GRANULAR ACTIVATED CARBON INCORPORATED WITH Zn²⁺ / NANO ZnO: STUDY OF ADSORPTION ISOTHERMS, POROSITY, KINETICS AND THERMODYNAMICS

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in

Environmental Chemistry Under the Faculty of Environmental Studies

Ву

JAYASREE. S (Register No.4088)

Under the Supervision and Guidance of

DR. V. SIVANANDAN ACHARI Associate Professor



SCHOOL OF ENVIRONMENTAL STUDIES COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY COCHIN-682 022, KERALA, INDIA.

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Ph.D. Thesis in Environmental Chemistry under the Faculty of Environmental Studies

Submitted by

Jayasree. S Research Scholar School of Environmental Studies Cochin University of Science and Technology Kochi – 682 022 Kerala, India Email: jayasreeprageesh@gmail.com

Supervising Guide

Dr. V. Sivanandan Achari Associate Professor School of Environmental Studies, Cochin University of Science and Technology Kochi – 682 022 Kerala, India Email:vsachari@gmail.com Phone: 0091-09495383342/0091-0484-2577311

School of Environmental Studies Cochin University of Science and Technology Kochi, Kerala, India 682 022

October 2017



SCHOOL OF ENVIRONMENTAL STUDIES

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY Cochin University P.O., Kochi - 682 022, Kerala, India Tel: 91-484-2577311, Fax: 91 – 484-2577311

DR. V. SIVANANDAN ACHARI Associate Professor in Environmental Chemistry/ Modeling/ Management (M) : 9495383342 / 0484 282548 / 0484 2577311 (R) : 0484 2306133 E-mail: vsachari@gmail.com, vsachari@cusat.ac.in

Date:30-10-2017



Certified that the work presented in the thesis entitled "Granular Activated Carbon Incorporated with Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics" is a bonafide work done by Ms. Jayasree. S under my supervision and guidance in the School of Environmental Studies, Cochin University of Science and Technology, Kochi-682 022 and that this work has not been included in any other thesis submitted previously for the award of any degree.

Dr. V. Sivanandan Achari Supervising Guide

Associate Professor Co-ordinator, UGC-SAP DRS (II) Programme School of Environmental Studies, Cochin University of Science and Technology Kochi – 682 022 Kerala, India

Declaration

I hereby declared that the work presented in this thesis entitled "Granular Activated Carbon Incorporated with Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics" is based on the original work done by me under the supervision of Dr. V. Sivanandan Achari, Associate Professor, Co-ordinator, UGC-SAP-DRS (II) Programme [2015 -2020], School of Environmental Studies, Cochin University of Science and Technology, Kochi-682 022 and has not been included in any other thesis submitted previously for the award of any degree.

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Jayasree. S

Research Scholar School of Environmental Studies Cochin University of Science and Technology Kochi – 682 022 Kerala, India



Coconut shell based granular activated carbons (GAC) have high adsorptive capacity due to their unique porous structure and very high selectivity for molecules and ions. Granular activated carbon is identified as an efficient material to refine contaminated water mostly in the tertiary stages of treatment process. Tailoring of physico chemical and structural properties observed as porosity, surface area and the surface complexes through activation / carbonisation / oxidation is a common practice to produce special granular activated carbons (GAC).

This doctoral thesis comprises research on a series of granular activated carbon based on coconut shell incorporated with Zn^{2+} ions (as $ZnCl_2$) and nano ZnO, activated at high temperatures (383 – 1273K) under super heated steam. Different batches of activated carbons were prepared in the laboratory under controlled conditions with specific Zn^{2+}/ZnO - carbon ratio as a function of temperature. Material properties, surface chemistry and adsorption efficiencies were determined using standard procedures followed; with a special emphasis to study of structure, adsorption isotherms, porosity/pore size distribution, kinetics and thermodynamics with respect to solid – gas (N₂ at 77K) and solid – liquid (phenol, *p* –nitrophenol & methylene blue) equilibria.

This doctoral thesis chapters mainly discusses the preparation, characterisation and adsorption studies of four different series of carbons prepared by chemical activation route are designated as GACZC, GACOZC, GACNZnO and GACONZnO series. The surface chemistry and physical structure of the resulting carbon was determined by FTIR, XPS, XRD, CHN and Boehm analytical methods. Surface morphology were observed by SEM and HRTEM analysis and appears to have enough highly developed porous structure.

The solid – gas equilibria (N₂ isotherms at 77K) of the new carbons have a Type I isotherm behaviour with H4 hysteresis loop common for materials with wider micropores. Further analysis using isotherm models of Brunauer Emmet Teller (BET), *I* plot, Langmuir, Freundlich, John, *t* – plot, Dubinin – Radushkevich, alpha S (α_s) and Barrett Joyner and Halenda (BJH) isotherm methods confirms that modified carbons GACZC series and GACNZnO series have extra microporosity; hence very high microporous surface area in the range 588.66 – 766.76 m²/g. The other carbon GACOZC and GACONZnO series, though microporosity is less, they have enough external surface area in the range 433.72 – 763.91 m²/g, are useful to separate large molecules.

The new carbons were successfully used for the adsorption of organic molecules in liquid phase (solid – liquid equilibria). The adsorption kinetics, equilibrium isotherm and thermodynamic studies are exhaustively conducted using the above carbon materials. This was done using phenol, p – nitrophenol and methylene blue (MB) in aqueous phase in bench scale batch reactors for a fixed carbon to substrate / adsorbate ratio. The resulting adsorption isotherms are analysed using isotherm models of Langmuir, Freundlich, Temkin, Dubinin – Radushkevich and John – Sivanandan Achari isotherm methods.

Contents

Chapter	ı 1	
INTRO	DUCTION	1 - 32
1.1	Activated Carbon	01
	1.1.1 Classification of Activated Carbon	
	1.1.2 Preparation of Activated Carbon	
	1.1.2.1 Physical Activation	
	1.1.2.2 Chemical Activation	
	1.1.3 Properties of Activated Carbon	
	1.1.3.1 Porous Structure of Activated Carbon	
	1.1.3.2 Surface Functional Groups	
	1.1.4 Applications of Activated Carbon	07
	1.1.5 Impregnated / Incorporated Activated Carbon	
	1.1.6 Zinc based Activated Carbon	10
1.2	Adsorption Process	11
	1.2.1 Physical Adsorption	12
	1.2.2 Chemical Adsorption	12
1.3	Types of Adsorption Isotherms	12
1.4	Adsorption Hysteresis Loop	14
1.5	Solid – Gas Adsorption Equilibria	15
	1.5.1 Adsorption Isotherm Models	16
	1.5.1.1 Langmuir Isotherm Model	
	1.5.1.2 Brunauer, Emmett and Teller (BET) Method	
	1.5.1.3 I point Method	17
	1.5.1.4 Dubinin-Radushkevich (D – R) Isotherm	17
	1.5.1.5 John Isotherm Method	
	1.5.1.6 Alpha S (α_s) Plots	
	1.5.1.7 <i>t</i> - <i>Plot</i> Method	
	1.5.1.8 Barrett Joyner Halenda (BJH) Method	
1.6	Solid – Liquid Adsorption Studies	19
1.7	Aim and Scope of the Study	21
1.8	Hypothesis	22
1.9	Structure of the Thesis	22
Refe	prences	27

MATEI	RIALS AND METHODS	. 33 - 65
2.1	Introduction	
2.2	Materials	
2.3	Methodology	
	2.3.1 Preparation of Granular Activated Carbon Native Form	
	(GAC383)	

	2.3.2	Preparation of Granular Activated Carbon Oxidized	
		Form (GACO383)	34
	2.3.3	Preparation of Nano Zinc Oxide (NZnO)	36
	2.3.4	Preparation of ZnCl ₂ Impregnated Granular Activated	
		Carbon Native Form (GACZC)	36
	2.3.5	Preparation of ZnCl ₂ Impregnated with Oxidised	
		Granular Activated Carbon (GACOZC)	36
	2.3.6	Preparation of Nano ZnO Impregnated Granular Activated	
		Carbon (GACNZnO)	38
	2.3.7	Preparation of Nano ZnO Impregnated with Oxidised	
		Granular activated carbon (GACONZnO)	38
2.4	Char	acterization Techniques	40
	2.4.1	Carbon Yield and Burn – off	40
	2.4.2	Boehm Titrations	41
	2.4.3	Elemental Analysis	42
	2.4.4	Fourier Transform Infrared (FTIR) Spectroscopy	42
	2.4.5	X-ray Photo Electron Spectroscopy (XPS)	42
	2.4.6	X –ray Diffraction Technique (XRD)	42
	2.4.7	Scanning Electron Microscopy (SEM)	43
	2.4.8	High Resolution Transmission Electron Microscopy	
		(HRTEM)	43
2.5	Adso	rption Studies (Solid – Gas & Solid – Liquid)	43
	2.5.1	Carbon – N ₂ Gas Adsorption (Solid - Gas Adsorption)	43
		2.5.1.1 Brunauer Emmett Teller (BET) Method	44
		2.5.1.2 BET Scatchard (I point) Method	45
		2.5.1.3 Langmuir Isotherm Method	46
		2.5.1.4 Freundlich Isotherm Method	46
		2.5.1.5 John Isotherm Method	47
		2.5.1.6 Alpha S (α_s) Method	47
		2.5.1.7 Dubinin - Radushkevich (D - R) Isotherm Method	48
		2.5.1.8 $t - plot$ Method	49
		2.5.1.9 BJH method	49
	2.5.2	Solid – Liquid Adsorption	50
		2.5.2.1 <i>Phenol</i>	50
		2.5.2.2 p – nitrophenol	50
		2.5.2.3 Methylene blue (MB)	51
		2.5.2.4 Adsorption Kinetics	52
		2.5.2.4.1 Pseudo First Order Kinetic Model	
		2.5.2.4.2 Pseudo Second Order Kinetic Model	
		2.5.2.4.5 Elovien Killette Model	
		2.5.2.4.5 Boyd Kinetic Model	
		2.5.2.5 Adsorption Isotherm Studies	
		2.5.2.5.1 Langmuir Isotherm Model	
		2.5.2.5.2 Freundlich Isotherm Model	57
		2.5.2.5.3 Temkin Isotherm	58

2.5.2.5.4 Dubinin – Radushkevich (D – R) Isotherm	59
2.5.2.5.5 John – Sivanandan Achari (J – SA) Isotherm	59
2.5.2.6 Adsorption Thermodynamics	59
2.6. Trace Elements – Adsorption study	61
2.7. Statistical Analysis of the Data	61
References	63

GRANU	JLAR ACTIVATED CARBON INCORPORATED			
WITH	Zn ²⁺ : PREPARATION, CHARACTERISATION AND			
ADSOF	RPTION STUDIES	7 - 184		
3.1	Introduction	67		
3.2	Characterization Studies of Granular Activated Carbon			
	Impregnated with Zinc Ions (GACZC). Native Form of			
	Carbon (GAC383) and Oxidized Carbon (GAC0383)	68		
	3.2.1 Effect of Impregnation Ratio on Zinc Ions (Zn^{2+}) /			
	GAC			
	3.2.2 Carbon Yield and Burn – off			
	3.2.3 Elemental Analysis			
	3.2.4 Surface Functional Group Analysis Using FTIR			
	Spectroscopy and Boehm Method	71		
	3.2.5 XPS Surface Analysis	73		
	3.2.6 XRD Analysis	77		
	3.2.7 Scanning Electron Microscopy (SEM)	79		
	3.2.8 Transmission Electron Microscopy			
3.3	Porosity Studies – Evaluation of Surface Area and Pore			
	Volume	84		
	3.3.1 Brunauer Emmet Teller (BET) Isotherm Analysis			
	3.3.2 <i>I</i> plot Method			
	3.3.3 Langmuir Isotherm Analysis	90		
	3.3.4 Freundlich Isotherm Analysis	91		
	3.3.5 John Isotherm Model Analysis	92		
	3.3.6 Alpha S (α_s) Isotherm Analysis			
	3.3.7 Dubinin-Radushkevich (D-R) isotherm Analysis			
	3.3.8 <i>t</i> - <i>plot</i> Isotherm Analysis	96		
	3.3.9 BJH Pore Size Distribution Studies			
3.4	Liquid Phase Adsorption Studies Using Carbon - GACZC			
	Series	100		
	3.4.1 Adsorption Studies – Phenol as Adsorbate	100		
	3.4.1.1 Adsorbent Dosage	100		
	3.4.1.2 Effect of Contact Time	101		
	3.4.1.3 Selection of GACZC for Phenol Adsorption	102		

	3.4.1.4	Adsorption Studies of GAC383, GACO383 and	
		GACZC107310	3
	3.4.1.5	Kinetic Modelling	4
		3.4.1.5.1 Pseudo First Order Model for Phenol	
		Adsorption10	4
		3.4.1.5.2 Pseudo Second Order Model for Phenol	
		Adsorption 10	7
		3.4.1.5.3 Intraparticle Diffusion Model for Phenol	
		Adsorption10	7
		3.4.1.5.4 Boyd Plot – Phenol	9
	3.4.1.6	Activation Energy11	1
	3.4.1.7	Adsorption Isotherm Studies of phenol	2
		3.4.1.7.1 Langmuir Isotherm – Phenol	4
		3.4.1.7.2 Freundlich Isotherm – Phenol	6
		3.4.1.7.3 Temkin Isotherm – Phenol on GAC383,	
		GACO383 and GACZC107311	8
		3.4.1.7.4 Dubinin- Radushkevich (D-R) Isotherm – Phenol	
		on GAC383, GACO383 and GACZC107311	9
	3.4.1.8	Thermodynamic Parameters for Phenol Adsorption 12	1
3.4.2	Adsorp	tion Studies of <i>p</i> –nitrophenol	3
	3.4.2.1	Effect of Contact Time	3
	3.4.2.2	Selection of Carbon 12	4
	3.4.2.3	Adsorption Kinetics	5
	0111210	3.4.2.3.1 Pseudo First and Second Order Kinetics:	Č
		p - nitrophenol	7
		3.4.2.3.2 Intraparticle Diffusion Model	7
		3.4.2.3.3 Elovich Kinetic Model for p - nitrophenol	
		Adsorption	8
	3.4.2.4	Activation Energy <i>p</i> - nitrophenol as Adsorbate	2
	3.4.2.5	Adsorption Isotherm Studies of <i>P</i> -nitrophenol as	
	0111210	Adsorbate 13	4
		3 4 2 5 1 Applications of Isotherm Models 13	5
	3426	Thermodynamic Parametrs 14	.1
343	Adsorp	tion Studies of Methylene Blue 14	2
5.1.5	3431	Effect of Carbon Dose 14	3
	3.4.3.1	Effect of Contact Time 14	3
	3/33	Selection of GACZC for Methylene Blue	5
	5.4.5.5	(MB) Adsorption 14	1
	3131	(MD) Adsorption Kinetics Study of Methylene	+
	5.4.5.4	Plue (MP) Adaption on New Carbons 14	1
	2 1 2 5	Activation Energy Using Mathylana Plus (MP) as	4
	5.4.5.5	A description Energy Using Methylene Dive (MD) as	1
	2126	Ausorioalian Isothorm Studios of Mathylana Dive	1
	3.4.3.0	Ausorption isotherm Studies of Methylene Blue (MP) on CAC7C1072 15	2
	2 4 2 7	(MD) OII GACZC10/5	3
	3.4.3.7	Adsorption Thermodynamics	U

3.5	Determination of Surface Area and Porosity of Modified	
	Carbons (GAC383, GACO383 and GACZC1073) Using	
	Liquid Phase Adsorption Isotherm Modelling	
	3.5.1 Langmuir Isotherm	163
	3.5.2 John – Sivanandan Achari Isotherm	165
	3.5.3 Brunauer Emmet Teller Method (BET)	167
	3.5.4 <i>I</i> plot Method	168
3.6	Adsorption of Trace Elements (Li, Mg, Al, Cr, Mn, Fe,	
	Co, Cu, Zn, As, Cd, Ba, Tl & Pb)	171
3.7	Statistical Analysis of the Data	172
3.8	Conclusions	178
Refe	erences	

GRANU	JLAR ACTIVATED CARBON OXIDISED AND	
INCOR	PORATED WITH Zn ²⁺ : PREPARATION,	
CHAR A	ACTERIZATION AND ADSORPTION STUDIES	35 - 276
4.1	Introduction	
4.2	Characterization Studies of GACOZC Series Carbons	
	4.2.1 Carbon Yield and Burn – off	
	4.2.2 Elemental Analysis	
	4.2.3 Surface Functional Group Analysis Using FTIR and	
	Boehm Methods	
	4.2.4 XPS Surface Analysis	191
	4.2.5 XRD Analysis	
	4.2.6 Scanning Electron Microscopy (SEM)	
	4.2.7 Transmission Electron Microscopy	
4.3	Porosity Studies – Evaluation of Surface Area and Pore	
	Volume	
	4.3.1 Brunauer Emmet Teller (BET) Isotherm	
	4.3.2 <i>I</i> Plot Method	
	4.3.3 Langmuir Isotherm	
	4.3.4 Freundlich Isotherm	
	4.3.5 John Isotherm Analysis	
	4.3.6 Alpha S (α_s) Isotherm	
	4.3.7 Dubinin-Radushkevich (D-R) Isotherm	
	4.3.8 De Boer <i>t</i> - plot	
	4.3.9 BJH Pore size Distribution	
4.4	Liquid Phase Adsorption Studies Using Carbon -	
	GACOZC Series	
	4.4.1 Adsorption Studies – Phenol as Adsorbate	
	4.4.1.1 Selection of GACOZC for Phenol Adsorption	
	4.4.1.2. Adsorption Kinetics	

		4.4.1.3	Activation Energy	
		4.4.1.4	Adsorption Isotherm Studies of Phenol	
			4.4.1.4.1 Adsorption Isotherm Modelling	220
		4.4.1.5	Thermodynamic Parameters for Phenol	
			Adsorption	226
	4.4.2	Adsorp	tion Studies of p – nitrophenol as Adsorbate	227
		4.4.2.1	Selection of Carbon	227
		4.4.2.2	Effect of Contact Time and Temperature	228
		4.4.2.3	Activation Energy Using p - nitrophenol as Adsorbate	
		4.4.2.4	Adsorption Isotherm Studies of <i>p</i> -nitrophenol as	
			Adsorbate	
		4.4.2.5	Thermodynamic Parameters	
	4.4.3	Adsorp	tion Studies of Methylene Blue (MB)	
		4.4.3. 1.	Selection of GACOZC for Methylene Blue (MB)	
			Adsorption	
		4.4.3.2	Adsorption Kinetics - Methylene Blue as Adsorbate	
		4.4.3.3	Activation Energy Using Methylene blue (MB) as	
			Adsorbate	250
		4.4.3.4	Adsorption Isotherm Studies of Methylene Blue	
			(MB) on GACOZC1073	251
		4.4.3.5	Adsorption Thermodynamics	256
4.5	Deter	minatic	on of Porosity and Surface Area of Modified	
	Carbo	ons (GA	C383, GACO383 and GACOZC1073) Using	
	Liqui	d Phase	Adsorption Isotherm Models	259
4.6	Adso	rption of	of Trace Elements (Li, Mg, Al, Cr, Mn, Fe,	
	Co, C	Cu, Zn, A	As, Cd, Ba, Tl & Pb)	
4.7	Statis	stical A	nalysis of the Data	
4.8	Conc	lusions.	-	271
Refe	rences	5		

GRAN	ULAR ACTIVATED CARBON INCORPORATED	
WITH	NANO ZnO: PREPARATION,	
CHAR A	ACTERIZATION AND ADSORPTION STUDIES 272	7 - 369
5.1	Introduction	277
5.2	Preparation of Nano Zinc Oxide (NZnO)	277
5.3	Characterization Studies of Nano Zinc Oxide	278
5.4	Effect of Impregnation Ratio on Nano Zinc Oxide / GAC	282
5.5	Characterisation Studies of Granular Activated Carbon	
	Impregnated with Nano Zinc Oxide (GACNZnO Series)	282
	5.5.1 Carbon Yield and Burn –off	283
	5.5.2 Elemental Analysis – CHNOS	283
	5.5.3 Surface Functional Group Analysis	284

	5.5.4 XPS Analysis	286
	5.5.5 XRD Analysis	288
	5.5.6 SEM Analysis	290
	5.5.7 TEM Analysis	290
5.6	Porosity Studies – Evaluation of Surface Area and Pore	
	Volume	291
	5.6.1 Brunauer Emmet Teller (BET) Isotherm Model	293
	5.6.2 I point Method	295
	5.6.3 Langmuir Isotherm	296
	5.6.4 Freundlich Isotherm	297
	5.6.5 John Isotherm Analysis	298
	5.6.6 Alpha S (α_s) Isotherm	298
	5.6.7 Dubinin Radushkevich (D – R) Isotherm	300
	5.6.8 $t - plot$ Method	301
	5.6.9 Barret Joyner Halenda (BJH) Pore Size Distribution	303
5.7	Liquid Phase Adsorption Study	305
	5.7.1 Adsorption Studies – Phenol as Adsorbate	305
	5.7.1.1 Selection of GACNZnO for Phenol Adsorption	305
	5.7.1.2 Effect of Temperature and Time on the Adsorption	
	of Phenol on GAC383, GACO383 and	
	GACNZnO1273	306
	5.7.1.3 Kinetic Modelling	307
	5.7.1.4 Adsorption Isotherm Studies of Phenol	313
	5.7.1.5 Thermodynamic Study	320
	5.7.2 Adsorption Studies of <i>p</i> –nitrophenol	321
	5.7.2.1 Selection of Carbon	322
	5.7.2.2 Adsorption Kinetics	322
	5.7.2.3 Adsorption Isotherm Studies of p - nitrophenol as	220
	Adsorbate	330
	5.7.2.4 Inermodynamic Parameters	330
	5.7.5 Adsolption Studies of Methylene Blue (MD)	227
	5.7.3.2 Adsorption Kinetics	337
	5.7.3.2 Adsorption Kinetics	338
	5 7 3 4 Thermodynamic Parameters	349
5.8	Determination of Surface Area and Porosity of Modified	
	Carbons Using Liquid Phase Adsorption Isotherm Modelling	352
5.9	Adsorption of Trace Elements (Li, Mg, Al, Cr, Mn, Fe,	
	Co, Cu, Zn, As, Cd, Ba, Tl & Pb)	359
5.10	Statistical Analysis of the Data	361
5.11	Conclusions	365
Refe	rences	366

Chapter	<i>i</i> 6		
GRANU	JLAR A	ACTIVATED CARBON OXIDISED AND	
INCOR	PORA	TED WITH NANO ZNO: PREPARATION.	
CHAR/	ACTER	ISATION AND ADSORPTION STUDIES	455
6.1	Introd	uction	.371
6.2	Chara	cterization Studies of GACONZnO	371
0.2	621	Carbon Yield and Burn - off	371
	622	Elemental Analysis	372
	623	Surface Functional Groups Analysis Using FTIR and Boehm	. 572
	0.2.0	Method	. 373
	6.2.4	XPS Analysis	.375
	6.2.5	XRD Analysis	.377
	6.2.6	Scanning Electron Microscopy	.379
	6.2.7	Transmission Electron Microscopy	. 380
6.3	Porosi	ity Studies – Evaluation of Surface Area and Pore	
	Volun	ne	.381
	631	Brunauer Emmet Teller (BET) Isotherm Model	382
	632	<i>I</i> plot method	383
	6.3.3	Langmuir Isotherm	.385
	6.3.4	Freundlich Isotherm	. 386
	6.3.5	John Isotherm	. 386
	6.3.6	Alpha S (α _s) Isotherm	. 388
	6.3.7	Dubinin - Radushkevich (D –R) Isotherm	. 388
	6.3.8	<i>t</i> - plot method	. 391
	6.3.9	BJH Pore Size Distribution	. 392
6.4	Liquid	Phase Adsorption Studies Using GACONZnO	.393
	6.4.1	Adsorption Studies – Phenol as Adsorbate	. 393
	(6.4.1.1 Selection of GACONZnO for Phenol Adsorption	394
	(6.4.1.2 Adsorption Kinetics	394
	(6.4.1.3 Activation Energy	401
	(6.4.1.4 Adsorption Isotherm Studies of Phenol	403
		6.4.1.4.1 Langmuir Isotherm Model	404
		6.4.1.4.2 Freundlich Isotherm Model	405
		6.4.1.4.3 Temkin Isotherm Model	408
		0.4.1.4.4 Dublinin - Radusinkevici (D-R) Isometini - Phenol	409
	612	Adsorption Studies of <i>n</i> _ nitronhanol	409
	0.4.2	6.4.2.1 Selection of Carbon from GACONZnO Series	411
	Ì	6422 Adsorption Kinetics	412
	, (6.4.2.3 Activation Energy p – nitrophenol as Adsorbate	
	(6.4.2.4 Adsorption Isotherm Studies, <i>p</i> -nitrophenol as	
		Adsorbate	419
	(6.4.2.5 Thermodynamic Parameters	425
	6.4.3	Adsorption Studies of Methylene Blue (MB)	. 426

	6.4.3.1	Selection of GACONZnO for Methylene Blue (MB)	
		Adsorption	426
	6.4.3.2	Adsorption Kinetics	427
	6.4.3.3	Activation Energy Using Methylene Blue (MB) as	
		Adsorbate	433
	6.4.3.4	Adsorption Isotherm Studies of Methylene Blue (MB)	
		on GACONZnO1273	434
	6.4.3.5	Adsorption Thermodynamics	438
6.5	Determination	on of Surface Area and Porosity of Modified	
	Carbons Usin	g Liquid Phase Adsorption Isotherm Modelling	441
6.6	Adsorption of	f Trace Elements (Li, Mg, Al, Cr, Mn, Fe,	
	Co, Cu, Zn, A	As, Cd, Ba, Tl & Pb)	445
6.7	Statistical Ar	nalysis of the Data	447
6.8	Conclusions		451
Refe	erence		453
apte	r 7		

List of Tables

Table 2.1:	Different series of granular activated carbon GAC prepared	39
Table 2.2:	Separation factor	57
Table 3.1:	Impregnation ratio X_{Zn} used, carbon yield and burn off obtained during the preparation of GACZC series	68
Table 3.2:	Surface functional groups and elemental composition of modified granular activated carbon GACZC series	70
Table 3.3:	The elemental composition of the modified granular activated carbons GAC383, GACO383 and GACZC1073 from XPS analysis	74
Table 3.4:	Assignment of binding energy values of the peaks in the C1s and O1s XPS spectrum of the surface functional groups in the modified granular activated carbons (GAC383, GACO383 and GACZC1073)	75
Table 3.5:	Structural parameters from X- ray diffraction studies	78
Table 3.6:	Textural characterisation of granular activated carbons studied	85
Table 3.7:	Surface area and Pore volume* of granular activated carbon impregnated with Zn^{2+} ions	87
Table 3.8:	Porosity parameters of granular activated carbon impregnated with Zn^{2+} ions calculated from Langmuir, Freundlich and John isotherm model	92
Table 3.9:	Dubinin – Radushkevich (D –R) and Alpha S (α_s) constants of the modified carbons	95
Table 3.10:	Surface area and pore size distribution using <i>t</i> - <i>plot</i> and <i>BJH</i> method	97
Table 3.11:	Comparison of the pseudo first and second order constants and parameters for the adsorption of phenol (C_0 : 250 mg/L)	106
Table 3.12:	Intraparticle diffusion constants for phenol adsorption on carbons GAC383, GAC0383 and GACZC1073 (C_0 : 250 mg/L)	108
Table 3.13:	Activation energy determined during adsorption of phenol on modified carbons	112
Table 3.14:	Langmuir, Freundlich and Temkin parameters of phenol adsorption on modified carbons (C ₀ : 25 - 3000 mg/L)	117
Table 3.15:	Dubinin - Radushkevich (D-R) Constant of phenol adsorption on carbons GAC383, GACO383 and GACZC1073	.120

Tab1e 3.16:	Thermodynamic parameters – Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the modified carbons
Table 3.17:	Kinetic parameters for the adsorption of p - nitrophenol on GAC383, GAC0383 and GACZC1073 (C ₀ : 250 mg/L)130
Table 3.18:	Activation energy of new carbons using <i>p</i> - nitrophenol as adsorbate
Table 3.19:	Langmuir, Freundlich, Temkin and Dubinin – Radushkevich isotherm parameters of p - nitrophenol on modified carbons (GAC383, GACO383 & GACZC1073)140
Table 3.20:	Thermodynamic parameters – Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS)
Table 3.21:	Kinetic constants for the adsorption of methylene blue adsorption (MB) on modified carbons (GAC383, GAC0383 and GACZC1073) at different temperatures (K) (C: 250 mg/L) 150
Table 3.22:	Activation energy of modified carbons using MB as
	adsorbate153
Table 3.23:	Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Adsorption Isotherm Model constant for methylene Blue (MB) on new carbons at different temperatures (K)
Table 3.24:	Thermodynamic parameters of GAC383, GACO383 and GACZC1073 for methylene blue (MB) adsorption at different temperatures $C_0: 25$ -1500 mg/L161
Table 3.25:	The porosity and surface area of the modified carbons using different isotherm models
Table 3.26:	Adsorption efficiency for removing trace elements by newly prepared carbons GAC383, GACO383 and GACZC1073
Table 3.27:	ANOVA table for the comparison of textural characterization of granular activated carbon taking GAC383 as control
Table 3.28:	ANOVA table for the comparison of textural characterization of granular activated carbon taking GACO383 as control
Table 3.29:	ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and <i>I</i> plot method) of granular activated carbon taking GAC383 as control
Table 3.30:	ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and <i>I</i> plot method) of granular activated carbon taking GACO383 as control

Table 3.31:	ANOVA table for the comparison of surface area obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and I plot method) of granular activated carbon taking GAC383 as control	175
Table 3.32:	ANOVA table for the comparison of surface area obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and <i>I</i> plot method) of granular activated carbon taking GACO383 as control	176
Table 3.33:	ANOVA table for the comparison of pore volume obtained by different methods (John Isotherm, Langmuir isotherm, Dubinin – Radushkevich isotherm and Alpha S) of granular activated carbon	176
Table 3.34:	ANOVA table for the comparison of surface area of modified carbons obtained by Langmuir isotherm and John isotherm models	178
Table 4.1:	Surface functional groups and elemental composition of modified granular activated carbons GACOZC series	187
Table 4.2.:	The elemental composition of the modified granular activated carbons GAC383, GACO383 and GACOZC1073 from XPS analysis	192
Table 4.3:	Structural parameters from X- ray diffraction studies	194
Table 4.4:	Textural characterization of granular activated carbons studied	201
Table 4.5:	Surface area and Pore volume* of granular activated carbon oxidized and impregnated with Zn^{2+} ions	202
Table 4.6:	Porosity parameters of granular activated carbon oxidized and impregnated with Zn^{2+} ions calculated from Langmuir, Freundlich and John model	205
Table 4.7:	Dubinin – Radushkevich $(D - R)$ and Alpha S (α_s) constants of the modified carbons	208
Table 4.8:	Surface area and pore size distribution using <i>t</i> - <i>plot</i> and <i>BJH method</i>	209
Table 4.9:	Comparison of the pseudo first and second order kinetic constants and parameters of adsorption of phenol for $C_0 = 250 \text{ mg/L}$	214
Table 4.10:	Intraparticle diffusion constant of phenol adsorption on carbons GAC383, GACO383 and GACOZC1073 for $C_0 = 250 \text{ mg/L}$	217
Table 4.11:	Determination of activation energy of phenol adsorption by GAC383, GACO383 and GACZC1073	219

Table 4 .12:	Langmuir, Freundlich, Temkin and Dubinin – Radushkevich $(D-R)$ parameters of phenol on modified carbons
Table 4.13:	Thermodynamic parameters – Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the modified carbons
Table 4.14:	Kinetic parameters for the adsorption of p - nitrophenol on GAC383, GACO383 and GACOZC1073 for $C_0 = 250 \text{ mg/L} \dots 233$
Table 4.15:	Activation energy of modified carbons using <i>p</i> - nitrophenol as adsorbate
Table 4.16:	Langmuir, Freundlich, Temkin and Dubinin – Radushkevich (D – R) isotherm parameters of p -nitrophenol on activated carbons
Table 4.17:	Thermodynamic parameters – Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of GACOZC1073243
Table 4.18:	Kinetic constants for the adsorption of methylene blue on modified carbons (GAC383, GACO383 and GACOZC1073) at different temperatures (C_0 : 250 mg/L)
Table 4.19:	Activation energy of modified carbons using MB as adsorbate
Table 4.20:	Langmuir, Freundlich, Temkin and Dubinin Radushkevich Adsorption Isotherm Model constant for methylene blue (MB) on new carbons at different temperatures (K)
Table 4.21:	Thermodynamic parameters of GAC383, GACO383 and GACOZC1073 for methylene blue (MB) adsorption at different temperatures for $C_0 = 25 - 1500 \text{ mg/L}$ 258
Table 4.22:	The porosity and surface area of the new modified carbons using standard isotherm models
Table 4.23:	Adsorption efficiency for removing trace elements by newly prepared carbons GAC383, GACO383 and GACOZC1073266
Table 4.24:	ANOVA table for the comparison of textural characterization of granular activated carbons
Table 4.25:	ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and I plot method) of granular activated carbons
Table 4.26:	ANOVA table for the comparison of pore volume obtained by different methods (John Isotherm, Langmuir isotherm, Dubinin – Radushkevich isotherm and alpha S) of granular activated carbon
Table 4.27:	ANOVA table for the comparison of porosity of granular activated carbon obtained by Langmuir and John – Sivanandan Achari isotherm model in liquid phase adsorption study

Table 4.28:	ANOVA table for the comparison of surface area of modified carbons obtained by Langmuir isotherm and John - Sivanandan Achari isotherm models
Table 5.1:	Estimation of particle size from the X-ray diffractograms of nano ZnO by using full width half maximum
Table 5.2:	Elemental composition of nano ZnO particles
Table 5.3:	Impregnation ratio X_{Zn} used, carbon yield, burn - off and elemental composition obtained during the preparation of carbon GACNZnO series
Table 5.4:	Elemental composition and surface functional groups of GACNZnO series
Table 5.5:	The elemental composition of the modified granular activated carbons GAC383, GAC0383 and GACNZn01273 from XPS analysis
Table 5.6:	Structural parameters from X- ray diffraction studies
Table 5.7:	Textural characteristion of granular activated carbons studied*; GACNZnO series
Table 5.8:	Surface area and pore volume* of modified granular activated carbon impregnated with nano ZnO
Table 5.9:	Porosity parameters of granular activated carbon impregnated with nano ZnO calculated from Langmuir, Freundlich and John isotherm model : GACNZnO series
Table 5.10:	Dubinin – Radushkevich (D-R) and Alpha S (α_s) constants of the modified carbons
Table 5.11:	Surface area and pore size distribution using <i>t</i> - <i>plot</i> and <i>BJH isotherm</i>
Table 5.12:	Comparison of the pseudo first and second order constants and parameters for the adsorption of phenol: $C_0 = 250 \text{ mg/L} \dots 308$
Table 5.13:	Intraparticle diffusion constants for phenol adsorption on carbons GAC383, GACO383 and GACNZnO1273 for C_0 = 250 mg/L
Table 5.14:	Activation energy determined during adsorption of phenol on GAC383, GACO383 and GACNZnO1273
Table 5.15:	Langmuir, Freundlich, Temkin and Dubinin – Radushkevich isotherm parameters of phenol on modified carbons
Table 5.16:	Thermodynamic parameters – Gibbs free energy, enthalpy and entropy for the adsorption of phenol on new carbons
Table 5.17:	Kinetic Parameters for the adsorption of p - nitrophenol on GAC383, GACO383 and GACNZnO1273; C ₀ = 250 mg/L

Table 5.18:	Activation energy for the adsorption of p – nitrophenol on modified carbons
Table 5.19:	Langmuir, Freundlich, Temkin and Dubinin – Radushkevich $(D-R)$ parameters of <i>p</i> -nitrophenol on modified carbons
Table 5.20:	Thermodynamic parameters – Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the modified carbons
Table 5.21:	Kinetic constants for the adsorption of methylene blue (MB) on modified carbons (GAC383, GACO383 and GACNZnO1073) at different temperatures (K); $C_0 = 250 \text{ mg/L} \dots 342$
Table 5.22:	Activation energy of surface modified carbons using methylene blue (MB) as adsorbate
Table 5.23:	Langmuir, Freundlich, Temkin and Dubinin - Radushkevich Isotherm model constants for methylene blue (MB) on new carbons at different temperatures (K)
Table 5.24:	Thermodynamic parameters of GAC383, GACO383 and GACNZnO1073 for methylene blue (MB) adsorption at different temperatures for initial concentration $C_0 = 25 - 1500 \text{ mg/L} \dots 351$
Table 5.25:	The porosity and surface area of the modified carbons using different isotherm models
Table 5.26:	Adsorption efficiency for removing trace elements by newly prepared carbons GAC383, GACO383 and GACNZnO1273
Table 5.27:	ANOVA table for the comparison of textural characterization of granular activated carbons
Table 5.28:	ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and <i>I</i> plot method) of granular activated carbons
Table 5.29:	ANOVA table for the comparison of pore volume obtained by different methods (John Isotherm, Langmuir isotherm, Dubinin – Radushkevich isotherm and alpha S) of granular activated carbon
Table 5.30:	ANOVA table for the comparison of porosity of granular activated carbon obtained by Langmuir and John – Sivanandan Achari isotherm models in liquid phase adsorption study
Table 5.31:	ANOVA table for the comparison of surface area of modified carbons obtained by Langmuir isotherm and John isotherm models

Table 6.1:	Surface functional groups and elemental composition of modified granular activated carbons
Table 6.2.:	The elemental composition of the modified granular activated carbons GAC383, GACO383 and GACONZnO1273 from XPS analysis
Table 6.3:	Structural parameters from X- ray diffraction studies
Table 6.4:	Textural characteristion of granular activated carbon*
Table 6.5:	Surface area and pore volume* of oxidized granular activated carbon impregnated with nano ZnO
Table 6.6:	Isotherm Parameters of Langmuir, Freundlich and John models N_2 (77K) for oxidized granular activated carbon impregnated with nano Zinc oxide (GACONZnO)
Table 6.7:	Dubinin – Radushkevich (D –R) and Alpha S (α_s) constants of the modified carbons
Table 6.8:	Surface area and pore size distribution using <i>t</i> - plot and BJH isotherm method for carbon GACONZnO
Table 6.9:	Comparison of the pseudo first and second order kinetic model for the adsorption of phenol (C_0 : 250 mg/L)
Table 6.10:	Intraparticle diffusion constant of phenol on modified carbons (C ₀ : 250 mg/L)400
Table 6.11:	Activation energy determined during adsorption of phenol on new modified carbons
Table 6 .12:	Langmuir,Freundlich,Temkin and Dubinin – Radushkevich (D –R) isotherm parameters of phenol adsorption by modified carbons for initial concentration $C_0 = 25 - 3000 \text{ mg/L} \dots 407$
Table 6.13:	Thermodynamic parameters – Gibb's free energy (ΔG) , enthalpy (ΔH) and entropy (ΔS) for the adsorption of phenol on carbons
Table 6.14:	Kinetic parameters for the adsorption of p - nitrophenol on GAC383, GAC0383 and GAC0NZnO1273 for initial concentration $C_0 = 250 \text{ mg/L}$
Table 6.15:	Activation energy determined during adsorption of <i>p</i> -nitrophenol on new modified carbons
Tablee 6.16:	Langmuir, Freundlich, Temkin and Dubinin - Radushkevich parameters of p -nitrophenol adsorption on modified carbons
Table 6.17:	Thermodynamic parameters – Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of GACONZnO1273

Table 6.18:	Kinetic constants for the adsorption of methylene blue (MB) on modified carbons (GAC383, GACO383 and GACONZnO1273) at different temperatures (C ₀ : 250 mg/L)431
Table 6.19:	Activation energy of modified carbons using methylene blue adsorption
Table 6.20:	Langmuir, Freundlich, Temkin and Dubinin - Radushkevichich isotherm (D-R) constants for methylene blue (MB) adsorption at different temperature (K)437
Table 6.21:	Thermodynamic parameters of GAC383, GACO383 and GACONZnO1273 for methylene blue (MB) adsorption at different temperatures
Table 6.22:	The porosity and surface area of the modified carbons using different isotherm models
Table 6.23:	Adsorption efficiency for removing trace elements by newly prepared carbons GAC383, GACO383 and GACONZnO1273
Table 6.24:	ANOVA table for the comparison of textural characterization of granular activated carbons
Table 6.25:	ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and I plot method) of granular activated carbons
Table 6.26:	ANOVA table for the comparison of pore volume obtained by different methods (John Isotherm, Langmuir isotherm, Alpha $S(\alpha_s)$ and Dubinin – Radushkevich isotherm) of granular activated carbons
Table 6.27:	ANOVA table for the comparison of porosity of granular activated carbon obtained by Langmuir and John – Sivanandan Achari isotherm model in liquid phase adsorption study
Table 6.28:	ANOVA table for the comparison of surface area of granular activated carbon obtained by Langmuir and John – Sivanandan Achari isotherm model in liquid phase adsorption study

List of Figures

Figure 1.1:	Schematic representation of pore structure of an activated carbon	05
Figure 1.2:	The surface functional groups present on the carbon	
8	surface	07
Figure 1.3:	Classification of physisorption isotherm types	14
Figure 1.4:	Classification of hysteresis loop	15
Figure 2.1:	GAC preparation boiling 0.5 N NaOH	35
Figure 2.2:	GAC washing with distilled water to neutralize the pH to	
	7.0 or near to it	35
Figure 2.3:	Granular Activated Carbon (GAC383)	35
Figure 2.4:	Oxidation of GAC383 with HNO ₃	35
Figure 2.5:	Impregnation of Nano ZnO on GAC383	37
Figure 2.6:	Steam activation of GAC under laboratory condition	37
Figure 2.7:	Carbonisation chamber	37
Figure 2.8:	Samples after activation and carbonization	37
Figure 2.9:	Methodology followed for the study of Granular	
	activated *GAC383, ⁺ GACO383	39
Figure 2.10:	Methodology followed for the study of granular activated	
	carbon (GAC383 / GACO383) incorporated with $ZnCl_2$ /	10
	nano ZnO	40
Figure 2.11:	Molecular structure of phenol	51
Figure 2.12:	Molecular structure of p – nitrophenol	51
Figure 2.13:	Molecular structure of methylene blue	51
Figure 3.1:	Carbon yield and burn off pattern of GACZC activated at	
	different temperatures	69
Figure 3.2(a):	FTIR spectra of GAC383	72
Figure 3.2(b):	FTIR spectra of GACO383	72
Figure 3.2(c):	FTIR spectra of GACZC activated at different temperatures	72
Figure 3.3:	XPS spectra of modified granular activated carbons	
	GAC383, GACO383 & GACZC1073 (a) C 1s peak (b)	70
	U Is peak	13
Figure $3.4(a)$:	XPS N Is spectra of modified granular activated carbons	74
\mathbf{E}'_{1}	UNC 7 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	74
Figure $3.4(b)$:	$\frac{1}{1} = \frac{1}{1} = \frac{1}$	/4
Figure 3.5:	Deconvoluted APS of GAC383 (a) U Is region & (b) U Is region	76
Figure 2 6.	Deconvoluted YDS of $GACO282$ (a) C is region by (b)	70
1 iguie 5.0.	O 1s region	76
	- 10 10 Gron	

Figure 3.7:	Deconvoluted XPS of GACZC1073 (a) C 1s region & (b) O 1s region	76
Figure 3.8(a):	X-ray diffractograms of GAC383	
Figure 3.8(b):	X-ray diffractograms of GACO383	
Figure 3.9:	X-ray diffractograms of (a) GACZC383, (b) GACZC473, (c) GACZC673, (d) GACZC873, (e) GACZC1073 and (f) GACZC1273	79
Figure 3.10:	SEM image of GAC383 (a) 100 μ m resolution (b) 50 μ m resolution (c) 10 μ m resolution and (d) 5 μ m resolution	80
Figure 3.11:	SEM image of GACO383 (a) 50 µm resolution and (b) 10 µm resolution	80
Figure 3.12:	SEM image of GACZC1073 (a) 100 μ m resolution (b) 50 μ m resolution (c) 10 μ m resolution and (d) 5 μ m resolution	
Figure 3.13:	TEM image of GAC383 (a) 200 nm resolution (b) 100 nm resolution (c) 50 nm resolution (d) 20 nm resolution	82
Figure 3.14:	TEM image of GACO383 (a) 200 nm resolution (b) 100 nm resolution (c) 50 nm resolution (d) 20 nm resolution	83
Figure 3.15:	TEM image of GACZC1073 (a) 20 nm resolution (b) 20 nm resolution (c) 5 nm resolution (d) 2 nm resolution	
Figure 3.16:	N_2 adsorption – desorption isotherm at 77K of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)	86
Figure 3.17:	BET isotherm plot of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)	88
Figure 3.18:	<i>I</i> plot of modified granular activated carbons (a) GAC383, (b) GAC0383, (c) GACZC873, (d) GACZC1073 & (e) GACZC1273	
Figure 3.19:	Langmuir isotherm plot of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073& GACZC1273)	93
Figure 3.20:	Freundlich isotherm plot of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073& GACZC1273)	93
Figure 3.21:	John isotherm plot of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)	93
Figure 3.22:	α_s isotherm plot of modified granular activated carbons (GAC383, GAC0383, GACZC873, GACZC1073 & GACZC1273)	

Figure 3.23:	Dubinin - Radushkevich (D – R) isotherm plot of modified granular activated carbons (GAC383, GAC0383, GACZC873, GACZC1073 & GACZC1273)96
Figure 3.24:	<i>t</i> - plot of modified granular activated carbons (GAC383, GAC0383, GAC2C873, GACZC1073 & GACZC1273)
Figure 3.25:	BJH adsorption cumulative pore volume of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)
Figure 3.26(a)	BJH desorption cumulative pore volume of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)
Figure 3.26(b)	BJH desorption dV/dlogW pore volume of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)
Figure 3.26(c)	BJH desorption dV/dW pore volume of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)
Figure 3.27:	Adsorbed quantity as a function of carbon dosage for the removal of phenol on GAC383 (C_0 : 1000 mg/L)101
Figure 3.28:	Effect of contact time for the adsorption of phenol by GAC383 & GACO383 (C ₀ : 1000 mg/L)101
Figure 3.29:	Comparison of adsorption efficiency of Zn^{2+} impregnated carbon GACZC series (C ₀ : 1000 mg/L)102
Figure 3.30:	Effect of contact time on the adsorption of phenol on GAC383 at different temperatures (C ₀ : 250 mg/L)103
Figure 3.31:	Effect of contact time on the adsorption of phenol on GACO383 at different temperatures (C_0 : 250 mg/L)103
Figure 3.32:	Effect of contact time on the adsorption of phenol on GACZC1073 at different temperatures (C_0 : 250 mg/L)104
Figure 3.33:	Psuedo first order kinetics of phenol on GAC383 at different temperatures (C_0 : 250 mg/L)105
Figure 3.34:	Psuedo first order kinetics of phenol on GACO383 at different temperatures (C_0 : 250 mg/L)105
Figure 3.35:	Pseudo first order kinetics of phenol on GACZC1073 at different temperatures (C ₀ : 250 mg/L)105
Figure 3.36:	Pseudo second order kinetics of phenol on GAC383 at different temperatures (C ₀ : 250 mg/L)105
Figure 3.37:	Pseudo second order kinetics of phenol on GACO383 at different temperatures (C_0 : 250 mg/L)106
Figure 3.38:	Pseudo second order kinetics of phenol on GACZC1073 at different temperatures (C ₀ : 250 mg/L)106

Figure 3.39:	Intraparticle diffusion model plot of phenol adsorption on GAC383 at temperatures (C ₀ : 250 mg/L)110
Figure 3.40:	Intraparticle diffusion model plot of phenol adsorption on GACO383 at temperatures (C_0 : 250 mg/L)110
Figure 3.41:	Intraparticle diffusion model plot of phenol adsorption on GACZC1073 at temperatures (C ₀ : 250 mg/L)110
Figure 3.42:	Boyd plots for phenol adsorption on GAC383 at different temperatures (C ₀ : 250 mg/L)110
Figure 3.43:	Boyd plots for phenol adsorption on GACO383 at different temperatures (C ₀ : 250 mg/L)111
Figure 3.44:	Boyd plots for phenol adsorption on GACZC1073 at different temperatures (C ₀ : 250 mg/L)111
Figure 3.45:	Plot of ln K_2 versus 1/T for the adsorption of phenol on new carbons (GAC383, GAC0383 and GACZC1073)112
Figure 3.46:	Adsorption of phenol on GAC383, GACO383 and GACZC1073 at 10^{0} C (C ₀ : 25 - 3000 mg/L)113
Figure 3.47:	Adsorption of phenol on GAC383, GACO383 and GACZC1073 at 20° C (C ₀ : 25 - 3000 mg/L)113
Figure 3.48:	Adsorption of phenol on GAC383, GACO383 and GACZC1073 at 30° C (C ₀ : 25 - 3000 mg/L)113
Figure 3.49:	Adsorption of phenol on GAC383, GACO383 and GACZC1073 at 40^{0} C (C ₀ : 25 - 3000 mg/L)113
Figure 3.50:	Adsorption of phenol on GAC383, GACO383 and GACZC1073 at 50° C (C ₀ : 25 - 3000 mg/L)114
Figure 3.51:	Langmuir isotherm model of phenol on GAC383 at different temperatures (C_0 : 25 - 3000 mg/L)115
Figure 3.52:	Langmuir isotherm model of phenol on GACO383 at different temperatures (C ₀ : 25 - 3000 mg/L)115
Figure 3.53:	Langmuir isotherm model of phenol on GACZC1073 at different temperatures (C ₀ : 25 - 3000 mg/L)116
Figure 3.54:	Freundlich isotherm model for phenol adsorption on GAC383 at different temperatures (C_0 : 25 - 3000 mg/L)116
Figure 3.55:	Freundlich isotherm model for phenol adsorption on GACO383 at different temperatures (C_0 : 25 - 3000 mg/L)116
Figure 3.56:	Freundlich isotherm model for phenol adsorption on GACZC1073 at different temperatures (C_0 : 25 - 3000 mg/L)116
Figure 3.57:	Temkin isotherm model of phenol on GAC383 at different temperatures (C ₀ : 25 - 3000 mg/L)
Figure 3.58:	Temkin isotherm model of phenol on GACO383 at different temperatures (C_0 : 25 - 3000 mg/L)118

Figure 3.59:	Temkin isotherm model of phenol on GACZC1073 at different temperatures (C ₀ : 25 - 3000 mg/L)119
Figure 3.60:	ΔG versus Temperature (<i>T</i>) for determination of thermodynamic parameters for the adsorption of phenol onto (a) GAC383, (b) GACO383 & (c) GACZC1073
Figure 3.61:	Effect of contact time for the adsorption of p – nitrophenol (GAC383 &GACO383) (C ₀ : 1000 mg/L)124
Figure 3.62:	Effect of contact time and amount of p -nitrophenol adsorbed for the adsorption on GACZC activated at different temperatures (C ₀ : 1000 mg/L)125
Figure 3.63:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACZC1073 at 10 ^o C (C ₀ : 250 mg/L)
Figure 3.64:	Effect of contact time on the adsorption of p - nitrophenol on GAC383, GACO383 and GACZC1073 at 20^{0} C (C ₀ : 250 mg/L)
Figure 3.65:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACZC1073 at 30 ^o C (C ₀ : 250 mg/L)
Figure 3.66:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACZC1073 at 40 ^o C (C ₀ : 250 mg/L)
Figure 3.67:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACZC1073 at 50 ^o C (C ₀ : 250 mg/L)
Figure 3.68:	Pseudo - first order kinetics of p -nitrophenol on GAC383 at temperatures (C ₀ : 250 mg/L)
Figure 3.69:	Pseudo - first order kinetics of p -nitrophenol on GACO383 at temperatures (C ₀ : 250 mg/L)128
Figure 3.70:	Pseudo - first order kinetics of p -nitrophenol on GACZC1073 at temperatures (C ₀ : 250 mg/L)129
Figure 3.71:	Ho - second order kinetics of p -nitrophenol on GAC383 at temperatures (C ₀ : 250 mg/L)129
Figure 3.72:	Ho - second order kinetics of p -nitrophenol on GACO383 at temperatures (C ₀ : 250 mg/L)129
Figure 3.73:	Ho - second order kinetics of p -nitrophenol on GACZC1073 at temperatures (C ₀ : 250 mg/L)129
Figure 3.74:	Intraparticle diffusion model of p -nitrophenol on GAC383 at different temperatures (C ₀ : 250 mg/L)131
Figure 3.75:	Intraparticle diffusion model of p -nitrophenol on GACO383 at different temperatures (C ₀ : 250 mg/L)131

Figure 3.76:	Intraparticle diffusion model of p -nitrophenol on GACZC1073 at different temperatures (C ₀ : 250 mg/L)131
Figure 3.77:	Elovich kinetic model of p – nitrophenol on GAC383 at different temperatures (C ₀ : 250 mg/L)131
Figure 3.78:	Elovich kinetic model of p - nitrophenol on GACO383 at different temperatures (C ₀ : 250 mg/L)
Figure 3.79:	Elovich kinetic model of p - nitrophenol on GACZC1073 at different temperatures (C ₀ : 250 mg/L)
Figure 3.80	Plot of ln K_2 versus 1/T for the adsorption of p - nitrophenol on GAC383 (C ₀ : 250 mg/L)133
Figure 3.81:	Plot of ln K_2 versus 1/T for the adsorption of p - nitrophenol on GACO383 (C ₀ : 250 mg/L)
Figure 3.82:	Plot of ln K_2 versus 1/T for the the adsorption of p - nitrophenol on GACZC1073 (C ₀ : 250 mg/L)133
Figure 3.83:	Adsorption isotherm of <i>p</i> - nitrophenol on GAC383, GACO383 & GACZC1073 at 10^{0} C (C ₀ : 25 - 3000 mg/L)
Figure 3.84:	Adsorption isotherm of <i>p</i> - nitrophenol on GAC383, GACO383 & GACZC1073 at 20^{0} C (C ₀ : 25 - 3000 mg/L)134
Figure 3.85:	Adsorption isotherm of <i>p</i> - nitrophenol on GAC383, GACO383 & GACZC1073 at 30^{0} C (C ₀ : 25 - 3000 mg/L)134
Figure 3.86:	Adsorption isotherm of <i>p</i> - nitrophenol on GAC383, GACO383 & GACZC1073 at 40^{0} C (C ₀ : 25 - 3000 mg/L)135
Figure 3.87:	Adsorption isotherm of <i>p</i> - nitrophenol on GAC383, GACO383 & GACZC1073 at 50^{0} C (C ₀ : 25 - 3000 mg/L)135
Figure 3.88:	Langmuir isotherm model of p - nitrophenol adsorption on GAC383 at different temperatures (C ₀ : 25 - 3000 mg/L)
Figure 3.89:	Langmuir isotherm model of p - nitrophenol adsorption on GACO383 at different temperatures (C ₀ : 25 - 3000 mg/L)137
Figure 3.90:	Langmuir isotherm model of p - nitrophenol adsorption on GACZC1073 at different temperatures (C ₀ : 25 - 3000
Figure 3.91:	mg/L)
Figure 3.92:	Separation factor of GACO383 under different initial concentration of p - nitrophenol at different temperatures (C ₀ : 25 - 3000 mg/L)
Figure 3.93:	Separation factor of GACZC1073 under different initial concentration of p - nitrophenol at different temperatures (C ₀ : 25 - 3000 mg/L)
Figure 3.94:	Freundlich isotherm model of p - nitrophenol adsorption on GAC383 at different temperatures (C ₀ : 25 - 3000 mg/L)
Figure 3.95:	Freundlich isotherm model of p - nitrophenol adsorption on GACO383 at different temperatures (C ₀ : 25 - 3000 mg/L)138
---------------	---
Figure 3.96:	Freundlich isotherm model of p - nitrophenol adsorption on GACZC1073 at different temperatures (C ₀ : 25 - 3000 mg/L)139
Figure 3.97:	Temkin isotherm model of p - nitrophenol adsorption on GAC383 at different temperatures (C ₀ : 25 - 3000 mg/L)139
Figure 3.98:	Temkin isotherm model of p - nitrophenol adsorption on GAC383 at different temperatures (C ₀ : 25 - 3000 mg/L)139
Figure 3.99:	Temkin isotherm model of p - nitrophenol adsorption on GAC383 at different temperatures (C ₀ : 25 - 3000 mg/L)139
Figure 3.100:	Plot of ln K_L versus 1/T for estimation of thermodynamic parameters for the adsorption of <i>p</i> - nitrophenol onto (a) GAC383, (b) GACO383 and (c) GACZC1073141
Figure 3.101:	Adsorbent dosage for the removal of methylene blue (MB) (C ₀ : 500 mg/L)143
Figure 3.102:	Effect of contact time for the adsorption of methylene blue (MB) on GAC383 & GACO383 (C ₀ : 500 mg/L)143
Figure 3.103:	Selection of carbons from the GACZC series for the adsorption of MB (C ₀ : 500mg/L)144
Figure 3.104:	Effect of contact time on the adsorption of MB on GAC383 at different temperatures (C_0 : 250 mg/L)146
Figure 3.105:	Effect of contact time on the adsorption of MB on GACO383 at different temperatures (C_0 : 250 mg/L)146
Figure 3.106:	Effect of contact time on the adsorption of MB on GACZC1073 at different temperatures (C_0 : 250 mg/L)146
Figure 3.107:	Pseudo -first order kinetics of MB on GAC383 at different temperatures (C_0: 250 mg/L) 147
Figure 3.108:	Pseudo -first order kinetics of MB on GACO383 at different temperatures (C_0: 250 mg/L)147
Figure 3.109:	Pseudo -first order kinetics of MB on GACZC1073 at different temperatures (C_0: 250 mg/L)147
Figure 3.110:	Psuedo second order kinetics of methylene blue adsorption on GAC383 at different temperatures (C ₀ : 250 mg/L)
Figure 3.111:	Psuedo second order kinetics of methylene blue adsorption on GACO383 at different temperatures $(C_0: 250 \text{ mg/L})$
Figure 3.112:	Psuedo second order kinetics of methylene blue adsorption on GACZC1073 at different temperatures (C_0 : 250 mg/L)
Figure 3.113:	Intraparticle diffusion model of methylene blue adsorption on GAC383 at different temperatures (C_0 : 250 mg/L)148

Figure 3.114:	Intraparticle diffusion model of methylene blue adsorption on GACO383 at different temperatures (C_0 : 250 mg/L)149
Figure 3.115:	Intraparticle diffusion model of methylene blue adsorption on GACZC1073 at different temperatures $(C_0: 250 \text{ mg/L})$
Figure 3.116:	Boyd plots for methylene blue adsorption on GAC383 at different temperatures (C_0 : 250 mg/L)151
Figure 3.117:	Boyd plots for methylene blue adsorption on GACO383 at different temperatures (C ₀ : 250 mg/L)151
Figure 3.118:	Boyd plots for methylene blue adsorption on GACZC1073 at different temperatures (C_0 : 250 mg/L)151
Figure 3.119:	Plot of ln K_2 versus 1/T for the adsorption of methylene blue on GAC383 (C_0 : 250 mg/L)
Figure 3.120:	Plot of ln K ₂ versus 1/T for the adsorption of methylene blue on GACO383 (C ₀ : 250 mg/L)
Figure 3.121:	Plot of ln K ₂ versus 1/T for the adsorption of methylene blue on GACZC1073 (C ₀ : 250 mg/L)152
Figure 3.122:	Adsorption isotherm of methylene blue (MB) adsorption on GAC383 at different temperatures for $C_0 : 25 - 1500 \text{ mg/L}$ 156
Figure 3.123:	Adsorption isotherm of methylene blue (MB) adsorption on GACO383 at different temperatures for C_0 : 25 -1500 mg/L
Figure 3.124:	Adsorption isotherm of methylene blue (MB) adsorption on GACZC1073 at different temperatures for C_0 : 25 - 1500 mg/l
Figure 3.125:	Langmuir isotherm model of methylene blue (MB) adsorption on GAC383 at different temperatures C_0 : 25 - 1500 mg/L
Figure 3.126:	Langmuir isotherm model of methylene blue (MB) adsorption on GACO383 at different temperatures C_0 : 25 -1500 mg/L
Figure 3.127:	Langmuir isotherm model of methylene blue (MB) adsorption on GACZC1073 at different temperatures C_0 : 25 -1500 mg/L
Figure 3.128:	Freundlich isotherm model of methylene blue (MB) adsorption on GAC383 at different temperatures $C_0: 25 - 1500 \text{ mg/L}$
Figure 3.129:	Freundlich isotherm model of methylene blue (MB) adsorption on GACO383 at different temperatures $C_0: 25$ -1500 mg/L
Figure 3.130:	Freundlich isotherm model of methylene blue (MB) adsorption on GACZC1073 at different temperatures $C_0: 25 - 1500 \text{ mg/L}$

Figure 3.131:	Temkin isotherm model of methylene blue (MB) adsorption on GAC383 at different temperatures $C_0 \colon 25$ -1500 mg/L158
Figure 3.132:	Temkin isotherm model of methylene blue (MB) adsorption on GACO383 at different temperatures $C_0: 25$ -1500 mg/L
Figure 3.133:	Temkin isotherm model of methylene blue (MB) adsorption on GACZC1073 at different temperatures C_0 : 25 -1500 mg/L
Figure 3.134:	lnK_D versus 1/T for the adsorption methylene blue (MB) on GAC383 for C ₀ : 25 -1500 mg/L162
Figure 3.135:	$lnK_{\rm D}$ versus 1/T for the adsorption methylene blue (MB) on GACO383 for C_0 : 25 -1500 mg/L 162
Figure 3.136:	lnK_D versus 1/T for the adsorption methylene blue (MB) on GACZC1073 for C_0 : 25 -1500 mg/L162
Figure 3.137:	Langmuir isotherm model at equilibrium temperature 30° C on (a) Phenol adsorption by granular activated carbons (b) <i>p</i> –nitrophenol adsorption by GAC383, GACO383 & GACZC1073 (c) methylene blue (MB)
Figure 3.138:	adsorption by GAC383, GACO383 & GACZC1073164 John Sivanandan Achari isotherm model for the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACZC1073 (d) John Sivanandan Achari isotherm model for the adsorption of p - nitrophenol on new carbons & John Sivanandan Achari isotherm model for the adsorption of methylene blue on (e) GAC383 (f) GACO383 & (g) GACZC1073
Figure 3.139:	BET and <i>I</i> plot model for the adsorption of Phenol (a) GAC383, (b) GACO383 and GACZC1073
Figure 3.140:	BET and <i>I</i> plot model for the adsorption of <i>p</i> - nitrophenol (a) GAC383, (b) GACO383 and (c) GACZC1073
Figure 3.141:	BET isotherm model for the adsorption of methylene blue (MB) on new carbons
Figure 3.142:	<i>I</i> plot model for the adsorption of methylene blue (MB) on new carbons
Figure 4.1:	Carbon yield and burn - off pattern of GACOZC series activated at different temperatures
Figure 4.2(a):	FTIR spectra of GAC383
Figure 4.2(b):	FTIR spectra of GACO383
Figure 4.3:	FTIR spectra of new carbons (a) GACOZC383, (b) GACOZC473, (c) GACOZC673, (d) GACOZC873, (e) GACOZC1073 & (f) GACOZC1273
	(c) Offeedeelors a (f) Offeedeel275190

Figure 4.4(a):	X-ray photoelectron spectra of GAC383	. 191
Figure 4.4(b):	X-ray photoelectron spectra of GACO383	. 191
Figure 4.4(c):	X-ray photoelectron spectra of GACZC1073	. 191
Figure 4.5(a):	High resolution C 1s spectrum of GACOZC1073	. 192
Figure 4.5(b):	High resolution O 1s spectrum of GACOZC1073	. 192
Figure 4.6(a):	X-ray diffractograms of GAC383	. 193
Figure 4.6(b):	X-ray diffractograms of GACO383	. 193
Figure 4.7:	X-ray diffractograms of modified carbons (a) GACOZC383,	
	(b) GACOZC473, (c) GACOZC673, (d) GACOZC873,	
	(e) GACOZC1073 and (f) GACOZC1273	. 194
Figure 4.8:	SEM image of 50 μm resolution (a) GAC383 (b) GACO383	
	& (c) GACOZC1073	. 196
Figure 4.9:	SEM image of 10 μ m resolution (a) GAC383 (b) GACO383	106
E	& (c) GACU2C10/5	. 190
Figure 4.10:	SEM image of 5 μ m resolution (a) GAC383 (b) GAC0383 & (c) GAC07C1073	197
Figure 4 11.	TEM image of 20 nm resolution (a) $GAC383$ (b) $GAC0383$. 177
11guie 4.11.	& (c) GACOZC1073	. 197
Figure 4.12:	TEM image of GACOZC1073 (a) 10 nm resolution (b) 5	, .
8	nm resolution (c) 2 nm resolution (d) 5 1/ nm Diffraction	
	pattern	. 198
Figure 4.13:	N_2 adsorption – desorption isotherm at 77K of modified	
	granular activated carbons (GAC383, GACO383,	
	GACOZC873& GACOZC1073)	. 199
Figure 4.14:	BET isotherm plot for modified granular activated	
	carbons (GAC383, GAC0383, GAC0ZC8/3 & GAC0ZC8/3 &	201
Figure 4 15:	L plot for modified groupular activated carbons (c) CAC292	. 201
Figure 4.15.	(b) $GACO383$ (c) $GACOZC873$ & (d) $GACOZC1073$	204
Figure 4 16 [.]	Monolaver adsorption capacity from BET and Iplot method	
inguie mio	using modified granular activated carbons (GAC383,	
	GACO383, GACOZC873 and GACOZC1073)	. 204
Figure 4.17:	Specific surface area calculated by BET and I plot method	
	using modified granular activated carbons (GAC383,	
	GACO383, GACOZC873 and GACOZC1073)	. 204
Figure 4.18:	Langmuir isotherm plot of modified granular activated	
	carbons (GAC383, GAC0383, GAC0ZC873&	200
E	UACUZCIU/3)	206
Figure 4.19:	carbons (GAC383 GAC0282 GAC07C972 %	
	GACOZC1073)	206
		. 200

Figure 4.20:	John isotherm plot of modified granular activated carbons (GAC383, GACO383, GACOZC873 & GACOZC1073)
Figure 4.21:	Alpha S (α_s) isotherm plot for modified granular activated carbons (GAC383, GACO383, GACOZC873 & GACOZC1073)
Figure 4.22:	Dubinin – Radushkevich (D-R) isotherm plot of modified granular activated carbons (GAC383, GACO383, GACOZC873 & GACOZC1073)
Figure 4.23:	<i>t - plot</i> of modified granular activated carbons (GAC383, GAC0383, GAC0ZC873 & GAC0ZC1073)
Figure 4.24:	BJH adsorption cumulative pore volume of modified granular activated carbons (GAC383, GACO383, GACO2C873& GACOZC1073)
Figure 4.25:	BJH desorption dV/dW pore volume of modified granular activated carbons (GAC383, GACO383, GACO2C873 & GACOZC1073)
Figure 4.26:	Comparison of adsorption efficiency of Zn^{2+} impregnated carbon GACOZC series (C ₀ : 1000 mg/L)212
Figure 4.27:	Effect of contact time on the adsorption of phenol on GAC383 at different temperatures for $C_0 = 250 \text{ mg/L}212$
Figure 4.28:	Effect of contact time on the adsorption of phenol on GACO383 at different temperatures for $C_0 = 250 \text{ mg/L} \dots 212$
Figure 4.29:	Effect of contact time on the adsorption of phenol on GACOZC1073 at different temperatures for $C_0 = 250$ mg/L
Figure 4.30:	Psuedo - first order kinetics of phenol (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$
Figure 4.31:	Ho second order kinetics of phenol on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$ 215
Figure 4.32:	Intraparticle diffusion model of Phenol on (a) GAC383 (b) GAC0383 & (c) GAC0ZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$
Figure 4.33:	Boyd plots for Phenol adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$
Figure 4.34:	Plot of ln K ₂ versus 1/T for the adsorption of phenol on modified activated carbons for $C_0 = 250 \text{ mg/L} \dots 219$
Figure 4.35:	Adsorption isotherm of GAC383 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$

Figure 4.36:	Adsorption isotherm of GACO383 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L} \dots 220$
Figure 4.37:	Adsorption isotherm of GACOZC1073 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L} \dots 220$
Figure 4.38:	Langmuir isotherm model of phenol (a) GAC383 (b) GAC0383 & (c) GAC0ZC1073 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$
Figure 4.39:	Freundlich isotherm model of phenol (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$
Figure 4.40:	Temkin isotherm model of phenol on GAC383 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$
Figure 4.41:	Temkin isotherm model of phenol on GACO383 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$ 224
Figure 4.42:	Temkin isotherm model of phenol on GACOZC1073 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$
Figure 4.43:	ΔG versus Temperature for the adsorption of phenol onto GAC383, GACO383 & GACOZC1073227
Figure 4.44:	Effect of contact time and amount of p -nitrophenol adsorbed for the adsorption on GACOZC activated at different temperatures (C ₀ = 1000 mg/L)
Figure 4.45:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACOZC1073 at 10 ^o C for $C_0 = 250 \text{ mg/L}$ 229
Figure 4.46:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACOZC1073 at 20 ^o C for $C_0 = 250 \text{ mg/L}$
Figure 4.47:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACOZC1073 at 30 ^o C for $C_0 = 250 \text{ mg/L}$
Figure 4.48:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACOZC1073 at 40 ^o C for $C_0 = 250 \text{ mg/L}$ 230
Figure 4.49:	Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACOZC1073 at 50 ^o C for $C_0 = 250 \text{ mg/L}$ 230
Figure 4.50:	Pseudo - first order kinetics of p -nitrophenol adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$ 232
Figure 4.51:	Pseudo - second order kinetics of p - nitrophenol adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for C ₀ = 250 mg/L

Figure 4.52:	Intraparticle diffusion model of <i>p</i> -nitrophenol adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250$ mg/L
Figure 4.53:	Elovich kinetic model of p –nitrophenol adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for C ₀ = 250 mg/L
Figure 4.54(a):Plot of lnK_2 versus $1/T$ for the estimation of activation energy for the adsorption of p -nitrophenol on GAC383 & GACO383 for $C_0 = 250 \text{ mg/L}$
Figure 4.54(b): Plot of lnK_2 versus $1/T$ for the estimation of activation energy for the adsorption of p -nitrophenol on GACOZC1073 for C ₀ = 250 mg/L
Figure 4.55:	Adsorption isotherm of p – nitrophenol on GAC383 at different temperatures for C ₀ = 25 - 3000 mg/L236
Figure 4.56:	Adsorption isotherm of p - nitrophenol on GACO383 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$
Figure 4.57:	Adsorption isotherm of p - nitrophenol on GACOZC1073 at different temperatures for C ₀ = 25 - 3000 mg/L
Figure 4.58:	Langmuir isotherm model of p – nitrophenol adsorption (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for C ₀ = 25 - 3000 mg/L239
Figure 4.59:	Separation factor of (a) GAC383, (b) GAC0383 & (c) GAC0ZC1073 under different initial concentration of p - nitrophenol at different temperatures for C ₀ = 25-3000 mg/L
Figure 4.60:	Freundlich isotherm model of p – nitrophenol adsorption (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_{r} = 25$, 3000 mg/l 241
Figure 4.61:	Temkin isotherm model of p – nitrophenol adsorption (a) GAC383 (b) GACO383 & (c) GACOZC1073 at
Figure 4.62:	different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$
Figure 4.63:	Selection of carbons from the GACOZC series for methylene blue (MB) adsorption $C_0 = 500 \text{ mg/L} \dots 244$
Figure 4.64:	Effect of contact time on the adsorption of methylene blue (MB) on GAC383 at different temperatures for $C_0 = 250 \text{ mg/L}$.
Figure 4.65:	Effect of contact time on the adsorption of methylene blue (MB) on GACO383 at different temperatures for $C_0 = 250 \text{ mg/L} \dots 245$

Figure 4.66:	Effect of contact time on the adsorption of methylene blue (MB) on GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$	245
Figure 4.67:	Psuedo -first order kinetics of methylene blue (MB) adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$	247
Figure 4.68:	Psuedo -second order kinetics of methylene blue (MB) adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$	247
Figure 4.69:	Intraparticle diffusion model of methylene blue (MB) adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$	249
Figure 4.70:	Boyd plots for methylene blue (MB) adsorption on (a) GAC383 (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$	249
Figure 4.71(a)	: Plot of $ln K_2$ versus $1/T$ for adsorption of methylene blue on GAC383 for $C_0 = 250 \text{ mg/L}$	250
Figure 4.71(b)): Plot of $ln K_2$ versus l/T for the adsorption of methylene blue on GACO383 for C ₀ = 250 mg/L	250
Figure 4.71(c)): Plot of $ln K_2$ versus $1/T$ for the adsorption of methylene blue on GACOZC1073 for $C_0 = 250 \text{ mg/L}$	250
Figure 4.72:	Adsorption isotherm of methylene blue (MB) adsorption on (a) GAC383, (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 25 - 1500 \text{ mg/L}$	253
Figure 4.73:	Langmuir isotherm model of methylene blue (MB) adsorption on (a) GAC383, (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 25$ -	
Figure 4.74:	1500 mg/L Freundlich isotherm model of methylene blue (MB) adsorption on (a) GAC383, (b) GACO383 & (c)	253
	GACO2C10/3 at different temperatures for $C_0 = 25 - 1500 \text{ mg/L}$	255
Figure 4.75:	Temkin isotherm model of methylene blue (MB) adsorption on (a) GAC383, (b) GACO383 & (c) GACOZC1073 at different temperatures for $C_0 = 25 - 1500 \text{ mg/J}$	255
Figure 4.76:	$ln K_D$ versus 1/T for the adsorption of methylene blue (MB) on GAC383 for C ₀ = 25 - 1500 mg/L	255
Figure 4.77:	$ln K_D$ versus 1/T for the adsorption of methylene blue (MB) GACO383 for $C_0 = 25 - 1500 \text{ mg/L}$	
Figure 4.78:	<i>ln</i> K_D versus 1/T for the adsorption of methylene blue (MB) GACOZC1073 for C ₀ = 25 - 1500 mg/L	257

Figure 4.79:	John SivanadanAchari (J-SA) isotherm plot for phenol, <i>p</i> – nitrophenol and methylene blue adsorption by GAC383	261
Figure 4.80:	John SivanadanAchari (J-SA) isotherm plot for phenol, p – nitrophenol and methylene blue adsorption by GACO383	261
Figure 4.81:	John SivanadanAchari (J-SA) isotherm plot for phenol, p – nitrophenol and methylene blue adsorption by GACOZC1073	261
Figure 4.82:	Langmuir isotherm model for the adsorption of Phenol by GAC383, GACO383 and GACOZC1073	262
Figure 4.83:	Langmuir isotherm model for the adsorption of p - nitrophenol by GAC383, GAC0383 and GAC0ZC1073	262
Figure 4.84:	Langmuir isotherm model for the adsorption of methylene blue by GAC383, GACO383and GACOZC1073	262
Figure 4.85:	BET and <i>I</i> plot model for the adsorption of Phenol (a) GAC383, (b) GACO383 and (c) GACOZC1073	263
Figure 4.86:	BET and <i>I</i> plot model for the adsorption of p - nitrophenol (a) GAC383, (b) GACO383 and (c) GACOZC1073	263
Figure 4.87:	The general isotherm and I plot of (a) GAC383 (b) GACO383 & (c) GACOZC1073 on MB adsorption	265
Figure 5.1:	Preparation of nano zinc oxide (NZnO)	278
Figure 5.2:	Nano zinc oxide (NZnO) prepared in the laboratory	278
Figure 5.3:	X -ray diffractograms of methanol mediated nano ZnO	279
Figure 5.4:	EDX spectrum of prepared nano ZnO	280
Figure 5.5:	SEM image of nano ZnO (a) 5 μm resolution (b) 1 μm resolution	281
Figure 5.6:	TEM image of nano ZnO (a) 100 nm magnification, (b) & (c) 50 nm magnification & (d) 20 nm magnification	281
Figure 5.7:	Carbon yield and burn - off pattern of GACNZnO activated at different temperatures	283
Figure 5.8:	The FTIR spectra of GACNZnO activated at different	
	temperatures	285
Figure 5.9:	XPS spectra of (a) GAC383, (b) GACO383 and (c) GACNZnO1273	286
Figure 5.10:	Deconvoluted XPS of GACNZnO1273 (a) C1s region (b) O1s region	287
Figure 5.11:	X-ray diffractograms of modified carbons(a) GACNZnO383, (b) GACNZnO473, (C) GACNZnO673, (d) GACNZnO873,	
	(e) GACNZnO1073 and (f) GACNZnO1273	289
Figure 5.12:	SEM image of GACNZnO1273 (a) 100 µm resolution (b) 50 µm resolution (c) 10 µm resolution and (d) 5 µm resolution	290
Figure 5.13:	TEM image of GACNZnO1273 (a) 10 nm resolution, (b) 5 nm resolution (c) 2 nm resolution (d) 5 1/ nm diffraction pattern	291

Figure 5.14:	N ₂ adsorption – desorption isotherm at 77K for modified granular activated carbons GAC383 & GAC0383	292
Figure 5.15:	N ₂ adsorption – desorption isotherm at 77K for modified granular activated carbons GACNZnO873, GACZNZnO1073 & GACNZnO1273	292
Figure 5.16:	BET isotherm model for the modified granular activated carbons of GACNZnO series	293
Figure 5.17:	<i>I</i> plot for modified granular activated carbons (a) GAC383 (b) GACO383 (c) GACNZnO873 (d) GACNZnO1073 & (e) GACNZnO1273	
Figure 5.18:	Comparison study of SA(BET) and SA(I) of the modified carbons of GACNZnO series	293
Figure 5.19:	Langmuir isotherm model for modified granular activated carbons (GAC383, GACO383, GACNZnOC873, GACNZnO1073 & GACNZnO1273)	299
Figure 5.20:	Freundlich isotherm model for modified granular activated carbons (GAC383, GAC0383, GACNZnOC873, GACNZnO1073 & GACNZnO1273)	299
Figure 5.21:	John isotherm model for modified granular activated carbons (GAC383, GACO383, GACNZnOC873, GACNZnO1073 & GACNZnO1273)	299
Figure 5.22:	Alpha S (α_s) plot for modified granular activated carbons (GAC383, GACO383, GACNZnOC873, GACNZnO1073 & GACNZnO1273)	
Figure 5.23:	Dubinin – Radushkevich (D – R) isotherm model for modified granular activated carbons (GAC383, GAC0383, GACNZnOC873, GACNZnO1073 & GACNZnO1273)	300
Figure 5.24:	Comparative study of micropore volume determined from α_s plot and D - R isotherm method	300
Figure 5.25:	<i>t</i> - <i>plot</i> of modified granular activated carbons (a) GAC383 & GACO383, (b) GACNZnO873, GACNZnO1073 & GACNZnO1273	302
Figure 5.26:	BJH Pore size distribution of modified granular activated carbons GAC383, GACO383, GACNZnO873, GACNZnO1073 & GACNZnO1273 (a) BJH adsorption cumulative pore volume against pore width & (b) BJH desorption cumulative pore volume against pore width (c) BJH desorption dV/dW pore volume versus pore width (d) BJH desorption dV/dlogW pore volume against pore width	303
Figure 5.27:	Amount of phenol adsorbed by members of GACNZnO series ($C_0 = 1000 \text{ mg/L}$)	306

Figure 5.28:	Effect of contact time on the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0 = 250$ mg/L	
Figure 5.29:	Psuedo - first order kinetics model for the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$	309
Figure 5.30:	Psuedo - second order kinetic model for the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$	309
Figure 5.31:	Intraparticle diffusion model for the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$.	
Figure 5.32:	Boyd kinetic model for the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$	
Figure 5.33:	plot of lnK_2 versus 1/T for the determination of activation energy for the adsorption of phenol on GAC383, GAC0383 & GACNZnO1273	
Figure 5.34:	Adsorption of phenol on GAC383, GACO383 and GACNZnO1273 at different temperature (a) 10° C, (b) 20° C (c) 30° C (d) 40° C & (e) 50° C for initial concentration C ₀ = 25 – 3000 mg/L	
Figure 5.35:	Langmuir isotherm model of phenol on (a) GAC383, (b) GAC0383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0: 25 - 3000 \text{ mg/L}$	
Figure 5.36:	Freundlich isotherm model of phenol on (a) GAC383, (b) GAC0383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0: 25 - 3000 \text{ mg/L}$	
Figure 5.37:	Temkin isotherm model of phenol on (a) GAC383, (b) GAC0383 & (c) GACNZnO1273 by different temperatures for $C_0: 25 - 3000 \text{ mg/L}$	
Figure 5.38:	ΔG versus Temperature for the determination of thermodynamic parameters for the adsorption of phenol by (a) GAC383, (b) GACO383 & (c) GACNZnO1273	
Figure 5.39:	Effect of contact time and amount of p -nitrophenol adsorbed for the adsorption on GACNZnO activated at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$	
Figure 5.40:	Effect of contact time on the adsorption of <i>p</i> -nitrophenol on GAC383, GACO383 and GACNZnO1273 at different temperature (a) 10° C, (b) 20° C, (c) 30° C, (d) 40° C & (e) 50° C for initia concentration C ₀ = 250 mg/L	

Figure 5.41:	Pseudo - first order kinetics of <i>p</i> -nitrophenol adsorption on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 at different temperatures ; $C_0 = 250 \text{ mg/L}$	326
Figure 5.42:	Pseudo - second order kinetics of p -nitrophenol adsorption on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 at different temperatures ; $C_0 = 250 \text{ mg/L}$	326
Figure 5.43:	Intraparticle diffusion model of p -nitrophenol adsorption on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 ; $C_0 = 250 \text{ mg/L}$	328
Figure 5.44:	Elovich kinetic model of p -nitrophenol adsorption on (a) GAC383 (b) GACO383 & (c) GACNZnO1273 ; C ₀ = 250 mg/L	328
Figure 5.45:	Activate on energy for the adsorption of p -nitrophenol on new carbons; $C_0 = 250 \text{ mg/L}$	
Figure 5.46:	Adsorption isotherm of (a) GAC383, (b) GAC0383 & (c) GACNZnO1273 at different temperature <i>P</i> -nitrophenol as adsorbate for initial concentration $C_0 = 25$ -3000 mg/L	331
Figure 5.47:	Langmuir isotherm model of p – nitrophenol adsorption on (a) GAC383, (b) GACO383 & (c) GACNZnO1273 at different temperatures for initial concentration C ₀ = 25 – 3000 mg/L	333
Figure 5.48:	separation factor of p – nitrophenol adsorption on (a) GAC383, (b) GACO383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0 = 25 - 3000 \text{ mg/L}$	333
Figure 5.49:	Freundlich isotherm model of p – nitrophenol adsorption on (a) GAC383, (b) GACO383 & (c) GACNZnO1273 at different temperatures for C ₀ = 25 – 3000 mg/L	334
Figure 5.50:	Temkin isotherm model of p – nitrophenol adsorption on (a) GAC383, (b) GACO383 & (c) GACNZnO1273 at different temperatures for C ₀ = 25 – 3000 mg/L	334
Figure 5.51:	plot of $\ln K_L$ versus 1/T for estimation of thermodynamic parameters for the adsorption of p - nitrophenol by GAC383, GAC0383 and GACNZnO1273	337
Figure 5.52:	Adsorption of carbon GACNZnO series for methylene blue (MB) as a function of time	338
Figure 5.53:	Effect of contact time on the adsorption of methylene blue on (a) GAC383, (b) GACO383 & (c) GACNZnO1073 at different temperatures for $C_0 = 250 \text{ mg/L}$	339

Figure 5.54:	Psuedo -first order kinetics of methylene blue (MB) adsorption by (a) GAC383, (b) GACO383 & (c) GACNZnO1073 at different temperatures ; $C_0 = 250 \text{ mg/L}$	1
Figure 5.55:	Psuedo – second order kinetics of methylene blue (MB) adsorption by (a) GAC383 , (b) GAC0383 & (c) GACNZnO1073 at different temperatures ; $C_0 = 250 \text{ mg/L}$	1
Figure 5.56:	intra particle diffusion model of methylene blue (MB) adsorption by (a) GAC383 , (b) GACO383 & (c) GACNZnO1073 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L} \dots 34$	13
Figure 5.57:	Boyd kinetic model of methylene blue (MB) adsorption by (a) GAC383 , (b) GAC0383 & (c) GACNZn01073 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$	13
Figure 5.58:	plot of <i>ln K</i> ₂ versus <i>1/T</i> for the adsorption of methylene blue (MB) on modified activated carbons (a) GAC383, (b) GACO383 and (c) GACNZnO1073	14
Figure 5.59:	Adsorption isotherm plot for methylene blue (MB) adsorption on (a) GAC383, (b) GAC0383 & (c) GACNZnO1073 at different temperatures for initial concentration $C_0 = 25 - 1500 \text{ mg/L} \dots 34$	15
Figure 5.60:	Langmuir isotherm model of methylene blue (MB) adsorption by (a) GAC383, (b) GACO383 & (c) GACNZnO1073 at different temperatures for initial concentration $C_0 = 25 - 1500 \text{ mg/L} \dots 34$	15
Figure 5.61:	Freundlich isotherm model of methylene blue (MB) adsorption by (a) GAC383, (b) GACO383 & (c) GACNZnO1073 at different temperatures for initial concentration $C_0 = 25 - 1500 \text{ mg/L}$	17
Figure 5.62:	Temkin isotherm model of methylene blue (MB) adsorption by (a) GAC383, (b) GACO383 & (c) GACNZnO1073 at different temperatures for initial concentration $C_0 = 25 - 1500 \text{ mg/L}$	17
Figure 5.63:	$ln K_D$ versus 1/T for the adsorption of methylene blue (MB) on GAC383 for initial concentration $C_0 = 25 - 1500 \text{ mg/L}$	50
Figure 5.64:	<i>ln K_D</i> versus 1/T for the adsorption of methylene blue (MB) on GACO383 for initial concentration $C_0 = 25 - 1500 \text{ mg/L}$	50
Figure 5.65:	<i>ln</i> K_D versus 1/T for the adsorption of methylene blue (MB) on GACNZnO1073 for initial concentration $C_0 = 25 - 1500 \text{ mg/L}$	50

Langmuir isotherm model for the adsorption of phenol by GAC383, GAC0383 and GACNZnO1273	355
Langmuir isotherm model for the adsorption of p - nitrophenol by GAC383, GAC0383 and GACNZnO1273	355
Langmuir isotherm model for the adsorption of MB by GAC383, GACO383 and GACNZnO1273	355
John Sivanadan Achari (J-SA) isotherm plot for the phenol adsorption (a) GACNZnO1273, (b) GAC383 & (c) GACO383	356
John Sivanadan Achari (J-SA) isotherm plot for the p - nitrophenol adsorption (a) GAC383(b) GACNZnO1273 & (c) GACO383	356
John Sivanadan Achari (J-SA) isotherm plot for the methylene blue adsorption (a) GAC383,(b) GACO383 & (c) GACNZnO1073	357
BET and I plot model for the adsorption of Phenol (a) GAC383, (b) GACO383 and GACNZnO1273	358
BET and I plot model for the adsorption of p - nitrophenol (a) GAC383, (b) GAC0383 and GACNZnO1273	358
BET isotherm model for the adsorption of methylene blue (MB) by GAC383, GACO383 and GACNZnO1273	359
The general isotherm and I plot for methylene blue adsorption on GACNZnO1073	359
The general isotherm and I plot for methylene blue adsorption on GAC383	359
The general isotherm and I plot for methylene blue adsorption on GACO383	359
Carbon yield and burn - off pattern of GACONZnO activated at different temperatures	372
FTIR spectra of GACONZnO activated at different temperatures	374
X-ray photoelectron spectra of (a) GAC383, (b) GAC0383 & (c) GAC0NZnO1273	376
High resolution C 1s spectrum of GACONZnO1273	377
High resolution O 1s spectrum of GACONZnO1273	377
X-ray difractograms of GACONZnO activated at different temperatures	378
SEM image of GACONZnO1273 (a) 100 μ m resolution (b) 50 μ m resolution (c) 50 μ m resolution of GAC383 and (d) 50 μ m resolution of GACO383	379
	Langmuir isotherm model for the adsorption of phenol by GAC383, GACO383 and GACNZnO1273 Langmuir isotherm model for the adsorption of P - nitrophenol by GAC383, GACO383 and GACNZnO1273 Langmuir isotherm model for the adsorption of MB by GAC383, GACO383 and GACNZnO1273 John Sivanadan Achari (J-SA) isotherm plot for the phenol adsorption (a) GACNZnO1273, (b) GAC383 & (c) GACO383 John Sivanadan Achari (J-SA) isotherm plot for the p - nitrophenol adsorption (a) GAC383(b) GACNZnO1273 & (c) GACO383 John Sivanadan Achari (J-SA) isotherm plot for the p - nitrophenol adsorption (a) GAC383(b) GACNZnO1273 & (c) GACO383 John Sivanadan Achari (J-SA) isotherm plot for the methylene blue adsorption (a) GAC383, (b) GACO383 & (c) GACNZnO1073 BET and I plot model for the adsorption of Phenol (a) GAC383, (b) GACO383 and GACNZnO1273 BET and I plot model for the adsorption of p - nitrophenol (a) GAC383, (b) GACO383 and GACNZnO1273 BET isotherm model for the adsorption of methylene blue (MB) by GAC383, GACO383 and GACNZnO1273 The general isotherm and I plot for methylene blue adsorption on GACNZnO1073 The general isotherm and I plot for methylene blue adsorption on GACO383 The general isotherm and I plot for methylene blue adsorption on GACO383 The general isotherm and I plot for methylene blue adsorption on GACO383 FTIR spectra of GACONZnO activated at different temperatures X-ray photoelectron spectra of (a) GAC383, (b) GACO383 & (c) GACONZnO1273 (a) GACO383, (b) GACO383 & (c) GACONZnO1273 (a) 100 µm resolution (b) 50 µm resolution (c) 50 µm resolution of GAC383 and (d) 50 µm resolution of GACO383

Figure 6.8:	TEM image of GACONZnO1273 (a) 20 nm resolution (b) 10 nm resolution (c) 5 nm resolution & (d) 2 nm resolution	380
Figure 6.9:	N ₂ adsorption – desorption isotherm at 77K of modified granular activated carbons (GAC383, GACO383, GACONZnO1073 & GACONZnO1273)	381
Figure 6.10:	BET isotherm model of modified granular activated carbons (GAC383, GACO383, GACONZnO1073 & GACONZnO1273)	383
Figure 6.11:	BET Scatchard isotherm model of modified granular activated carbons (a) GAC383, (b) GACO383, (c) GACONZnO1073 & (d) GACONZnO1273)	384
Figure 6.12:	Monolayer adsorption capacity from BET and <i>I</i> plot method using modified granular activated carbons (GAC383, GAC0383, GAC0NZnO1073 and GAC0NZnO1273)	
Figure 6.13:	Specific surface area calculated from BET and I plot method using modified granular activated carbons (GAC383, GAC0383, GAC0NZnO1073 and GAC0NZnO1273)	
Figure 6.14:	Langmuir isotherm model of modified granular activated carbon GACONZnO	387
Figure 6.15:	Freundlich model of modified granular activated carbon GACONZnO	387
Figure 6.16:	John Isotherm model of modified granular activated carbon GACONZnO	387
Figure 6.17:	Alpha S (α_s) isotherm model of modified granular activated carbons GACONZnO	387
Figure 6.18:	D - R Isotherm of modified granular activated carbons (GAC383, GACO383, GACONZnO1073 & GACONZnO1273)	390
Figure 6.19:	Micropore volume calculated by D - R isotherm and α_s using modified granular activated carbons (GAC383, GAC0383, GAC0NZn01073 & GAC0NZn01273)	390
Figure 6.20:	<i>t</i> - plot model of modified granular activated carbons (a) GAC383, (b) GAC0383, (c) GAC0NZn01073 & (d) GAC0NZn01273	
Figure 6.21:	BJH adsorption cumulative pore volume of modified granular activated carbons (GAC383, GACO383, GACO383, GACONZnO1073 & GACONZnO1273)	392
Figure 6.22:	BJH desorption dv/dlogW pore volume of modified granular activated carbons (GAC383, GACO383, GACONZnO1073, & GACONZnO1273)	393
	•	

Figure 6.23:	Amount of phenol adsorbed by different types of nano ZnO impregnated on oxidised granular activated carbons, GACONZnO Series ($C_0 = 1000 \text{ mg/L}$)	394
Figure 6.24:	Effect of contact time on the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACONZnO1273 at different temperatures for C_0 : 250 mg/L	395
Figure 6.25:	Pseudo first order kinetics of phenol adsorption on (a) GAC383, (b) GAC0383 & (c) GAC0NZnO1273 at different temperatures (C_0 : 250 mg/L)	398
Figure 6.26:	Pseudo second order kinetics of phenol adsorption on (a) GAC383, (b) GAC0383 & (c) GAC0NZn01273 at different temperatures (C_0 : 250 mg/L)	398
Figure 6.27:	Intraparticle diffusion model of phenol adsorption on (a) GAC383, (b) GAC0383 & (c) GAC0NZn01273 at different temperatures (C_0 : 250 mg/L)	399
Figure 6.28:	Boyd plot for phenol adsorption on (a) GAC383, (b) GAC0383 & (c) GAC0NZn01273 at different temperatures (C_0 : 250 mg/L)	399
Figure 6.29:	Plot of ln K_2 versus 1/T for the adsorption of phenol on modified activated carbons (a) GAC383, (b) GAC0383 and (c) GAC0NZnO1273	402
Figure 6.30:	Adsorption isotherm of phenol on GAC383, GACO383 & GACONZnO1273 at different temperatures (a) 10° C (b) 20° C (c) 30° C (d) 40° C & (e) 50° C for initial concentration $C_{0} = 25 - 3000$ mg/L	403
Figure 6.31:	Langmuir isotherm plots of phenol by (a) GAC383, (b) GAC0383 & (C) GACONZn01273at different temperatures for initial concentration $C_0 = 25 - 3000$ mg/l	406
Figure 6.32:	Freundlich isotherm plots of phenol by (a) GAC383, (b) GAC0383 & (C) GAC0NZn01273at different temperatures for initial concentration $C_0 = 25 - 3000$ mg/L	406
Figure 6.33:	Temkin isotherm model of phenol by (a) GAC383, (b) GAC0383 & (C) GACONZnO1273 at different temperatures for initial concentration $C_0 = 25 - 3000 \text{ mg/L}$	
Figure 6.34:	ΔG versus Temperature for determination of thermodynamic parameters for the adsorption of phenol by (a) GAC383, (b) GAC0383 & (c) GACONZn01273	411
Figure 6.35:	Effect of contact time and amount adsorbed for the adsorption of p -nitrophenol on GACONZnO activated at different temperatures	412

Figure 6.36:	Effect of contact time on the adsorption of <i>p</i> -nitrophenol on GAC383, GACO383 and GACONZnO1273 at different temperatures (a) 10^{0} C, (b) 20^{0} C, (c) 30^{0} C, (d) 40^{0} C & (e) 50^{0} C for initial concentration C ₀ = 250 mg/L
Figure 6.37:	Pseudo - first order kinetics of p -nitrophenol adsorption by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}414$
Figure 6.38:	Pseudo - second order kinetics of p -nitrophenol adsorption by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$
Figure 6.39:	Intraparticle diffusion model of <i>p</i> -nitrophenol adsorption by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L} \dots 416$
Figure 6.40:	Elovich kinetic model of p -nitrophenol adsorption by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L} \dots 416$
Figure 6.41:	Plot of ln K_2 versus 1/T for the adsorption of p - nitrophenol on modified granular activated carbons
Figure 6.42:	Adsorption isotherm of p - nitrophenol adsorption on (a) GAC383, (b) GAC0383 & (c) GAC0NZnO1273 at different temperatures for initial concentration $C_0 = 25 - 3000 \text{mg/L}$
Figure 6.43:	Langmuir isotherm model of p – nitrophenol adsorption by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 at different temperatures for initial concentration C ₀ : 25 – 3000 mg/L
Figure 6.44:	Separation factor of p – nitrophenol adsorption by (a) GAC383, (b) GAC0383 & (c) GAC0NZn01273 at different temperatures for initial concentration C ₀ : 25 – 3000 mg/L
Figure 6.45:	Freundlich isotherm model of p – nitrophenol adsorption by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 at different temperatures for initial concentration C ₀ : 25 – 3000 mg/L
Figure 6.46:	Temkin isotherm model of p – nitrophenol adsoption by (a) GAC383, (b) GACO383 & (c) GACNZnO1273 at different temperatures for initial concentration C ₀ : 25 – 3000 mg/L
Figure 6.47:	Plot of ln K_L versus 1/T for for the adsorption of p – nitrophenol onto GAC383, GAC0383 and GAC0NZnO1273

Figure 6.48:	Selection of carbon from GACONZnO ($C_0 = 500 \text{ mg/L}$)
Figure 6.49:	Effect of contact time on the adsorption of methylene blue (MB) by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 at different temperatures (C ₀ : 250 mg/L)427
Figure 6.50:	Psuedo first order kinetics of methylene blue (MB) adsorption by (a) GAC383 , (b) GACO383 & (c) GACONZnO1273 at different temperatures (C ₀ : 250 mg/L)430
Figure 6.51:	Psuedo second order kinetics of methylene blue (MB) adsorption by (a) GAC383 , (b) GACO383 & (c) GACONZnO1273 at different temperatures (C_0 : 250 mg/L)
Figure 6.52:	Intraparticle diffusion model of methylene blue (MB) adsorption by (a) GAC383, (b) GAC0383 & (c) GAC0NZn01273 at different temperatures (C_0 : 250 mg/() = 422
Figure 6.53:	Boyd Kinetic model of methylene blue (MB) adsorption by (a) GAC383 , (b) GACO383 & (c) GACONZnO1273 at different temperatures (C ₀ : 250 mg/L)
Figure 6.54:	Plot of ln K ₂ versus 1/T for the adsorption of methylene blue (MB) on modified activated carbons
Figure 6.55:	Adsorption isotherm plot for methylene blue (MB) adsorption by (a) GAC383, (b) GACO383 & (c) GACONZnO1073 at different temperatures for initial concentration $C_0 = 25 - 3000 \text{ mg/L}$
Figure 6.56:	Langmuir isotherm plot for methylene blue (MB) adsorption by (a) GAC383, (b) GAC0383 & (c) GAC0NZn01073 at different temperatures for initial concentration $C_0 = 25 - 3000 \text{ mg/L}$
Figure 6.57:	Freundlich Isotherm plot for methylene blue (MB) adsorption by (a) GAC383, (b) GAC0383 & (c) GAC0NZn01273 at different temperatures for initial concentration $C_0 = 25 - 3000 \text{ mg/L}$
Figure 6.58:	Temkin Isotherm plot for methylene blue (MB) adsorption by (a) GAC383, (b) GAC0383 & (c) GAC0NZnO1273 at different temperatures for initial concentration $C_0 = 25 - 3000 \text{ mg/L}$
Figure 6.59:	<i>ln K_D</i> versus <i>1/T</i> for the adsorption of methylene blue by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 for $C_0 = 25 - 3000 \text{ mg/L}$
Figure 6.60:	Langmuir isotherm model for the adsorption of Phenol by GAC383, GACO383 and GACNZnO1273

Figure 6.61:	Langmuir isotherm model for the adsorption of p - nitrophenol by GAC383, GACO383 and GACNZnO1273442
Figure 6.62:	Langmuir isotherm model for the adsorption of methylene blue by GAC383, GACO383 and GACNZnO1273442
Figure 6.63:	John - Sivanadan Achari (J-SA) isotherm plot for (a) phenol (b) p – nitrophenol and (c) methylene blue adsorption by GACONZnO1273 443
Figure 6.64:	BET and I plot model for the adsorption of (a) phenol, (b) p – nitrophenol and (c) MB

List of Abbreviations

A	Equilibrium binding constant
ACPV	Adsorption cumulative pore volume
ADCSA	Adsorption cumulative surface area
a_L	Parameter of the Langmuir isotherm
ANOVA	Analysis of variance
A _s	External surface area (m ² /g)
В	Temkin isotherm constant
BET	Brunauer-Emmett-Teller method
BJH	Barrett Joyner Halenda method
b _T	Variation of adsorption energy
C_0	Initial concentration
C _e	Equilibrium concentration
DCPV	Desorption cumulative pore volume
DCSA	Desorption cumulative surface area
D _e	Diffusion coefficient
D-R	Dubinin-Radushkevich isotherm model
E_0	Mean free energy
Ea	Activation Energy
F	Variance ratio
GAC	Granular Activated Carbon
J-SA	John-Sivanandan Achari isotherm model
\mathbf{k}_1	First order rate constant
\mathbf{k}_2	Second order rate constant
K _D	Distribution coefficient
$K_{\rm F}$	Freundlich adsorption capacity
K _{id}	Intra particle diffusion coefficient
K _L	Langmuir constant related to adsorption energy
L	Pore width (nm)
LSD	Least significant difference
М	Mass of adsorbent
MB	Methylene Blue
ms	Mean square

n	Freundlich factor affecting intensity of adsorption	
P value	Significance level	
Р	Pressure	
p/p_0	Relative Pressure	
PSD	Pore size distribution	
q_e	Amount adsorbed at equilibrium	
qecal	Amount adsorbed from calculation	
q _e exp	Amount adsorbed from experiment	
q_m (D-R)	$Micropore\ adsorption\ capacity\ in\ Dubinin-Radushkevich\ isotherm$	
q_m (J-SA)	Monolayer adsorption capacity in J-SA isotherm plot.	
q_{max}	Monolayer adsorption capacity in Langmuir isotherm	
R	Gas constant	
\mathbf{R}^2	Correlation co-efficient	
R _a	Particle radius	
R _L	Dimensionless constant separation factor	
SA (BET)	BET surface area	
SA (D-R)	Dubinin-Radushkevich surface area (m ² /g)	
SA (I)	I plot surface area (m ² /g)	
SA(L)	Langmuir Surface area (m ² /g)	
SA ext	External surface area in t- plot method	
SA_{mi}	Micropore surface area in t- plot method	
SA _{mi} (D-R)	Micropore surface area in t- plot method	
t	Time	
Т	Temperature (K)	
V	Adsorbed volume (solid-gas equilibrium)	
V_{I}	Monolayer volume in I point	
$V_m (\alpha_S)$	Micropore volume in alpha S	
$V_m(BET)$	Monolayer volume in BET	
$V_{m}(L)$	Monolayer volume in Langmuir	
V _m (J)	Monolayer volume in John isotherm plot	
V _{mes}	Mesopore volume	
$\mathbf{V}_{\mathrm{mic}}$	Micropore volume	
$V_{mse}(J)$	Pore volume due to molecular sieve effect in John isothermplot	
V _t	Total pore volume	

X_{Zn}	Zinc incorporation ratio
α	Initial adsorption rate
αs	Alpha S method
α	Initial adsorption rate
β	Extent of surface coverage
ΔG	Gibbs free energy
ΔH	Enthalpy change
ΔS	Entroly change
3	Polanyi potential

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Chapter **1** INTRODUCTION

1.1 Activated Carbon

Activated carbons are group of carbonaceous porous material, prepared by carbonization and activation of organic substances of mainly biological in origin. They are unique and versatile materials having a large surface area, microporous structure, good adsorption capacity and degree of surface reactivity [1]. These are widely used in separation and purification of gases and liquids. Their important applications relate to removal of color, odor, taste, undesirable organic impurities from potable waters, for the treatment of domestic and industrial wastewater, solvent recovery and in air pollution control operations as well as for various industrial purposes.

Coconut shell based granular activated carbons (GAC) have high adsorptive capacity exhibited by its unique porous structure and very high selectivity. Hence, activated carbon filtration using modified granular activated carbon is identified as an efficient method to refine contaminated water essentially in the tertiary stages of treatment. Tailoring of physico chemical properties such as porosity, surface area and the surface morphology through secondary activation stage is a common practice to enhance adsorption efficiency. Properties of activated carbon depend significantly on porosity and surface area brought about by the activation process followed and the nature of native carbon char used.

1.1.1 Classification of Activated Carbon

Activated carbon used for water treatment is available in two main types: powdered activated carbon (PAC) and granular activated carbon (GAC). The particle size of powdered activated carbon is smaller ranges from 0.015 to 0.025 mm. Powdered activated carbon is highly efficient for waste water treatment, but it is less practiced being not easy to separate from the waste stream at the end of the unit operations. Powdered activated carbons are mainly obtained by the activation of raw material like wood sawdust and other lignocellulosic materials [2]. The Granular Activated carbon (GAC) has a particle size between 0.6 - 4 mm. Most industrial purposes use GAC due to the fact that the GAC is easy to be isolated from the bulk fluid, by screening or classification [3]. Granular activated carbons are mainly prepared from relatively high density materials such as coconut shell, coal and stones.

1.1.2 Preparation of Activated Carbon

Carbonization and activation are the two major steps involved in the preparation of an activated carbon. Carbonization is a heat treatment process to convert the basic material (mainly coal / wood) into solid char in the absence of air at a temperature range of 400 - 600 °C. The pores generated by carbonization process showed narrow pores or pores blocked by tarry substances. The carbonized product is then activated by physical or chemical method to improve the porous structure of an activated carbon. Preparation of activated carbon can be achieved by two activation procedures namely, physical activation and chemical activation.

1.1.2.1 Physical Activation

During the activation process, the carbonized material (char) is exposed to an inert atmosphere at a high temperature (800 -1000 °C) for the burn – off of volatile components from residual carbon char. This result to a consolidation of micro crystalline structures of the carbon product with high porosity mainly micro / mesoporous. Steam, air and CO_2 are mainly used as activating agents for physical activation process and it is endothermic and easy to control. The following reactions take place between steam / air and carbon matrix.

$$C + H_2 O \rightarrow CO + H_2$$

$$\Delta H = +117 \text{ kJ/mol}$$
(1.1)

$$C + 2H_2O \quad CO_2 + H_2$$

$$\Delta H = +117 \text{ kJ/mol} \tag{1.2}$$

The higher activation temperature produces controlled amount of air into the furnace to burn CO and H_2 produced during the activation process [4].

$$CO + 1/2 \quad O_2 \to CO_2$$

$$\Delta H = -285 \text{ kJ/mol} \tag{1.3}$$

$$H_2 + 1/2 O_2 \rightarrow H_2 O$$

$$\Delta H = -238 \text{ kJ/mol}$$
(1.4)

Steam activated carbons have larger adsorptive capacity and wider pore size distribution compared to others.

1.1.2.2 Chemical Activation

In the chemical activation process the carbonisation and activation are carried out simultaneously in a single step. In this process the raw material is first impregnated with strongly dehydrating and oxidising agents such as zinc chloride (ZnCl₂), potassium hydroxide (KOH), sodium hydroxide (NaOH), phosphoric acid (H₃PO₄) etc. After impregnation, the material is thermally activated at a temperature 400 – 800⁰C. The main advantages of chemical activation against physical activation are the shortest activation time, relatively lower temperature, higher carbon yield

3

and development of high porosity [5]. Zinc chloride (ZnCl₂) is regarded as an ideal chemical agent; it improves the adsorption capacity and bulk density of the activated carbon obtained.

1.1.3 Properties of Activated Carbon

Carbon exists in different allotropic forms such as carbine, graphitic carbon, non – graphitic carbon, nanotubes and diamond. This distinction is due to the arrangement of the carbon atoms in their crystal structure. Activated carbon is a non graphitic type; they are hard and low density materials, cannot be transformed into crystalline graphite even at very high temperature (3000°C). The low density of non graphitizing materials (activated carbons) is because of high porous structure and large internal surface area [6].

1.1.3.1 Porous Structure of Activated Carbon

Activated carbons have porous structure with different size and shapes. According to IUPAC [7, 8], pores are classified into three different groups to their sizes [Figure 1.1]. Micropores are pores with width not exceeding 2 nm, mesopores are pores with 2 - 50 nm and macropores are pores hiving width greater than 50 nm. The micropores are further divided into super micropores with width ranging from 0.7 - 2 nm and ultramicropores with width not exceeding 0.7 nm. During activation macropores are formed first, then mesopores and finally micropores are generated. The macropores are formed by the oxidation of weak points and portions on the external surface of the raw material. Mesopres are generated as secondary channels within the walls of the macropore structure and micropores are formed by the burn – off of the planes within the micro crystalline structure of the raw material used [9]. Porous structure of activated carbons has different shape; mainly ink bottle shape, capillaries open at both ends or with one end closed, regular slit shaped, V - shaped etc.



Figure 1.1: Schematic representation of pore structure of an activated carbon

The total pore volume (cm³/g) and pore size distribution (d_v/d_r) are the two major components for adsorption. Activated carbons have a broad pore size distribution. Activated carbon prepared by same method from different material exhibit quite different pore size distributions decided by the nature of basic material used. The pore size distribution is mainly determined by mercury porosimetry which is effective for pore size ranging from 3.6 nm up to about few millimetres. The micropores and mesopores are identified by using nitrogen adsorption desorption isotherm studied at 77K. The interlayer space between hexagonal carbon layers of activated carbon are determined by XRD analysis. The extrinsic pores on the surface of carbon materials are obtained by using microscopic techniques such as SEM, TEM, AFM etc. [10].

Depending upon the raw material used, the proportion of micropores, mesopores and macropores present on an activated carbon varies. For a coconut shell based carbon, major proportion dominates the micropores, hence phenol like organic molecule can easily access micropors. Wood and peat based carbon have more meso and macro porosity and these are used as ideal adsorbent for separating large molecules as well as for color removal from liquid phase [11].

5

Chapter 1

1.1.3.2 Surface Functional Groups

The physical characteristics such as porosity and specific surface area not only influence the adsorption. But also the chemical properties such as functional groups play an important role in adsorption. The heteroatom are bonded to the edges and corners of carbon surface form carbon oxygen, carbon - nitrogen, carbon - sulphur and carbon - halogen surface complexes and are called surface groups. These functional groups are responsible for surface properties of most activated carbons. Garten and Weis (1957) [12] was the first researchers, proposed that oxygen is present in the carbon surface in the form of functional groups. Groups can be generated by thermal or chemical treatment of activated carbon, mostly by chemical treatment of nitric acid, phosphoric acid, ozone, carbon dioxide, hydrogen peroxide etc. [13]. Activated carbon surface compounds have three types of oxygen containing groups; acidic, basic and neutral types. The acidic surface functional groups are mainly carboxyls, phenols and lactones. Their presence enhances the hydrophilic and polar character. These types of carbons are efficiently used for the removal of heavy metals. Pyrones and chromenes are the common basic surface oxygen groups. Neutral groups are created by the irreversible chemisorptions of oxygen at the ethylene type (-C=C-) unsaturated sites present on carbon surfaces. The acidic functional groups are formed when carbon is treated with oxygen at high temperature. Basic surface oxides are formed when a carbon surface is released from all surface compounds upon activating at higher temperature. The decomposition of surface acidic functional groups such as carboxylic, phenolic and lactone groups gives rise to the creation of active sites at the edges of the graphene layer. Upon cooling in an inert atmosphere and re-exposure to air and oxygen is fixed on these active sties in the form of basic groups like pyrones and chromene [14].



Figure 1.2: The surface functional groups present on the carbon surface [3]

The carbon surface functional groups are detected and characterised by analytical techniques such as temperature programmed desorption method, fourier transform infrared spectroscopy, X –ray photoelectron spectroscopy (XPS) etc.

1.1.4 Applications of Activated Carbon

Activated carbons are versatile solid adsorbent and their important applications includes drinking water treatment, industrial waste water treatment, air purification, solvent recovery, food processing, metallurgy, recovery of gold and silver and a variety of gas phase applications. Nearly 80% of the total use of activated carbon is meant for liquid – phase applications. Adsorption efficiency of an activated carbon depends on both physical and chemical characteristics. This includes the nature and source of raw material, method of preparation, porosity, surface area, surface functional groups, crystallinity etc. Microporous carbons are useful for gas phase applications. Mesoporous carbon (wider micropores and mesopores) is efficient for liquid phase applications.

Chapter 1

Prauchner and Rodriguez – Reinoso (2012) [15] reported that coconut shell based granular activated carbons exhibit high porosity by using physical and chemical activation method during their preparations. In physical activation process with CO_2 gas can tailor the narrower pore size distribution. Chemical activation with H_3PO_4 or $ZnCl_2$ produces higher packing density, higher mechanical strength and larger proportion of mesopores. Higher packing density shows a positive effect on adsorption efficiency of granular activated carbon. The mean pore radius is higher in H_3PO_4 activated carbons than activation with $ZnCl_2$.

Krishnaiah et al. (2015) [16] studied the modification of commercial activated carbon using phosphoric acid impregnation and examined the removal efficiency of 2,4 - dichlorophenol from aqueous phase. Higher activation temperature shows lower percentage yield of modified carbons (500 to 700°C). Those, prepared with phosphoric acid impregnation ratio (Xp - 1.2) and activation temperature (500°C) showed the highest percentage (93.65%) for the removal of 50 ppm concentration of 2, 4 - dichlorophenol.

Azevedo et al. (2007) [17] reported that microporous activated carbon prepared from coconut shell using chemical activation with zinc chloride followed by physisorption is regarded as better adsorbent for natural gas storage applications.

Equilibrium isotherm and kinetic studies of phenol adsorption on physico chemically (CO₂- KOH) activated coconut shell carbon with well defined pores are reported by Mohd Din et al. (2009) [18]. The activation factors highly influence the adsorption capacity of phenol (205.8 mg/g).

Cazetta et al. (2011) [19] reported that coconut shell based carbon, activated (with NaOH) showed higher surface area efficient for methylene blue removal. Hu et al. (2001) [20] studied, coconut shell and palm shell based carbon, activated with KOH having high surface area and larger proportion of mesopores showed large uptake of erythrosine red.

9

1.1.5 Impregnated / Incorporated Activated Carbon

Impregnated / incorporated activated carbons are carbonaceous adsorbents which have chemicals finely distributed on their internal surface. The impregnation optimizes the existing properties of the activated carbon giving a synergism between the chemicals and the carbon. This facilitated the cost effective removal of certain impurities from gas streams which would be impossible otherwise. Qualities of impregnated activated carbon are utilised in the field of gas purification, civil and military gas purification systems and catalysis [21]

The presence of arsenic in drinking water is one of the greatest threats to public health. The aim of this experimental investigation was to study the removal efficiency of As⁵⁺ from water by application of ironimpregnated activated carbon (Fe-AC). Surface treatment of activated carbon with an iron salt was carried out by impregnation method and thermo - chemical reactions with using of 100 mM FeCl₃ solution. The results indicated that Fe-AC is one of the suitable adsorbents can be used for the treatment of arsenic contaminated water [22].

In one of the studies [23] activated carbon was impregnated with different concentrations of $SnCl_2.2H_2O$. Native and impregnated activated carbons were analysed by means of physical adsorption and XPS and were tested for CO gas adsorption in a pressure swing adsorption (PSA) system. The adsorption isotherms of N₂ at 77 K were Type I revealed that all are microporous carbons. The surface area, pore volume and pore size distribution were considerably reduced with impregnation. The impregnated activated carbon showed a very good adsorption for CO gas compared to the unimpregnated native form.

Deflouridation of drinking water was carried out by the continuous flow of adsorption mode at room temperature. Four carbon columns were prepared by the impregnation of ZrOCl₂, alum, CaCl₂ and Borax on

Chapter 1

activated coconut shell charcoal. Known fluoride influent water was run into the column at a constant rate of 4 L/h and a constant level of water was maintained. Samples of the treated water collected for analysis by the ion selective electrode method. In this study Zirconium ion impregnated coconut shell charcoal showed maximum fluoride uptake and proved to be the most effective defluridating agent followed by CaCl₂ and alum [24].

Adsorption studies of basic and zinc chloride (ZnCl₂) impreganted coconut shell granular activated carbon (GAC) for nitrate removal from water has been known [25]. The adsorption capacity has been 1.7 mg/g (basic carbon) and 10.2 mg/g (zinc chloride impregnated carbon). Results of the present study recommend that the adsorption process using ZnCl₂ treated coconut shell GAC might be a promising innovative technology in future for nitrates removal from drinking water.

1.1.6 Zinc Based Activated Carbon

Zinc chloride (ZnCl₂), Zinc oxide (ZnO), zinc acetate (Zn(CH₃COO)₂) etc. impregnated activated carbons are used in many applications in adsorption studies for solid – gas and solid – liquid equilibrium. Khalili et al. (2000) [26] reported the paper mill sludge impregnated with zinc chloride produce micro and mesoporous carbons. Zinc chloride impregnation improved the properties of mesoporosity. Subha and Namasivayam (2009) [27] reported that activated carbon prepared from coir pith using zinc chloride impregnation improves the percentage removal of 2, 4 - dichloro phenol. Hu and Srinivasan (2001) [28] reported that coconut shell based carbon chemicaly activated with ZnCl₂ produced high micro and mesoporous activated carbon, efficient for phenol and large molecular erythrosine red. Karthick et al. (2014) [29] studied production of activated carbon using Jatropha curcas by ZnCl₂ activation method. They reported that it is a cost

effective method and it is better adsorbent for the removal of basic dye (Rhodamine B) and reactive dye (Procion Orange).

Kikuchi et al. (2006) [30] reported that ZnO loaded activated carbon an effective adsorbent for Pb²⁺ removal from aqueous solutions. ZnO loading increases the specific surface area due to the enhancement of mesopore surface area. ZnO creates hydroxyl group on activated carbon is responsible for Pb^{2+} adsorption. Jahanbakhsh and Ebrahimi (2016) [31] studied that modified activated carbon with ZnO nanoparticles is used for the removal of acid green 25 dye from aqueous solutions. Activated carbon prepared from waste tire by chemical and heat treatment in N₂ atmosphere shows high adsorption capacity for acid green 25 (306.83mg/g) than for the basic carbon (111.3mg/g). Marahal et al. (2015) [32] observed that ZnO nanoparticles loaded activated carbon is used for adsorptive removal of uric acid. Ghaedi et al. (2013) [33] conducted a study to prepare a novel adsorbent for the removal of malachite green from aqueous solution by ZnO nanoparticle loaded activated carbon (ZnO - NP - AC), have high surface area and various functional groups, enhanced the adsorption potential. Achari (1998) extensively studied adsorption behaviour of ZnCl₂ impregnated activated carbon for N₂, CO₂, phenols and heavy metal ions [36]

1.2 Adsorption Process

According to IUPAC (2015) [8], Adsorption is defined as the enrichment of atoms, molecules or ions in the vicinity of an interface. The adsorption process, a surface phenomena where the gas or liquid particles bind to the solid surface is termed as an *adsorbent* and *adsorbate* is the compound that retained by adsorbent. Silica gel, alumina, activated carbon, zeolites etc. are commonly used adsorbents for adsorption. Adsorption processes are mainly classified into *physical adsorption* and *chemical adsorption* depending upon the force of attraction between adsorbate and adsorbent.

11

1.2.1 Physical Adsorption

During physisorption, the force of attraction between adsorbent and adsorbate is weak Van der Waals forces of attraction [34]. The physical adsorption process begins with monolayer formation, then multilayer and later pore filling. In the case of physisorption $\Delta H < 40$ kJ/mol. Physisorption process is reversible and rapidly attains equilibrium.

1.2.2 Chemical Adsorption

In chemisorptions, the force of attraction between adsorbate and adsorbent is chemical forces of attraction [35]. Chemisorptions lead to the formation of monolayer. The enthalpy change is much higher (40 - 400KJ/mol). The adsorbent and adsorbate interaction occurs by covalent bond, the chemisorptions is weak and if interaction are ionic in nature chemisorptions is strong.

1.3 Types of Adsorption Isotherms

According to IUPAC (1985) [7] recommendations physisorption isotherm data are classified into six types. The graphical representation of an adsorption isotherm data is in the amount of gas adsorbed (cm³/g or mmol/g) against the relative pressure (p/p_0).

Type I Isotherm: This isotherm is applicable to microporous solids such as for activated carbons, molecular sieve zeolites and porous oxides. Type I isotherm is concave to relative pressure axis and the amount adsorbed approaches a limiting value. Figure 1.3 shows Type I (a) and Type I (b) isotherm. The Type I (a) isotherm is given by microporous solids having mainly *narrow micropores* and the pore width is less than *1.0 nm* and Type I (b) isotherms are originate with materials having broad range including *wider micropores* and *narrow mesopores* less than *2.5 nm*.


- *Type II Isotherm:* This isotherm is designated to non porous or macroporous adsorbent. The pattern of this isotherm is initially to concave to the relative pressure (p/p_0) axis, then the relative pressure increases becomes linear and finally convex to the X - axis. This shape is the result of unrestricted monolayer – multilayer adsorption up to high p/p_0 .
- Type III Isotherm: This isotherm is given by nonporous or macroporus solid and it is convex to the X axis. Weak adsorbent – adsorbate interactions occurs in Type III isotherm.
- *Type IV Isotherm:* This isotherm is specified in mesoporus materials such as oxide gels, industrial adsorbent and molecular sieves. Its initial region is related to Type II isotherm, but at high relative pressure pore condensation occurs. In the case of Type IV (a) isotherm capillary condensation is accompanied by hysteresis loop and Type IV (b) isotherm are inclined to smaller width mesopores, conical and cylindrical mesopores.
- *Type V* Isotherm: The shape of this isotherm is similar to Type III isotherm and there is only weak adsorbent - adsorbate interaction. This isotherm shows a hysteresis loop associated with pore filling mechanism. Type V isotherm is perceived for water adsorption on hydrophobic micro and mesoporous materials.
- *Type VI Isotherm:* This isotherm is a step wise isotherm, indicated layer by layer adsorption on a highly uniform surface. Each step height represents the volume of gas adsorbed layer. The sharpness of this step is dependent upon the system and the temperature.



Figure 1.3: Classification of physisorption isotherm Types [7]

1.4 Adsorption Hysteresis Loop

Hysteresis loop is located in the multilayer physisorption isotherm where the capillary condensation occurs. The hysteresis loops are classified into six types [8] are H1, H2 (a), H2 (b), H3, H4, H5 & H6 shown in Figure 1.4. The H1 hysteresis loop is shown in materials with a narrow range of uniform mesopores. The adsorbent materials such as mesoporous carbon, template silica and some controlled pore glasses are shown this type loop. Ink bottled shaped pores shown H1 hysteresis loop. H2 hysteresis is more complex pore structure and loop is broad and it is

15

observed with a long and a flat plateau with a steep desorption branch. H2 (a) hysteresis loop is found in silica gels and some porous glasses and H2 (b) is observed in mesocellular and mesoporous silicas. H3 hysteresis loops are associated with macroporous materials. H4 hysteresis loop is associated with Type I and Type II isotherm. This loop is observed in micro and mesoporus carbons, mesoporous zeolites. H5 hysteresis loop is not uncommon. This type of loop is seen in open and partially blocked mesopore structures.



Figure 1.4: Classification of Hysteresis Loop [8]

1.5 Solid – Gas Adsorption Equilibria

Solid – gas equilibrium adsorption studies are the most widely used techniques for the characterisation of porous materials. The general adsorption isotherm pattern gives information about adsorbent – adsorbate interaction. Gases such as N_2 , Ar, Kr, CO₂, CO, water vapor and low

Chapter 1

boiling aliphatic hydrocarbons and alcohols are also used. Nitrogen gas is commonly used adsorbate to determine the surface area, porosity and pore size distribution of any solid material [36].

1.5.1 Adsorption Isotherm Models

The nitrogen adsorption – desorption isotherm data at 77K are applied to different isotherm models such as Langmuir isotherm model, Brunauer Emmett and Teller (BET) isotherm model, I point method, Dubinin – Radushkevich (D –R) Isotherm model, t - *plot* model, John isotherm model, Barret Joyner Halenda (BJH) method and Alpha S (α_s) method to determine the surface area, pore width, pore volume, pore area etc.

1.5.1.1 Langmuir Isotherm Model

Langmuir isotherm model [37] is the first developed theoretical model for adsorption isotherm and it assumes monolayer adsorption capacity of the solid material. It is more applicable for Type I microporous materials. The mathematical model of this model is expressed as

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m} \tag{1.5}$$

where *P* is the pressure, *V* is the amount of gas adsorbed (cm³/g STP), V_m is the monolayer adsorption capacity (cm³/g STP) and b is the Langmuir energy constant.

1.5.1.2 Brunauer, Emmett and Teller (BET) Method

The specific surface area and porosity of any porous solid material are calculated by using BET method [38]. The multilayer adsorption is first proposed by Brunauer, Emmett and Teller. This equation is expressed as

Introduction

$$\frac{1}{V(\frac{p_{o}}{p}-1)} = \frac{1}{V_{m}C} + \frac{C-1}{V_{m}C} (\frac{p}{p_{o}})$$
(1.6)

where V is the amount of gas adsorbed (cm³/g STP), p/p_0 is the relative pressure, C is the adsorption constant and V_m is the monolayer volume (cm³/g STP).

1.5.1.3 I point Method

The BET Scatchard plot or I point method is used to determine the microporosity and mesoporosity of any porous solids [39]. In the case of I plot the original BET equation is rearranged in the form

$$\left[V\left(1 - \frac{p}{p_0}\right)\right] / \frac{p}{p_0} = CV_m - (C - 1)\left[V(1 - \frac{p}{p_0})\right]$$
(1.7)

A plot of $[V(1 - \frac{p}{p_0})] / \frac{p}{p_0}$ versus $[V(1 - \frac{p}{p_0})]$ gives an inclined

V shaped graph. The inversion point projected on the horizontal axis corresponds to the monolayer volume (V_m) .

1.5.1.4 Dubinin-Radushkevich (D – R) Isotherm

Most of the microporous materials contain a wide range of pores present, micropores and mesopores. The shape of the isotherm pattern is Type I with H4 hysteresis loop. The micropore filling occurs at low relative pressure range. This type of materials, Dubinin - Radushkevich isotherm equation [40] is most useful model to determine micropore volume and micropore surface area. The equation is represented as

$$logV = logV_0 - D \log^2(p_0 / p)$$
(1.8)

The D – R isotherm plot logV versus $log^2 (p_0/p)$ gives slope D and intercept $log V_0$. V_0 is the micropore volume (cm³/g) and D is the constant related to microporous structure.

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 17

1.5.1.5 John Isotherm Method

An Indian Scientist John developed a semi empirical isotherm model to evaluate the adsorption parameters of any porous materials [36,41]. The equation is given by

$$\log\log P = C + n\log V \tag{1.9}$$

where *P* is the Pressure, *V* is the amount of gas adsorbed (cm³/g STP), *C* and *n* are John isotherm constant.

1.5.1.6 Alpha S (α_s) Plots

Gregg and Sing (1982) [42] proposed an Alpha S (α_s) method, by comparing the adsorption isotherm under test to a standard isotherm in a reduced form. The external surface area calculated from the slope of this plot. The equation is written as

$$A_{s} = 2.86 \text{ V} / \alpha_{s} \tag{1.10}$$

where V/α_s is the slope of the α_s plot and 2.86 is the correction factor obtained by calibrating against the BET area of sooty silica.

1.5.1.7 *t* - *Plot* Method

Lippens and De Boer (1964) [43] proposed t - *plot* method, a graphical relationship expressed as a universal t curve in which the thickness of the surface is considered identical to that on the reference surface at all relative pressure. The thickness of the adsorbed layer can be obtained by the equation

$$t = [13.99 / (0.034 - \log (p/p_0))]^{0.5}$$
(1.7)

where *t* is thickness and p/p_0 is the relative pressure. The *t* - *plot* method amount adsorbed against thickness gives slope (External surface area – SA_{Ext}) and intercepts (micropre volume - V_{mi}).

1.5.1.8 Barret Joyner Halenda (BJH) Method

The BJH method is based on Kelvin equation, the pore size, pore width and area of distribution are obtained from the adsorption desorption isotherm data [44]. The Kelvin equation provides the relationship between pore radius (r_p) and adsorbed layer thickness (t) and the meniscus radius (r_k)

$$r_{p} = t + r_{K} = t - \frac{4.5}{\log(P/P_{0})}$$
(1.8)

The cumulative surface area is calculated by using the equation

$$SA_{CUM}, (m^2/g) = 2\sum v_{pi} / \sum r_{pi}$$
(1.9)

1.6 Solid – Liquid Adsorption Studies

To design a batch or fixed bed absorber reactor system adsorption kinetics, isotherm and thermodynamic features of the process are very important. Adsorption kinetics involve the determination of the rate at which pollutants are removed from solution media onto carbon surface [45]. The time dependant kinetic data are applied to different kinetic models such as pseudo first order model, pseudo second order model, intraparticle diffusion model and Boyd kinetic model are used to determine the rate constant and for the study of adsorption mechanism. Studies on adsorption isotherms are essential to understand how adsorbate interacts with adsorbent material and are critical in optimizing the use of adsorbent [46]. The general liquid phase adsorption data, amount adsorbed (q_e) and equilibrium concentration (C_e) is applied to different isotherm models like Langmuir, Freundlich, Temkin, John - Sivanandan Achari Isotherm models [47, 48, 49, 50] to evaluate the adsorption efficiency of the porous materials like activated carbon. Temperature influences the adsorption process. The prominent thermodynamic parameters such as change in

Chapter 1

enthalpy, entropy and free energy change are mostly determined in adsorption science [51]. Review of research work discussed the practices followed for the preparation, characterisation and adsorption efficiency studies of the granular activated carbon, activated / impregnated with different chemical agents, the special nature of porous carbon product obtained in a general perspective. Structural characterisation such as crystallinity, elemental composition, surface functional groups, etc. using different characterisation techniques is enumerated. Solid – gas equilibrium studies are used to determine surface area and porosity of these adsorbent materials and solid – liquid adsorption studies used to calculate the efficiency of this porous material and to identify the process of adsorption (physical / chemical).

Specially modified granular activated carbons incorporated with Zn^{2+} , Ce^{2+} , Zr^{2+} , CeO_2 are known. Chemical activation using these materials promotes more porous structure on carbon surface, hence improved efficiency. New carbon produced are collected, graded, classified and characterized based on pertinent parameters. Regarding a carbon material, burn off, yield, porosity, surface area and adsorption efficiency are very essential to choose to meet the purposes. Different batches of activated carbons prepared in the laboratory under controlled conditions with a specific carbon metal ratio are important to decide the properties.

This study comprises research on a series of granular activated carbon incorporated with $ZnCl_2$ and nano ZnO activated under an inert atmosphere provided by superheated steam. Different batches of activated carbons prepared in the laboratory under controlled conditions with specific carbon – metal oxide ratio as a function of temperature. Physico - chemical characterisation and adsorption efficiency were determined using standard procedures followed, with a special emphasis on study of structure,

adsorption isotherms, porosity / pore size distribution, kinetics and thermodynamics with respect to solid – gas and solid – liquid equilibria.

1.7 Aim and Scope of the Study

Major Objectives of the Study

The main objective of this research work is to evaluate the relative adsorption potential of coconut shell based granular activated carbons newly developed under a set of chemical activation conditions.

The study comprises

- Modification of granular activated carbons (GAC) to develop new series of carbon product materials and to evaluate their adsorption efficiency using solid – gas and solid – liquid equilibria.
- Characterisation studies of GAC impregnated with ZnCl₂ and ZnO nano materials with respect to structure, the porosity, pore size distribution and specific surface area.
- 3) Evaluation of adsorption isotherm behavior of the modified carbon materials under kinetic and equilibrium isotherm conditions.
- 4) Evaluation of adsorption efficiency of granular activated carbons by studying kinetics, isotherm and thermodynamics of adsorption using phenol, p nitro phenol and methylene blue as adsorbate.
- Evaluation of adsorption efficiency of granular activated carbon using BET, *I plot*, Langmuir, Freundlich, Dubinin – Radushkevich, Alpha S (α_s), *t* - *plot*, BJH, John, John – Sivanandan Achari isotherm models.
- Adsorption evaluation of carbon materials using ground water having trace elements; Li, Mg, Al, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Ba, Tl & Pb under their concentrations.

In this research study there are 24 numbers of carbons are prepared under different activation conditions. These materials are graded, classified and characterized based on rigorous analyses with respect to burn off, yield, porosity, structure, surface area and adsorption efficiency.

1.8 Hypothesis

- 1. Whether there is any significant difference between the total pore volume, micropore volume and mesopore volume for different modified granular activated carbons (GACZC, GACOZC, GACNZnO and GACONZnO) and in comparison with the native form of granular activated carbon (GAC).
- 2. Whether there is any significant difference between porosity and surface area using solid gas equilibria using N₂ gas adsorption at 77K, evaluated using different isotherm models; BET isotherm, I plot method, Langmuir isotherm, John isotherm, α_s plot, *t plot* for modified granular activated carbons and in comparison with the native form of granular activated carbon.
- 3. Whether there is any relation between the adsorption temperature and adsorption efficiency for the modified granular activated carbons (GACZC, GACOZC, GACNZnO and GACONZnO).
- Whether there is any significant difference between porosity and surface area determined using Langmuir isotherm and John – Sivanandan Achari isotherm (J-SA) for newly prepared granular activated carbons from solid – liquid equilibria.

1.9 Structure of the Thesis

- Chapter 1: Introduction
- Chapter 2: Materials and Methods
- Chapter 3: Granular Activated Carbon Incorporated with Zn²⁺: Preparation, Characterisation and Adsorption Studies

- Chapter 4: Granular Activated Carbon Oxidised and Incorporated with Zn²⁺: Preparation, Characterisation and Adsorption Studies
- Chapter 5: Granular Activated Carbon Incorporated with Nano ZnO: Preparation, Characterisation and Adsorption Studies
- Chapter 6: Granular Activated Carbon Oxidised and Incorporated with Nano ZnO: Preparation, Characterisation and Adsorption Studies
- Chapter 7: Summary and Conclusion

These chapters are followed by a brief description of "Future Scope of the Study".

The chapters and their contents are presented accordingly in the following sections.

Chapter 1 Introduction

This chapter gives a brief account on activated carbon their preparation, classification, properties and application in various fields. This chapter describes the theory of determination of porosity, pore volume and surface area by using different isotherm models applying in solid – gas equilibria studies as per IUPAC criteria. Significance of solid – liquid adsorption studies in separation, purification and adsorption reactor operation to identify the adsorption phenomena. This chapter ends with the discussion on the objective of the study, hypothesis and the structure of the thesis.

Chapter 2 Materials and Methods

This chapter mainly describes the methodology/ experimental procedures followed for this research work. It includes materials, methods, instrumentation and theory followed for the preparation, characterisation and adsorption studies. This

is followed by the detailed description of solid – gas and solid – liquid adsorption studies. It also describes the features of different isotherm models for the determination of porosity, pore size and surface area of new carbon materials. The experimental methods followed to study the liquid phase adsorption under kinetic and equilibrium conditions. The methods used for statistical analysis are also presented at the end of this chapter.

Chapter 3 Granular Activated Carbon Incorporated with Zn²⁺: Preparation, Characterisation and Adsorption Studies

This chapter discusses the preparation, characterisation and adsorption studies of granular activated carbon incorporated with zinc ions (Zn^{2+}) . The physico chemical characterization such as porosity, surface area, surface functional groups, surface morphology, crystallinity etc. as evidence by their textural characterizations done by N₂ adsorption – desorption isotherm analysis, FTIR, XPS, XRD, SEM, TEM, elemental analysis etc. are discussed in this chapter. Porosity and surface area were critically analysed by different isotherm models such as Brunauer Emmett Teller (BET), I plot, Langmuir, Freunlich, John, a_s, Dubinin – Radushkevich (D-R), t - plot, Barrett- Joyner Halenda (BJH) method etc. This chapter also discusses the application of liquid phase adsorption studies including adsorption kinetics, isotherm and thermodynamics of the new granular activated carbons by using phenol, p – nitrophenol and methylene blue as adsorbate. It discusses, the different kinetic equations, isotherm models and thermodynamic parameters to determine the mechanism and the adsorption process of the newly prepared activated carbons.

Granular Activated Carbon Oxidised and Incorporated Chapter 4 with Zn²⁺: Preparation, Characterisation and Adsorption **Studies**

This chapter comprises, the oxidation, impregnation, thermal activation, physico chemical characterization such as porosity, surface area, surface functional groups, surface morphology, crystallinity etc. as evidenced by their textural characterizations done by N₂ adsorption – desorption isotherm analysis, FTIR, XPS, XRD, SEM, TEM, elemental analysis etc. The nitrogen adsorption – desorption isotherm data are applied to different isotherm models such as Brunauer Emmett Teller (BET), I plot, Langmuir, Freunlich, John, alpha S (α_s), Dubinin – Radushkevich (D-R), t - plot, Barrett Joyner Halenda (BJH) method etc. to decide surface area, porosity and pore size distribution. The liquid phase adsorption towards phenol, p – nitro phenol and methylene blue are discussed under different sections. Adsorption kinetics models such as Lagergren first order, Ho second order, intraparticle diffusion model, Boyd model etc. are applied to determine the rate constant and adsorption mechanism. Equilibrium phenol, p – nitro phenol and methylene blue adsorption data are analysed using Langmuir, Freundlich, Temkin and Dubinin - Radushkevich, John -Sivanandan Achari isotherm models. The constants and parameters are determined to interpret adsorption mechanism. This chapter also discusses the thermodynamic parameters such as activation energy (E_a) , change in enthalpy (ΔH) , entropy (ΔS) and Gibbs free energy change (ΔG) of the modified carbons with respect to liquid phase adsorption study.

Chapter 5 Granular activated carbon incorporated with nano ZnO: Preparation, Characterisation and Adsorption Studies

This chapter mainly describes the preparation of nano sized, crystalline and hexagonal shaped zinc oxide and further procedures to preparation of GACNZnO series granular activated carbon and their characterisation study using different physico chemical methods. It discusses the porosity studies of modified granular activated carbons using nitrogen adsorption desorption isotherm at 77K. Isotherm models such as Brunauer Emmett Teller (BET), I plot, Langmuir, Freunlich, John, α_s , Dubinin – Radushkevich (D-R), *t* - *plot*, Barrett Joyner Halenda (BJH) method are applied, evaluated and discussed. The liquid phase adsorption of phenol, p –nitrophenol and methylene blue (MB) by modified carbons (GACNZNO) are investigated. This chapter also discusses monolyer adsorption capacity and the reaction mechanism based on kinetic, isotherm and thermodynamic studies. A comparison of adsorption efficiency of this GACNZnO series is presented along with GAC383 and GACO383.

Chapter 6 Granular Activated Carbon Oxidised and Incorporated with nano ZnO: Preparation, Characterisation and Adsorption Studies

This chapter comprises study of granular activated carbon oxidised and incorporated with nano zinc oxide (GACONZnO series). They are characterized by using different physico - chemical methods such as porosity, surface area, surface functional groups, surface morphology, crystallinity etc. as evidenced by their textural characterizations done by N_2 adsorption – desorption isotherm analysis at 77K, FTIR, XPS, XRD, SEM, TEM, elemental analysis etc. Solid – gas and

solid – liquid adsorption equilibria studies are elaborately discussed with respect to adsorption parameters. The surface area, porosity, pore size distribution are done by different isotherm models for nitrogen adsorption desorption isotherm studies at 77K. Adsorption kinetics, adsorption isotherm and thermodynamic behaviour of these carbon materials are discussed based on phenol, p - nitrophenol and methylene blue (MB) adsorption.

Chapter 7 Summary and Conclusion

This chapter summarises the major findings and conclusions of this research based on statistical interpretation of results. Relative merits of new activation treatment, variation of physico - chemical and surface properties; crystallinity, surface morphology, specific surface area, porosity, pore size distribution and adsorption efficiency studies are examined.

The thesis concludes with a brief description of "Future Scope of the Study" and "Concluding Remarks".

The respective chapters are being concluded with a brief chapter summary and references.

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Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 31

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32

Chapter **2** MATERIALS AND METHODS

2.1 Introduction

This chapter discusses the detailed description of the scientific methods followed for the preparation of granular activated carbon based on coconut shell under chemical / physical activation methods and the standard operation procedures for characterization and adsorption studies are presented of these modified carbons.

2.2 Materials

The coconut shell based granular activated carbons (manufactured by Indo German Carbon Industry, Cochin, India) of size 12 * 40 AWUSS have been used as the starting material for the preparation of a new series of carbon. Specifications of the starting carbon used in the present study as supplied by the manufacturer are graded (WTE124), type (Granular), iodine number (1100 mg/g), apparent density (0.50 g/cc), surface area (1150 m²/g), ash content (4%), moisture (5%) and pH (9 -11). Chemicals and reagent of AR grade finest quality are preferred and used throughout this research work. Zinc chloride (ZnCl₂) almost 99.9% purity used in this study was manufactured from E. Merck. Nano ZnO has been prepared under laboratory conditions using solvothermal method. The standard solution of phenol, p – nitrophenol and methylene blue were prepared by

Chapter 2

dissolving this organic solutes and dye on distilled water. Contaminated ground water taken from the Puttingal fire accident station, Kollam on April 2016 used for adsorption study of trace elements.

2.3 Methodology

2.3.1 Preparation of Granular Activated Carbon Native Form (GAC383)

100 g of granular activated carbon precursor was weighed and taken in a conical flask and then it is washed with 300 ml distilled water for 3 times. 200 ml of 0.5 N NaOH is added to it and boiled for 1 hr (Figure 2.1) washed again with distilled water for 3 times and boiled with distilled water for 1 hr. Cooled and again add 0. 5 N HCl to this carbons and washed with distilled water for 3 - 4 times and boiled with distilled water for another 1 hr. Carbon and its content are cooled and washed, then this is filled with a glass column (length 45 cm and width 5 cm) and washed with distilled water until the pH is get neutralized to pH 7.0 or near to it (Figure 2.2) dried in an oven at 110^{0} C, and this carbon native is designated as GAC383 (Figure 2.3) is the basic reference material used throughout the study.

2.3.2 Preparation of Granular Activated Carbon Oxidized Form (GACO383)

The GAC383 can be oxidized with 12.94% HNO₃. The oxidation was done in a reaction mixture containing 100 g of GAC383, 540 ml of distilled water and 130 ml of HNO₃. It is refluxed for 3hours. After the filtration the procedure was repeated 1 hour for further oxidation under reflux. Then the carbon samples were washed with distilled water continuously till the pH at 7.0 or near to it and the carbons dried at 110° C and labelled as GACO383 and used under this name throughout the study [1, 2].



Figure 2.1: GAC preparation boiling 0.5 N NaOH

Figure 2.2: GAC washing with distilled water to neutralize the pH to 7.0 or near to it.



Figure 2.3: Granular Activated Carbon Figure 2.4: Oxidation of GAC383 with (GAC383) HNO₃

Commercially available zinc chloride (ZnCl₂) and laboratory prepared nano ZnO is used as the activating agent to impregnate the native carbon and nitric acid oxidized carbon and to prepare different series of granular activated carbon. The nano sized ZnO was prepared by using 0.1 M zinc acetate and 0.15 M oxalic acid in methanol as solvent [3,4]. Preparation and characterization of nano zinc oxide are given below and also discussed in chapter 5. There are four series of granular activated carbon (GACZC, GACOZC GACNZnO, and GACONZnO) are prepared under laboratory conditions.

2.3.3 Preparation of Nano Zinc Oxide (NZnO)

The nano sized ZnO powder was prepared by using 0.1 M zinc acetate $[Zn (CH_3COO)_2. 2H_2O]$ and 0.15 M oxalic acid $[H_2C_2O_4. 2H_2O]$ in methanol as solvent. Oxalic acid was mixed with zinc acetate under stirring at 120 rpm at 17 hours at room temperature. The intermediate zinc oxalate was formed (equation 2.1), and it's centrifuged at 5000 rpm and washed with acetone for 3 or 4 times to remove impurities and dried in an oven at $110^{\circ}C$ to remove excess water. Nano zinc oxide was prepared by the decomposition of synthesized zinc oxalate at $450^{\circ}C$ in a muffle furnace for 2 hours (equation 2.2)

$$Zn(CH_{3}COO)_{2} \cdot 2H_{2}O + H_{2}C_{2}O_{4} \cdot 2H_{2}O \longrightarrow ZnC_{2}O_{4} \cdot 2H_{2}O + 2CH_{3}COOH + 2H_{2}O$$
(2.1)

$$ZnC_2O_4.2H_2O + \frac{1}{2}O_2 \longrightarrow ZnO + 2CO_2 + 2H_2O$$

$$(2.2)$$

2.3.4 Preparation of ZnCl₂ Impregnated Granular activated Carbon Native Form (GACZC)

An amount of 0.035g of the zinc chloride $(Zn / GAC ratio (X_{Zn}) = 0.02 \text{ g})$ was mixed with 50 ml water and taken in a burette. The ZnCl₂ solution was added drop wise into the conical flask containing 10 g granular activated carbon mixed with 50 ml water. The addition is accompanied by stirring with a magnetic stirrer at a temperature of 80^oC for 1hr. The sample was then dried in an oven and cooled to room temperature. The product is represented as GACZC. The same procedure has been followed for ZnCl₂, 0.07, 0.14, 0.28, 0.56 and 0.84 g for every 10 g of GAC.

2.3.5 Preparation of ZnCl₂ impregnated with Oxidised Granular activated Carbon (GACOZC)

An amount of 0.035g of the Zinc chloride $(Zn/GAC ratio(X_{Zn}) = 0.02g)$ was mixed with 50 ml water and taken in a burette. The ZnCl₂ solution was added drop wise into the conical flask containing 10 g oxidised activated

carbon mixed with 50 ml water. The addition is accompanied by stirring with a magnetic stirrer at a temperature of 80° C for 1hr. The sample was then dried in oven and cooled to room temperature. The product is represented as GACOZC.



 Figure 2.5: Impregnation of nano ZnO
 Figure 2.6: Steam activation of GAC under laboratory condition



Figure 2.7: Carbonisation chamber



Figure 2.8: Samples after activation and carbonization

2.3.6 Preparation of Nano ZnO Impregnated Granular Activated Carbon (GACNZnO)

An amount equal to 0.025 g of the nano-zinc oxide (Zn/ GAC ratio $(X_{Zn}) = 0.02$ g) prepared to be mixed with 50 ml methanol and taken in a burette. The nano zinc oxide solution was added drop wise into the conical flask containing 10 g granular activated carbon (GAC383) mixed with 50ml methanol (Figure 2.5). The addition is accompanied by stirring with a magnetic stirrer at a temperature of 80^oC for 1hr. The sample was then dried in oven and cooled to room temperature. The product is represented as GACNZnO. The same procedure is done on different ratios 0.05, 0.1, 0.2, 0.4, 0.6, 1 and 2 g of nano zinc oxide impregnated granular activated carbon.

2.3.7 Preparation of Nano ZnO Impregnated with Oxidised Granular Activated Carbon (GACONZnO)

An amount of 10 g of granular activated carbon in its oxidized form (GACO383) mixed with 50 ml of methanol taken in a conical flask. 0.025 g of nano zinc oxide solution was added drop wise into the conical flask. The addition is accompanied by stirring by a magnetic stirrer at a temperature of 80° C for 1 hr. The sample was then dried in oven and cooled to room temperature. The product is represented as GACONZnO.

The four series of granular activated carbon, namely GACZC, GACOZC GACNZnO, and GACONZnO are prepared. Each series consists of six carbon samples is steam activated at different temperature ranging from $110 - 1000^{0}$ C [383K, 473K, 673K, 873K, 1073K and 1273K] in a temperature – controlled muffle furnace (Figure 2.6 & 2.7). After the activation process, these carbons are kept in this furnace to attain the room temperature and these carbons are collected and stored in a desiccator for further characterization and adsorption studies (Figure 2.8).

SI No:	Granular activated carbon [native form]	HNO ₃ oxidised granular activated carbon [Oxidised form]	ZnCl2incorporated granular carbon activated at different temperature	ZnCl ₂ incorporated oxidized carbon activated at different temperature	Nano ZnO incorporated granular carbon activated at different temperature	Nano ZnO incorporated oxidised carbon activated at different temperature
1			GACZC383	GACOZC383	GACNZnO383	GACONZnO383
2	GAC383	GACO383	GACZC473	GACOZC473	GACNZnO473	GACONZnO473
3			GACZC673	GACOZC673	GACNZnO673	GACONZnO673
4			GACZC873	GACOZC873	GACNZnO873	GACONZnO873
5			GACZC1073	GACOZC1073	GACNZnO1073	GACONZnO1073
6			GACZC1273	GACOZC1273	GACNZnO1273	GACONZnO1273

Table 2.1: Different series of granular activated carbon GAC prepared



Figure 2.9: Methodology followed for the study of granular activated carbon*GAC383, ⁺GACO383

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 39





Figure 2.10: Methodology followed for the study of granular activated carbon (GAC383 / GAC0383) incorporated with ZnCl₂/ nano ZnO

2.4 Characterization Techniques

2.4.1 Carbon Yield and Burn - off

The $ZnCl_2$ and Nano ZnO impregnated carbons (4 series of GAC's) are carbonized under super-heated steam (steam activation) in a temperature controlled muffle furnace at different temperature ranging from 473K to 1273K, the yield and burn off are determined [5].

$$Carbonyield = \frac{W_{ac}}{W_{bc}} \times 100\%$$
(2.3)

 W_{ac} is the weight of carbon after steam activation and W_{bc} is the initial weight of carbon.

Burn - off is defined as the weight difference between the raw sample (W_0) and activated sample, (W_1) divided by the weight of the raw sample.

$$Burn - off = \frac{W_0 - W_1}{W_0} \times 100\%$$
(2.4)

2.4.2 Boehm Titrations

Boehm's titration technique was used for the selective quantification of carboxylic, lactonic, and phenolic groups on the modified granular activated carbons [6]. These groups can be distinguished by their neutralization behavior with aqueous NaHCO₃, Na₂CO₃ and NaOH. The surface basicity of all the carbons was also determined on the basis of HCl consumption.

a. Carboxyls

An amount equal to 0.150 g of powdered granular activated carbons was shaken with 30 ml of 0.05 N NaHCO₃ for 20 hrs. The contents were separated and the filtrate collected. An aliquot of the collected solution was mixed with excess of 0.05 N HCl and the CO_2 gas formed was boiled off and back titrated with standard NaOH.

b. Lactones

Granular activated carbons (0.15 g) powdered form was shaken thoroughly with 30 ml of 0.05 M Na₂CO₃ solutions for 20 hrs and the contents separated. An aliquot of the solution was mixed excess of 0.05 M HCl and the CO₂ boiled off and back titrated with a standard NaOH solution.

c. Phenols

An amount equal to 0.150 g of the powdered form of modified granular activated carbons was shaken with 30 ml of 0.05 N NaOH for 20 hrs. An aliquot of the solution is titrated against standard HCl.

d. Bases

An amount 0.150 g of modified carbons was shaken with 30 ml of 0.05 M HCl and the filtrate was titrated with standard NaOH.

2.4.3 Elemental Analysis

The elemental composition [C, H, N & O] of the modified granular activated carbons were done by using Elemental Vario EL III.

2.4.4 Fourier Transform Infrared (FTIR) Spectroscopy

Characterization of surface functional groups of the modified granular activated carbons qualitatively analyzed using Fourier Transform Infrared Spectroscopy (Thermo Nicolet Avatar 370). The spectral range is $4000-400 \text{ cm}^{-1}$ and with resolution 4 cm⁻¹.

2.4.5 X-ray Photo Electron Spectroscopy (XPS)

The surface functional groups of the modified granular activated carbons are qualitatively determined by XPS method and the percentage composition of the carbon are also obtained by this method. Axis Supra (XPS) surface analysis instrument is used for this purpose.

2.4.6 X- ray Diffraction Technique (XRD)

X - ray Powder Diffractometry is one of the most powerful and established technique for material structural analysis. The crystallinity of GAC are determined using X - ray Powder Diffractometer (Bruker AXS D8 Advance). The x - ray source is Cu and the wavelength used for the determination of crystallinity of the modified carbons is 1.5406 A^0 , an angle range is 360° . From the XRD we can determine interlayer spacing d_{002} using Bragg equation as follows.

$$n\,\lambda = 2\,d\,\sin\theta\tag{2.5}$$

where λ - wavelength of X-ray radiation, n - an integer, d - spacing of the crystal planes and θ - scattering angle or peak position

The crystallite size along c-axis L_c and the size of the layer planes L_a are determined using Scherrer equation.

$$L = \frac{k \lambda}{\beta \, Cos\theta} \tag{2.6}$$

where *L* is L_c or L_a , *B* is the half width of the diffraction peak in radians and *k* is the shape factor and the values of k = 0.9 and 1.84 are used for calculation of L_c and L_a respectively.

2.4.7 Scanning Electron Microscopy (SEM)

The surface morphology was done by using Scanning Electron Microscope (SEM) JEOL Model JSM - 6390LV. The Scanning Electron Microscope uses an electron beam of surface imaging.

2.4.8 High Resolution Transmission Electron Microscopy (HRTEM)

High Resolution Transmission Electron Microscope (HRTEM) model Jeol /JEM 2100 are used for the surface morphological studies of modified granular activated carbons and prepared nano ZnO. TEM image is formed from the interaction of the electrons transmitted through the carbon surface.

2.5 Adsorption Studies (Solid – Gas & Solid – Liquid)

2.5.1 Carbon – N₂ Gas Adsorption (Solid - Gas Adsorption)

Physisorption structural characterisation such as pore structure (V_{t} , V_{mic} , V_{mes} and pore width) and surface area were done by using nitrogen

Chapter 2

adsorption – desorption isotherm at liquid nitrogen temperature 77K using Micrometrics (Tristar 3000 V6. 07A). The nitrogen adsorption isotherm data applied to different isotherm models such as Brunauer Emmet Teller (BET) method, *I* plot method, Langmuir isotherm, Freundlich Isotherm, John Isotherm, *t* –plot, Dubinin – Radushkevich isotherm, alpha S (α_s) method and Barret Joyner and Halenda (BJH) method to determine surface area and porosity of these modified granular activated carbons.

The surface area is determined by using BET method, *I* plot method, Langmuir isotherm and John isotherm etc, the micropore surface area are determined by t - plot method and Dubinin Radushkevich isotherm method. The total pore volume measured by at relative pressure 0.9 (p/p_0) and mesopore volume was calculated by subtracting t - plot micropore volume from the total pore volume. The BJH method is commonly used to pore size distribution of the modified granular activated carbons. These isothermal equations are discussed in detail in the following sections.

2.5.1.1 Brunauer Emmett Teller (BET) Method

Brunauer, Emmett and Teller were the first to make advancement in the possibility of using gas adsorption for the determination of surface area of porous adsorbents. The simplified form of the BET equation [7] is expressed as

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \left(\frac{p}{p_0}\right)$$
(2.7)

The linear form of this BET equation is

$$\frac{1}{V(\frac{p_0}{p}-1)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} (\frac{p}{p_0})$$
(2.8)

44

where V is the amount adsorbed (mmol/g), V_m is the monolayer capacity (mmol/g), C is the BET constant and it is related to the energy of adsorption in the first adsorbed layer. The C parameter indicates the magnitude of adsorbent – adsorbate interaction. The BET isotherm plot

$$\frac{1}{V(\frac{p_0}{p}-1)}$$
 against with intercept $\frac{1}{V_m C}$ and slope $\frac{C-1}{V_m C}$.

The monlayer volume V_m and C are obtained from the slope and intercept

$$C = \frac{Slope + intercept}{intercept}$$
(2.9)

$$V_m = \frac{l}{Slope + intercept}$$
(2.10)

The specific surface area of the modified granular activated carbons is determined by using the monolayer adsorption capacity (V_m) ,

$$SA(BET) = \frac{v_m (cm^3 / g STP) \times 6.023 \times 10^{23} (molecules / mole) \times 0.162 \times 10^{-18} (m^2 / N_2 molecule)}{22414 (cm^3 / mol)}$$
(2.11)

2.5.1.2 BET - Scatchard Plot (I point) Method

In the case of BET- Scatchard plot [8] the original BET equation is rearranged in the form

$$[V(1 - \frac{p}{p_0})] / \frac{p}{p_0} = CV_m - (C - 1)[V(1 - \frac{p}{p_0})]$$
(2.12)

A plot of $[V(1 - \frac{p}{p_0})] / \frac{p}{p_0}$ versus $[V(1 - \frac{p}{p_0})]$ gives an inclined

V shaped graph. The inversion point projected on the horizontal axis corresponds to the monolyer volume (V_m). The specific surface area (*SA* (*I*)) is calculated from V_m is

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 45

$$SA(I) = 4.353 V_m$$
 (2.13)

Where,

$$4.353 = \frac{6.023 \times 10^{23} (\text{ molecules / mole}) \times 0.162 \times 10^{-18} (\text{m}^2 / N_2 \text{molecule})}{22414 (\text{ cm}^3 / \text{mol})}$$
(2.14)

2.5.1.3 Langmuir Isotherm Method

The Langmuir isotherm model is first developed adsorption isotherm applicable to chemisorption, but it also applied to physisorption Type I isotherm. The Langmuir equation is

$$\frac{V}{V_m} = \frac{b P}{l + b P}$$
(2.15)

This equation (2.15) can be rearranged in the linear form

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m}$$
(2.16)

Where *P* is the absolute pressure (mmHg), *V* is the volume adsorbed (mmol/g), V_m is the monolayer adsorption capacity (mmol/g) and *b* is the Langmuir energy constant [9].

The Langmuir surface area (SA(L)) is calculated from the Langmuir monlayer volume

$$SA(L) = \frac{v_m (cm^3 / g STP) \times 6.023 \times 10^{23} (molecules / mole) \times 0.162 \times 10^{-18} (m^2 / N_2 molecule)}{22414 (cm^3 / mol)}$$
(2.17)

2.5.1.4 Freundlich Isotherm Method

Freundlich isotherm model [10] is an empirical isotherm and is generally expressed as

$$V = K_F P^{1/n} \tag{2.18}$$

Where K_F and *n* are Freunlich constants, *V* is the volume of gas adsorbed (mmol/g), *P* is the absolute pressure (mmHg).

This equation is linearized by logarithm to transforms give

$$\log V = \log K_F + 1/n \log P \tag{2.19}$$

The parameter K_F is an indicator of adsorption capacity and n is the adsorption intensity. Both of these adsorption parameters are obtained from the linear plot of *log V* against *log P*.

2.5.1.5 John Isotherm Method

The John isotherm model is generally applied in the various adsorption system and is expressed as

$$log log P = C + n \log V \tag{2.20}$$

From the plot of *loglog P* against *log V* gives a straight line with slope *n* and intercept *C*, where *C* and *n* are regarded as John isotherm constants. The limiting micropore volume $V_m(J)$ are calculated by extrapolating the straight line connecting to the lower point of *loglog P* [11, 12].

2.5.1.6 Alpha S (α_s) Method

The external surface area of an adsorbent material is calculated by using α_s method [13]. An Alpha S (α_s) plot is obtained by plotting the amount adsorbed by the granular activated carbons (mmol/g) against α_s , the reduced standard adsorption. The surface area is calculated by using the equation

$$A_{\rm s} = 2.86 \, V \,/\,\alpha_{\rm s} \tag{2.21}$$

where V/α_s the slope of the Alpha S (α_s) plot and 2.86 is the correction factor obtained by calibrating against the BET area of sooty silica.

Granular Activated Carbon Incorporated With Zn $^{2+}$ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 47

2.5.1.7 Dubinin - Radushkevich (D - R) Isotherm Method

In order to determine the micropore volume and pore width of any microporus materials the Dubinin – Radushkevich (D-R) isotherm method is generally used [14]. The D-R equation is written as follows

$$logV = logV_0 - D \log^2(p_0 / p)$$
(2.22)

where, V - volume of nitrogen adsorbed at each relative pressure, V_0 - micropore volume from D-R isotherm, D - constant related to micropore structure

$$D = 2.303 \left(\frac{RT}{\beta E_0}\right)^2$$
(2.23)

R – gas constant, T – Temperature, β - affinity coefficient of N₂ gas (0.33) and E_0 - characteristic energy of modified carbons

A plot of $\log V$ versus $\log^2(p_0 / p)$ gives a straight line with intercept V_0 (micropore volume). The characteristic energy is calculated by using the equation

$$E_0 = \sqrt{\frac{2.303 RT}{m \beta}} \tag{2.24}$$

where, *m* is the slope of the D-R isotherm plot. The characteristic energy related to pore width (L_{av}) of the modified carbons using McEnaney equation [15]

$$L_{av} = 6.6 - 1.79 \ln E_0 \tag{2.25}$$

In the case of slit shape micropores the surface area is calculated by using the following equation

$$S_{mi} (m^2 / g) = 2 * 10^3 V_0 (cm^3 / g) / L_{av} (nm)$$
(2.26)
2.5.1.8 *t* – *plot* Method

The micropore volume and external surface area of carbon materials are calculated by Lippeens and De – Boer (1964) [16] t - *plot* method. The statistical thickness 't' of the adsorbed layer in the modified carbons as a function of amount adsorbed (mmol/g) at a given relative pressure (p/p_0).

$$t = \left[\frac{13.99}{(0.034 - \log(p/p_0))} \right]^{0.5}$$
(2.27)

The *t* - *plot* amount adsorbed against thickness gives slope (External surface area – SA_{Ext}) and intercept (micropre volume - V_{mi}).

$$SA_{EXT} = \frac{slope(cm^{3} / g - A^{0}STP) \times (10^{10} A^{0} / m) \times (Dcm^{3} liquid / cm^{3} STP)}{F \times 10^{6} (cm^{3} / m^{3})}$$
(2.28)

$$V_{mi} = intercept (cm^{3} / g STP) \times D(cm^{3} liquid / cm^{3} STP)$$
(2.29)

Where *D* is the density conversion factor (0.0015468) and *F* is the surface area correction factor = 1. The micropore surface area is obtained by subtracting the external surface area from BET surface area.

$$SA_{mi} = SA_{BET} - SA_{Ext} \tag{2.30}$$

2.5.1.9 BJH Method

Barret Joyner and Halenda (BJH) analysis is a pore size distribution determination method [17], typically applied to nitrogen adsorption desorption data measured at 77K on porous materials. It uses the modified Kelvin equation to relate the amount adsorbed (mmol/g) at each relative pressure (p/p_0) is decreased from a high to low value to the size of pores. The pore analysis consists of determining the average pore size, average pore volume and pore size or pore volume distribution.

The Kelvin equation provides the relationship between pore radius (r_P) and adsorbed layer thickness (t) and the meniscus radius (r_K)

$$r_p = t + r_K = t - \frac{4.5}{\log(P / P_0)}$$
(2.31)

Granular Activated Carbon Incorporated With Zn $^{2+}$ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 49

The cumulative surface area is calculated by using the equation

$$SA_{CUM} (m^2 / g) = 2\Sigma v_{pi} / \Sigma r_{pi}$$

$$(2.32)$$

2.5.2 Solid – Liquid Adsorption

Optimization of adsorption process thereafter for the design of unit operations, the adsorption kinetics, equilibrium isotherm studies and thermodynamic studies are very important. In this regard, equilibrium and kinetic adsorption behavior and temperature effect of these modified granular activated carbons are made using phenol, p – nitrophenol and methylene blue from the aqueous phase in bench scale batch reactors [18].

2.5.2.1 Phenol

Phenol is a derivative of benzene can be used as raw material for various industries such as petrochemicals, oil refineries, plastics, pharmaceuticals, etc. It is an organic pollutant in the list of priority pollutants by the US EPA, they are aromatic hydrocarbon residues and are considered to be carcinogenic and causes unpleasant taste and odor at very low concentrations. BIS (Bureau of Indian Standard) maintains a desirable limit of 0.001 mg/L in drinking water.

2.5.2.2 *p* – nitrophenol

p – nitrophenol is a phenolic compound that has a nitro group on the para position of the hydroxyl group on the benzene ring and it decreases the water solubility. The roles of p -nitrophenol in the chemical manufacturing industry is enormous and are generally produced as a by-product from various industries. It is used to manufacture drugs, fungicides, insecticides and dyes are darken to leather. Short term inhalation of p – nitrophenol in humans cause headaches, drowsiness, nausea and cyanosis. It also causes eye and skin irritation.

2.5.2.3 Methylene Blue (MB)

Methylene blue (MB) is a cationic dye extensively used in many processes involved in manufacturing industries: textile, rubber, paper, plastic, cosmetic, microbiology, diagnostics etc. These industries use dyes and pigments to color and promote their products. These dyes are colour imparting high molecular weight organic pollutants and the presence of even a very minute amount. Low as 1ppm of coloring substances in water makes it undesirable due to its change in aesthetic appearance. Their presence affects the aquatic ecosystems. The discharge of colored effluent from industries into natural streams causes some serious toxicological and environmental consequences. Potential health effects of methylene blue (MB) appear as disorders related to eyes, gastrointestinal and respiratory tract, increased heart rate, vomiting, shock, jaundice, tissue necrosis etc.





Figure 2.11: Molecular structure of phenol

Figure 2.12: Molecular structure of *p* - nitrophenol



Figure 2.13: Molecular structure of methylene blue

2.5.2.4 Adsorption Kinetics

The adsorption kinetics were studied using an initial concentration of adsorbate (Phenol, p – nitrophenol and methylene blue (MB)) 250 mg/L shakes for contact time ranges from 10 - 720 minutes using a temperature controlled water bath shaker. The study conducted at different temperature (10, 20, 30, 40 and 50^oC), 1.0 g/L adsorbent dosage (modified GAC's) was weighed and placed in a 100 ml screw cap conical flask containing 50 ml solution of adsorbate. For isotherm study, shaking / contact time is controlled as 600 minutes as equilibration time. After the desired contact time (10, 20, 30, 40, 60, 120, 240, 360, 480, 600 and 720 and minutes) GAC were filtered using Whatmann No.1 filter paper. The concentration of the filtrate was measured for residual phenol, p – nitrophenol and methylene blue concentration using a UV-Visible Spectrophotometer (Cary 50 Probe, manufactured by Varian Industries) at 268 nm, 317 nm and 650 nm respectively.

The amount of phenol, p –nitrophenol and methylene blue (MB) adsorbed by GACs are determined by using the mass balance equation represented as

$$q_{e} = \frac{v(C_{0} - C_{e})}{m}$$
(2.33)

 q_e is the mount adsorbed (mg/g), C_e is the final concentration in solution (mg/L), C_0 is the initial concentration in solution (mg/L), v is the volume of the solution (L) and *m* is the adsorbent mass (g). These experimental data are applied to different kinetic equations such as pseudo first order kinetic model, Ho second order kinetic model, intrparticle diffusion model, Boyd model and Elovich kinetic model to determine the mechanism of adsorption and rate of adsorption process.

2.5.2.4.1 Pseudo First Order Kinetic Model

Lagergren's pseudo first order kinetic equation [19] is widely used as an adsorption kinetic model

$$\frac{d q_t}{d t} = K_1(q_e - q_t)$$
(2.34)

After integration and applying boundary conditions t = 0, t = t and $q_t = 0$ to $q_t = q_0$ the equation (2.34) is changed to the equation (2.35).

$$ln(q_e - q_t) = ln q_e - K_I t \tag{2.35}$$

where q_t and q_e are the amount adsorbed (mg/g) at any time and at equilibrium respectively, K_1 is the pseudo first order rate constant. A linear plot $ln (q_e-q_t)$ versus time (*t*) gives a slope (K_1) and intercept ($ln q_e$), from this intercept the amount adsorbed obtained (q_ecal).

2.5.2.4.2 Pseudo Second Order Kinetic Model

Ho and Mckcay (1998) [20] defined pseudo second order kinetic model based on equilibrium adsorption expressed as

$$\frac{d q_t}{d t} = K_2 (q_e - q_t)^2$$
(2.36)

Integrate this equation (2.36) for the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_0$ yield equation (2.37).

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t$$
(2.37)

This equation has been rearranged into a linear form

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$
(2.38)

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 53

A straight line plot of t/q_t versus t gives slope $(1/q_e)$ and intercept $(1/K_2q_e^2)$, q_e is the amount adsorbed $(q_e \ cal)$ obtained from the pseudo second order kinetic model and K_2 is the second order rate constant. The model is valid only the $q_e \ cal$ should equal to the adsorption capacity obtained from the experimental kinetic data.

2.5.2.4.3 Elovich Kinetic Model

Elovich kinetic equation [21] is given as

$$\frac{d q_t}{d t} = \frac{1}{\beta} \ln \left(\alpha \beta \right) + \frac{1}{\beta} \ln t$$
(2.39)

Integrating this rate equation with respect to the boundary conditions t=0 to t=t and $q_t=0$ to $q_t=q_0$ yield equation (2.40)

$$q_{t} = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$$
(2.40)

 α is the initial adsorption rate and β is the extent of surface coverage obtained from the linear plot of q_t against ln t. $1/\beta$ is the slope and $1/\beta$ ($ln\alpha\beta$) is the intercept.

2.5.2.4.4 Intraparticle Diffusion Model

To determine the rate controlling step and diffusion mechanism of an adsorption process the intraparticle diffusion model is commonly used. Weber and Morris (1962) [22] intraparticle diffusion model is applied given as

$$q_t = K_{id} t^{1/2} + C (2.41)$$

where K_{id} is the intrapartice diffusion constant (mg/gmin) and *C* is a constant related to the thickness of the boundary layer. For the intraparticle diffusion plots amount adsorbed at different time interval versus the square root of time (q_t vs $t^{1/2}$), the first portion is ascribed to surface

adsorption and the second linear portion is attributed to intra particle diffusion.

2.5.2.4.5 Boyd Kinetic Model

The actual governing rate of the adsorption process is evaluated by Boyd kinetic model [23]. The Boyd kinetic model is expressed as

$$F = I - (6 / \pi^2) e^{-B_t}$$
(2.42)

Where *F* is the fraction of the amount adsorbed at a time (t) in a minute. Rearranging the equation (2.42) and gives equation (2.43)

$$I - F = (6 / \pi^2) e^{-B_t}$$
(2.43)

or

$$B_{t} = -0.4977 - \ln(1 - F) \tag{2.44}$$

Applying the equation

$$F = \frac{q_t}{q_e} \tag{2.45}$$

$$B_t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \tag{2.46}$$

The B_t is calculated from equation (2.44). A linear plot of B_t against t is used to identify whether the adsorption process is mainly controlled (intraparticle or surface diffusion).

$$B = \frac{\pi^2 D_i}{r^2} \tag{2.47}$$

The diffusivity coefficient (D_i) is calculated from the slope (B) of the plot, *r* is the radius of the adsorbent.

2.5.2.5 Adsorption Isotherm Studies

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 55

Chapter 2

The batch experiments of the adsorption isotherms were conducted at different temperature (10, 20, 30, 40 and 50^{0} C) in a 100 ml screw cap conical flask. Carbon granules equivalent to ratio of 1.0 g/L (50 mg/50 ml adsorbent dosage) were weighed and placed in the flask containing a solution of phenol and *p* -nitrophenol of a desired concentration (25, 50, 75, 100, 150, 250, 500, 750, 1000, 1250, 1500, 2000, 2500 and 3000 mg/L) in a temperature controlled bath shaker and for methylene blue the concentration ranging from 25 – 1500 mg/L. For adsorption isotherm study, shaking time was fixed at 480 minutes (phenol and *p* – nitrophenol) and 680 minutes (methylene blue) based on preliminary studies conducted for the determination of equilibration time. After shaking the suspension was filtered using Whatmann No.1 filter paper. The concentration of the filtrate was measured using a UV-Visible Spectrophotometer at 268 nm (phenol), 317 nm (*p* – nitrophenol) and 650 nm (methylene blue).

Adsorption isotherm studies are very essential to understand how adsorbate interacts with carbon granules and are critical in optimizing the use of adsorbent. The equilibrium experimental isotherm data apply to different isotherm models such as Langmuir isotherm model, Freundlich isotherm model, Temkin isotherm model, Dubinin – Radushkevich isotherm model and John – Sivanandan Achari isotherm models to evaluate the fitness of this model and which is more useful for the design of a reaction system. These models are commonly used to determine the critical constant and identify the process of adsorption.

2.5.2.5.1 Langmuir Isotherm Model

In liquid phase adsorption isotherm studies Langmuir model is represented as [1, 24]

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{2.48}$$

Adsorption capacity and energy parameters derived from isotherms are very useful to design a single batch adsorption reactor system. The linear form of Langmuir model is plotted by using this equation (2.48)

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{2.49}$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbate in solution, q_e is the amount adsorbed per unit weight of adsorbent (GAC), K_L (L/g) and a_L are Langmuir constants. A linear plot of $C_{e'}/q_e$ against C_e gives slope (a_L/K_L) and intercepts $(1/K_L)$. The monolayer adsorption capacity (q_{max}) is obtained from the reciprocal of the slope (a_L/K_L) and the Langmuir energy constant calculated from the reciprocal of the intercept.

The dimensionless separation factor (R_L) is calculated by using Langmuir isotherm constants is defined as [24]

$$R_{L} = \frac{1}{1 + a_{L} C_{0}}$$
(2.50)

Where a_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution (mg/L). The separation factor (R_L) gives an idea about the favorability of an adsorption process as shown in Table 2.2.

Table 2.2: Separation factor					
R _L Favorability of adsorption process					
$R_{L} > 1$	Unfavorable				
$R_{L} = 1$	Linear				
$0 < R_L < 1$	Favorable				
$R_{L} = 0$	Irriversible				

2.5.2.5.2 Freundlich Isotherm Model

Freundlich isotherm model [10] is an empirical isotherm equation based on heterogenous surface and satisfactory application for lower concentration of adsorbate solution and it is generally expressed as

$$q_e = K_F C_e^{1/n}$$
 (2.51)

The logarithmic form of this Freundlich isotherm is given by equation (2.50)

$$\log q_e = \log K_F + 1/n \log C_e \tag{2.52}$$

where C_e (mg/l) is the equilibrium concentration and q_e (mg/g) is the amount adsorbed, K_F is the adsorption capacity and l/n is the adsorption intensity constant. The Freundlich constants are obtained from the logarithmic plot of $log q_e$ versus $log C_e$.

2.5.2.5.3 Temkin Isotherm

Temkin isotherm describes the adsorbent – adsorbate interactions [25] which assumes that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin model is expressed as

$$q_e = \frac{RT}{b} \ln(AC_e)$$
(2.53)

The linear form of Temkin isotherm is

$$q_e = B \ln A + B \ln C_e \tag{2.54}$$

$$B = \frac{RT}{b_T} \tag{2.55}$$

A Temkin plot q_e versus $ln \ C_e$ yields a straight line with B as the slope and $B \ lnA$ as the interept. A is the binding energy constant (L/g) and B is related to the heat of adsorption. b_T is the variation of adsorption energy. R is the gas constant (8.314 J/mol K) and T is the absolute temperature in Kelvin.

2.5.2.5.4 Dubinin – Radushkevich (D – R) Isotherm

The Dubinin - Radushkevich (D-R) isotherm equation is generally expressed as

$$q_e = q_m exp - (\beta \varepsilon^2) \tag{2.56}$$

The linear form of D - R model is [26]

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{2.57}$$

 q_e is the amount adsorbed, q_m is the adsorption capacity, and ε is the polyani potential is related to the equilibrium concentration is equal to $RT ln(1+\frac{1}{C})$, R is the gas constant (8.314 J/mol K), T is the absolute

temperature and β is a constant related to mean adsorption energy (E_0) [27].

$$E_0 = \frac{1}{\sqrt{2\beta}} \tag{2.58}$$

2.5.2.5.5 John – Sivanandan Achari (J –SA) Isotherm

John – Sivanandan Achari (J – SA) isotherm model is applied in solid - liquid equilibria [28, 29, 30]. The linear form of J-SA isotherm equation is

$$\log\log C_e = C + n\log q_e \tag{2.59}$$

Where C and n are the intercept and slope of the plot loglog C_e against log q_e , C is the J-SA isotherm constant and n is the adsorbability constant.

2.5.2.6 Adsorption Thermodynamics

The thermodynamic parameters such as change in enthalpy (ΔH) , entropy (ΔS) and standard Gibbs free energy change (ΔG) for phenol and p –nitrophenol adsorption by these carbons are calculated by using Van't Chapter 2

Hoff equation and activation energy (E_a) calculated from Arrhenius equation.

$$lnK_{L} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(2.60)

$$\Delta G = -RTlnK_L \tag{2.61}$$

$$lnK_2 = lnK_0 - \frac{E_a}{RT}$$
(2.62)

 K_L is the Langmuir energy constant, *T* is the absolute temperature (283, 293, 303, 313 and 323) and *R* is the universal gas constant (8.314 J/K mol). The ΔH and ΔS are obtained from the slope and intercept of the linear plot of $ln K_L$ versus 1/T [31]. The Arrhemius activation energy (*Ea*) calculated from the slope of the linear plot $ln K_2$ against 1/T. K_2 is the second order rate constant.

The thermodynamic parameters such as ΔG , ΔH and ΔS are calculated from the distribution coefficient (K_D) [1] for each initial methylene blue concentrations by using the relationship

$$lnK_D = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$
(2.63)

$$\Delta G = \Delta H - T \,\Delta S \tag{2.64}$$

$$K_D = \frac{C_{solid}}{C_{liquid}}$$
(2.65)

Where K_D is the distribution coefficient, C_{solid} is the equilibrium concentration on adsorbent and C_{liquid} is the equilibrium concentration in solution. The value of ΔH and ΔS are calculated from the slope and intercept of the linear plot $ln K_D$ against the reciprocal of temperature (1/T).

2.6 Trace Elements – Adsorption Study

Adsorption evaluation of carbon materials using contaminated ground water having trace elements; Li, Mg, Al, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Ba, Tl & Pb are determined by batch experiments. Initial and final concentration (after adsorption) is determined by Inductively Coupled Plasma – Mass Spectrometer (ICP –MS). This instrument is capable of scanning the mass range of 5 to 250 amu with a minimum resolution capability of 1 amu peak width at 5 % peak height.

2.7 Statistical Analysis of the Data

The data collected for the study were compiled and analysed statistically using the following tests.

- 1) Student's independent 't' test for comparison of means
- 2) Two factor ANOVA Technique for comparison of Row and Column effects
- 3) Three factors ANOVA Technique for Comparison of Group means
- 4) *'t'* test for testing the significance of correlation coefficient

The formula used for comparison of means in students' independent' test is

$$t = \frac{\sqrt{x_1 - x_2}}{\sqrt{\frac{S^2}{n_1} + \frac{S^2}{n_2}}}$$
(2.66)

Where $\overline{x_1}$ and $\overline{x_2}$ are the means of the two samples, n_1 and n_2 are the size of the samples and S^2 is the pooled variance. This 't' is having Degrees of freedom $n_1+n_2 - 2$.

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 61

The mathematical model used for framing the two factor ANOVA is

$$X_{ij} = \mu + \alpha_i + \beta_j + E_{ij} \tag{2.67}$$

where x_{ij} – observation in the ith row and jth column, μ – overall effect, α_i – ith row effect, $\beta_j - j^{th}$ column effect and E_{ij} – random error

Wherever each treatment effects were found to be a significant difference (LSD) at the 5% level of significance were calculated in order to separate out significant treatment effect.

The mathematical model framed for the three factor ANOVA is

$$X_{ijk} = \mu + \alpha_i + \beta_j + r_k + E_{ijk}$$

$$r_k - k^{\text{th}} \text{ treatment effect}$$

$$(2.68)$$

Karl Pearson's coefficient of correlation was calculated using the formula

$$r = \frac{n\Sigma xy - (\Sigma_i x) (\Sigma_i y)}{\sqrt{n\Sigma x^2 - (\Sigma x_i)} x \sqrt{n\Sigma y^2 - (\Sigma y_i)}}$$
(2.69)

The significance of the correlation coefficient was tested using the 't' test

$$t = \frac{r \, x \, \sqrt{n - 2}}{\sqrt{1 - r^2}} \tag{2.70}$$

Having degrees of freedom (n-2).



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Chapter 2

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Chapter **3**

67

GRANULAR ACTIVATED CARBON INCORPORATED WITH Zn²⁺: PREPARATION, CHARACTERISATION AND ADSORPTION STUDIES

3.1 Introduction

Coconut shell based granular activated carbons (GAC) have a high adsorptive capacity exhibited by its unique porous structure and very high selectivity. Development of extra porosity of carbon by chemical / physical (Zn^{2+} ions or any metal salt / steam, CO_2 or N_2) activation will improve its efficiency. The resulting material utilised as a commercial product for many manufacturing and service industries. Zinc chloride is one of the most commonly used chemical activating agents for the production of highly micro – mesoporous carbons. Zn^{2+} ions enhance the porosity and proportion of surface functional groups. These carbons are efficient to purify wastewater containing organic pollutants and dyes preferably in the tertiary stages of the drinking water or effluent treatment operations. In this study adsorption behavior of a series of granular activated carbon impregnated with Zn^{2+} ions produced / activated at different temperature are elaborately discussed. Their characterisation and adsorption efficiency were determined using standard procedures based on experimental or theoretical basis.

This chapter discusses the preparation, characterisation and adsorption studies of a new series carbon designated as GAC383, GACO383, GACZC383, GACZC473, GACZC673, GACZC873, GACZC1073 and GACZC1273 which are prepared in our laboratory are mentioned here under.

3.2 Characterization Studies of Granular Activated carbon Impregnated with Zinc Ions (GACZC), Native Form of Carbon (GAC383) and Oxidized Carbon (GAC0383)

The adsorption efficiency of an activated carbon depends on its porous structure and surface chemistry. The granular activated carbon suitable for waste water treatment (adsorption process) is largely decided by the physico - chemical properties; determined by characterization studies of porosity, surface area, surface functional groups, surface morphology and crystallinity etc.

3.2.1 Effect of Impregnation Ratio on Zinc Ions (Zn²⁺) / GAC

An amount of 10g of GAC have been impregnated with different ratios of zinc ions and carbonised to determine the carbon yield, burn off at activation temperature 600^{0} C are shown in Table 3.1. It is seen that as weight of zinc increases, there is no much difference in the percentage of yield and burn off. The overall burn off percentage is in the range of 21.73 - 24.54%. However, an optimum yields with a minimum Zn²⁺ ion is obtained for $X_{zn} = 0.0017$. So the preparation of Zn impregnated granular activated carbons have been done in the ratio selected $X_{Zn} = 0.0017$ for further studies of modification, characterisation and adsorption efficiency evaluation.

Carbon	Weight of ZnCl ₂ (g)	Weight of Zinc (g)	X _{Zn} = gzn ²⁺ /g of carbon	Carbon yield (%)	Burn off (%)
	0.03	0.017	0.0017	77.74	22.26
	0.07	0.034	0.0034	76.53	23.47
GACZC873	0.14	0.067	0.0067	78.27	21.73
	0.28	0.134	0.0134	75.46	24.54
	0.56	0.269	0.0269	76.58	23.42
	0.84	0.403	0.0403	77.27	22.26

 $\label{eq:table 3.1: Impregnation ratio X_{Zn} used, carbon yield and burn off obtained during the preparation of GACZC series$

3.2.2 Carbon Yield and Burn – off

Carbon yield and burn - off of the granular activated carbon impregnated with Zn^{2+} ions ($X_{Zn} = 0.0017$) modified under different activation temperature is shown in Figure 3.1. Carbon yield decreases as the temperature of steam activation goes up. A lesser yield at higher temperature was essentially due to the devolatization of the carbon material upon heating [1]. The steam activation of GACZC series shows a very stable and steady burn - off pattern. It increases from 19% to 23% at 1273K. The burn - off promotes enough porosity and high surface area to the carbon produced.



Figure 3.1: Carbon yield and burn - off pattern of GACZC activated at different temperatures

3.2.3 Elemental Analysis

Elemental analysis of the modified granular activated carbons shows that it has carbon (65 - 95 %), Hydrogen (0.1 - 2.6 %), Nitrogen (0.1 - 0.6 %)and oxygen (5 - 31 %). GACZC1073 carbon has highest carbon percentage (94.5%). As carbon content of the activated carbon increase it is generally expected that the surface area may be high. High carbon content and high surface area are most desired qualities of carbon it enhances the adsorption

Chapter 3

capacity of most modified carbons [2]. In this study the granular activated carbon impregnated with zinc chloride activated at high temperature possesses less percentage of nitrogen and oxygen (Table 3.2). It is known that, as the temperature increases the more surface oxides were removed from carbon surfaces [3]. All the selected carbons in this study show nitrogen is less than 1%. For a typical activated carbon, as regards to nitrogen content is normally less than 1%. In a study nitric acid oxidation (for carbon GACO383) enhanced the oxygen content and decreased the content of elemental carbon and may lead to decrease of surface area. Carbonisation up to 1073K gives interesting features; the percentage of hydrogen, nitrogen and oxygen decreases with increasing temperature for the selected zinc impregnated (X_{Zn}) carbon ratio. Decrease in these compositions of elements indicated that the successive pyrolytic decomposition of surface functional groups on the carbon surface. However a slight increase is visible in the elemental composition at 1273K. The surface chemistry of these modified carbons is further evaluated by using the Boehm method and FTIR analysis.

Carbon	Carboxylic (meq/g)	Lactones (meq/g)	Phenolic (meq/g)	Base (meq/g)	C%	%Н	N%	0%
GAC383	0.40	0.17	0.45	0.50	89.43	0.60	0.36	9.61
GACO383	1.38	1.34	2.10	0.20	65.10	2.61	0.58	31.71
GACZC383	0.47	0.32	0.75	0.30	75.52	0.41	0.20	23.87
GACZC473	0.52	0.32	0.70	0.55	89.64	0.21	0.17	9.98
GACZC673	0.61	0.11	0.62	0.55	88.21	0.09	0.14	11.56
GACZC873	0.66	0.11	0.53	0.60	91.76	0.08	0.24	7.92
GACZC1073	0.39	0.10	0.20	0.90	94.67	0.09	0.11	5.13
GACZC1273	0.42	0.11	0.34	0.75	94.08	0.13	0.10	5.69

 Table 3.2: Surface functional groups and elemental composition of modified granular activated carbon GACZC series

School of Environmental Studies, Cochin University of Science and Technology

3.2.4 Surface Functional Group Analysis Using FTIR Spectroscopy and Boehm Method

Identification of surface functional groups has been analyzed by Fourier Transform Infrared spectroscopy and quantitatively measured using Boehm titration method. Boehm's titration technique was used for the selective quantification of carboxylic, lactonic, phenolic and carbonyl groups [4] present in the carbon surface (Table 3.2). It is seen that GACO383 (nitric acid oxidized form) have a high proportion of acidic groups; carboxylic (1.38 meq/g), phenolic (2.10 meq/g), lactonic (1.34 meq/g). This is due to generation of extra groups by acid oxidation [5]. It is known that high thermal treatment decreases the acidic functional complexes and in the presence of metals, the carbonyl group increases. However, activation at high temperature with Zn^{2+} ions decrease the proportion of acidic surface functional groups but enhances the carbonyl group.

The FTIR spectra of modified carbons (GAC383 and GAC0383) are shown in Figure 3.2 (a) and (b). The band at 3426 cm⁻¹ (GAC383) and 3437 cm⁻¹ (GAC0383) are assigned to O-H stretching vibrations. The bands at 2924 cm⁻¹ is attributed to the C-H interaction with the surface of GAC0383 and it is absent in GAC383 (native carbon). The peaks 1628 cm⁻¹ (GAC383) and 1631 cm⁻¹(GAC0383) are corresponds to the mono or distributed C=C. The weak band at 1397 cm⁻¹ only present in GAC0383 indicate the N-H group in the form of -CO-NH is showing the existence of nitrogen functional groups. Altogether, modifications of carbon (GAC0383) with nitric acid increase proportion of the acidic functional groups. It might be caused by the chemisorptions of oxygen on the newly generated sites which are refreshed by acid, removing the initially occupied inorganics [6].





Figure 3.2 (a): FTIR spectra of GAC383

Figure 3.2 (b): FTIR spectra of GACO383



Figure 3.2 (c): FTIR spectra of GACZC activated at different temperatures

The FTIR spectra of granular activated carbon impregnated with Zn^{2+} ions and activated at different temperature ranging from 383K - 1273K (GACZC series) are shown in Figure 3.2 (c). These zinc impregnated carbons showed the major absorption bands at 3403 – 3445 cm⁻¹, 2926 cm⁻¹, 1622 – 1637 cm⁻¹, 1020 – 1033 cm⁻¹ and 450-650 cm⁻¹. The first band at 3403 – 3445 cm⁻¹ is a broad peak that is attributed to O – H stretching vibration of hydroxyl groups. The peak at 2926 cm⁻¹ is assigned to C – H symmetrical and asymmetric stretching of residual methylene groups on the surface of GACZC. The band at 1622 – 1637 cm⁻¹ ascribed to aromatic

ring stretching or highly conjugated C=O is stretching, prominent and broad at all. The bands in the range of 1020 - 1033 cm⁻¹ are a strong band of C - O group in alcohol, phenol, ether or ester is visible on new carbons. These bands disappear as the activation temperature increases. There is a peak at 571cm⁻¹ and any of these between 450 - 650 cm⁻¹ are attributed to the out of plane C-H bending mode. The presence of these spectral regions indicated that alkaline groups and cyclic ketones and their derivatives are formed during activation by zinc ions. These groups are significant on activation up to 873K, and are observable in the FTIR spectra (Figure 3.2 (c)).

3.2.5 XPS Surface Analysis

The modified granular activated carbons are further characterized by using X- ray Photoelectron Spectroscopy (XPS) measurements to obtain the elemental composition of these carbons (Table 3.3) and the chemical functional groups on the surface (Table 3.4). The percentage of carbon is obtained by the area of the C 1s spectrum of modified carbons (Figure 3.3 (a)) is GAC383 – 92.96%, GACO383 – 86.54% and GACZC1073 – 97.69%. It shows that zinc ions impregnation and activation at 1073K (GACZC1073) increases the percentage of carbon content.



Figure 3.3: XPS spectra of modified granular activated carbons GAC383, GACO383 & GACZC1073 (a) C 1s peak (b) O 1s peak

73

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics





Figure 3.4 (a): XPS N 1s spectra of modified granular activated carbons GACO383

Figure 3.4 (b): XPS Zn 2p spectra of GACZC1073

The O 1s spectrum of the modified carbons is shown in Figure 3.3 (b). The atomic concentration of oxygen is higher at GACO383 that is the nitric acid oxidised form (12.86%). The XPS analysis shows that the GAC383 contains 92.96% carbon and 7.04% oxygen. The atomic concentration of zinc is calculated from the area of Zn 2p (Figure 3.4 (b)) of GACZC1073 is 0.02%.

Table 3.3: The elemental composition of the modified granular activated carbonsGAC383, GAC0383 and GACZC1073 from XPS analysis

Carbon	Position Binding energy (eV) C 1s	C%	Position Binding energy (eV) O 1s	0%0	Position Binding energy (eV) N 1s	N%	Position Binding energy (eV) Zn 2p	Zn%
GAC383	284	92.96	532	7.04	-	-	-	-
GACO383	284	86.54	532	12.86	400	0.60	-	-
GACZC1073	284	97.69	531	2.29	-	-	1022	0.02

e						,
Functional group	GAC383		GAC	O383	GACZC1073	
	C 1s	O 1s	C 1s	O 1s	C 1s	O 1s
Aliphatic carbon	284.07		284.26		284.02	
	284.39	-	284.72	-	284.09	-
	284.66				284.40	
					284.47	
Aromatic Carbon			285.26		285.07	
	285.15	-	285.67	-	285.80	-
					285.97	
Hydroxyl	286.13	-	286.13	-	286.71	-
Carbonyl	287.10	-	-	-	-	-
Metal oxide (ZnO)	-	-	-	-	-	530.90
Ketone, lactone,						
carbonyl	-	531.71	-	531.65	-	531.62
		532.52		532.22		
Ester	-	532.59	-	532.33	-	532.56
				532.97		
Ether oxygen	-	533.65	-	533.86	-	533.33
				533.59		
Carboxyl	-	534.56	-	534.42	-	534.57
				534.91		
Chemisorbed oxygen	-	536.16	-	-	-	536.16

Table 3.4 :	Assignment of binding energy values of the peaks in the C1s and O1s
	XPS spectrum of the surface functional groups in the modified
	granular activated carbons (GAC383, GACO383 and GACZC1073)

The C 1s broad peaks indicate the presence of different carbon species at the surface of granular activated carbons, GAC383 (Figure 3.5 (a), GAC0383 (Figure 3.6 (a) and GACZC1073 (Figure 3.7 (a)). It shows that the spectra were deconvoluted into different components such as aliphatic carbon (284.07 - 284.72 eV), aromatic carbon (285.07 - 285.97 eV), hydroxyl (286.13 - 286.71 eV) and carbonyl (287.1 eV) [7].





Figure 3.5: Deconvoluted XPS of GAC383 (a) C 1s region & (b) O 1s region



Figure 3.6: Deconvoluted XPS of GACO383 (a) C 1s region & (b) O 1s region



Figure 3.7: Deconvoluted XPS of GACZC1073 (a) C 1s region & (b) O 1s region

The O 1s peaks are deconvoluted into different components for GAC383 (Figure 3.5 (b)), GACO383 (Figure 3.6 (b)) and GACZC1073 (Figure 3.7 (b)). The O 1s peaks are indicating the presence of different chemical states of oxygen on the surface of these modified carbons (Table 3.4). The carbons show a peak at 531.62 - 531.71 eV is ascribed to ketone and lactone groups. The GAC383 shows a binding energy 532.52 - 532.59 eV, GACO383 – 532.22 to 532.97 eV and GACZC1073 – 532.56 eV attributes to ester groups. The binding energy between 533.33 - 533.86 eV is ascribed to ether like oxygen groups. The binding energy 534.56 - 534.91 eV is present in these granular activated carbons are attributed to carboxyl groups [8].

3.2.6 XRD Analysis

X-ray diffractograms for GAC383, GACO383 and GACZC series activated at (383, 473, 673, 873, 1073 and 1273K) are shown in Figure 3.8–3.9. Diffractograms among the carbon members show no visible differences. Diffraction peaks around 24 and 43^0 are assigned to the reflection from (002) and (10) planes, respectively. The occurrence of these broad peaks indicates crystallised structure and better layer alignment [9] for all the granular activated carbons. From the XRD profiles interlayer spacing d_{002} is determined using the Bragg equation as follows.

$$d_{002} = \frac{\lambda}{2\,\sin\theta} \tag{3.1}$$

Where, λ - wavelength of X-ray radiation and Θ – scattering angle or peak position. It is known that the interlayer distance of a typical graphitic structure is 0.335nm [10]. In the case of GAC reported in this study, the peak at $2\theta = 24^{\circ} - 25^{\circ}$ corresponds to an interlayer distance in the range of 0.35 – 0.38 nm (Table 3.5). This indicates that new carbons exist as non-graphitized forms.

	P		.,	
Carbon	20	L _c (nm)	L _a (nm)	d ₀₀₂ (nm)
GAC383	24.46	1.14	2.28	0.36
GACO383	24.98	0.97	1.94	0.35
GACZC383	25.37	1.36	2.72	0.35
GACZC473	24.05	1.10	2.20	0.37
GACZC673	24.40	1.18	2.38	0.36
GACZC873	23.57	1.20	2.39	0.38
GACZC1073	24.14	1.29	2.59	0.37
GACZC1273	23.78	1.29	2.58	0.37

Table 3.5: Structural parameters from X- ray diffraction studies

The crystallite size along c-axis L_c and the size of the layer planes L_a are determined using Scherrer equation.

$$D = \frac{k \lambda}{\beta \cos \theta} \tag{3.2}$$

Where *L* is either L_c or L_a , β is the half width of the diffraction peak in radians, θ is the scattering angle and *k* is the shape factor and the values of k = 0.9 (for L_c) and 1.84 (for L_a) are used for calculation. As regards to structure, L_c is the stack height and L_a is the stack width are presented in Table 3.5. The graphitic carbons are formed as stack width of around 1.0 - 2.0 nm [11]. The new modified carbons show stack height is in the range of 0.97 - 1.36 nm and stackwidth 1.94 - 2.59 nm. Results show that distinct difference from the graphitic sheets rather than our modified carbons.



of GAC383

Figure 3.8(b): X-ray diffractograms of GACO383



Figure 3.9: X-ray diffractograms of (a) GACZC383, (b) GACZC473, (c) GACZC673, (d) GACZC873, (e) GACZC1073 and (f) GACZC1273

3.2.7 Scanning Electron Microscopy (SEM)

Surface morphology and physical properties of the modified carbons (GAC383, GACO383, and GACZC1073) are studied using Scanning Electron Microscopy (SEM). SEM is useful for obtaining the surface features: size, shape and porosity of the carbon. Figure 3.10 - 3.12 shows the SEM image of modified carbons GAC383, GACO383 and GACZC1073 respectively at different resolutions (5 µm, 10 µm, 50 µm and 100 µm). GACZC1073 shows a greater proportion of pores on surfaces; hence there is a more possibility for a high pollutant / adsorbate to be adsorbed into these pores [12]. Compared to others, GACO383 (HNO₃ oxidised form) has a smooth surface features. In Figure 3.11 (a), shows that acid oxidation increases the pore width and surface structure is more uniform. This has to be further evaluated through pore analysis in a later section. Such carbon has a less Micropore volume has to be verified through *t* - *plot* analysis. GACO383 already has a large proportion of the surface oxygen complex

on the surface, as the pores are subjected to oxidative degradation by HNO_3 that ultimately causes widening of the existing pores.



Figure 3.10: SEM image of GAC383 (a) 100 μm resolution (b) 50 μm resolution (c) 10 μm resolution and (d) 5 μm resolution



Figure 3.11: SEM image of GACO383 (a) 50 μm resolution and (b) 10 μm resolution

Granular activated carbon incorporated with Zn²⁺: preparation, characterisation and adsorption studies



Figure 3.12: SEM image of GACZC1073 (a) 100 μm resolution (b) 50 μm resolution (c) 10 μm resolution and (d) 5 μm resolution

3.2.8 Transmission Electron Microscopy

High Resolution Transmission Microscopy (HRTEM) is also used as a tool for the porosity and surface properties of the modified carbons (GAC383, GACO383, and GACZC1073). HRTEM image of the native carbon GAC383 (Figure 3.13) indicated that it has a uniform microporosity. At 20 nm resolution, the pores were getting visible due to the high electron density field of micropore area. These pores were inherent throughout the surface and are slit-shaped. They were seats of high energy sites of graphene layers. Figure 3.13 (c & d) shows fringes and irregular pattern of carbon. Nitric acid oxidized carbon (GACO383) showed a predominant distribution of pores and graphitic spaces become

visible in the TEM image (Figure 3.14). HRTEM images of Zn^{2+} ions impregnated granular activated carbon shown in Figure 3.15 (a-d). It is clear that these carbons are highly microporous in nature.



Figure 3.13: TEM image of GAC383 (a) 200 nm resolution (b) 100 nm resolution (c) 50 nm resolution (d) 20 nm resolution





Figure 3.14: TEM image of GACO383 (a) 200 nm resolution (b) 100 nm resolution (c) 50 nm resolution (d) 20 nm resolution

Chapter 3



Figure 3.15: TEM image of GACZC1073 (a) 20 nm resolution (b) 20 nm resolution (c) 5 nm resolution (d) 2 nm resolution

3.3 Porosity Studies – Evaluation of Surface Area and Pore Volume

Physical characterization of pore structure (V_b , V_{mic} , V_{mes} and *pore width*) and surface area were done using nitrogen adsorption – desorption isotherm at liquid nitrogen at 77K by gravimetric method. Figure 3.16 shows the nitrogen adsorption – desorption isotherm for the newly modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273). On close examination of the isotherm profiles, it is seen that these carbons show Type I isotherm behavior, according to BDDT (Brunauer, Deming,
Deming, and Teller) classification [13]. This type of isotherm curves are characteristics of the existence of only strong interactions between the N₂ gas and carbon surface, because of high adsorption capacity at a low relative pressure as per IUPAC 2015 classification. Type I isotherm is a very common feature in granular activated carbons. Type I isotherm with H4 hysteresis loop indicates that the initially micropore filling occurs during N₂ adsorption, it is followed by multilayer physisorption and then capillary condensation is prevalent [14]. From the nitrogen adsorption desorption plot, it clear that at the relative pressure, 0.2 the micropore filling is completed. Then the mesopores are filled and to form a narrow hysteresis loop at high p/p_0 as identical as H4 type. The H4 hysteresis loop is visible for all granular activated carbons modified by our laboratory (GAC383, GACO383 & GACZC series) conditions. This indicates the presence of wider micropores or mesopores. H4 hysteresis loop also shows the existence of slit shaped pores prominent to contribute microporous.

Carbon	$\frac{V_t}{[cm^3g^{-1}]}$	V_{mic} [cm ³ g ⁻¹]	V_{mes} $[cm^{3}g^{-1}]$	Vmic/ Vt (%)	Vmes/ Vt (%)	Pore Width (nm)			
GAC383	0.573	0.351	0.222	61.26	38.74	1.77			
GACO383	0.526	0.297	0.229	56.46	43.54	1.77			
GACZC873	0.541	0.378	0.163	69.87	30.13	1.70			
GACZC1073	0.569	0.400	0.170	70.30	29.70	1.70			
GACZC1273	0.602	0.379	0.223	62.96	37.04	1.74			
$V_{x}(cm^{3} / g STP) = \frac{V_{x}(cm^{3} / g) \times 22414 \times 0.808}{28}$ *Vx- Vx Vmig Vmag									

To evaluate the physical characteristics of the modified carbons such as porosity and surface area, we used different isotherm models such as BET, *I* plot, Langmuir, Freundlich, John, Alpha S (α_s), Dubinin – Radushkevich (D – R), *t* - *plot*, BJH method are applied to N₂ data presented in Figure 3.16.



Figure 3.16: N₂ adsorption – desorption isotherm at 77K of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)

3.3.1 Brunauer Emmet Teller (BET) Isotherm Analysis

Brunauer Emmet Teller (BET) Isotherm method [13] was used to determine the specific surface area of new GAC. The BET equation for multilayer adsorption can be written as

$$\frac{1}{V(\frac{p_0}{p}-1)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \left(\frac{p}{p_0}\right)$$
(3.3)

Where p – gas pressure, V –amount of nitrogen gas adsorbed on the carbon surface at each pressure P, p_0 - saturation pressure, V_m – monolayer volume and C – constant related to the heat of the first – layer of adsorption.

The monolayer volume V_m and the constant C were calculated using a plot of $\frac{1}{V(\frac{p_0}{p}-1)}$ versus $\frac{p}{p_0}$. Practically, the linearity of the BET

isotherm plot is always restricted to a part of the isotherm. The extent of

linearity of BET isotherm depends on both adsorbent (modified carbons) and adsorbate (N_2 gas) interaction and the operational temperature (77K) [15]. For many porous materials, the range of linearity is for relative pressure of 0.05-0.3, but for granular activated carbons it is limited to relative pressures less than 0.1 [16]. The BET *C* parameter of these modified carbons is positive only in the relative pressure range of 0.05 to 0.1 and it is shown in Table 3.7. That indicates the completion of monolayer coverage occurs at this relative pressure. Based on this we calculated the specific surface area using BET equation at a relative pressure range of 0.05 to 0.1. To ascertain more information on porosity we used BET - Scatchard plot (*I plot*) method.

	p/p ₀	, upto 0.	1	p/	p ₀ upto	0.3			
Carbon	SA (BET) (m ² g ⁻¹)	V _m (BET) (cm ³ g ⁻¹	C	SA (BET) (m ² g ⁻¹)	V _m (BET) (cm ³ g ⁻¹	C	SA (I) (m ² g ⁻¹)	$\mathbf{V}_{\mathbf{m}}(\mathbf{I})$ ($\mathbf{cm}^{3}\mathbf{g}^{-1}$)	
GAC383	1298.5	0.461	524	996.8	0.354	-81.58	1271.2	0.457	
GACO383	1186.5	0.421	439	973.3	0.346	-118.59	1163.7	0.411	
GACZC873	1266.4	0.449	798	1029.9	0.366	-104.82	1248.8	0.447	
GACZC1073	1335.0	0.474	759	1083.4	0.385	-104.14	1316.8	0.471	
GACZC1273	1382.1	0.491	548	1127.5	0.400	-111.22	1355.2	0.482	
$*V_m(cm^3 / g STP) = \frac{V_m(cm^3 / g) \times 22414 \times 0.808}{28}$									

 Table 3.7:
 Surface area and Pore volume* of granular activated carbon impregnated with Zn²⁺ ions

The total pore volume of the modified carbons is measured by at relative pressure 0.98 (p/p_0) and shown in Table 3.6. It is clear that granular activated carbon GAC383 shows total pore volume 0.573 cm³g⁻¹ and it decreases with nitric acid oxidation GACO383 (0.526 cm³g⁻¹), hence shows the lower BET surface area. This means, nitric acid oxidation increases the proportion of acidic surface functional groups and suppresses

the micropore development on the surface and enlarges or widen the pore structure. Consequently mesopore volume increases. The BET isotherm model of granular activated carbon impregnated with zinc ions at higher temperature is shown in Figure 3.17. The BET surface area and pore volume are calculated and presented in Table 3.7. The activation temperature applied varies from 873 to 1273K the BET surface area (1266 – 1382 m²/g) and pore volume (0.29 - 0.32 cm³g⁻¹) increases. Activation systematically enhances the pore development.



Figure 3.17: BET isotherm plot of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)

3.3.2 I plot Method

In normal BET method the linear part has to be located within a range, and it depends on the adsorbent nature. It is very difficult to calculate the monolayer volume and surface area if the material has mesoporosity in presence microporous or vice versa. In such cases the BET - Scatchard plot (*I plot*) method is very useful [17]. The main advantage of *I plot* is without any knowledge on *C* value we can calculate the monolayer adsorption capacity V_m directly from the graph. Following this principle, a

plot of $[V(1 - \frac{p}{p_0})] / \frac{p}{p_0}$ versus $[V(1 - \frac{p}{p_0})]$ gives an inclined V shaped graph for modified carbons (GAC383, GACO383, GACZC873, GACZC1073 and GACZC1273) shown in Figure 3.18.



Figure 3.18: *I* plot of modified granular activated carbons (a) GAC383, (b) GAC0383, (c) GACZC873, (d) GACZC1073 & (e) GACZC1273

The extrapolation of the *I point* towards the *x* axis directly give $V_m(I)$ and is exactly same as of BET plot. The surface area [SA (I)] calculated

from the $V_m(I)$ using the equation (SA $(I) = 4.353V_m$) and all shown in Table 3.7.

$$\left[V\left(1 - \frac{p}{p_0}\right)\right] / \frac{p}{p_0} = CV_m - (C - 1)\left[V(1 - \frac{p}{p_0})\right]$$
(3.4)

The monolayer volume $(V_m(I))$ and surface area (SA(I)) is more comparable to BET pore volume and surface area, that indicates that the modified carbons are highly microporus in character. These modified carbons have a high surface area and pore volume, hence suitable for gaseous and liquid phase adsorption applications.

3.3.3 Langmuir Isotherm Analysis

The Langmuir isotherm model is applicable only on homogenous surface. The isotherm based on monolayer adsorption capacity that is only one molecule can adsorb on a site. The granular activated carbons are characterized by using this model. The mathematical equation of the Langmuir isotherm is [18]

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m}$$
(3.5)

P – Pressure of N₂ gas, V – amount adsorbed per unit mass of modified granular activated carbons at relative pressure (mmolg⁻¹), V_m – Monolayer adsorption capacity and b - Langmuir energy constant

The monolayer volume V_m and Langmuir energy constant can be calculated using a plot of $\frac{P}{V}$ versus *P* (Figure 3.19).

The Langmuir surface area (SA (L)) calculated by using the equation

Granular activated carbon incorporated with Zn^{2+} : preparation, characterisation and adsorption studies

$$SA(L) = \frac{V_L a n}{V_{STP}}$$
(3.6)

$$SA = \frac{V_m (cm^3 / g STP) x 0.162 x 10^{-18} (m^2 / N_2 molecule) x (6.023 x 10^{23})}{22414 (cm^3 / mol)}$$
(3.7)

The modified carbons show high monolayer volume and high correlation coefficient (R^2 -0.99) indicates the modified carbons have homogenous surface. It is seen that for the zinc impregnated carbons, as the activation temperature increases from 873 to 1273K the Langmuir surface area and porosity also increases. The nitric acid oxidised form GACO383 has a less Langmuir surface area that indicates nitric acid impregnation decreases the surface area and adsorption monolayer.

3.3.4 Freundlich Isotherm Analysis

The N_2 gas adsorption data of modified carbons (GAC383, GAC0383, GAC2C873, GACZC1073 and GACZC1273) were evaluated using Freundlich isotherm model [19] is given by

$$\log V = \log K_{\rm F} + 1/n \log P \tag{3.8}$$

Where, V – amount adsorbed per unit mass of modified granular activated carbons at relative pressure (mmolg⁻¹), P – Pressure of N₂ gas, K_F – adsorption capacity and 1/n – related to adsorption intensity.

The Figure 3.20 shows the Freundlich isotherm plot of modified granular activated carbons log P against log V. The Freundlich constants are tabulated in Table 3.8. The correlation coefficient obtained from the linear isotherm plot of Langmuir isotherm model ($R^2 = 0.99$) yields a much better fit than Freundlich isotherm model ($R^2 = 0.94 - 0.97$). This indicates the nitrogen adsorption takes place at the homogenous surface of the modified granular activated carbons (GAC383, GACO383, GACZC873,

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

GACZC1073 and GACZC1273). The adsorption intensity (n) is high with positive value (12.68–17.19) indicating that the adsorption mechanism follows physisorption process. The adsorption capacity (K_F) increases with activation temperature.

3.3.5 John Isotherm Model Analysis

John isotherm model [20] for solid - gas equilibria is represented as

$$loglog P = C + n \log V \tag{3.9}$$

A plot of *log V* versus *loglog P* gives a straight line from the slope we get adsorbability constant (*n*) and John isotherm constant *C* from intercept. The limiting micropore volume $[V_m (J)]$ calculated from extrapolating the straight line connecting to the y axis (Figure 3.21). The $V_m (J)$ value is more comparable with $V_m (L)$ and the surface area of John *SA* (*J*) and Langmuir also comparable that indicate the modified carbons are highly microporous in nature.

	Langn	nuir Isotl Model	Freundlich Isotherm Model			John Isotherm Model				
Carbon	SA (L) (m ² g ⁻¹)	V _m (L) (cm ³ g ⁻¹ STP)	\mathbf{R}^2	KF	а	${f R}^2$	SA (J) (m ² g ⁻¹)	V _m (J) (cm ³ g ⁻¹ STP)	и	\mathbb{R}^2
GAC383	1598.2	367.1	0.99	231.44	13.91	0.97	1610.0	369.9	3.22	0.99
GACO383	1476.6	339.0	0.99	202.74	12.68	0.97	1503.9	345.5	2.84	0.99
GACZC873	1514.6	347.9	0.99	240.15	17.19	0.95	1522.6	349.8	3.89	0.99
GACZC1073	1594.8	366.4	0.99	252.34	17.08	0.94	1608.6	369.53	3.85	0.99
GACZC1273	1685.2	387.1	0.99	248.81	14.50	0.96	1700.4	390.60	3.31	0.99
$V_m (cm^3 / g) = \frac{V_m (cm^3 / g STP) \times 28}{22414 \times 0.808}$										

Table 3.8: Porosity parameters of granular activated carbon impregnated with Zn²⁺ ions calculated from Langmuir, Freundlich and John isotherm model



Figure 3.21: John isotherm plot of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073& GACZC1273) **Figure 3.22:** α_s isotherm plot of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)

93

3.3.6 Alpha S (α_s) Isotherm Analysis

The Alpha S (α_s) plot is developed by Gregg and Sing (1982) [21] by plotting the amount of nitrogen adsorbed against α_s , the reduced standard

adsorption. The nitrogen uptake (V_{ad}) at each p/p_0 divided by that at 0.4 p/p_0 gives the α_s values. The α_s isotherm plot of modified granular activated carbons is shown in Figure 3.22. The surface area of the α_s plot calculated by using the equation

$$A_s = 2.86 \frac{V}{\alpha_s} \tag{3.10}$$

$$A_s = 2.86 * Slope$$
 (3.11)

The value 2.86 has been obtained by calibration against the BET area of sooty silica's. The α_s micropore volume (V_{mi}) and surface area (A_s) of modified carbons (GAC383, GACO383, GACZC873, GACZC1073 and GACZC1273) are given in Table 3.9. The nitric acid oxidation (GACO383) shows comparatively less micropore volume and surface area compared to other carbons. Nitric acid oxidation suppresses the surface area compared to other carbons. The zinc ions impregnated granular activated carbons shows that micropore volume and surface area from the α_s isotherm method increases with increasing activation temperature.

3.3.7 Dubinin - Radushkevich (D-R) isotherm Analysis

The micropore surface area and micropore volume of modified carbons can be determined by using Dubinin Radushkovich (D - R) isotherm method [22].

$$\log V = \log V_0 - D \log^2(p_0 / p)$$
(3.12)

V - Amount of nitrogen adsorbed at each relative pressure, V_0 – micropore volume from D-R isotherm and D – constant related to micropore structure

$$D = 2.303 \left(\frac{RT}{\beta E_0}\right)^2$$
(3.13)



R – gas constant, T – Temperature, β - affinity coefficient of N₂ gas (0.33) and E_0 - characteristic energy of modified carbons

A plot of *log V* versus $log^2(p_0 / p)$ of modified carbons GAC383, GACO383, GACZC873, GACZC1073 and GACZC1273 are shown in Figure 3.23. The micropore volume (V_0) and characteristic energy E_0 calculated from the intercept and slope of the D-R isotherm. The characteristic energy related to pore width of the modified carbons is determined using McEnaney equation [23]

$$L_{av} = 6.6 - 1.79 \ln E_0 \tag{3.14}$$

The D – R micropore volume of the modified carbons are comparable with micropore volume calculated from α_s plot, further confirms the modified carbons are micro porous in nature. The characteristic energy is in the range of 15.02–16.84 kJ/mol, reveals that the adsorption occurs by a physisorption mechanism. The microporous surface area calculated from D – R plot is more compared with *t* - *plot* micropore surface area.

Table 3.9: Dubinin – Radushkevich (D –R) and Alpha S (α_s) constants of the modified carbons

Carbon		D-F	$\alpha_{\rm s}$ Isotherm						
	L _{av} (D-R) (nm)	E ₀ (D-R) (kJ/mol)	V ₀ * (D-R) (ml/g)	S _{mi} (D-R) (m ² /g)	R ²	V _{mi} * (ml/g)	$\begin{array}{c} \mathbf{A_s} \\ (\mathbf{m^2/g}) \end{array}$		
GAC383	1.68	15.62	0.543	646.51	0.99	0.543	1005.26		
GACO383	1.75	15.02	0.500	570.22	0.98	0.503	930.30		
GACZC873	1.54	16.84	0.525	679.92	0.99	0.524	969.86		
GACZC1073	1.56	16.73	0.554	711.53	0.99	0.550	1016.52		
GACZC1273	1.66	15.79	0.576	694.76	0.99	0.576	1065.93		
$*V_{m}(cm^{3} / g STP) = \frac{V_{m}(cm^{3} / g) \times 22414 \times 0.808}{28}$									

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

<u>95</u>

Chapter 3

The granular activated carbon impregnated with Zn^{2+} ions and activated at 1073K shows the high micropore surface area compared to other carbons from this series. The pore width (L_{av}) of the modified carbons shown in Table 3.9 truly is in the range of (1.5 – 1.8 nm). These pore width indicate that these carbons are microporous in nature.



Figure 3.23: Dubinin - Radushkevich (D – R) isotherm plot of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)



3.3.8 *t* - *plot* Isotherm Analysis

Lippens and De- Boer (1964) t - plot methods [24] were used to determine the micropore volume and external surface area of modified granular activated carbons using adsorbed thickness calculations (Figure 3.24). The V_{mi} and SA_{ext} are determined by using the relationship

$$t = [13.99 / (0.034 - \log(p / p_0))]^{0.5}$$
(3.15)

Where *t* is the thickness of the pores of granular activated carbons and p/p_0 is the relative pressure of nitrogen adsorption desorption isotherm at 77K.

Granular activated carbon impregnated with Zn^{2+} ions / activated at 1073K (GACZC1073) shows highest micropore volume and lowest external surface area (Table 3.10) and these carbons has more carbon content and high basic groups differ from other carbon studied. Here during activation Zn^{2+} has to be incorporated into the interior of the GAC particles, where it inhibits the expected contraction with increasing temperature (1073K). Which implies that Zn^{2+} may act as a template for the creation of microporosity on carbon granules. Hence, granular activated carbon incorporated with Zn^{2+} ions and activated at 1073K (GACZC1273), micropore volume and high micropore surface area compared to other carbons. As the activation temperature of 1273K (GACZC1273), micropore volume becomes less than that observed for activation at 1073 (GACZC1073), but increases the external surface area, that means Zn^{2+} ions impregnated granular activated carbon activation at 1073K (GACZC1073) produce high microporous carbon.

		t Plot		BJH Isotherm						
Carbon	V _{mi} (cm ³ /g)	SA_{ext} (m ² /g)	${ m SA}_{ m mi}$ $({ m m}^2/{ m g})$	ADCSA (m ² /g)	DECSA (m ² /g)	ADCPV (cm ³ /g)	DECPV (cm ³ /g)	Pore Width Ad (nm)	Pore Width De (nm)	
GAC383	0.351	408.10	588.66	226.21	220.52	0.138	0.134	2.44	2.43	
GACO383	0.297	433.72	540.59	250.00	242.84	0.142	0.137	2.28	2.25	
GACZC873	0.378	305.84	724.10	166.77	176.62	0.099	0.101	2.36	2.29	
GACZC1073	0.400	316.60	766.76	172.78	184.91	0.103	0.107	2.38	2.31	
GACZC1273	0.379	419.99	707.47	229.03	234.69	0.135	0.136	2.36	2.32	

Table 3.10: Surface area and pore size distribution using t - plot and BJH method

3.3.9 BJH Pore Size Distribution Studies

The pore size distribution of modified carbons is determined according to the BJH method from the H4 hysteresis loop, based on the Kelvin equation [25].

$$r_{p} = t + r_{k} = t - \frac{4.5}{\log (p/p_{0})}$$
(3.16)

 r_p is the pore radius of the new carbons, *t* is the thickness of the adsorbed layer and r_k is the meniscus radius and p/p_0 is the relative pressure.

The Figure 3.25 shows the BJH adsorption isotherm plot and Figure 3.26 (a, b & C) depicts the BJH desorption isotherm plot of new carbons (GAC383, GACO383, GACZC873, GACZC1073 and GACZC1273). The BJH method is commonly used to determine the mesopore volume of porous carbons. The pore diameter ranging from 0 to 3000 A^0 for BJH adsorption and 0 to 200 A^0 for BJH desorption studies is determined. The average pore width of the starting material GAC383 was determined from BJH adsorption – desorption model is 2.44 nm and 2.43 nm respectively. GAC383 is oxidised with nitric acid, GACO383 decrease the pore width 2.28 nm (adsorption) and 2.25 nm (desorption) method. The new carbons, zinc incorporated and activated at higher temperature (GACZC873, GACZC1073 and GACZC1273) the average pore width ranges from 2.36 nm to 2.38 nm for BJH adsorption studies and 2.29 nm to 2.32 nm for BJH desorption studies.

The cumulative surface area of these new carbons is calculated by using the equation

$$SA_{cum}(m^2 / g) = 2\sum V_{pi} \sum r_{pi}$$
(3.17)

The adsorption cumulative surface area for new carbons; GAC383 (226.21 m^2/g), GACO383 (250 m^2/g), GACZC873 (166.77 m^2/g), GACZC1073 (172.78 m^2/g) and GACZC1273 (234.69 m^2/g) and BJH desorption cumulative surface area for these carbons; GAC383 (220.52 m^2/g), GACO383 (242.84 m^2/g), GACZC873 (176.62 m^2/g), GACZC1073 (184.91 m^2/g) and GACZC1273 (234.69 m^2/g).



Figure 3.25 : BJH adsorption cumulative Figure 3.26 (a): BJH desorption pore volume of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)

cumulative pore volume of modified granular activated carbons (GAC383, GACO383, GACZC873, GACZC1073 & GACZC1273)

220



Chapter 3

The BJH pore size distribution indicates that the new carbons are predominantly micro and mesoporous and it is more efficient for liquid phase adsorption studies (treatment of drinking water / wastewater system).

3.4 Liquid Phase Adsorption Studies Using Carbon - GACZC Series

Batch adsorption processes using the new series of carbon are exhaustively done under laboratory conditions to evaluate kinetics, isotherms and thermodynamics. Phenol, p – nitrophenol and methylene blue (MB) are selected for liquid phase adsorption studies. Batch experiments (bench scale) were carried out as a function of initial concentration and contact time to test the adsorption efficiency of each one of the series.

3.4.1 Adsorption Studies – Phenol as Adsorbate

Adsorption studies of phenol include determining the adsorbent dose, contact time, nature of carbon selected for adsorption studies such as adsorption kinetics, isotherm and thermodynamics.

3.4.1.1 Adsorbent Dosage

To determine the optimum dose of carbon (GAC383), 1000 mg/L of the phenol solution was shaken with weight of GAC383 ranging from 1 g/L to 20 g/L at constant temperature (30° C) for a period of 8 hrs. The Figure 3.27 shows that phenol removal decreases with increasing the dose of GAC383. For small carbon doses, a small area of external surface is available for adsorption. Therefore, it exists a large driving force from the phenol solution per unit mass of GAC383 in the aqueous phase. A higher solution gradient with smaller solid concentration enhanced the accumulation inside the particles [5]. So in all the succeeding phenol adsorption isotherms and kinetic studies the adsorbent dose is fixed as 1 g/L.



Figure 3.27: Adsorbed quantity as a function of carbon dosage for the removal of phenol on GAC383 (C₀: 1000 mg/L)

3.4.1.2 Effect of Contact Time

Batch adsorption studies are done using 50 ml of the 1000 mg/L concentration of phenol solution as adsorbate and GAC383 and GAC0383 are adsorbent, keeping carbon dose 1 g/L.



Figure 3.28: Effect of contact time for the adsorption of phenol by GAC383 & GACO383 (C₀: 1000 mg/L)

Granular Activated Carbon Incorporated With Zn $^{2+}$ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 101

Chapter 3

Figure 3.28 shows the amount of phenol uptake at different time intervals (q_t) mg/g versus the contact time (t) in minutes. Adsorption increases with time after 480 minutes (8 hours) there is no significant amount of phenol is removed from the solution. This time is fixed as equilibration time, to conduct further isotherm studies.

3.4.1.3 Selection of GACZC for Phenol Adsorption

Selection of GACZC series for phenol adsorption was studied using an initial concentration of 1000 mg/L phenol after 8 hr equilibration period (Figure 3.29). The filtrate was measured by a UV – Visible spectrophotometer at 268 nm. Granular activated carbon impregnated with Zn^{2+} ions and activated at different temperature ranging from 383K to 1273K named as GACZC383, GACZC473, GACZC673, GACZC873, GACZC1073 and GACZC1273 respectively. From this series GACZC1073 shows highest phenol adsorption efficiency compared to others. It has very high carbon content (94%), have a high proportion of basic surface groups (0.90 meq/g) and enough micro porous surface area (766.76 m²/g) which enhances the adsorption capacity.



3.4.1.4 Adsorption Studies of GAC383, GACO383 and GACZC1073

Adsorptions of phenol on the above modified carbons are studying for an initial concentration of 250 mg/L solution at neutral pH to determine the effects of temperature and time. The shaking period ranges from 10 minute to 600minutes at temperatures 10^{0} C, 20^{0} C, 30^{0} C, 40^{0} C and 50^{0} C. Adsorbed amount (q_{t}) against time (t) for selected temperature was plotted for GAC383 (Figure 3.30), GACO383 (Figure 3.31) and GACZC1073 (Figure 3.32). Adsorption is more as the temperature rises because the number of active sites of modified carbons are enhanced; it improves the phenol adsorption efficiency [26]. Granular activated carbon, activated with Zn^{2+} ions at 1073 (GACZC1073) shows higher adsorption capacity compared to others. This indicates impregnation and activation of carbon with Zn^{2+} ions improved the phenol adsorption capacity.



Figure 3.30: Effect of contact time on the adsorption of phenol on GAC383 at different temperatures (C₀: 250 mg/L)

Figure 3.31: Effect of contact time on the adsorption of phenol on GACO383 at different temperatures (C₀: 250 mg/L)





Figure 3.32: Effect of contact time on the adsorption of phenol on GACZC1073 at different temperatures (C₀: 250 mg/L)

3.4.1.5 Kinetic Modelling

Adsorption kinetic studies of GAC – phenol system provide insight into chemical property changes in tune of time measured as its reaction rate. Kinetic studies provides knowledge on the involvement of GAC surface chemistry and the rate of removal of phenolic pollutants. This time dependent experimental data of kinetics were analyzed using different kinetic models: pseudo first order, pseudo second order, intraparticle diffusion and Boyd model to examine the mechanism of adsorption.

3.4.1.5.1 Pseudo First Order Model for Phenol Adsorption

Among the kinetic models known to study adsorption systems Lagergen model, one of the general and usually followed for solute adsorption was applied. This model is expressed in a linear form [27]

$$ln(q_e - q_t) = ln q_e - K_1 t \tag{3.18}$$

Where K_1 (min⁻¹) is the pseudo – first order rate constant, t (min) the contact time, q_t and q_e are the amount of phenol adsorbed at any time t and at equilibrium respectively for the granular activated carbon under study. A plot of ln (q_e - q_t) against t at different temperatures is shown for GAC383 (Figure 3.33), GACO383 (Figure 3.34) and GACZC1073 (Figure 3.35).

From the slope K_1 and from the intercept $q_e cal$ are evaluated and given in Table 3.11. It is seen that $q_e cal$ is lower than $q_e exp$ and the regression is also less, means first order is not applicable for the adsorption of phenol for the new carbon adsorption system. The first order rate constant (K_1) is almost same for all carbon studied at all temperatures.



Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics







Table 3.11: Comparison of the pseudo first and second order constants and
parameters for the adsorption of phenol (C₀: 250 mg/L)

Cashar	Т	q _e exp	Pseud	o First O Kinetics	rder	Pseudo Second Order kinetics			
Cardon	(K)	(mg/g)	q _e cal (mg/g)	K ₁ (min ⁻¹)	\mathbf{R}^2	q _e cal (mg/g)	K_2*10^4 (gmg ¹ min ⁻¹)	\mathbf{R}^2	
	283	121.61	86.99	0.007	0.96	135.14	1.24	0.99	
GAC383	293	126.41	88.72	0.007	0.97	137.93	1.40	0.99	
	303	129.99	84.02	0.007	0.95	139.47	1.59	0.99	
	313	134.93	84.76	0.007	0.96	143.06	1.83	0.99	
	323	138.76	80.16	0.007	0.95	145.14	2.09	0.99	
	283	118.38	75.83	0.006	0.94	124.53	1.80	0.99	
	293	122.27	73.27	0.005	0.93	126.42	2.10	0.99	
GACO383	303	125.99	71.43	0.006	0.93	130.21	2.30	0.99	
	313	129.63	70.72	0.006	0.94	133.69	2.50	0.99	
	323	132.84	69.31	0.006	0.95	136.43	2.70	0.99	
	283	139.79	98.18	0.007	0.97	146.20	1.29	0.99	
	293	147.13	94.27	0.007	0.97	150.83	1.46	0.99	
GACZC1073	303	156.68	73.70	0.005	0.93	160.51	1.52	0.99	
	313	167.04	74.32	0.005	0.88	173.31	1.71	0.99	
	323	174.79	78.08	0.006	0.94	181.16	1.74	0.99	

3.4.1.5.2 Pseudo Second Order Model for Phenol Adsorption

Ho and Mckay (1999) [28] presented an adsorption based pseudo – second order rate law expression for how the reaction rate depends on the adsorption capacity on solid phase but not the concentration of adsorbate. The model can be represented in the following form

$$\frac{t}{q_{t}} = \frac{1}{K_{2}q_{e}^{2}} + \frac{t}{q_{e}}$$
(3.19)

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), *t* is the reaction time (min), q_t (mg/g) is the amount adsorbed at time *t*, K_2 is the equilibrium rate constant of pseudo second order adsorption $(gmg^{-1}min^{-1})$. This model is used to express the kinetics of phenol adsorption on the new carbons. Where the graph t/q_t versus *t* gives a straight line for all the carbons studied at different temperature are shown in Figure 3.36, 3.37 and 3.38. From the slope the amount of phenol adsorbed at equilibrium q_ecal and from the intercept K_2 is determined (Table 3.11). The correlation coefficient (R^2) for pseudo second order kinetic model was relatively high and its calculated q_ecal (equilibrium adsorption capacity) is more comparable with q_eexp than the calculated q_e for the first order kinetics. This suggests that the batch reactor system consisting of new GAC follows pseudo second order kinetic model. The new treatment system is efficient and is related to carbon behavior [29].

3.4.1.5.3 Intraparticle Diffusion Model for Phenol Adsorption

Weber and Morris (1963) [30] proposed an intraparticle diffusion model to predict the rate controlling step of an adsorption process. When mass transfer is the controlling step, it is important to identify the diffusion mechanism. According to intraparticle diffusion model, the initial rate of diffusion is given by the following equation:

$$q_t = K_{id} t^{0.5} + C (3.20)$$

Granular Activated Carbon Incorporated With Zn $^{2+}$ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 107

Chapter 3

Where qt (mg/g) is the amount of phenol adsorbed at any time t, K_{id} (mg g⁻¹ min^{-1/2}) is the intra particle diffusion constant and C (mg/g) is the boundary layer thickness. Intraparticle diffusion model for the adsorption of phenol on GAC383 (Figure 3.39), GACO383 (Figure 3.40) and GACZC1073 (Figure 3.41) at different temperatures are given. It is seen that, there are two straight line portions; first is attributed to surface diffusion and the second linear portion is attributed to intra particle diffusion. The K_{id1} for the modified GAC (Table 3.12) is higher than the K_{id2} of all GAC indicating that pore diffusion is a slow step. The intercept of the second linear portion is proportional to the boundary layer thickness (C_2) for the modified carbons at different temperature ranging from 10 to 50°C are GAC383 (52.67 - 76.33 mg/g), GACO383 (56.42 - 80.12 mg/g) and GACZC1273 (52.68 - 96.11 mg/g). The boundary layer thickness increases with temperature; because temperature enhances the proportion of active sites of the modified carbon's surface.

			Intrapar	ticle diff	usion constan	nt						
Carbon	Т (К)	K _{id1} (mgg ⁻¹ min ^{-1/2})	$\underset{(mgg^{-1})}{C_1}$	\mathbf{R}^2	K _{id2} (mgg ⁻¹ min ^{-1/2})	C2 -1 (mgg ⁻)	\mathbf{R}^2					
	283	14.49	-29.90	0.97	3.22	52.67	0.98					
	293	14.40	-24.96	0.99	3.36	54.82	0.98					
GAC383	303	15.33	-25.13	0.97	3.18	61.59	0.98					
	313	14.29	-13.35	0.99	3.17	67.43	0.97					
	323	14.16	-6.98	0.99	2.88	76.33	0.99					
	283	11.28	-10.05	0.98	2.77	56.42	0.99					
	293	11.05	-3.68	0.99	2.68	61.33	0.97					
GACO383	303	11.32	0.30	0.99	2.43	71.14	0.98					
	313	11.15	6.68	0.98	2.43	75.56	0.99					
	323	10.49	15.03	0.99	2.37	80.12	0.99					
	283	14.74	-23.19	0.99	3.79	52.68	0.94					
	293	14.63	-16.91	0.98	3.53	64.20	0.90					
GACZC1073	303	15.75	-15.85	0.99	3.50	74.99	0.92					
	313	15.08	0.54	0.99	3.52	89.29	0.99					
	323	14.70	8.74	0.99	3.58	96.11	0.99					

 Table 3.12: Intraparticle diffusion constants for phenol adsorption on carbons GAC383, GAC0383 and GACZC1073 (C₀: 250 mg/L)

School of Environmental Studies, Cochin University of Science and Technology

3.4.1.5.4 Boyd Plot – Phenol

It is seen from the intra particle diffusion model of phenol on modified granular activated carbons, that two straight lines that are distinct for surface adsorption and intraparticle diffusion. This prompts to determine which step is the actual step for adsorption of phenol on new modified carbons [31]. The Boyd kinetic equation is given by

$$F = 1 \left(\frac{6}{\pi^2} \right) \exp(-B_t)$$
(3.21)

$$F = \frac{q_t}{q_e} \tag{3.22}$$

F is the fraction of solute adsorbed at any time t, q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the amount adsorbed at equilibrium (mg/g) and B_t is a mathematical function of F. Substituting in equation (3.22) in equation (3.21) and it simplifies

$$B_t = -0.4977 - \ln(1 - F) \tag{3.23}$$

 B_t calculated by the equation (3.23). B_t plotted against time t (Figure 3.42, 3.43 and 3.44) it shows that the plot was linear but do not pass through the origin. This confirms that, for the selected aqueous phenol concentration, external mass transport governs the adsorption process at all temperatures studied [32].





Figure 3.43: Boyd plots for phenol adsorption on GACO383 at different temperatures $(C_0: 250 \text{ mg/L})$

Figure 3.44: Boyd plots for phenol adsorption on GACZC1073 at different temperatures (C₀: 250 mg/L)

3.4.1.6 Activation Energy

The activation energy E_a for phenol adsorption was determined by the Arrhenius method.

$$\ln K_2 = \ln K_0 - \frac{E_a}{RT} \tag{3.24}$$

Where E_a is the activation energy, R is the gas constant and T is the adsorption temperature. K_2 is the rate constant obtained from the pseudo second order kinetic model. A plot of $ln K_2$ against l/T gives a straight line (Figure 3.45) from the slope, Arrhenius activation energy (E_a) calculated (Table 3.13) based on equation 3.24. The activation energy gives an idea about the mechanism of adsorption is physisorption (5 – 40 kJ mol⁻¹) or chemisorption (40 – 800 kJ mol⁻¹) [33]. In our study, the activation energy of phenol is less than 40 kJmol⁻¹. This reveals that the adsorption of phenol on GAC383 (10 kJ mol⁻¹), GACO383 (7.59 kJ mol⁻¹) and GACZC1073 (5.87 kJ mol⁻¹) follows physisorption.

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 1111





Figure 3.45: Plot of ln K_2 versus 1/T for the adsorption of phenol on new carbons (GAC383, GAC0383 and GACZC1073)

 Table 3.13: Activation energy determined during adsorption of phenol on modified carbons.

Carbon	E _a (kJ mol ⁻¹)	K ₀
GAC383	10.00	0.0086
GACO383	7.59	0.0046
GACZC1073	5.87	0.0016

3.4.1.7 Adsorption Isotherm Studies of phenol

Adsorption isotherm studies were carried out different initial concentration ranging from 25 to 3000 mg/L of phenol on GAC383, GACO383 and GACZC1073. The Figure 3.46 to 3.50 shows the isotherm plots, where the amount of phenol adsorbed per gram of adsorbent (q_e) versus the equilibrium concentration (C_e). Adsorption capacity increases with phenol concentration as well as with respect to temperature. It is observed that, adsorptive capacity varies in the order GACZC1073 > GAC383 > GACO383. This reveals that carbon with Zn²⁺ ions and activated / carbonized at 1073K have a more adsorption efficiency among the carbon selected and studied.





Figure 3.48: Adsorption of phenol on GAC383,GACO383 and GACZC1073 at 30^{0} C (C₀: 25 - 3000 mg/L)

Figure 3.49: Adsorption of phenol on GAC383, GAC0383 and GACZC1073 at 40^{0} C (C₀: 25 - 3000 mg/L)





Figure 3.50: Adsorption of phenol on GAC383, GACO383 and GACZC1073 at 50° C (C₀: 25 - 3000 mg/L)

Oxidized carbon (GACO383) shows the less phenol adsorption compared to others. This is because, GACO383 is more hydrophilic, due to polar oxygen (carboxylic) groups, act as ideal sites for water clusters compared to phenol molecule to build up hydrogen – bonding. GACO383 is having predominantly micro and mesopores, hydrogen – bonding can effectively reduce the affinity of the phenol molecules into the inner pore structure [34]. Dispersive type $\pi - \pi$ interaction plays a dominant role in the physisorption mechanism of phenol adsorption. GACZC1073 have more basic groups on the surface; it enhances the π electron density and the phenol adsorption capacity [35]. Adsorption is prominent with temperature rise, shows that the adsorption of phenol onto new carbon is endothermic in nature.

Equilibrium isotherm data are further processed to fit the standard adsorption models of Langmuir, Freundlich, Temkin and D-R isotherms.

3.4.1.7.1 Langmuir Isotherm - Phenol

Langmuir isotherm is a mathematical construct to model the adsorption efficiency of activated carbon. The form of the model used in this study is

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e \tag{3.25}$$

Where q_e (mg/g) and C_e (mg/L) are the amount of phenol adsorbed per gram of modified carbons and equilibrium concentration respectively. The Langmuir constant K_L (L/g) is the energy of adsorption and K_L/a_L (q_{max}) is the monolayer adsorption capacity. A plot of C_e/q_e against C_e assumes straight lines (Figure 3.51, 3.52 and 3.53). From the slope, monolayer adsorption capacity q_{max} (mg/g) and from the intercept K_L as (L/g) and are listed in Table 3.14. The high correlation coefficient on applying Langmuir isotherm (R²-0.99) indicates the homogenous nature of carbon surface. GACZC has the higher adsorption capacity measured as 343.64 mg/g (10^oC), 378.78 mg/g (20^oC), 408.16 mg/g (30^oC), 432.90 mg/g (40^oC) and 454.55 mg/g (50^oC) compared to others. This is because, these carbons shows more basic surface groups (0.90 meq/g), preferably high carbon content (94%) and high micropore surface area (766.76 m²/g) determined from t - *plot* method. This means, surface functional groups and surface area controls the adsorption.



Figure 3.51: Langmuir isotherm
model of phenol on
GAC383 at different
temperatures
 $(C_0: 25 - 3000 \text{ mg/L})$ Figu

Figure 3.52: Langmuir isotherm model of phenol on GACO383 at different temperatures $(C_0: 25 - 3000 \text{ mg/L})$

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 115





Figure 3.53: Langmuir isotherm model of phenol on GACZC1073 at different temperatures (C₀: 25 - 3000 mg/L)

Figure 3.54: Freundlich isotherm model for phenol adsorption on GAC383 at different temperatures (C₀: 25 - 3000 mg/L)



GACZC1073 at different temperatures (C₀: 25 - 3000 mg/L)

3.5

3.4.1.7.2 Freundlich Isotherm – Phenol

(C₀: 25 - 3000 mg/L)

Isothermal variation of specific adsorption of phenol on GAC383, GACO383 and GACZC1073 has been evaluated using Freundlich isotherm model.

$$\log q_e = \log K_F + 1/n \log C_e \tag{3.26}$$

Where C_e (mg/L) is the equilibrium concentration of phenol and q_e (mg/g) is the amount of phenol adsorbed at equilibrium. The intercept is the adsorption capacity K_F (mgg⁻¹) and slope 1/n is relates to the measure of adsorption intensity. A plot of log q_e versus log C_e shown in Figure 3.54 - 3.56 and the adsorption constants and parameters are evaluated and given in Table 3.14.

Table 3.14: Langmuir, Freundlich and Temkin parameters of phenol on modified carbons (C₀: 25 - 3000 mg/l)

	т	Langmuir isotherm Constants			Freundlich isotherm Constants			Temkin isotherm Constants			
Carbon	(K)	q _{max} (mgg ⁻¹)	K _L (1 mg ⁻¹)	\mathbf{R}^2	$\mathbf{K}_{\mathbf{F}}$ (mgg ⁻¹)	1/n	\mathbf{R}^{2}	A (l/mg)	B	b T (J/mol)	\mathbb{R}^2
	283	266.67	2.33	0.99	16.38	0.385	0.93	0.190	43.10	52.66	0.98
CAC292	293	284.90	2.48	0.99	16.74	0.391	0.94	0.188	46.14	49.19	0.98
GAC383	303	312.50	2.48	0.99	16.73	0.402	0.98	0.175	50.47	44.97	0.99
	313	336.70	2.53	0.99	17.00	0.410	0.95	0.171	53.96	42.06	0.98
	323	352.12	2.68	0.99	17.38	0.413	0.95	0.172	56.33	40.29	0.98
	283	188.32	2.17	0.99	19.16	0.316	0.89	0.370	27.90	81.35	0.99
C A CO202	293	199.60	2.34	0.99	19.87	0.320	0.89	0.370	29.61	76.64	0.99
GAC0383	303	209.64	2.48	0.99	20.71	0.321	0.89	0.380	30.98	73.26	0.99
	313	225.73	2.52	0.99	21.13	0.328	0.90	0.360	33.34	68.08	0.99
	323	236.97	2.59	0.99	21.66	0.331	0.90	0.360	34.88	65.07	0.99
	283	343.64	2.24	0.99	19.53	0.385	0.95	0.204	51.07	44.45	0.97
G + G7 G10 50	293	378.78	2.52	0.99	20.96	0.389	0.98	0.217	55.67	40.77	0.99
GACZC1073	303	408.16	3.36	0.99	25.17	0.380	0.96	0.288	58.78	38.62	0.97
	313	432.90	3.85	0.99	29.06	0.370	0.96	0.366	60.13	37.75	0.98
	323	454.55	4.50	0.99	32.54	0.364	0.94	0.440	62.01	36.60	0.98

Isotherm study (10° C to 50° C) enhanced the adsorption capacity (K_F) of the modified carbons; temperature favours the adsorption of phenol on modified carbons. The Freundlich constant l/n is less than one (l/n < 1)means it is classified to Langmuirian isotherm. In the case of Langmuir type

Chapter 3

isotherm the ratio between the concentrations of the phenol remaining in solution and adsorbed on the granular activated carbons, decreases when the concentration of phenol increases providing a concave curve to x - axis (Figure 3.46 to 3.50). The correlation coefficient ($R^2 = 0.99$) of Langmuir isotherm model yields a better fit than the Freundlich isotherm model (R^2 ranges from 0.89 - 0.98) in all cases of study conducted. It indicates that phenol adsorption takes place at the specific homogeneous surface of the granular activated carbons (GAC383, GACO383 and GACZC1073) and the adsorption reaction results in the formation of a monolayer coverage of the adsorbed molecules.

3.4.1.7.3 Temkin Isotherm – Phenol on GAC383, GACO383 and GACZC1073

Phenol adsorption of new carbon systems is characterized by using Temkin isotherm model [36]. It assumes that, the heat of adsorption decreases linearly with the coverage due to effective adsorbent – adsorbate interaction. The adsorption process is characterized by a uniform distribution of binding energies, up to some maximum binding energy [37].





Figure 3.59: Temkin isotherm model of phenol on GACZC1073 at different temperatures (C₀: 25 - 3000 mg/L)

The linear form of this model is expressed as:

$$q_{e} = B \ln A + B \ln C_{e} \tag{3.27}$$

$$B = \frac{RT}{b_T} \tag{3.28}$$

A is the equilibrium binding constant (L/mg) and B is related to heat of adsorption are calculated from the intercept and slope of the Temkin isotherm plot obtained by plotting q_e versus $ln C_e$ (Figure 3.57 – 3.59). The variation of the adsorption energy (b_T) is calculated from the equation (3.26). The Temkin constants are calculated and presented in Table 3.14. The adsorption energy (b_T) is less than 80 kJ/mol for the carbons studied. That indicates, adsorption of phenol on modified carbons occurs by physical adsorption such as weak Van der Waals force of attraction between phenol and modified carbons [38].

3.4.1.7.4 Dubinin- Radushkevich (D-R) Isotherm – Phenol on GAC383, GACO383 and GACZC1073

The D - R isotherm is applied on phenol adsorption on modified carbons to determine the energy distribution onto a heterogeneous surface.

This model is applied only at lower concentrations phenol adsorbed. The linear of D - R equation is expressed as:

$$\ln q_e = \ln Q_D - \beta \varepsilon^2 \tag{3.29}$$

Where Q_D is the theoretical maximum adsorption capacity (mol/g), β is the Dubinin – Radushkevich isotherm constant (mol²/kJ²), ε is the Polanyi potential and is equal to

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{3.30}$$

R is the universal gas constant, *T* is the Temperature and C_e is the equilibrium phenol concentration.

		Dubinin	- Radushkevich	(D-R) constan	its
Carbon	T (K)	Q _D (D-R)	E ₀ (D-R)	β (mol ² J ⁻²⁾	\mathbf{R}^2
		(mg/g)	(kJ/mol)		
GAC383	283	55.52	0.267	7.03	0.98
	293	56.62	0.288	6.01	0.98
	303	57.39	0.293	5.83	0.98
	313	58.39	0.339	4.34	0.98
	323	59.22	0.362	3.81	0.98
	283	54.89	0.247	8.19	0.98
CAC0292	293	56.10	0.273	6.71	0.98
GACO383	303	57.41	0.301	5.50	0.98
	313	58.76	0.328	4.65	0.98
	323	59.29	0.359	3.89	0.98
	283	62.74	0.330	4.58	0.99
$C \wedge C \overline{C} C 1 0 \overline{C} 2$	293	63.35	0.377	3.51	0.98
GACZCI073	303	66.03	0.561	1.59	0.99
	313	68.80	0.696	1.03	0.99
	323	79.98	0.700	1.02	0.99

Table 3.15: Dubinin - Radushkevich (D-R) constant of phenol on carbonsGAC383, GAC0383 and GACZC1073

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The constant β gives a knowledge about the mean free energy E_0 (kJ/mol) of adsorption per phenol molecule when it is transferred to the surface of the modified carbons from infinity, in the solution phase, can be calculated using the relationship [39].

$$E_0 = \frac{1}{(2\beta)^{1/2}}$$
(3.31)

The mean free energy indicates adsorption occurs by ion exchange or physical adsorption. Adsorption follows the ion exchange mechanism ($E_0 \, 8$ - 16 kJ/mol) and physical adsorption ($E_0 < 8$ kJ/mol) according to mean free energy measured. Phenol adsorption occurs on the new carbons by physical adsorption; because the mean free energy less than 8 kJ/mol shown in Table 3.15. The phenol adsorption capacity (Q_D) as regards to Dubinin – Radushkevich isotherm model increases with temperature being GACZC1073 has a maximum value among the series.

3.4.1.8 Thermodynamic Parameters for Phenol Adsorption

The mechanism of adsorption can be interpreted based on thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). They were calculated from the Langmuir isotherms parameter (K_L) by using the Van't Hoff equation (3.32 & 3.33). The temperature effect on the adsorption of phenol was studied at 5 different temperatures (10^oC, 20^oC, 30^oC, 40^oC and 50^oC). From the general adsorption isotherm (Figure 3.46 to 3.50) it is seen that with the temperature, there is a rise in phenol adsorption capacity, due to the endothermic nature of the adsorption process.

$$\Delta G = -RT \ln K_L \tag{3.32}$$

$$\Delta G = \Delta H - T \,\Delta S \tag{3.33}$$

Chapter 3

 ΔS and ΔH are calculated by using the intercept and slope of the plot ΔG versus *T* (Figure 3.60) for phenol adsorption on GAC383, GACO383 and GACZC1073 (Table 3.16). The magnitude of the standard enthalpy change gives an insight whether adsorption is physical or chemical in nature. ΔH indicates that, adsorption of phenol on GAC's were endothermic in nature as it is positive. Temperature enhances the pore accessibility on carbon surface; it increases the adsorption capacity of phenol at higher temperature. For most physisorption, the ΔH is approximately 80 kJ/mol and for chemisorption $\Delta H > 80$ kJ/mol. The enthalpy of phenol adsorption on the carbon studied < 20 kJ/mol, reveals that this adsorption process is physical. The positive value of entropy change (ΔS) reflects a good affinity towards the carbon surface and the increasing randomness at the solid-solution interface during the adsorption process [40].

(enuopy	(25) 01	une mou	incu cai	00115	
Carbon		ΔG	G (kJmol	⁻¹)		ΔН	ΔS
	283	293	303	313	323	(kJmol ⁻¹)	(Jmol ⁻¹ K ⁻¹)
GAC383	-194	-2.18	-2.24	-2.35	-2.59	2.26	14.93
GACO383	-1.82	-2.07	-2.29	-2.41	-2.55	3.30	18.26
GACZC1073	-1.90	-2.27	-3.06	-3.51	-4.04	12.93	51.40

Table 3.16: Thermodynamic parameters – Gibbs free energy (ΔG) , enthalpy (ΔH) and entropy (ΔS) of the modified carbons

Gibbs free energy change (ΔG) confirms the feasibility and spontaneity of the adsorption process. The ΔG lies between -20 and 0 kJ/mol shows adsorption is physisorption and the free energy change is in the range of -20 and 80 kJ/mol means the adsorption process follows physisorption together with chemisorptions. The Gibbs free energy change decreases with temperatures are in between -20 and 0 kJ/mol. From these phenol adsorption data on modified carbons, it is identified that the adsorption process occurs more favorable at higher temperature (323K), due to the endothermic nature of the adsorption process.



Figure 3.60: ΔG versus Temperature (T) for determination of thermodynamic parameters for the adsorption of phenol onto (a) GAC383, (b) GACO383 & (c) GACZC1073

3.4.2 Adsorption Studies of *p* –nitrophenol

Batch experiments, studies of p – nitrophenol adsorption were carried out as a function of concentration, time, temperature and equilibrium conditions using modified granular activated carbons.

3.4.2.1 Effect of Contact Time

Adsorption kinetics, equilibrium isotherm and thermodynamic studies are very important for the optimization of adsorption process for the design of unit operation [41]. The Figure 3.61 shows the effect of

Chapter 3

contact time on the removal of GAC383 and GACO383. The plots of amount adsorbed against time in minutes are single, smooth and it leads to saturation. This type of graph indicates the monolayer coverage of p –nitrophenol on the surface of GACs. The maximum amount of p – nitrophenol adsorbed corresponding to the equilibrium (8 hrs) is found to be GAC383 (300 mg/g) and GACO383 (188 mg/g). The result shows that carbon–oxygen surface groups on GACs influences the adsorptions of p - nitrophenol. The amount of acidic surface groups was enhanced by oxidation with nitric acid and it suppresses the adsorption of p – nitrophenol.



Figure 3.61: Effect of contact time for the adsorption of *p* – nitrophenol (GAC383 &GACO383) (C₀: 1000 mg/L)

3.4.2.2 Selection of Carbon

Relative adsorption efficiency of GACZC carbon series is tested to decide the best from the group. The initial concentration (1000 mg/L) of p – nitrophenol is used to plot quantity adsorbed at different time interval, ranging from 10 to 600 minutes for this selection study. The final concentration of adsorbate remained was measured by a UV – Visible

spectrophotometer at 317 nm. Figure 3.62 clearly shows that GACZC1073 has the higher adsorption capacity compared to other carbon members of this series.



Figure 3.62: Effect of contact time and amount of p -nitrophenol adsorbed for the adsorption on GACZC activated at different temperatures (C₀: 1000 mg/L)

3.4.2.3 Adsorption Kinetics

The adsorption kinetic study of p – nitrophenol on three carbons (GAC383, GACO383 and GACZC1073) were done using initial concentration (250mg/L) at different temperature 10^oC, 20^oC, 30^oC, 40^oC and 50^oC (Figure 3.63 – 3.67). Among the three carbons, Zn²⁺ impregnated granular activated carbon, activated at 1073K (GACZC1073) shows highest adsorption capacity in all temperatures studied. More than 90% p – nitrophenol is known removed using GACZC1073 at 8 hrs equilibration period. The time dependent data are applied to different kinetic models (pseudo first order model, Ho second order model, Weber intraparticle diffusion model and Elovich kinetic model) to identify the mechanism of adsorption on modified carbons.







Figure 3.63: Effect of contact time on the adsorption of p-nitrophenol on AC383, GACO383 and GACZC1073 at 10^oC (C₀: 250 mg/L)







Figure 3.65: Effect of contact time on
the adsorption of
p-nitrophenol on GAC383,
GAC0383 and
GACZC1073 at 30°C (C0:
250 mg/L)Figure 3.66: Effect of contact time on
the adsorption of
p-nitrophenol on
GAC383, GAC0383 and
GACZC1073 at 40°C
(C0: 250 mg/L)



Figure 3.67: Effect of contact time on the adsorption of *p* -nitrophenol on GAC383, GACO383 and GACZC1073 at 50^oC (C₀: 250 mg/L)

3.4.2.3.1 Pseudo First and Second Order Kinetics: *p* – nitrophenol

The Figure 3.68 to 3.73 shows the first and second order model plot for GAC383, GACO383 and GACZC1073. The pseudo first order and Ho second order kinetic parameters for the adsorption of p - nitro phenol on modified granular activated carbons are calculated and shown in Table 3.17. The q_e experimental are more comparable with q_e calculated obtained from the pseudo second order kinetic model and the correlation coefficient (R^2) value obtained from this model is found to be higher than that of first order model applied. This means the adsorption of p – nitrophenol on modified GAC follows Ho second order kinetics [42]. Adsorption is controlled by the square of unoccupied sites on granular activated carbons. The $q_e cal$ and K_2 obtained from the pseudo second order kinetic model increases with temperature indicates it is an endothermic adsorption.

3.4.2.3.2 Intraparticle Diffusion Model

Intraparticle diffusion model [30] used to study the diffusion mechanism. Intraparticle diffusion plot of GAC383, GACO383 and GACZC1073 are shown in Figure 3.74, 3.75 and 3.76 respectively. It shows two straight line portions, the first one is attributed to surface diffusion and the second portion is represented pore diffusion. The K_{id1} from Table 3.17 is

higher than the K_{id2} of all GAC at temperatures studied, indicating that pore diffusion is a slow step. Boundary layer thickness increases with temperature shows that temperature favors p – nitrophenol adsorption.

3.4.2.3.3 Elovich Kinetic Model for *p* - nitrophenol Adsorption

The simplest form of Elovich model [43] is represented by

$$q_{t} = \frac{1}{\beta} (\ln \alpha \beta) + \frac{1}{\beta} \ln t$$
(3.34)

The initial rate constant α (mg g⁻¹min⁻¹) and desorption constant β (g mg⁻¹) are obtained from the intercept and slope of the plot of q_t versus ln t (Figure 3.77 -3.79). According to Elovich model, GACZC1073 shows higher initial adsorption rate (α) and lower desorption (β) compared to other carbons. Zn²⁺ ions impregnation increases more adsorption sites on the surface of granular activated carbon and it increases the overall adsorption efficiency. Initial adsorption rate α increases with temperature means more active sites are formed on the carbon surface. GACZC1073 shows highest value (50.6 at 50⁰C) shown in Table 3.17. The desorption constant β for all temperatures are almost same, indicates that there is no change in the desorption of p – nitrophenol on modified carbons with respect to temperature.





Chapter 3

Carbon			First or	der kin	etics	Seco ki	nd orde netics		-	ıtrapart	ticle dif	fusion c	constant		Elovi	ich Cons	tant
		((₁	(,		(₁ .	s-(-s		(^{2/1-} nim			(^{2/1-} nim			(¹⁻ nim	(₁	
	(K) T	ថិ/ਡੋਘ) dxə ^ə b	lsəsp ggm)	(min ⁻¹ K1	_z ط	lsəsp ggm)	(ճաճ _լ 1813 1813	εz	(m88 K ^{iq1}	c	r,R	(w88 ₁ K ^{iqz}	۲	zΒ	(ມຣີຣີ ຜ	(Smg g	₂8
GAC383	283	201.92	153.84	0.007	0.98	221.24	7.59	0.99	16.69	-15.98	0.98	5.64	79.51	66.0	9.04	0.023	0.99
	293	209.76	151.53	0.006	0.98	225.73	8.50	66.0	16.69	-7.49	0.98	5.51	89.37	66.0	11.06	0.023	66.0
	303	213.44	151.29	0.007	0.98	228.83	9.20	66.0	16.80	-2.21	0.97	5.34	97.64	66.0	12.76	0.023	0.99
	313	216.53	151.04	0.008	0.98	231.48	10.18	66.0	15.96	9.13	0.96	5.08	107.66	66.0	15.43	0.024	66.0
	323	219.02	143.17	0.008	0.98	232.02	11.46	66.0	17.13	69.6	0.97	4.75	116.88	66.0	18.60	0.024	0.99
GC0383	283	119.50	82.71	0.005	0.91	129.53	12.38	0.99	13.35	-28.15	0.98	2.99	51.47	0.97	5.12	0.038	0.97
	293	124.52	84.52	0.006	0.93	133.33	14.16	66.0	12.90	-20.54	96.0	3.06	55.88	66.0	6.28	0.038	0.97
	303	129.30	84.24	0.006	0.93	136.80	15.58	66.0	12.89	-15.83	0.97	2.99	62.04	66.0	7.50	0.038	0.97
	313	133.78	81.11	0.006	0.94	139.86	18.80	66.0	12.44	-5.21	96.0	2.97	68.11	66.0	10.75	0.040	0.98
	323	138.59	78.20	0.006	0.94	142.45	21.26	66.0	11.93	4.89	0.99	3.21	67.38	66.0	15.66	0.042	66.0
GACZC1073	283	211.86	167.63	0.006	0.97	236.41	5.37	66.0	19.49	-36.77	0.98	7.35	50.32	66.0	7.39	0.021	0.98
	293	220.75	155.46	0.006	0.96	236.97	7.45	0.99	19.88	-24.30	0.98	5.74	91.73	66.0	10.35	0.022	0.99
	303	229.45	129.34	0.006	0.87	238.66	11.34	66.0	26.56	-35.02	0.95	4.18	133.47	96.0	18.24	0.023	0.94
	313	237.45	134.40	0.006	0.97	245.70	13.15	66.0	18.30	23.36	0.95	5.07	127.10	66.0	30.57	0.025	0.99
	323	240.35	117.95	0.006	0.94	246.31	16.89	0.99	19.31	31.49	0.97	3.74	156.91	66.0	50.61	0.027	86.0

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Figure 3.74: Intraparticle diffusion model of p -nitrophenol on GAC383 at different temperatures (C₀: 250 mg/L)



Figure 3.75: Intraparticle diffusion model of p -nitrophenol on GACO383 at different temperatures (C₀: 250 mg/L)



model of p -nitrophenol on GACZC1073 at different temperatures (C₀: 250 mg/L)



6.5





3.4.2.4 Activation Energy *p*-nitrophenol as Adsorbate

The activation energy of modified carbons (GAC383, GACO383 and GACZC1073) is determined by using the Arrhenius equation based on the second order rate constant (K_2). Linear plot $ln K_2$ versus l/T for the estimation of activation energy for the adsorption of p - nitrophenol are made in Figure 3.80 GAC383, 3.81 GACO383 & 3.82 GACZC1073. Arrhenius activation energy (E_a) and the temperature independent factor (K_0) was calculated and summarized in Table 3.18. The activation energy of modified carbons calculated from p – nitrophenol adsorption is less than 40 kJ/mol indicating that adsorption is physisorption. The positive activation energy indicates that energy barriers are present in the p - nitrophenol adsorption by granular activated carbons (GAC383 – 7.63 kJ/mol, GAC0383 – 10.35 kJ/mol and GACZC1073 – 21.80 kJ/mol) and that the reaction is endothermic.





Figure 3.82: Plot of $\ln K_2$ versus 1/T for the adsorption of *p* -nitrophenol on GACZC1073 (C₀: 250 mg/L)

Table 3.18: A	Activation	energy of I	new carbons	using p -	nitropheno	l as adsorbate
		01		01		

Carbon	$E_a (kJmol^{-1})$	Ko	R	
GAC383	7.63	0.003	0.95	
GACO383	10.35	0.009	0.97	
GACZC1073	21.80	0.585	0.99	

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 133

3.4.2.5 Adsorption Isotherm Studies of *p*-nitrophenol as Adsorbate

The Figure 3.83 - 3.87 shows the isotherm plot for *p*- nitrophenol removal of the new GAC's at different temperature, were amount of *p*- nitrophenol adsorbed per gram of adsorbent (*q_e*) versus the equilibration concentration (*C_e*) are plotted. The isotherm has a steep rising phase in the beginning followed by saturation at higher initial concentration typical for Type I microporous materials as per IUPAC (2015) classification [44]. The temperature has an influence on the adsorption of *p* – nitrophenol on new carbons (GAC383, GACO383 and GACZC1073).



Figure 3.85: Adsorption isotherm of *p*- nitrophenol on GAC383, GACO383 & GACZC1073 at 30° C (C₀: 25 - 3000 mg/L)

Granular activated carbon incorporated with Zn²⁺: preparation, characterisation and adsorption studies



3.4.2.5.1 Applications of Isotherm Models

Equilibrium isotherm at different temperatures (10^{0} C, 20^{0} C, 30^{0} C, 40^{0} C and 50^{0} C) are applied to isotherm models such as Langmuir isotherm model, Freundlich isotherm model, Temkin model and Dubinin – Radushkevich model to calculate the adsorption capacity and other structural constants by p – nitrophenol adsorption. The Figure 3.88 -3.90 shows the Langmuir isotherm plot for the adsorption of p – nitrophenol on modified granular activated carbons GAC383, GACO383 and GACZC1073 respectively at different temperature.

Langmuir isotherm model for the modified carbons shows linear over the whole range of p - nitrophenol concentration studied with a high correlation coefficient (0.99). It suggests that Langmuir isotherm is a good model for p - nitrophenol adsorption on modified carbons. Monolayer adsorption capacity (q_{max}) increases with increasing temperature for all the carbon studied (Table 3.19). GACZC1073 shows highest monolayer adsorption capacity (420 to 529 mg/g) compared to native and oxidised form of carbons.

The dimensionless separation factor (R_L) , express the essential characteristic of the Langmuir equation is calculated by the equation (3.35),

$$R_{L} = \frac{1}{1 + a_{L} C_{0}}$$
(3.35)

 a_L is the Langmuir constant and C_0 is the initial concentration of p - nitrophenol. $R_L > 1$ means adsorption to be unfavourable, $R_L = 1$ adsorption is linear, $0 < R_L < 1$ means favourable and $R_L = 0$ adsorption to be unfavourable. From the Figure 3.91 – 3.93, all the R_L lies between zero and one indicating that the adsorption process was favorable in all initial concentration and temperatures studied.

Freundlich isotherm model of modified carbons GAC383, GACO383 and GACZC1073 on p - nitrophenol adsorption is presented in Figure 3.94, 3.95 & 3.96 respectively. This model is used for heterogenous surface energy system and is presented here for adsorption isotherm studies at a different temperature range. From the linear form of the model, determined the adsorption capacity (K_F) and adsorption intensity (n). The adsorption capacity K_F increases with temperature as it is an endothermic process. In most of the cases the adsorption intensity n lies in the range 1 - 10 shows, the beneficial adsorption [45]. In our study, the n is the range of 2.91 – 4.26 represents the favourable adsorption of p - nitrophenol on modified carbons.

Temkin isotherm model of the modified carbons (GAC383, GAC0383 and GACZC1073) is shown in Figure 3.97 – 3.99. The equilibrium binding constant (*A*) and the constant related to the heat of adsorption (*B*) are presented in Table 3.19. The correlation coefficient (R^2) is 0.99 in all temperatures studied for p – nitrophenol adsorption on modified carbons. The variation of the adsorption energy (b_T) decreases with increasing temperature of all the carbons.

The Dubinin – Radushkevich (D - R) isotherm model is fitted to data giving more thrust to the lower concentration of p – nitrophenol adsorption on modified carbons. The D – R isotherm parameters are shown in Table 3.19.

The maximum adsorption capacity (Q_D) increases with temperature. From these studies, GACZC1073 shows highest adsorption capacity compared to others. The adsorption energy calculated from the D – R isotherm is < 8kJ/mol. This means, this adsorption of p – nitrophenol on new granular activated carbon is physical in character.



Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics







Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

¹³⁹

Chapter 3

	F	Langm	uir isothe nstants	E	Freundlic	ch isot stants	herm	Temk	in isothe	rm consta	ants	Dubin	in – Radush Const	kevich isoth ants	erm
Carbon	- (¥	q _{max} (mgg ⁻¹)	K _L (Lmg ⁻¹)	R²	\mathbf{K}_{F} (mgg ⁻¹)	=	R²	A _T (L/mg)	в	b _T (J/mol)	\mathbf{R}^2	Q _D (D-R) (mgg ⁻¹)	E ₀ (D-R) (kJmol ⁻¹)	K' (mol²J²)	\mathbf{R}^2
GAC383	283	272.48	7.61	66.0	53.49	4.26	0.86	5.54	29.56	76.79	0.98	75.77	1.47	0.232	66.0
	293	304.88	8.36	66.0	55.01	4.06	0.88	4.50	33.62	67.50	66.0	77.02	1.66	0.182	66.0
	303	340.14	9.03	0.99	56.58	3.88	0.89	3.78	38.01	59.71	66.0	78.21	1.85	0.146	66.0
	313	377.36	9.40	66.0	58.14	3.73	16.0	3.31	42.44	53.48	66.0	79.53	2.03	0.121	66.0
	323	403.23	10.69	0.99	59.90	3.64	16.0	3.15	45.86	49.49	66.0	81.24	2.19	0.10	66.0
	283	201.61	2.06	66.0	18.48	3.05	0.93	0.31	30.27	74.99	66.0	49.61	0.329	4.63	0.97
	293	213.22	2.14	66.0	18.93	3.01	0.93	0.31	31.94	71.07	66.0	50.62	0.355	3.97	0.97
GACU383	303	224.22	2.23	0.99	19.33	2.97	0.93	0.30	33.60	67.55	66.0	51.31	0.386	3.35	0.97
	313	235.29	2.31	0.99	19.67	2.94	0.93	0.30	35.26	64.37	66.0	52.08	0.414	2.92	0.97
	323	245.70	2.41	66.0	20.04	2.91	0.94	0.29	36.82	61.64	66.0	52.74	0.446	2.51	0.97
	283	420.17	5.82	0.99	57.09	3.63	0.92	2.61	45.52	49.86	66.0	79.30	1.76	4.37	66.0
	293	454.55	7 <i>.</i> .7	66.0	59.18	3.50	0.93	2.50	50.57	44.89	66.0	86.97	1.83	4.47	66.0
GACZC10/3	303	490.20	9.67	0.99	66.45	3.57	16.0	3.20	53.61	42.34	66.0	87.11	2.16	4.47	0.99
	313	510.20	11.88	66.0	74.42	3.68	0.92	4.58	53.97	42.06	0.99	99.04	2.62	4.60	66.0
	323	529.10	14.53	0.99	81.33	3.68	0.91	5.97	55.24	41.09	66.0	112.74	2.71	4.73	66.0

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3.4.2.6 Thermodynamic Parametrs

The energetics of adsorption of *p*- nitrophenol on the above carbon (GAC383, GACO383 and GACZC1073) is determined by thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). These parameters were calculated from the Langmuir isotherm constants (K_L) by using the Van't Hoff equation. The temperature effect on the adsorption of *p*- nitrophenol was studied at 5 different temperatures (10^oC, 20^oC, 30^oC, 40^oC and 50^oC) shown in Figure 3.100 (a) GAC383, (b) GACO383 and (c) GACZC1073.



Figure 3.100: plot of $\ln K_L$ versus 1/T for the adsorption of *p*- nitrophenol onto (a) GAC383, (b) GAC0383 and (c) GACZC1073

Granular Activated Carbon Incorporated With Zn $^{2+}$ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 141

Chapter 3

The values of ΔS and ΔH are calculated from the intercept and slope of the plot $ln K_L$ versus 1/T for p - nitrophenol adsorption on different GACs and are given in Table 3.20. The positive ΔH indicates that adsorption of p – nitrophenol on GAC were endothermic in nature. Temperature enhances the rate of diffusion of the adsorbate molecule across the external boundary layer and into the internal pores of the adsorbate, due to the decrease in the viscosity of the solution [46]. The increase in the adsorption capacity of granular activated carbons with temperature may be attributed to the pore size enlargement. The magnitude of the standard enthalpy change, gives an idea whether adsorption is physical or chemical in nature of carbon surfaces. ΔH of the new GAC is less than 40 kJ/mol indicates adsorption of p – nitrophenol follows physisorption mechanism. The positive entropy change (ΔS) reflects a good affinity towards the GAC and the increasing randomness at the solidsolution interface during adsorption. The negative ΔG confirms the feasibility and spontaneity of the adsorption process. ΔG decreases with adsorption temperatures. From these, we ascertain that the adsorption process is more favorable at higher temperature (323K), due to the endothermic nature of the GAC – para nitrophenol adsorption system [47, 48].

		Δ	G (kJm	ol ⁻¹)		ΔΗ	ΔS
Carbon	283	293	303	313	323	(kJmol ⁻¹)	(Jmol ⁻¹ K ⁻¹)
GAC383	-4.78	-5.17	-5.54	-5.83	-6.36	6.02	38.18
GACO383	-1.70	-1.85	-2.02	-2.18	-2.36	2.96	16.45
GACZC1073	-4.14	-4.99	-5.71	-6.44	-7.19	17.16	75.44

Table 3.20: Estimation of thermodynamic parameters – Gibbs free energy (ΔG),
enthalpy (ΔH) and entropy (ΔS)

3.4.3 Adsorption Studies of Methylene Blue

The adsorption efficiency of modified carbons (GAC383, GACO383 and GACZC1073) is determined by using adsorption kinetics, isotherm and thermodynamic study of a cationic dye methylene blue (MB) as adsorbate.

3.4.3.1 Effect of Carbon Dose

The Figure 3.101 shows the effect of carbon dose on the adsorption of methylene blue (MB) on GAC383 where different weight (1 g/L, 2 g/L, 4 g/L and 6 g/L) dose of carbon was used for 500 mg/L concentrations of MB at 30° C. The adsorption percentage decreases with mass of GAC383, because at a smaller adsorbent dosage fraction of active sites saturated with MB increases [49]. The amount adsorbed decreases from 156.46 mg/g to 74.36mg/g with weight dose of 1 g/L to 6 g/L of GAC383 (Figure 3.68). Accordingly, a carbon mass of 1 g/L was used throughout the whole adsorption studies of MB on new modified granular activated carbons.

3.4.3.2 Effect of Contact Time

The adsorption of methylene blue on modified carbons was determined as a function of contact time. The amount of MB adsorbed (q_t) against *time* (in minutes) for an initial concentration of MB, 500mg/L for GAC383 and GACO383 (Figure 3.102). Adsorption progresses with time, after 600 minutes there is no further change in the adsorption of MB, fixed as the equilibrium time for the MB isotherm and thermodynamic studies.



Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 143

3.4.3.3 Selection of GACZC for Methylene Blue (MB) Adsorption

To identify an efficient carbon from the GACZC series adsorption using methylene blue (Figure 3.103) was done for an initial concentration (500mg/L). After 10 hrs shaking periods the filtrate was measured for equilibrium concentration. It is seen that from the carbons series, GACZC1073 shows highest MB adsorption compared to others.



Figure 3.103: Selection of carbons from the GACZC series for the adsorption of MB (C₀: 500 mg/L)

3.4.3.4 Adsorption Kinetics Study of Methylene Blue (MB) Adsorption on New Carbons

Adsorption kinetic studies of the new carbon GAC383, GACO383, and GACZC1073 are made to determine the rate at which MB is removed from aqueous media onto modified carbon surface. The time dependent data were shown in Figure 3.104 - 3.106 at different temperatures studied at 250 mg/L for MB concentration. The temperature enhances the adsorption capacity of all the carbon studied for MB adsorption. This time dependent data analysed using different kinetic models: pseudo first order,

pseudo second order, intraparticle diffusion and Boyd models are used to examine the mechanism of MB adsorption on carbon surface.

Lagergen pseudo first order model is used first as the model equation. A plot of $ln (q_e-q_t)$ versess t (Figure 3.107 - 3.109) gives a straight line, from the slope K_l and $q_e cal$ from the intercept evaluated. $q_e cal$ is lower than $q_e exp$ and the regression is also less (Table 3.20). This means the first order kinetic model is not applicable to the study of adsorption of MB for the new carbon adsorption system. The second order Kinetic model (Ho second order model) is used to express the kinetics of MB adsorption for the new carbon adsorption system as the graph t/qt verses t gives a straight line for all the carbons (Figure 3.110 - 3.112). The second order kinetic parameters and correlation coefficient are determined from the linear plot given in Table 3.21. It is seen that, correlation coefficient (R^2) for pseudo second order kinetic model is relatively high. Equilibrium adsorption capacity $(q_e cal)$ is more comparable with $q_e exp$ than the $q_e cal$ for the first order kinetics for MB adsorption. This suggests that batch reactor consisting of new GAC - MB adsorption system follows pseudo second order kinetic model. This infers that the new treatment system is comparatively efficient and is related to carbon behavior [29]. Weber and Morris (1963) [30] intraparticle diffusion model is used to predict the rate controlling step for Methylene Blue adsorption. When mass transfer is the controlling step for adsorption of MB, it is important to identify the diffusion mechanism. The Figure 3.113 - 3.115 shows the intraparticle diffusion model for the adsorption of MB on granular activated carbons GAC383, GACO383 and GACZC1073 respectively. It is seen that, there are two straight line portions; the first part is attributed to surface diffusion and the second linear portion is attributed to intra particle diffusion. The Table 3.21 shows the surface diffusion constant (K_{idl}) are higher than intraparticle diffusion constant (K_{id2}). It indicates that, pore diffusion is a slow step compared to surface diffusion. The boundary layer thickness increases with temperature in all cases.





Figure 3.104: Effect of contact time on the adsorption of MB on GAC383 at different temperatures (C₀: 250 mg/L)





Figure 3.106: Effect of contact time on the adsorption of MB on GACZC1073 at different temperatures $(C_0: 250 \text{ mg/L})$



Figure 3.107: Pseudo -first order kinetics Figure 3.108: Pseudo -first order kinetics of MB on GAC383 at different temperatures (C₀: 250 mg/L)

of MB on GACO383 at different temperatures (C₀: 250 mg/L)



Figure 3.109: Pseudo -first order kinetics of MB on GACZC1073 at different temperatures (C₀: 250 mg/L)





Figure 3.110: Psuedo second order kinetics of methylene blue on GAC383 at different temperatures $(C_0: 250 \text{ mg/L})$



Figure 3.111: Psuedo second order kinetics of methylene blue on GACO383 at different temperatures (C₀: 250 mg/L)







Figure 3.113: Intraparticle diffusion model of methylene blue on GAC383 at different temperatures (C₀: 250 mg/L)



Figure 3.114:Intraparticle diffusion
model of methylene blue
on GACO383 at different
temperatures
 $(C_0: 250 \text{ mg/L})$ Figure 3.115:Intraparticle diffusion
model of methylene
blue on GACZC1073 at
different temperatures
 $(C_0: 250 \text{ mg/L})$

Boyd kinetic model is used to evaluate the diffusion mechanism of MB adsorption and diffusivity coefficient (D_e). The Boyd model B_t versus *time* already discussed in the earlier section of this chapter (for the phenol adsorption). Diffusivity coefficient D_e calculated by using the equation

$$B = \frac{\pi^2 De}{r^2} \tag{3.36}$$

B is calculated from the slope of plot (Figure: 3.116 - 3.118), *B_t* versus *time* for the adsorption of MB on GAC383, GACO383 and GACZC1073 respectively at different temperature studied. *r* is the radius of granular carbons. Table 3.21 shows that diffusivity coefficient increases as a function of temperature. This is due to the difference in the mobility force on the MB particle with rise in temperature [50].

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 149

Chapter 3

ivated AC)			First o c	order Kin onstants	etics	Seco kinetic	ond ord s const	er ants	-	Intrapar	ticle dif	fusion co	Instants		Boy kin cons	'd's etic tant
Granular Act O nodra O	(K) T	(છ્રુછ) કુલ્યો	(ฮิ/ฮิɯ) bรงป	K ¹	۲ ₃	(Bam) becal	K ⁵ *10-+	۲ ₂	(min ^{1,1} nim ^{1,1} 28m)) K _{id1}	cı	ג ²	(mgg ⁻¹ nim ^{-1,2}) K _{id2}	C2	۲ ₃	(cm ₅ 8 ₋₁) D°*104	εz
	283	102.05	60.38	0.005	0.94	104.38	2.42	0.99	8.49	1.76	96.0	2.07	50.67	0.97	1.33	0.94
	293	116.77	64.49	0.005	0.98	118.76	2.46	66.0	7.24	21.22	0.97	2.48	56.37	66.0	1.33	0.98
GAC383	303	124.24	67.07	0.005	0.94	126.42	2.52	0.99	5.78	38.04	66.0	2.61	61.14	0.97	1.50	0.94
	313	132.00	66.07	0.005	0.98	133.87	2.57	66.0	5.59	45.81	66.0	2.72	66.48	66.0	1.38	0.98
	323	138.08	67.84	0.005	0.96	140.25	2.73	0.99	6.07	49.34	96.0	2.47	78.76	66.0	1.57	0.96
	283	80.60	53.52	0.004	0.96	82.37	2.33	0.99	5.66	2.99	0.98	2.21	25.73	0.99	1.17	0.96
	293	90.92	54.31	0.004	0.97	16.16	2.57	0.99	5.15	15.65	0.98	2.35	32.81	96.0	1.17	76.0
GAC0383	303	98.13	54.75	0.004	0.98	99.80	2.75	0.99	5.29	20.75	66.0	2.05	47.28	66.0	1.24	0.98
	313	110.64	56.84	0.004	0.95	110.38	2.78	0.99	6.37	24.83	66.0	2.25	53.67	0.97	1.10	0.95
	323	117.76	53.85	0.004	0.94	118.06	3.32	0.99	7.52	27.33	96.0	1.78	72.52	66.0	1.22	0.94
	283	107.92	78.06	0.004	0.95	112.99	1.17	0.99	9.04	-14.94	0.99	2.74	36.77	96.0	1.07	0.95
	293	129.46	87.31	0.004	96.0	132.63	1.30	0.99	11.26	-10.65	66.0	3.56	39.94	66.0	1.09	96.0
GACZC1073	303	148.15	91.81	0.005	0.97	151.75	1.48	0.99	10.84	6.39	96.0	3.30	66.02	66.0	1.25	76.0
	313	165.18	97.56	0.005	0.96	168.63	1.54	0.99	10.87	22.58	0.95	3.80	72.47	66.0	1.36	96.0
		171.02	00 67	0 005	100			0000		0000						

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3.4.3. 5 Activation Energy Using Methylene Blue (MB) as Adsorbate

The activation energy for the removal MB using modified carbons are determined using Arrhenius plot (Figure 3.119 - 3.121) for the modified

Chapter 3

-8.18

carbons. The activation energy (E_a) is positive and magnitude indicates that MB adsorption on modified carbons is endothermic and is a physisorption process.



(C₀: 250 mg/L)



Carbon	E _a (kJmol ⁻¹)	K ₀	R
GAC383	2.11	0.001	0.95
GACO383	5.98	0.003	0.95
GACZC1073	6.16	0.002	0.98

 Table 3.22: Activation energy of modified carbons using MB as adsorbate

3.4.3.6 Adsorption Isotherm studies of Methylene Blue (MB) on **GACZC1073**

Adsorption isotherm studies are done to determine how methylene blue (MB) interacts with carbon surfaces and are critical in optimizing the use of carbon. The Figure 3.122 - 3.124 shows the isotherm plots for MB removal. Adsorbed amount per gram of GAC (q_e) versus the equilibrium concentration (C_e) are plotted at different temperatures. The adsorption isotherm has distinct shapes decided by MB dye interaction on carbon surface. Plots shows Type I isotherm behaviour as per IUPAC, means no strong competition between water and the MB occurs to occupy the carbon surfaces. Adsorption capacity of carbon varies according to the order GACZC1073 > GAC383 > GAC0383. This indicates, that granular activated carbon incorporated with Zn²⁺ ions activated / carbonized at 1073K have more adsorption efficiency among the selected group of carbons. It is known that there are two types of adsorption mechanisms prominent during the adsorption of dye on carbon [51]. First is the electrostatic interaction between MB molecules and carbon surface groups. Other is dispersive interactions between dye and carbon surface layers. Being, methylene blue is a cationic dye, adsorption occurs through a mechanism of $\pi - \pi$ dispersive interaction, where delocalised π electrons of carbon surface and free electrons of the MB molecules (aromatic rings and -N=C-C=C- or -N=N bonds) are involved. Among the three carbons, GACO383 - the nitric acid oxidised form, shows less MB uptake. This indicates that, the carbon has highest

Chapter 3

surface acidity (with respect to Boehm titration data, Table 3.2) is a valid reason for lower adsorption of MB cationic dye. Whereas, carbon GACZC1073 shows highest adsorption capacity among the group studied, as its surface are relatively having good proportion of basic (γ pyrone like) groups. Their presence further contributes to the dispersive interaction of MB as they are already known to plays a dominant role in the adsorption mechanism of dyes [6].

To design a single batch adsorption reactor system to study efficiency of new carbon to remove MB dye from contaminated water under equilibrium isotherm conditions. Linear adsorption isotherm models such as Langmuir, Freundlich and Temkin isotherm are applied.

Langmuir isotherm model is commonly used to determine the adsorption efficiency of activated carbons. A plot of C_e/q_e versus C_e assumes straight lines (Figure 3.125, 3.126 and 3.127). From the slope, monolayer adsorption capacity q_{max} (mg/g) and from the intercept K_L as (L/mg) are determined (Table 3.23). High correlation coefficient is obtained for this adsorption process on applying Langmuir isotherm $(R^2 - 0.99)$ to new carbons – MB system indicates the homogenous nature of carbon surface. GACZC1073 has higher monolayer adsorption capacities; 207.90 mg/g (10⁰C), 235.85 mg/g (20⁰C), 248.76 mg/g (30⁰C), 270.27 mg/g (40⁰C) and 303.03 mg/g (50⁰C). This is because this carbon has more basic surface group (0.90 meq/g), preferably high carbon content (95%). This means, nature and content of Surface functional groups and specific surface area mainly control the adsorption of MB on the new modified carbons.

Specific adsorption of Methylene Blue (MB) on new granular activated carbon has been evaluated using Freundlich isotherm model. A plot of $logq_e$ versus $logC_e$ is shown in Figure 3.128 – 3.130 for the new carbon studied, l/n is the slope and K_F is the intercept of the

isotherms are evaluated (Table 3.23). These modified carbon shows 1/nis less than 1.0 means it is a normal Langmuir isotherm given by Types I porous materials. Adsorption capacity K_F increases with temperature indicate that adsorption of MB on new carbons is an endothermic process.

The heat of cationic dye methylene blue adsorption (MB) is related to surface coverage of MB onto modified carbons due to the adsorbent - adsorbate interaction. This was studied using Temkin isotherm model (Figure 3.131, 3.132 & 3.133). A linear plot of q_e versus lnC_e gives an intercept of A (equilibrium binding constant) and slope B (related to heat of adsorption) are given in Table 3.23. The B is increased with increasing temperature from 283 to 323K, it indicates adsorption is an endothermic process. Correlation coefficient is found to be more or less than 0.99.

The Langmuir, Freundlich and Temkin isotherm constants are useful for calculating the monolayer adsorption capacity, favourability, binding energy respectively for the removal of MB using new carbons. Dubinin - Radushkevich (D - R) isotherm model is useful to determine the adsorption process is physical or chemical using the mean adsorption energy (E_0) the Dubinin - Radushkevich Constant. The mean adsorption energy ($E_0 < 8$ kJ/mol) refers to adsorption process is physical or $E_0 > 8$ kJ/mol chemical adsorption occurs. Table 3.23 shows the $E_0 < 8$ kJ/mol for the adsorption of MB on modified carbons (GAC383, GACO383 and GACZC1073). This means the removal of MB using modified carbons is physical adsorption process.





Figure 3.122: Adsorption isotherm of methylene blue (MB) adsorption on GAC383 at different temperatures for $C_0: 25$ -1500 mg/L



Figure 3.123: Adsorption isotherm of methylene blue (MB) adsorption on GACO383 at different temperatures $C_0: 25 -1500 \text{ mg/L}$



Figure 3.124: Adsorption isotherm of methylene blue (MB) adsorption on GACZC1073 at different temperatures $C_0: 25 - 1500 \text{ mg/L}$



Figure 3.125: Langmuir isotherm model of methylene blue (MB) adsorption on GAC383 at different temperatures $C_0: 25 - 1500 \text{ mg/L}$


Figure 3.126: Langmuir isotherm model of methylene blue (MB) adsorption on GACO383 at different temperatures C₀: 25 -1500 mg/L



Figure 3.127: Langmuir isotherm model of methylene blue (MB) adsorption on GACZC1073 at different temperatures C₀: 25 -1500 mg/L



Figure 3.128: Freundlich isotherm model Figure 3.129: Freundlich isotherm of methylene blue (MB) adsorption on GAC383 at different temperatures C₀: 25 -1500 mg/L



model of methylene blue (MB) adsorption on GACO383 at different temperatures C₀: 25 -1500 mg/L



of methylene blue (MB) adsorption on GACZC1073 at different temperatures C₀: 25 -1500 mg/L







Figure 3.132: Temkin isotherm model of Figure 3.133: Temkin isotherm model methylene blue (MB) adsorption on GACO383 at different temperatures C₀: 25 -1500 mg/L

of methylene blue (MB) adsorption on GACZC1073 at different temperatures C₀: 25 -1500 mg/L

		Langm C(uir isoth onstants	erm	Freu	ndlich i Constai	sotheri nts	E	Temk	in isothe	erm Con	stant	Dub	inin – Ra (D – R) C	idushkević onstant	_
Carbon	T (K)	_{ռջա} թ	(₋ ՏաՂ) K ^r	εz	(שפפ ^{יו}) א _ו	u/I	u	κ	(¹ -ชิฑป) A	B	b _r (Jmol ⁻¹)	_z ع	Q _D (D-K) (mgg ⁻¹)	(D-K) (ド Ղաօլ _{-լ}) E ⁰	(աօլ ₅ -ը) K,	r ² R2
	283	150.60	3.74	0.99	37.67	0.200	1.58	96.0	9.50	15.15	149.85	0.97	57.43	2.75	0.0659	0.97
	293	169.49	4.54	66.0	40.65	0.209	1.61	96.0	9.36	17.17	132.20	0.98	58.83	3.26	0.0471	0.96
UAC383	303	11001	4.80	0.99	42.90	0.217	1.63	0.99	8.68	19.16	118.48	96.0	60.30	3.74	0.0356	0.96
	313	209.64	5.13	66.0	45.34	0.223	1.66	0.99	8.61	20.92	108.48	0.95	61.58	4.20	0.0282	0.96
	323	229.35	5.51	66.0	47.80	0.223	1.68	66.0	8.59	22.71	99.95	0.94	62.78	4.67	0.0228	0.97
	283	107.99	2.89	0.99	35.09	0.159	6.27	0.97	12.08	13.66	166.17	0.98	54.15	2.77	0.0650	0.98
	293	122.40	3.37	0.99	37.67	0.169	5.92	96.0	11.93	15.34	147.94	0.98	56.25	3.14	0.0506	0.98
UACU383	303	138.70	3.60	0.99	39.84	0.178	5.61	0.98	11.26	17.05	133.14	76.0	57.98	3.49	0.0410	0.97
	313	154.32	4.31	0.99	42.34	0.188	5.33	96.0	11.55	18.19	124.76	0.97	59.50	3.79	0.0348	0.97
	323	172.41	4.59	0.99	44.58	0.195	5.12	66.0	9.36	21.28	106.67	0.95	60.98	4.08	0.0300	0.97
	283	207.90	2.27	0.99	53.89	0.209	4.78	96.0	0.98	25.00	90.78	0.88	53.95	1.44	0.2400	0.99
	293	235.85	3.60	66.0	26.62	0.282	3.55	76.0	2.36	25.81	87.93	0.89	60.52	1.57	0.2039	0.97
GACZC1073	303	248.76	5.35	0.99	31.98	0.286	3.50	0.98	5.59	25.77	88.07	0.95	61.62	2.78	0.0646	0.98
	313	270.27	7.06	0.99	41.26	0.263	3.80	0.98	6:59	27.90	81.36	96.0	64.35	3.78	0.0350	0.97
	323	303.03	90.6	0.99	51.03	0.248	4.04	0.97	39.23	25.24	89.91	0.92	64.37	8.20	0.0074	96.0

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics **159**

3.4.3.7 Adsorption Thermodynamics

The adsorption of methylene blue (MB) on GAC383, GACO383 and GACZC1073 at different temperature shows that adsorption increases with increasing temperature. The MB adsorption isotherm studies are carried out using the concentration ranging from 25 - 1500mg/l and the temperature studied are 10^{0} C, 20^{0} C, 30^{0} C, 40^{0} C and 50^{0} C. The thermodynamic parameters such as enthalpy, entropy and Gibbs free energy change are calculated by using these equations.

$$K_D = \frac{C_{solid}}{C_{liquid}}$$
(3.37)

$$lnK_D = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$
(3.38)

$$\Delta G = \Delta H - T \Delta S \tag{3.39}$$

Where K_D is the distribution coefficient, C_{solid} is the equilibrium concentration of the MB on modified carbons and C_{liquid} is the equilibrium concentration of the MB in solution. The Figure 3.134 – 3.136 shows the logarithmic variation of distribution coefficient versus reciprocal of temperature (1/T) in Kelvin scale. Table 3.24 shows the thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of modified carbons for MB adsorption at different temperature and different concentration. ΔS and ΔH decreases with increasing concentration. The ΔS is positive means increase in disorder of carbon – dye solution interface of material during the adsorption system studied and the strong affinity of modified carbons towards MB. The standard free energy for physisorption is in the range of -20 to 0 kJ/mol and chemisorptions varies from -80 to -400 kJ/mol.

Granular activated carbon incorporated with Zn^{2+} : preparation, characterisation and adsorption studies

	tempera	tures C_0 :	25 - 150	JU mg/L				
		<u>,</u>			$\Delta \mathbf{G}$	G (kJmol	¹)	
Carbon	C ₀	∆S J ¹⁻ lomL)	∆H (kJmoľ	283	293	303	313	323
	25	105.61	19.29	-1.0.59	-11.65	-12.71	-13.76	-14.82
	50	90.76	18.29	-7.40	-8.31	-9.22	-10.12	-11.03
	75	78.53	18.05	-4.17	-4.96	-5.75	-6.53	-7.32
	100	60.48	14.21	-2.91	-3.52	4.12	-4.73	-5.33
GAC383	150	52.66	13.94	-0.96	-1.49	-2.01	-2.54	-3.07
	200	44.03	12.57	0.11	-0.33	-0.77	-1.21	-1.65
	250	35.23	10.75	0.78	0.43	0.08	-0.28	-0.63
	350	30.70	10.37	1.68	1.37	1.07	0.76	0.45
	500	26.33	10.01	2.56	2.29	2.03	1.77	1.50
	750	21.21	9.55	3.55	3.33	3.12	2.91	2.70
	1000	18.04	9.34	4.23	4.05	3.87	3.69	3.51
	1250	16.41	9.40	4.76	4.59	4.43	4.26	4.10
	1500	14.38	9.23	5.16	5.02	4.88	4.73	4.59
	25	105.26	19.34	-10.45	-11.50	-12.56	-13.61	-14.66
	50	91.24	18.65	-7.17	-8.08	-9.00	-9.91	-10.82
	75	75.12	18.34	-2.92	-3.67	-4.42	-5.18	-5.93
	100	66.65	17.65	-1.22	-1.88	-2.55	-3.22	-3.88
	150	57.04	16.53	0.39	-0.19	-0.76	-1.33	⁻¹ .90
GACO383	200	44.16	13.72	1.22	0.78	0.34	-0.10	-0.54
	250	36.32	12.03	1.75	1.39	1.02	0.66	0.30
	350	28.28	10.61	2.61	2.32	2.04	1.76	1.47
	500	24.76	10.50	3.50	3.25	3.00	2.75	2.51
	750	21.11	10.45	4.47	4.26	4.05	3.84	3.63
	1000	17.62	10.11	5.13	4.95	4.77	4.60	4.42
	1250	15.05	9.88	5.62	5.47	5.32	5.17	5.01
	1500	13.37	9.81	6.03	5.89	5.76	5.63	5.49
	25	317.50	83.47	-6.38	-9.56	-12.73	-15.91	-19.08
	50	193.96	49.13	-5.76	-7.70	-9.64	-11.58	-13.52
	75	167.09	44.71	-2.57	-4.24	-5.91	-7.58	-9.26
	100	188.05	52.14	-1.08	-2.96	-4.84	-6.72	-8.60
GACZC1073	150	179.71	50.98	0.12	-1.68	-3.47	-5.27	-7.07
	200	99.45	28.50	0.36	-0.64	-1.63	-2.62	-3.62
	250	71.65	20.85	0.57	-0.15	-0.86	-1.58	-2.30
	350	59.95	18.31	1.34	0.74	0.14	-0.46	-1.06
	500	37.37	12.53	1.96	1.58	1.21	0.83	0.46
	750	28.54	11.00	2.92	2.64	2.35	2.07	1.78
	1000	20.72	9.35	3.48	3.28	3.07	2.86	2.65
	1250	18.89	9.31	3.96	3.77	3.58	3.39	3.21
	1500	17.47	9.31	4.37	4.19	4.02	3.84	3.67

Table 3.24: Thermodynamic parameters of GAC383, GACO383 and GACZC1073 for methylene blue (MB) adsorption at different temperatures C_0 : 25 - 1500 mg/L

Granular Activated Carbon Incorporated With Zn $^{2+}$ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 161

Chapter 3

The ΔG values of MB on modified carbons ranging from decreases with increasing temperature and higher in higher concentration. It indicates, adsorption is spontaneous means adsorption system does not require energy from external source. ΔG increases with methylene blue (MB) adsorbate concentration. This indicates at higher concentrations, the spontaneity of adsorption decreases. As the temperature increases, ΔG also decreases. The enthalpy increases with temperature means adsorption is endothermic.



Figure 3.134: lnK_D versus 1/T for the adsorption methylene blue (MB) on GAC383 for C_0 : 25 -1500 mg/L

Figure 3.135: lnK_D versus 1/T for the adsorption methylene blue (MB) on GACO383 for C_0 : 25 -1500 mg/L



Figure 3.136: lnK_D versus 1/T for the adsorption methylene blue (MB) on GACO383 for C_0 : 25 -1500 mg/L

3.5 Determination of Surface Area and Porosity of Modified Carbons (GAC383, GACO383 and GACZC1073) Using Liquid Phase Adsorption Isotherm Modelling

Porosity and surface area are the most important characteristic features of a carbon material in adsorption science. Most well known method for determination of surface area and porosity is nitrogen gas adsorption desorption study at 77K. The resulting isotherms are analysed using established isotherm models such as BET, t - plot, Dubinin - Radushkevich isotherm, Langmuir etc. In this study, Phenol, p – nitrophenol and methylene blue (MB) are used as adsorbates to determine the adsorption efficiency, specific surface area and adsorption capacity of the modified carbons GAC383, GACO383 and GACZC1073. Earlier sections discussed adsorption isotherm studies of materials under different temperatures. The specific surface area of modified carbon (GAC383, GACO383 and GACZC1073) are determined by using different isotherm models such as Langmuir, John – Sivanandan Achari isotherm, BET and I plot applied for the adsorption studies of phenol, p – nitrophenol and Methylene blue at a temperature of 30° C.

3.5.1 Langmuir Isotherm

Langmuir isotherm model is the first introduced isotherm model in the adsorption characteristics of an adsorbent. Langmuir monolayer adsorption capacity is calculated using an equation

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e \tag{3.40}$$

Langmuir isotherm model is graphically represented as $C_{e/a}$ versus equilibrium concentration (C_e) (Figure 3.137), the reciprocal of the slope is monolayer adsorption capacity (q_{max}) . The Langmuir surface area of the modified carbons are calculated by using this q_{max} for the adsorption of

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 163



$$SA_{L}(m^{2} / g) = \frac{q_{max}(g / g) \times 6.022 \times 10^{23} (molecules / mole) \times 0.522 \times 10^{-18} (nm^{2} / Phenol molecule)}{94.11124}$$
(3.41)

$$SA_{L} (m^{2}/g) = \frac{q_{max} (g/g) \times 6.022 \times 10^{23} (molecules / mole) \times 0.525 \times 10^{-18} (nm^{2} / p - nitrophenol molecule)}{139.11}$$
(3.42)

$$SA_{L}(m^{2}/g) = \frac{q_{max}(g/g) \times 6.022 \times 10^{23} (molecules / mole) \times 1.2 \times 10^{-18} (mm^{2} / MB molecule)}{318.90}$$
(3.43)

$$Porosity = \frac{q_{max}(mg / g)}{Density of adsorbate}$$
(3.44)



Figure 3.137: Langmuir isotherm model at equilibrium temperature 30°C on

- (a) Phenol adsorption by granular activated carbons
- (b) *p* –nitrophenol adsorption by GAC383, GACO383 & GACZC1073
- (c) Methylene Blue (MB) adsorption by GAC383, GACO383 & GACZC1073

The porosity and surface area of modified carbon using Langmuir isotherm model is shown in Table 3.25. The porosity of modified carbons is higher for p - nitrophenol compared to phenol and methylene blue (MB). Presence of nitro group on phenol structure enhances its adsorption on carbon surface because; it has less solubility in water. Molecular structure of methylene blue (MB) is large, its pore and surface accessibility is reduced hence surface area and adsorption capacities evaluated are less for the carbon.

3.5.2 John – Sivanandan Achari Isotherm

This isotherm model known to be suitable to express liquid phase equilibrium adsorption phenomenon by granular activated carbons given by [5, 52, 53, 54]

$$\log\log C_e = C + n\log q_e \tag{3.44}$$

The isotherms (Figure 3.138 (a) - (f)) are constructed for carbon phenol, carbon - para nitrophenol & carbon - methylene blue adsorption system by plotting ' C_e ' in loglog and ' q_e ' in log form. The parameter n is the measure of adsorption energy, $q_e \pmod{g}$ is the amount of adsorbate (phenol, p - nitrophenol & dye adsorbed at equilibrium and C_e (mg/L) is the equilibrium concentration. Logarithm of limiting micro pore volume [monlayer adsorption capacity, q (J-SA)] is obtained by extrapolating the straight line connecting the lower points to loglog C_e .



Figure 3.138: John Sivanandan Achari isotherm model for the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACZC1073 (d) John Sivanandan Achari isotherm model for the adsorption of p - nitrophenol on new carbons & John Sivanandan Achari isotherm model for the adsorption of methylene blue on (e) GAC383 (f) GACO383 & (g) GACZC1073

The John – Sivanandan Achari (J - SA) surface area of modified carbons are calculated by using the equations shown below

$$SA_{J-SA}(m^{2}/g) = \frac{q_{m(J-SA)}(g/g) \times 6.022 \times 10^{23} (molecules / mole) \times 0.522 \times 10^{-18} (nm^{2} / Phenol molecule)}{94.11124}$$
(3.44)

$$SA_{J-SA}(m^{2}/g) = \frac{q_{m(J-SA)}(g/g) \times 6.022 \times 10^{23} \text{ (molecules / mole)} \times 0.525 \times 10^{-18} \text{ (mm^{2}/p-nitrophenol molecule)}}{139.11}$$
(3.45)

$$SA_{J-SA}(m^2 / g) = \frac{q_{m(J-SA)}(g / g) \times 6.022 \times 10^{23} (molecules / mole) \times 1.2 \times 10^{-18} (mm^2 / MB molecule)}{318.90}$$
(3.46)

$$Porosity = \frac{q_{m} (J-SA)^{(mg / g)}}{Density of \ adsorbate}$$
(3.47)

The porosity of Langmuir isotherm and John – Sivanandan Achari isotherm (J-SA) are found to be quiet comparable for these modified granular activated carbons (GAC383, GACO383 and GACZC1073) towards phenol, p – nitrophenol and methylene blue (MB). It indicates that these carbons are having Type I isotherm character and are highly microporous in nature.

3.5.3 Brunauer Emmet Teller Method (BET)

The BET isotherm model is used to determine the surface area and porosity of the modified carbons GAC383, GACO383 and GACZC1073. BET isotherm model in liquid phase is expressed as

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{K_b Q_m} + (\frac{K_b - 1}{K_b Q_m})(\frac{C_e}{C_s})$$
(3.48)

Where C_e is the concentration of methylene blue (MB) in solution (mg/L), C_s is the saturation concentration of MB (mg/L), q_e is the amount of MB adsorbed (mg/g), Q_m is the complete monolayer adsorption capacity from the BET plot and K_b is the constant related to the energy of interaction with

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 167

the surface [55]. The surface area calculated by the monolayer adsorption value Q_m using the equation

$$SA_{BET}(m^{2} / g) = \frac{Q_{m (BET)}(g / g) \times 6.022 \times 10^{23} (molecules / mole) \times 0.522 \times 10^{-18} (mm^{2} / Phenol molecule)}{94.11124}$$
(3.49)

$$SA_{BET} (m^2 / g) = \frac{Q_{m (BET)} (g / g) \times 6.022 \times 10^{23} (molecules / mole) \times 0.525 \times 10^{-18} (mn^2 / p - nitrophenol molecule)}{139.11}$$
(3.50)

$$SA_{BET} (m^{2} / g) = \frac{Q_{m (BET)} (g / g) \times 6.022 \times 10^{23} (molecules / mole) \times 1.2 \times 10^{-18} (mm^{2} / MB molecule)}{318.90}$$
(3.51)

$$Porosity = \frac{Q_m (BET)^{(mg / g)}}{Density of adsorbate}$$
(3.52)

The The surface area and porosity of the modified carbons using BET isotherm model in phenol. p -nitrophenol and methylene blue (MB) are shown in Table 3.25. Here, we see that the porosity and surface areas of modified carbons are higher in phenol adsorption compared to other adsorbate. Because the cross sectional area and molecular weight of phenol is less compared to other adsorbate.

3.5.4 I plot Method

BET scatchard plot or I plot in liquid phase is expressed as

$$\left[q_{e}\left(1-\frac{C_{e}}{C_{s}}\right)\right]/\frac{C_{e}}{C_{s}} = Cq_{m}-(C-1)\left[q_{e}\left(1-\frac{C_{e}}{C_{s}}\right)\right]$$
(3.53)

From the monolayer adsorption capacity of modified carbons surface area are calculated using the equation

$$SA_{I} (m^{2} / g) = \frac{q_{m} (I) (g / g) \times 6.022 \times 10^{23} (molecules / mole) \times 0.522 \times 10^{-18} (mm^{2} / Phenol molecule)}{94.11124}$$
(3.54)

$$SA_{I}(m^{2}/g) = \frac{q_{m(l)}(g/g) \times 6.022 \times 10^{23} (molecules/mole) \times 0.525 \times 10^{-18} (mm^{2}/p - nitrophenol molecule)}{139.11}$$
(3.55)

$$SA_{I}(m^{2} / g) = \frac{q_{m(I)}(g / g) \times 6.022 \times 10^{23} (molecules / mole) \times 1.2 \times 10^{-18} (nm^{2} / MB molecule)}{318.90}$$
(3.56)

School of Environmental Studies, Cochin University of Science and Technology

Porosity =
$$\frac{q_{\text{Iplot}}(\text{mg/g})}{\text{Density of adsorbate}}$$
 (3.57)

The porosity and surface area of modified carbons using the BET isotherm model and BET scatchard plot (I plot) model for phenol, p - nitrophenol and MB are comparable that indicate these modified carbons (GAC383, GACO383 and GACZC1073) are microporous in nature.

Table 3.25: The porosity and surface area of the modified carbons using different isotherm models

	Donosity		Phenol		p	- nitropł	nenol	Me	thylene I	Blue
Isotherm Models	(cm ^{3/} g) and Surface area (m ² /g)	GAC383	GACO383	GACZC1073	GAC383	GACO383	GACZC1073	GAC383	GAC0383	GACZC1073
Langmuir	q _{max} (L)	312.5	209.6	408.2	340.1	224.2	490.2	190.1	138.7	248.8
(L)	$V_m(L)$	0.452	0.303	0.590	0.425	0.28	0.613	0.300	0.219	0.393
	SA (L)	1043.9	700.4	1363.6	773.2	509.7	1114.3	430.9	314.4	563.8
John	q _m (J-SA)	310.5	217.4	400.4	357.8	232.2	502.70	190.1	135.7	252.9
Sivanandan Achari(J –	V _m (J-SA)	0.449	0.314	0.579	0.448	0.29	0.629	0.300	0.214	0.399
SA)	SA(J-SA)	1037.2	726.2	1337.7	813.2	527.7	1142.6	430.8	307.5	573.1
Bruaner	q _m (BET)	190.2	135.6	215.8	190.1	135.7	252.9	115.8	84.2	150.5
Emmet Teller (BET)	V _m (BET)	0.275	0.195	0.312	0.284	0.175	0.377	0.183	0.133	0.237
	SA (BET)	635.3	452.9	720.9	515.9	318.2	573.1	262.4	190.8	341.1
BET	q _m (Iplot)	189.9	137.6	215.7	236.5	140.1	308.5	117.3	86.54	155.6
Scatchard Plot(I plot)	V _m (I plot)	0.273	0.199	0.312	0.296	0.175	0.386	0.185	0.136	0.245
	SA(I plot)	634.5	459.5	720.7	537.5	318.4	701.3	265.9	196.1	352.6





School of Environmental Studies, Cochin University of Science and Technology

Granular activated carbon incorporated with Zn²⁺: preparation, characterisation and adsorption studies







3.6 Adsorption of Trace Elements (Li, Mg, Al, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Ba, Tl & Pb)

Adsorption efficiency of carbon GAC383, GACO383 and GACZC1073 are tested using a ground water sample having trace metals in concentrations (Li – 1.3 μ g/L, Mg – 1220.04 μ g/L, Al - 42.88 μ g/L, Cr - 0.27 µg/L, Mn - 103.5 µg/L, Fe - 2884.22 µg/L, Co - 1.01 µg/L, Cu - 1.06 µg/L, Zn - 12355.72 µg/L, As - 0.06 µg/L, Cd - 0.04 µg/L, Ba - 186.02 μ g/L, Tl - 0.04 μ g/L and Pb - 2.4 μ g/L). This has been collected from a region whose water quality parameters are known, Batch experiment were done, 100 ml of ground water mixed with 0.1 g of carbon. For this study, contact time is controlled as 480 minutes as equilibration stime, After the desired contact time these carbons were filtered and the final concentration is determined by ICP – MS. The percentage adsorption efficiency of these new carbons are evaluated and are shown in Table 3.26. From the Table it is clear that GACO383 shows more than 90% efficiency to remove most of the heavy metals such as manganese (Mn), aluminium (Al), Iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and barium (Ba). The carbon GACZC depicts that more than 90% removal efficiency against trace elements Fe (9932%), Zn (99.32%) and Pb (98.75%). More of the trace elements removed by GACZC1073 shows higher than 50% efficiency.

		GAC	383	GACO)383	GACZ	C1073
Trace elements	Initial concentration (µg/l)	Amount adsorbed (µg/g)	Percentage efficiency (%)	Amount adsorbed (μg/g)	Percentage efficiency (%)	Amount adsorbed (μg/g)	Percentage efficiency (%)
Li	1.30	0.23	17.69	0.63	48.46	0.33	25.38
Mg	1220.04	17.7	1.45	939.66	77.02	158.79	13.02
Al	42.88	36.89	86.03	39.58	92.30	31.99	75.66
Cr	0.27	0.09	33.33	0.2	74.07	0.1	37.04
Mn	103.5	73.39	70.91	100.5	97.10	39.86	38.51
Fe	2884.22	2860.18	99.17	2873	99.61	2873.22	99.62
Co	1.01	0.71	70.30	0.94	93.07	0.8	79.21
Cu	1.06	0.05	4.72	1.02	96.23	0.94	88.68
Zn	12355.72	12143.04	98.28	12345.92	99.92	12271.14	99.32
As	0.06	0.02	33.33	0.04	66.67	0.035	58.33
Cd	0.04	0.01	25.00	0.02	50.00	0.03	75.00
Ba	186.02	91.04	48.94	183.25	98.51	133.53	71.78
T1	0.04	0.03	75.00	0.03	75.00	0.03	75.00
Pb	2.4	2.3	95.83	1.61	67.08	2.37	98.75

Table 3.26:	Adsorption	efficiency	for removing	trace e	elements	by n	newly	prepared
	carbons GA	AC383, GA	ACO383 and C	GACZC	C1073			

3.7 Statistical Analysis of the Data

Results of statistical tests conducted to check the various hypotheses, suggested in the chapter 1, give the following results:

Hypothesis 1: Whether there is any significant difference between the total pore volume, micropore volume and mesopore volume for different modified granular activated carbons (GACZC) and in comparison with the native form of granular activated carbon (GAC) and carbon oxidised with nitric acid (GACO383).

The comparison of textural characterization obtained by two way ANOVA test and the sum of squares (*ss*), degree of freedom (*df*), mean square (*ms*), variance ratio (*F*) and level of significance (*P*–value) are shown in the Table 3.27 (GAC 383 as control) and Table 3.28 (GACO383 as control). The inferences are given below.

 Table 3.27: ANOVA table for the comparison of textural characterization of granular activated carbon taking GAC383 as control

Source	SS	df	ms	F	P-value
Total	121716.0454	11			
Carbons	1054.4651	3	351.4884	1.322	P>0.05
Pore volumes	119066.3184	2	59533.1592	223.92	P<0.001
Residual	1595.269	6	265.8770		

Inferences

- (a) There is significant difference between V_t , V_{mic} and V_{mes} (P<0.001). Total pore volume is significantly higher than other two, mesopore volume is significantly lower compared to the other two.
- (b) There is no significant difference between the carbon GAC's (P>0.05)

Table 3.28: ANOVA table for the comparison of textural characterization of granular activated carbon taking GACO383 as control

Source	SS	df	ms	F	P-value
Total	116428.2515	11			
Carbons	1882.2571	3	627.4190	1.028	P>0.05
Pore volumes	110885.4717	2	55442.7359	90.877	P<0.001
Residual	36605227	6	610.0871		

Inferences

- (a) There is significant difference between volumes. Total pore volume is significantly higher than the rest (P<0.001). Mesopore volume is significantly lower than others.
- (b) There is no significant difference between the carbons GAC's (P>0.05).

(c) Comparison of mean percentage of microporosity (V_{mic}/V_t) and mesoporosity (V_{mes}/V_t) the mean percentage of microporosity is significantly higher than that of mesoporosity (t = 7.519, df =8, P<0.001)

Hypothesis 2: Whether there is any significant difference between porosity and surface area using Solid – gas equilibria using N₂ gas adsorption at 77K, evaluated using different isotherm models; BET isotherm, I plot method, Langmuir isotherm, John isotherm, α_s plot, *t* - plot for modified granular activated carbons and in comparison with the native form of granular activated carbon.

To prove this hypothesis two way ANOVA method is used. The adsorption capacity, surface area and pore volume obtained by establishing isotherm models such as Langmuir, John isotherm, Dubinin – Radushkevich isotherm, BET isotherm, *I plot*, Alpha S (α_s). The results are presented in Table 3.29 (GAC383 as control for adsorption capacity), Table 3.30 (GAC0383 as control for adsorption capacity), Table 3.31 (GAC383 as control for surface area), Table 3.32 (GAC0383 as control for surface area), Table 3.32 (GAC0383 as control for surface area), Table 3.33 (GAC383 as control for pore volume) and Table 3.34 (GAC0383 as control for pore volume). The inferences are given below.

Table 3.29: ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and *I* plot method) of granular activated carbon taking GAC383 as control

Source	SS	df	ms	F	P-value
Total	20228.9538	15			
Carbons	2139.8949	3	713.2983	38.947	P<0.001
Adsorption capacity	17924.2261	3	5974.7420	326.225	P<0.001
Residual	164.8328	9	18.3148		

Inferences

(a) There is significant difference between porosity (P<0.001). GACZC1273 is having significantly higher adsorption capacity compared to others.

(b) There is significant difference between methods (P < 0.001). John isotherm and Langmuir isotherm methods depicted significantly higher value compared to the other two. BET isotherm method and *I plot* method are having significantly lower value (P < 0.001).

Table 3.30: ANOVA table for the comparison of adsorption capacity obtained by
different methods (John Isotherm, Langmuir isotherm, BET isotherm and
I plot method) of granular activated carbon taking GACO383 as control

Source	SS	df	ms	F	P-value
Total	23763.0543	15			
Carbons	5475.6364	3	1825.2121	64.02	P < 0.001
Adsorption capacity	18030.8469	3	6010.2823	210.83	P<0.001
Residual	256.5710	9	28.5079		

Inferences

- (a) There is significant difference between the adsorption capacities. GACZC1073 and GACZC1273 are significantly higher than the rest with respect to porosity (P< 0.001).</p>
- (b) John isotherm and Langmuir isotherm methods give significantly higher value than the rest (P < 0.001).

Table 3.31: ANOVA table for the comparison of surface area obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and *I* plot method) of granular activated carbon taking GAC383 as control

Source	SS	df	ms	F	P-value
Total	394089.73	15			
Carbons	41541.99	3	13847.3317	41.273	P < 0.001
Adsorption capacity	349528.19	3	116509.3967	347.266	P < 0.001
Residual	3019.55	9	335.5050		

Inferences

- (a) There is significant difference in the surface area (P< 0.001) GACZC1273 is having significantly higher surface area compared to others.
- (b) In John isotherm and Langmuir isotherm method showed significantly higher surface area compared to others (P< 0.001). *SA* (*BET*) and *SA* (*I*plot) is hiaving significantly lower surface area (P<0.001).

Table 3.32: ANOVA table for the comparison of surface area obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and *I plot* method) of granular activated carbon taking GACO383 as control

Source	SS	df	ms	F	P-value
Total	440177.830	15			
Carbons	90040.835	3	30013.6117	93.03	P<0.001
Adsorption capacity	347233.395	3	115744.4650	358.762	P<0.001
Residual	2905.600	9	322.6222		

Table 3.33: ANOVA table for the comparison of pore volume obtained by
different methods (John Isotherm, Langmuir isotherm, Dubinin –
Radushkevich isotherm and Alpha S) of granular activated carbon

g		10		Б	D 1
Source	SS	đľ	ms	F	P-value
Total	6439.1471	19			
Carbons	5300.2055	4	1325.0514	225.6292	P<0.001
Adsorption capacity	1068.4693	3	356.1564	60.646	P<0.001
Residual	70.4723	12	5.8727		

Inferences

- (a) GACZC1273 is having significantly higher surface area (P<0.001) and GACO383 is having significantly less surface area (P<0.001).
- (b) Surface area is significantly higher in Langmuir and John isotherm methods and significantly lower in BET and I plot methods (P<0.001).

Inferences

- (a) GACZC1273 is having significantly higher pore volume and GACO383 is having significantly lower pore volume (P<0.001).
- (b) Micropore volume calculated by Alpha S plot method and Dubinin Radushkevich methods are having significantly higher value than the other two methods (P<0.001) though between them the difference is not significant.



Hypothesis 3: Whether there is any relation between the adsorption temperature and adsorption efficiency for the modified granular activated carbons (GACZC).

Pearson correlation coefficient (r) and Student's t test are used to prove the relation of adsorption temperature and adsorption efficiency. From the above test, attained following inferences:

There is significant positive correlation between temperature and adsorption of phenol on GACZC 1073 (r =0.9953, t = 17.79, df = 3, P <0.01). This indicates that as temperature increases adsorption of phenol also increases.

There is significant positive correlation between temperature and adsorption of p-nitro phenol on on GACZC 1073 (r =0.9888, t = 11.49, df = 3, P < 0.01). This indicates that as temperature increases adsorption of *p*-nitro phenol also increases.

There is significant positive correlation between temperature and adsorption of MB on GACZC 1073 (r = 0.9903, t = 12.36, df = 3, P < 0.01). This indicates that as temperature increases adsorption of MB also increases.

Hypothesis 4: Whether there is any significant difference between surface area determined using Langmuir isotherm and John – Sivanandan Achari isotherm (J-SA) for newly prepared granular activated carbons from solid liquid equilibria.

Langmuir and John – Sivanandan Achari isotherm model for phenol, p – nitrophenol and methylene blue adsorption on modified carbons are tested by three way ANOVA test. Results are shown in Table 3.34. Inferences are given below.

Chapter 3

isoth	erm models				
Source	Ss	df	ms	F	p-value
Total	1945017.2812	17			
Methods	371.7356	1	371.7356	0.048	$P \hspace{0.1in} > \hspace{-0.1in} 0.5$
Carbon	755024.5745	2	377512.2873	49.0346	P < 0.001
P, PNP & MB	1097234.2878	2	548617.1439	71.2592	P < 0.001
Residual	92386.6833	12	7698.8903		

Table 3.34: ANOVA table for the comparison of surface area of modified carbons obtained by Langmuir isotherm and John – Sivanandan Achari isotherm models

Inferences

- (a) There is no significant difference in surface area between Langmuir and John Sivanandan Achari isotherm models (P > 0.5).
- (b) Between carbons the surface area is significant (P< 0.001). In GACZC1073 the surface area is significantly higher than that in GAC383 and GAC0383 (P< 0.001).
- (c) The surface area differ significantly between phenol (P), p nitrophenol (PNP) and methylene blue (MB). In phenol, the surface area is significantly greater that in PNP and MB (P< 0.001)

3.8 Conclusions

Granular activated carbon impregnated with Zn^{2+} ions ($X_{zn} = 0.0017$) has unique and distinct surface characteristics, structural features and adsorption efficiency in solid – gas and solid – liquid equilibria studies. The steam activation of GACZC series shows a very stable and steady burn off pattern (12% to 23% at 1273K). GACZC1073 shows high percentage of elemental carbon (94.68%) and lesser percentage of oxygen (5.13%). The percentage of basic groups formed varies with activation temperature; GACZC1073 shows high basic groups (0.90 meq/g). The FTIR spectra show a peak at 571 cm⁻¹ and any of these between 450 – 650 cm⁻¹ are attributed to the out of plane C-H bending mode. The presence of these

spectral regions indicated that alkaline groups and cyclic ketones and their derivatives are formed during activation with zinc ions. These groups are significant during activation upto 873K; are observable in the FTIR spectra. The XPS surface analysis confirms that chemical and thermal activation (GACZC1073) has highest carbon percentage (97.69%) and a very lesser amount of zinc (0.02%). The interlayer distance (d_{002}) of these granular activated carbons lies in a range of 0.35 - 0.38 nm indicate that these carbons are non – graphitised carbons. SEM image of GAC shows well developed pores on surfaces where there is a more possibility for pollutant / adsorbate to beadsorbed into these pores. TEM image of the native carbon (GAC383) and zinc impregnated carbon (GACZC1073) are highly microporous in nature.

The modified granular activated carbon (GACZC) shows a Type I isotherm behaviour with H4 hysteresis loop indicate the presence of wider pores. The *I plot* surface area are more comparable with *BET* surface area means the modified carbons are highly microporous in character. The pore width calculated by Dubinin - Radushkevich (D - R) method (1.56 -1.75nm) and BET (1.70 -1.77) shows that these granular activated carbons are microporous in nature. GACZC series at higher activation temperature (GACZC873, GACZC1073 & GACZC1273) GACZC1073 shows higher micropore volume (0.40 cm³/g) and micropore surface area (766.76m²/g) from the t plot method. BJH pore size distribution method shows the pore width in the range of 2.10 to 2.50nm. The nitrogen adsorption – desorption isotherm method indicate that the new carbons are predominantly wider microporous these carbons are more applicable for waste water treatment. Kinetic studies showed that that adsorption of phenol, p - nitro phenol and methylene blue followed pseudo- second order model. Two phases in the intraparticle diffusion suggest that the adsorption process proceeds by surface adsorption and intraparticle diffusion.

Thermodynamic parameters such as enthalpy change, free energy change and entropy change showed that the adsorption process of phenol, p - nitrophenol and methylene blue has been endothermic and spontaneous. Agreement of Langmuir and John – Sivanandan Achari isotherm with single phase adsorption and agreeing values for critical constant indicate that the granular activated carbon materials newly prepared incorporated with Zn²⁺ ions are greatly microporous.

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Chapter 4

GRANULAR ACTIVATED CARBON OXIDISED AND INCORPORATED WITH Zn²⁺: PREPARATION, CHARACTERISATION AND ADSORPTION STUDIES

4.1 Introduction

Nitric acid is a powerful oxidising agent. Nitric acid oxidation of granular activated carbons increases the oxygen containing functional groups and changes the physical and chemical nature of carbon. Surface modification using nitric acid to remove the mineral content and improved the hydrophilic character of carbons [1]. The resulting surface chemistry, porosity and surface area affect the adsorption efficiency of a carbon. The granular activated carbon (GAC383) impregnated with Zn^{2+} ions and activated at different temperature showed that the adsorption capacity of carbon in gaseous and liquid phase is enhanced. In this chapter, the adsorption efficiency of oxidized carbon (GACO383) impregnated with Zn^{2+} ions are elaborately discussed as a new series. Physico - chemical characterization and adsorption efficiency of this new activated carbon series consists of GACOZC383, GACOZC473, GACOZC673, GACOZC873, GACOZC1073 and GACOZC1273 are presented. Together with a comparison of adsorption efficiency with respect to GAC383 and GACO383 analyzed. The methodologies followed for these carbon materials were already discussed in the chapter 2.

4.2 Characterization Studies of GACOZC Series Carbons

The characterization studies of GACOZC series are done with respect to established standard methods of analysis. These includes, the oxidation, impregnation, thermal activation, physico chemical characterization such as porosity, surface area, surface functional groups, surface morphology, crystallinity etc. as evidenced by their textural characterizations done by N_2 adsorption – desorption isotherm analysis, FTIR, XPS, XRD, SEM, TEM, elemental analysis etc.

4.2.1 Carbon Yield and Burn - Off

The carbon yield and burn - off of the oxidized granular activated carbon impregnated with Zn^{2+} ions and activated at different temperature are shown in Figure 4.1.



Figure 4.1: Carbon yield and burn - off pattern of GACOZC series activated at different temperatures

It is seen that the activation decreases the carbon yield and burn off increases. The less yield noticed at high temperature was essentially due to the structural reorientation of the carbon upon heating. Carbon activated at 1073K (GACOZC1073 -28.73%) and 1273K (GACOZC1273- 28.13%) has no much difference in the burn - off. It appears that thermal, structural stabilization occurs at the activation temperature of 1073K (GACOZC1073) as evidenced by carbon yield and burn - off results.

4.2.2 Elemental Analysis

The chemical composition of the modified carbons GACOZC series and basic GAC383, GACO383 are determined by elemental analysis and are presented in Table 4.1. Nitric acid oxidation decreases the carbon content from GAC383 (89.43%) to GACO383 (65.10%). The content of oxygen (31.71%), hydrogen (2.61%) and nitrogen (0.58%) are increased after nitric acid oxidation. Nitric acid oxidation also enhanced the oxygen surface groups as it determined by Boehm titration and FTIR spectroscopic analysis. In the case of GACOZC series of carbons - oxidation and impregnation with zinc ions decrease the carbon content first. Thermal activation enhances the carbon content 64.41% to 84.07%. Whereas, content of hydrogen decreases from 2.16 - 0.52%, nitrogen 0.64 - 0.17% and oxygen 32.97 - 14.82% upon thermal activation. Because, the steam activation increases the pyrolytic decomposition of non - carbon elements and it increases the percentage of elemental carbon (GACOZC1073 – 84.07%) [2].

Carbon	Carboxylic (meq/g)	Lactones (meq/g)	Phenolic (meq/g)	Base (meq/g)	C%	Н%	N%	0%
GAC383	0.40	0.17	0.45	0.50	89.43	0.60	0.36	09.61
GACO383	1.38	1.34	2.10	0.20	65.10	2.61	0.58	31.71
GACOZC383	1.38	1.27	1.64	0.20	64.41	2.16	0.59	32.97
GACOZC473	1.33	1.12	1.52	0.25	72.76	0.67	0.64	26.40
GACOZC673	0.92	1.03	0.94	0.34	76.34	0.61	0.59	22.85
GACOZC873	0.59	0.98	0.64	0.39	75.98	0.77	0.46	22.66
GACOZC1073	0.23	0.94	0.17	0.43	84.07	0.52	0.17	14.82
GACOZC1273	0.26	0.96	0.24	0.40	83.54	0.57	0.20	15.25

 Table 4.1: Surface functional groups and elemental composition of modified granular activated carbons GACOZC series

Granular Activated Carbon Incorporated With Zn $^{2+}$ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 187

4.2.3 Surface Functional Group Analysis Using FTIR and Boehm Methods

The surface functional groups of the modified carbons are quantitatively determined by using Boehm titration methods and are shown in Table 4.1. The oxidation of nitric acid increases the oxygenated acidic functional groups such as carboxylic (1.38 meq/g), lactonic (1.34 meq/g) and phenolic (2.10 meq/g) groups on the surface of GACO383. This carbon impregnated with zinc ions (GACOZC series) has higher acidic functional groups compared to starting carbon GAC383. Steam activation at higher temperature enhances the basicity of carbon. Hence, acidic functional groups such as carboxylic, phenolic and laconic groups are less. From the series, GACOZC383 shows high carboxylic (1.38 meq/g), phenolic (1.27 meq/g) and lactonic (1.64 meq/g) groups. Thermal activation reduced the functional groups. GACOZC1073 showed lesser carboxylic (0.23 meq/g), phenolic (0.94 meq/g) and lactonic (0.17 meq/g) groups on their surfaces. Because heat treatment caused the acidic functional groups removed as they are less stable oxygen functional groups on the carbons surface [3]. But activation at 1273K, the proportion of these acidic functional groups is slightly enhanced. This is better as granular activated carbon with low acidic functional groups and high basicity has been known best for adsorption of organic compounds.

The presence of various surface functional groups on the modified carbon surface is determined by Fourier transform Infrared Spectroscopic (FTIR) method. The FTIR spectra were taken in the transmission band mode in the range of $4000 - 500 \text{ cm}^{-1}$. The FTIR spectra of GAC383 and GAC0383 are shown in Figure 4.2 (a) and (b) respectively. The broad peaks of GAC383 (3426 cm⁻¹) and GAC0383 (3440 cm⁻¹) are the O - H stretching vibration of hydrogen bonds. The bands at 2924 cm⁻¹ range is attributed to C - H interaction with the surface of GAC0383 and it is absent in GAC383. The peaks shows GAC383 (1626 cm⁻¹) and GAC0383

(1631 cm⁻¹) is attributed to the mono or distributed C = C bond. A strong peak at 1120 cm⁻¹ is the asymmetric stretch of COC on the surface of GACO383. The band present GACO383 (1030 cm⁻¹) is related to the C – OH stretching vibration. The Figure 4.2 (b) shows that nitric acid oxidation increases the intensity of acidic surface functional groups.



The FTIR spectra of GACOZC are shown in Figure 4.3. The band at 3433 - 3437 cm⁻¹ is due to O–H stretching vibration of hydroxyl groups. The two bands 2924 cm⁻¹ and 2857 cm⁻¹ is only present in lower activation temperature of the carbons GACOZC383, GACOZC473 and GACOZC673 only. This peak is assigned to C–H symmetric and asymmetric stretching of residual methylene groups on the surface of GACOZC. As the activation temperature increases the intensity of peak disappear on the carbon surface. The band in the range of 1703 - 1735cm⁻¹ is because of C=O stretching vibration of ketones and aldehydes present on all the carbons. The strong band in the range of 1613 - 1635 cm⁻¹ is related to either C=C or C=N of the aromatic region of the modified carbons [4]. The modified carbons at a higher activation temperature shows a stretching vibration of 1515 cm⁻¹ (GACOZC873), 1511 cm⁻¹ (GACOZC1073) and 1520 cm⁻¹

quinine structures [5]. The band in the range of $1450 - 1460 \text{ cm}^{-1}$ of the modified carbon, indicating that a series of overlapping absorption bands attributed to the stretching vibration of hydroxyl groups and in plane vibrations of C–H structures [6].



Figure 4.3: FTIR spectra of new carbons (a) GACOZC383, (b) GACOZC473, (c) GACOZC673, (d) GACOZC873, (e) GACOZC1073 & (f) GACOZC1273

The bands between $921 - 1059 \text{ cm}^{-1}$ are a strong band of C–O of primary alcohol and primary amine in the structure of GACOZC series of carbon. The peaks in the range of $500 - 650 \text{ cm}^{-1}$ are attributed to the out of plane C-H bending mode. The band in the range of $403 - 421 \text{ cm}^{-1}$ is attributed to basic groups such as cyclic ketones and other ketone derivatives. These sharp peak points are only seen at higher activation temperature.

4.2.4 XPS Surface Analysis

The elemental compositions of the granular activated carbons are obtained by the XPS method (Table 4.2). Figure 4.4 (a) – (c) shows the wide spectrum of XPS of the granular activated carbons. The table shows that the percentage of carbon is higher with oxidation, activation and impregnation with Zn^{2+} ions (GACOZC1073 – 96.92%). The percentage of oxygen is obtained from the area of the O 1s spectrum of modified carbons are GAC383 – 7.04%, GACO383 – 12.86% and GACOZC1073 – 2.71%. GACOZC1073 shows a lesser amount of zinc atoms (0.06%) at a peak (binding energy – 1021 eV).



Figure 4.4 (a): X-ray photoelectron spectra of GAC383

Figure 4.4 (b): X-ray photoelectron spectra of GACO383



Figure 4.4 (c): X-ray photoelectron spectra of GACOZC1073

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

Chapter 4

 Table 4.2.:
 The elemental composition of the modified granular activated carbons

 GAC383, GACO383 and GACOZC1073 from XPS analysis

Carbon	С%	0%	N%	Zn%
GAC383	92.96	7.04	-	-
GACO383	86.54	12.86	0.60	-
GACOZC1073	96.88	2.71	0.35	0.06

The detailed study of the surface chemistry of carbon (284 eV) and oxygen (532 eV) was deconvoluted using Gaussian – Lorentzian peaks. The high resolution C 1s spectrum of GACOZC1073 (Figure 4.5 (a)) deconvoluted into six major components. The strong bands at 284.49 eV is prescribed to aliphatic carbon. The binding energy (285.10 - 285.87 eV) is corresponding to aromatic carbon. Carboxyl and ester groups are present in a peak at 288.45 eV and the binding energy 290.30 eV is ascribed to a satellite signal due to the π - π shake up in aromatic rings [7].



The high resolution O 1s spectrum of GACOZC1073 is deconvoluted into seven major components (Figure 4.5(b)). The carbon GACOZC1073
shows a peak at binding energy 530.72 eV corresponds to C=O bonds. The peak at 531.7 eV is ascribed to alcohols and esters. The peak at 533.16 - 533.63 eV is due to the presence of ethers and the chemisorbed oxygen shows a peak in the binding energy in the range of 535.56 - 536.54 eV.

4.2.5 XRD Analysis

The X - ray diffraction pattern of the modified carbons is shown in Figure 4.6 and 4.7. The modified carbons GAC383, GACO383, GACOZC383, GACOZC473, GACOZC673, GACOZC873, GACOZC1073 and GACOZC1273 show two peaks at around $2\theta = 23.86 - 25.07^0$ and $2\theta = 43^0$. These peaks are assigned to the reflection from (002) plane and (10) plane respectively. The shape of the XRD profile shows that there are no significant changes in the structure of these modified carbon studied. It indicates that the structure of these modified carbons is being retained after oxidation, impregnation and activation treatments. The interlayer distance (d_{002}) of the modified carbons calculated by using Bragg's equation is shown in Table 4.3. The d_{002} value at the peak $2\theta = 23.86 - 25.07^0$ is in the range of 0.35 -0.37 nm. The d_{002} value of a typical graphitic structure is 0.335 nm. The carbons studied are having greater than this, indicate that these carbons exist as non – graphitized forms and these have well defined porosity.



of GAC383

Figure 4.6 (b): X-ray diffractograms of GACO383

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics



Figure 4.7: X-ray diffractograms of modified carbons (a) GACOZC383, (b) GACOZC473, (c) GACOZC673, (d) GACOZC873, (e) GACOZC1073 and (f) GACOZC1273

The crystalline size of these carbons is obtained from the Scherer equation. The stack height (L_c) and stack width (L_a) are tabulated in Table 4.3. The GACOZC series of the carbons shows stack height in the range 1.11 - 1.48 nm and stack width in the range of 2.22 - 2.96 nm. The stack widths are higher than a typical graphitic carbon (1.00 - 2.00 nm).

	1		5	
Carbon	20	L _c (nm)	L _a (nm)	d ₀₀₂ (nm)
GAC383	24.46	1.14	2.28	0.36
GACO383	24.98	0.97	1.94	0.35
GACOZC383	25.07	1.48	2.96	0.36
GACOZC473	24.50	1.27	2.53	0.36
GACOZC673	23.86	1.11	2.22	0.37
GACOZC873	24.89	1.17	2.34	0.36
GACOZC1073	24.59	1.14	2.30	0.36
GACOZC1273	24.59	1.14	2.27	0.36

Table 4.3: Structural parameters from X- ray diffraction studies

4.2.6 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is commonly used for the visualization of a porous structure of carbon materials. The Figure 4.8 -4.10 shows the different resolution of scanning electron micrograph image of the modified carbons GAC383, GACO383 and GACOZC1073. These carbons show some white dots on the surface, indicate the presence of some inorganic compounds in the starting material. The Figure 4.8 shows the image of 50 µm resolution of these modified carbons. It is clear that the Figure 4.8 (a) the coconut shell based native form of carbon (GAC383) shows a well - defined pore structure and these carbons oxidised with nitric acid (GACO383) seen in Figure 4.8 (b) shows wider pores but disordered due to the oxidative destruction of the carbon surface. This carbon impregnated with zinc ions and activated at 1073K (GACOZC1073) shown in Figure 4.8 (c) has a wider pores with well – interconnected under all resolutions. It is clear that pore widening occurred after impregnation and activation as well as during nitric acid oxidisation of carbon. The SEM image of 5µm resolution of GACOZC1073 (Fig 4.10 (c)) shows that pore surface is in the range of $0.84 - 4.84 \mu m$.

4.2.7 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is used to determine the actual structure of coconut shell based granular activated carbons. The high resolution (20 nm) TEM image of modified carbons GAC383 (Figure 4.11 (a)), GACO383 (Figure 4.11 (b)) and GACOZC1073 (Figure 4.11 (c)). The SEM and TEM image shows that the native form of carbon (GAC383) is having a uniform microporostiy [8].

Chapter 4



Figure 4.8: SEM image of 50 μm resolution (a) GAC383 (b) GACO383 & (c) GACOZC1073



Figure 4.9: SEM image of 10 μm resolution (a) GAC383 (b) GACO383 & (c) GACOZC1073

Granular Activated Carbon Oxidised and Incorporated with Zn²⁺: Preparation, Characterization ...



Figure 4.10: SEM image of 5 μm resolution (a) GAC383 (b) GACO383 & (c) GACOZC1073



Figure 4.11: TEM image of 20 nm resolution (a) GAC383 (b) GACO383 & (c) GACOZC1073

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 197

Chapter 4



Figure 4.12: TEM image of GACOZC1073 (a) 10 nm resolution (b) 5 nm resolution (c) 2 nm resolution (d) 5 1/ nm Diffraction pattern

The nitric acid oxidized form GACO383 shows a disordered pore structure. This nitric oxidized carbon impregnated with zinc ions (GACOZC1073) at different resolution is shown in Figure 4.12 (a) for resolution 10 nm, (b) for resolution 5 nm, (c) for resolution 2 nm & (d) diffraction pattern. The impregnation, oxidation and activation show a regular pore structure. The parallel lines are shown on the surface of carbon indicate that the pores are slit – shaped [6]. The diffraction pattern of GACOZC shows that this carbon is an amorphous material as evidenced by the XRD pattern.

4.3 Porosity Studies – Evaluation of Surface Area and Pore Volume

The Figure 4.13 illustrates the nitrogen adsorption desorption isotherms at 77K on the modified granular activated carbons (GAC383, GAC0383, GAC0ZC873 and GAC0ZC1073). For the carbons GAC0ZC873 and GAC0ZC1073 activated at 600 and 800⁰C respectively, the amount of nitrogen adsorbed increases with relative pressure. The isotherms show a Type I profile with H4 hysteresis loop, indicate that the nitric acid impregnation and activation with zinc ions increases the presence of wide micropores and mesopores.



Figure 4.13: N₂ adsorption – desorption isotherm at 77K of modified granular activated carbons (GAC383, GACO383, GACO2C873 & GACOZC1073)

The Figure 4.13 shows the H4 hysteresis loop appeared at a relative pressure > 0.4 shows that these GACOZC carbons contains slit shaped pores with capillary condensation and well developed micro and mesoporosity [9]. The total pore volume, t - plot micropore volume and mesopore volume of the modified carbons are presented in Table 4.4. The total pore volume increases with increasing activation temperature. It is

known that nitric acid oxidation, Zn^{2+} impregnation and steam activation decreases the microporosity and increases the mesoporosity [10]. The proportion of mesopore to total pore volume ratio (V_{mes}/V_{tot}) variation in the order GACOZC1073 (63%). > GACOZC873 (58%) > GACO383 (43%) > GAC383 (38%).

These nitrogen adsorption – desorption data of the modified carbons are applied to different isotherm models and to calculate the surface area, pore volume and pore width.

4.3.1 Brunauer Emmet Teller (BET) Isotherm

The porosity and surface area are calculated by using BET isotherm model for the granular activated carbon oxidized and further impregnated with Zn^{2+} ions (GACOZC873 and GACOZC1073) activated at higher temperatures.

$$\frac{1}{V(\frac{p_0}{p}-1)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} (\frac{p}{p_0})$$
(4.1)

It is compared with native form of carbon (GAC383) and oxidized form (GACO383) and the calculated constants are presented in Table 4.4. The characteristic BET model plots are shown in Figure 4.14 upto a relative pressure ($p/p_0 - 0.1$). The surface area ($SA_{BET} - 1305.39 \text{ m}^2/\text{g}$) and porosity ($V_{BET} - 0.3918 \text{ cm}^3/\text{g}$) increases with activation temperature at 1073. This BET isotherm data are compared with BET Scatchard plot method (*I plot*). Based on the trials and observations up to 0.1 relative pressure is used for the surface area and porosity calculation, because the *C* parameter is only +ve at this relative pressure onwards; that means up to this relative pressure monolayer adsorption is fulfilled.



Carbon	V _t [cm ³ g ⁻¹]	V _{mic} [cm ³ g ⁻¹]	V ^{mes} [cm ³ g ⁻¹]	Vmic/Vt (%)	Vmes/Vt (%)	Pore Width (nm)
GAC383	0. 573	0.351	0.2222	61.26	38.74	1.77
GACO383	0.526	0.297	0.2291	56.46	43.54	1.77
GACOZC1073	0.560	0.231	0.329	41.19	58.81	1.91
GACOZC1273	0.604	0.221	0.382	36.66	63.34	1.92
$V_m(cm^3 / g ST)$	$TP) = \frac{V_m(c)}{V_m(c)}$	m^3 / g)	x 22414 x 28	:0.808		

Table 4.4: Textural characterization of granular activated carbons studied

The average pore radius was calculated using the formula

$$d_{av} = 4V_t / S \tag{4.2}$$

 V_t is the total pore volume and S denote BET surface area. The pore width of the modified carbons are GAC383 (1.77 nm), GACO383 (1.77 nm), GACOZC873 (1.91 nm) and GACOZC1073 (1.92 nm). This indicates that all the carbons are microporous but having wider micropores. Temperature activation, oxidation and impregnation enlarge the pore structure.



Figure 4.14: BET isotherm plot for modified granular activated carbons (GAC383, GACO383, GACOZC873 & GACOZC1073

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 201

4.3.2 I Plot Method

The BET scatchard plot (I plot method) $[V(1 - \frac{p}{p_0})] / \frac{p}{p_0}$ vs. $[V(1 - \frac{p}{p_0})]$ gives an inclined V shaped graph of modified carbons (GAC383, GACO383, GACOZC873 and GACOZC1073) shown in Figure 4.15 (a), (b), (c) & (d) respectively.

$$[V(1 - \frac{p}{p_0})] / \frac{p}{p_0} = CV_m - (C - 1)[V(1 - \frac{p}{p_0})]$$
(4.3)

By the extrapolation of the I point towards the x axis, we directly get V_{mic} (I). The V_{mic} (I) is exactly the same of V_m (*BET*) at the BET parameter *C* is positive. The V_m and *SA* of BET and the same obtained from *I plot* are comparable shown in Figure 4.16 (adsorption capacity versus modified carbons) and 4.17 (surface area versus modified carbons).

Table 4.5: Surface area and Pore volume* of granular activated carbon oxidized
and impregnated with Zn^{2+} ions

	BET (p/p ₀ upto	0.1)	BET (p	/p ₀ upto	0.3)	I p	lot
Carbon	SA (BET) (m ² g ⁻¹)	V _m (BET) (cm ³ g ⁻¹	C	SA (BET) (m ² g ⁻¹)	V _m (BET) (cm ³ g ⁻¹	C	SA (I) (m ² g ⁻¹)	$V_{mic}(I)$ (Cm^3g^{-1})
GAC383	1298.5	0.461	524	996.75	0.354	-81	1271.2	0.457
GACO383	1186.5	0.421	439	973.31	0.346	-118	1163.7	0.412
GACOZC873	1216.1	0.432	303	1018.26	0.362	-148	1186.4	0.421
GACOZC1073	1305.4	0.464	263	1103.23	0.392	-167	1268.4	0.451
$V_m(cm^3 / g S)$	STP) = -	$V_m(cm^3)$	/g)	x 22414 28	x 0.808	8		

4.3.3 Langmuir Isotherm

The laboratory modified carbons GAC383, GACO383, GACOZC873 and GACOZC1073 are applied to the Langmuir isotherm model analysis. A straight line plot of P/V against P gives a monolayer volume $[V_m(L)]$ from the slope and Langmuir energy constant K_L from the intercept.

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m} \tag{4.4}$$

The Langmuir isotherm plots are shown in Figure 4.18. It gives a straight line with high correlation coefficient (R^2 - 0.99) for all the carbons, indicate that these carbon surfaces are homogenous nature. The Table 4.6 shows the monolayer volume [$V_m(L)$] and Langmuir surface area [SA (L)] of modified carbons. GACOZC1073 shown higher Langmuir surface area (1709.41 m²/g) compared to other carbons GACOZC873 (1581.17 m²/g), GAC383 (1598.24 m²/g) and GACO383 (1476.58 m²/g). The oxidation decreases the pore volume and surface area because of the blockage of pores due to nitric acid oxidation. Impregnation, acid oxidation and activation at 1073K increase the porosity and surface area of carbon, hence enhances the adsorption efficiency of solid – liquid equilibrium adsorption.

4.3.4 Freundlich Isotherm

The nitrogen adsorption data of the modified carbons are applied with Freundlich isotherm and the linear plot of log V against log P (Figure 4.19) and the characteristic constants are measured (Table 4.6).

$$\log V = \log K_F + 1 / n \log P \tag{4.5}$$

The correlation coefficient $(R^2 - 0.97 \text{ and } 0.98)$ and adsorption intensity *n* is in the range of 9.3 – 13.9 indicate that adsorption occurs through physisorption mechanism.

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 203





Figure 4.15: I plot for modified granular activated carbons (a) GAC383, (b) GACO383, (c) GACOZC873 & (d) GACOZC1073



GACO383, GACOZC873

and GACOZC1073)

modified granular activated carbons (GAC383, GACO383, GACOZC873 and GACOZC1073)

Surface Area (m²/g) a

800

600

4.3.5 John Isotherm Analysis

The John isotherm plot of *log V* against *loglog P* gives a straight line (Figure 4.20) for the modified carbons GAC383, GACO383, GACOZC873 and GACOZC1073. The absorbability constant (n) obtained from the slope of the plot are presented in Table 4.6.

$$loglog P = C + n \log V \tag{4.6}$$

The limiting micropore volume $[V_m (J)]$ calculated from extrapolating the straight line connecting to the y axis of the plot. The $[V_m (J)]$ and $[V_m (L)]$ are comparable that indicate these modified carbons contains microporosity. The surface area calculated from John isotherm models is GAC383 (1610.0 m²/g), GACO383 (1503.9 m²/g), GACOZC873 (1582.1 m²/g) and GACOZC1073 (1709.7 m²/g). The surface area of modified carbons calculated by Langmuir and John method is comparable and percentage variation is less than 20% shows these carbons are Type I pattern.

Table 4.6: Porosity parameters of granular activated carbon oxidized and impregnated with Zn^{2+} ions calculated from Langmuir, Freundlich and John model

	Langm	uir Isoth Model	erm	Fre Isothe	eundlich erm Mo	ı del	Johi	n Isother	m Moo	lel
Carbon	SA(L) (m^2g^{-1})	V _m (L) (cm ³ g ⁻¹ STP)	\mathbb{R}^2	\mathbf{K}_{F}	n	\mathbb{R}^2	SA (J) (m ² g ⁻¹)	V _m (J) (cm ³ g ⁻¹ STP)	u	\mathbb{R}^2
GAC383	1598.2	367.14	0.99	231.44	13.91	0.97	1610.0	369.85	3.22	0.99
GACO383	1476.6	339.19	0.99	202.74	12.68	0.97	1503.9	345.48	2.84	0.99
GACOZC873	1581.2	363.22	0.99	186.69	9.92	0.98	1582.1	363.43	2.20	0.99
GACOZC1073	1709.4	392.68	0.99	193.03	9.27	0.98	1709.7	392.75	2.05	0.99
$V_m (cm^3 / g) =$	$\frac{V_m (cm^3)}{2244}$	/ g STP) 4 x 0.808	x 28							

4.3.6 Alpha S (α_s) Isotherm

Sing and Coworkers (1986) [11] proposed an Alpha S (α_s) plot for the determination of micropore volume and external surface area of the porous materials.

$$A_s = 2.86 \frac{V}{\alpha_s} \tag{4.7}$$

The Figure 4.21 shows the α_s plot of the modified carbons GAC383, GACO383, GACOZC873 and GACOZC1073. The micropore volume and surface area calculated are shown in Table 4.7. The micropore volume of the α_s plot of GAC383 (351.21 cm³/g STP or 0.543 ml/g), GACO383 (325.34 cm³/g STP or 0.503 ml/g), GACOZC873 (345.39 cm³/g STP or 0.534 ml/g) & GACOZC1073 (373.85 cm³/g STP or 0.578 ml/g) is comparable with D-R micropore volume GAC383 (351.21 cm³/g STP or 0.543 ml/g), GACO383 (323.40 cm³/g STP or 0.504 ml/g), GACOZC873 (336.34 cm³/g STP or 0.520 ml/g) and GACOZC1073 (363.50 cm³/g STP or 0.562 ml/g). The micropore volume increases with activation temperature from 873 to 1073 K.





4.3.7 Dubinin Radushkevich (D-R) Isotherm

The micropore surface area and characteristic energy are calculated by using Dubinin Radushkevich isotherm method. This method is based on Polanyi's potential theory.

$$logV = logV_0 - D \log^2(p_0 / p)$$
(4.8)

$$D = 2.303 \left(\frac{RT}{\beta E_0}\right)^2$$
(4.9)

$$L_{av} = 6.6 - 1.79 \ln E_0 \tag{4.10}$$

The Figure 4.22 shows a linear plot of logV against $log^2(p_0/p)$ of the modified carbons GAC383, GACO383, GACOZC873 and GACOZC1073. The characteristic energy (E_0) is in the range of 13 - 16 kJ/mol indicating that these carbons are adsorbing nitrogen by physisorption mechanism. The pore width (L) is less than 2nm for all the carbons studied, GAC383 (1.68 nm), GACO383 (1.75 nm), GACOZC873 (1.93 nm) and GACOZC1073 (1.99 nm) it indicates that pores are wider after oxidation, impregnation and activation process. The micropore surface (S_{mi}) area calculated by using D-R method is decreased with higher pore width (L) and decreasing energy (E_0) . The correlation coefficient is in the range of 0.96 – 0.97. The porewidth calculated by BET method and D-R are comparable.

Table 4.7: Dubinin – Radushkevich (D - R) and Alpha S (α_s) constants of the modified carbons

Carbon		D-R	Isotherm			as Is	otherm
	L (D-R) (nm)	E ₀ (D-R) (kJ/mol)	V ₀ * (D-R) (ml/g)	S_{mi} (D-R) (m^2/g)	R^2	V_{mi}^{*} (ml/g)	$\begin{array}{c} A_s \\ (m^2/g) \end{array}$
GAC383	1.68	15.62	0.543	646.43	0.97	0.543	1005.26
GACO383	1.75	15.02	0.500	571.43	0.96	0.503	930.00
GACOZC873	1.93	13.61	0.520	538.86	0.96	0.534	987.05
GACOZC1073	1.99	13.09	0.562	564.82	0.96	0.578	1068.31
$V_m(cm^3 / g ST)$	$P) = \frac{V_m(cn)}{cn}$	n^3 / g) x 22 28	2414 x 0.8	808		·	

4.3.8 De Boer *t* - *plot*

Lippens and de - Boer t - plot (1965) [12] method is used to determine the external surface area and micropore volume from the intercept and slope of the linear plot of nitrogen adsorbed against thickness.

$$t = [13.99 / (0.034 - \log(p / p_0))]^{0.5}$$
(4.11)

The t - plot of the carbons GAC383, GACO383, GACOZC873 and GACOZC1073 are shown in Figure 4.23. The t - plot micropore volume and micropore surface area decreases with carbon oxidised, impregnated with Zn^{2+} ions activated in 873 and 1073K, GACOZC873 (V_{mi} – 0.231 cm³/g and SA_{mi} – 380. 94 m²/g) and GACOZC1073 (V_{mi} – 0.221 cm³/g and SA_{mi} –349.3 m²/g). The external surface calculated by the *t* - *plot* method is higher in GACOZC873 (637.71 m^2/g) and GACOZC1073 (752.33 m^2/g). From the t - plot method it is clear that oxidation with nitric acid impregnated with zinc ions activated at higher temperature 873 and 1073K enhances the external surface area.

		t Plot			E	BJH Isotl	nerm		
Carbon	V _{mi*} (cm ³ /g)	${ m SA}_{ m ext}$ $({ m m}^2/{ m g})$	${\rm SA}_{\rm mi}$ (m ² /g)	ADCSA (m ² /g)	DECSA (m ² /g)	ADCPV (cm ³ /g)	DECPV (cm ³ /g)	Pore Width Ad (nm)	Pore Width De (nm)
GAC383	0.351	408.1	588.66	226.21	220.52	0.138	0.134	2.44	2.43
GACO383	0.297	433.72	540.59	250.00	242.84	0.142	0.137	2.28	2.25
GACOZC873	0.231	637.71	380.94	229.03	234.69	0.135	0.136	2.36	2.32
GACOZC1073	0.221	752.33	349.03	371.69	348.64	0.204	0.194	2.20	2.23
$V_m(cm^3 / g S)$	$TP = \frac{V_{j}}{V_{j}}$	$m_m(cm^3 / g)$) x 22414 28	4 x 0.808					

Table 4.8: Surface area and pore size distribution using t - plot and BJH method

Chapter 4

4.3.9 BJH Pore Size Distribution

The pore size distribution of the modified granular activated carbons such as GAC383, GACO383, GACOZC873 and GACOZC1073 are determined by Barret Joyner Halenda (BJH) method [13]. BJH method is commonly used for mesoporus carbon materials. The BJH adsorption – desorption pore volume, pore size and surface area are measured using adsorption – desorption isotherm of N_2 uptake by modified carbons as a function of pore diameter.



The pore size distribution of the modified carbons is presented in Table 4.8. The adsorption cumulative surface area $(371.69 \text{ m}^2/\text{g})$ and cumulative pore volume $(0.204 \text{ cm}^3/\text{g})$ are higher in GACOZC1073 and adsorption pore width (2.20 nm) is less. These carbon shows desorption cumulative surface area (348.64 m²/g) and the desorption cumulative pore volume (0.194 cm³/g) is higher and desorption pore width (2.23 nm) is less. BJH adsorption and desorption cumulative pore volume against pore

width of the modified carbons GAC383, GACO383, GACOZC873 and GACOZC1073 are shown in Figure 4.24 and 4.25. The Pore width calculated by BJH adsorption (2.20 - 2.44 nm) and desorption (2.23 - 2.43 nm) method. The BJH surface area, pore volume and pore width of adsorption and desorption are almost same for all the carbons studied indicate that nitrogen adsorption on these carbons follows physisorption mechanism.

4.4 Liquid Phase Adsorption Studies Using Carbon - GACOZC Series

To determine the liquid phase adsorption efficiency of oxidised granular activated carbon impregnated with zinc ions (GACOZC series) adsorption kinetics, adsorption isotherm and thermodynamic studies are done using phenol, p - nitrophenol and methylene blue as adsorbate.

4.4.1 Adsorption Studies – Phenol as Adsorbate

An adsorption study of phenol includes a selection of carbon, adsorption kinetics, adsorption isotherms and thermodynamic study using the modified carbons GAC383, GACO383 and GACOZC series.

4.4.1.1 Selection of GACOZC for Phenol Adsorption

Initial concentration of 1000 mg/l phenol was used as adsorbate to select a carbon from GACOZC series for the detailed adsorption studies of phenol. The Figure 4.26 shows the amount adsorbed versus carbons from GACOZC series. It is clear that GACOZC1073 (223.52 mg/g) shows higher phenol adsorption efficiency compared to other carbons. GACOZC shows high carbon content, high BET surface area and high total pore volume than other carbons, these factors influence the adsorption capacity of phenol.







4.4.1. 2. Adsorption Kinetics

The adsorption kinetic study of phenol on three carbons (GAC383, GAC0383, and GAC0ZC1073) was undertaken using initial concentration (250 mg/L) at different temperature ranging from $10 - 50^{\circ}$ C.







Figure 4.28: Effect of contact time on the adsorption of phenol on GACO383 at different temperatures for $C_0 = 250 \text{ mg/L}$



Figure 4.29: Effect of contact time on the adsorption of phenol on GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$

The Figure 4.25, 4.26 and 4.27 shows the phenol uptake behavior as a function of time and temperature. Phenol adsorption on these carbons increases with respect to temperature and time. These time dependent data are applied in different kinetic models such as pseudo first order, Ho second order, Weber intra particle diffusion model and Boyd model to identify the mechanism of adsorption on modified carbons.

The pseudo first order kinetic model was applied on the adsorption of phenol on these modified carbons and are shown in Figure 4.30 (a) - (c).

$$ln(q_e - q_t) = ln q_e - K_1 t \tag{4.12}$$

The first order rate constant (K_1) and amount adsorbed calculated from first order equation $(q_e cal)$ are given in Table 4.9. The first order rate constant is almost same for all the carbons studied at all temperatures. The amount adsorbed $(q_e exp)$ determined from the batch kinetic study at different temperature is not comparable with q_e calculated $(q_e cal)$ obtained from the pseudo first order kinetic model whose correlation coefficient $(R^2 ranges 0.93 - 0.97)$ is also less. This means, the adsorption of phenol on these modified carbons, not agreed to Lagergren first order kinetic model [14, 15].

The temperature dependent kinetic data of phenol adsorption on these modified carbons are applied to Ho second order kinetic model and shown in Figure 4.31 (a) - (c).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$
(4.13)

These carbons depict the second order rate constant (K_2) and q_e calculated $(q_e cal)$ increases with temperature (Table 4.9). This indicates the endothermic nature of adsorption. The amount adsorbed $(q_e exp)$ determined from the phenol batch kinetic study is more comparable with q_e calculated $(q_e cal)$ obtained from the pseudo second order kinetic model whose correlation coefficient $(R^2=0.99)$ is excellent. Therefore, the adsorption of phenol on modified carbons follows the second order kinetic model.

Table 4.9: Comparison of the pseudo first and second order kinetic constants and
parameters of adsorption of phenol for $C_0 = 250 \text{ mg/L}$

	т	<i>a</i>	First o	order Kine	etics	Se	cond order kinet	ics
Carbon	(K)	q _e exp (mg/g)	q _e cal (mg/g)	K ₁ (min ⁻¹)	\mathbf{R}^2	q _e cal (mg/g)	K_2*10^4 (gmg ¹ min ⁻¹)	\mathbf{R}^2
	283	121.61	86.99	0.007	0.96	135.14	1.24	0.99
	293	126.41	88.72	0.007	0.97	137.93	1.40	0.99
GAC383	303	129.99	84.02	0.007	0.95	139.47	1.59	0.99
	313	134.93	84.76	0.007	0.96	143.06	1.83	0.99
	323	138.76	80.16	0.007	0.95	145.14	2.09	0.99
	283	118.38	75.83	0.006	0.94	124.53	1.80	0.99
	293	122.27	73.27	0.005	0.93	126.42	2.10	0.99
GACO383	303	125.99	71.43	0.006	0.93	130.21	2.30	0.99
	313	129.63	70.72	0.006	0.94	133.69	2.50	0.99
	323	132.84	69.31	0.006	0.95	136.43	2.70	0.99
	283	120.16	85.53	0.005	0.95	129.53	1.30	0.99
	293	124.16	87.97	0.007	0.97	134.77	1.50	0.99
GACOZC1073	303	128.71	83.17	0.006	0.96	136.61	1.70	0.99
	313	131.15	78.40	0.007	0.94	137.55	2.10	0.99
	323	136.46	79.11	0.007	0.96	142.25	2.20	0.99





School of Environmental Studies, Cochin University of Science and Technology

The first and second order kinetic model cannot identify the diffusion mechanism of phenol adsorption on these modified carbons; hence intraparticle diffusion model [16] is applied to identify the diffusion mechanism.

$$q_t = K_{id} t^{0.5} + C \tag{4.14}$$

The Figure 4.32 (a) - (c) shows the intraparticle diffusion model for these modified carbons at different temperature studied. The phenol adsorption process is a complex mechanism governed by one or more process such as film diffusion (first linear portion in the Figure 4.32) and intra particle diffusion (second linear portion of the plot 4.32). The Intra particle diffusion constant (Table 4.10) shows that transport rate for stage 1 is higher than second stage, $K_{id1} > K_{id2}$ for all the carbons studied at selected temperatures.

			Intrapart	ticle diffu	ision const	tant	
Carbon	Т (К)	K _{idl} mgg ⁻¹ min ^{-1/2}	C ₁ (mg/g)	\mathbb{R}^{2}	K _{id2} -1 mgg-1 min ^{-1/2}	C ₂ (mg/g)	${f R}^2$
	283	14.49	-29.90	0.97	3.22	52.67	0.98
	293	14.40	-24.96	0.99	3.36	54.82	0.98
GAC383	303	15.33	-25.13	0.97	3.18	61.59	0.98
	313	14.29	-13.35	0.99	3.17	67.43	0.97
	323	14.16	-6.98	0.99	2.88	76.33	0.99
	283	11.28	-10.05	0.98	2.77	56.42	0.99
	293	11.05	-3.68	0.99	2.68	61.33	0.97
GACO383	303	11.32	0.30	0.99	2.43	71.14	0.98
	313	11.15	6.68	0.98	2.43	75.56	0.99
	323	10.49	15.03	0.99	2.37	80.12	0.99
	283	10.55	-13.23	0.97	3.14	49.57	0.99
	293	12.66	-17.82	0.95	3.09	57.33	0.99
GACOZC1073	303	12.80	-12.55	0.97	2.99	63.39	0.99
	313	12.52	-5.02	0.98	2.35	78.89	0.99
	323	11.52	5.43	0.98	2.53	80.72	0.99

Table 4.10: Intraparticle diffusion constant of phenol adsorption on carbons GAC383, GACO383 and GACOZC1073 for $C_0 = 250 \text{ mg/L}$

Chapter 4

The phenol molecules first get adsorbed at the surface of the carbons. This is the fastest step and afterwards, transport / migrate slowly through the micropores to the active sites of these carbons. The slowest intra particle diffusion step is the rate limiting step for the adsorption of phenol on these modified carbons. At higher temperature, the intercept of the second linear plot is also higher, means larger the boundary layer thickness (C_2).

The kinetic data of phenol adsorption were analysed by using Boyd kinetic model to determine the rate controlling step.

$$B_t = -0.4977 - \ln(1 - F) \tag{4.15}$$

A plot of B_t against *time*, Figure 4.33 (a) to (c) showed that these points were scattered and the plot did not pass through the origin. This means the adsorption of phenol on these carbons (GAC383, GACO383 and GACOZC1073) governed by external mass transport and intraparticle diffusion was the rate limiting step for this adsorption process [17]

4.4.1.3 Activation Energy

The Figure 4.34 showed the activation energy, calculated using the second order rate constant (k_2) of phenol adsorption against the function of temperature.

$$\ln K_2 = \ln K_0 - \frac{E_a}{RT} \tag{4.16}$$

The activation energy of all carbons (Table 4.11) is positive that indicate adsorption is endothermic in character. The *Ea* (kJmol⁻¹) is in the range of 7.59 - 10.72 kJmol⁻¹ indicates that phenol adsorption on modified carbons follows physisorption mechanism.





Figure 4.34: plot of lnK_2 versus 1/T for the adsorption of phenol on modified activated carbons for $C_0 = 250 \text{ mg/L}$

Table 4.11: Determination of activation energy of phenol adsorption by GAC383,GAC0383 and GAC0ZC1073

Carbon	$E_a (kJmol^{-1})$	\mathbf{K}_{0}
GAC383	10.00	0.0086
GACO383	7.59	0.0046
GACOZC1073	10.72	0.0121

4.4.1.4 Adsorption Isotherm Studies of Phenol

Adsorption isotherms are more applicable to the description of the interaction between phenol molecule and modified carbons. Amount of phenol adsorbed (q_e) against equilibrium concentration (C_e) of these granular activated carbons are shown in Figure 4.35 (GAC383), Figure 4.36 (GAC0383) and Figure 4.37 (GAC0ZC1073). The phenol adsorbed increases in increasing temperature, the same trend shown for all the carbons studied. All the carbons show a Type I behaviors as per IUPAC classification.





Eigure 4.35: Adsorption isotherm of GAC383 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$

Figure 4.36: Adsorption isotherm of GACO383 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$



Figure 4.37: Adsorption isotherm of GACOZC1073 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$

4.4.1.4.1 Adsorption Isotherm Modelling

Equilibrium phenol adsorption data are applied in the different isotherm model such as Langmuir, Freundlich, Temkin and Dubinin – Radushkevich. The constants obtained from these isotherm models provide important information on the phenol adsorption mechanism and surface properties of these modified carbons.

The Langmuir isotherm model applicable only for homogenous surface of activated carbons. From this, monolayer adsorption capacity (q_{max}) of the modified carbons and Langmuir energy constant (K_L) is calculated. This isotherm model of modified carbons is shown in Figure 4.38 (a), (b) & (c).

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e \tag{4.17}$$

The q_{max} and K_L of phenol adsorption on modified carbons are presented in Table 4.12. Monolayer adsorption capacity increases with increasing temperature according to the order GAC383 (266.67 -352.12 mg/g) > GACOZC1073 (245.10 - 333.33 mg/g) > GACO383 (188.32 - 236.97 mg/g). This indicates native form of granular activated carbon has the highest adsorption efficiency among the group selected for isotherm study. GAC383 has relatively high carbon content, high BET surface area, low acidic functional groups compared to other two carbons therefore it increases the phenol adsorption compared to others. Nitric acid oxidation increases the acidic surface functional groups and suppresses the adsorption capacity of phenol. Acid oxidation, impregnation with Zn^{2+} ions and steam activation (GACOZC1073) increases the carbon content, basic groups and BET surface area than GACO383. This is the reason for phenol adsorption is higher in GACOZC1073 than GACO383.

The adsorption capacity (K_F) and adsorption intensity or adsorbability constant (n) were calculated from the intercept and slope of the Freundlich isotherm model of the modified carbons presented in Figure 4.39 (a), (b) & (c).





$$\log q_e = \log K_F + 1 / n \log C_e \tag{4.18}$$

The Freundlich parameter '*n*' is a heterogeneity factor, indicate that whether the phenol adsorption is linear (n = 1), if it is chemisorption (n < 1) and for favorable physisorption process (n > 1). The adsorption intensity (n > 1) for phenol (Table 4.12) indicates adsorption is favorable at different temperature studied. The slope 1/n is less than one indicating that phenol adsorption by modified carbons is a Langmuirian type [18]. The adsorption capacity (K_F) increases with increasing temperature of all the carbons. The correlation coefficient $(R^2 = 0.89 - 0.98)$ for all the carbon studied. It indicates that isotherm model is not applicable for this phenol adsorption study.

Temkin isotherm models are used to study the heat of adsorption and carbon – phenol interaction on adsorption isotherm.

$$q_e = B \ln A + B \ln C_e \tag{4.19}$$

$$B = \frac{RT}{b_T} \tag{4.20}$$

Temkin plot q_e versus $ln C_e$ was shown in Figure 4.40, 4.41 & 4.42. The equilibrium binding constant (*A*) and heat of adsorption (*B*) are given in Table 4.12. The heat of adsorption (*B*) increases with temperature for all the three carbons studied, indicating endothermic adsorption [19]. The adsorption energy (b_T) calculated from the heat of adsorption (*B*) is decreases with temperature. The value of b_T is lower than 80 kJ/mol indicate a physical adsorption process. It confirms that adsorption occurs through weak Van der Waals force of interaction between modified carbons and phenol.

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 223





Figure 4.40: Temkin isotherm model of phenol on GAC383 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$





Figure 4.42: Temkin isotherm model of phenol on GACOZC1073 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$

The Dubinin - Radushkevich isotherm parameters are calculated from the plot of $ln q_e$ versus ε^2 of the modified carbons.

$$\ln q_e = \ln Q_D - \beta \varepsilon^2 \tag{4.21}$$

The activity coefficient (β) from the slope of the plot and maximum adsorption capacity (q_m) from the intercept is shown in Table 4.12.



		Langm	uir Cons	tants	Fr C	eundlic	ч "	Ē	emkin C	onstants		Dubini	n - Radus Consta	hkevich ints	(D-R)
Carbon	T (K)	_{xem} p (¹⁻ ըցցա)	(_ן 3שק) א ^ר	_z א	(աճճ _{ւլ}) K ^ե	u	z¥	_T A (کسع)	В	լլօա/բ) Д	zង	(աճ\ճ) (D-K) Ծ ^թ	(ԷՂ\ሠ၀) (D-K) E ⁰	(աօլ _{շԴ} շյօա) է	τ'ষ
	283	266.67	2.33	66.0	16.38	2.60	0.93	0.1898	43.10	52.66	0.98	55.52	0.2668	7.03	0.98
	293	284.90	2.48	66.0	16.74	2.56	0.94	0.1875	46.14	49.19	96.0	56.62	0.2883	6.01	0.98
GAC383	303	312.50	2.48	66.0	16.73	2.49	96.0	0.1747	50.47	44.97	0.99	57.39	0.2929	5.83	0.98
	313	336.70	2.53	66.0	17.00	2.44	0.95	0.1708	53.96	42.06	0.98	58.39	0.3395	4.34	0.98
	323	352.12	2.68	66.0	17.38	2.42	0.95	0.1724	56.33	40.29	0.98	59.22	0.3624	3.81	0.98
	283	188.32	2.17	0.99	19.16	3.17	0.89	0.3697	27.90	81.35	0.99	54.89	0.2471	8.19	0.98
	293	199.60	2.34	66.0	19.87	3.13	0.89	0.3698	29.61	76.64	0.99	56.10	0.2730	6.71	0.98
UALUJ8J	303	209.64	2.48	66.0	20.71	3.12	0.89	0.3799	30.98	73.26	0.99	57.41	0.3016	5.50	0.98
	313	225.73	2.52	66.0	21.13	3.05	06.0	0.3602	33.34	68.08	0.99	58.76	0.3277	4.65	0.98
	323	236.97	2.59	66.0	21.66	3.02	06.0	0.3595	34.88	65.07	0.99	59.29	0.3586	3.89	0.98
	283	245.10	1.78	0.99	18.20	2.86	0.93	0.2408	36.22	62.66	0.99	59.66	0.0168	7.57	0.99
	293	273.97	1.85	66.0	19.21	2.81	0.93	0.2396	39.89	56.90	0.99	66.27	0.0151	6.96	0.99
GALUZUIU/3	303	304.88	2.00	66.0	20.73	2.79	0.94	0.2488	43.58	52.08	86.0	75.64	0.0132	5.81	0.99
	313	318.47	2.27	66.0	23.72	2.88	0.94	0.3102	44.17	51.38	86.0	75.69	0.0132	3.70	0.98
	323	333.33	2.49	66.0	25.66	2.91	0.94	0.3476	45.58	49.80	0.98	75.73	0.0132	2.58	0.99

Chapter 4

The activity coefficient (β) gives the mean free energy (E_0) of adsorption per phenol molecule when it is transferred to the surface of the granular carbons from infinity in the solution. The adsorption capacity (Q_D) increases with temperature indicate that adsorption is endothermic. The activity coefficient increases with temperature reveals that, temperature enhances the efficiency of carbon. In our study, the magnitude of mean energy (E_0) is found to vary within the range for GAC383 (0.27 - 0.36 kJ/mol), GACO383 (0.24 – 0.35 kJ/mol) and GACOZC1073 (0.01 – 0.02 kJ/mol). This mean energy is less than 8 kJ/mol reveals that the phenol adsorption process follows physical adsorption.

4.4.1.5 Thermodynamic Parameters for Phenol Adsorption

The thermodynamic parameters such as change in enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) are calculated and presented in Table 4.13.

$$\Delta G = -RT \ln K_L \tag{4.22}$$

$$\Delta G = \Delta H - T \,\Delta S \tag{4.23}$$

The enthalpy change (ΔH) and entropy change (ΔS) was determined from the slope and intercept of the plot ΔG versus Temperature (Figure 4.43). The Gibbs free energy decreases with increasing temperature indicating that adsorption is endothermic and the negative confirms the spontaneity of the adsorption process. The ΔH is less than 40 kJ/mol for all the carbon studied reveals that phenol adsorption occurs through a physical process. The positive ΔS reflects a good affinity between phenol molecule and modified carbons.





Figure 4.43: ΔG versus Temperature for estimation of thermodynamic parameters for the adsorption of phenol onto GAC383, GACO383 & GACOZC1073

Table 4.13: Thermodynamic parameters – Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the modified carbons

Carbon		Δ	G (kJma	ol ⁻¹)		ΔΗ	ΔS
	283	293	303	313	323	(kJmol ⁻¹)	(Jmol ⁻¹ K ⁻¹)
GAC383	-1.94	-2.18	-2.24	-2.35	-2.59	2.26	14.93
GACO383	-1.82	-2.07	-2.29	-2.41	-2.55	3.30	18.26
GACOZC1073	-1.35	-1.51	-1.75	-2.14	-2.46	6.79	28.49

4.4.2 Adsorption Studies of *p* – nitrophenol as Adsorbate

Adsorption studies of p – nitrophenol includes a selection of carbon, adsorption kinetics, adsorption isotherms and thermodynamic study using these modified carbons GAC383, GACO383 and GACOZC series.

4.4.2.1 Selection of Carbon

Select a carbon from the second series (GACOZC) for the detailed p – nitrophenol adsorption studies such as isotherm, kinetics and thermodynamics, initial concentration of 1000 mg/L are used. The Figure 4.44 shows the effect of amount adsorbed against different contact time for the adsorption of p –nitophenol on GACOZC series. Figure shows that contact time increases adsorption also, after 8 hr there is no much increase

in the p –nitrophenol adsorption, hence fixed for equilibration period for isotherm study. From this series, carbon GACOZC1073 shows highest adsorption capacity, selected for detailed adsorption studies and compared the efficiency with GAC383 and GACO383.



Figure 4.44: Effect of contact time and amount of *p* -nitrophenol adsorbed for the adsorption on GACOZC activated at different temperatures ($C_0 = 1000 \text{ mg/L}$)

4.4.2.2 Effect of Contact Time and Temperature

The study of contact time for p – nitrophenol adsorption by modified carbons was helpful to acquire the kinetic parameters and it is essential for the determination of the efficiency of a carbon used in a wastewater treatment unit. The Figure 4.45 - 4.49 shows the variation of amount adsorbed (q_t) as a function of time in minute for various carbons (GAC383, GACO383 and GACOZC1073) at different temperature ranging from 10^oC to 50^oC. The amount adsorbed from batch kinetic study (q_eexp) of GAC383 (in the range of 201.92 – 219.02 mg/g), GACO383 (in the range 119.50 – 138.59 mg/g) and GACOZC1073 (in the range of 165.29 – 205.61 mg/g) under selected temperature studied. All these three carbons show the same trend as time and temperature enhances absorption. Among carbons GAC383 shows the highest absorption rate compared to others.


The percentage of carbon content and less number of acidic functional groups promote the p – nitrophenol adsorption efficiency of GAC383. GACOZC1073 shows high BET surface area, mesopore volume, carbon content and basic groups compared to GACO383. So p –nitrophenol adsorption capacity is higher in GACOZC1073 than GACO383.



Figure 4.45: Effect of contact time on
the adsorption of
p -nitrophenol on
GAC383, GACO383
and GACOZC1073 at
 10^{0} C for C₀ = 250 mg/LFigure 4.46: Effect of contact time on
the adsorption of
p -nitrophenol on
GAC383, GACO383 and
GACOZC1073 at
for C₀ = 250 mg/L





Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 229





These time dependent experimental data applied to different kinetic model such as pseudo first order model, Ho second order model, intraparticle diffusion model and Elovich model to identify the mechanism of p – nitrophenol adsorption on modified carbons (GAC383, GACO383 and GACOZC1073).

The Figure 4.50 (a) - (c) shows a straight line plot of $ln (q_e-q_t)$ versus time (*t* in minute). The pseudo first order rate constant (K_1) from the slope and an equilibrium adsorption capacity (q_ecal) from the intercept are shown in Table 4.14. The first order rate constant (K_1) is almost same for all the temperature and carbon studied, GAC383 (0.006 min⁻¹), GACO383 (0.005 min⁻¹) and GACOZC1073 (0.006 min⁻¹). The amount adsorbed (q_eexp) determined from the p – nitrophenol adsorption kinetic study is more deviated with q_e calculated (q_ecal) obtained from the pseudo first order kinetic model and the correlation coefficient (R^2 ranges 0.91 – 0.98) shows that Lagergren first order model fails to interpret this experimental data.

The applicability of the Ho second order model is examined by a plot of t/q_t against *time* [Figure 4.51 (a), (b) & (c)]. The second order rate

constant (K_2) and amount adsorbed (q_ecal) from the intercept and slope of the plot respectively are given (Table 4.14). The amount adsorbed (q_eexp) are more comparable with q_e calculated (q_ecal) obtained from the pseudo second order kinetic model and high correlation coefficient ($R^2 - 0.99$) indicates that these models are applicable for prediction of the behavior of p –nitrophenol adsorption on activated carbons (GAC383, GACO383 and GACOZC1073) [20]. The amount adsorbed (q_ecal) and rate constant (K_2) increases with temperature, reveals the endothermic nature of adsorption.

The intraparticle diffusion plot of amount adsorbed at various time intervals (q_i) versus square root of time ($t^{1/2}$) for modified carbons at different temperature ranging from 10⁰C to 50⁰C [Figure 4.52 (a) – (c)]. It shows two straight line portions, the first sharper point is attributed to p –nitrophenol diffusion through the external surface of the adsorbent called film (external) diffusion and the second line describes the gradual adsorption stage, corresponding to p –nitrophenol diffusion inside the pores of the granular activated carbons. The slope and intercept of the linear fit used to calculate the diffusion coefficient (*kid*) and boundary layer thickness (*C*) given in Table 4.14. The K_{id1} (ranges 8.77 -17.13 mgg⁻¹min^{-1/2}) is higher than the *kid*₂ (ranges 2.97 - 5.64 mgg⁻¹min^{-1/2}) for all carbons indicating that pore diffusion is a slow step. The slowest intra particle diffusion step is the rate limiting step for the adsorption of p - nitrophenol on new modified carbons.

The initial adsorption rate (α) and desorption constant (β) calculated from the intercept and slope of the plot of q_t versus ln t of p - nitrophenol adsorption by activated carbons at different temperatures (Figure 4.53). The initial adsorption rate and desorption constant increases with temperature for all the carbons studied the evidence that endothermic and physical nature of p- nitrophenol adsorption process. The Elovich constant α for temperature studies are in the range of GAC383 (9.04 -18.60 mg/g), GACO383 (5.12 -15.66 mg/g) and GACOZC1073 (5.33 - 22.60 mg/g). All three carbons selected have good correlation and coefficient is in the range ($R^2 : 0.97 - 0.99$).



			i													1	
			First o	rder kin	etics	Sec	cond ord kinetics	er	5 10	Intrapa	rticle di	ffusion c	constant		Elo	vich Con	stant
Carbon	(K)	(වි/වි dx	ы (¹ -99	(¹⁻ ni		al 12 ⁻¹)	²⁻ 01*) *10 ⁻⁵		ו (^{גען-} nim ¹ 33	(¹ -88		(^{1/1-} nim ¹ 33	(¹ -29		(¹⁻ nim ¹ gg	(¹⁻ ១ព	
	T	u) ə°b	u) ə ^ə b	ա) 'X	Ъz	u) ə ^ə b	(81) K ⁷	ъ	ա) K ^{iq}	ա) 'ጋ	ъ	u) K ^{iq}	ա) Շշ	zΒ	ພ) ກ	(Bu b	r,M
GAC383	283	201.92	153.84	0.007	0.98	221.24	7.59	0.99	16.69	-15.98	0.98	5.64	79.51	0.99	9.04	0.023	0.99
	293	209.76	151.53	0.006	0.98	225.73	8.50	0.99	16.69	-7.49	0.98	5.51	89.37	0.99	11.06	0.023	0.99
	303	213.44	15129	0.007	0.98	228.83	9.20	0.99	16.80	-2.21	0.97	5.34	97.64	0.99	12.76	0.023	0.99
	313	216.53	151.04	0.008	0.98	231.48	10.18	0.99	15.96	9.13	0.96	5.08	107.66	0.99	15.43	0.024	0.99
	323	219.02	143.17	0.008	0.98	232.02	11.46	66.0	17.13	69.6	0.97	4.75	116.88	66.0	18.60	0.024	0.99
GCO383	283	119.50	82.71	0.005	0.91	129.53	12.38	0.99	13.35	-28.15	0.98	2.99	51.47	0.97	5.12	0.038	0.97
	293	124.52	84.52	0.006	0.93	133.33	14.16	0.99	12.90	-20.54	0.96	3.06	55.88	0.99	6.28	0.038	0.97
	303	129.30	84.24	0.006	0.93	136.80	15.58	0.99	12.89	-15.83	0.97	2.99	62.04	66.0	7.50	0.038	0.97
	313	133.78	81.11	0.006	0.94	139.86	18.80	0.99	12.44	-5.21	0.96	2.97	68.11	0.99	10.75	0.040	0.98
	323	138.59	78.20	0.006	0.94	142.45	21.26	0.99	11.93	4.89	66.0	3.21	67.38	66.0	15.66	0.042	66.0
GACOZC1073	283	165.29	133.64	0.006	0.98	188.68	6.03	0.99	14.42	-27.5	0.96	5.41	46.00	0.99	5.33	0.026	0.99
	293	173.02	131.45	0.006	0.98	189.75	7.97	0.99	13.34	-12.8	0.99	4.94	63.56	0.99	6.89	0.027	0.99
	303	181.64	151.54	0.006	0.98	199.20	10.37	0.99	8.77	28.67	0.89	4.91	80.75	0.91	11.64	0.027	0.97
	313	191.61	121.52	0.006	0.97	200.80	11.88	0.99	13.18	13.47	0.98	4.61	89.24	0.99	14.62	0.028	0.99
	323	205.61	116.79	0.006	0.94	211.86	14.29	0.99	16.71	11.36	0.97	4.26	110.32	0.99	22.60	0.028	0.98

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 233



4.4.2.3 Activation Energy Using *p* - nitrophenol as Adsorbate

The pseudo second order model is correctly interpreting the experimental data, and the second order rate constant was applied in the Arrhenius equation and calculates activation energy. A plot of $ln K_2$ versus 1/T gives a straight line (Figure 4.54). From the slope of the plot Arrhenius activation energy of the activated carbons are calculated, for GAC383 (7.63 kJmol⁻¹), GACO383 (1.35 kJmol⁻¹) and GACOZC1073 (16.22 kJmol⁻¹). This $E_a < 40 \text{ kJmol}^{-1}$ means the adsorption of p – nitrophenol on modified carbons shows a physical adsorption process. Adsorption occurs through the physical process indicate the equilibrium rapidly attained and it is a reversible process [21]. The positive activation energy for the adsorption of p –nitrophenol by modified carbons depicts that it is an endothermic process.



Table 4	.15:	Activation	energy	of mo	odified	carbons	using p	-nitrophend	ol as adsorbate
			01				01	· · · · · ·	

Carbon	E _a (KJmol-1)	Ko	R
GAC383	7.63	0.0019	0.9549
GACO383	10.35	0.0098	0.9704
GACOZC1073	16.22	0.0613	0.9916

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 235

4.4.2.4 Adsorption Isotherm Studies of *p*-nitrophenol as Adsorbate

Studies on adsorption isotherms are essential to understand how p - nitrophenol interaction with carbon granules and are critical in optimizing the use of adsorbent. The experimental adsorption isotherm studies are conducted at an equilibrium time of 8hr for different concentration of p – nitrophenol ranges from 25 – 3000 mg/L. Temperature studies at a range of 10 - 50^oC and dosage of GAC383, GACO383 and GACOZC1073 were 1 g/L. Adsorption increases with substrate concentration and temperature. Temperature rise activates more active sites on the carbon surface and it enhances the adsorption capacity [22]. The relationship between the amount of p – nitrophenol adsorbed (q_e) and its concentration in the liquid phase at equilibrium (C_e) are plot (Figure 4.55 - 4.57). Type I isotherm features are prominent for all carbons studied at selected temperatures.





Figure 4.57: Adsorption isotherm of p - nitrophenol on GACOZC1073 at different temperatures for $C_0 = 25 - 3000 \text{ mg/L}$

Experimental data are applied to different isotherm models such as Langmuir isotherm, Freundlich isotherm, Temkin isotherm and Dubinin – Radushkevich isotherm equation and to evaluate the adsorptive characteristic features of the granular activated carbons (GAC383, GAC0383 and GAC0ZC1073).

The Figure 4.58 (a) for GAC383, 4.58 (b) for GAC0383 and 4.58 (c) for GAC0ZC1073 shows a straight line plot of C_e/q_e versus C_e of p –nitrophenol adsorption at different temperature. The Langmuir constant q_{max} , K_L and a_L are presented in Table 4.16. The monolayer adsorption capacity (q_{max}) increases, according to the order GAC0ZC1073 (322.58 – 414.94 mg/g) > GAC383 (272.45 - 403.23 mg/g) > GAC0383 (201.61 – 245.70 mg/g). This indicates granular activated carbon oxidized form impregnated with Zn²⁺ ions and steam activated at 1073K has the highest adsorption efficiency among the group selected for isotherm study. The adsorption efficiency of GAC0ZC1073 was depended on several factors such as high BET surface area (1101 m²/g), total pore volume (390.67 cm³/g STP or 0.6036 cm³/g), high distribution of micropores (36.66%) and

Chapter 4

mesopores (63.34%) and basic groups (0.53 meq/g). The correlation coefficients (R^2 -0.99) for all the carbons studied at all temperatures indicate that carbon surface is energetically homogeneous.

The dimensionless separation factor (R_L) calculated by Langmuir constant (a_L) for the activated carbons on p – nitrophenol adsorption. The Figure 4.59 shows that the R_L is in the range of 0 – 1. This confirms that adsorption is favorable for all the carbons studied at all temperatures.

Freundlich empirical isotherm model is applied for the adsorption of the activated carbons and are plotted in Figure 4.60 (a) – (c). Freundlich adsorption capacity (K_F) and exponent of linearity (1/n) is calculated from the intercept and slope of the straight line plot log q_e against log C_e . The linearity constant (1/n) < 1 for activated carbons studied are listed in Table 4.16 indicate that adsorption is favorable and are having Langmuirian type isotherm features. The adsorption capacity (K_F) increases with temperature indicate that adsorption is an endothermic process. The correlation coefficient (R^2 ranges between 0.86 - 0.94) implies that experimental data of p - nitrophenol adsorption does not follow good agreement with Freundlich model [23].

Temkin isotherm model is applied to determine the heat of p -nitrophenol adsorption and the interaction between activated carbon surface and p-nitrophenol. The heat of adsorption constant (*B*) and equilibrium binding constant (*A*) is calculated from the slope and intercept of a straight line plot of q_e against $ln \ C_e$ [Figure 4.61(a) – (c)]. The correlation coefficient (R^2) and Temkin parameters are presented in Table 4.16. The heat of adsorption constant (*B*) increase with temperature for all the carbons studied shows the endothermic adsorption character. Table 4.16 shows that the Temkin constant (b_T) is less than 80 kJ/mol indicate physical adsorption.





Chapter 4

		Lan	gmuir C	onstant	s	ξŬ	eundlic	– ~	É	emkin C	onstant	s	Dubin	in – Rad Consta	ushkev nts	ich
Carbon	T (K)	_{xem} p (¹ 22m)	(բաճ _{-լ}) К ^г	յե (¹⁻ ջավ)	rع ع	(աճճ _լ) K ^ե	u/I	זעז,	(լ.Ճավ) Կ	В	ւղ 11-լօալ)	zB	(ឆ/ਡੋɯ) ^w b	(ɣŋ\moj) E ⁰	(wol ₅ 1 ₋₅₎ Kʻ	_₹ צ
	283	272.48	7.61	0.028	0.99	53.49	0.235	0.86	5.54	29.56	76.79	0.98	75.77	1.47	0.23	0.99
	293	304.88	8.36	0.027	0.99	55.01	0.246	0.88	4.50	33.62	67.50	66.0	77.02	1.66	0.18	0.99
GAC383	303	340.14	9.03	0.027	0.99	56.58	0.258	0.89	3.78	38.01	59.71	0.99	78.21	1.85	0.14	0.99
	313	377.36	9.40	0.025	0.99	58.14	0.268	16.0	3.31	42.44	53.48	66.0	79.53	2.03	0.12	0.99
	323	403.23	10.69	0.027	0.99	59.90	0.275	16.0	3.15	45.86	49.49	66.0	81.24	2.19	0.10	0.99
	283	201.61	2.06	0.010	0.99	18.48	0.328	0.93	0.31	30.27	74.99	0.99	49.61	0.329	4.63	0.97
	293	213.22	2.14	0.010	0.99	18.93	0.332	0.93	0.31	31.94	71.07	0.99	50.62	0.355	3.97	0.97
GACO383	303	224.22	2.23	0.010	0.99	19.33	0.337	0.93	0.30	33.60	67.55	0.99	51.31	0.386	3.35	0.97
	313	235.29	2.31	0.010	0.99	19.67	0.340	0.93	0.30	35.26	64.37	66.0	52.08	0.414	2.92	0.97
	323	245.70	2.41	0.010	0.99	20.04	0.344	0.94	0.29	36.82	61.64	66.0	52.74	0.446	2.51	0.97
	283	322.58	4.09	0.013	0.99	39.74	0.287	06.0	1.10	39.41	57.59	0.99	137.08	0.510	4.92	0.98
	293	354.61	4.55	0.013	0.99	40.96	0.297	06.0	1.03	43.76	51.87	66.0	137.36	0.565	4.92	0.96
GACOZC1073	303	377.36	5.16	0.014	0.99	42.69	0.301	06.0	1.06	46.69	48.62	66.0	139.80	0.630	4.94	0.97
	313	400.00	5.85	0.015	0.99	47.69	0.295	0.89	1.35	48.13	47.15	66.0	140.19	0.736	4.94	0.97
	323	416.67	7.09	0.017	0.99	54.16	0.287	0.89	1.92	48.85	46.47	66 0	158.26	7.09.0	5 06	0.99

School of Environmental Studies, Cochin University of Science and Technology



Chapter 4

Dubinin – Radushkevich isotherm model is commonly used to determine the adsorption energy of an adsorption process and to determine the p –nitophenol adsorption by activated cabons are physical or chemical process. The D –R isotherm constant are given in Table 4.16. The adsorption capacity q_m increases with temperature for all the activated carbons. The magnitude of adsorption capacity increases in the order of GACOZC1073 (137 – 158 mg/g) > GAC383 (75 – 81 mg/g) > GACO383 (49 – 52 mg/g). This model is applied only lower concentration of p –nitrophenol as adsorbate.

4.4.2. 5 Thermodynamic Parameters

To determine the thermodynamic parameters such as change in enthalpy (ΔH), entropy (ΔS) and Gibbs free energy change (ΔG) using different temperature effect on adsorption of p – nitrophenol on these modified carbons. Temperature used for this study is 10°C, 20°C, 30°C, 40° C and 50° C. These thermodynamic parameters are calculated using the Van't Hoff equation. The ΔH and ΔS are obtained from the slope and intercept of the plot lnK_L versus 1/T and are shown in Figure 4.62. Table 4.17, it is clear that the ΔG decreases with temperature and all the carbons show negative value confirms that the adsorptions by granular activated carbons are spontaneous and is favourable for higher temperature. The positive ΔH and ΔS indicated that adsorption is endothermic and no structural changes occur in the carbon -p- nitrophenol solution interface [24]. At higher temperatures the Gibbs free energy change is more negative implies that greater driving force is required for the adsorption of p – nitrophenol by modifying carbons. All these carbons show ΔH < 40 kJ/mol indicate that the adsoprtion process occurs through physical forces only.





Figure 4.62: Plot of $ln K_L$ versus 1/T for determination of thermodynamic parameters for the adsorption of p - nitrophenol by GAC383, GAC0383 and GAC0ZC1073

Table 4.17: Thermodynamic parameters – Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of GACOZC1073

		Δ	G (kJmo	l ⁻¹)		ΔΗ	ΔS
Carbon	283	293	303	313	323	(kJmol ⁻¹)	(Jmol ⁻¹ K ⁻¹)
GAC383	-4.78	-5.17	-5.54	-5.83	-6.36	6.02	38.18
GACO383	-1.70	-1.85	-2.02	-2.18	-2.36	2.96	16.45
GACOZC1073	-3.31	-3.69	-4.13	-4.60	-5.26	10.23	47.62

4.4.3 Adsorption Studies of Methylene Blue (MB)

The adsorption capacity of modified carbons (GAC383, GACO383 and GACOZC series) is determined by using adsorption kinetics, isotherm and thermodynamic study of a cationic dye Methylene Blue (MB) as adsorbate.

4.4.3.1 Selection of GACOZC for Methylene Blue (MB) Adsorption

The selection of a carbon from the GACOZC series for the detailed study of adsorption of MB was conducted by initial concentration of 500 mg/L MB solution for 10 hours equilibration period in a lab scale study.

Final concentration was measured in a UV Visible spectrophotometer at 650 nm. GACOZC1073 shows highest adsorption capacity compared to others (Figure 4.63). The adsorption efficiency is higher in the range of 14 - 38% than other carbons from the same series.



Figure 4.63: Selection of carbons from the GACOZC series for methylene blue (MB) adsorption $C_0 = 500 \text{ mg/L}$

4.4.3.2 Adsorption Kinetics – Methylene Blue as Adsorbate

Adsorption kinetics study is very important because it gives vital information on how fast the MB adsorption process requires to reach equilibrium. The effect of activation temperature on the methylene blue adsorption kinetics on granular activated carbons GAC383 (Figure 4.64), GACO383 (Figure 4.65) and GACOZC1073 (Figure 4.66). The initial concentration of MB used is 250 mg/L. Figure shows that methylene blue adsorption increases with time and temperature. Temperature increases the mobility of the methylene blue dye molecule also improves [25].



Figure 4.66: Effect of contact time on the adsorption of methylene blue (MB) on GACOZC1073 at different temperatures for $C_0 = 250 \text{ mg/L}$

These time dependent experimental data are applied in different kinetic equations such as pseudo first order, Ho second order, intraparticle diffusion model and Boyd model find the rate constant and the mechanism of adsorption. The first order rate constant (K_1) and amount adsorbed

Chapter 4

 (q_ecal) from the slope and intercept of the linear plot $ln (q_e - q_t)$ versus *time* in minutes (Figure 4.67). The experimental data are not comparable with calculated q_e from the first order and the correlation coefficient is less than 0.99 for all the carbons studied indicates that first order kinetics is not following experimental data. The correlation coefficient ($R^2 - 0.99$) obtained for the straight line plot of t/q_t versus t (Figure 4.68) suggests that, the adsorption of MB on modified carbons follows pseudo second order kinetic model [26]. The adsorption capacity (q_ecal) and second order rate constant (K_2) increases with temperature means MB adsorption by granular activated carbons is an endothermic process. The batch kinetic data are agreed with a calculated adsorption capacity of second order as shown in Table 4.18.

The first and second order kinetic model cannot identify the diffusion mechanism of MB adsorption on carbons GAC383, GACO383 and GACOZC1073. Weber intraparticle diffusion model is applied to predict the rate controlling step for MB adsorption on activated carbons. Weber and Morris (1963) intraparticle diffusion model [16], qt against square root of time $(t^{1/2})$ gives two straight line portions (Figure 4.69). The first portion is attributed to external diffusion and the second linear portion is attributed to pore diffusion [27]. The diffusion coefficient (K_{idl}) from the first linear portion is higher than the intraparticle diffusion coefficient (K_{id2}) shown in Table 4.18. The lower Kid_2 suggest that the intraparticle diffusion is the rate controlling step for the adsorption of MB on carbons. The boundary layer thickness determined for the intercept of the plot increases with temperature. The correlation coefficient of intraparticle diffusion model is in the range of $(R^2 = 0.95 \cdot 0.99)$. Boyd model is used to determine the diffusivity coefficient (D_i) from the straight line plot of B_t versus time (Figure 4.70). As the temperature increases, the diffusivity coefficient almost higher indicate that temperature influence the MB adsorption. The correlation coefficient (R^2) is in the range of 0.94 - 0.99 for all the carbons studied at different temperature. Lower R^2 indicates that the external diffusion is not the sole rate limiting step.



			i				-									
bəted			First c	order kind onstants	etics	Seco. kinetic	nd orde s consta	r nts	Intr	aparticle	diffusio	n kinetic	s constar	ıts	Boyd ki constan	netic ts
svitsA relunerS Sarbon	(K) L	(S/Zw) dxə°t	(ສ/ສົມ) ວັ	'N	782	(B/g) Jecal	±401*2×10*	z 8	(^{1/1} -nim ⁻¹ 22m) K _{id1}	LC.	z	(^{1/1} . 1/2. 1/2.	^z C	z	(₁₋ s _z wə) +-01×°0	z
	283	102.05	60.38	0.0048	0.94	104.38	2.42	0.99	8.49	1.76	0.98	2.07	50.67	0.97	1.33	0.94
	293	116.77	64.49	0.0048	0.98	118.76	2.46	0.99	7.24	21.22	0.97	2.48	56.37	0.99	1.33	0.98
GAC383	303	124.24	67.07	0.0054	0.94	126.42	2.52	0.99	5.78	38.04	0.99	2.61	61.14	76.0	1.50	0.94
	313	132.00	66.07	0.0049	0.98	133.87	2.57	0.99	5.59	45.81	0.99	2.72	66.48	0.99	1.38	0.98
	323	138.08	67.84	0.0056	96.0	140.25	2.73	0.99	6.07	49.34	0.98	2.47	78.76	66.0	1.57	0.96
	283	80.60	53.52	0.0042	0.96	82.37	2.33	0.99	5.66	2.99	0.98	2.21	25.73	66.0	1.17	0.96
	293	90.92	54.31	0.0042	0.97	16.16	2.57	0.99	5.15	15.65	0.98	2.35	32.81	0.98	1.17	0.97
GACO383	303	98.13	54.75	0.0044	0.98	99.80	2.75	0.99	5.29	20.75	0.99	2.05	47.28	66.0	1.24	0.98
	313	110.64	56.84	0.0039	0.95	110.38	2.78	0.99	6.37	24.83	0.99	2.25	53.67	0.97	1.10	0.95
	323	117.76	53.85	0.0044	0.94	118.06	3.32	66.0	7.52	27.33	0.98	1.78	72.52	0.99	1.22	0.94
	283	93.75	71.80	0.0048	0.97	101.42	1.27	0.99	8.40	-15.24	0.99	2.61	29.49	0.98	1.07	0.98
	293	109.90	78.68	0.0047	0.98	115.74	1.41	66.0	7.99	-3.10	0.99	2.90	38.80	0.99	1.16	66.0
GACOZC1073	303	120.19	75.61	0.0040	0.95	121.36	1.73	66.0	6.12	18.65	0.95	2.81	48.44	0.95	0.92	0.97
	313	128.37	77.97	0.0046	96.0	131.06	1.84	0.99	8.98	11.16	0.98	2.92	56.25	66.0	1.1	0.95
	323	139.90	77.23	0.0049	0.98	142.45	2.08	0.99	8.41	26.81	0.98	2.84	70.68	0.99	1.19	0.99

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4.4.3.3 Activation Energy using Methylene blue (MB) as Adsorbate

A linear plot of lnK_2 against 1/T for the estimation of activation energy for the adsorption of MB on granular activated carbons is shown in Figure 4.71 (a) GAC383, (b) GACO383 and (c) GACOZC1073.



Figure 4.71 (c): Plot of $ln K_2$ versus 1/T for the adsorption of methylene blue on GACOZC1073 for C₀ = 250 mg/L

The activation energy (E_a) is an important parameter to determine the type of adsorption. The E_a is in the range of 0 - 40 kJ/mol indicate MB adsorption is a physical process and $E_a > 40$ kJ/mol adsorption occurs

through chemical process. The activation energy obtained by the adsorption of MB on modified carbons (Table 4.19) GAC383 (E_a - 2.11 kJ/mol), GAC0383 (E_a - 5.98 kJ/mol) and GAC0ZC1073 (E_a - 9.59 kJ/mol). Thus the adsorption of MB by these modified carbons occurs through physical adsorption. The positive E_a means it is an endothermic process the energy that gain for an adsorption to occur.

Table 4.19: Activation energy of modified carbons using MB as adsorbate

Carbon	$E_a(kJmol^{-1})$	K ₀	R
GAC383	2.11	0.0006	0.95
GACO383	5.98	0.0029	0.95
GACOZC1073	9.59	0.0074	0.98

4.4.3.4 Adsorption Isotherm Studies of Methylene Blue (MB) on GACOZC1073

The adsorption isotherm studies of methylene blue give information about how these molecules distribute between the MB solution phase and the carbon surface when the adsorption process occur after a 10 hr calibration period. The Figure 4.72 (a) - GAC383, Figure 4.72 (b) -GACO383 and Figure 4.72 (c) - GACOZC1073 shows the typical Type I isotherm of amount adsorbed (q_e) against concentration at equilibrium (C_e) of MB dye at different temperature ranging from 10 - 50^oC. The adsorption efficiency of MB enhances with adsorption temperature point out that it is an endothermic process. These equilibrium adsorption data are applied to different isotherm equations such Langmuir, Freundlich, Temkin and Dubinin - Radushkevich to determine the adsorption capacity of the activated carbons and critical constants to evaluate the characteristic features of these carbons for the adsorption of MB.

A Langmuir isotherm gives information about the monolayer adsorption capacity of the modified carbons with homogenous active sites. A linear plot

Chapter 4

of $C_{e'}q_{e}$ against C_{e} for the MB adsorption by GAC383, GACO383 and GACOZC1073 are shown in Figure 4.73. The monolayer adsorption capacity (q_{max}) calculated from the slope and Langmuir energy constant (K_L) from the intercept is shown in Table 4.20. The q_{max} and K_L increases with temperature for all the carbon studied. The correlation coefficient ($R^2 - 0.99$) indicates that removal of MB occurs by homogenous surface of the activated carbons. The q_{max} of the activated carbons at different temperature ranging from $10-50^{\circ}$ C is GAC383 (150.60 mg/g, 169.49 mg/g, 190.11 mg/g, 209.64 mg/g and 229.35 mg/g), GACO383 (107.99 mg/g, 122.40 mg/g, 138.70 mg/g, 154.32 mg/g and 172.41 mg/g) and GACOZC1073 (175.75 mg/g, 190.84 mg/g, 199.20 mg/g, 213.22 mg/g and 225.23 mg/g). The π - π dispersive interaction plays a dominant role on the adsorption of MB type cationic dye, where adsorption forms through delocalized π electrons on carbon surface and free electrons of the MB molecules. Highly acidic surface groups present on the GACO383 surface [carboxylic (1.38meq), phenolic (1.34 meq/g) and lactonic (2.10 meq/g) and low basic groups (0.20 meq/g)] decrease the adsorption capacity of MB. The GACOZC1073 shows the higher adsorption capacity of MB, but the variation is not as much as high as compared to GAC383. The percentage of mesoporosity, BET surface area and basicity influence the efficiency of MB adsorption by GACOZC1073 [28].

Freundlich isotherm plot of $log q_e$ versus $log C_e$ gives a straight line with a slope l/n (Freundlich constant) and intercept K_F (adsorption capacity) shown in Figure 4.74 (a) for GAC383, 4.74 (b) for GACO383 and 4.74 (c) for GACOZC1073. The Freundlich isotherm constant is given in Table 4.20. The K_F increases with temperature indicating the endothermic adsorption of MB by activated carbons. The linearity constant l/n is less than one indicates a favourable Langmuir type adsorption. The correlation coefficient (R^2) of Freundlich is less than Langmuir correlation coefficient so adsorption is favourable for homogenous surface.





Chapter 4

		Langm	uir Con.	stants	Fr	eundlich	Constan	ts	L	emkin C	onstants		Dubin	in – Rac Consta	lushkev ints	ich
Carbon	(K) L	(₁₋ 88ш) ^{хти} Б	(₁₋ 8ш7) א ^ר	<i>3</i> ح	(נוגר _{ין}) א ^{רב}	u/I	u	₇ ع	(₁₋ 87) V	(Joml) B	(10mL) Td	<i>2</i> ع	(₁₋ 88ш) ^ш Ь	(KJmol ₁) E [©]	(uol ₅ 25) K،	_z א
	283	150.60	3.74	0.99	37.67	0.200	1.58	0.98	9.50	15.15	149.85	0.97	57.43	2.75	0.066	0.97
	293	169.49	4.54	66.0	40.65	0.209	1.61	0.98	9.36	17.17	132.20	0.98	58.83	3.26	0.047	0.96
UAU383	303	11.061	4.80	66.0	42.90	0.217	1.63	0.99	8.68	19.16	118.48	0.96	60.30	3.74	0.036	0.96
	313	209.64	5.13	0.99	45.34	0.223	1.66	0.99	8.61	20.92	108.48	0.95	61.58	4.20	0.028	0.96
	323	229.35	5.51	66.0	47.80	0.228	1.68	0.99	8.59	22.71	99.95	0.94	62.78	4.67	0.023	0.97
	283	107.99	2.89	0.99	35.09	0.159	6.27	0.97	12.08	13.66	166.17	0.98	54.15	2.77	0.065	0.98
	293	122.40	3.37	66.0	37.67	0.169	5.92	0.98	11.93	15.34	147.94	0.98	56.25	3.14	0.051	0.98
UALU383	303	138.70	3.60	66.0	39.84	0.178	5.61	0.98	11.26	17.05	133.14	0.97	57.98	3.49	0.041	0.97
	313	154.32	4.31	66.0	42.34	0.188	5.33	0.98	11.55	18.19	124.76	0.97	59.50	3.79	0.035	0.97
	323	172.41	4.59	66.0	44.58	0.195	5.12	0.99	9.36	21.28	106.67	0.95	60.98	4.08	0.030	0.97
	283	175.75	1.89	0.99	24.08	0.270	3.70	0.98	1.03	20.91	108.53	0.88	45.25	2.15	0.108	0.95
	293	190.84	2.35	0.99	25.44	0.280	3.58	0.97	1.08	23.13	98.14	0.87	46.90	2.49	0.081	0.94
GACOZC1073	303	199.20	2.91	0.99	27.59	0.278	3.60	0.95	1.34	23.99	94.63	0.85	48.08	3.09	0.052	0.95
	313	213.22	3.80	66.0	33.29	0.267	3.75	0.99	2.09	24.72	91.82	06.0	54.01	3.31	0.046	0.94
	323	225.23	4.93	66 0	36.47	0.267	3.74	0.99	2.54	26.10	86.96	0.93	55.52	3.64	0.038	0.94

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Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

Chapter 4

The heat of MB adsorption / MB – granular activated carbons interaction on equilibrium adsorption isotherm were studied by using Temkin isotherm model shown in Figure 4.75 (a) – (c). A linear plot of q_e versus lnC_e gives an intercept of A (equilibrium binding constant) and slope B (related to heat of adsorption) are given in Table 4.20. The heat of adsorption constant (B) increases with temperature for all the carbons studied, for GAC383 (15.15 - 22.71 Jmol⁻²), GACO383 (13.66 – 21.28 Jmol⁻²) and GACOZC1073 (20.91 - 26.10 Jmol⁻²) indicate that MB adsorption is an endothermic process. The Table 4.18 shows that $b_T < 80 kJ/mol$ indicate that adsorption mainly follows physisorption mechanism. The correlation coefficient is found to be more or less than 0.99 in all cases.

Dubinin - Radushkevich (D-R) isotherm model is used to determine the adsorption mechanism of carbons using mean adsorption energy E_0 . The mean adsorption energy is less than 8 kJ/mol for all the carbons (Table 4.20) further indicates that adsorption follows physisorption mechanism. The q_m increases with temperature reveals that adsorption is an endothermic process. This isotherm model is applicable only lower concentration of MB dye and the adsorption capacity q_m of GAC383 (57.43 – 62.78 mg/g), GACO383 (54.15 - 60.98 mg/g) and GACOZC1073 (45.25 - 55.52 mg/g). In case of lower concentration GAC383 shows higher adsorption capacity and the correlation coefficient (R^2 ranges between 0.94 – 0.98).

4.4.3.5 Adsorption Thermodynamics

The thermodynamic parameters such as change in enthalpy (ΔH), entropy (ΔS) and Gibbs free energy change (ΔG) of GAC383, GACO383 and GACOZC1073 on Methylene Blue adsorption are calculated using distribution coefficient (K_D) applied in Van't Hoff equation. The change in enthalpy and entropy of these activated carbons is obtained from the intercept and slope of the straight line plot of lnK_D against 1/T (Figure 4.76 – 4.78). The thermodynamic constants ΔG , ΔH and ΔS are presented in Table 4.21. The ΔG decreases with temperature indicating that MB adsorption efficiency enhances at higher adsorption temperature. The ΔG is positive for higher concentration of MB studied, indicating that system gained energy from an external source. The ΔH is positive means adsorption is endothermic and it is less than 40 kJ/mol for all the carbons at all concentration studied indicate a physisorption mechanism. The ΔS is positive reflects a good affinity of the methylene blue particles towards modified carbons.



Figure 4.76: $ln K_D$ versus 1/T for the adsorption of methylene blue (MB) on GAC383 for $C_0 = 25 - 1500$ mg/L

Figure 4.77: $ln K_D$ versus 1/T for the adsorption of methylene blue (MB) GACO383 for $C_0 = 25 - 1500 \text{ mg/L}$

257



blue (MB) GACOZC1073 for $C_0 = 25 - 1500 \text{ mg/L}$

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

Carbon	$\frac{0-23}{C_{2}}$	- 1500 mg/				AG (kIm	ol ⁻¹)	
Curbon		$(Jmol^{-1}K^{-1})$	(kJmol ⁻¹)	283	293	303	313	323
	25	105.61	19.29	-10.59	-11.65	-12.71	-13.76	-14.82
	50	90.76	18.29	-7.40	-8.31	-9.22	-10.12	-11.03
	75	78.53	18.05	-4.17	-4.96	-5.75	-6.53	-7.32
	100	60.48	14.21	-2.91	-3.52	-4.12	-4.73	-5.33
	150	52.66	13.94	-0.96	-1.49	-2.01	-2.54	-3.07
GAC383	200	44.03	12.57	0.11	-0.33	-0.77	-1.21	-1.65
	250	35.23	10.75	0.78	0.43	0.08	-0.28	-0.63
	350	30.70	10.37	1.68	1.37	1.07	0.76	0.45
	500	26.33	10.01	2.56	2.29	2.03	1.77	1.50
	750	21.21	9.55	3.55	3.33	3.12	2.91	2.70
	1000	18.04	9.34	4.23	4.05	3.87	3.69	3.51
	1250	16.41	9.40	4.76	4.59	4.43	4.26	4.10
	1500	14.38	9.23	5.16	5.02	4.88	4.73	4.59
	25	105.26	19.34	-10.45	-11.50	-12.56	-13.61	-14.66
	50	91.24	18.65	-7.17	-8.08	-9.00	-9.91	-10.82
	75	75.12	18.34	-2.92	-3.67	-4.42	-5.18	-5.93
	100	66.65	17.65	-1.22	-1.88	-2.55	-3.22	-3.88
	150	57.04	16.53	0.39	-0.19	-0.76	-1.33	-1.90
CAC0292	200	44.16	13.72	1.22	0.78	0.34	-0.10	-0.54
GACOS85	250	36.32	12.03	1.75	1.39	1.02	0.66	0.30
	350	28.28	10.61	2.61	2.32	2.04	1.76	1.47
	500	24.76	10.50	3.50	3.25	3.00	2.75	2.51
	750	21.11	10.45	4.47	4.26	4.05	3.84	3.63
	1000	17.62	10.11	5.13	4.95	4.77	4.60	4.42
	1250	15.05	9.88	5.62	5.47	5.32	5.17	5.01
	1500	13.37	9.81	6.03	5.89	5.76	5.63	5.49
	25	99.48	19.31	-8.84	-9.84	-10.83	-11.83	-12.82
	50	91.07	22.74	-3.03	-3.95	-4.86	-5.77	-6.68
	75	87.78	23.47	-1.37	-2.25	-3.13	-4.01	-4.88
	100	69.69	19.20	-0.52	-1.22	-1.91	-2.61	-3.31
	150	50.78	14.74	0.38	-0.13	-0.64	-1.15	-1.66
010701072	200	47.35	14.19	0.80	0.32	-0.15	-0.62	-1.10
GACOZCI0/3	250	44.42	13.70	1.13	0.68	0.24	-0.20	-0.65
	350	36.21	11.91	1.67	1.30	0.94	0.58	0.22
	500	29.51	10.88	2.53	2.24	1.94	1.65	1.35
	750	18.26	8.59	3.42	3.24	3.06	2.88	2.69
	1000	10.44	6.98	4.02	3.92	3.82	3.71	3.61
	1250	4.90	5.82	4.43	4.38	4.33	4.28	4.24
	1500	3.22	5.73	4.82	4.79	4.75	4.72	4.69

Table 4.21: Thermodynamic parameters of GAC383, GACO383 and GACOZC1073 for methylene blue (MB) adsorption at different temperatures for $C_0 = 25 - 1500 \text{ mg/L}$

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4.6 Determination of Porosity and Surface Area of Modified Carbons (GAC383, GACO383 and GACOZC1073) Using Liquid Phase Adsorption Isotherm Models

The porosity and surface area of the modified carbons GAC383, GAC0383 and GAC0ZC1073 are determined using adsorption isotherm models such as Langmuir, John – Sivanandan Achari (J –SA), Brunauer Emmet and Teller (BET) and BET - Scatchard plot (*I plot*) in liquid phase adsorption study. The adsorbate used as phenol, p - nitrophenol and methylene blue.

$$SA(m^{2} / g) = \frac{q_{m}(g / g) \times 6.022 \times 10^{23} (molecules / mole) \times a \times 10^{-18} (nm^{2} / molecule)}{Molecular weight of adsorbate}$$
(4.24)

$$Porosity = \frac{q_m(mg / g)}{Density of \ adsorbate}$$
(4.25)

The Figure 4.79 – 4.81 is the John – Sivanandan Achari (J - SA) isotherm plot for the adsorption of phenol, p – nitrophenol and methylene blue (MB) adsorption of GAC383, GACO383 and GACOZC1073 respectively. The limiting micropore volume calculated by J – SA method by extrapolating the straight line connecting to the lower point of *loglog C_e* is shown in Table 4.22. The $q_m(J-SA)$ for GAC383 (phenol – 310.5 mg/g, p – nitrophenol – 357.80 mg/g and MB – 190.10 mg/g), GACO383 (phenol – 217.40 mg/g, p – nitrophenol – 232.20 mg/g and MB – 135.70 mg/g) and GACOZC1073 (phenol – 307.00 mg/g, p – nitrophenol – 386.72 mg/g and MB – 201.47 mg/g). Compared to these adsorbates p –nitrophenol adsorption is higher for three carbons studied. One reason is the introduction of the nitro group on the para position of phenol increases the adsorption of p -nitrophenol due to decrease the water solubility. MB is a large molecule compared to phenol and p – nitrophenol that reason adsorption decreases. Using the $q_m(J-SA)$ specific surface area is determined

SA (J-SA) and presented in Table 4.22. The SA (J-SA) for GAC383 (Phenol – 1037.2 m²/g, p – nitrophenol – 813.2 m²/g and MB – 430.8 m²/g), GACO383 (phenol – 726.2 m²/g, p – nitrophenol – 527.7 m²/g and MB – 307.5 m²/g) and GACOZC1073 (Phenol – 1025.4 m²/g, p – nitrophenol – 878.9 m²/g and MB – 456.54 m²/g). The surface area of phenol is higher compared to other adsorbate calculated by this method. The molecular weight varies as phenol (94.11 g/mol) < p - nitrophenol (139.11 g/mol) < MB (318.90 g/mol) is a reason for high surface observed for phenol than others.

The monolayer adsorption capacity q_{max} are calculated from the Langmuir isotherm model are shown in Table 4.22. The linear plot of C_e/q_e versus C_e of the modified carbons for phenol, p –nitrophenol and MB adsorption are shown in Figure 4.82 – 4.84. The monolayer adsorption capacity varies in the order p – nitrophenol > phenol > methylene blue (MB). The monolayer adsorption capacity and surface area of Langmuir method is comparable with limiting micropore volume and surface area of John – Sivanandan Achari (J –SA) method indicating that the modified carbons are having Type I character and have microporosity [29, 30,31,32]

BET and *I plot* method are applied for the liquid phase adsorption and the porosity and surface area evaluated. The q_m (BET) and q_m (I plot) equal comparable at the range of C_e/C_s equals to 0.3 where *C* parameter of BET is observed positive.

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Figure 4.79: John Sivanadan Achari (J-SA) isotherm plot for phenol, *p* – nitrophenol and methylene blue adsorption by GAC383



Figure 4.80: John Sivanadan Achari (J-SA) isotherm plot for phenol, *p* – nitrophenol and methylene blue adsorption by GACO383



Figure 4.81: John Sivanadan Achari (J-SA) isotherm plot for phenol, p - nitrophenol and methylene blue adsorption by GACOZC1073





gure 4.84: Langmuir isotherm model for the adsorption of methylene blue by GAC383, GACO383and GACOZC1073



Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

			Phenol		<i>p</i> - n	itroph	enol	Me	thylene	Blue
Isotherm Models	Porosity and Surface area	GAC383	GACO383	GACOZC1073	GAC383	GACO383	GACOZC1073	GAC383	GACO383	GACOZC1073
	q _{max} (L) (mg/g)	312.5	209.6	304.88	340.1	224.2	377.35	190.1	138.7	199.20
Langmuir (L)	SA (L) (m ² /g)	1043.9	700.4	1018.35	773.2	509.7	857.60	430.9	314.4	451.40
	Porosity (cm ³ /g)	0.452	0.303	0.441	0.425	0.280	0.472	0.316	0.231	0.331
John	q _m (J- SA)	310.5	217.4	307.00	357.8	232.2	386.72	190.1	135.7	201.47
Sivanandan Achari	SA (J- SA)	1037.2	726.2	1025.44	813.2	527.7	878.90	430.8	307.5	456.54
(J –SA)	Porosity (cm ³ /g)	0.449	0.314	0.444	0.448	0.290	0.484	0.316	0.226	0.335
Brunauer -	q _m (BET)	190.2	135.6	164.58	227.1	140.0	231.91	115.8	84.2	126.34
Emmet - Teller	SA (BET)	635.3	452.9	549.73	515.9	318.2	527.06	262.4	190.8	286.29
(BE1)	Porosity (cm ³ /g)	0.275	0.196	0.238	0.284	0.175	0.290	0.193	0.140	0.210
BET	q _m (I plot)	189.9	137.6	160.64	233.31	140.1	231.26	117.3	86.54	125.48
Scatchard plot	SA (I plot)	634.5	459.5	536.57	530.24	318.4	525.58	265.9	196.1	349.88
(I plot)	Porosity (cm ³ /g)	0.274	0.199	0.232	0.292	0.175	0.289	0.195	0.144	0.209

Table 4.22: The porosity and surface area of the new modified carbons using standard isotherm models

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Figure 4.87: The general isotherm and I plot of (a) GAC383 (b) GAC0383 & (c) GAC0ZC1073 on MB adsorption

4.6 Adsorption of Trace Elements (Li, Mg, Al, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Ba, Tl & Pb)

Adsorption efficiency of carbon GAC383, GACO383 and GACOZC1273 are tested using a ground water sample having trace metals in concentrations (Li – 1.3 μ g/L, Mg – 1220.04 μ g/L, Al - 42.88 μ g/L, Cr – 0.27 μ g/L, Mn – 103.5 μ g/L, Fe – 2884.22 μ g/L, Co – 1.01 μ g/L, Cu – 1.06 μ g/L, Zn – 12355.72 μ g/L, As – 0.06 μ g/L, Cd – 0.04 μ g/L, Ba – 186.02 μ g/L, Tl – 0.04 μ g/L and Pb – 2.4 μ g/L). This has been collected from a region whose water quality parameters are known. Batch experiment were done, 100 ml of ground water mixed with 0.1 g of carbon. For this study, shaking time is controlled as 480 minutes as equilibration

time. After the desired contact time these carbons were filtered and the final concentration is determined by ICP – MS. The percentage adsorption efficiency of these new carbons are evaluated and are shown in Table 4.23. The results show that GACO383 has more than 90% efficiency to remove most of the heavy metals such as Mn, Al, Fe, Co, Cu, Zn and Ba. The carbon GACOZC depicts that more than 90% removal efficiency against trace elements Fe, Cu, Zn and Pb. GACOZC1073 shows more than 60% efficiency for other trace elements tested except magnesium (Mg).

		GAC	383	GACO)383	GACOZ	C1073
Trace elements	Initial concentrati on (µg/l)	Amount adsorbed (µg/g)	Percentage efficiency (%)	Amount adsorbed (µg/g)	Percentage efficiency (%)	Amount adsorbed (µg/g)	Percentage efficiency (%)
Li	1.3	0.23	17.69	0.63	48.46	1.19	91.54
Mg	1220.04	17.7	1.45	939.66	77.02	213.37	17.49
Al	42.88	36.89	86.03	39.58	92.30	33.9	80.18
Cr	0.27	0.09	33.33	0.2	74.07	0.18	66.67
Mn	103.5	73.39	70.91	100.5	97.10	70.74	68.35
Fe	2884.22	2860.18	99.17	2873	99.61	2872	99.58
Co	1.01	0.71	70.30	0.94	93.07	0.86	85.15
Cu	1.06	0.05	4.72	1.02	96.23	1.00	94.34
Zn	12355.72	12143.04	98.28	12345.92	99.92	12285.18	99.43
As	0.06	0.02	33.33	0.04	66.67	0.04	66.67
Cd	0.04	0.01	25.00	0.02	50.00	0.03	75.00
Ba	186.02	91.04	48.94	183.25	98.51	131.88	70.90
T1	0.04	0.03	75.00	0.03	75.00	0.03	75.00
Pb	2.4	2.3	95.83	1.61	67.08	2.28	95.00

 Table 4.23: Adsorption efficiency for removing trace elements by newly prepared carbons GAC383, GACO383 and GACOZC1073

4.7 **Statistical Analysis of the Data**

Results of statistical tests conducted to check the various hypothesis, suggested in the chapter 1, give the following results:

Hypothesis 1: Whether there is any significant difference between the total pore volume, micropore volume and mesopore volume for different modified granular activated carbons (GACOZC) and in comparison with the native form of granular activated carbon (GAC) and carbon oxidised with nitric acid (GACO383 [ANOVA TEST].

The comparison of textural characterization obtained by two way ANOVA test and the sum of squares (ss), degree of freedom (df), mean square (ms), variance ration (F) and level of significance (p - value) are shown in the Table 4.24 and the inferences are given below.

8		-			
Source	SS	df	ms	F	p-value
Total	103176.5353	11			
Carbons	1723.8726	3	574.6242	0.289	P>0.05
Pore volumes	89550.2472	2	44775.1236	22.571	P<0.001
Residual	11902.4155	6	1983.7359		

Table 4.24: ANOVA table for the comparison of textural characterization of granular activated carbons

Inferences

- There is no significant difference between carbon and textural (a) characterization (P > 0.05)
- (b) There is significant difference between textural characterisation (P <0.001). Total pore volume (V_t) is significantly higher than V_{mic} and V_{mes} (P < 0.001).



Chapter 4

Hypothesis 2: Whether there is any significant difference between porosity and surface area using Solid – gas equilibria using N₂ gas adsorption at 77K, evaluated using different isotherm models; BET isotherm, I plot method, Langmuir isotherm, John isotherm, α_s plot, t plot for modified granular activated carbons and in comparison with the native form of granular activated carbon.

To prove this hypothesis two way ANOVA method is used. The adsorption capacity, surface area and pore volume obtained by establishing isotherm models such as Langmuir, John isotherm, Dubinin – Radushkevich isotherm, BET isotherm, I plot, alpha S (α_s). The results are presented in Table 4.25 and inferences are given below.

Table 4.25: ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and I plot method) of granular activated carbons

Source	SS	df	ms	F	p-value
Total	2530168.8566	7			
Carbons	2394634.8168	1	2394634.8168	178.``363	P<0.001
Adsorption capacity	95257.2623	3	31752.4208	2.365	P>0.05
Residual	40276.7775	3	13425.5925		

Inferences

- (a) There is no significant difference between the different methods (P>0.05)
- (b) There is significant difference in the adsorption capacity. John isotherm method the surface area is significantly higher than the rest (P < 0.001)



Source	SS	df	ms	F	p-value
Total	5341.8157	15			
Carbons	2556.8656	3	852.2885	5.177	P<0.05
Pore volume	1303.2406	3	434.4135	2.639	P>0.05
Residual	1481.7095	9	164.6344		

Table 4.26: ANOVA table for the comparison of pore volume obtained by
different methods (John Isotherm, Langmuir isotherm, Dubinin –
Radushkevich isotherm and alpha S) of granular activated carbon

Inferences

- (a) There is no significant difference between methods in estimating pore volume (P > 0.05)
- (b) There exists significant difference between granular activated carbons (P < 0.05)
- (c) GACOZC1073 are having significantly higher pore volume compared to the other two (P < 0.05).

Hypothesis 3: Whether there is any relation between the adsorption temperature and adsorption efficiency for the modified granular activated carbons (GACOZC).

Pearson correlation coefficient (r) and Student's t test are used to prove the relation of adsorption temperature and adsorption efficiency. From the above test, attained following inferences:

There is a significant positive correlation between temperature and adsorption of phenol on GACOZC 1073 (r = 0.9833, t = 9.3520, df = 3, P < 0.01). This indicates that temperature enhances the phenol adsorption.

There is a significant positive correlation between temperature and adsorption of *p* - nitro phenol on GACOZC 1073 (r = 0.99345, t = 15.0544, df = 3, P < 0.01). This indicates that *p*-nitro phenol adsorption increases with temperature.

There is significant positive correlation between temperature and adsorption of MB on GACOZC 1073 (r = 0.9973, t = 23.50574, df = 3, P < 0.01). This indicates that as temperature increases adsorption of MB also enhanced.

Hypothesis 4: Whether there is any significant difference between porosity and surface area determined using Langmuir isotherm and John – Sivanandan Achari isotherm (J-SA) for newly prepared granular activated carbons from solid – liquid equilibria

Langmuir and John – Sivanandan Achari isotherm model for phenol, p – nitrophenol and methylene blue adsorption on modified carbons are tested by three way ANOVA test. Results are shown in Table 4.27 and Table 4.28. Inferences are given below.

Source ss df ms F p-value									
carbon obtained by Langmuir and John – Sivanandan Achari isotherm model in liquid phase adsorption study									
Table 4.27: ANOVA table	e for the c	comparis	on of poros	ity of gran	ular activated				

Source	SS	df	ms	F	p-value
Total	0.12616	17			
Methods	0.00017	1	0.00017	0.378	P > 0.05
Carbons	0.07420	2	0.03710	82.444	P < 0.001
Phenol, <i>p</i> –nitrophenol & methylene blue	0.04637	2	0.02319	103.044	P< 0.001
Residual	0.00542	12	0.00045		

Inferences

- (a) There is no significant difference in porosity as estimated by Langmuir and John Sivanandan Achari isotherm methods (P > 0.05).
- (b) Carbons differ significantly in porosity (P < 0.001). GACOZC1073 showed significantly higher volume compared to the other two (P < 0.001).
- (c) Phenol, p nitrophenol and methylene blue also showed a significant difference in porosity (P < 0.001). Phenol and p nitrophenol showed significantly higher porosity than methylene blue (P < 0.001).

Granular Activated Carbon Oxidised and Incorporated with Zn²⁺: Preparation, Characterization ...

isother	rm models				
Source	SS	df	ms	F	p-value
Total	1144644.5717	17			
Methods	596.6210	1	596.6210	0.202	P > 0.5
Carbon	259770.3812	2	129885.1906	44.059	P < 0.001
Phenol, p – nitrophenol and methylene blue	848901.8643	2	424450.9322	143.980	P < 0.001
Residual	35375.7052	12	2947.9754		

Table 4.28: ANOVA table for the comparison of surface area of modified carbons obtained by Langmuir isotherm and John - Sivanandan Achari isotherm models

Inferences

- (a) There is no significant difference in surface area between Langmuir and John Sivanandan Achari isotherm methods (P > 0.05).
- (b) Surface area differs significantly between carbons (P < 0.001). GACOZC1073 is having significantly higher surface area compared to the other two carbons (P < 0.001).
- (c) Phenol, p nitrophenol and methylene blue also differ significantly higher in phenol compared to p nitrophenol and methylene blue (P < 0.001).

4.8 Conclusions

The granular activated carbon oxidized with nitric acid (GACO) and incorporated with Zn^{2+} ions and steam activated at different temperatures from GACOZC series of carbon having Type I characteristics evidenced by H4 hysteresis of microporosity. Activation decreases the carbon yield and enhances the carbon percentage (64.41% - 86.54%). Boehm method shows acidic functional groups such as carboxylic, lactonic and phenolic groups are higher at lower activation temperature and steam activation enhances the basicity. Carbons at higher activation temperature (GACOZC1073 and GACOZC1273) shows a band in the range of 403 – 421 cm⁻¹ is attributed to the basic groups such as cyclic ketones and other

Chapter 4

ketone derivatives. The X-ray photoelectron spectroscopy XPS method depicts that the percentage of carbon (GACOZC1073 - 96.92%) is high which is oxidized, activated at 1073K and impregnation with Zn^{2+} ions. GACOZC1073 shows a lesser percentage of zinc atoms (0.06%) as evidenced by a peak (Binding energy - 1021eV). The GACOZC carbon series studied are having greater interlayer distance ($d_{002} > 0.335$ nm) indicate that carbons exist as non - graphitized forms and these are having well defined porosity. The SEM and TEM analysis shows a regular pore structure throughout the surface of these microporous carbons. Pores are widening and well interconnected under all resolutions. GACOZC1073 shows a high external surface area (752.33 m^2/g) compared to GAC383 and GACO383. In other words, these metal ions incorporated oxidised carbon have an average pore width in the range (1.93 nm - 1.99 nm)obtained by Dubinin - Radushkevich isotherm method confirms the presence of slit shaped micropores (1.9 - 2.0 nm). BJH pore size distribution studies (PSD) showed that adsorption wide or the coarse pore diameter ranges 2.20-2.44 nm and desorption pore width ranges 2.20 -2.36 nm for these granular activated carbons.

Among GACOZC series studied, GACOZC1073 has a higher adsorption efficiency for phenol (304.88 mg/g), p – nitrophenol (377.35 mg/g) and methylene blue (199.20 mg/g). Adsorption kinetic studies showed that that adsorption of phenol, p - nitrophenol and methylene blue (MB) followed pseudo- second order model. The adsorption capacity obtained from different isotherm models (Langmuir, Freundlich, Temkin & Dubinin – Radushkevich isotherm) increases with adsorption temperature indicates the endothermic nature of adsorption. The mean free energy < 8 kJ / mol reveal that phenol, p – nitrophenol and methylene blue (MB) adsorption by GAC follows physical adsorption. Thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) showed that the adsorption



process of phenol, p - nitrophenol and methylene blue was endothermic and spontaneous.

Two way ANOVA test for porosity and surface area studies solid – gas equilibria showed, there is a significant difference between pore volume and surface area obtained from different carbons. GACOZC1073 having significantly higher porosity and surface area compared to GAC383 and GACO383. The three way ANOVA test for the liquid phase adsorption study indicate that there is no significant difference between porosity and surface area calculated by different isotherm models (Langmuir and John – Sivanandan Achari isotherm) and significant difference in porosity and surface area between carbons. There is a significant positive correlation between temperature and adsorption of phenol, p – nitrophenol and methylene blue.

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Chapter 5 GRANULAR ACTIVATED CARBON INCORPORATED WITH NANO ZnO: PREPARATION, CHARACTERISATION AND ADSORPTION STUDIES

5.1 Introduction

This chapter discusses the preparation, characterisation and adsorption properties of specially modified granular activated carbon incorporated with nano zinc oxide under an inert atmosphere provided by super - heated steam. Zinc oxide nano particles are commonly used in the preparation of electronic, magnetic and catalytic materials. It exhibits high catalytic efficiency and strong adsorption capacity [1]. Zinc oxide changed to nano size as it can have the surface area and porosity, could be incorporated into its porous structure. This advantage is seldom used in carbon material science as it may influence the efficiency of granular activated carbon in adsorption studies. In this study the activated carbon GAC383 is incorporated with laboratory prepared nano zinc oxide and activated at different temperature. The resulting carbon is named as GACNZnO383, GACNZnO473, GACNZnO673, GACNZnO873, GACNZnO1073 and GACNZnO1273.This group of carbon are designated as GACNZnO series.

5.2 Preparation of Nano Zinc Oxide (NZnO)

The nano sized ZnO powder was prepared by using 0.1 M zinc acetate [Zn (CH₃COO) ₂. 2H₂O] and 0.15 M oxalic acid [$H_2C_2O_4$. 2H₂O]

Chapter 5

in methanol as solvent [2, 3]. Oxalic acid was mixed with zinc acetate under stirring at 120 rpm at 17 hours at room temperature (Figure 5.1). The intermediate zinc oxalate was formed (Equation 5.1), and it is centrifuged at 5000 rpm and washed with acetone for 3 or 4 times to remove impurities and dried in an oven at 110° C to remove excess water. Nano zinc oxide was prepared by the decomposition of synthesized zinc oxalate at 450° C in a muffle furnace for 2 hours (Equation 5.2).

$$Zn(CH_{3}COO)_{2} \cdot 2H_{2}O + H_{2}C_{2}O_{4} \cdot 2H_{2}O \longrightarrow ZnC_{2}O_{4} \cdot 2H_{2}O + 2CH_{3}COOH + 2H_{2}O$$
(5.1)

 $ZnC_2O_4.2H_2O + \frac{1}{2}O_2 \longrightarrow ZnO + 2CO_2 + 2H_2O$

Figure 5.1: Preparation of nano zinc oxide (NZnO)



(5.2)

Figure 5.2: Nano zinc oxide (NZnO) prepared in the laboratory

5.3 Characterisation Studies of Nano Zinc Oxide

Laboratory prepared nano zinc oxide *NZnO* (Figure 5.2) was characterized by using XRD, SEM, EDAX and TEM analysis to determine the crystallinity and surface morphology.

X - ray diffraction patterns of zinc oxide nano particles prepared in methanol as solvents are shown in Figure 5.3. The characteristic peaks at



the scattering angles $2\theta = 31.83^{\circ}$, 34.47° , 36.23° , 47.48° , 56.58° , 62.83° , 67.96° , 69.04° corresponds to the reflection from the crystal planes (100), (002), (101), (102), (110), (103), (112) and (201). It indicates that these newly prepared nano ZnO is in hexagonal phase with wurtizite structure [4].



Figure 5.3: X -ray diffractograms of methanol mediated nano ZnO

Phase	Width FWHM	20	hkl	Particle size (nm)
	0.420	31.83	100	18.00
	0.380	34.47	002	19.76
ZnO	0.628	36.24	101	11.90
	0.643	47.48	102	11.19
	0.665	56.58	110	10.41
	0.744	62.83	103	9.02
	0.620	67.96	112	10.51

 Table 5.1:
 Estimation of particle size from the X-ray diffractograms of nano ZnO by using full width half maximum

The crystalline size of this nano particle is calculated by using Scherrer formula.

$$D = k(\frac{\lambda}{\beta \cos\theta}) \tag{5.3}$$

k is a constant equal to 0.89, λ is the wavelength (0.15406 nm), β is the full width half maximum and θ is the scattering angle. The crystalline size

of these ZnO particles calculated and presented in Table 5.1. The prepared nano zinc oxide particle size ranges from 9.02 to 19.76 nm.

Figure 5.4 shows the energy dispersive X- ray spectra (EDAX) of nano ZnO and the Table 5.2 depicts the composition of various elements in this prepared nano ZnO sample. The prepared nano zinc oxide particles have Zn (57.85%) and O (42.15%).



Figure 5.4: EDX spectrum of prepared nano ZnO

(Kev)	Mass%	Atom%
0.525	15.13	42.15
8.63	84.87	57.85
	100	100
	(Kev) 0.525 8.63	(Kev) Mass% 0.525 15.13 8.63 84.87 100

Table 5.2: Elemental composition of nano ZnO particles

The Scanning Electron Microscopic (SEM) image of the nano ZnO particles is shown in Figure 5.5 (a) for 5 μ m resolution and 5.5 (b) for 1 μ m resolution respectively. This image shows that the prepared nano zinc oxide particles are spherical in shape and have uniform distribution.

Granular Activated Carbon Incorporated with Nano ZnO: Preparation, Characterization...



Figure 5.5: SEM image of nano ZnO (a) 5 µm resolution (b) 1 µm resolution



Figure 5.6: TEM image of nano ZnO (a) 100 nm magnification, (b) & (c) 50 nm magnification & (d) 20 nm magnification

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 281

High Resolution Transmission Electron Micrograph (HRTEM) is shown in Figure 5.6 under different resolutions. It shows that, the particles are spherical in nature and homogeneous. The particles are shown in the range of 10 - 20 nm. These results are closely matched with XRD (Table 5.1). That means the prepared nano zinc oxide is crystalline and is in hexagonal shape [5]. The low particle size and crystalline structure indicate that, solvent plays a key role in the formation of crystallites of nano zinc oxide particles.

5.4 Effect of Impregnation Ratio on Nano Zinc Oxide / GAC

An amount of 10 g of GAC have been impregnated with different weight of the nano zinc oxide and activated at 873K, and to determine the carbon yield, burn - off and elemental composition (Table 5.3). The result shows that there is no much difference in the percentage of carbon yield, burn - off and elemental carbon. So we choose 0.025 g nano zinc oxide to be impregnated with 10 g of carbons for the preparation of a new series of carbons.

Table 5.3: Impregnation ratio X_{Zn} used, carbon yield, burn - off and elemental
composition obtained during the preparation of carbon GACNZnO
series

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Carbon	Weight of NZnO (g)	X _{Zn} = g zn / g of carbon	Carbon yield (%)	Burn - off (%)	C%	Н%	N%	%0
	0.025	0.0017	83.15	16.85	89.13	0.11	0.18	10.58
	0.05	0.0034	82.59	17.41	86.42	0.11	0.21	13.26
	0.10	0.0067	82.78	17.22	89.96	0.20	0.28	9.56
GACNZnO873	0.20	0.0134	83.16	16.84	89.53	0.25	0.39	9.83
	0.40	0.0269	83.51	16.49	89.76	0.17	0.28	9.79
	0.60	0.0403	83.73	16.27	90.37	0.16	0.40	9.07

5.5 Characterisation Studies of Granular Activated Carbon Impregnated with Nano Zinc Oxide (GACNZnO Series)

The nano sized, crystalline and hexagonal shaped zinc oxide are incorporated to native form of carbon (GAC383) and activated at different temperatures (GACNZnO series) are characterized by using different physico - chemical methods.

5.5.1 Carbon Yield and Burn - off

The Figure 5.7 shows the carbon yield and burn – off pattern of granular activated carbons (GAC383) impregnated with nano zinc oxide (GACNZnO series). The burn – off increases and carbon yield decreases with activation temperature. Non - volatile organic compounds are eliminated at higher activation temperature, to result burn - off increase and yield decrease [6]. The activation takes place in the external and the micropore surface of the granular activated carbon. High thermal activation generates new pores on the surface and the inner pores form wider [7].



5.5.2 Elemental Analysis – CHNOS

The elemental composition of the GACNZnO series is shown in Table 5.4. Thermal activation increases the percentage burn - off due to the removal of non - carbon elements and it enhances the elemental carbon

composition (79.26 – 92.56%). The heteroatom such as hydrogen (0.52 - 0.12%), nitrogen (0.52 - 0.11%) and oxygen (19.88 - 7.17%) decreases with increasing activation temperature from 383-1273K.

SI No:	Carbon	C%	H%	N%	0%0	Carboxylic (meq/g)	Lactones (meq/g)	Phenolic (meq/g)	Base (meq/g)
1	GAC383	89.43	0.60	0.36	9.61	0.40	0.17	0.45	0.50
2	GACO383	65.10	2.61	0.58	31.71	1.38	1.34	2.10	0.20
3	GACNZnO383	79.26	0.52	0.34	19.88	0.42	0.24	0.49	0.45
4	GACNZnO473	81.21	0.34	0.22	18.23	0.40	0.14	0.38	0.55
5	GACNZnO673	84.57	0.14	0.18	15.11	0.35	0.15	0.24	0.55
6	GACNZnO873	89.13	0.11	0.18	10.58	0.30	0.12	0.19	0.65
7	GACNZnO1073	91.91	0.16	0.14	7.79	0.26	0.10	0.15	0.95
8	GACNZnO1273	92.56	0.12	0.11	7.17	0.22	0.11	0.08	0.95

 Table 5.4: Elemental composition and surface functional groups of GACNZnO series

5.5.3 Surface Functional Group Analysis

Characterisation of surface functional groups qualitatively analyzed using Fourier Transform Infrared spectroscopy (FTIR) and quantitatively measured using the Boehm titration method. The FTIR spectra of GACNZnO series are shown in Figure 5.8. The GACNZnO series shows a band between $3426 - 3434 \text{ cm}^{-1}$ [GACNZnO383 (3434 cm^{-1}), GACNZnO473 (3429 cm^{-1}), GACNZnO673 (3429 cm^{-1}), GACNZnO1073 (3434 cm^{-1}) and GACNZnO1273 (3426 cm^{-1})] is ascribed to O – H stretching vibration of hydroxyl groups. The vibration band at 2924 - 2927 cm⁻¹ are attributed to C – H stretching vibration of alkyl groups is absent in lower activation temperatures (GACNZnO383 & GACNZnO473). All the carbons shows a broad band at $1622 - 1637 \text{ cm}^{-1}$ due to aromatic ring stretching or highly conjugated C=C stretching vibrations of olefins. The vibration band at $1400 - 1450 \text{ cm}^{-1}$ is assigned to the presence of

carboxylic groups. Higher activation temperature shows lesser bandwidth. The GACNZnO series of carbon shows band at 1100- 1200 cm⁻¹, is attributed to stretching vibration of primary, secondary and tertiary alcohols, esters and ethers [8]. Activation temperature increases a band observed at 590 - 650 cm⁻¹ is ascribed to the out plane C – H bending mode and a band at a range of 450 - 500 cm⁻¹ is attributed to ZnO stretching.



Figure 5.8: The FTIR spectra of GACNZnO activated at different temperatures

The Table 5.4 shows the acidic and basic functional groups present on these modified granular activated carbons (GAC383, GACO383 and GACNZnO series). Granular activated carbon impregnated with nano ZnO (GACNZnO383) increases the acidic functional groups and decrease the basicity at a small level compared to native form of carbons (GAC383). The steam activation decreases these acidic functional groups and enhances the basic groups. The FTIR spectrum shows that the intensity of acidic functional groups is lesser at higher activation temperature (GACNZnO1273). This carbon shows carboxylic (0.22 meq/g), phenolic (0.01 meq/g), lactonic (0.08 meq/g) and basic (0.95 meq/g) groups. Results show that basic groups increases at higher activation temperatures in the presence of nano ZnO.

5.5.4 XPS Analysis

Table 5.5 shows that elemental carbon was the most abundant constituent in these samples characterised by XPS method. GACNZnO1273 shows highest carbon content (94.35%), lesser oxygen (5.64%) and a smaller percentage of zinc (0.01%). Nitrogen is not detected in this sample. It indicated that zinc impregnation and higher activation removed the surface oxides.

Table 5.5:The elemental composition of the modified granular activated carbons
GAC383, GAC0383 and GACNZnO1273 from XPS analysis

Carbon	C%	O%	N%	Zn%
GAC383	92.96	7.04	-	-
GACO383	86.54	12.86	0.60	-
GACNZnO1273	94.35	5.64	-	0.01



Figure 5.9: XPS spectra of (a) GAC383, (b) GACO383 and (c) GACNZnO1273

Figure 5.9 shows the XPS spectra of GAC383, GACO383 and GACNZnO1273. The elemental compositions of the carbon GACNZnO1273 are obtained from C 1s peak (284 eV).



Figure 5.10: Deconvoluted XPS of GACNZnO1273 (a) C1s region (b) O1s region

C 1s deconvoluted into several components (Figure 5.10 (a)) with binding energy corresponding to aliphatic carbon (283.69 - 284.66 eV), aromatic carbon (285.15 - 285.83 eV), hydroxyl groups (286.16 eV), carbonyl groups (287.11 eV), carboxyl or ester groups (288.32 – 289.56 eV) and a satellite signal due to the π - π shake up in aromatic rings (290.93 eV) [9]. Figure 5.10 (b) shows the deconvoluted O 1s spectra of GACNZnO1273. A peak around 529.50 -530.30 eV shows the presence of metal oxide. The binding energy 531.28 -532.92 eV is observed the presence of carbonyl groups. A peak at binding energy (533.62 eV) depicts the existence of oxygen singly bonded to carbon in ethers and phenols. The peak around 535.96 -537.17 eV shows the presence of chemisorbed oxygen [10].



5.5.5 XRD Analysis

The XRD pattern of GACNZnO series carbons is shown in Figure 5.11. All these carbons show broad peaks at $2\theta = 23.88 - 24.95^{\circ}$ and $2\theta = 43.56 - 44.07^{\circ}$. These peaks are assigned to the reflection from (002) and (10) plane respectively indicates the carbonaceous crystalline structure, forms a better alignment [11]. The structural parameters of these modified carbons (GACNZnO series) are calculated at $2\theta = 23.88 - 24.95^{\circ}$ and presented in Table 5.6. The d_{002} of these GACNZnO series ($d_{002} = 0.36 - 0.37$ nm) shows higher than a typical graphitic carbon (0.335 nm). These non – graphitic carbons have high adsorption efficiency compared to graphitic carbons. The GACNZnO series the stack height ($L_c = 1.11 - 1.55$ nm) and stack width ($L_a = 2.22 - 3.10$ nm) are obtained from the Scherrer equation (Table 5.6). A typical graphitic carbon the stack width is near to 1 - 2 nm, this indicates that these GACNZnO series carbons are amorphous and highly efficient adsorbents.

Carbon	20	L _c (nm)	L _a (nm)	d ₀₀₂ (nm)
GAC383	24.46	1.14	2.28	0.36
GACO383	24.98	0.97	1.94	0.35
GACNZnO383	23.99	1.11	2.22	0.37
GACNZnO473	24.41	1.55	3.10	0.36
GACNZnO673	24.07	1.11	2.22	0.37
GACNZnO873	24.84	1.29	2.58	0.36
GACNZnO1073	24.14	1.29	2.59	0.37
GACNZnO1273	23.85	1.29	2.59	0.37

Table 5.6: Structural parameters from X- ray diffraction studies



Chapter 5

5.5.6 SEM Analysis

Scanning Electron Microscopy is used for the detection of surface morphology and physical characteristics of GACNZnO carbon. The nano zinc oxide impregnation and activation at higher temperature (GACNZnO1273) show a well - developed pore structure (Figure 5.12). Chemical and physical activation process developed the new pores and the existing pores are widening. The zinc oxide nano particles are present in the carbon surface at all resolutions and the presence of nano zinc oxide at higher activation creates more microporosity.



Figure 5.12: SEM image of GACNZnO1273 (a) 100 μm resolution (b) 50 μm resolution (c) 10 μm resolution and (d) 5 μm resolution

5.5.7 TEM Analysis

Figure 5.13 shows the TEM images of modified granular activated carbon (GACNZnO1273) at different resolution. It shows that activation

and incorporation increases the porosity, dark regions are the presence of carbons and light region indicates the presence of the pores. The native (GAC383) and oxidized carbon (GAC0383) already discussed in chapter 3 and 4.



Figure 5.13: TEM image of GACNZnO1273 (a) 10 nm resolution, (b) 5 nm resolution (c) 2 nm resolution (d) 5 1/ nm diffraction pattern

5.6 Porosity Studies – Evaluation of Surface Area and Pore Volume

The Figure 5.14 shows the nitrogen adsorption - desorption isotherm pattern for GAC383 and GACO383, amount adsorbed against different relative pressure. Figure 5.15 depicts the isotherm behavior of granular activated carbon impregnated with nano zinc oxide and activated at 873K (GACNZnO873), 1073K (GACNZnO1073) and 1273K (GACNZnO1273).

Chapter 5

It shows that the activation temperature enhances the amount of nitrogen adsorbed. These carbons show Type I isotherm and H4 hysteresis loop indicate the presence of micro and mesopores. H4 hysteresis loops indicate the presence of slit shaped pores [12].



This nitrogen adsorption – desorption isotherm data of these modified carbons are applied to different isotherm model to identify the surface area, pore volume, pore size distribution etc.

The total pore volume obtained from the relative pressure ($p/p_0 = 0.98$) are shown in Table 5.7. The pore volume increases with activation temperature from 873 - 1273K. Compared to GAC383, the percentage of micropore volume is higher and lesser mesopore volume. Pore width calculated by BET method is in the range of 1.71 -1.74 nm



Granular Activated Carbon Incorporated with Nano ZnO: Preparation, Characterization...

GACIN	LIIO series					
Carbon	V _t [cm ³ g ⁻¹]	V _{mic} [cm ³ g ⁻¹]	V _{mes} [cm ³ g ⁻¹]	Vmic/Vt (%)	Vmes/Vt (%)	Pore Width (nm)
GAC383	0.573	0.351	0.2222	61.26	38.74	1.77
GACO383	0.526	0.297	0.2291	56.46	43.54	1.77
GACNZnO873	0.526	0.328	0.198	62.34	37.66	1.74
GACNZnO1073	0.571	0.355	0.216	62.22	37.78	1.72
GACNZnO1273	0.602	0.403	0.199	67.05	32.95	1.71
$*V_m(cm^3 / g STP)=$	$=\frac{V_m(cm^3)}{2}$	g) x 2241 28	14 x 0.808			

 Table 5.7:
 Textural characteristion of granular activated carbons studied*;

 GACNZnO series
 Gacenary

5.6.1 Brunauer Emmet Teller (BET) Isotherm Model

The Figure 5.16 shows the BET isotherm plot of $1 / [V(p_0 / p) - 1]$ against relative pressure ($p/p_0 = 0.1$) for the modified carbons (GAC383, GAC0383, GACNZnO873, GACNZnO1073 and GACNZnO1273)



Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 293







The porosity and surface area calculated from BET model are shown in Table 5.8. The V_m (*BET*) and *SA* (*BET*) obtained for the modified granular activated carbons are *GACNZnO873* V_m (*BET*) - 277.93 cm³/g STP & *SA* (*BET*) - 1209.88 m²/g), GACNZnO1073 V_m (*BET*) - 304.99 cm³/g STP & *SA* (*BET*) - 1326.99 m²/g) and GACNZnO1273 V_m (*BET*) -277.93 cm³/g STP & *SA* (*BET*) - 1381.79 m²/g). The surface area and monolayer adsorption capacity increase with activation temperatures.

5.6.2 I point Method

The BET - Scatcharad plot or *I point* method $[V(1 - p/p_0)/(p/p_0)]$] against p/p_0 of the modified carbons are shown in Figure 5.17 (a) GAC383, (b) GACO383, (c) GACNZnO873, (d) GACNZnO1073 and (e) GACNZnO1273.

$$[V(1 - \frac{p}{p_0})] / \frac{p}{p_0} = CV_m - (C - 1)[V(1 - \frac{p}{p_0})]$$
(5.5)

The V_{mic} (*I*) obtained from the inversion point of the plot are presented in Table 5.8.

	p/j	p ₀ upto 0.1		p	o/p ₀ upto 0		-	
Carbon	$\begin{array}{c} SA \ (BET) \\ (m^2 \ g^{-1}) \end{array}$	$V_{m}(BET)$ ($cm^{3}g^{-1}$ STP)	C	$\begin{array}{c} SA \ (BET) \\ (m^2 \ g^{-1}) \end{array}$	$\begin{array}{l} V_{m}(BET) \\ (cm^{3}g^{-1} \\ STP) \end{array}$	С	$\sum_{(m^2 g^{-1})}$	$V_{mic}(I)$ (cm ³ g ⁻¹ ST)
GAC383	1298.5	298.31	524	996.8	228.97	-81.58	1271.2	295.40
GACO383	1186.5	279.35	439	973.3	223.79	-118.59	1163.7	266.35
GACNZnO873	1209.9	277.93	510	992.5	228.02	-117.00	1188.1	272.92
GACNZnO1073	1326.9	304.83	533	1083.5	249.00	-113.00	1295.3	297.56
GACNZnO1273	1403.6	322.43	601	1135.1	260.74	-104.95	1381.8	317.42
$*V_{m}(cm^{3}g STP) = \frac{V_{m}(cm^{3}g) \times 22414 \times 0.808}{28}$								

 Table 5.8: Surface area and pore volume* of modified granular activated carbon impregnated with nano ZnO

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 295

The surface area calculated from this inversion point of these modified carbons is GAC383 (1271.18 m^2/g), GACO383 (1163.70 m^2/g), GACNZnO873 (1188.08 m^2/g), GACNZnO1073 (1295.34 m^2/g) and GACNZnO1273 (1381.79 m^2/g).

A comparative study of surface area determined by using BET and I plot method for the modified carbons (GAC383, GACO383, GACNZnO873, GACNZnO1073 and GACNZnO1273) is shown in Figure 5.18 [13]. A perfect matching is observed in all cases of new carbons studied. The correlation coefficient between the carbons of this plot are $R^2 = 0.99$.

5.6.3 Langmuir Isotherm

The Langmuir isotherm models for the modified carbons are shown in Figure 5.19 and the constants are presented in Table 5.9.

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m}$$
(5.6)

The Langmuir adsorption capacity (V_m) and Langmuir energy constant (K_L) are calculated from the slope and intercept of a straight line plot P/V against P. The $V_m(L)$ of the modified carbons are GAC383 (367.14 cm³/g STP), GACO383 (330.19 cm³/g STP), GACNZnO873 (360.06 cm³/g STP), GACNZnO1073 (370.11cm³/g STP) and GACNZnO1273 (388.12 cm³/g STP). The correlation coefficient ($R^2 = 0.99$) for all the carbons indicates that nitrogen adsorption occurs through a homogenous surface of the modified carbons. Langmuir isotherm model (Figure 5.17) shows that adsorption capacity increases with activation temperature. The Langmuir surface area calculated from the monolayer adsorption capacity is GAC383 (1598.24 m²/g), GACO383 (1476.58 m²/g), GACNZnO873 (1567.40 m²/g), GACNZnO1073 (1611.20 m²/g) and GACNZnO1273 (1689.70 m²/g).

5.6.4 Freundlich Isotherm

The empirical isotherm model Freundlich applied to nitrogen isotherm data for the modified granular activated carbons are shown in Figure 5.20 and the Freundlich constants are presented in Table 5.9.

$$\log V = \log K_F + 1 / n \log P \tag{5.7}$$

The correlation coefficient (R^2 is in the range of 0.95 – 0.97) indicate that Langmuir adsorption isotherm is more comparable with experimental data of nitrogen isotherm for these carbons. The adsorption capacity (K_F) increases with increasing activation temperature in the order GACNZnO1273 (258.40 cm³/g STP) > GACNZnO1073 (237.49 cm³/g STP) > GACNZnO873 (214.48 cm³/g STP). The adsorption intensity nranges between 12.58 - 15.57 indicate that N2 adsorption by modified carbon is a physisorption process.

Table 5.9: Porosity parameters of granular activated carbon impregnated with nano ZnO ions calculated from Langmuir, Freundlich and John isotherm model : GACNZnO series

Carbon	Langmuir Isotherm Model			Freundlich Isotherm Model			John Isotherm Model			
	$\begin{array}{c} SA\left(L\right)\\ (m^{2}g^{-1})\end{array}$	$V_m(L)^*$ (cm ³ g ⁻¹ STP)	\mathbf{R}^{2}	K _F (cm ³ g ⁻¹ STP)	u	\mathbf{R}^2	$\frac{SA (J)}{(m^2 g^{-1})}$	$V_m(J)^*$ (cm ³ g ⁻¹ STP)	u	\mathbf{R}^2
GAC383	1598.2	367.1	0.99	231.4	13.91	0.97	1610.0	369.9	3.22	0.99
GACO383	1476.6	339.0	0.99	202.7	12.68	0.97	1503.9	345.5	2.84	0.99
GACNZnO873	1567.4	360.0	0.99	214.5	14.28	0.97	1498.0	344.1	3.13	0.99
GACNZnO1073	1611.2	370.1	0.99	237.5	14.55	0.97	1616.0	371.2	3.21	0.99
GACNZnO1273	1689.7	388.1	0.99	258.4	15.57	0.95	1695.0	389.4	3.55	0.99
$V_m (cm^3 / g) = \frac{V_1}{V_1}$	$\frac{n}{22414}$	g STP) x x 0.808	28							

5.6.5 John Isotherm Analysis

The Figure 5.21 shows the John isotherm model log V against loglog P for the modified granular activated carbons. The limiting micropore volume $V_m(J)$ calculated from John isotherm model is comparable with Langmuir adsorption capacity $V_m(L)$ indicate that these modified carbons are highly microporous.

$$log log P = C + n \log V \tag{5.8}$$

The surface area obtained from John isotherm model are GAC383 (1610.00 m²/g), GACO383 (1503.90 m²/g), GACNZnO873 (1498.00 m²/g), GACNZnO1073 (1616.00 m²/g) and GACNZnO1273 (1695.01 m²/g).

5.6.6 Alpha S (α_s) Isotherm

The micropore volume and external surface area of these modified granular activated carbons (GAC383, GACO383, GACNZnO873, GACNZnO1073 & GACNZnO1273) are calculated by α_s isotherm method (Table 5.10).

$$A_s = 2.86 \frac{V}{\alpha_s} \tag{5.9}$$

Linear plots of volume of nitrogen adsorbed against α_s are shown in Figure 5.22. The surface area determined from this method (A_s) for the modified carbons are GAC383 (1005.26 m²/g), GACO383 (930.30 m²/g), GACNZnO873 (935.93 m²/g), GACNZnO1073 (1026.08 m²/g) and GACNZnO1273 (1074.01 m²/g).









5.6.7 Dubinin Radushkevich (D – R) Isotherm

Dubinin Radushkevich isotherm model (Figure 5.23) is commonly used to determine the microporous surface area and to determine the process of adsorption using mean activation energy.

$$logV = logV_0 - D \log^2(p_0 / p)$$
(5.10)

$$D = 2.303 \left(\frac{RT}{\beta E_0}\right)^2$$
(5.11)

$$L_{av} = 6.6 - 1.79 \ln E_0 \tag{5.12}$$

The microporus surface area (S_{mi}), micropore volume (V_0), mean activation energy (E_0) and pore width (L) obtained for the modified carbons are GAC383 (646.63 m²/g, 351.21 cm³/g STP or 0.543 ml/g, 15.62 kJ/mol and 1.68 nm), GACO383 (571.43 m²/g, 323.40 cm³/g STP or 0.500 ml/g,
15.57 kJ/mol and 1.75 nm), GACNZnO873 (600.65 m²/g, 327.48 cm³/g STP or 0.506 ml/g, 15.57 kJ/mol and 1.69 nm) GACNZnO1073 (662.79 m²/g, 358.98 cm³/g STP or 0.555 ml/g, 15.68 kJ/mol and 1.67 nm) and GACNZnO1273 (716.73 m²/g, 378.38 cm³/g STP or 0.585 ml/g, 16.04 kJ/mol and 1.63 nm). The nano Zinc oxide impregnation and activation at higher temperature for these modified carbons shows higher micropore volume and micropore surface area and lower pore width. The mean activation energy of these modified carbons shows adsorption of nitrogen by these carbons follows physical process.

Table 5.10: Dubinin – Radushkevich (D-R) and alpha S (α_s) constants of the modified carbons

Carbon		D-l	R Isothern	n		a _s Ise	otherm
	L (D-R) (nm)	E ₀ (D-R) (kJ/mol)	V ₀ * (D-R) (ml/g)	S_{mi} (D-R) (m^2/g)	R ²	V_{mi}^{*} (ml/g)	$\begin{array}{c} A_s \\ (m^2/g) \end{array}$
GAC383	1.68	15.62	0.543	646.43	0.97	0.543	1005.26
GACO383	1.75	15.02	0.500	571.43	0.96	0.503	930.30
GACNZnO873	1.69	15.57	0.506	600.65	0.99	0.506	935.93
GACNZnO1073	1.67	15.68	0.555	662.79	0.99	0.555	1026.08
GACNZnO1273	1.63	16.04	0.585	716.73	0.99	0.581	1074.01
$V_m(cm^3 / g STP) =$	$=\frac{V_m(cm^3)}{cm^3}$	/g)x224 28	414 x 0.80	08			

The Figure 5.24 shows the agreement of micropore volume from the D-R method and α_s for all these modified carbon studied, as it shows a straight line plot with a high correlation coefficient ($R^2 = 0.99$). It indicates that the micropore volume calculated from these two methods is almost same.

5.6.8 *t* – *plot* Method

The Figure 5.25 (a) GAC383 and GACO383 and (b) GACNZnO873, GACNZnO1073 and GACNZnO1273 shows the t - *plot* model, adsorbed quantity (mmol/g) against the thickness of the modified granular activated carbons.

$$t = [13.99 / (0.034 - \log(p / p_0))]^{0.5}$$
(5.13)

The micropore volume, external surface area and mesopore surface area are presented in Table 5.11. The external surface area (SA_{ext}) obtained from t - plot method are GAC383 (408.10 m²/g), GACO383 (433.72 m²/g), GACNZnO873 (377.11 m²/g), GACNZnO1073 (424.10 m²/g) and GACNZnO1273 (374.44 m^2/g). The micropore surface area calculated by subtracting external surface area from BET surface area for the modified GAC383 (588.66 m^2/g), GACO383 (540.59 m^2/g), carbons are (617.13 m²/g), GACNZnO1073 (659.68 m²/g) and GACNZnO873 GACNZnO1273 (760.64 m²/g). It shows that GACNZnO1273shows higher micropore surface area and GACNZnO1073 higher external surface area for the GACNZnO series studied at higher activation temperatures. The micropore surface area calculated from D - R method and t - plot method are comparable and error percentage < 10.



Figure 5.25: *t - plot* of modified granular activated carbons (a) GAC383 & GAC0383, (b) GACNZn0873, GACNZn01073 & GACNZn01273



Figure 5.26: BJH Pore size distribution of modified granular activated carbons GAC383, GACO383, GACNZnO873, GACNZnO1073 & GACNZnO1273 (a) BJH adsorption cumulative pore volume against pore width & (b) BJH desorption cumulative pore volume against pore width (c) BJH desorption dV/dW pore volume versus pore width (d) BJH desorption dV/dlogW pore volume against pore width

5.6.9 Barret Joyner Halenda (BJH) Pore Size Distribution

The pore size distribution of the modified carbons is obtained by BJH adsorption - desorption plot (Figure 5.26) using the pore volume against pore width. The modified carbons have a pore width in the range of 1.65 - 1.75 nm is using D - R and BET method, but the BJH pore size distribution shown in Figure 5.26 (d), the pore size is in the range of 25 - 35 A⁰ (2.5 - 3.5 nm). The pore width calculated from BJH adsorption and

desorption method for the modified carbons are GAC383 (2.44 nm & 2.43 nm), GACO383 (2.28 nm & 2.25 nm), GACNZnO873 (2.29 nm & 2.23 nm), GACNZnO1073 (2.20 nm & 2.15 nm) and GACNZnO1273 (2.35 nm & 2.28 nm). The result shows that the modified carbons have a pore width ranges from 2.0 - 2.5 nm, which indicate that mesopore are also present in these modified carbons [14].

The cumulative surface area of these new carbons are calculated by using the equation

$$SA_{cum}(m^2 / g) = 2\sum V_{pi} \sum r_{pi}$$
 (5.14)

The cumulative adsorption and desorption surface area obtained from these modified carbons are GAC383 (226.21 m²/g & 220.52 m²/g), GACO383 (250.00 m²/g, 242.84 m²/g), GACNZnO873 (207.65 m²/g, 217.95 m²/g), GACNZnO1073 (230.72 m²/g, 242.43 m²/g) and GACNZnO1273 (203.34 m²/g, 217.43 m²/g). The adsorption desorption pore volume is in the range 0.119-0.142 cm³/g.

Table 5.11: Surface area and pore size distribution using t - plot and BJH isotherm

		t Plot			J	BJH Isot	herm		
Carbon	V _{mi*} (cm ³ /g)	$\frac{SA_{ext}}{(m^2/g)}$	$\frac{{\rm SA}_{\rm mi}}{({\rm m}^2/{\rm g})}$	ADCSA (m ² /g)	DECSA (m ² /g)	ADCPV* (cm ³ /g)	DECPV* (cm ³ /g)	Pore Width Ad (nm)	Pore Width De (nm)
GAC383	0.351	408.10	588.66	226.21	220.52	0.138	0.134	2.44	2.43
GACO383	0.297	433.72	540.59	250.00	242.84	0.142	0.137	2.28	2.25
GACNZnO873	0.328	377.11	617.13	207.65	217.95	0.119	0.122	2.29	2.23
GACNZnO1073	0.355	424.10	659.68	230.72	242.43	0.127	0.130	2.20	2.15
GACNZnO1273	0.404	374.44	760.64	203.34	217.43	0.119	0.124	2.35	2.28
$V_m(cm^3 / g ST)$	$(P) = \frac{V_m}{M}$	(cm^3 / g)	$\frac{1}{28}$) x 224	14 x 0.80	08				

5.7 Liquid Phase Adsorption Study

The liquid phase adsorption of phenol, p –nitrophenol and methylene blue (MB) by modified carbons (GACNZnO) are investigated. For this detailed study of adsorbent (GACNZnO) and adsorbate (phenol, p –nitrophenol and methylene blue) interaction, a carbon having a good adsorption capacity is selected from GACNZnO series as a better adsorbent.

5.7.1 Adsorption Studies – Phenol as Adsorbate

An adsorption study of phenol includes selection of carbon, adsorption kinetics, adsorption isotherms and thermodynamic study using the GACNZnO and comparison study using GAC383 and GACO383 is being done.

5.7.1.1 Selection of GACNZnO for Phenol Adsorption

GACNZnO carbon from series (GACNZnO383. Select а GACNZNO473. GACNZnO673. GACNZnO873, GACNZnO1073 & GACNZnO1273) an initial concentration of 1000 mg/L phenol is used as adsorbate after 8 hr equilibration period. The amount adsorbed (mg/g) against the modified carbons are shown in Figure 5.27. It shows that the adsorption efficiency of GACNZnO series increases with activation temperature. GACNZNO1273 (297.65 mg/g) shows highest removal efficiency for phenol than other carbons. This carbon shows a high basic group (0.85 meq/g), carbon content (92.56%), BET surface area (1135.08 m²/g) micropore volume (261.31 cm³/g STP or 0.404 cm³/g) and micropore surface area $(760.64 \text{ m}^2/\text{g})$ compared to others.





Figure 5.27: Amount of phenol adsorbed by members of GACNZnO series ($C_0 = 1000 \text{ mg/L}$)

5.7.1.2 Effect of Temperature and Time on the Adsorption of Phenol on GAC383, GACO383 and GACNZnO1273:

The Figure 5.28 (a) GAC383, (b) GACO383 and (c) GACNZnO1273 presents the effect of concentration on contact time on the phenol adsorption for different temperature ranging from 10° C to 50° C. It indicates that time and temperature enhances the removal of phenol. Phenol adsorption equilibrium was attained at 8 hr. The amount adsorbed at equilibrium (*q_eexp*) at temperatures are ranging from GAC383 (121.61–138.76 mg/g), GACO383 (118.38-132.84 mg/g) and GACNZnO (129.87-165.88 mg/g). The GACNZnO1273 shows highest adsorption capacity compared to others. Nano zinc oxide impregnation and activation increases the microporosity and it enhances the adsorption efficiency.





Figure 5.28: Effect of contact time on the adsorption of phenol on (a) GAC383 (b) GAC0383 & (c) GACNZnO1273 at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$

5.7.1.3 Kinetic Modelling

The time dependant phenol adsorption data (Figure 5.28) are subjected to different kinetic models such as Lagergren first order, Ho second order, Weber intraparticle diffusion model and Boyd model determine the adsorption mechanism and rate controlling step for the adsorption of phenol by modifying carbons (GAC383, GACO383 & GACNZnO1273).

Lagergren pseudo first order model [15] is applied for the phenol adsorption on these modified carbons GAC383, GACO383 and GACNZnO1273.

$$ln(q_{e} - q_{t}) = ln q_{e} - K_{1} t$$
(5.15)

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 307

A linear plot of $ln (q_e - q_t)$ against time *t* is shown in Figure 5.29 (a), (b) & (c). From the slope and intercept of the straight line plot gives a first order rate constant (K_1) and amount adsorbed (q_ecal) are presented in Table 5.12. The correlation coefficient of a first order model of phenol adsorption is less than 0.99 (R^2 ranges 0.87 - 0.96). The batch kinetic data (q_eexp) did not agree with the q_e calculated (q_ecal) of the first order. This indicates that the adsorption of GAC383, GACO383 and GACNZnO1273 on phenol did not follow this model.

The Table 5.12 shows the amount adsorbed ($q_e cal$) and second order rate constant (K_2) gives the slope and intercept of the straight line plot of t/q_t vs t (Figure 5.30 (a), (b) & (c)).

Carbon	T	q _e exp	First o	order Kine	etics	Seco	ond order kinet	ics
	(K)	(<i>mg/g</i>)	<i>q_ecal</i> (mg/g)	$\frac{K_1}{(min^{-1})}$	R^2	q _e cal (mg/g)	K_2*10^4 (gmg ¹ min ⁻¹)	R^2
	283	121.61	86.99	0.007	0.96	135.14	1.24	0.99
	293	126.41	88.72	0.007	0.97	137.93	1.40	0.99
GAC383	303	129.99	84.02	0.007	0.95	139.47	1.59	0.99
	313	134.93	84.76	0.007	0.96	143.06	1.83	0.99
	323	138.76	80.16	0.007	0.95	145.14	2.09	0.99
	283	118.38	75.83	0.006	0.94	124.53	1.80	0.99
	293	122.27	73.27	0.005	0.93	126.42	2.10	0.99
GACO383	303	125.99	71.43	0.006	0.93	130.21	2.30	0.99
	313	129.63	70.72	0.006	0.94	133.69	2.50	0.99
	323	132.84	69.31	0.006	0.95	136.43	2.70	0.99
	283	129.87	69.50	0.006	0.96	133.69	2.70	0.99
	293	136.68	63.28	0.005	0.95	137.55	3.10	0.99
GACNZnO1273	303	142.44	63.09	0.005	0.92	143.06	3.10	0.99
	313	154.41	59.73	0.005	0.87	155.28	3.60	0.99
	323	165.88	65.00	0.007	0.94	169.20	3.80	0.99

Table 5.12: Comparison of the pseudo first and second order constants and parameters for the adsorption of phenol: $C_0 = 250 \text{ mg/L}$





$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$
(5.16)

The second order rate constant (K_2) and amount adsorbed $(q_e cal)$ increases with temperature indicating that the adsorption is an endothermic process. The q_e calculated $(q_e cal)$ from the second order model are close to experimental data $(q_e exp)$ and the correlation coefficient $(R^2 = 0.99)$ for all the carbons studied. It indicates that the pseudo second order model follows phenol adsorption by the selected carbon at the temperature studied.

Weber and Morris (1963) [16] intraparticle diffusion model is used to determine the adsorption mechanism and the rate controlling step for the adsorption of phenol by modified carbons.

$$q_t = K_{id} t^{0.5} + C \tag{5.17}$$

The amount adsorbed against the square root of time gives two straight line portions as shown in Figure 5.31 (a) (b) & (c). The first portion is attributed to surface adsorption and the second linear portion is attributed to intraparticle diffusion. The K_{id1} (ranges 8.57 - 15.33 mgg⁻¹min^{-1/2}) is higher than the K_{id2} (ranges 1.95 - 3.66 mgg⁻¹min^{-1/2}) for all carbons indicating that pore diffusion is a slow step (Table 5.13). Slow step is the rate controlling step for the adsorption of phenol on modified carbons. The boundary layer thickness increases with temperature for the carbon studied. The boundary layer effect obtained from the particle diffusion step is a greater effect than the surface diffusion steps shown in Table 5.13 [17]. Higher the intercept higher the boundary layer thickness and it ranges from GAC383 (52.67 – 76.33 mg/g), GACO383 (56.42 - 80.12 mg/g) and GACNZnO1273 (72.73 -123.76 mg/g) at temperatures studied.

Chapter 5

			Intrap	article d	liffusion co	onstant	
Carbon	T (K)	$\mathbf{K}_{\mathrm{id1}}$ (\mathbf{mgg}^{-1} $\mathbf{min}^{-1/2}$)	C ₁ (mgg ⁻¹)	\mathbf{R}^{2}	${f K_{id2}} ({f mgg}^{-1})$	C ₂ (mgg ⁻¹)	\mathbf{R}^2
	283	14.49	-29.90	0.97	3.22	52.67	0.98
	293	14.40	-24.96	0.99	3.36	54.82	0.98
GAC383	303	15.33	-25.13	0.97	3.18	61.59	0.98
	313	14.29	-13.35	0.99	3.17	67.43	0.97
	323	14.16	-6.98	0.99	2.88	76.33	0.99
	283	11.28	-10.05	0.98	2.77	56.42	0.99
	293	11.05	-3.68	0.99	2.68	61.33	0.97
GACO383	303	11.32	0.299	0.99	2.43	71.14	0.98
	313	11.15	6.68	0.98	2.43	75.56	0.99
	323	10.49	15.03	0.99	2.37	80.12	0.99
	283	10.27	14.05	0.99	2.61	72.73	0.99
	293	8.57	33.99	0.98	2.76	74.71	0.99
GACNZnO1273	303	9.17	36.18	0.98	2.64	82.47	0.96
	313	11.78	36.04	0.95	2.28	102.71	0.96
	323	11.74	46.13	0.97	1.95	123.76	0.99

Table 5.13: Intraparticle diffusion constants for phenol adsorption on carbonsGAC383, GAC0383 and GACNZnO1273 for $C_0 = 250 \text{ mg/L}$

The Figure 5.32 (a), (b) & (c) shows the Boyd model for the phenol adsorption by modified granular activated carbons GAC383, GACO383 and GACNZnO1273 respectively.

$$B_t = -0.4977 - \ln(1 - F) \tag{5.18}$$

A plot of *Bt* versus *time* shows that plots were scattered and do not pass through the origin. It indicates that the phenol adsorption by modified carbons governed by external mass transport or surface diffusion and intraparticle diffusion is the rate controlling step [18].

The activation energy of phenol adsorption by modified carbons are determined by using the second order rate constant and it is based on Arrhenius equation.



Granular Activated Carbon Incorporated with Nano ZnO: Preparation, Characterization...

$$\ln K_2 = \ln K_0 - \frac{E_a}{RT} \tag{5.19}$$

The second order rate constant (K_2) increases with temperature. A plot of lnK_2 against 1/T gives the activation energy from the slope of the plot (Figure 5.33). Table 5.14 shows activation energy (E_a) obtained from this Arrhenius plot are GAC383 (10.00 kJ/mol), GACO383 (7.59 kJ/mol) and GACNZnO1273 (6.61 kJ/mol). The $E_a < 40$ kJ/mol indicates that the adsorption of phenol by these modified carbons follows physisorption.



Figure 5.33: plot of lnK_2 versus1/T for the determination of activation energy for the adsorption of phenol on GAC383, GACO383 & GACNZnO1273

Table 5.14: Activation energy determined during adsorption of phenol on
GAC383, GACO383 and GACNZnO1273

Carbon	E _a (kJmol ⁻¹)	K ₀
GAC383	10.00	0.0086
GACO383	7.59	0.0046
GACNZnO1273	6.61	0.0045

5.7.1.4 Adsorption Isotherm Studies of Phenol

The Figure 5.34 (a) – (e) shows the general isotherm plot at different adsorption temperature (10^{0} C - 50^{0} C). The amount adsorbed at equilibrium

 (q_e) against phenol concentration at equilibrium (C_e) shows a Type I isotherm pattern. The amount of phenol adsorption enhances with initial concentrations and temperature. The standard isotherm model (Figure 5.34) shows that GACNZnO1273 shows highest phenol adsorption capacity compared to other two carbons. GACNZnO1273 has a carbon content (92.56%), basic group (0.95 meq/g), BET surface area (1403.60 m²/g), micropore volume (261.31 cm³/g STP or 0.404 cm³/g) and micropore surface area (760.64 m²/g). These factors contribute to improve the phenol adsorption capacity.

This equilibrium isotherm data apply to different isotherm models such as Langmuir isotherm, Freundlich isotherm, Temkin isotherm and Dubinin – Radushkevich isotherm to determine the characteristic constant and maximum adsorption capacity.

Langmuir isotherm based on the assumption that the adsorption occurs in homogeneous surface of the carbon with uniform distribution of energy level.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e \tag{5.20}$$

Langmuir concept is that adsorption occurs only in one site leads to monolayer adsorption. The monolayer adsorption capacity (q_{max}) and Langmuir energy constant (K_L) calculated from the slope and intercept are presented in Table 5.15. A linear plot of C_e/q_e versus Ce is shown in Figure 5.35 (a), (b) & (c). The q_{max} and K_L increases with temperature indicating that adsorption is endothermic. The monolayer adsorption capacity increases with temperature in the order GACNZnO1273 (330.03 – 414.94 mg/g) > GAC383 (266.37 – 352.17 mg/g) > GACO383 (188.32 – 236.97 mg/g). GACNZnO1273 shows the highest monolayer adsorption capacity compared to other two carbons. The BET surface area, carbon percentage and basic surface functional groups play a dominant role for the adsorption of phenol by modified carbons.



Figure 5.34: Adsorption of phenol on GAC383, GACO383 and GACNZnO1273 at different temperature (a) 10^{0} C, (b) 20^{0} C (c) 30^{0} C (d) 40^{0} C & (e) 50^{0} C for initial concentration C₀ = 25 - 3000 mg/L

The Figure 5.36 (a), (b) & (c) shows straight lines plot of $log q_e$ against $log C_e$ for the adsorption of phenol on modified carbons at different temperature ranging from 10 - 50^oC.

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics **315**



	Tab	ole 5.15:	Langn	nuir, Fre	eundlich,	Temkiı	1 and D	ubinin –	Radushk	evich isc	otherm p	oaramete	LS		
		Langm	uir Con	stants	Freund	lich Con	stants	É	emkin Co	onstants		Dubi	nin Radı Consta	ushkevi nts	ch
Carbon	(K) L	(mgg ⁻¹) اسعد	(ן של _{-ז}) א ^ר	۲ ²	(w88 ₋₁) K ^k	u	В ₅	(Sm/l) A	В	(Iom/L) DT	к	Q _D (D-R) (mgg ⁻¹)	(кาшоl ₋₁) (D-К) Е ⁰	(mol ₅ 1- ²⁾ B	В ₅
	283	266.67	2.33	0.99	16.38	2.60	0.93	0.189	43.10	52.66	0.98	55.52	0.267	7.03	0.98
	293	284.90	2.48	0.99	16.74	2.56	0.94	0.188	46.14	49.19	96.0	56.62	0.289	6.01	0.98
UAU303	303	312.50	2.48	66.0	16.73	2.49	96.0	0.175	50.47	44.97	66.0	57.39	0.293	5.83	0.98
	313	336.70	2.53	0.99	17.00	2.44	0.95	0.171	53.96	42.06	0.98	58.39	0.340	4.34	0.98
	323	352.12	2.68	66.0	17.38	2.42	0.95	0.172	56.33	40.29	96.0	59.22	0.362	3.81	86.0
	283	188.32	2.17	0.99	19.16	3.17	0.89	0.370	27.90	81.35	66.0	54.89	0.247	8.19	0.98
	293	199.60	2.34	0.99	19.87	3.13	0.89	0.370	29.61	76.64	66.0	56.10	0.273	6.71	0.98
UACU383	303	209.64	2.48	66.0	20.71	3.12	0.89	0.379	30.98	73.26	66.0	57.41	0.302	5.50	0.98
	313	225.73	2.52	66.0	21.13	3.05	06.0	0.360	33.34	68.08	66.0	58.76	0.328	4.65	0.98
	323	236.97	2.59	66.0	21.66	3.02	06.0	0.360	34.88	65.07	66.0	59.29	0.359	3.89	0.98
	283	330.03	2.25	0.99	18.74	2.59	96.0	0.200	49.95	45.44	96.0	56.20	0.429	2.71	0.98
	293	344.83	2.45	66.0	19.98	2.60	0.97	0.216	51.56	44.02	0.97	56.22	0.473	2.24	0.97
CI2100200	303	383.14	2.81	66.0	25.03	2.73	0.98	0.310	53.02	42.81	0.94	58.35	0.863	0.67	0.95
	313	398.41	3.40	0.99	29.08	2.82	0.97	0.412	53.66	42.30	66.0	59.65	1.08	0.43	0.95
	323	414.94	3.90	0.99	33.42	2.92	0.97	0.539	53.90	42.11	66.0	62.66	1.27	0.31	0.95

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics **317**

$$\log q_e = \log K_F + 1 / n \log C_e \tag{5.21}$$

The adsorption capacity (K_F) and process intensity (n) were calculated from the slope and intercept of the Freundlich plot and are presented in Table 5.15. The n > 1 indicate that adsorption is favourable for all the carbons studied. The K_F increases with temperature indicate that adsorption of phenol is endothermic nature. The correlation coefficient $(R^2 = 0.99)$ was found to be high for the Langmuir isotherm model compared to the Freundlich model applied $(R^2 ranges 0.87 - 0.98)$. It indicates that phenol adsorption occurs on a homogenous carbon surface.

The Figure 5.37 (a), (b) & (c) shows the Temkin plot of q_e versus lnC_e for the adsorption of phenol by modified carbons.

$$q_e = B \ln A + B \ln C_e \tag{5.22}$$

$$B = \frac{RT}{b_T}$$
(5.23)

The equilibrium binding constant (*A*) and a constant related to heat of adsorption (*B*) gives the intercept and slope of the plot respectively and are listed in Table 5.15. The heat of adsorption (*B*) increases with temperature for phenol adsorption by modified carbons, GAC383 (43.10 - 56.33), GACO383 (30.98 - 34.88) and GACNZnO1273 (36.22 - 45.58). It indicates that adsorption is endothermic and the adsorption energy (b_T) decreases with temperature and it is less than 80 kJ/mol indicating that adsorption occurs through physical force of attraction.





Figure 5.37: Temkin isotherm model of phenol on (a) GAC383, (b) GACO383 & (c) GACNZnO1273 by different temperatures for C₀: 25 – 3000 mg/L

The Dubinin - Radushkevich (D-R) isotherm model for phenol adsorption is applied only in the case of lower concentration of phenol adsorption on modified carbons.

$$lnq_e = lnQ_D - \beta\varepsilon^2 \tag{5.24}$$

$$E_0 = \frac{1}{(2\beta)^{1/2}}$$
(5.25)

The D - R constant are calculated and presented in Table 5.15. The adsorption capacity (q_m) increases with temperature for all the modified

Chapter 5

carbons studied. The mean activation energy (E_0) calculated from the activity coefficient (β) is less than 8 kJ/mol indicating that adsorption of phenol by modified carbons show physisorption mechanism.

5.7.1.5 Thermodynamic Study

The thermodynamic parameters such as Gibbs free energy change (ΔG) , change in enthalpy (ΔH) and entropy (ΔS) are calculated and presented in Table 5.16.



Figure 5.38: ΔG versus Temperature for the determination of thermodynamic parameters for the adsorption of phenol by (a) GAC383, (b) GAC0383 & (c) GACNZnO1273

 $\Delta G = -RT lnK_{T}$ (5.26)

$$\Delta G = \Delta H - T \,\Delta S \tag{5.27}$$

A plot of ΔG against Temperature (T) gives a straight line plot with slope ΔS and intercept ΔH are shown in Figure 5.38. The ΔG calculated using Langmuir constant (K_L) decreases with increasing temperature indicating that adsorption is favorable at higher temperature and the negative results implied the feasibility and spontaneous nature of the adsorption of phenol.

The positive ΔH (GAC383 = 2.26 kJmol⁻¹, GACO383 = 3.30 kJmol⁻¹ and GACNZnO1273 = 10.91 kJmol⁻¹) indicating that adsorption is endothermic and it is less than 40 kJ/mol identified that adsorption of phenol by modified carbons occurs though weak Van der Walls interactions that means adsorption is physisorption. The positive ΔS $(GAC383 = 14.93 \text{ Jmol}^{-1}\text{K}^{-1}, GACO383 = 18.26 \text{ Jmol}^{-1}\text{K}^{-1}$ and GACNZnO1273 = 44.92 $\text{Jmol}^{-1}\text{K}^{-1}$) indicate that adsorption leads more randomness.

Table 5.16: Thermodynamic parameters – Gibbs free energy, enthalpy and entropy for the adsorption of phenol on new carbons

Carbon		ΔΟ	G (kJmol ⁻¹)		ΔH	ΔS
Carbon	283	293	303	313	323	(kJmol ⁻¹)	(Jmol ⁻¹ K ⁻¹)
GAC383	-1.94	-2.18	-2.24	-2.35	-2.59	2.26	14.93
GACO383	-1.82	-2.07	-2.29	-2.41	-2.55	3.30	18.26
GACONZnO1273	-1.91	-2.19	-2.60	-3.18	-3.65	10.91	44.92

5.7.2 Adsorption Studies of *p* –nitrophenol

The adsorption studies of p – nitrophenol includes the selection of carbon, adsorption kinetics, isotherm and thermodynamic studies using the native form of carbon (GAC383), oxidized carbon (GAC0383) and native form impregnated with nano ZnO and activated at different temperatures (GACNZnO series).

5.7.2.1 Selection of Carbon

Select a carbon from GACNZnO series for the detailed study for the removal of p – nitrophenol in the liquid phase adsorption using an initial concentration of 1000 mg/L p – nitrophenol at different time interval ranging from 10 minutes to 600 minutes. The removal of p –nitrophenol increases with respect to time. The Figure 5.39 shows that GACNZnO1273 shows higher adsorption capacity compared to other carbon from this series. GACNZnO1273 show high basic group content (0.95 meq/g) and a high carbon percentage (92.56%), BET surface area (1403.60 m²/g), total pore volume (375.95 cm³/g STP or 0.602 cm³/g) compared to other carbons.



Figure 5.39: Effect of contact time and amount of *p* -nitrophenol adsorbed for the adsorption on GACNZNO activated at different temperatures for initial concentration $C_0 = 250 \text{ mg/L}$

5.7.2.2 Adsorption Kinetics

The adsorption kinetic studies of p – nitrophenol on modified carbons (GAC383, GACO383 and GACNZnO1273) were studied using an initial concentration of 250 mg/L at different temperature ranging from 10, 20, 30, 40 and 50^oC. The amount adsorbed (q_e) against different time interval of modified carbons at different temperature is shown in Figure 5.40 (a) – (e). The amount adsorbed increases with time and temperature.





Figure 5.40: Effect of contact time on the adsorption of p -nitrophenol on GAC383, GACO383 and GACNZnO1273 at different temperature (a) 10^{0} C, (b) 20^{0} C, (c) 30^{0} C, (d) 40^{0} C & (e) 50^{0} C for initia concentration C₀ = 250 mg/L

Chapter 5

GACNZnO1273 shows higher p – nitrophenol adsorption (q_e) compared to other carbons studied. Removal of p - nitrophenol from aqueous media to GACNZnO1273 surface increases with temperature (10^{0} C – 84.19%, 20^{0} C – 85.78%, 30^{0} C – 86.61%, 40^{0} C – 92.83% and 50^{0} C – 95.54%). The percentage removal increases in the range of GAC383 (80 - 87%) and GACO383 (47 - 55%). The oxidised carbon GACO383 shows lowest adsorption capacity because of the electrostatic repulsion between the acidic surface functional groups on GACO383 and p –nitrophenol.

These time depend adsorption data are applied to different kinetic models such as pseudo first order model, Ho second order, intraparticle diffusion model and Elovich model to determine the mechanism of p – nitrophenol adsorption on surface modified carbons (GAC383, GAC0383 and GACNZn01273).

Pseudo first order kinetic model $ln(q_e - q_t)$ against t (minute) at different temperature for the adsorption of p – nitrophenol are shown in Figure 5.41 (a) GAC383, (b) GACO383 and (c) GACNZnO1273. The first order rate constant (K_1), calculated adsorption capacity (q_ecal) and correlation coefficient (R^2) are shown in Table 5.17. The experimental kinetic data (q_eexp) is not comparable with calculated q_e of pseudo first order and the R^2 ranges 0.94 – 0.98 indicate that, the experimental data of p – nitrophenol adsorption do not follow first order mechanism.

Ho second order kinetic model shows the straight line plot (Figure 5.42 (a) – (c)) of t/q_t against t for the adsorption of p – nitrophenol on modified carbons (GAC383, GACO383 and GACNZnO1273). The second order rate constant (K_2) and amount adsorbed (q_ecal) from the intercept and slope of Ho second order model are presented in Table 5.17. The q_ecal for the modified carbons are GAC383 (221.20 - 232.00 mg/g), GACO383 (129.50 - 142.50 mg/g) and GACNZnO1273 (233.64 – 249.38

mg/g). The high correlation coefficient ($R^2 = 0.99$) and good agreement between $q_e exp$ from the batch kinetic data and $q_e cal$ from the second order model for adsorption of p – nitrophenol, that follows pseudo second order model.

The first and second order kinetic model cannot identify the diffusion mechanism and rate controlling step so we used Weber intrparticle diffusion model. The Figure 5.43 (a), (b) & (c) shows a linear plot of q_t against square root of t ($t^{1/2}$) gives two straight lines. The first part is attributed to surface diffusion and second linear portion shows intraparticle diffusion. The surface diffusion constant (K_{idl}) and intraparticle diffusion constant (K_{id2}) are given in Table 5.17. The K_{idl} > K_{id2} for the adsorption of p - nitrophenol on carbons studied. It indicates that the intraparticle diffusion is the slowest step identified for p – nitrophenol adsorption and it is the rate controlling step. The intercept of the second portion (C_2) that is the measure of boundary layer thickness, it shows that GAC383 (79.5 -116.9 mg/g), GACO383 (51.5 -67.4 mg/g) and GACNZnO1273 (72.7 -138.8 mg/g) at different temperature studied.



·/Tic Algert					Indiac		domini								00°, 00		
			First ord	er Kinetio	S	Second o	rder kine	tics	Intrapart	icle diffus	sion con	stant			Elovich (onstant	
Carbon	T (K)	(ອີ/ອີເພ) dxə ^ə b	(mธุร ⁻¹) คุณป	(שוּש _{ין}) א ^י	۶z	գ,cal (mgg ⁻¹)	(500 s ^{01,1}) K ³ *102	۶	K ^{id1})) אנוער ^{1/2}) (אנוער	(աճճ _{-լ}) Ը'	z۲	(^{ניז]} מיש _{ועד}) א	(աճճ _{-լ}) Ը ^շ	۶	a (¹⁻ nim ¹ 92m)	(BuB) (J	ß²
	283	201.92	153.84	0.007	0.98	221.24	7.59	66.0	16.69	-15.98	96.0	5.64	79.51	66.0	9.04	0.023	66.0
	293	209.76	151.53	0.007	0.98	225.73	8.50	0.99	16.69	-7.49	0.98	5.51	89.37	0.99	11.06	0.023	0.99
GAC383	303	213.44	151.29	0.007	0.98	228.83	9.20	660	16.80	-2.21	76.0	5.34	97.64	66.0	12.76	0.023	66.0
	313	216.53	151.04	0.008	0.98	231.48	10.18	0.99	15.96	9.13	0.96	5.08	107.66	0.99	15.43	0.024	0.99
	323	219.02	143.17	0.008	0.98	232.02	11.46	66.0	17.13	69.6	0.97	4.75	116.88	66.0	18.60	0.024	66.0
	283	119.50	82.71	0.005	0.91	129.53	12.38	0.99	13.35	-28.15	0.98	2.99	51.47	0.97	5.12	0.038	0.97
	293	124.52	84.52	0.006	0.93	133.33	14.16	66.0	12.90	-20.54	0.96	3.06	55.88	66.0	6.28	0.038	0.97
GC0383	303	129.30	84.24	0.006	0.93	136.80	15.58	66.0	12.89	-15.83	0.97	2.99	62.04	0.99	7.50	0.038	0.97
	313	133.78	81.11	0.006	0.94	139.86	18.80	0.99	12.44	-5.21	96.0	2.97	68.11	0.99	10.75	0.040	96.0
	323	138.59	78.20	0.006	0.94	142.50	21.26	0.99	11.93	4.89	66.0	3.21	67.38	66.0	15.66	0.042	66.0
	283	210.47	161.3	0.006	0.96	233.64	5.78	0.99	16.69	-15.98	0.98	5.64	79.51	0.99	9.04	0.021	0.98
	293	217.44	160.9	0.007	96.0	240.96	6.71	66.0	20.12	-31.19	0.94	4.82	110.9	0.99	9.14	0.020	0.98
GACNZnO1273	303	226.73	149.0	0.007	0.95	241.55	9.45	0.99	21.68	-20.61	0.99	4.49	126.8	0.99	13.96	0.022	0.98
	313	232.08	137.6	0.006	0.94	242.13	11.84	66.0	20.48	-0.12	66.0	4.26	136.5	0.99	21.05	0.023	0.98
	323	238.86	139.1	0.007	0.96	249.38	12.45	0.99	20.45	8.56	66.0	4.57	138.8	0.99	25.66	0.023	96.0

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics **327**



Elovich kinetic model (Figure 5.44 (a) GAC383, (b) GACO383) and (c) GACNZnO1273) shows a linear relationship between amounts of p – nitrophenol adsorbed at different time intervals (q_t) against natural logarithm of a different time in minutes (ln t). The initial adsorption rate (α) and desorption constant (β) are determined from the intercept and slope of the Elovich model. The initial adsorption rate increases with temperature for GAC383 (9.00 – 18.61 mgg⁻¹min⁻¹), GACO383 (5.10 – 15.70 mgg⁻¹min⁻¹) and GACNZnO1273 (7.61 -25.66 mgg⁻¹min⁻¹). Adsorption capacity and initial adsorption rate increases with temperature, is due to the enhancement of mobility of p - nitrophenol from solution phases to the carbon surface [19].



Figure 5.45: Activate on energy for the adsorption of *p* -nitrophenol on new carbons; $C_0 = 250 \text{ mg/L}$

The activation energy (E_a) for the adsorption of p – nitrophenol on modified carbons (GAC383, GACO383 and GACNZnO1273) is calculated from the Ho second order rate constant (K_2) using Arrhenius equation. A straight line plot of $ln k_2$ versus 1/T of the p -nitrophenol adsorption for GAC383, GACO383 and GACNZnO1273 are shown in Figure 5.45 (a), (b) & (c) respectively. The activation energy obtained from the slope of the plot is presented in Table 5.18. The activation energy (E_a) calculated for GAC383 (7.63 kJmol⁻¹), GACO383 (10.35 kJmol⁻¹) and GACNZnO1273 (16.02 kJmol⁻¹), it is less than 40 kJmol⁻¹ indicating that the mechanism of p – nitrophenol adsorption by these carbons are physisorption.

 $E_a(kJmol^{-1})$ K R Carbon **GAC383** 7.63 0.0019 0.955 GACO383 10.35 0.0098 0.970 GACNZnO1273 16.02 0.0518 0.980

Table 5.18: Activation energy for the adsorption of p – nitrophenol on modified carbons

5.7.2.3 Adsorption Isotherm Studies of *p*- nitrophenol as Adsorbate

To design an adsorption reactor system for the removal of p – nitrophenol solution, equilibrium isotherm studies are also essential and to understand how p- nitrophenol interact with carbon surface and critical to optimize the use of these granular activated carbons. Figure 5.46 (a) – (c) shows the amount adsorbed at equilibrium (q_e) against equilibrium concentration (C_e) of p – nitrophenol adsorption by these carbons at different temperature (10 – 50^oC). The figure shows that the adsorption capacity enhanced by adsorption temperature and solution concentration. The experimental isotherm data obtained by p – nitrophenol adsorption of these carbons SType I isotherm pattern.

These experimental isotherm data apply to known isotherm models such as Langmuir, Freundlich, Temkin and Dubinin – Radushkevich to determine the mechanism of p- nitrophenol adsorption on these modified carbons and characteristic constants related to adsorption.





Figure 5.46: Adsorption isotherm of (a) GAC383, (b) GACO383 & (c) GACNZnO1273 at different temperatures *P*- nitrophenol as adsorbate for initial concentration $C_0 = 25$ -3000 mg/L

The Langmuir isotherm model is used to determine the maximum adsorption capacity of p – nitrophenol equivalent to monolayer coverage. The maximum monolayer adsorption capacity (q_{max}) and surface energy constant (K_L) are determined from the slope and intercept of the linear plot (Figure 5.47 (a), (b) & (c)) and are presented in Table 5.19. The monolayer adsorption capacity increases with temperature for GAC383 (272.48 - 403.23 mg/g), GACO383 (201.61 - 245.70 mg/g) and GACNZnO1273 (390.63 -510.20 mg/g). Acceleration of some slow adsorption steps and creation more active sites on the surface of these modified carbons are the main reason of higher q_{max} at higher temperature [20]. GACNZnO1273

Chapter 5

shows highest adsorption capacity compared to others. Adsorption of p – nitrophenol on carbons occurs through electrostatic interaction between negatively charged phenoxide group and positive charge on the carbon surface. The basic surface functional groups and the low percentage of oxygen increase the positive charge on the GACNZnO1273 surface leads to higher adsorption capacity compared to GAC383 and GACO383. High BET surface area and total pore volume also promote the more adsorption efficiency of this carbon (GACNZnO1273). The Langmuir energy constant becomes more with temperature indicate that adsorption is an endothermic process. The high correlation coefficient ($R^2 = 0.99$) shows that p – nitrophenol adsorption occurs on the homogenous surface of carbons.

The favorability of p – nitrophenol adsorption on new modified carbons is determined by using separation factor (R_L) calculating from Langmuir constant (a_L) [21]. The Factor R_L against initial concentration (C_0) of modified carbons GAC383 (5.48 a), GACO383 (5.48 b) and GACNZnO1273 (5.48 c) shows that the R_L lies between 0 and 1. It means p – nitrophenol adsorption is favourable at all concentration and adsorption temperatures.

Freundlich isotherm model applied on the p – nitrophenol adsorption on all modified carbons. A straight line plot of $log q_e$ versus $log C_e$ of these modified carbons are shown in Figure 5.49 (a), (b) & (c). The Freundlich parameters are shown in Table 5.19. The adsorption capacity (K_F) increases with temperature indicating that higher temperature is favourable for adsorption of p – nitrophenol. The correlation coefficients ($R^2 - 0.86 -$ 0.94) of these isotherm is less than that of Langmuir correlation coefficient ($R^2 - 0.99$) reveals that adsorption of p –nitophenol on new modified carbons are Langmuirian type [22 & 23].







		La	ngmuir C	Constants		Fr C	eundlich onstants		Ţ	emkin C	onstants		Dubini	in - Rad Consta	ushkev nts	ich
Carbon	(K) T	(₁₋ 88ш) хош Б	(₁₋ 8ш7) ⁷ Н	ג. (ג.קש ^{רו})	۶	(₁₋ 88ш) ^Л У	и	B 2	(Sui/J) ¹ V	Я	(loml) Jd	₇ 8	(188u) (U-U) (D-U)	(к]шо[₁) Е%D-В)	(uol _z Lz) K	B ₅
	283	272.48	7.61	0.028	0.99	53.49	0.235	0.86	5.54	29.56	76.79	0.98	75.77	1.47	0.23	0.99
	293	304.88	8.36	0.027	0.99	55.01	0.246	0.88	4.50	33.62	67.50	0.99	77.02	1.66	0.18	0.99
GAC383	303	340.14	9.03	0.027	0.99	56.58	0.258	0.89	3.78	38.01	59.71	0.99	78.21	1.85	0.14	66.0
	313	377.36	9.40	0.025	0.99	58.14	0.268	16.0	3.31	42.44	53.48	0.99	79.53	2.03	0.12	66.0
	323	403.23	10.69	0.027	0.99	59.90	0.275	0.91	3.15	45.86	49.49	0.99	81.24	2.19	0.10	0.99
	283	201.61	2.06	0.010	0.99	18.48	0.328	0.93	0.31	30.27	74.99	0.99	49.61	0.33	4.63	0.97
	293	213.22	2.14	0.010	0.99	18.93	0.332	0.93	0.31	31.94	71.07	0.99	50.62	0.35	3.97	0.97
GACO383	303	224.22	2.23	0.010	0.99	19.33	0.337	0.93	0.30	33.60	67.55	0.99	51.31	0.38	3.35	0.97
	313	235.29	2.31	0.010	0.99	19.67	0.340	0.93	0.30	35.26	64.37	0.99	52.08	0.41	2.92	76.0
	323	245.70	2.41	0.010	0.99	20.04	0.344	0.94	0.29	36.82	61.64	0.99	52.74	0.45	2.51	0.97
	283	390.63	5.71	0.015	0.99	53.51	0.275	0.92	2.34	43.31	52.41	0.99	85.66	1.46	0.23	0.99
	293	429.18	6.08	0.014	0.99	55.08	0.284	0.93	2.18	47.70	47.58	0.98	85.95	1.63	0.19	0.99
GACNZn01273	303	471.70	7.68	0.016	0.99	66.04	0.273	0.93	3.67	49.30	46.04	0.98	106.62	2.22	0.10	96.0
	313	492.61	9.21	0.019	0.99	75.85	0.262	0.92	5.74	49.54	45.82	0.98	120.79	2.54	0.08	0.98
	323	510.20	10.19	0.020	0.99	82.09	0.257	0.92	7.33	50.20	45.21	0.98	121.57	2.81	0.06	76.0

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics **335**

The Temkin isotherm plot of q_e versus $ln C_e$ are shown in Figure 5.50 (a), (b) & (c) and the equilibrium binding constant (*A*) and heat of adsorption constant (*B*) from the intercept and slope of the plot are tabulated and presented in Table 5.19. The constant related to heat of adsorption (*B*) of these carbons GAC383 (29.56 – 45.86), GACO383 (30.27 - 36.82) and GACNZnO1273 (43.31 – 50.20) increases with temperature signifying that adsorption is an endothermic process. Temkin isotherm constant (b_T) is less than 80 kJ/mol indicating that adsorption is a physical process.

The Dubinin Radushkevich (D - R) isotherm applied only to lower concentration of p – nitrophenol adsorption on modified carbons. This isotherm helps to understand adsorption is a physical or chemical process. The mean activation energy (E_0) calculated from D-R isotherm model is less than 8kJ/mol indicating that p – nitrophenol adsorption occurs through weak Van der Waals force of attraction. The adsorption capacity (q_m) increases with temperature indicate adsorption is an endothermic character.

5.7.2.4 Thermodynamic Parameters

The thermodynamic parameters such as Gibbs free energy change (ΔG) , enthalpy (ΔH) and entropy (ΔS) are calculated and presented in Table 5.20. The ΔH and ΔS calculated from the linear plot of lnK_2 versus l/T are shown in Figure 5.51.

The ΔG decreases with increasing temperature indicating that adsorption process is favorable at higher temperature. The negative ΔG confirms the feasibility and spontaneous nature of p – nitrophenol adsorption on carbons [24 & 25]. The positive ΔH indicate that adsorption is an endothermic process and it is less than 40 kJ/mol indicating that adsorption of p – nitrophenol on these carbons GAC383 (6.02 kJ/mol), GACO383 (2.96 kJ/mol) and GACNZnO1273 (6.56 kJ/mol) shows physisorption process. The positive ΔS depicts the increasing randomness at the carbon – p - nitrophenol solution interface during the adsorption.


Figure 5.51: plot of lnK_L versus 1/T for estimation of thermodynamic parameters for the adsorption of p - nitrophenol by GAC383, GAC0383 and GACNZnO1273

Table 5.20: Estimation of thermodynamic parameters – Gibbs free energy (ΔG), enthalpy(ΔH) and entropy (ΔS) of GANZnO1273

		Δ	G (kJmol	l ⁻¹)		ΔH	ΔS
Carbon	283	293	303	313	323	(kJmol ⁻¹)	(Jmol ⁻¹ K ⁻¹)
GAC383	4.78	-5.17	-5.54	-5.83	-6.36	6.02	38.18
GACO383	-1.70	-1.85	-2.02	-2.18	-2.36	2.96	16.45
GACNZnO1273	-4.75	-5.16	-5.57	-5.86	-6.40	6.54	39.89

5.7.3 Adsorption Studies of Methylene Blue (MB)

Adsorption efficiency of granular activated carbon incorporated with nano zinc oxide with different activation temperature (GACNZnO series) using methylene blue as adsorbate is discussed. Selection of carbon, adsorption kinetics, adsorption isotherms and thermodynamic studies are done.

5.7.3.1 Selection of Carbon

Adsorption studies of methylene blue (MB) using an initial concentration of 500 mg/L at 30° C for maximum 720 minutes shaking period. The Figure 5.52 shows that removal of MB from solution is enhanced with time maximum of 10 hours. From the GACNZnO series

the amount of methylene blue adsorption increases in the order of GACNZnO1073 > GACNZnO1273 > GACNZnO873 > GACNZnO673 > GACNZnO473 > GACNZnO473 > GACNZnO383. GACNZnO1073 shows high adsorption capacity compared to others because this carbon has high carbon content (91.91%), high basic group (0.95 meq/g), mesopore volume and mesopore surface area. It enhances the adsorption efficiency of methylene blue.



Figure 5.52: Adsorption of carbon GACNZnO series for methylene blue (MB) as a function of time.

5.7.3.2 Adsorption Kinetics

The amount adsorbed at different time (q_t) as a function of time (t) at different temperature are presented in Figure 5.53 (a) GAC383, (b) GAC0383 and (c) GACNZnO1073. The amount adsorbed at equilibrium $(q_e exp)$ are presented in Table 5.21 It confirms that removal of MB from solution increases in the order GACNZnO1073 (115.63 -190.36 mg/g) > GAC383 (102.05 - 138.08 mg/g) > GACO383 (80.68 - 117.64 mg/g) at different temperature temperatures (10 - 50^oC). Data applied to different kinetic models to determine the physical or chemical characteristics of modified carbons and to study mechanisms of MB adsorption.





Figure 5.53: Effect of contact time on the adsorption of methylene blue on (a) GAC383, (b) GAC0383 & (c) GACNZnO1073 at different temperatures for $C_0 = 250 \text{ mg/L}$

The Lagergren first order rate constant (K_1) and adsorption capacity (q_ecal) are obtained by using a straight line plot $ln (q_e-q_t)$ versus t are shown in Figure 5.54 (a) - (c) and the constants are presented in Table 5.21. The experimental kinetic data (q_eexp) are not comparable with the amount adsorbed from first order equation (q_ecal) and the correlation coefficient is less $(R^2 ranging from 0.92 - 0.98)$ for all carbons at all temperatures studied indicating that first order kinetics is not follows batch kinetic data. The kinetic data are further applied to Ho second order model. The pseudo second order rate constant (K_2) and adsorption capacity (q_ecal) are deliberated from the intercept and slope of the plot t/q_t versus t for the adsorption of MB on these modified carbons (Figure 5.55 (a), (b) &(c)). The rate constant K_2 and q_ecal increases with temperature indicate that adsorption is an endothermic process.

The methylene blue adsorbed by batch kinetic ($q_e exp$) are comparable with a calculated amount of MB adsorbed by applying a second order model ($q_e cal$) and $R^2 = 0.99$. Means, Ho second order model follows the experimental kinetic data for MB adsorption on these carbons studied. The adsorption capacity is higher in GACNZnO1073 than other carbons.

The Figure 5.56 (a), (b) & (c) shows the intraparticle diffusion model q_t against $t^{1/2}$ gives two straight line portions. The first portion shows surface diffusion and the second linear portion is ascribed to intraparticle diffusion. The slope of the first portion (surface diffusion coefficient K_{id1}) is higher than the second portion (intraparticle diffusion coefficient K_{id2}). The K_{id1} of the modified carbon at different temperature studied are in the range of GAC383 (5.59 - 8.49 mgg⁻¹min^{-1/2}), GACO383 (5.15 - 6.37 mgg⁻¹min^{-1/2}) and GACNZnO1073 (7.52 - 13.50 mgg⁻¹min^{-1/2}) and the K_{id2} of these carbons are GAC383(2.07 - 2.72 mgg⁻¹min^{-1/2}), GACO383(1.78 - 2.35 mgg⁻¹min^{-1/2}) and GACNZnO1073 (1.99-2.98 mgg⁻¹min^{-1/2}). It points out that, second portion is the slowest step and intraparticle diffusion is the rate controlling step for the adsorption of MB. The intercept of the second portion is the high means thickness of the boundary layer also high. The constant C₂ of these carbons is GAC383 (50.67 - 78.76 mg/g), GACO383 (25.73 - 72.52 mg/g) and GACNZnO1273 (42.99 - 139.22 mg/g).

Boyd kinetic model is used to calculate the diffusivity coefficient (D_e) of MB adsorption. A straight line plot of B_t versus t are shown in Figure 5.57 (a) – (c) and the diffusion coefficient calculated from the slope of the plot are presented in Table 5.21. The diffusivity coefficients (D_e) for the MB adsorption by these carbons are GAC383 ($1.33*10^{-4} - 1.50*10^{-4}$ cm²s⁻¹), GACO383 ($1.17*10^{-4} - 1.22*10^{-4}$ cm²s⁻¹) and GACNZnO1073 ($1.36*10^{-4} - 1.44*10^{-4}$ cm²s⁻¹). The correlation coefficient (R^2) is in the range of 0.92 – 0.98. The plot is almost linear and does not pass through the origin reveals that MB adsorptions are governed by external mass transport and particle diffusion is the rate controlling step [26, 27].



Chapter 5

			First or	der Kine	tics	Second o	rder kii	netics	Intrap	urticle di	ffusion	constan			Boyd n	lodel
Carbon	T (K)	(ສີ/ສີພ) dxə ^ə b	(g/gm) gecal	¹ N	zষ	(g/gm) (g/gm)	K ⁵ *10 ⁴	ß2	(^{1/1} -nim ¹ 22m) K _{id1}	(ພຣີ\ຣີ) C ¹	κ	(^{1/1} -nim ^{-1/2}) K ^{idz}	(mg/g) C2	۲z	(cm ₅ 2.1) D°*10+	zظ
	283	102.05	60.38	0.005	0.94	104.38	2.42	0.99	8.49	1.76	96.0	2.07	50.67	0.97	1.33	0.94
	293	116.77	64.49	0.005	0.98	118.76	2.46	0.99	7.24	21.22	0.97	2.48	56.37	0.99	1.33	0.98
GAC383	303	124.24	67.07	0.005	0.94	126.42	2.52	66.0	5.78	38.04	66.0	2.61	61.14	0.97	1.50	0.94
	313	132.00	66.07	0.005	0.98	133.87	2.57	0.99	5.59	45.81	0.99	2.72	66.48	0.99	1.38	0.98
	323	138.08	67.84	0.006	96.0	140.25	2.73	66.0	6.07	49.34	0.98	2.47	78.76	66.0	1.57	0.96
	283	80.60	53.52	0.004	0.96	82.37	2.33	0.99	5.66	2.99	0.98	2.21	25.73	0.99	1.17	0.96
	293	90.92	54.31	0.004	0.97	91.91	2.57	66.0	5.15	15.65	96.0	2.35	32.81	0.98	1.17	0.97
GAC0383	303	98.13	54.75	0.004	0.98	99.80	2.75	66.0	5.29	20.75	0.99	2.05	47.28	66.0	1.24	0.98
	313	110.64	56.84	0.004	0.95	110.38	2.78	66.0	6.37	24.83	0.99	2.25	53.67	76.0	1.10	0.95
	323	117.76	53.85	0.004	0.94	118.06	3.32	66.0	7.52	27.33	0.98	1.78	72.52	66.0	1.22	0.94
	283	115.93	84.17	0.005	0.98	123.15	1.27	0.99	9.41	-9.66	0.94	2.98	42.99	0.99	1.36	0.98
	293	135.10	89.24	0.004	0.97	138.31	1.40	66.0	8.85	8.00	0.99	3.52	47.42	66.0	1.19	0.97
GACNZn01073	303	166.67	85.83	0.004	0.94	168.35	1.90	66.0	13.34	13.28	0.99	2.67	98.68	66.0	1.24	0.94
	313	183.51	86.68	0.004	0.93	184.50	2.01	0.99	14.28	23.27	0.99	2.69	114.84	66.0	1.21	0.93
	323	190.36	88.32	0.005	0.92	193.42	2.07	66.0	13.50	31.66	0.95	1.99	139.22	66.0	1.44	0.92

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The activation energy (E_a) for the adsorption of MB on carbons are calculated from the slope of the plot $ln K_2$ against l/T are shown in Figure 5.58 (a) - (c). The E_a of carbons GAC383 (2.11 kJ/mol), GACO383 (5.98 kJ/mol) and GACNZnO1073 (9.59 kJ/mol). Table shows that $E_a < 40 kJ/mol$ for all carbon studied conclude that, MB interaction with carbons is a physical process.



Figure 5.58: plot of *ln K*₂ versus *1/T* for the adsorption of methylene blue (MB) on modified activated carbons (a) GAC383, (b) GAC0383 and (c) GACNZnO1073

Table 5.22: Activation energy of surface modified carbons using methylene blue (MB) as adsorbate

Carbon	$E_a (kJmol^{-1})$	\mathbf{K}_{0}	R
GAC383	2.11	0.0006	0.95
GACO383	5.98	0.0030	0.95
GACNZnO1073	9.59	0.0074	0.98

5.7.3.3 Adsorption Isotherm Studies

The equilibrium amount adsorbed (q_e) against concentration at equilibrium (C_e) of MB adsorption at temperatures $(10 - 50^{0}C)$ are shown in Figure 5.59 (a) GAC383, (b) GACO383 and (c) GACNZnO1073. The MB adsorption increases with solution concentration and adsorption temperature, an indication for endothermic process. The general isotherm (Figure 5.59) shows a Type I isotherm pattern. These equilibrium data are applied to different isothermal models such as Langmuir isotherm, Freundlich Isotherm, Temkin isotherm and Dubinin – Radushkevich isotherm to determine the characteristic constant and identify the mechanism of adsorption (physical or chemical).





Chapter 5

		Langmu	iir Cons	tants	Freu	ndlich (Consta	nts	L	emkin C	Constant		Dubir	iin – Rad Consta	ushkevi nt	ch
Carbon	T (K)	(₁₋ 88ш) ^{хти} в	(₁₋ 8ш7) ⁷ У	۶zظ	(wsg ⁻¹) K _F	u/I	u	κ²	(_{เ-} ธิพๅ) V	В	, (Jmol ¹⁾) Ե	۲ ²	(աճճ _{-լ}) (D-K) Ծ ^ո	(k1mol. ₁) (D-K) E ⁰	(mol ₅ 1_5) K,	κ
	283	150.60	3.74	0.99	37.67	0.200	4.99	0.98	9.50	15.15	149.85	0.97	57.43	2.75	0.066	0.97
	293	169.49	4.54	0.99	40.65	0.209	4.78	0.98	9.36	17.17	132.20	0.98	58.83	3.26	0.047	0.96
UAC383	303	190.11	4.80	0.99	42.90	0.217	4.61	0.99	89.8	19.16	118.48	0.96	60.30	3.74	0.036	0.96
	313	209.64	5.13	0.99	45.34	0.223	4.49	66.0	8.61	20.92	108.48	0.95	61.58	4.20	0.028	0.96
	323	229.35	5.51	0.99	47.80	0.228	4.40	66.0	8.59	22.71	99.95	0.94	62.78	4.67	0.023	0.97
	283	107.99	2.89	0.99	35.09	0.159	6.27	0.97	12.08	13.66	166.17	0.98	54.15	2.77	0.065	0.98
	293	122.40	3.37	0.99	37.67	0.169	5.92	0.98	11.93	15.34	147.94	0.98	56.25	3.14	0.051	0.98
UACU383	303	138.70	3.60	66.0	39.84	0.178	5.61	0.98	11.26	17.05	133.14	76.0	57.98	3.49	0.041	0.97
	313	154.32	4.31	0.99	42.34	0.188	5.33	0.98	11.55	18.19	124.76	76.0	59.50	3.79	0.035	0.97
	323	172.41	4.59	0.99	44.58	0.195	5.12	66.0	9.36	21.28	106.67	0.95	60.98	4.08	0.030	0.97
	283	221.73	2.60	0.99	35.80	0.241	4.15	0.97	4.84	21.59	105.11	0.98	51.64	5.07	0.019	0.95
	293	246.31	4.22	66.0	45.93	0.231	4.32	66.0	5.18	23.13	98.12	0.98	58.12	5.89	0.014	0.93
GACNZnO1073	303	261.10	7.12	0.99	62.06	0.204	4.89	66.0	6.67	21.76	104.30	76.0	64.06	7.85	0.008	0.97
	313	288.18	8.93	0.99	69.16	0.205	4.87	66.0	6.71	23.39	97.05	76.0	64.04	9.02	0.006	0.96
	323	324.68	11.71	0.99	88.33	0.189	5.30	86.0	7.52	23.59	96.21	0.95	65.27	11.6	0.004	0.96

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The Figure 5.60 (a) GAC383, (b) GAC0383 and (c) GACNZnO1073 shows the Langmuir isotherm plot C_e/q_e against C_e for the MB adsorption at temperature $(10 - 50^{\circ}C)$. The monolayer adsorption capacity (q_{max}) and Langmuir energy constant (K_L) are calculated from the slope and intercept of the plot and are presented in Table 5.23. The q_{max} and K_L increases with temperature indicating that adsorption is an endothermic process. The q_{max} of these modified carbon at 10° C for GAC383 (150.60 mg/g), GACO383 (107.99 mg/g) and GACNZnO1073 (221.73 mg/g), 20⁰C for GAC383 (169.49 mg/g), GACO383 (122.40 mg/g) and GACNZnO1073(246.31 mg/g), 30° C for GAC383 (190.11 mg/g), GACO383 (138.70 mg/g) and GACNZnO1073 (261.10 mg/g), 40^oC for GAC383 (209.64 mg/g), GACO383 (154.32 mg/g) and GACNZnO1073 (288.18 mg/g) and 50^oC for GAC383 (229.35 mg/g), GACO383 (172.41 mg/g) and GACNZnO1073 (324.68 mg/g). All these carbons studied at temperature $10 - 50^{\circ}$ C, GACNZnO1073 shows highest adsorption capacity. This carbons show mesopore volume, mesoproe surface area, basicity and percentage of the carbon content is higher compared to others. These factors enhance the removal of MB dye by GACNZnO1073. The correlation coefficient ($R^2 = 0.99$) for all the carbons studied indicate that equilibrium isotherm data are applicable for Langmuir isotherm model [28]. The Freundlich isotherm model was used to estimate the adsorption capacity (K_F) and adsorption intensity (n) of the MB on the carbon (GAC383, GACO383 and GACNZnO1073) surface is presented in Table 5.23. The equilibrium data from the batch isotherm study of MB adsorption were plotted log q_e against log C_e (Figure 5.61). The K_F increases with temperature indicate that temperature enhances the mobility of MB molecules from solution to carbon phase. The *n* is in the range of 1 - 10 indicate favourable adsorption and the l/n is less than 1 assumes that it is a Langmuir type isotherm. In the MB adsorption isotherm study by these three carbons the n (4.15 - 6.27) and 1/n (0.159 - 0.241). The correlation coefficient ($R^2 = 0.97$) - 0.99) for all the carbons.

Temkin isotherm plot for MB adsorption on GAC383, GACO383 and GACNZnO1073 are shown in Figure 5.62 (a) – (c). The Temkin parameters such as equilibrium binding constant (*A*), heat of adsorption (*B*) and Temkin energy constant (b_T) are presented in Table 5.23. The heat of adsorption increases with temperature indicates that adsorption is an endothermic process. The $b_T < 80 \text{ kJ/mol}$ reveals that MB adsorption on these modified carbons shows a physical adsorption process. Dubinin – Radushkevich (D-R) isotherm model is also used to identify the adsorption is physical or chemical nature. The mean adsorption energy calculated from D - R plot (Table 5.23) is less than 8 kJ/mol indicating that adsorption is a physical process. The adsorption capacity (Q_D) increases with increasing temperature. The Q_D for various carbons at different temperature (10 – 50^oC) are GAC383 (57.43 - 62.78 mg/g) GACO383 (54.15 – 60.98 mg/g) and GACNZnO1073 (51.64 – 65.27 mg/g).

5.7.3.4 Thermodynamic Parameters

Thermodynamic parameters such as standard free energy change (ΔG) , enthalpy (ΔH) and entropy change are calculated by using the distribution constant (K_D) applying in Van't Hoff equation and are presented in Table 5.24. The change in enthalpy (ΔH) and entropy (ΔS) calculated from the slope and intercept of the plot $ln K_D$ against 1/T (Figure 5.63 – 5.65). The positive enthalpy for all carbons at all concentration indicates that adsorption of MB by these carbons are endothermic process. The positive entropy indicates that increasing randomness of these modified carbons – dye solution interface and the strong affinity between MB and modified carbons. The ΔG of MB on modified carbons decrease with rise of temperature and more for large concentration. At lower concentration the ΔG is almost negative for all three carbon selected, indicates a spontaneous nature of adsorption. The positive ΔG at higher concentration indicate that the presence of an energy barrier and the

adsorption was unspontaneous and percentage of adsorption decreases at higher concentration studied, but with temperature increases the Gibbs free energy change also decreases that means adsorption is favourable a higher temperature.



Figure 5.63: $ln K_D$ versus 1/T for the adsorption of methylene blue (MB) on GAC383 for initial concentration $C_0 = 25 - 1500 \text{ mg/L}$





Figure 5.65: *ln* K_D versus 1/T for the adsorption of methylene blue (MB) on GACNZnO1073 for initial concentration $C_0 = 25 - 1500 \text{ mg/L}$

^					Δ	G (kJmo	ol ⁻¹)	
Carbon	C ₀	∆S (Jmol ⁻¹ K ⁻¹)	∆H (kJmol ⁻¹)	283	293	303	313	323
	25	105.61	19.29	-10.59	-11.65	-12.71	-13.76	-14.82
	50	90.76	18.29	-7.40	-8.31	-9.22	-10.12	-11.03
	75	78.53	18.05	-4.17	-4.96	-5.75	-6.53	-7.3
GAC383	100	60.48	14.21	-2.91	-3.52	-4.10	-4.73	-5.33
	150	52.66	13.94	-0.96	-1.49	-2.01	-2.54	-3.07
	200	44.03	12.57	0.11	-0.33	-0.77	-1.21	-1.65
	250	35.23	10.75	0.78	0.43	0.08	-0.28	-0.63
	350	30.70	10.37	1.68	1.37	1.07	0.76	0.45
	500	26.33	10.01	2.56	2.29	2.03	1.77	1.50
	750	21.21	9.55	3.55	3.33	3.12	2.91	2.70
	1000	18.04	9.34	4.23	4.05	3.87	3.69	3.51
	1250	16.41	9.40	4.76	4.59	4.43	4.26	4.10
	1500	14.38	9.23	5.16	5.02	4.88	4.73	4.59
	25	105.26	19.34	-10.45	-11.50	-12.56	-13.61	-14.66
	50	91.24	18.65	-7.17	-8.08	-9.00	-9.91	-10.82
	75	75.12	18.34	-2.92	-3.67	-4.42	-5.18	-5.93
	100	66.65	17.65	-1.22	-1.88	-2.55	-3.22	-3.88
	150	57.04	10.53	0.39	-0.19	-0.76	-1.33	-1.90
CAC0383	200	36 32	12.03	1.22	0.78	1.02	-0.10	-0.34
GAC0303	350	28.28	10.61	2.61	2 32	2.02	1.76	1 47
	500	24.76	10.50	3.50	3.25	3.00	2.75	2.51
	750	21.11	10.45	4.47	4.26	4.05	3.84	3.63
	1000	17.62	10.11	5.13	4.95	4.77	4.60	4.42
	1250	15.05	9.88	5.62	5.47	5.32	5.17	5.01
	1500	13.37	9.81	6.03	5.89	5.76	5.63	5.49
	25	335.80	82.37	-12.68	-16.02	-19.38	-22.74	-26.09
	50	300.63	79.48	-5.44	-8.44	-11.44	-14.44	-17.44
	/5	194.39	58.07	-3.5/	-5.52	-/.46	-9.40	-11.35
	100	214.41	50.51	-1./1	-5.65	-5.99	-0.14	-10.28
	200	209.67	21.20	0.17	-1.92	-4.02	-0.12	-8.21
GACNZnO1073	250	94.87	27.29	0.02	-1.09	-2.19 -1 54	-3.30	-4.40 _3.43
51101.21101010	350	68.47	20.46	1.09	0.40	-0.28	-0.97	-1.65
	500	45.77	14.81	1.86	1.40	0.94	0.49	0.03
	750	30.44	11.37	2.75	2.45	2.15	1.84	1.54
	1000	24.56	10.27	3.32	3.07	2.83	2.58	2.34
	1250	21.14	9.77	3.79	3.58	3.36	3.15	2.94
	1500	18.43	9.42	4.20	4.02	3.84	3.65	3.47

Table 5.24:	Thermodynamic parameters of GAC383, GACO383 and
	GACNZnO1073 for methylene blue (MB) adsorption at different
	temperatures for initial concentration $C_0 = 25 - 1500 \text{ mg/L}$

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 351

5.8 Determination of Surface Area and Porosity of Modified Carbons Using Liquid Phase Adsorption Isotherm Modelling

The surface area and porosity of GAC383, GAC0383, GACNZnO1073 and GACNZnO1273 are determined by using adsorption isotherm models in liquid phase adsorption study. The adsorbate used as phenol, p - nitrophenol and methylene blue (MB). The Figure 5.66 (phenol), 5.67 (p - nitrophenol) and 5.68 (MB) is the Langmuir isotherm plot for the adsorption. The monolayer adsorption capacity (q_{max}) and surface area (SA) of the modified carbons using phenol adsorption for GAC383 (q_{max} - 312.5 mg/g & SA - 1043.90 m²/g), GAC0383 (q_{max} -209.60 mg/g & SA - 700.40 m²/g) and GACNZnO1273 (q_{max} - 383.15 mg/g & SA – 1279.79 m²/g), p –nitrophenol adsorption for GAC383 (q_{max} $-340.10 \text{ mg/g} \& \text{SA} - 773.20 \text{ m}^2/\text{g}$), GACO383 (q_{max} - 224.20 mg/g & $SA - 509.70 \text{ m}^2\text{/g}$ and $GACNZnO1273 (q_{max} - 471.70 \text{ mg/g} \& SA -$ 1072.03 $m^2/g)\,$ and MB adsorption for GAC383 $(q_{max}-190.10~mg/g$ & SA $-430.90 \text{ m}^2/\text{g}$), GACO383 (q_{max} $-138.70 \text{ mg/g} \& \text{SA} - 314.40 \text{ m}^2/\text{g}$), and GACNZnO1073 ($q_{max} - 261.10 \text{ mg/g} \& \text{SA} - 591.64 \text{ m}^2/\text{g}$). Among three adsorbate used, phenol is a small molecule that results the highest surface area observed for phenol adsorption. Compared to Phenol, p – nitrophenol is less water soluble hence p –nitrophenol adsorption by these modified carbons show highest monolayer adsorption capacity. In the case of the MB, being a large molecule adsorption efficiency decrease. Compared to native and oxidised form of carbon native carbon impregnated nano zinc oxide (GACNZnO 1073 & GACNZnO1273) has a higher adsorption capacity and surface area of liquid phase study. These carbons have a high percentage of carbon content, basic group, BET surface area, micropore volume, micropore surface area, mesopore surface area - enhances the adsorption efficiency in liquid phase.



John – Sivanandan Achari (J –SA) isotherm [29, 30] plot for the modified granular activated carbons are shown in Figure 5.69 - 5.71. Isotherm plots have only one phase unique for microporous carbon materials, with well defined correlation. The limiting micropore volume q_m (J-SA) obtained for the J –SA plot is tabulated in Table 5.25. The micropore volume and SA calculated by J - SA isotherm model for the modified carbons are GAC383 (Phenol – 310.5 mg/g & 1037.20 m²/g, p – nitrophenol - 357.80 mg/g & 813.20 m²/g and MB - 190.10 mg/g & 430.80 m²/g). For GACO383 (Phenol – 217.40 mg/g & 726.20 m²/g, p- nitrophenol - 232.20 mg/g & 527.70 m²/g and MB - 135.70 mg/g & $307.50 \text{ m}^2/\text{g}$). Whereas for GACNZnO1273 (Phenol - 379.49 mg/g & 1267.56 m²/g, p – nitrophenol – 471.73 mg/g & 1072.10 m²/g) .GACNZnO1073 is having qm (J-SA) - 266.32 mg/g & SA - 603.49 m²/g for methylene blue adsorption. Langmuir monolayer adsorption capacity and SA (L) are comparable with the limiting micropore volume and SA (J-SA) from the John Sivanandan Achari (J -SA) isotherm model indicate that these modified carbons are highly microporous.

Figure 5.72 – 5.77 shows the BET and I plot method applied in phenol, p –nitrophenol and methylene blue adsorption on new carbons. The porosity and surface area are obtained are presented in Table 5.25. In liquid phase adsorption the porosity and surface area of BET and I plot method are comparable at the range of $C_{e'}/C_s - 0.3$ here the C parameter of BET is positive.



Chapter 5

Isotherm	Porosity and		Phenol			p - nitroph	enol	Methyle	ene blue	
Models	Surface area	GAC383	GAC0383	GACNZn01273	GAC383	GAC0383	GACNZn01273	GAC383	GAC0383	GACNZnO1073
Langmuir (L)	q _{max} (L) (mg/g)	312.5	209.6	383.15	340.1	224.2	471.70	190.1	138.7	261.10
	Porosity (L) (cm ³ /g)	0.452	0.303	0.554	0.425	0.280	0.590	0.300	0.219	0.412
	SA(L) m ² /g	1043.9	700.4	1279.79	773.2	509.7	1072.03	430.9	314.4	591.64
John Sivananda	q _{max} (J-SA) (mg/g)	310.5	217.4	379.49	357.8	232.2	471.73	190.1	135.7	266.32
n Achari (J-SA)	Porosity (J-SA) (cm ³ /g)	0.449	0.314	0.548	0.448	0290	0.590	0.300	0.219	0.420
e S	SA (J-SA) m ² /g	1037.2	726.2	1267.56	813.2	527.7	1072.10	430.8	307.5	603.49
Bruaner Emmet	q _{max} (BET) (mg/g)	190.2	135.6	215.78	227.1	140.0	274.17	115.8	84.2	161.35
Teller (BET)	Porosity (BET) (cm ³ /o)	0.275	0.195	0.312	0.284	0.175	0.343	0.183	0.133	0.268
	SA (BET) m ² /g	635.3	452.9	720.74	515.9	318.2	623.10	262.4	190.8	365.63
BET scatchard	q _{max} (I plot) (mg/g)	189.9	137.6	213.33	233.31	140.1	276.55	117.3	86.54	165.78
piot (I plot)	Porosity (I plot) (cm ³ /g)	0.273	0.199	0.308	0.296	0.175	0.346	0.185	0.136	0.276
	SA (I plot) m ² /g	634.5	459.5	712.56	537.5	318.4	628.51	265.9	196.1	375.66



Figure 5.68: Langmuir isotherm model for the adsorption of MB by GAC383, GACO383 and GACNZnO1073











Chapter 5









Figure 5.75: The general isotherm and I plot for methylene blue adsorption on GACNZnO1073



Figure 5.76: The general isotherm and I plot for methylene blue adsorption on GAC383



Q (1-C /C

Figure 5.77: The general isotherm and I plot for methylene blue adsorption on GACO383

5.9 Adsorption of Trace Elements (Li, Mg, Al, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Ba, Tl & Pb)

Adsorption efficiency of carbon GAC383, GACO383 and GACONZnO1273 are tested using a ground water sample having trace metals in concentrations (Li – 1.3 μ g/L, Mg – 1220.04 μ g/L, Al - 42.88 μ g/L, Cr – 0.27 μ g/L, Mn – 103.5 μ g/L, Fe – 2884.22 μ g/L, Co – 1.01 μ g/L,

Cu – 1.06 µg/L, Zn – 12355.72 µg/L, As – 0.06 µg/L, Cd – 0.04 µg/L, Ba – 186.02 µg/L, Tl – 0.04 µg/L and Pb – 2.4 µg/L). This has been collected from a region whose water quality parameters are known, Batch experiment were done, 100 ml of ground water mixed with 0.1 g of carbon. For this study shaking, contact time is controlled as 540 minutes as equilibration time. After the desired contact time these carbons were filtered and the final concentration is determined by ICP – MS. The initial concentration, amount adsorbed and removal efficiency is shown in Table 5.26. The results show that more than 95% efficiency to remove most of the heavy metals such as Fe, Cu, Zn for all the carbons studied. Except magnesium (Mg), all the trace elements studied shows that, GACNZnO have 50% removal efficiency.

		GAC	383	GACO)383	GACNZ	nO1273
Trace elements	Initial concentration (µg/l)	Amount adsorbed (µg/g)	Percentage efficiency (%)	Amount adsorbed (µg/g)	Percentage efficiency (%)	Amount adsorbed (µg/g)	Percentage efficiency (%)
Li	1.3	0.23	17.69	0.63	48.46	0.75	57.69
Mg	1220.04	17.7	1.45	939.66	77.02	150.17	12.31
Al	42.88	36.89	86.03	39.58	92.30	31.93	75.52
Cr	0.27	0.09	33.33	0.2	74.07	0.15	55.56
Mn	103.5	73.39	70.91	100.5	97.10	74.88	72.35
Fe	2884.22	2860.18	99.17	2873	99.61	2872.66	99.60
Co	1.01	0.71	70.30	0.94	93.07	0.81	80.20
Cu	1.06	0.05	4.72	1.02	96.23	0.82	77.36
Zn	12355.72	12143.04	98.28	12345.92	99.92	12290.55	99.47
As	0.06	0.02	33.33	0.04	66.67	0.025	41.67
Cd	0.04	0.01	25.00	0.02	50.00	0.02	50.00
Ва	186.02	91.04	48.94	183.25	98.51	137.94	74.15
T1	0.04	0.03	75.00	0.03	75.00	0.03	75.00
Pb	2.4	2.3	95.83	1.61	67.08	2.36	98.33

Table 5.26: Adsorption efficiency for removing trace elements by newly preparedcarbons GAC383, GAC0383 and GACNZnO1273

School of Environmental Studies, Cochin University of Science and Technology

5.10 Statistical Analysis of the Data

Results of statistical tests conducted to check the various hypotheses, suggested in the chapter 1, give the following results:

Hypothesis 1: Whether there is any significant difference between the total pore volume, micropore volume and mesopore volume for different modified granular activated carbons (GACNZnO) and in comparison with the native form of granular activated carbon (GAC) and carbon oxidised with nitric acid (GACO383).

To prove this hypothesis, two way ANOVA test is used. The comparison of textural characterizations (micropore volume, mesopore volume and Total pore volume) obtained from ANOVA tests are shown in the Table 5.27. From this statistical analysis *ss* (sum of squares), *df* (degree of freedom), *ms* (mean square), *F* (variance ratio) and p - value (level of significance) are obtained and the inferences are listed below.

Table 5.27: ANOVA table for the comparison of textural characterization of granular activated carbons

Source	SS	df	ms	F	p-value
Total	132646.4154	14			
Carbons	2434.8662	4	608.7166	2.160	p>0.05
Pore volumes	127956.8772	2	63978.4386	227.008	P<0.001
Residual	2254.6720	8	281.8340		

Inferences

- (a) There is no significant difference between the carbon s (p>0.05).
- (b) The pore volumes differ significantly (p < 0.001). Total pore volume is significantly higher than micropore and mesopore volumes (p < 0.001).
- (a) Comparison of microporosity and mesoporosity showed that the mean percentage microporosity is significantly higher than that of mesoporosity (t = 12.993, df = 8, p < 0.001)

Hypothesis 2: Whether there is any significant difference between porosity and surface area using Solid – gas equilibria using N₂ gas adsorption at 77K, evaluated using different isotherm models; BET isotherm, I plot method, Langmuir isotherm, John isotherm, α_s plot, t plot for modified granular activated carbons and in comparison with the native form of granular activated carbon.

To prove hypothesis II, two way ANOVA test is used. The comparison study of adsorption capacity and pore volume obtained by different isotherm models (John isotherm, Langmuir isotherm, BET isotherm and I plot) is taken for two way ANOVA test. From this statistical analysis *ss* (sum of squares), *df* (degree of freedom), *ms* (mean square), *F* (variance ratio) and p - value (level of significance) are obtained (Table 5.28 & 5.29) and the inferences are listed below.

Table 5.28: ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and I plot method) of granular activated carbons

Source	SS	df	ms	F	p-value
Total	12763987.7267	39			
Carbons	83394.2839	4	20848.5710	3.523	P < 0.05
Models	373499.7246	3	9337.8210	15.777	P < 0.001
Residual	183465.1940	31	5918.2321	2048.522	

Inferences

- (a) Among carbons GACNZnO1273 is significantly higher than the rest (p < 0.05)
- (b) Among models, Langmuir isotherm model and John isotherm have significantly higher pore volumes than others (p < 0.001)
- (c) Regarding adsorption capacity, adsorption capacity calculated using Langmuir isotherm model is significantly higher, followed by John isotherm model (p < 0.001).



Table 5.29: <i>A</i>	ANOVA	table f	for the	comparison	of pore	volume	obtained	by
Ċ	lifferent	method	s (Johr	Isotherm,	Langmuin	· isotherm	, Dubinir	1 –
F	Radushke	vich iso	therm a	nd alpha S)	of granula	r activated	l carbon	

Source	SS	df	ms	F	p-value
Total	7529.4797	19			
Carbons	4047.7849	4	1011.9462	6.808	P<0.01
Adsorption capacity	1698.0963	3	566.0321	3.808	P<0.05
Residual	1783.5985	12	148.6332		

Inferences

- (a) Among carbons GACNZnO is significantly higher than the rest (p < 0.01).
- (b) Among models, V_m and V_J given significantly higher values than the rest (p < 0.05)

Hypothesis 3: Whether there is any relation between the adsorption temperature and adsorption efficiency for the modified granular activated carbons (GACNZnO).

Pearson correlation coefficient (r) and Student's t test are used to prove the relation of adsorption temperature and adsorption efficiency. From the above test, attained following inferences:

There is significant positive correlation between temperature and adsorption of phenol on GACNZnO1273 (r = 0.98544, t = 10.0377, df = 3, P < 0.01). This indicates that phenol adsorption increases with temperature.

There is significant positive correlation between temperature and adsorption of p - nitro phenol on on GACNZnO1273 (r = 0.9829, t = 9.2484, df = 3, P < 0.01). This reveals s that as temperature enhances the p - nitrophenol adsorption.

There is significant positive correlation between temperature and adsorption of methylene blue (MB) on GACNZnO1073 (r =0.98886,

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 363

t = 11.50919, df = 3, P < 0.01). This indicates that methylene blue adsorption enhances with temperature.

Hypothesis 4: Whether there is any significant difference between porosity and surface area determined using Langmuir isotherm and John – Sivanandan Achari isotherm (J-SA) for newly prepared granular activated carbons from solid – liquid equilibria.

The comparison of porosity and surface area of granular activated carbon obtained by Langmuir and John – Sivanandan Achari (J –SA) isotherm models for the study of phenol, $_{\rm p}$ –nitrophenol and methylene blue adsorption are tested by using three way ANOVA technique. Table 5.30 (porosity) and Table 5.31 (surface area) attributed the results of the above test and the inferences are given below.

Table 5.30: ANOVA table for the comparison of porosity of granular activated carbon obtained by Langmuir and John – Sivanandan Achari isotherm models in liquid phase adsorption study

Source	66	df	me	F	n_voluo
Source	33	ui	1115	Г	p-value
Total	0.25659	17	0.00008		
Methods	0.00008	1	0.09301	0.073	p > 0.05
Carbons	0.18601	2	0.02870	85.326	P < 0.001
Phenol, p –nitrophenol	0.05739	2	0.00109	26.325	p < 0.001
& methylene blue					
Residual	0.01311	12			

Inferences

- (a) There is no significant difference in porosity between Langmuir and John Sivanandan Achari isotherm methods (p > 0.05).
- (b) Porosity between carbons is significant (p < 0.001). GACNZnO1273 exhibited high porosity than the other two carbons studied (GAC383 & GACO383).
- (c) Phenol, p nitrophenol and methylene blue also showed a significant difference in porosity (p < 0.001). Phenol and p nitrophenol is having significantly higher volume than methylene blue (p < 0.001).

Source	SS	df	ms	F	p-value
Total	1673389.00059	17			
Methods	270.5913	1	270.5913	0.061	p > 0.5
Carbon	653869.6279	2	326934.8140	73.445	p < 0.001
Phenol, <i>p</i> – nitrophenol and methylene blue	96781.7376	2	483915.8688	108.710	P < 0.001
Residual	53417.0491	12	4451.4208		

 Table 5.31: ANOVA table for the comparison of surface area of modified carbons obtained by Langmuir isotherm and John isotherm models

Inferences

- (a) There is no significant difference in surface area between Langmuir and John Sivanandan Achari isotherm methods (p > 0.05).
- (b) Between the carbons there is significant difference in surface area (p < 0.001). GACNZnO1273 is having higher surface area than the other two (p < 0.001).
- (c) Surface area differs significantly between phenol, p nitrophenol and methylene blue (p < 0.001). Phenol is having significantly higher surface area than the other two adsorbate studied (p < 0.001).

5.11 Conclusions

GACNZnO series of carbon has distinct burn off with an activation temperature goes up to 1273K. The fixed carbon content (79.26 – 95.26%) is high with basic groups (0.45 – 0.95 meq/g). The surface morphological studies show that laboratory prepared nano ZnO is hexagonal phase with wurtizite structure and the particle size range of 10 – 20nm. Nano zinc oxide incorporated on granular activated carbon (GACNZnO series) has good porosity. Carbon activated at 1273 (GACNZnO1273) has highest microporosity and excellent adsorption efficiency. The nitrogen adsorption – desorption isotherm pattern shows Type I with H4 hysteresis loop, indicate the presence of super micropores. The micropore volume calculated by D – R method and alpha S (α_s) method confirms the presence

of micropores. It is seen that GACNZNO1273 shows higher micropore surface area (760.64 m^2/g) and GACNZnO1073 bears higher external surface area (424.10 m^2/g). On applying adsorption theoretical calculation based established model, the limiting micropore volume (V_m(J)) obtained for John isotherm model as compared with Langmuir adsorption capacity $(V_m(L))$ in all cases. This indicates that GACNZnO carbons are highly microporous. GACNZnO1273 is found most useful for the removal of phenol and p – nitrophenol and GACNZnO1073 for methylene blue (MB) compared to other granular activated carbons (GAC383 & GACO383). Between the John – Sivanandan Achari (J – SA) and Langmuir isotherms tested with the phenol, p – nitrophenol and methylene blue (MB) have high correlation. This further confirms homogenous microporous carbon behaviors ideal for separation, purification and removal of contaminants. Thermodynamic parameters such as enthalpy change, free energy change and entropy change showed that the adsorption process of phenol, p nitrophenol and methylene blue was endothermic and spontaneous. The statistical three way ANOVA analysis in solid - liquid adsorption equilibria reveals that there is no significant difference between Langmuir and John – Sivanandan Achari isotherm models (p > 0.05). Pearson correlation proves that, there is a significant positive correlation between temperature and adsorption of phenol, p –nitrophenol and methylene blue adsorption on new carbons.

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GRANULAR ACTIVATED CARBON OXIDISED AND INCORPORATED WITH NANO ZnO: PREPARATION, CHARACTERISATION AND ADSORPTION STUDIES

6.1 Introduction

This chapter of the thesis discusses the adsorption efficiency of a new series of oxidized carbon (GACO383) impregnated and activated with nano ZnO. Nitric acid oxidized carbon were surface loaded with nano ZnO and activated at different temperature under an inert atmosphere provided by super - heated steam. Physico chemical characterization and adsorption efficiency of this carbon group designated as GACONZnO383, GACONZnO473, GACONZnO673, GACONZnO873, GACONZnO1073 and GACONZnO1273 are systematically presented along with basic forms GAC383 and GACO383.

6.2 Characterization Studies of GACONZnO

The nano zinc oxide (nano ZnO) is incorporated on nitric acid oxidised carbon (GACO383) and activated at different temperatures referred to as (GACONZnO) series are characterized by different analytical methods.

6.2.1 Carbon Yield and Burn - off

The carbon yield and burn - off of the oxidized granular activated carbon that has been impregnated with nano ZnO ($X_{Zn} = 0.0017$) and activated under different temperature is shown in Figure 6.1. It shows that

a very stable and steady burn - off pattern for GACONZnO series. Higher activation temperature decreases the carbon yield and increases the burn - off. Carbon yield decreases from 95.16 - 72.11% at 1273K. Decreased carbon yield at higher activation temperatures was essentially due to the structural reorientation of the carbon structures upon heating.



Figure 6.1: Carbon yield and burn - off pattern of GACONZnO activated at different temperatures

6.2.2 Elemental Analysis

The elemental composition of the modified carbons GACONZnO series along with basic GAC383, GACO383 are determined (Table 6.1). Activation temperature has a pronounced impact on fixed carbon content varies from 66.52 - 89.84%. The content of hetero atoms ranges as hydrogen (2.11 - 0.19%), nitrogen (0.51 - 0.42%) and oxygen (29.76 – 9.28%) decreases with increasing activation temperature from 383-1273K.


Carbon	Carboxylic (meq/g)	Lactones (meq/g)	Phenolic (meq/g)	Base (meq/g)	C%	Н%	N%	0%
GAC383	0.40	0.17	0.45	0.50	89.43	0.60	0.36	09.61
GACO383	1.38	1.34	2.10	0.20	65.10	2.61	0.58	31.71
GACONZnO383	1.26	1.15	1.34	0.22	66.52	2.11	0.51	29.76
GACONZnO473	1.01	1.02	1.28	0.26	73.10	1.01	0.48	25.31
GACONZnO673	0.85	0.96	0.87	0.31	75.27	0.65	0.40	23.48
GACONZnO873	0.66	0.98	0.70	0.36	82.65	0.29	0.44	16.42
GACONZnO1073	0.36	0.61	0.23	0.40	88.17	0.28	0.44	10.91
GACONZnO1273	0.32	0.53	0.20	0.48	89.84	0.19	0.42	9.28

Table 6.1: Surface functional groups and elemental composition of modified granular activated carbons

6.2.3 Surface Functional Groups Analysis Using FTIR and Boehm Method

The surface functional groups of the modified carbons are quantitatively determined by using Boehm titration methods (Table 6.1) and qualitatively analyzed by FTIR method (Figure 6.2). The nitric acid oxidized carbon (GACO383) impregnated with nano zinc oxide (GACONZnO series) have higher acidic functional groups compared to starting carbon GAC383. From this fourth series of carbon, GACONZnO383 shows high carboxylic (1.26 meq/g), phenolic (1.34 meq/g) and lactonic (1.15 meq/g) groups. At higher thermal activation reduced the functional groups. GACONZnO1273 has lesser carboxylic (0.32 meq/g), phenolic (0.53 meq/g) and lactonic (0.20 meq/g) groups on carbon surface. Heating under inert conditions (steam activation) decrease the acidic surface functional groups, due to their thermal dissociation [1].





Figure 6.2: FTIR spectra of GACONZnO activated at different temperatures

The nano zinc oxide impregnated oxidized carbons showed the major absorption bands at 3421 - 3441 cm⁻¹, 2924 cm⁻¹, 2364 cm⁻¹, 1710 - 1717 cm^{-1} , 1628 -1637 cm⁻¹, 1554 - 1578 cm⁻¹, 1181 cm⁻¹, 1031 - 1062 cm^{-1} and 554 - 611 cm^{-1} . The first band at 3421 - 3441 cm^{-1} is a broad peak that is attributed to O – H stretching vibration of hydroxyl groups. The peak at 2924 cm^{-1} is assigned to C – H symmetrical and asymmetric stretching of residual methylene groups on the surface of GACONZnO. The band in the range of 1710 -1717 cm^{-1} is attributed to C=O stretching vibration of ketones and aldehydes. All the carbon is prominent with these broad peaks. The peak at 1628 -1637 cm⁻¹ is attributed to the presence of carbonyl groups. The bands between 1554 - 1578 cm⁻¹ are associated with the presence of aromatic rings attributed to quinone structures. The broad bands at 1031 - 1062 cm⁻¹ are a strong band of C – O of alcohol or amine in the structure of GACONZnO series of carbon. There is a peak range from 554 - 611 cm⁻¹ are attributed to the out of the plane C-H bending mode at higher activation temperature. This peak is due to the presence of alkaline groups of cyclic ketones and their derivatives of the carbon surface at higher activation temperature [2].



6.2.4 XPS Analysis

The X - ray photo electron spectroscopic studies are carried out to find more surface structural information about the elemental composition (Table 6.2) and the presence of carbon and oxygen surface functional groups (Figure 6.4 & 6.5) on the GACONZnO surface. Table 6.2 shows that nitric acid oxidation (GACO383) decreases the percentage of carbon (86.54%) and increase the percentage of oxygen (12.86%) and nitrogen (0.60%) compared to native carbon (GAC383). This GACO383 incorporated with nano zinc oxide and activated at higher temperature increases the percentage of carbon (93.59%) and shows a small percentage of zinc in the carbon surface at 1022eV. It indicates the presence of Zn²⁺ in the ZnO wurtzite structure, on the new carbon [3].

6/16505; 6/160									
Carbon	С%	0%	N%	Zn%					
GAC383	92.96	7.04	-	-					
GACO383	86.54	12.86	0.60	-					
GACONZnO1273	93.59	5.84	0.28	0.29					

 Table 6.2.:
 The elemental composition of the modified granular activated carbons
 GAC383, GAC0383 and GAC0NZnO1273 from XPS analysis

The C 1s and O 1s spectrum of prepared granular activated carbons are deconvoluted into different components and to determine the carbon oxygen surface functional groups presents on this carbon surface. Figure 6.4 and 6.5 shows the deconvoluted C 1s and O 1s spectra of GACONZnO1273.





Figure 6.3: X-ray photoelectron spectra of (a) GAC383, (b) GAC0383 & (C) GACONZn01273

The high resolution C 1s spectra are deconvoluted into 8 major components. The peak at 283.94 – 284.49 eV is attributed to the presence of graphitic carbon, the peak at 284.85 – 285.60 eV is the occurrence of amorphous carbons. The presence of hydroxyl, phenolic and alcoholic groups and a peak at 286.28 – 287.45 eV is attributed to the presence of carboxyl and esters on the carbon surface. A peak at 288.97 – 290.89 eV corresponds to the presence of π - π * transition in the aromatic rings of the GACONZnO surface. The O 1s peak at 532 eV is deconvoluted into different components and it shows a different peak in a range of 530.2 eV to 535.27 eV. The peak at 530.20 – 531.15 eV is the presence of C=O of carboxylic groups, peak at 532.46 – 533.22 eV shows the occurrence of C-

OH groups. Another peak in the range of 534.2 - 535.3 eV is attributed to the presence of chemisobed oxygen on the carbon surface [4].



6.2.5 XRD Analysis

The XRD profile shows that there are no significant changes in the structure of these new modified carbon studied (Figure 6.6). The interlayer distance (d_{002}) at the peak $2\theta = 23.86 - 25.07^0$ is in the range of 0.35 - 0.37 nm shows a higher value than a typical graphitic carbon (0.335 nm). The interlayer distance is greater than 0.335nm indicate that these carbons exist as non – graphitized forms and these are well defined porous adsorbers. The stack height (L_c) and stack width (L_a) are determined using Scherrer equation (Table 6.3). The GACONZnO series, the carbons shows stack height in the range 1.11 – 1.48 nm and stack width in the range of 2.22 – 2.96 nm.

Figure 6.3 shows the X-ray diffraction pattern of carbon GACONZnO series. The broad peak around $2\theta = 24.97 - 25.22^{\circ}$ and $2\theta = 43 - 44^{\circ}$ on all carbons indicate the well crystallized surface of carbon *related to (002) and (100)* surface.

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 377



School of Environmental Studies, Cochin University of Science and Technology

Granular Activated Carbon Oxidised and Incorporated with Nano ZnO: Preparation, ...

Carbon	20	L _a (nm)	$L_{c}(nm)$	d ₀₀₂ (nm)
GAC383	24.46	2.28	1.14	0.36
GACO383	24.98	1.94	0.97	0.35
GACONZnO383	24.97	2.76	1.37	0.35
GACONZnO473	24.73	2.59	1.29	0.36
GACONZnO673	25.22	2.29	1.14	0.35
GACONZnO873	25.08	2.24	1.12	0.35
GACONZnO1073	24.66	2.21	1.11	0.36
GACONZnO1273	24.77	2.30	1.15	0.36

Table 6.3: Structural parameters from X- ray diffraction studies

6.2.6 Scanning Electron Microscopy

The scanning electron microscopic images of the modified carbons are shown in Figure 6.7. The Figure 6.7 (a) and (b) shows the different magnifications of the carbon GACONZnO1273. It shows that pores are wide and open after oxidation, followed by activation with nano ZnO at higher temperature compared to native form GAC383 (Figure 6.7 (c)) and oxidized forms GACO383 (Figure 6.7 (d)) of carbon.



SEM image of GACONZnO1273 (a) 100 µm resolution (b) 50 µm resolution Figure 6.7: (c) 50 µm resolution of GAC383 and (d) 50 µm resolution of GACO383

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 379

6.2.7 Transmission Electron Microscopy

The TEM image (Figure 6.8) shows this new attempt of ZnO incorporation, oxidation and activation gives a regular pore structure. The dark regions are the bulk surface of the carbon and light regions are the porous structure. Figure 6.8 (d) clearly shows the parallel lines indicate that, the pores are slit shaped.



Figure 6.8: TEM image of GACONZnO1273 (a) 20 nm resolution (b) 10 nm resolution (c) 5 nm resolution & (d) 2 nm resolution



6.3 Porosity Studies – Evaluation of Surface Area and Pore volume

The adsorption of nitrogen at liquid temperature (77K) provides a sensitive quantitative technique for specific surface area determination and other textural properties of the carbons as regards to pore size, total pore volume and pore size distribution. The Figure 6.9 shows the nitrogen adsorption - desorption isotherm for the modified granular activated carbons (GAC383, GACO383, GACONZnO1073 and GACONZnO1273). The amount of nitrogen adsorbed increases with pressure and it show a Type I isotherm with H4 hysteresis loop. It indicates the presence of micro and meso pores. The total pore volume, t - plot micropore volume and mesopore volume of carbons are presented in Table 6.4. The total pore volume increases with activation temperature. It is known that nitric acid oxidation, Zn^{2+} impregnation and steam activation decrease the microporosity and increases the mesoporosity [5]. The percentage mesopore to total pore volume ratio (V_{mes} / V_{tot}) increases in the order GACONZnO1273 (65.14%) > GACONZnO1073 (59.49%) > GACO383 (43.56%) > GAC383 (38.80%).



Figure 6.9: N₂ adsorption – desorption isotherm at 77K of modified granular activated carbons (GAC383, GACO383, GACONZnO1073 & GACONZnO1273)

These nitrogen adsorption – desorption data of the modified carbons were applied to fit with different isotherm models such as Brunauer Emmett Teller (BET) method, BET Scatchard plot, Langmuir isotherm method, Freundlich isotherm method, John isotherm method, De – Boer t - plot etc. used to calculate the porosity, surface area, pore volume and pore width.

Carbon	V _t [Cm ³ g ⁻¹]	V _{mic} [Cm ³ g ⁻¹]	V _{mes} [Cm ³ g ⁻¹]	Vmic/Vt (%)	Vmes/Vt (%)	Pore Width (nm)
GAC383	0.573	0.351	0.222	61.26	38.74	1.77
GACO383	0.526	0.297	0.229	56.46	43.54	1.77
GACONZnO1073	0.554	0.224	0.329	40.51	59.49	1.92
GACONZnO1273	0.595	0.207	0.387	34.86	65.14	1.92
$V_m(cm^3 / g STP) = \frac{V_m}{V_m}$	$f_m(cm^3 / g)$	x 22414 x 28	:0.808			

Table 6.4: Textural characteristion of granular activated carbon*

6.3.1 Burnauer Emmet Teller (BET) Isotherm Model

The Figure 6.10 shows the BET isotherm plot of $1 / [V(p_0 / p) - 1]$ against relative pressure (p/p_0) for the modified carbons (GAC383, GAC0383, GAC0NZnO1073 and GACONZnO1273).

$$\frac{1}{V(\frac{p_0}{p}-1)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} (\frac{p}{p_0})$$
(6.1)

For a material with Type I isotherm features, the BET isotherm model is applied only at relative pressure up to 0.1. The porosity and surface area are calculated from BET equation (Table 6.5). The V_m (*BET*) and *SA* (*BET*) obtained for the new granular activated carbons are GACONZnO1073 [V_m (*BET*) - 0.427 cm³/g or 276.18 cm³/g STP , *SA* (*BET*) - 1200.74 m²/g], GACONZnO1273 [V_m (*BET*) - 0.455 cm³/g or 294.29 cm³/g STP, *SA* (*BET*) -1281.10 m²/g]. The pore radius of the modified carbon is calculated from BET surface area. The pore radius of the carbons is GAC383 (1.77 nm), GACO383 (1.77 nm), GACONZnO1073 (1.92 nm) and GACONZnO1273 (1.92 nm). The pore radius shows that all the carbons are microporous but having wider pores. High temperature activation, oxidation and impregnation procedures enlarge the pore structure.



Figure 6.10: BET isotherm model of modified granular activated carbons (GAC383, GACO383, GACONZnO1073 & GACONZnO1273)

Table 6.5:	Surface	area	and	pore	volume*	of	modified	granular	activated
	carbon i	mpre	gnate	d with	$n Zn^{2+}$			-	

	p/p ₀ upto 0.1		p/	p ₀ upto 0.				
Carbon	$\begin{array}{c} SA \\ (BET) \\ (m^2 g^{-1}) \end{array}$	V_{m} (BET) ($cm^{3}g^{-1}$	C	$\begin{array}{c} SA \\ (BET) \\ (m^2 g^{-1}) \end{array}$	V_m (BET) (cm ³ g ⁻¹	C	$\mathop{\rm SA}_{(m^2 g^{-1})}^{(I)}$	$\begin{array}{c} V_{m}\left(I\right)\\ (Cm^{3}g^{-1})\end{array}$
GAC383	1298.5	298.18	524	996.75	228.97	-81.58	1271.2	291.45
GACO383	1186.5	272.30	439	973.31	223.79	-118.59	1163.7	265.71
GACONZnO1073	1200.7	275.54	798	1166.3	236.73	-104.82	1248.8	266.35
GACONZnO1273	1281.1	294.30	759	1240.5	249.02	-104.14	1316.8	285.43
$*V_m (cm^3 / g) = \frac{V_h}{2}$	$m (cm^3 / g)$	STP) x 28	3					

6.3.2 I plot method

The BET - Scatchard plot (*I* plot) for the modified granular activated carbons (GAC383, GACO383, GACONZnO1073 and GACONZnO1273) provided inclined *V* shape graphs (Figure 6.11).

$$[V(1 - \frac{p}{p_0})] / \frac{p}{p_0} = CV_m - (C - 1)[V(1 - \frac{p}{p_0})]$$
(6.2)

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 383

The projection of the I - point on the V (1-P) axis corresponds exactly to the Vm (I) directly from the I plot. The surface area calculated from the V_m (I) for the modified carbon is GAC383 (1271.18 m²/g), GACO383 (1163.70 m²/g), GACONZnO1073 (1166.31 m²/g) and GACONZnO1273 (1240.49 m²/g).

Study of porosity and surface area obtained by BET and I plot method for the modified carbons (GAC383, GACO383, GACONZnO1073 and GACONZnO1273) are shown in Figure 6.12 (adsorption capacity versus modified carbons) and Figure 6.13 (surface area versus modified carbons). Identical features are observed in all cases of carbons studied for V_m as well as SA.



Figure 6.11: BET Scatchard isotherm model of modified granular activated carbons (a) GAC383, (b) GACO383, (c) GACONZnO1073 & (d) GACONZnO1273)





- Figure 6.12: Monolayer adsorption capacity from BET and Iplot method using modified granular activated carbons (GAC383, GACO383, GACONZnO1073 and GACONZnO1273)
- Figure 6.13: Specific surface area calculated from BET and I plot method using modified granular activated carbons (GAC383, GACO383, GACONZnO1073 and GACONZnO1273)

6.3.3 Langmuir Isotherm

The Langmuir isotherm models for GAC383, GACO383, GACONZnO1073 and GACONZnO1273 are shown in Figure 6.14 and the constants are presented in Table 6.6.

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m} \tag{6.3}$$

The Langmuir adsorption capacity V_m (*L*) and energy constant (K_L) are calculated from the slope and intercept of the straight line plot *P/V* against *P*. The correlation coefficient (R^2 =0.99) for all the carbons indicates that nitrogen adsorption occurs in homogenous surface of the modified carbons. The Langmuir surface area calculated from the V_m (*L*) is GAC383 (1598.24 m²/g), GACO383 (1476.58 m²/g), GACONZnO1073 (1523.27 m²/g) and GACONZnO1273 (1641.16 m²/g).

6.3.4 Freundlich Isotherm

The Freundlich empirical isotherm model applied to nitrogen isotherm data for the modified granular activated carbons as log V against log P (Figure 6.15). The adsorption capacity (K_F) and adsorption intensity (n) are calculated (Table 6.6).

$$logV = log K_F + 1 / n logP \tag{6.4}$$

The correlation coefficient (R^2 is in the range of 0.97 - 0.98) reveals that Langmuir adsorption isotherm ($R^2 = 0.99$) is more comparable with experimental data of nitrogen isotherm for these carbons. The adsorption intensity *n* (9.07 -13.91) shows that N₂ adsorption by modified carbon is a physisorption process.

Table 6.6: Isotherm Parameters of Langmuir, Freundlich and John models N2(77K) for oxidized granular activated carbon impregnated with nanoZinc oxide (GACONZnO)

	Langmuir Isotherm Model		Freund	Freundlich Isotherm Model			John Isotherm Model		
Carbon	() ()	() ¹⁻					(¹		
	SA (1 (m ² g ⁻	$V_m(L (cm^3 g^2))$	R^2	K_{F}	u	R^2	SA (J (m ² g ⁻	V _m (J (cm ³ g STP)	\mathbf{R}^2
GAC383	1598.2	367.14	0.99	231.44	13.91	0.97	1610.03	369.85	0.99
GACO383	1476.6	339.19	0.99	202.74	12.68	0.97	1503.94	345.48	0.99
GACONZnO1073	1523.3	349.92	0.99	182.91	9.56	0.98	1546.78	355.32	0.99
GACONZnO1273	1641.2	377.00	0.99	190.20	9.07	0.98	1672.37	384.17	0.99
$*V_m (cm^3 / g)$	$=\frac{V_m(cn)}{V_m(cn)}$	$n^3 / g ST$	$(P) \times 2\delta$	8					
	22	414×0.8	08						

6.3.5 John Isotherm

Structural characterization of the new carbon materials are done by well knowm semi empirical Indian isotherm model by renowned adsorption scientist Joh [6].

$$loglog P = C + n \log V \tag{6.5}$$

The John isotherm plots are shown in Figure 6.16 and the results are shown in Table 6.6, the micropore volume $[V_m(J) cm^3/g STP]$ and surface area [SA (J)] obtained for the modified carbons are GAC383 – 369.85 cm³/g STP (1610.03 m²/g), GACO383 - 345.48 cm³/g STP (1503.64 m²/g), GACONZnO1073 – 355.32 cm³/g STP (1546.78 m²/g) and GACONZnO1273 – 384.17 cm³/g STP (1672.37 m²/g). The surface area of modified carbons calculated by Langmuir and John method is comparable and variation is less than 20%, shows these carbons are Type I materials.



Figure 6.14:Langmuir isotherm model of granular activated carbon GACONZnO



Figure 6.15: Freundlich model of granular activated carbon GACONZnO



Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 387

6.3.6 Alpha S (α_s) Isotherm

The Alpha S (α_s) plot is developed by Gregg and Sing (1982) [7] by plotting the amount of nitrogen adsorbed against α_s , the reduced standard adsorption. The nitrogen uptake (V_{ad}) at each p/p₀ divided by that at 0.4 p/p₀ gives the α_s values. The Figure 6.17 shows the α_s plot of the modified carbons GAC383, GACO383, GACONZnO1073 and GACONZnO1273.

$$A_s = 2.86 \frac{V}{\alpha_s} \tag{6.6}$$

The micropore volume (V_{mi}) and external surface area (A_s) are calculated (Table 6.7) by using the plot, the amount of nitrogen adsorbed against alpha S (α_s). The surface area determined from this method (A_s) for the modified carbons are GAC383 (1005.26 m²/g), GACO383 (930.30 m²/g), GACONZnO1073 (948.01 m²/g) and GACONZnO1273 (1050.41 m²/g).

6.3.7 Dubinin - Radushkevich (D - R) Isotherm

Dubinin - Radushkevich isotherm equation [8] is the most useful model to determine micropore volume and micropore surface area. The equation is represented as

$$logV = logV_0 - D log^2(p_0 / p)$$
(6.7)

$$D = 2.303 \left(\frac{RT}{\beta E_0}\right)^2$$
(6.8)

$$L_{av} = 6.6 - 1.79 \ln E_0 \tag{6.9}$$

The Figure 6.18 shows a linear plot of log V against $log^2 (p_0/p)$ of the modified carbons GAC383, GACO383, GACONZnO1073 and GACONZnO1273. The micropore surface area (S_{mi}) and characteristic energy (E_0) are shown in Table 6.7. The characteristic energy (E_0) is in the range of 12.94 -15.62 kJ/mol, indicating that these carbons are adsorbing nitrogen by physisorption mechanism. The micropore volume $(V_0 \ cm^3/g)$ and micropore surface area (S_{mi}) obtained for the modified carbons are GAC383 -0.543 cm³/g or 351.21 cm³/g STP (646.43 m²/g), GACO383 -0.500 cm³/g or 351.21 cm³/g STP (571.43 m²/g), GACONZnO1073 - $0.514\ cm^3/g\ or\ 332.46\ cm^3/g\ STP\ (530.04\ m^2/g)$ and GACONZnO1273 - $0.552 \text{ cm}^3/\text{g or } 357.04 \text{ cm}^3/\text{g STP}$ (557.06 m²/g). The pore width (L) is less than 2 nm for all the carbons studied, GAC383 (1.68 nm), GAC0383 (1.75 nm), GACONZnO1073 (1.94 nm) and GACONZnO1273 (1.98 nm) confirms that pores are widened after oxidation, impregnation and activation process.

		D	α _s Is	$a_{\rm s}$ Isotherm			
Carbon	L (D-R) (nm)	E ₀ (D-R) (kJ/mol)	V ₀ (D-R) (ml/g)	$S_{mi}(D-R)$ (m^2/g)	R^{2}	V _{mi} (ml/g)	A_s (m^2/g)
GAC383	1.68	15.62	0.543	646.43	0.97	0.543	1005.26
GACO383	1.75	15.02	0.500	571.43	0.96	0.503	930.00
GACONZnO1073	1.94	13.25	0.514	530.04	0.97	0.512	948.01
GACONZnO1273	1.98	12.94	0.552	557.06	0.96	0.568	1050.41
$*V_m(cm^3 g / STP) = \frac{V_m(cm^3 g / STP)}{V_m(cm^3 g / STP)}$	cm ³ / g) x 2241- 28	4 x 0.808				

Table 6.7: Dubinin – Radushkevich (D –R) and alpha S (α_s) constants of the modified carbons

The Figure 6.19 shows the result of the study of micropore volume from the D-R and α_s method for all the modified carbon studied. It shows that the micropore volume calculated from these two methods is almost same.







Figure 6.18: D - R Isotherm of modified granular activated carbons (GAC383, GACO383, GACONZnO1073 & GACONZnO1273)



Figure 6.19: Micropore volume calculated by D - R isotherm and α_s using modified granular activated carbons (GAC383, GACO383, GACONZnO1073 & GACONZnO1273)



Figure 6.20: t plot model of modified granular activated carbons (a) GAC383, (b) GAC0383, (c) GAC0NZn01073 & (d) GAC0NZn01273

6.3.8 *t* - *plot* Method

Lippens and De Boer (1964) [9] proposed t - *plot* method, a graphical relationship expressed as a universal t curve in which the thickness of the surface is considered identical to that on the reference surface at all relative pressure. The thickness of the adsorbed layer can be obtained by the equation

$$t = [13.99 / (0.034 - \log(p / p_0))]^{0.5}$$
(6.10)

The Figure 6.20 (a) GAC383, (b) GAC0383, (c) GAC0NZnO1073 and (d) GAC0NZnO1273 shows the t - *plot* isotherm plots, amount adsorbed against the thickness of the adsorbed layer of N₂ at 77K for modified granular activated carbons. The micropore volume, external surface area and mesopore surface area evaluated are presented in Table 6.8.

BJH Method t - plot ore Width Ad ore Width De Carbon Ξ. GAC383 0.134 0.3505 408.10 588.66 226.21 220.52 0.138 2.44 2.43 0.2968 2.28 2.25 GACO383 433.72 540.59 250.00 242.84 0.142 0.137 GACONZnO1073 0.2242 635.44 373.81 370.63 353.23 0.204 0.196 2.20 2.22 GACONZnO1273 0.2072 763.91 300.88 438.01 434.40 0.235 0.232 2.14 2.13 $V_m(cm^3 / g) \times 22414 \times 0.808$ $V_{m}(cm^{3} / g STP) =$ 28

 Table 6.8: Surface area and pore size distribution using t plot and BJH isotherm method for carbon GACONZnO

The external surface area (SA_{ext}) obtained from t - plot method are GAC383 (408.10 m²/g), GACO383 (433.72 m²/g), GACNZnO1073 (635.44 m²/g) and GACONZnO1273 (763.91 m²/g). The micropore surface area calculated by subtracting the external surface area from a BET surface area for the modified carbons is GAC383 (588.66 m²/g),

GACO383 (540.59 m²/g), GACONZnO1073 (373.81 m²/g) and GAOCNZnO1273 (300.88 m²/g). From the *t* - plot method, it is clear that oxidation with nitric acid activation with nano ZnO activated at higher temperature 1073 and 1273K enhances the external surface area.

6.3.9 BJH Pore Size Distribution

The pore size distribution of the modified carbons is obtained by BJH adsorption - desorption plot (Figure 6.21 & 6.22) using the pore volume against pore width. The pore width calculated from BJH adsorption and desorption method for the modified carbons is GAC383 (2.44 nm & 2.43 nm), GACO383 (2.28 nm & 2.25 nm), GACONZnO1073 (2.20 nm & 2.22 nm) and GACONZnO1273 (2.14 nm & 2.13 nm). The pore width shows that the modified carbons have a pore width range from 2.0 - 2.5 nm, which indicate the presence of mesopores. Cumulative adsorption and desorption surface area obtained from these modified carbons are GAC383 (226.21 m²/g & 220.52 m²/g), GACO383 (250.00 m²/g & 242.84 m²/g), GACONZnO1073 (230.72 m²/g & 242.43 m²/g) and GACONZnO1273 (203.34 m²/g & 217.43 m²/g). It is observed that the adsorption desorption pore volume measured is in the range 0.119 - 0.142 cm³/g.



Figure 6.21: BJH adsorption cumulative porevolume of modified granular activated carbons (GAC383, GACO383, GACONZnO1073, &GACONZnO1273)



Figure 6.22: BJH desorption dv/dlogW pore volume of modified granular activated carbons (GAC383, GACO383, GACONZnO1073, & GACONZnO1273)

6.4 Liquid Phase Adsorption Studies Using GACONZnO

The adsorption efficiency and profile of GACONZnO series is determined by using liquid phase adsorption studies by phenol, p – nitrophenol and methyelene blue (MB) as adsorbate, followed by test for adsorption of trace metals from contaminated ground water.

6.4.1 Adsorption Studies – Phenol as Adsorbate

The adsorption studies of phenol by new GACONZnO carbon, includes adsorption kinetics, isotherms, thermodynamics study and further selection of best carbon from this series.

6.4.1.1 Selection of GACONZnO for Phenol Adsorption

Selected a carbon from GACONZnO series for the detailed phenol adsorption studies. The batch experiments were done by using initial phenol concentration of 1000 mg/L. After 8 hrs shaking period the filtrate was measured for C_e (mg/L) using a UV - Visible spectrophotometer at 268 nm and the amount adsorbed (q_e - mg/g) are calculated. The q_e obtained is marked against GACONZnO series as shown in Figure 6.23. It is clear that, GACONZnO1273 shows highest phenol adsorption capacity compared to other carbons from this series. This carbon has shown highest BET surface area, mesopore surface area, elemental carbon and high amount of basic group compared to others.



Figure 6.23: Amount of phenol adsorbed by different types of nano ZnO impregnated on oxidised granular activated carbons, GACONZNO Series ($C_0 = 1000 \text{ mg/L}$)

6.4.1.2 Adsorption Kinetics

The batch kinetic data on phenol uptake at different time interval (q_t) against *time (minute)* for different adsorption temperature of the modified

carbons are shown in Figure 6.24 (a) GAC383, (b) GACO383 and (c) GACONZnO1273.



Figure 6.24: Effect of contact time on the adsorption of phenol on (a) GAC383 (b) GACO383 & (c) GACONZnO1273 at different temperatures for C_0 : 250 mg/L

The phenol adsorption rapidly increased with a contact time of 10 - 480 minutes for adsorption temperatures $10 - 50^{0}$ C. There is no change in adsorption capacity after increasing the time up to 480 minutes, so the equilibrium isotherm studies are done by 8hr equilibration period. The equilibrium adsorption capacity ($q_e exp$) presented in Table 6.9 shows

that, GACNZnO1273 have higher adsorption affinity for phenol removal compared to the oxidised form of carbon (GACO383). The time and temperature dependant data are applied to different kinetic models such as a pseudo first order model, Ho second order model, Weber intraparticle diffusion model and Boyd model to determine the rate of phenol uptake and to identify the physical and chemical properties.

Pseudo first order kinetic model ln (q_e - q_t) against time for the phenol adsorption by modified carbons are shown in Figure 6.25 (a) GAC383, (b) GAC0383 and (c) GAC0NZnO1273.

$$ln(q_e - q_t) = ln q_e - K_1 t \tag{6.11}$$

The equilibrium adsorption capacity calculated $(q_e cal)$ and first order rate constant (K_1) are determined and presented in Table 6.9. It shows that the $q_e cal$, are not comparable with $q_e exp$ obtained from the batch kinetic data and the correlation coefficient $(R^2 ranges from 0.88 - 0.97)$ indicate, phenol adsorption by these modified carbons not follows Lagergren first order kinetic model.

The Figure 6.26 (a), (b) & (c) depicts the pseudo second order kinetic model for the phenol adsorption by modified granular activated carbons.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$
(6.12)

The second order kinetic constants are presented in Table 6.9. The rate constant K_2 increases with rising temperature from 10 to 50^oC, indicate that phenol adsorption by these modified carbons favorable at higher temperature. The q_ecal obtained from this model is also increased with temperature and it is more comparable with adsorption capacity for the time dependent data (q_eexp). The correlation coefficient ($R^2 = 0.99$) for all

cases of carbon at all temperatures identifies that Ho second order kinetic model follows the experimental data for phenol adsorption by these modified carbons (GAC383, GACO383 and GACONZnO1273). The $q_e cal$ obtained from Ho second order kinetic model are marked, varies in the order GAC383 (135.14 - 145.14 mg/g), GACO383 (124.53 - 136.43 mg/g) and GACONZnO1273 (129.70 - 145.77 mg/g).

			First o	rder Kin	etics	Second	order ki	netics
Carbon	T (K)	q _{eexp} (mg/g)	q _{ecal} (mg/g)	K1 (min ⁻¹)	\mathbb{R}^{2}	q _{ecal} (mg/g)	${ m K}_2^{*10^4}$ (gmg ¹ min ⁻¹)	\mathbb{R}^{2}
	283	121.61	86.99	0.007	0.96	135.14	1.24	0.99
	293	126.41	88.72	0.007	0.97	137.93	1.40	0.99
GAC383	303	129.99	84.02	0.007	0.95	139.47	1.59	0.99
	313	134.93	84.76	0.007	0.96	143.06	1.83	0.99
	323	138.76	80.16	0.007	0.95	145.14	2.09	0.99
	283	118.38	75.83	0.006	0.94	124.53	1.80	0.99
	293	122.27	73.27	0.005	0.93	126.42	2.10	0.99
GACO383	303	125.99	71.43	0.006	0.93	130.21	2.30	0.99
	313	129.63	70.72	0.006	0.94	133.69	2.50	0.99
	323	132.84	69.31	0.006	0.95	136.43	2.70	0.99
	283	123.72	74.10	0.007	0.96	129.70	1.56	0.99
	293	127.35	62.37	0.006	0.91	130.21	1.97	0.99
GACONZnO1273	303	134.85	61.54	0.006	0.97	135.32	2.72	0.99
	313	140.20	60.74	0.005	0.88	139.86	2.80	0.99
	323	144.50	64.22	0.006	0.94	145.77	2.83	0.99

Table 6.9: Comparison of the pseudo first and second order kinetic model for the adsorption of phenol (C_0 : 250 mg/L)





School of Environmental Studies, Cochin University of Science and Technology



Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

To determine the diffusion mechanism of phenol adsorption by modified granular activated carbons intraparticle diffusion model is applied.

$$q_t = K_{id} t^{0.5} + C \tag{6.13}$$

The intraparticle diffusion model amount of phenol adsorbed at different time interval (q_t) versus the square root of time $(t^{1/2})$ are shown in Figure 6.27 (a) – (c). It shows two straight line portions, the first portion is the region of the surface or instantaneous adsorption and the second portion is the slow, gradual adsorption step, controlled by intraparticle diffusion [10]. The surface adsorption (K_{id1}) and intraparticle diffusion constant (K_{id2}) are shown in Table 6.10.

		Intraparticle diffusion constant							
Carbon	Т (К)	K _{id1} mgg ⁻¹ min ^{-1/2}	C_1 (mgg ⁻¹)	\mathbb{R}^2	K _{id2} mgg- ¹ min ^{-1/2}	C_2 (mgg ⁻¹)	\mathbf{R}^{2}		
	283	14.49	-29.90	0.97	3.22	52.67	0.98		
	293	14.40	-24.96	0.99	3.36	54.82	0.98		
GAC383	303	15.33	-25.13	0.97	3.18	61.59	0.98		
	313	14.29	-13.35	0.99	3.17	67.43	0.97		
	323	14.16	-6.98	0.99	2.88	76.33	0.99		
	283	11.28	-10.05	0.98	2.77	56.42	0.99		
	293	11.05	-3.68	0.99	2.68	61.33	0.97		
GACO383	303	11.32	0.299	0.99	2.43	71.14	0.98		
	313	11.15	6.68	0.98	2.43	75.56	0.99		
	323	10.49	15.03	0.99	2.37	80.12	0.99		
	283	11.12	-9.73	0.98	3.31	48.97	0.98		
	293	12.62	-9.09	0.99	3.16	55.02	0.96		
GACONZnO1273	303	8.08	31.07	0.99	2.91	68.49	0.97		
	313	9.53	26.35	0.93	2.44	82.15	0.87		
	323	9.55	31.14	0.95	2.54	86.39	0.96		

Table 6.10: Intraparticle diffusion constant of phenol on modified carbons $(C_0: 250 \text{ mg/L})$

School of Environmental Studies, Cochin University of Science and Technology

The K_{id1} of these carbons under different temperatures ranges as GAC383 (14.16 - 15.33 mgg⁻¹min^{-1/2}), GACO383 (10.49 - 11.28 mgg⁻¹min^{-1/2}) and GACONZnO1273 (8.08 - 12.62 mgg⁻¹min^{-1/2}). The K_{id2} obtained are GAC383 (2.88 - 3.36 mgg⁻¹min^{-1/2}), GACO383 (2.37 - 2.77 mgg⁻¹min^{-1/2}) and GACONZnO1273 (2.44 - 3.31 mgg⁻¹min^{-1/2}). The $K_{id1} > K_{id2}$ indicate that intraparticle diffusion is the slowest and it is the rate controlling step for the adsorption of phenol by these modified granular activated carbon studied. The intercept of the second linear portion is proportional to the boundary layer thickness (C_2) for the modified carbons for different temperatures ranging from 10 to 50°C are GAC383 (52.97 - 76.33 mg/g), GACO383 (56.42 - 80.12 mg/g) and GACONZnO1273 (48.97 - 86.39 mg/g). The adsorption temperature increases the boundary layer thickness for the adsorption systems.

The Boyd model is used to determine the actual rate controlling step involved in the adsorption of phenol.

$$B_t = -0.4977 - \ln(1 - F) \tag{6.14}$$

A linear plot of B_t against time (*t*) is shown in Figure 6.28 (a) GAC383, (b) GAC0383 and (c) GAC0NZnO1273 for the phenol adsorption data. The line of these plots at different temperatures (10 – 50^oC) did not pass through the origin; means that external mass transport was mainly governed by the adsorption process of phenol on carbons and intraparticle diffusion is the slowest step and the rate controlling step [11].

6.4.1.3 Activation Energy

Activation energy is determined from pseudo second order rate constant of phenol for the adsorption using the Arrhenius equation.

$$\ln K_2 = \ln K_0 - \frac{E_a}{RT} \tag{6.15}$$

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 401

A linear plot of $ln K_2$ against l/T (Figure 6.29) gives activation energy from the slope (Table 6.11).The E_a of these modified carbons is GAC383 (10.00 kJ/mol), GACO383 (7.59 kJ/mol) and GACONZnO1273 (11.89 kJ/mol). The positive activation energy confirms that adsorption is an endothermic process and being $E_a < 40 kJ/mol$ means adsorption is a physical process. Less amount of activation energy (E_a) shows that the rate is controlled by an intraparticle diffusion mechanism [12].



Figure 6.29: plot of lnK₂ versus 1/T for the for the adsorption of phenol on modified activated carbons (a) GAC383, (b) GACO383 and (c) GACONZnO1273

Table 6.11:	Activation energy	determined	during	adsorption	of phenol	on new
	modified carbons					

Carbon	$E_a(kJmol^{-1})$	K ₀
GAC383	10.00	0.008
GACO383	7.59	0.005
GACONZnO1273	11.89	0.026

6.4.1.4 Adsorption Isotherm studies of phenol

The equilibrium adsorption isotherm data constants and parameters are most essential for the testing and evaluation of the performance of the batch reactor system studied.



Figure 6.30: Adsorption isotherm of phenol on GAC383, GACO383 & GACONZnO1273 at different temperatures (a) 10° C (b) 20° C (c) 30° C (d) 40° C & (e) 50° C for initial concentration $C_0 = 25 - 3000$ mg/L

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 403

Figure 6.30 (a), (b) & (c) shows the equilibrium adsorption isotherm data of the modified carbons GAC383, GACO383 and GACONZnO1273 for the adsorption of phenol, at different temperatures $(10^{\circ}C, 20^{\circ}C, 30^{\circ}C, 40^{\circ}C$ and $50^{\circ}C$). The figure shows a Type I isotherm pattern according to the IUPAC classification [13]. Compared to oxidized form of carbon (GACO383), the carbon impregnated with nano zinc oxide and activated at 1273 (GACONZnO1273) shows higher phenol adsorption efficiency at all temperatures. It is seen that impregnation and activation decrease the proportion of acidic functional groups and the fixed carbon percentage highly influenced the adsorption efficiency.

These phenol adsorption equilibrium data are treated with different isotherm equations such as Langmuir, Freundlich isotherm, Temkin and Dubinin – Radushkevich isotherm models. Most isotherm model constants are related to the adsorption capacity (q_m) and surface properties of these modified carbons studied.

6.4.1.4.1 Langmuir Isotherm Model

The monolayer adsorption capacity (q_{max}) and Langmuir energy constants (K_L) of the modified granular activated carbons are obtained from the slope and intercept of the linear plot of C_e/q_e versus C_e are shown in Figure 6.31 (a) – (c) and the constant are presented in Table 6.12.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e \tag{6.16}$$

The q_{max} and K_L increase with temperature convinces that the adsorption of phenol by GAC383, GACO383 and GACONZnO1273 is an endothermic process. The adsorption capacity is enhanced with respect to temperature due to the enlargement of the pore sizes or creation of more active sites on the carbon surface [14]. Carbon GACONZnO1273 shows maximum adsorption capacity ranges from 260.42 – 334.45 mg/g and

native carbon GAC383 shows little higher adsorption capacity (266.67 – 352.12 mg/g). These two carbons show the same percentage of fixed carbon (89%) and pyrones (0.45 -0.50 meq/g). But in *t* - *plot* micropore surface area was higher in GAC383 (588.66 m²/g) and has lower external surface area (408.10 m²/g). Whereas GACONZnO1273 has micropore surface area (373.81 m²/g) and shows a higher external surface area (761.00 m²/g). The total surface area calculated as 1134.81 m²/g for GACONZnO1273 whereas that of GAC383 is 1096.76 m²/g. The excess external surface area has reduced the phenol uptake of this carbon modified. The correlation coefficient ($R^2 - 0.99$) indicates the experimental equilibrium data are in good agreement with the Langmuir isotherm model and the phenol adsorption occurs on homogenous surface of these modified carbons.

6.4.1.4.2 Freundlich Isotherm Model

The slope and intercept of the linear plots of $log q_e$ against $log C_e$ at different temperatures (Figure 6.32 (a), (b) & (c)) ranging from 10 - 50^oC are used to calculate adsorption capacity (K_F) and adsorption intensity (n) of Freundlich isotherm model.

$$\log q_e = \log K_F + 1/n \log C_e \tag{6.17}$$

The adsorption capacity K_F increases with temperature, indicate that it is an endothermic process. The adsorption intensity "*n*" gives an idea about the favorable nature of adsorption. The *n* is in the range of 2 - 10 represents good adsorption, 1 - 2 moderately difficult and n < 1 is poor adsorption [15]. In our study, the carbon materials are good adsorbent for phenol adsorption, *n* is in the range of 2.42 - 3.17. The correlation coefficient of Langmuir isotherm model ($R^2 = 0.99$) showed that it is better fitted than Freundlich model ($R^2 = 0.89 - 0.95$) for phenol adsorption studies.

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 405



Lable 0.14: Lang carbo	null, ri ns for i	initial con	t entratic	anu ur m C ₀ =	= 25 – 3(Nauus 100 mg	/L	(N-U) I	ISOUICIII	і рагані	cicis u	I pileiuu	ausorpuo		outtien
		Langm C6	uir isoth nstants	erm	Freund Ci	lich iso mstant	therm	L	emkin is Consta	otherm unts		Dubi	inin – Rad isother D-R) Con	lushkevi m ıstants	ch
Carbon		G	(,		(((10	۱- ₅)	
	T (K)	^{xem} b	(ן ש5 <u>.</u> א ^ר	zط	(سکھ لا ^ہ	u/I	_z α	(Sɯ/J) V	B	(լօա/բ) ք	_z α	(ш&\& (D-В) (D-В)	(кา\ш (D-В) Е ⁰	r _z low) g	zΉ
	283	266.67	2.33	0.99	16.38	2.60	0.93	0.189	43.10	52.66	0.98	55.52	0.267	7.03	0.98
	293	284.90	2.48	66.0	16.74	2.56	0.94	0.188	46.14	49.19	0.98	56.62	0.288	6.01	0.98
UAC383	303	312.50	2.48	66.0	16.73	2.49	0.98	0.175	50.47	44.97	66.0	57.39	0.293	5.83	0.98
	313	336.70	2.53	66.0	17.00	2.44	0.95	0.171	53.96	42.06	0.98	58.39	0.339	4.34	0.98
	323	352.12	2.68	66.0	17.38	2.42	0.95	0.172	56.33	40.29	0.98	59.22	0.362	3.81	0.98
	283	188.32	2.17	0.99	19.16	3.17	0.89	0.370	27.90	81.35	0.99	54.89	0.247	8.19	0.98
	293	199.60	2.34	66.0	19.87	3.13	0.89	0.370	29.61	76.64	0.99	56.10	0.273	6.71	0.98
COCUDED.	303	209.64	2.48	66.0	20.71	3.12	0.89	0.379	30.98	73.26	0.99	57.41	0.302	5.50	0.98
	313	225.73	2.52	66.0	21.13	3.05	06.0	0.360	33.34	68.08	0.99	58.76	0.328	4.65	0.98
	323	236.97	2.59	0.99	21.66	3.02	06.0	0.360	34.88	65.07	0.99	59.29	0.359	3.89	0.98
	283	260.42	2.01	0.99	17.90	2.76	0.94	0.219	39.69	57.19	0.98	60.53	0.265	7.15	0.98
	293	271.74	2.13	0.99	18.57	2.75	0.93	0.225	41.33	54.91	0.99	62.84	0.273	6.71	0.98
UACUNZIIU12/3	303	298.51	2.19	0.99	18.97	2.68	0.94	0.216	45.07	50.36	0.99	65.94	0.282	6.29	0.99
	313	318.47	2.63	66.0	20.75	2.68	0.93	0.242	48.00	47.29	0.99	66.25	0.335	4.45	0.98
	323	334.45	2.87	0.99	22.53	2.71	0.93	0.271	49.51	45.84	0.98	68.35	0.389	3.30	0.99

6.4.1.4.3 Temkin Isotherm Model

Temkin isotherm model was used to test the phenol adsorption potential of the granular activated carbons GAC383, GACO383 and GACONZnO1273 (Figure 6.33). It assumes that, the heat of adsorption decreases linearly with the coverage due to effective adsorbent – adsorbate interaction.



Figure 6.33: Temkin isotherm model of phenol by (a) GAC383, (b) GAC0383 & (C) GAC0NZn01273 at different temperatures for initial concentration $C_0 = 25 - 3000 \text{ mg/L}$

$$q_e = B \ln A + B \ln C_e \tag{6.18}$$

$$B = \frac{RT}{b_T} \tag{6.19}$$
The Temkin isotherm constants (*A*, *B* & b_T) are calculated for phenol adsorption (Table 6.12). The constant *B* increases with temperature indicate that adsorption is an endothermic process. The adsorption energy (b_T) is less than 80 kJ/mol means adsorption of phenol here occurs by the physical forces of attraction.

6.4.1.4.4 Dubinin - Radushkevich (D-R) Isotherm - Phenol

The Dubinin – Radushkevich (D-R) isotherm helps to understand the phenol adsorption occurs by granular activated carbon is a physical or chemical process.

$$lnq_e = lnQ_D - \beta\varepsilon^2 \tag{6.20}$$

$$E_0 = \frac{I}{(2\beta)^{1/2}}$$
(6.21)

The adsorption characteristic energy (E_0) calculated (Table 6.13), it is in the range 0.2668 – 0.3898 kJ/mol shows that phenol adsorption is a physical process. The adsorption capacity (Q_D) increases with temperature means adsorption is an endothermic process. The Q_D for granular activated carbons are GACONZnO1273 (60.53 – 68.30 mg/g), GAC383 (55.52 – 59.22 mg/g) and GACO383 (54.89 – 59.29 mg/g). The correlation coefficient (R^2) for D - R model is in the range of 0.98 - 0.99 for the lower concentration of phenol adsorption by these carbons studied.

6.4.1.5 Thermodynamic Parameters for Phenol Adsorption

The thermodynamic behaviour for the adsorption of phenol by modified granular activated carbons (GAC383, GAO383 and GACONZnO1273) was analysed using Van't Hoff equation.

$$\Delta G = -RT \ln K_L \tag{6.22}$$

$$\Delta G = \Delta H - T \Delta S \tag{6.23}$$

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 409

Chapter 6

The Gibbs free energy change (ΔG) decreases with increasing temperature. The ΔG of this new carbons are GAC383 (-1.94 to -2.59 kJ/mol), GACO383 (-1.82 to -2.55 kJ/mol) and GACONZnO1273 (-1.64 to -2.52 kJ/mol). The negative ΔG indicates the spontaneous nature of adsorption.

		Δ	G (kJmo	⁻¹)			
Carbon	283	293	303	313	323	AH (kJmol ⁻¹)	ΔS (Jmol ⁻¹ K ⁻¹)
GAC383	-1.94	-2.18	-2.24	-2.35	-2.59	2.26	14.93
GACO383	-1.82	-2.07	-2.29	-2.41	-2.55	3.30	18.26
GACONZnO1273	-1.64	-1.84	-1.98	-2.52	-2.83	7.12	30.64

Table 6.13: Thermodynamic parameters – Gibb's free energy(ΔG) , enthalpy(ΔH)and entropy (ΔS) for the adsorption of phenol on carbons

The enthalpy change (ΔH) and entropy change (ΔS) are calculated (Table 6.12) from the intercept and slope of the plot ΔG against 1/T (Figure 6.34). The result reveals that the ΔH obtained for the adsorption of phenol onto modified granular activated carbons are positive. The positive enthalpy change indicates that adsorption is an endothermic process. The $\Delta H < 80 \ kJ/mol$ for all the carbons studied. It reveals that, phenol adsorption is a physisorption process. This means, phenol adsorption occurs due to the deterioration of weak Van der Waals forces between the active sites on the activated carbon and phenol molecule. The positive ΔS correspond to the increase in the degree of freedom of adsorbed species.



Figure 6.34: ΔG versus Temperature for determination of thermodynamic parameters for the adsorption of phenol by (a) GAC383, (b) GAC0383 & (c) GACONZnO1273

6.4.2 Adsorption Studies of *p* –nitrophenol

The adsorption studies of p – nitrophenol by modified granular activated carbons GAC383, GACO383 and GACONZnO series includes the selection of carbon, adsorption kinetics, isotherm and thermodynamic study.

6.4.2.1 Selection of Carbon from GACONZnO Series

To select a best carbon from GACONZnO series efficient for the adsorption of p – nitrophenol, batch study has been done for an initial concentration 1000 mg/L as a function of time. The final concentration of p – nitrophenol at each time interval (ranging from 10 minutes to 600minutes)

was measured by a UV – Visible spectrophotometer at 317 nm. Adsorption of p – nitrophenol increases with time and GACONZnO1273 shows higher removal efficiency compared to other carbon members of this GACONZnO series (Figure 6.35).



Figure 6.35: Effect of contact time and amount adsorbed for the adsorption of *p* - nitrophenol on GACONZnO activated at different temperatures

6.4.2.2 Adsorption Kinetics

The Figure 6.36 (a), (b), (c), (d) & (e) presents the plot of p - nitrophenol adsorbed ($q_t mg/g$) versus contact time (t) for an initial concentration of 250 mg/L at different temperature ranging from 10^oC to 50^oC. The amount of p – nitrophenol adsorbed from batch experimental study ($q_e exp$) for GAC383 varies in the range of 201.92 – 219.02 mg/g whereas for GAC0383, it is in the range 119.50 – 138.59 mg/g and for GAC0NZnO1273, and it is in the range of 168.46 – 208.30 mg/g under different temperatures studied. All these modified granular activated carbons show the same trend as adsorption capacity enhances with time and temperature. These time dependent data are subjected to different kinetic models such as pseudo first order model, Ho second order kinetic model, Intraparticle diffusion model and Elovich kinetic model to identify the mechanism of adsorption and rate constants.



Figure 6.36: Effect of contact time on the adsorption of *p* -nitrophenol on GAC383, GAC0383 and GAC0NZnO1273 at different temperatures (a) 10° C, (b) 20° C, (c) 30° C, (d) 40° C & (e) 50° C for initial concentration C₀ = 250 mg/L

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 413



) D													Ĩ
Carbon			First o	rder Kin	etics	Sec	ond orde kinetics	ar		Intrapar	ticle dil	fusion c	onstant		Elovic	ch Cons	tant
	(K) L	mg/g) leexp	lecal (^{ecal}	ر، (¹⁻ nim	28	(¹ -92m) (ecal	² -01 ⁴ 2) 2×10 ⁻⁵	z 2	(^{2/1-} nim ¹ 22m	ו <mark>י 12</mark> ניב	7	(^{2/1-} nim ¹ 22m)	(¹ -22m) ג ^ב	z ?	ו נ ^ד חוֹש ^י))	៩៣៩ ₋₁) ទ	7
	283	201.92	153.84	0.007	0.98	221.24	7.59	0.99	16.69	-15.98	0.98	5.64	79.51	0.99	9.04	0.023	0.99
	293	209.76	151.53	0.006	0.98	225.73	8.50	0.99	16.69	-7.49	0.98	5.51	89.37	0.99	11.06	0.023	66.0
GAC383	303	213.44	151.29	0.007	0.98	228.83	9.20	0.99	16.80	-2.21	0.97	5.34	97.64	0.99	12.76	0.023	0.99
	313	216.53	151.04	0.008	0.98	231.48	10.18	0.99	15.96	9.13	96.0	5.08	107.66	0.99	15.43	0.024	66.0
	323	219.02	143.17	0.008	0.98	232.02	11.46	0.99	17.13	69.6	0.97	4.75	116.88	0.99	18.60	0.024	66.0
	283	119.50	82.71	0.005	0.91	129.53	12.38	0.99	13.35	-28.15	0.98	2.99	51.47	0.97	5.12	0.038	0.97
	293	124.52	84.52	0.006	0.93	133.33	14.16	0.99	12.90	-20.54	0.96	3.06	55.88	0.99	6.28	0.038	0.97
GC0383	303	129.30	84.24	0.006	0.93	136.80	15.58	0.99	12.89	-15.83	0.97	2.99	62.04	0.99	7.50	0.038	0.97
	313	133.78	81.11	0.006	0.94	139.86	18.80	0.99	12.44	-5.21	0.96	2.97	68.11	0.99	10.75	0.040	0.98
	323	138.59	78.20	0.006	0.94	142.45	21.26	0.99	11.93	4.89	0.99	3.21	67.38	0.99	15.66	0.042	66.0
	283	168.42	128.62	0.006	0.97	186.57	8.12	0.99	11.60	-6.23	0.99	4.10	77.52	0.99	6.64	0.027	0.99
	293	179.1	129.81	0.008	0.98	193.42	9.52	66.0	14.09	-7.28	66.0	4.76	74.95	66.0	8.52	0.026	86.0
GACONZnO1273	303	188.1	129.43	0.006	0.96	199.20	10.90	66.0	13.18	7.94	0.99	4.54	87.40	0.94	12.31	0.028	0.98
	313	195.56	117.41	0.007	0.95	205.34	14.02	66.0	17.83	-2.74	96.0	3.58	116.93	0.99	17.50	0.027	0.97
	323	208.3	120.97	0.007	96.0	217.39	14.63	66.0	17.90	7.96	66.0	3.84	124.28	0.99	23.05	0.027	86.0



School of Environmental Studies, Cochin University of Science and Technology

The pseudo first order kinetic model proposed by Lagergren (1898) [16] have been applied for the p – nitrophenol adsorption kinetics by modified carbons. A linear plot of $ln (q_e - q_t)$ versus t (minutes) (Figure 6.37 (a) –(c)) from the slope as the first order rate constant (K_I) and from the intercept, amount adsorbed (q_ecal). The theoretical p – nitrophenol adsorbed (q_ecal) from this model is compared with experimental q_eexp . The experimental data deviate from the theoretical data (q_ecal). It shows that this model fails to predict the p -nitrophenol adsorption by these modified carbons at all contact time studies.

The equilibrium adsorption capacity $(q_e cal)$ and the second order rate constant (K_2) determined from a straight line plot of t/q_t against *time* (Figure 6.38 (a), (b) & (c)). The second order kinetic constant and correlation coefficients are listed in Table 6.14. The amount adsorbed $(q_e exp)$ are more comparable with q_e calculated $(q_e cal)$ obtained from the pseudo second order kinetic model and high correlation coefficient $(R^2 - 0.99)$ indicate that p – nitrophenol adsorption process is more favorable by pseudo second order kinetic model for all the carbons studied.

To investigate the diffusion mechanism of p – nitrophenol adsorption process an intraparticle diffusion model was used. Using the experimental kinetic data, by plotting the amount adsorbed at different time interval (q_t) versus $t^{1/2}$, two straight portions are obtained (Figure 6.39 (a) –(c)). The first portion indicates the surface adsorption and the second linear region are attributed to pore diffusion. The diffusion constant and boundary layer thickness are shown in Table 6.14. The intercept of the second portion (C_2) that is the boundary layer thickness shows high values for the modified carbons GAC383 (79.5 -116.9 mg/g), GACO383 (51.5 – 67.4 mg/g) and GACONZnO1273 (77.52 - 124.28 mg/g) at different temperature ranging from 10 – 50°C. The $K_{id1} > K_{id2}$ for the adsorption of p - nitrophenol on these three carbons studied. It makes us to believe that the intraparticle

Chapter 6

diffusion is the slowest step for p – nitrophenol adsorption. Also it is the rate controlling step for these modified carbon studied.

Figure 6.40 (a), (b) & (c) presents the plot of amount of p – nitrophenol adsorbed at different time interval (q_t) against natural logarithm of time (ln t). The Elovich kinetic constants and correlation coefficients are calculated (Table 6.13). The initial adsorption rate (α) increases with temperature means adsorption is an endothermic process. The surface active sites become more active with temperature and p –nitrophenol removal percentage increases. The Elovich constant α for different temperature are in the range of GAC383 (9.04 - 18.60 mg/g), GACO383 (5.12 - 15.66 mg/g) and GACONZnO1273 (6.64 - 23.35 mg/g). All these three carbons show correlation coefficient is in the range ($R^2 - 0.97 \cdot 0.99$).

6.4.2.3 Activation Energy - p – nitrophenol as Adsorbate

The activation energy (E_a) of p – nitrophenol adsorption by granular activated carbons is obtained from Arrhenius plot, $ln K_2$ versus l/T (Figure 6.41). The energy of activation (E_a) for the modified carbons is GAC383 (7.65 kJ/mol), GACO383 (10.35 kJ/mol) and GACONZnO1273 (11.90 kJ/mol). The calculated Ea < 40 kJ/mol indicate that p –nitrophenol adsorption onto modified carbon is a physical adsorption process.



Figure 6.41: Plot of $ln K_2$ versus 1/T for the adsorption of p -nitrophenol on modified granular activated carbons

on new	modified carbons		
Carbon	E _a (kJmol-1)	K ₀	\mathbf{R}^2
GAC383	7.63	0.002	0.99
GACO383	10.35	0.009	0.99
GACONZnO1273	11.90	0.013	0.97

Table 6.15: Activation energy determined during adsorption of p -nitrophenolon new modified carbons

6.4.2.4 Adsorption Isotherm Studies, P- nitrophenol as Adsorbate

The adsorption isotherm indicates how p –nitrophenol molecules distribute between p-nitrophenol solution phase and carbon surface when the adsorption process reaches at an equilibrium state.



Figure 6.42: Adsorption isotherm of *p*- nitrophenol adsorption on (a) GAC383, (b) GAC0383 & (c) GAC0NZn01273 at different temperatures for initial concentration $C_0 = 25 - 3000$ mg/L

Granular Activated Carbon Incorporated With Zn $^{2+}$ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 419

Chapter 6

The Figure 6.42 (a), (b) & (c) shows a plot of amount adsorbed (q_e) against equilibrium concentration (C_e) for GAC383, GACO383 and GACONZnO1273 for 10 - 50^oC. The Figure shows that temperature and the initial concentration influences the adsorption efficiency of p – nitrophenol. These isotherm experimental data applied to different isotherm models such as Langmuir isotherm, Freundlich isotherm, Temkin isotherm and Dubinin – Radushkevich isotherm models and to evaluate correlation between amounts of p –nitrophenol adsorbed against equilibrium concentration.

The Langmuir isotherm model shows a linear plot of C_{e}/q_{e} versus C_{e} for p – nitrophenol adsorption (Figure 6.43 (a), (b) & (c)) and the parameters are presented (Table 6.16). The Langmuir energy constant (K_L) and monolayer adsorption capacity (q_{max}) increases with temperature show that adsorption is an endothermic process. Temperature enhances the proportion of active sites on the surface of these carbons as it enlarges the sizes of pores and hence adsorption efficiency enhances. The q_{max} of the modified carbons are GAC383 (272.48 - 403.23 mg/g), GACO383 (201.61 245.70 mg/g) and GACONZnO1273 (293.25-390.63 mg/g) at temperature ranging from 10 - 50° C. It means that GACONZnO1273 has the highest adsorption efficiency among the group selected for p – nitrophenol isotherm study. The efficiency of GACONZnO1273 depends on several factors such as high BET surface area (1064 m^2/g), total pore volume (0.595 cm³/g), high distribution of micro (34.86%) and mesopores (65.14%). The correlation coefficient $(R^2 - 0.99)$ for all the carbons studied at all temperatures indicating that carbon surface is energetically homogeneous.

The essential characteristics of Langmuir isotherm model is the determination of separation factor (R_L). The Figure R_L against initial concentration (C_0) of modified carbons GAC383 (6.44 a), GACO383 (6.44



b) and GACNZnO1273 (6.44 c) shows that the R_L lies between 0 and 1. Adsorption is most favored at all initial concentrations and temperatures.

The Freundlich isotherm model was applied for the adsorption of p –nitrophenol by GAC383 (Figure 6.45 (a)), GACO383 (Figure 6.45 (b)) and GACONZnO1273 (Figure 6.45 (c)). The Freundlich isotherm parameters such as adsorption capacity (K_F) , adsorption intensity (n) and correlation coefficient are calculated and tabulated in Table 6.16. The adsorption capacity increases with temperature due to the pore enlargement. The correlation coefficients $(R^2 = 0.86 - 0.94)$ of these isotherm is less than that of the Langmuir correlation coefficient (R^2 - 0.99) shows that adsorption of p –nitophenol on modified carbons are Langmuir type [17].

The Figure 6.46 (a), (b) & (c) shows the Temkin isotherm plot, q_e against $ln C_e$ for the modified carbon at different temperature (10 - 50^oC). The equilibrium binding constant (A), heat of adsorption constant (B) and adsorption energy (b_T) are calculated from the Temkin plot (Table 6.16). The B increases with temperature for modified carbons, GAC383 (29.56 – 45.86), GACO383 (30.27 - 36.82) and GACNZnO1273 (43.31 - 50.20). It indicates, the prominence of endothermic character of adsorption. Temkin isotherm constant (b_T) is less than 80 kJ/mol indicating that adsorption is a physical process.

The Dubinin – Radushkevich isotherm helps to understand adsorption is a physical or chemical process. The mean activation energy (E_0) calculated from D - R isotherm model (Table 6.16) identified that $E_0 < 8$ kJ/mol means p – nitrophenol adsorption by modified carbons occurs through weak Van der Waals force of attraction. The adsorption capacity (Q_D) increases with increasing temperature indicate than adsorption is an endothermic character.



Carbon T $\frac{1}{2}$			angmuir (Constants		Ere Co	eundlic	h s	L	emkin (Constant	s	Dub	inin – R: (D -R) C	adushke	vich
GAC383 272.48 7.61 0.028 0.99 55.49 4.26 293 304.88 8.36 0.027 0.99 55.01 4.06 293 304.88 8.36 0.026 0.99 55.58 3.88 313 340.14 9.03 0.026 0.99 56.58 3.88 313 340.14 9.03 0.027 0.99 56.58 3.88 313 347.36 9.40 0.027 0.99 56.58 3.88 323 403.23 10.69 0.027 0.99 56.58 3.88 233 201.61 2.06 0.010 0.99 18.93 3.01 GAC0383 303 224.22 2.14 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 313 235.29 2.41 0.010 0.99 19.67 2.94 323 293.255 2.41	E A	տր որ	(רש _{לין}) א ^ר	(רשמ _{ין}) זיי	zΒ	(wSS ₋₁) K ^k	u	zB2	₁ - դր	В	Td (Joml)	εz	(Ճ/Ճա) ^ա b	(۲۹\mol) E ⁰	(mol ₅ 1- ₅₎ K'	r ²
GAC383 304.88 8.36 0.027 0.99 55.01 4.06 GAC383 303 340.14 9.03 0.026 0.99 56.58 3.88 313 377.36 9.40 0.025 0.99 56.58 3.83 313 377.36 9.40 0.025 0.99 56.58 3.83 323 403.23 10.69 0.027 0.99 59.90 3.64 233 201.61 2.06 0.010 0.99 18.93 3.01 293 213.22 2.14 0.010 0.99 18.93 3.01 303 224.22 2.31 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 310 2.91 0.010	28	3 272.48	7.61	0.028	66.0	53.49	4.26	0.86	5.54	29.56	76.79	96.0	75.77	1.47	0.23	66.0
GAC383 303 340.14 9.03 0.026 0.99 56.58 3.88 313 377.36 9.40 0.025 0.99 58.14 3.73 313 377.36 9.40 0.027 0.99 58.14 3.73 323 403.23 10.69 0.027 0.99 58.90 3.64 323 201.61 2.06 0.010 0.99 18.48 3.05 283 201.61 2.06 0.010 0.99 18.93 3.01 293 213.22 2.14 0.010 0.99 18.93 3.01 303 224.22 2.31 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 19.67 2.94 333 293.25 2.64 1.002 0.99 3.06 3.01 GACONZn01273 303 344.83	29	3 304.88	8.36	0.027	66.0	55.01	4.06	0.88	4.50	33.62	67.50	66.0	77.02	1.66	0.18	66.0
313 377.36 9.40 0.025 0.99 58.14 3.73 323 403.23 10.69 0.027 0.99 59.90 3.64 283 201.61 2.06 0.010 0.99 59.90 3.64 283 201.61 2.06 0.010 0.99 18.93 3.01 293 213.22 2.14 0.010 0.99 18.93 3.01 303 224.22 2.31 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 19.67 2.94 323 293.25 2.64 1.002 0.99 31.08 3.32 GACONZnO1273 303 344.83 4.83 0.999 0.990 3.69 313 367.65 4.89 0.999 0.999 3.03 3.89	30	3 340.14	9.03	0.026	66.0	56.58	3.88	0.89	3.78	38.01	59.71	66.0	78.21	1.85	0.14	66.0
323 403.23 10.69 0.027 0.99 59.90 3.64 283 201.61 2.06 0.010 0.99 18.48 3.05 293 201.61 2.06 0.010 0.99 18.93 3.01 293 213.22 2.14 0.010 0.99 18.93 3.01 303 224.22 2.31 0.010 0.99 19.33 2.97 313 235.29 2.31 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 19.67 2.94 323 293.25 2.64 1.002 0.99 31.08 3.32 GACONZnO1273 303 344.83 4.83 0.999 0.999 36.03 3.89 GACONZnO1273 313 367.65 4.89 0.999 0.999 53.03 3.89	31	3 377.36	9.40	0.025	66.0	58.14	3.73	0.91	3.31	42.44	53.48	66.0	79.53	2.03	0.12	66.0
GAC0383 201.61 2.06 0.010 0.99 18.48 3.05 GAC0383 293 213.22 2.14 0.010 0.99 18.93 3.01 303 224.22 2.23 0.010 0.99 18.93 3.01 313 235.29 2.31 0.010 0.99 19.33 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 19.67 2.94 323 235.25 2.41 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 20.04 2.91 293 320.51 3.49 0.999 0.999 3.03 3.67 303 344.83 4.83 0.999 0.999 3.69 3.61 313 367.65 4.89 0.999 0.999 53.03 3.81	32	3 403.23	10.69	0.027	66.0	59.90	3.64	16.0	3.15	45.86	49.49	66.0	81.24	2.19	0.10	0.99
GAC0383 293 213.22 2.14 0.010 0.99 18.93 3.01 GAC0383 303 224.22 2.23 0.010 0.99 19.33 2.97 313 235.29 2.31 0.010 0.99 19.67 2.94 313 235.29 2.31 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 19.67 2.94 283 293.25 2.64 1.002 0.99 31.08 3.32 GACONZn01273 303 344.83 4.83 0.999 0.99 3.09 3.69 313 367.65 4.89 0.999 0.99 53.03 3.89	28	3 201.61	2.06	0.010	0.99	18.48	3.05	0.93	0.31	30.27	74.99	0.99	49.61	0.329	4.63	0.97
GACO383 303 224.22 2.23 0.010 0.99 19.33 2.97 313 235.29 2.31 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 20.04 2.91 283 293.25 2.64 1.002 0.99 31.08 3.32 293 320.51 3.49 0.999 0.99 40.90 3.60 313 367.65 4.89 0.999 0.99 53.03 3.89 313 367.65 4.89 0.999 0.99 56.52 3.91	29	3 213.22	2.14	0.010	66.0	18.93	3.01	0.93	0.31	31.94	71.07	66.0	50.62	0.355	3.97	0.97
313 235.29 2.31 0.010 0.99 19.67 2.94 323 245.70 2.41 0.010 0.99 20.04 2.91 323 245.70 2.41 0.010 0.99 20.04 2.91 283 293.25 2.64 1.002 0.99 31.08 3.32 293 320.51 3.49 0.999 0.999 0.99 36.0 293 320.51 3.49 0.999 0.999 36.0 3.60 303 344.83 4.83 0.999 0.99 53.03 3.89 313 367.65 4.89 0.999 0.99 53.03 3.89 273 306.2 5.00 1.000 6.99 56.52 3.91	30	3 224.22	2.23	0.010	66.0	19.33	2.97	0.93	0.30	33.60	67.55	66.0	51.31	0.386	3.35	0.97
323 245.70 2.41 0.010 0.99 20.04 2.91 283 293.25 2.64 1.002 0.99 31.08 3.32 293 320.51 3.49 0.999 0.99 40.90 3.60 293 320.51 3.49 0.999 0.99 40.90 3.60 303 344.83 4.83 0.999 0.99 3.60 3.69 313 367.65 4.89 0.999 0.99 53.03 3.89 272 260.52 5.00 1.000 6.09 56.52 3.91	31	3 235.29	2.31	0.010	66.0	19.67	2.94	0.93	0.30	35.26	64.37	66.0	52.08	0.414	2.92	0.97
283 293.25 2.64 1.002 0.99 31.08 3.32 293 320.51 3.49 0.999 0.99 40.90 3.60 293 320.51 3.49 0.999 0.99 40.90 3.60 303 344.83 4.83 0.999 0.99 53.03 3.89 313 367.65 4.89 0.999 0.99 55.52 3.91	32	3 245.70	2.41	0.010	0.99	20.04	2.91	0.94	0.29	36.82	61.64	66.0	52.74	0.446	2.51	0.97
GACONZnO1273 293 320.51 3.49 0.999 0.99 40.90 3.60 303 344.83 4.83 0.999 0.99 55.03 3.89 313 367.65 4.89 0.999 0.99 56.52 3.91	28	3 293.25	2.64	1.002	0.99	31.08	3.32	0.92	0.66	37.12	61.14	96.0	81.76	0.510	1.90	0.86
GACONZADU1273 303 344.83 4.83 0.999 0.99 53.03 3.89 313 367.65 4.89 0.999 0.99 56.52 3.91 222 220.62 6.02 1.000 6.01 60.19 2.94	29	320.51	3.49	666.0	66.0	40.90	3.60	0.92	1.35	37.16	61.08	0.98	88.68	0.930	0.58	0.97
313 367.65 4.89 0.999 0.99 56.52 3.91	273 30	3 344.83	4.83	0.999	66.0	53.03	3.89	0.92	3.12	36.76	61.75	66.0	92.39	1.33	0.28	0.91
272 200.62 5.07 1.000 50.10 2.07	31	3 367.65	4.89	666.0	66.0	56.52	3.91	0.92	3.53	38.21	59.39	86.0	93.71	1.82	0.15	66.0
40°C 01°CC 66°D 000°T 76°C 00°D6C 67°C	32	3 390.63	5.92	1.000	0.99	59.18	3.84	0.94	3.75	40.73	42.11	66.0	94.88	2.05	0.12	0.99



6.4.2.5 Thermodynamic Parameters

The enthalpy change (ΔH) and entropy change (ΔS) are calculated (Table 6.17) from the linear plot $ln K_L$ versus 1/T (Figure 6.47). The positive value of ΔH indicates that adsorption is an endothermic process and it is less than 40 kJ/mol indicating that adsorption of p – nitrophenol on these carbons varies with the limit; GAC383 (6.02 kJ/mol), GACO383 (2.96 kJ/mol) and GACONZnO1273 (14.93 kJ/mol), shows occurences of physisorption process. The positive value of ΔS shows the increasing randomness at the carbon - nitrophenol solution interface during the adsorption reaction. The standard free energy change (ΔG) is negative for the modified carbon studied for p – nitrophenol adsorption, as it varies GAC383 (-4.78 to -6.36kJ/mol), GACO383 (-1.70 to -2.36 kJ/mol) and GACONZnO1273 (- 2.28 to -4.77 kJ/mol). The negative value increases with temperature confirm that the adsorptions by modified carbons are spontaneous and are favourable at higher temperature [18].



Figure 6.47: plot of $\ln K_L$ versus 1/T for for the adsorption of p – nitrophenol onto GAC383, GACO383 and GACONZnO1273

Table 6.17:	Thermodynamic	parameters -	Gibbs	free	energy	$(\Delta G),$	enthalpy
	(ΔH) and entropy	y (ΔS) of GAC	ONZnO	1273			

		Δ	G (kJmo	l ⁻¹)		ΔH	ΔS
Carbon	283	293	303	313	323	(kJmol ⁻¹)	(Jmol ⁻¹ K ⁻¹)
GAC383	-4.78	-5.17	-5.54	-5.83	-6.36	6.02	38.18
GACO383	-1.70	-1.85	-2.02	-2.18	-2.36	2.96	16.45
GACONZnO1273	-2.28	-3.05	-3.96	-4.13	-4.77	14.93	61.27

Granular Activated Carbon Incorporated With Zn^{2+} / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 425

6.4.3 Adsorption Studies of Methylene Blue (MB)

Study of selection of carbon, adsorption kinetics, adsorption isotherms and thermodynamic studies is done to evaluate the adsorption efficiency of granular activated carbon GACONZnO formed with nano zinc oxide with different activation temperature.

6.4.3.1 Selection of GACONZnO for Methylene Blue (MB) Adsorption

To select a best carbon from GACONZnO series all are subjected to adsorption test for an initial concentration of 500 mg/L methylene blue for an equilibration period of 10 hrs. The amount adsorbed (mg/g) against the modified carbons are presented in Figure 6.48. The Figure shows that the adsorption capacity increases with nature of carbon incorporated and activated at temperatures 383 - 1273K. GACONZnO1273 shows highest adsorption efficiency for MB removal than other carbons.



Figure 6.48: Selection of carbon form GACONZnO (C₀ -500 mg/L)



6.4.3.2 Adsorption Kinetics

The Figure 6.49 (a), (b) & (c) shows the effect of activation temperature on the methylene blue adsoprtion kinetics. It is seen that time dependent data are single, smooth and continuous leading to saturation. It indicate the formation of possible monolayer coverage of methylene blue dye on the surface of GAC383, GACO383 and GACONZnO1273 [19].



Figure 6.49: Effect of contact time on the adsorption of methylene blue (MB) by (a) GAC383, (b) GACO383 & (c) GACONZnO1273 at different temperatures (C₀ : 250 mg/L)



Chapter 6

These time dependant data are applied to different kinetic models such as pseudo first order, pseudo second order model, intraparticle diffusion model and Boyd kinetic model to determine the critical constants and the mechanism of MB adsorption.

Figure 6.50 (a), (b) & (c) shows a straight line plot for $ln (q_e-q_t)$ versus t for the modified granular activated carbons (GAC383, GACO383 and GACONZnO1273). The Lagergren first order rate constant (K_1) and adsorption capacity $(q_e cal)$ are calculated (Table 6.18). The experimental adsorption capacity $(q_e exp)$ are not comparable with calculated adsorption capacity $(q_e cal)$ and the correlation coefficient (R^2 ranges from 0.94 - 0.98) for all carbons at all temperatures indicating that first order kinetics is not followed [20]. Further data are applied to Ho second order model (Figure 6.51 (a), (b) & (c)). The pseudo second order rate constant (K_2) and adsorption capacity (q_e) are calculated from the intercept and slope of the plot t/q_t against t for the adsorption of MB on these carbons. The rate constant K_2 and $q_e cal$ increases with temperature suggest that adsorption is an endothermic process. The adsorption capacity from the batch kinetic data is comparable with calculated adsorption capacity of the second order kinetics $(q_e cal)$ and $R^2 = 0.99$ indicate that Ho second order model follows the experimental kinetic data for MB adsorption on these carbons GAC383, GACO383 and GACONZnO1073.

The first and second order model cannot identify the diffusion mechanism so we use intra particle diffusion model to identify the diffusion mechanism of MB adsorption. The Figure 6.52 (a), (b) & (c) shows the intraparticle diffusion model as q_t against $t^{1/2}$ gives two straight line portions. The first portion shows surface diffusion and the second linear portion is ascribed to intraparticle diffusion. The slope of the first portion (surface diffusion coefficient K_{idl}) is higher than the

second portion (intraparticle diffusion coefficient K_{id2}). The K_{id1} of the modified carbon at different temperature studied are in the range of GAC383 (5.59 - 8.49 mgg⁻¹min^{-1/2}), GACO383 (5.15 - 6.37 mgg⁻¹min^{-1/2}) ^{1/2}) and GACONZnO1273 (5.01 - 8.39 mgg⁻¹min^{-1/2}) and the K_{id2} of these carbons are GAC383 $(2.07 - 2.72 \text{ mgg}^{-1}\text{min}^{-1/2})$, GAC0383 $(1.78 \text{ mg}^{-1}\text{min}^{-1/2})$ $-2.35 \text{ mgg}^{-1}\text{min}^{-1/2}$) and GACONZnO1273 (2.67 $-3.03 \text{ mgg}^{-1}\text{min}^{-1/2}$). It indicates that second portion is the slowest step and intraparticle diffusion is the rate controlling step for the adsorption of MB by new modified carbons studied. The intercept of the second portion is high indicate that, the boundary layer thickness is also have high value. Adsorption temperature increases from 10 to 50° C the boundary layer thickness also increases for GAC383 (50.67 - 78.76 mg/g), GAC0383 (25.73 – 72.52 mg/g) and GACONZnO1273 (34.80 – 74.29 mg/g).

The Figure 6.53 (a), (b) & (c) shows the Boyd kinetic model, B_t versus t for the modified granular activated carbons at different temperature ranging from $10 - 50^{\circ}$ C. The diffusivity coefficient is calculated from the slope of the Boyd plot (Table 6.18). The correlation coefficient (R^2) is in the range of 0.93 - 0.99. The plot is almost linear and does not pass through the origin indicate that MB adsorptions on the modified carbons are governed by external mass transport and particle diffusion being the second is the rate controlling step.





Carbon			First	order kir	letics	Second	order ki	netics	1999-199	Intrapart	ticle diff.	usion co	nstant		R i Ki	oyd ietic odel
	(K) T	(5/5m) ^{dxəə} b	(g\gm) (รุงรุณ)	¹ K ¹	τ <mark>υ</mark>	qecal (B'2m)	(gmg ⁻¹ min ⁻¹) K ₂ *10 ⁻⁴	_z א	(איז ^{ון, וועד} (איז איז) איז איז איז איז איז איז א	(աճ\ճ) Ը ^ւ	τu	(uim ^{-1/2}) K ^{idz}	(ա ճ\ճ) Ը ⁷	τ <mark>Σ</mark>	(cm ₅ 1 ₁) D°*104	۲z
	283	102.05	60.38	0.005	0.94	104.38	2.42	0.99	8.49	1.76	86.0	2.07	50.67	0.97	1.33	0.94
	293	116.77	64.49	0.005	0.98	118.76	2.46	0.99	7.24	21.22	0.97	2.48	56.37	0.99	1.33	0.98
GAC383	303	124.24	67.07	0.005	0.94	126.42	2.52	0.99	5.78	38.04	66.0	2.61	61.14	0.97	1.50	0.94
	313	132.00	66.07	0.005	0.98	133.87	2.57	66.0	5.59	45.81	0.99	2.72	66.48	0.99	1.38	0.98
	323	138.08	67.84	0.006	96.0	140.25	2.73	0.99	6.07	49.34	0.98	2.47	78.76	0.99	1.57	0.96
	283	80.60	53.52	0.004	0.96	82.37	2.33	0.99	5.66	2.99	0.98	2.21	25.73	0.99	1.17	0.96
	293	90.92	54.31	0.004	0.97	91.91	2.57	66.0	5.15	15.65	0.98	2.35	32.81	0.98	1.17	0.97
GACO383	303	98.13	54.75	0.004	0.98	99.80	2.75	66.0	5.29	20.75	66.0	2.05	47.28	0.99	1.24	0.98
	313	110.64	56.84	0.004	0.95	110.38	2.78	66.0	6.37	24.83	66.0	2.25	53.67	0.97	1.10	0.95
	323	117.76	53.85	0.004	0.94	118.06	3.32	66.0	7.52	27.33	0.98	1.78	72.52	0.99	1.22	0.94
	283	100.84	74.02	0.005	0.97	106.84	1.39	66.0	8.25	-9.58	76.0	2.67	34.80	0.99	1.05	0.98
	293	113.10	79.51	0.005	0.95	118.06	1.62	0.99	8.39	1.53	0.97	3.03	39.92	0.99	1.27	0.93
GACONZnO1273	303	126.71	72.14	0.005	0.98	129.70	2.11	66.0	5.01	36.19	0.76	2.48	65.88	0.99	1.20	0.99
	313	133.60	72.23	0.004	0.99	134.95	2.15	66.0	5.03	42.53	0.99	2.76	65.15	0.99	1.06	0.98
	323	142.19	74.47	0.005	0.98	144 51	01 0	0 00	6 60	41.75	0 00	2 7 R	0C 7L	000	112	0.98



6.4.3.3 Activation Energy Using Methylene Blue (MB) as Adsorbate

A linear plot of lnK_2 against l/T for the estimation of activation energy (E_a) for the adsorption of methylene blue (MB) on modified carbons is shown in Figure 6.54 (a) GAC383, (b) GAC0383 and (c) GACONZnO1273. The activation energy obtained by the adsorption of methylene blue on modified carbons (Table 6.19) for GAC383 (E_a - 2.11 kJ/mol), GAC0383 (E_a - 5.98 kJ/mol) and GAC0NZnO1273 (E_a - 9.13 kJ/mol). It means the adsorption of MB by these modified carbons occurs through physical adsorption (E_a is in the range of 0 – 40 kJ/mol).



Figure 6.54: plot of lnK₂ versus 1/T for the adsorption of methylene blue (MB) on modified activated carbons

Table 6.19: Activation energy of modified carbons using methylene blue adsorption

Carbon	$E_a(kJmol^{-1})$	K ₀	R
GAC383	2.11	0.001	0.95
GACO383	5.98	0.003	0.95
GACONZnO1273	9.13	0.007	0.93

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 433

6.4.3.4 Adsorption Isotherm Studies of methylene blue (MB) on GACONZnO1273

The Figure 6.55 (a) GAC383, (b) GACO383 and (c) GACOZC1073 shows the typical Type I isotherm of amount adsorbed (q_e) versus concentration at equilibrium (C_e) of methylene blue dye at different temperature ranging from 10 - 50^oC. The adsorption efficiency of methylene blue (MB) enhances with temperature means, it is an endothermic process. These equilibrium adsorption data are applied to different isotherm equations such Langmuir, Freundlich, Temkin and Dubinin – Radushkevich (D – R) to determine the adsorption capaciand critical constants to evaluate the characteristic features of modified carbons with respect to MB adsorption.

Langmuir isotherm model, a linear plot of C_{e}/q_{e} against C_{e} for the methylene blue (MB) adsorption by GAC383, GACO383 and GACONZnO1273 are shown in Figure 6.56 (a), (b) & (c). The monolayer adsorption capacity (q_{max}) calculated from the slope and Langmuir energy constant (K_L) from the intercept of the Langmuir isotherm model (Table 6.20). The q_{max} and K_L increases with temperature for all the carbon studied. The correlation coefficient ($R^2 - 0.99$) indicates MB adsorption occurs on a homogenous surface possessed by modified carbons. The q_m carbons at temperature $10 - 50^{\circ}$ C ranges GACONZnO1273 (189.04 mg/g, 197.63 mg/g, 208.77 mg/g, 217.77 mg/g and 232.02 mg/g), For carbon GAC383 (150.60 mg/g, 169.49 mg/g, 190.11 mg/g, 209.64 mg/g and 229.35 mg/g), and for it varies as GACO383 (107.99 mg/g, 122.40 mg/g, 138.70 mg/g, 154.32 mg/g and 172.41 mg/g). It is seen that GACONZnO1273 shows the highest adsorption capacity of MB. The percentage of mesoporosity, BET surface area and basicity influence the efficiency of MB adsorption by GACONZnO1273.







		Langm	uir Con	stants	Frei	Indlich C	Constar	ıts	an Kind	Temkin (Constant	201404	Dubinin	- Radushl Consta	kevich (D nt	- R)
Carbon	T (K)	(₁₋ 88m) xmu	(_{г-} 8ш7) ^Т у	28	(₁₋ 88ш) ⁴ У	u/]	1	285	(₁₋ 81117) V	8	("Ioml") Td	5	נאדם <u>)</u> ה-א-ע) ס ^ה	(k]wol 1) (D-K) E ⁰	(נוסו _ג ג _ב) אי	28
	283	150.60	3.74	0.99	37.67	0.2003	1.58	0.98	9.50	15.15	149.85	0.97	57.43	2.75	0.0659	0.97
	293	169.49	4.54	0.99	40.65	0.2091	1.61	0.98	9.36	17.17	132.20	0.98	58.83	3.26	0.0471	0.96
GAC383	303	190.11	4.80	0.99	42.90	0.2169	1.63	0.99	8.68	19.16	118.48	96.0	60.30	3.74	0.0356	0.96
	313	209.64	5.13	0.99	45.34	0.2225	1.66	0.99	8.61	20.92	108.48	0.95	61.58	4.20	0.0282	0.96
	323	229.35	5.51	66.0	47.80	0.2275	1.68	66.0	8.59	22.71	99.95	0.94	62.78	4.67	0.0228	0.97
	283	107.99	2.89	0.99	35.09	0.1594	6.27	0.97	12.08	13.66	166.17	0.98	54.15	2.77	0.0650	0.98
	293	122.40	3.37	0.99	37.67	0.1690	5.92	0.98	11.93	15.34	147.94	96.0	56.25	3.14	0.0506	0.98
UACU383	303	138.70	3.60	66.0	39.84	0.1783	5.61	0.98	11.26	17.05	133.14	76.0	57.98	3.49	0.0410	0.97
	313	154.32	4.31	0.99	42.34	0.1876	5.33	0.98	11.55	18.19	124.76	0.97	59.50	3.79	0.0348	0.97
	323	172.41	4.59	66.0	44.58	0.1954	5.12	66.0	9.36	21.28	106.67	0.95	60.98	4.08	0.0300	0.97
	283	189.04	1.75	0.99	20.77	0.3001	3.33	0.97	0.60	24.04	94.43	0.86	42.59	1.76	0.1621	0.98
	293	197.63	2.28	66.0	24.60	0.2886	3.46	0.98	06.0	24.40	93.03	96.0	46.80	2.14	0.1094	0.95
GACONZnO1273	303	208.77	3.54	0.99	37.75	0.2392	4.18	0.98	4.34	21.40	106.05	0.89	52.68	4.50	0.0247	0.96
	313	212.77	4.54	0.99	43.22	0.2274	4.40	66.0	7.61	20.99	108.13	0.91	56.22	4.87	0.0211	96.0
	373	232.02	5.70	66 0	53 89	0 2091	4 78	0 00	18 56	20.91	108 52	0 03	63 35	5 50	0.0166	20.05

Chapter 6

The Freundlich isotherm model for MB adsorption by modified carbons (Figure 6.57 (a), (b) & (c)). The adsorption capacity (K_F) and adsorption intensity (*n*) of the MB by the carbon (GAC383, GACO383 and GACONZnO1273) surface are presented in Table 6.20. The K_F increases with temperature as it enhances the mobility of MB molecules from solution to carbon phase. The adsorption intensity '*n*' for MB adsorption is in the range of 1.58 – 6.27 indicate MB adsorption is most favourable with correlation coefficient ($R^2 = 0.97$ -0.99).

The Temkin isotherm plot (q_e versus $ln C_e$) for the modified carbons (GAC383, GACO383 and GACONZnO1273) is shown in Figure 6.58 (a), (b) & (c) respectively. The constants A (equilibrium binding constant, L/mg), B (related to heat of adsorption J/mol) and b_T (variation of adsorption energy, kJ/mol) are listed in Table 6.20. The Table shows that the correlation coefficient is ($\mathbb{R}^2 - 0.86 - 0.98$). The low adsorption energy (0.093 - 0.166 kJ/mol) for this adsorption study indicates that a weak Van der Waals force of interaction occurs between MB molecule and modified carbons.

The Dubinin – Radushkevich (D-R) isotherm is applied to MB adsorption by these carbons to determine the adsorption energy (E_0) and adsorption capacity (Q_D). Table 6.20 shows that adsorption capacity increases with temperature means adsorption is an endothermic process. The E_0 is less than 8 kJ/mol indicate that MB adsorption by GACONZnO1273 is a physical adsorption.

6.4.3.5 Adsorption Thermodynamics

The thermodynamic parameters such as change in enthalpy (ΔH), change in entropy (ΔS) and Gibbs free energy (ΔG) are calculated at different temperatures (10^oC, 20^oC, 30^oC, 40^oC & 50^oC). Methylene blue (MB) adsorption by modified carbon shows that adsorption efficiency enhances with temperature.



Figure 6.59: lnK_D versus 1/T for the adsorption of methylene blue by (a) GAC383, (b) GAC0383 & (c) GACONZnO1273 for C₀ = 25 - 3000 mg/L

The ΔH increases with temperature show the endothermic nature of adsorption. The enthalpy change is less than 40 kJ/mol indicates MB adsorption is a physical process. The positive ΔS implies the increasing disorder and randomness at the solid – solution interface. The Gibbs free energy change decreases with temperature is identified. It indicates that the efficiency of MB removal by modified carbons is more at higher activation temperature. This is due to the enlargement of pore structure and adsorbent size at higher adsorption temperatures [21].



Chapter 6

 Table 6.21:
 Thermodynamic parameters of GAC383, GACO383 and GACONZnO1273 for methylene blue (MB) adsorption at different temperatures

Carbon		1)			Δ	G (kJmol	-1)	
	(l/gr	ol ⁻¹ K	ol ⁻¹)					
	C ₀ (n	∆S (Jmo	∆H (kJm	283	293	303	313	323
	25	105.61	19.29	-10.59	-11.65	-12.71	-13.76	-14.82
	50	90.76	18.29	-7.40	-8.31	-9.22	-10.12	-11.03
	75	78.53	18.05	-4.17	-4.96	-5.75	-6.53	-7.32
	100	60.48	14.21	-2.91	-3.52	-4.12	-4.73	-5.33
GAC383	150	52.66	13.94	-0.96	-1.49	-2.01	-2.54	-3.07
	200	44.03	12.57	0.11	-0.33	-0.77	-1.21	-1.65
	250	35.23	10.75	0.78	0.43	0.08	-0.28	-0.63
	350	30.70	10.37	1.68	1.37	1.07	0.76	0.45
	500	26.33	10.01	2.56	2.29	2.03	1.77	1.50
	750	21.21	9.55	3.55	3.33	3.12	2.91	2.70
	1000	18.04	9.34	4.23	4.05	3.87	3.69	3.51
	1250	16.41	9.40	4.76	4.59	4.43	4.26	4.10
	1500	14.38	9.23	5.16	5.02	4.88	4.73	4.59
	25	105.26	19.34	-10.45	-11.50	-12.56	-13.61	-14.66
	50	91.24	18.65	-7.17	-8.08	-9.00	-9.91	-10.82
	75	75.12	18.34	-2.92	-3.67	-4.42	-5.18	-5.93
	100	66.65	17.65	-1.22	-1.88	-2.55	-3.22	-3.88
	150	57.04	16.53	0.39	-0.19	-0.76	-1.33	-1.90
GACO383	200	44.16	13.72	1.22	0.78	0.34	-0.10	-0.54
	250	36.32	12.03	1.75	1.39	1.02	0.66	0.30
	350	28.28	10.61	2.61	2.32	2.04	1.76	1.47
	500	24.76	10.50	3.50	3.25	3.00	2.75	2.51
	750	21.11	10.45	4.47	4.26	4.05	3.84	3.63
	1000	17.62	10.11	5.13	4.95	4.77	4.60	4.42
	1250	15.05	9.88	5.62	5.47	5.32	5.17	5.01
	1500	13.37	9.81	6.03	5.89	5.76	5.63	5.49
	25	243.05	61.02	-7.77	-10.20	-12.63	-15.06	-17.49
	50	217.41	59.13	-2.40	-4.58	-6.75	-8.93	-11.10
	75	190.29	53.57	-0.28	-2.18	-4.09	-5.99	-7.89
	100	130.47	36.52	-0.40	-1.71	-3.01	-4.32	-5.62
GACONZnO1273	150	90.01	25.88	0.41	-0.49	-1.39	-2.29	-3.19
	200	64.63	19.20	0.91	0.26	-0.38	-1.03	-1.68
	250	42.44	12.89	0.88	0.46	0.04	-0.39	-0.81
	350	32.06	10.66	1.59	1.27	0.95	0.62	0.30
	500	24.95	9.54	2.48	2.23	1.99	1.74	1.49
	750	13.12	7.01	3.30	3.17	3.03	2.90	2.77
	1000	5.11	5.27	3.82	3.77	3.72	3.67	3.62
	1250	4.70	5.62	4.29	4.25	4.20	4.15	4.10
	1500	3.08	5.56	4.69	4.66	4.63	4.60	4.57

School of Environmental Studies, Cochin University of Science and Technology

6.5 Determination of Surface Area and Porosity of Modified **Carbons using Liquid Phase Adsorption Isotherm** Modelling

The porosity and surface area of the modified carbons GAC383, GACO383 and GACONZnO1273 are determined by using different adsorption isotherm models such as Langmuir, John – Sivannandan Achari (J -SA), Brunauer Emmet and Teller (BET) and BET Scatchard plot (I plot) in liquid phase adsorption study. The adsorbate used as phenol, p nitrophenol and Methylene Blue. The Figure 6.60- 6.62 is the Langmuir (L) isotherm plot for the adsorption of phenol, p – nitrophenol and MB adsorption by GAC383, GACO383 and GACONZnO1273 respectively. The monolayer adsorption capacity q_m (L) are calculated from the Langmuir isotherm model are shown in Table 6.22. The monolayer adsorption capacity increasing in the order p – nitrophenol > phenol > methylene blue. GACONZnO1273 shows highest porosity and surface area compared to GACO383. Figure 6.63 depicts the John - Sivanandan Achari (J -SA) isotherm plot for the adsorption of these organic compounds and dye. The limiting micropore volume calculated by this method is comparable with Langmuir monolayer adsorption capacity, indicating that the modified carbons are microporous in character. The surface area and porosity calculated by BET and I plot method is comparable (Figure 6.64, Table 6.22) reveals that this carbons are highly porous.







Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics

			Phenol		<i>p</i> -	nitrophe	enol	M	ethylene	blue
Isotherm Models	Porosity and Surface area	GAC383	GACO383	GACONZnO1273	GAC383	GACO383	GACONZnO1273	GAC383	GACO383	GACONZnO1273
Langmuir (L)	q _{max} (L) (mg/g)	312.5	209.6	298.51	340.1	224.2	344.83	190.1	138.7	208.77
	Porosity (L) (cm ³ /g)	0.452	0.303	0.431	0.425	0.280	0.431	0.300	0.219	0.347
	SA (L) (m²/g)	1043.9	700.4	997.6	773.2	509.7	783.69	430.9	314.4	473.08
John Sivanand	q _{max} (J-SA) (mg/g)	310.5	217.4	304.64	357.8	232.2	343.48	190.1	135.7	210.37
an Achari (J –SA)	Porosity (J- SA) (cm ³ /g)	0.449	0.314	0.440	0.448	0290	0.430	0.300	0.219	0.350
	SA (J-SA) (m²/g)	1037.2	726.2	1017.6	813.2	527.7	780.63	430.8	307.5	476.71
Bruaner Emmet	q _{max} (BET) (mg/g)	190.2	135.6	168.77	227.1	140.0	201.04	115.8	84.2	115.66
(BET)	Porosity (BET) (cm ³ /g)	0.275	0.195	0.244	0.284	0.175	0.251	0.183	0.133	0.192
	SA (BET) (m²/g)	635.3	452.9	563.72	515.9	318.2	456.90	262.4	190.8	262.09
BET scatchard	q _{max} (I plot) (mg/g)	189.9	137.6	166.44	233.31	140.1	217.21	117.3	86.54	117.16
plot (I plot)	Porosity(I plot)(cm ³ /g)	0.273	0.199	0.240	0.296	0.175	0.272	0.185	0.136	0.195
	SA (I plot) (m²/g)	634.5	459.5	555.94	537.5	318.4	493.65	265.9	196.1	265.49

Table 6.22:	The porosity	^r and surfac	e area	of the	modified	carbons	using	different
	isotherm mo	dels						

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Figure 6.64: BET and I plot model for the adsorption of (a) Phenol, (b) p – nitrophenol and (c) MB

6.6 Adsorption of Trace Elements (Li, Mg, Al, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Ba, Tl & Pb)

Adsorption efficiency of carbon GAC383, GACO383 and GACONZnO1273 are tested using a ground water sample having trace metals in concentrations (Li – 1.3 μ g/L, Mg – 1220.04 μ g/L, Al - 42.88 μ g/L, Cr – 0.27 μ g/L, Mn – 103.5 μ g/L, Fe – 2884.22 μ g/L, Co – 1.01 μ g/L, Cu – 1.06 μ g/L, Zn – 12355.72 μ g/L, As – 0.06 μ g/L, Cd – 0.04 μ g/L, Ba – 186.02 μ g/L, Tl – 0.04 μ g/L and Pb – 2.4 μ g/L). This has been collected from a region whose water quality parameters are known, Batch experiment were done, 100 ml of ground water mixed with 0.1 g of carbon.

For this study shaking, contact time is controlled as 540 minutes as equilibration time, After the desired contact time these carbons were filtered and the final concentration is determined by ICP – MS. The percentage adsorption efficiency of these new carbons are evaluated and are shown in Table 6.23. Significant observations are, the heavy metals Fe and Zn shows higher removal efficiency towards GAC383 (Fe – 99.17% & Zn – 98.28 %), GACO383 (99.61 % & 99.92 %) and GACONZnO1273 (99.86% & Zn – 99.59%). GACO383 shows higher removal efficiency towards all the trace elemts studies more than 65% except Li (48.46%) and Cd (50.00%). The Carbon GACONZnO depicts higher efficiency towards Li (84.62%), Pb (95.00%) and Cd (75.00%) compared to GAC383 and GACO383. All the trace elements studied shows that, GACONZnO1273 have more than 60% removal efficiency for this low concentration.

		GAC	383	GACO)383	GACONZnO1273		
Trace elements	Initial concentrati on (µg/l)	Amount adsorbed (µg/g)	Percentage efficiency (%)	Amount adsorbed (µg/g)	Percentage efficiency (%)	Amount adsorbed (µg/g)	Percentage efficiency (%)	
Li	1.3	0.23	17.69	0.63	48.46	1.1	84.62	
Mg	1220.04	17.7	1.45	939.66	77.02	721.69	59.15	
Al	42.88	36.89	86.03	39.58	92.30	33	78.05	
Cr	0.27	0.09	33.33	0.2	74.07	0.21	77.78	
Mn	103.5	73.39	70.91	100.5	97.10	96.1	92.85	
Fe	2884.22	2860.18	99.17	2873	99.61	2880.21	99.86	
Co	1.01	0.71	70.30	0.94	93.07	0.95	94.06	
Cu	1.06	0.05	4.72	1.02	96.23	0.98	92.45	
Zn	12355.72	12143.04	98.28	12345.92	99.92	12304.71	99.59	
As	0.06	0.02	33.33	0.04	66.67	0.04	66.67	
Cd	0.04	0.01	25.00	0.02	50.00	0.03	75.00	
Ba	186.02	91.04	48.94	183.25	98.51	177.76	95.56	
Tl	0.04	0.03	75.00	0.03	75.00	0.03	75.00	
Pb	2.4	2.3	95.83	1.61	67.08	2.28	95.00	

Table 6.23:Adsorption efficiency for removing trace elements by newly
prepared carbons GAC383, GACO383 and GACONZnO1273

School of Environmental Studies, Cochin University of Science and Technology

446

6.7 Statistical Analysis of the Data

Results of statistical tests conducted to prove the various hypothesis, suggested in the chapter 1, give the following results:

Hypothesis 1: Whether there is any significant difference between the total pore volume, micropore volume and mesopore volume for different modified granular activated carbons (GACNZnO) and in comparison with the native form of granular activated carbon (GAC) and carbon oxidised with nitric acid (GACO383).

The comparison of textural properties of carbons such as micropore volume, mesopore volume and total pore volume were by two way ANOVA test observations are shown in the Table 6.24. From this statistical analysis *ss* (sum of squares), *df* (degree of freedom), *ms* (mean square), *F* (variance ratio) and p - value (level of significance) obtained and the inferences are given below.

 Table 6.24:
 ANOVA table for the comparison of textural characterization of granular activated carbons

Source	SS	df	ms	F	p-value
Total	103385.1923	11			
Carbons	1419.7323	3	473.2441	0.213	P > 0.05
Pore volumes	88653.1651	2	44326.5826	19.975	P < 0.001
Residual	13312.2949	6	2218.7158		

Inferences

- (a) There is no significant difference between the carbons (p > 0.05).
- (b) Pore volumes exhibited a significant difference (p < 0.001) $V_{t is}$ significantly higher than the other two and V_{mic} is significantly lower (p < 0.001).
- (c) There is no significant difference in between the mean percentage of microporosity and mesoporosity (t = 0.392, df = 6, p > 0.05).

Hypothesis 2: Whether there is any significant difference between porosity and surface area using solid – gas equilibria using N₂ gas adsorption at 77K, evaluated using different isotherm models; BET isotherm, *I plot* method, Langmuir isotherm, John isotherm, α_s plot, *t* - *plot* for modified granular activated carbons and in comparison with the native form of granular activated carbon.

To prove this hypothesis two way ANOVA test is used. The comparison of adsorption capacity, surface area and pore volume obtained by different isotherm models (John isotherm, Langmuir isotherm, BET isotherm, I plot, alpha S (α_s) and Dubinin – Radushkevich isotherm) are taken for two way ANOVA test and presented in Table 6.25 and 6.26. The inferences are given below.

Table 6.25: ANOVA table for the comparison of adsorption capacity obtained by different methods (John Isotherm, Langmuir isotherm, BET isotherm and I plot method) of granular activated carbons

Source	SS	df	ms	F	p-value
Total	5897212.8243	15			
Carbons	24613.5013	3	8204.0043	8.144	P < 0.01
Models	836.5110	1	836.5110	0.830	P > 0.05
Residual	10073.9185	10	1007.3919		

Inferences

- (a) Among carbons GACONZnO1273 followed by GAC383 is significantly higher than the other two (p < 0.01).
- (b) There is no difference between the models (p > 0.05).



Table 6.26:	ANOVA table for the comparison of pore volume obtained by different methods (John Isotherm, Langmuir isotherm, alpha $S(\alpha_s)$ and Dubinin – Radushkevich isotherm) of granular activated carbons								
Source	SS	df	ms	F	p-value				
Total	5041.4602	15							
Carbons	3530.6109	3	1176.8703	196.781	P<0.001				
Pore volumes	1457.0237	3	485.6746	81.208	P<0.001				
Residual	53 8256	9	5 9806						

Inferences

- (a) Among carbons GACONZnO1273 is significantly higher than the rest, followed by GAC383 (p < 0.001).
- (b) Among pore volumes, Langmuir and John isotherm models showed significantly higher value than Dubinin - Radushkevich and alpha S plot.

Hypothesis 3: Whether there is any relation between the adsorption temperature and adsorption efficiency for the modified granular activated carbons (GACONZnO).

Pearson correlation coefficient (r) and Student's t test are used to prove the relation of adsorption temperature and adsorption efficiency. From the above test, the inferences are given below.

There is significant positive correlation between temperature and adsorption of phenol on GACONZnO 1273 (r =0.99384, t = 15.5302, df = 3, P <0.01). This indicate that phenol adsorption increases with temperature

There is significant positive correlation between temperature and adsorption of p-nitro phenol on on GACONZnO 1273 (r =0.999301, t = 46.29571, df = 3, P <0.01). This indicates that temperature enhances the *p*-nitro phenol adsorption.

There is significant positive correlation between temperature and adsorption of MB on GACONZnO 1273 (r =0.9786, t = 8.237124, df = 3,

P < 0.01). This indicates that as temperature increases adsorption of MB also enhanced.

Hypothesis 4: Whether there is any significant difference between porosity and surface area determined using Langmuir isotherm and John – Sivanandan Achari isotherm (J-SA) for newly prepared granular activated carbons from solid – liquid equilibria.

Langmuir and John – Sivanandan Achari (J –SA) isotherm models for liquid phase adsorption study are tested by using three way ANOVA technique. Results of three way ANOVA test for porosity and surface area of phenol, p – nitrophenol and methylene blue are presented in Table 6.27 and 6.28 and the inferences are listed below.

Table 6.27: ANOVA table for the comparison of porosity of granular activated carbon obtained by Langmuir and John – Sivanandan Achari isotherm model in liquid phase adsorption study

Source	SS	df	ms	F	p-value
Total	0.1149	17	0.0002		
Methods	0.0002	1	0.0341	0.667	p > 0.05
Carbons	0.0682	2	0.0215	113.667	P < 0.001
Phenol, <i>p</i> –nitrophenol	0.0429	2	0.0003	71.500	p < 0.001
& methylene blue					-
Residual	0.0036	12			

Inferences

- (a) There is no significant difference in porosity between Langmuir and John Sivanandan Achari isotherm methods (p > 0.05).
- (b) Porosity differe significantly between carbons (p < 0.001). GACONZnO1273 showed significantly higher porosity than the other two (GAC383 and GACO383).
- (c) Between phenol, p –nitrophenol and methylene blue also there is significant difference in adsorption capacity (p <0.001). Porosity is significantly higher in p nitrophenol followed by phenol (p <0.001).

Both isotherm Langmuir and John – Sivanandan Achari (J –SA) provide very agreeing values for monolayer adsorption capacity and limiting micropore quantity adsorbed is having unique isotherm behaviors.

		1	1	1 2	
Source	SS	df	ms	F	p-value
Total	0.1149	17	0.0002		
Methods	0.0002	1	0.0341	0.667	p > 0.05
Carbons	0.0682	2	0.0215	113.667	P < 0.001
Phenol, p –nitrophenol & methylene blue	0.0429	2	0.0003	71.500	p < 0.001
Residual	0.0036	12			

Table 6.28:ANOVA table for the comparison of surface area of
activated carbon obtained by Langmuir and John – Sivanandan
Achari isotherm model in liquid phase adsorption study

Inferences

- (a) Specific surface area does not differ significantly between Langmuir and John Sivanandan Achari isotherm methods (p > 0.05).
- (b) Among carbons there is significant difference in surface area (p < 0.001). Surface area in GACONZnO1273 and GAC383 is significantly greater that in GACO383.
- (c) Between phenol, p –nitrophenol and methylene blue, the surface area differs significantly (p < 0.001). Surface area is significantly higher in phenol than in p –nitrophenol and MB (p < 0.001).

Langmuir and John – Sivanandan Achari isotherms provide very good agreement in specific surface area reveals unique isotherm behavior.

6.8 Conclusions

The nitric acid oxidized granular activated carbon incorporated with nano ZnO (GACONZnO series) has good adsorption capacity as it has sufficient porosity and specific surface area. Thermal activation decreases the carbon yield and enhances the carbon content 66.52% to 89.84%.

GACONZnO series depicts higher acidic functional groups (carboxylic – 1.26 meq/g, lactonic 1.15 meq/g and phenolic 1.34 meq/g) and thermal activation reduces their presence (carboxylic – 0.32 meq/g, phenolic – 0.53 meq/g and lactonic – 0.20 meq/g). The XPS spectra of GACONZnO shows that percentage of carbon increases with activation temperature (C – 93.59%) and decrease the percentage of oxygen (5.84%) and nitrogen (0.28%) compared to nitric acid oxidized carbon (GACO383). A peak at 1022eV depicts the presence of Zn in the form of ZnO in wurtizite structure.

The broad peak at $2\theta = 24.97 - 25.22^{\circ}$ and $2\theta = 43 - 44^{\circ}$ on all carbons in the GACONZnO series indicate the well crystallized surface of carbon related to (002) and (100) surface. The stack width > 2nm reveals that carbons are non graphitized forms and are efficient adsorbers. The surface morphological studies show that pores are widened after oxidation, incorporation and activation at higher temperature (GACONZnO 1273).

The nitrogen adsorption – desorption isotherm studies infers that GACONZnO has Type I isotherm behavior with H4 hysteresis loop. The total pore volume increases with activation temperature. The proportion mesopore to total pore volume ratio (V_{mes}/V_{tot}) increases in the order GACONZnO1273 (65.14%) > GACONZnO1073 (59.49%) > GACO383 (43.56%) > GAC383 (38.80%). The external and micropore surface area obtained from t - plot method reveals that nitric acid oxidation, zinc incorporation and steam activation at higher temperature enhances the external surface area and a decrease in micropore surface area.

The adsorption efficiency of GACONZnO series is tested by liquid phase adsorption studies using phenol, p – nitrophenol and methylene blue. GACONZnO1273 showed higher adsorption efficiency for phenol (298.51 mg/g), p – nitrophenol (344.83 mg/g) and methylene blue (208.77 mg/g). Kinetic studies showed that that adsorption of phenol, p - nitrophenol and MB followed pseudo- second order model. Two phases in the intraparticle



diffusion has been distinct suggest, that the adsorption process proceeds by surface adsorption and intraparticle diffusion. Elovich kinetic model shows that initial adsorption rate increase with temperature.

The adsorption capacity obtained from different isotherm models (Langmuir, Freundlich, Temkin & Dubinin – Radushkevich isotherm) increases with activation temperature that indicates the endothermic nature of adsorption. The mean free energy < 8kJ/mol reveals that phenol, p – nitrophenol and MB adsorption by GAC follows physical adsorption. Thermodynamic parameters such as enthalpy change, free energy change and entropy change showed that the adsorption process of phenol, p – nitrophenol and methylene blue is endothermic and spontaneous. There is no significant difference between Langmuir and John – Sivanandan Achari Isotherm models of the carbon studied for phenol, p – nitrophenol and methylene blue adsorption. Hence both isotherm models are unique in their behavior to test the adsorption efficiency of this new series of catbon evidenced by their structural and statistical parameters.

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Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 453

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SUMMARY AND CONCLUSION

Coconut shell based granular activated carbon procured, purified and dried at 383K, labelled as GAC383. It has been oxidised with nitric acid to obtain modified carbon GACO383. Both of these are further incorporated with either Zn²⁺ or nano ZnO and activated at various temperatures 383 – 1273K. Four different series of carbons were thereby newly prepared and subjected to adsorption analysis and batch tests. The purpose has been to synthesise a new group of specially modified and nano material incorporated microporous carbon material for separation and purification of gas and liquid. The new carbon series are GACZC, GACOZC, GACNZnO and GACONZnO. The complete and exhaustive study of these carbons form the major content of this bound thesis.

Carbons all are well characterized for their physico – chemical properties and surface morphologies. They are all subjected to solid – gas and solid – liquid kinetic and equilibrium adsorption studies. The adsorption efficiency of new porous carbon materials depends upon factors such as pore size, surface area and surface chemistry. This chapter is to summarise the major findings and conclusions of this doctoral research along with statistical interpretation of results. The relative merits of new chemical activation treatment, variation of physico - chemical and surface properties: crystallinity, surface morphology, specific surface area, porosity, pore size distribution are enumerated and adsorption isotherm

studies of these four prominent series of carbons GACZC, GACOZC, GACNZnO and GACONZnO are examined.

GACZC Series

Granular activated carbon incorporated with Zn^{2+} ions ($X_{zn} = 0.0017$) and activated at different temperature ranges from 383 -1273K had distinct surface structures, discrete pore features and adsorption efficiency – revealed by solid – gas and solid – liquid equilibria studies. The thermal activation of GACZC series resulted a very stable and steady burn – off pattern; 19% at 473K (GACZC473) to 23% at 1273K (GACZC1273). The burn – off promoted enough porosity and surface area to the resulted carbon.

GACZC1073 has a high elemental carbon percentage (94.68%) with less oxygen (5.13%). The surface functional groups present in the GACZC series are; carboxyl (0.39 - 0.66 meq/g), lactones (0.10 - 0.32 meq/g), phenols (0.20 - 0.75 meg/g) and bases (0.30 - 0.90 meg/g). High thermal treatment decreased the amount of acidic functional groups and activation in presence Zn^{2+} ions, made the carbonyl groups became more. The FTIR spectra $(450 - 650 \text{ cm}^{-1})$ indicated the presence of alkaline groups, cyclic ketones and their derivatives, interpreted during activation by zinc ions. The XPS surface analysis showed that zinc ions and activation at 1073K (GACZC1073) improved the percentage of carbon content (97.69%). The atomic concentration of zinc in GACZC1073 is 0.02%. The C 1s and O 1s spectrum of these new carbons are deconvoluted into different peaks. It is attributed to the presence of carboxyl, carbonyl, metal oxide, ketones and lactones on the surface of carbon. The crystalline size and interlayer distance obtained by XRD method indicate that carbons of GACZC series are truly non – graphitic carbons.

Surface morphological studies of GACZC1073 (SEM image) show a greater proportion of pores on the surfaces. There is a more possibility for

a high uptake of pollutants and adsorbate into these pores. HRTEM image of these carbons shows that all carbons are highly microporus in nature.

The nitrogen adsorption – desorption isotherm studies exhibited a Type I isotherm profile with H4 hysteresis loop for the prepared carbons (GAC383, GACO383 and GACZC series). At a low relative pressure (0.2) the micropore filling occurs, then the mesopores are filled and to form a narrow hysteresis loop (H4) at high relative pressure. H4 hysteresis loop is due to the existence of slit shaped pores regarded as prominent micropores.

The monolayer volume and specific surface area calculated by I plot method is more comparable with the BET method at a low relative pressure (0.1) indicates that these carbons are highly microporus in character. The Langmuir isotherm, the monolayer volume $V_m(L)$ and John isotherm, the limiting micropore volume $V_m(J)$ calculated are comparable. This reveals that these new GACZC carbons are highly microporus in nature. The GACZC1273 shows highest monolayer volume and surface area calculated by BET method, I plot method, Langmuir isotherm and John isotherm models, compared to other carbon of the series.

The characteristic free energy (E_0) calculated from Dubinin – Radushkevich (D –R) isotherm method reveals that, the adsorption occurs by a physisorption mechanism. The pore width calculated by this method is in the range of 1.50 - 1.80 nm. The micropore surface area calculated from D - R and t - plot method are comparable. GACZC1073 shows the higher micropore surface area (766.76 m²/g) compared to others.

The new carbons, GACZC873, GACZC1073 and GACZC1273 have average pore width ranges from 2.36 nm to 2.38 nm based on BJH adsorption studies and 2.29 nm to 2.32 nm from BJH desorption studies. The new carbons predominantly have wider micropores, hence are more suitable for wastewater treatment.

The solid – liquid adsorption equilibria studies revealed that GACZC1073 has higher adsorption efficiency for phenol, p – nitrophenol and methylene blue compared to other carbon among this series.

Zinc incorporated granular activated carbon, activated at 1073K (GACZC1073) shows higher phenol adsorption capacity (408.20 mg/g) and specific surface area (1363.60 m²/g). This carbons show high carbon content (94%), have a high proportion of basic surface groups (0.90 meq). Also enough microporous surface area (766.76 m²/g) which enhances the adsorption capacity. This carbon is also efficient for the p – nitrophenol adsorption (capacity 490.20 mg/g) and methylene blue adsorption (capacity 248.80 mg/g).

Kinetic studies show that the adsorption of phenol, p - nitro phenol and methylene blue followed pseudo second order model. It suggests that the batch reactor system consisting of new GAC follows pseudo second order kinetic model. Two phases in the intraparticle diffusion suggest that the adsorption process proceeds by surface adsorption and intraparticle diffusion. Zinc ions incorporated granular activated carbon (GACZC1073) had more adsorption sites on the surface and it enhances the overall adsorption efficiency against phenol, p – nitrophenol and methylene blue. The initial adsorption rate increases with temperature means, more active sites are formed on the carbon surface.

The negative Gibbs free energy change (ΔG) confirms the feasibility and spontaneity of the adsorption process. The activation energy and enthalpy change show that adsorption of phenol, p – nitrophenol and methylene blue were endothermic in nature. The mean activation energy from Dubinin – Radushkevich isotherm model, Arrhenius equation and enthalpy change from Van't Hoff equation reveals that interaction occurs by a physisorption mechanism. The positive entropy change (ΔS) reflects a good affinity towards GACZC1073 and the increasing randomness at the solid – solution interface during adsorption.

Agreement of Langmuir and John – Sivanandan Achari isotherms with single phase adsorption and comparable critical constants shows that the granular activated carbon incorporated with Zn^{2+} ions are greatly microporous.

GACOZC Series

The characterization and adsorption studies of granular activated carbon oxidized with nitric acid (GACO) and incorporated with Zn^{2+} ions – consists of activated carbon GACOZC series are critically evaluated. The steam activation decreased the carbon yield and increased the burn off. For GACOZC series of carbons, oxidation and further impregnation with zinc ions decreased the carbon content first. Thermal activation enhanced the carbon content 64.41% to 86.54%. Whereas, the content of hydrogen decreases from 2.16% - 0.57%, nitrogen 0.67 - 0.52% and oxygen 32 – 12% upon thermal activation.

Among the GACOZC series, GACOZC383 showed a high amount of carboxylic (1.38 meq/g), phenolic (1.27 meq/g) and lactonic (1.64 meq/g) groups. Thermal activation reduced the properties of acidic functional groups. GACOZC1073 showed lesser carboxylic (0.23 meq/g), phenolic (0.94 meq/g) and lactonic (0.17 meq/g) groups on their surfaces. The elemental compositions of GACOZC1073 obtained by XPS method are carbon (96.88%), oxygen (2.71%), nitrogen (0.35%) and zinc (0.06%). The XRD profile of GACOZC383, GACOZC473, GACOZC673, GACOZC873, GACOZC1073 and GACOZC1273 show two peaks at around $2\theta = 23.86 - 25.07^{0}$ and $2\theta = 43^{0}$. The d₀₀₂ value of the peak $2\theta = 23.86 - 25.07^{0}$ is in the range of 0.35 - 0.37 nm. Being, it is greater than 0.335 nm (graphitic carbon), infers that, these carbons exist as non – graphitized forms with well defined porous structures.

The SEM image shows that the pore widening occurred in nitric acid oxidised carbon during impregnation and activation under steam at high temperature. The TEM image of GACOZC showed a regular pore structure. The parallel linear grains are visibe on the surface of carbon indicate that the pores are slit – shaped. The diffraction pattern of GACOZC showed that, this carbon is amorphous material in nature as evidenced by the XRD pattern.

The amount of nitrogen adsorbed increased with relative pressure and the isotherm shows a Type I profile with H4 hysteresis loop. Nitric acid impregnation and activation with zinc ions increased the presence of wider micropores. The total pore volume become high with the rise of activation temperature.

The pore width of the granular activated carbons is obtained by applying BET surface area on N_2 isotherm and has GACOZC873 (1.9 nm) and GACOZC1073 (1.92 nm). This indicates that, all carbons are microporous but having wider micropores. Activation temperature, oxidation and presence of impregnation ion Zn^{2+} enlarge the pore structure.

Isotherm modelling of solid – gas phase reveals that impregnation, oxidation and activation at 1073K (GACOZC1073) increase the porosity and specific surface area of the carbon. The external surface area obtained from t - plot method is higher in GACOZC873 (673.71 m²/g) and GACOZC1073 (752.33 m²/g). Nitric acid oxidised carbon incorporated with zinc ions and activated at higher temperature revealed a mesopore volume and external surface area. The BJH adsorption – desorption pore width of GACOZC is in the range of 2.20 – 2.36 nm. The BJH cumulative surface area, pore volume and pore width of adsorption and desorption are same for all the carbon studied, shows that nitrogen adsorption process is physisorption.



From the carbons of GACOZC series studied, GACOZC1073 had higher adsorption efficiency for phenol, p – nitrophenol and methylene blue. GACOZC1073 showed a, high BET surface area, total pore volume, less acidic functional groups and high elemental carbon. These factors enhanced the adsorption efficiency against phenol, p –nitrophenol and methylene blue studied in batch tests. Adsorption kinetic studies showed that the adsorption of phenol, p - nitrophenol and methylene blue followed pseudo second order model. The Boyd model shows that, external mass transport mainly governs the adsorption process and the intraparticle diffusion was the rate limiting step. The dimensionless separation factor calculated by Langmuir constant, R_L is in the range of 0 – 1 confirms that, adsorption is favorable for all the carbon studied at all temperatures. The correlation coefficient of (R^2) of Freundlich isotherm is less reveals that adsorption is favorable for homogeneous surface.

The adsorption capacity obtained from different isotherm models (Langmuir, Freundlich, Temkin & Dubinin – Radushkevich isotherm) increases with activation temperature common to the endothermic nature of adsorption. The mean free energy < 8 kJ/mol reveals that, phenol, p – nitrophenol and MB adsorption by GAC follows physical adsorption. Thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) showed that, the adsorption process of phenol, p – nitrophenol and methylene blue is endothermic and spontaneous.

The pore volume and specific surface area calculated by Langmuir and John - Sivanandan Achari Isotherm methods are comparable as these carbons are Type I porous material. For liquid phase adsorption, the monolayer adsorption capacity varies in the order p –nitrophenol > phenol > methylene blue.

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and ThermodynamiCS 463

GACNZnO Series

The GACNZnO series, the carbon yield decreased with activation temperature and increased the fixed carbon content (79.26 – 95.26%) and basic groups (0.45 – 0.95 meq/g). GACNZnO1273 shows highest carbon content (94.35%), lesser oxygen and a smaller percentage of zinc (0.01%). The stack width (L_a - 2.22 to 3.10 nm) is obtained from the XRD analysis reveals that, GACNZnO series carbons are amorphous and highly efficient adsorbents. The SEM image shows that the nano zinc oxide impregnation and activation at higher temperature created more microporosity.

The nitrogen adsorption – desorption isotherm pattern showed Type I with H4 hysteresis loop because of the presence of slit shaped wider micropores. The critical evaluation of isotherm constants of BET and *I* plot method revealed that, the members of GACNZnO series of the activated carbon group are convincingly microporous. From this series of carbon studied, GACNZnO1273 showed a higher microporous surface area (760. 64 m²/g). GACNZnO1073 depicted a higher mesopore volume (139.71 cm³/g STP or 0.216 cm³/g) and external surface (424.10 m²/g) area compared to other carbon studied. The pore width obtained by Dubinin – Radushkevich isotherm method and BET method is within the range (1.63 nm – 1.69 nm). This confirms that, these materials are highly micro porous with a great proportion of micropore volume (62.34–67.55%).

GACNZnO1273 has highest carbon content (92.56%), basic group (0.95 meq/g), BET surface area (1403.60 m²/g), micropore volume (261.31 cm³/g STP or 0.404 cm³/g) and micropore surface area (760.64 m²/g). These factors greately improve their phenol and p – nitrophenol adsorption capacity. Kinetic studies showed that the adsorption of phenol, p - nitro phenol and methylene blue (MB) followed the pseudo-second order model. Implies that adsorption is controlled by the square of unoccupied sites on granular activated carbons. The Langmuir isotherm

shows high correlation coefficient ($R^2 = 0.99$) means that, phenol, p – nitrophenol and methylene blue (MB) adsorption occurs in the homogenous surface of the granular activated carbons.

Thermodynamic parameters such as enthalpy change (ΔH) , free energy change (ΔG) and entropy change (ΔS) and activation energy (E_a) showed that the adsorption process of phenol, *p* - nitrophenol and methylene blue is endothermic, physiosorption and spontaneous.

The porosity and specific surface area of GACNZnO1273, obtained from different isotherm models are comparable shows that this carbon is having Type I character and efficient for solid –liquid adsorption studies.

GACONZnO Series

Nano ZnO is incorporated with GACO383 and activated at different temperatures (383 - 1273K), form a new group of carbon, GACONZnO series was generated. This series shows a very stable and steady burn - off pattern. Thermal activation enhanced the burn – off and elemental carbon content (66.52 % to 89.84 %.). From this fourth series of carbon, it is seen thatGACONZnO383 shows high carboxylic (1.26 meq/g), phenolic (1.34 meq/g) and lactonic (1.15 meq/g) groups. Thermal activation reduced the content of surface functional groups. The deconvoluted C 1s and O 1s spectrum of GACONZnO1273 depicts the presence of surface functional groups includes carboxyls, phenols, lactones, chemisorbed oxygen, etc. The interlayer distance (d_{002}) of new carbon series are greater than 0.335 nm. This shows that these carbons exist as non – graphitized forms and are well defined absorbers. The surface morphological studies (SEM and TEM) show that pores are widened after treatment with nitric acid oxidation, chemical (nano ZnO) and physical activation (steam activation). The porosity evaluation studies using nitrogen adsorption – desorption isotherm method shows that GACONZnO carbons are having Type I

character and H4 hysteresis loops are present. The total pore volume and mesopore volume are enhanced with activation temperature. Oxidised carbon (GACO383) impregnated with nano ZnO and activated at 1273K (GACONZnO1273) shows high mesoporosity and hence very high external surface area (763.91 m²/g). The pore width calculated by Dubinin – Radushkevich isotherm method shows average pore width remains within the range (1.94 nm – 1.98 nm). Barret Joyner Halenda (BJH) method of pore size distribution studies (PSD) showed that the adsorption pore diameter ranges 2.14 – 2.20 nm and desorption pore width ranges 2.13 - 2.22 nm for carbons of this group.

From the GACONZnO series, GACONZnO1273 has higher adsorption efficiency of phenol (298.51 mg/g), p – nitrophenol (344.83 mg/g) and methylene blue (208.77 mg/g). Kinetic studies showed that the adsorption of phenol, p - nitrophenol and MB followed the pseudo- second order model. Two phases in the intraparticle diffusion suggest that the adsorption process proceeds by surface adsorption and intraparticle diffusion. Boyd kinetic model results reveal that external mass transport mainly governs the adsorption and particle diffusion is the rate limiting step. The Elovich kinetic model shows that initial adsorption rate increase with temperature.

The adsorption capacity obtained from different isotherm models (Langmuir, Freundlich, Temkin & Dubinin – Radushkevich isotherm) increases with activation temperature as for endothermic nature of adsorption. Activation energy (E_a) and enthalpy change (ΔH) is less than 40 kJ/mol reveals that phenol, p –nitrophenol and MB adsorption by GACONZnO1273 follows physical adsorption. The negative Gibbs free energy change indicates that adsorption on new carbons show a spontaneous process. The positive entropy change means adsorption increased the randomness at the solid – solution interface. There is no

significant difference between Langmuir and John – Sivanandan Achari Isotherm models for these carbon studied for phenol, p – nitrophenol and methylene blue adsorption as these are having Type I character.

Statistical Analysis: Solid – Gas and Solid – Liquid Equilibria

Solid - gas (N₂ adsorption isotherm data at 77 K) and solid – liquid (phenol, p – nitrophenol and methylene blue adsorption) equilibria on chemically activated carbon using Zn²⁺ and ZnO were compiled and analyzed statistically using the two factor ANOVA technique, three factor ANOVA technique and 't' test for testing the significance of correlation coefficient.

For GACZC series, there is a significant difference between the adsorption capacities and surface area, as regards toGACZC1073 and GACZC1273 are significantly higher than the rest with respect to porosity and surface area (p < 0.001). Temperature effect towards the adsorption of phenol, p- nitrophenol and methylene blue (MB) are tested by Pearson correlation coefficient and student's t test. There is significant positive correlation between temperature and adsorption of phenol (r = 0.9953, t = 17.79, df = 3, P <0.01), p - nitro phenol (r =0.9888, t = 11.49, df = 3, P < 0.01) and methylene blue (r = 0.9903, t = 12.36, df = 3, P < 0.01) on GACZC. This indicates that adsorption of phenol, p - nitro phenol and methylene blue are enhanced with temperature. Solid - liquid phase adsorption isotherm data are analyzed with Langmuir and John -Sivanandan Achari isotherm method. Statistical analysis proved that, there is no significant difference in porvolume and surface area between Langmuir and John – Sivanandan Achari isotherm models (P > 0.5). Between carbons the surface area is significant (P < 0.001). In GACZC1073 the surface area is significantly higher than that in GAC383 and GACO383 (P < 0.001). The surface area differs significantly between phenol (P), p -nitrophenol (PNP) and methylene blue (MB). In phenol adsorption, the surface area is significantly greater than for PNP and MB (P < 0.001).

For carbon GACOZC series, two way ANOVA test for porosity and surface area studies based on solid – gas equilibria showed that, there is a significant difference between pore volume and surface area obtained for each members of carbons. GACOZC1073 is having significantly higher pore volume and surface area compared to GAC383 and GACO383. The three way ANOVA test for the liquid phase adsorption study indicate that, there is no significant difference between porosity and surface area calculated by different isotherm models (Langmuir and John – Sivanandan Achari isotherm) and significant difference in porosity and surface area between carbons. There is a significant positive correlation between temperature and adsorption of phenol, p – nitrophenol and methylene blue.

For carbon GACNZnO series, GACNZnO1273 is significantly higher adsorption capacity than the rest (P < 0.05). The adsorption capacity and surface area obtained from different isotherm models reveals that, Langmuir isotherm model and John isotherm have significantly higher porosity and surface area than others (P < 0.001). Pearson correlation and student't' test proves that, there is a significant positive correlation between temperature and adsorption of phenol, p –nitrophenol and methylene blue adsorption on new carbons. The statistical three way ANOVA analysis in solid – liquid adsorption equilibria reveals that there is no significant difference between Langmuir and John – Sivanandan Achari isotherm models (P > 0.05). Between the carbons tested for porosity and surface area, GACNZnO1273 is having higher porosity and surface area than the other two (P < 0.001). Phenol, p – nitrophenol and methylene blue also showed a significant difference in porosity (P < 0.001). Phenol and p – nitrophenol is having significantly higher pore volume than methylene blue (P < 0.001).

For carbon GACONZnO series, solid – gas equilibria based on N₂ gas adsorption at 77K shows significant difference between porosity and surface area evaluated by isotherm models; BET isotherm, *I* plot method, Langmuir isotherm, John isotherm, α_s plot, *t* plot. Once the data is tested by two way ANOVA method, GACONZnO1273 shows significantly higher porosity and surface than others (P < 0.01). For solid – liquid phase adsorption study, three way ANOVA is used. There is no significant difference in porosity and surface area between Langmuir and John – Sivanandan Achari isotherm methods (P > 0.05). Porosity and surface area differ significantly between carbons (P < 0.001). GACONZnO1273 showed significantly higher porosity than the other two (GAC383 and GACO383).

Conclusions

- New granular activated carbon materials (GACZC, GACOZC, GACNZnO and GACONZnO series) based on coconut shell oxidized with HNO₃, incorporated with Zn²⁺ ions and nano ZnO produced marked changes in the structure, porosity, surface area, pore size distribution and adsorption efficiency.
- All the modified carbons have non-graphitized carbon structure as evidenced by XRD profile ($d_{002}\approx 0.35$).
- All the modified carbons show Type I isotherm profile with H4 hysteresis loop
- Zn²⁺ ions / nano ZnO based carbon oxidation results in pore widening (1.92 -1.99 nm) at high temperature, and their distribution is uniform and homogenous on the carbon surface.
- Native carbon (GAC383) impregnated with Zn²⁺ / nano ZnO activated carbon shows high microporosity and hence very high microporous surface area (588.66 766.76 m²/g).

Granular Activated Carbon Incorporated With Zn²⁺ / Nano ZnO: Study of Adsorption Isotherms, Porosity, Kinetics and Thermodynamics 469

- Oxidized carbon (GACO383) impregnated with Zn²⁺ / ZnO activated carbon shows a high external surface area (433.72 763.91 m²/g).
- GACZC1073 is more useful for the removal of phenol (P) and p nitro phenol (PNP) compared to other granular activated carbons. The adsorption capacity of phenol varies, according to the order GACZC1073 (408.16 mg/g) > GACNZnO1073 (383.15 mg/g) > GAC383 (312.50 mg/g) > GACOZC1073 (304.88 mg/g) > GACONZnO1073 (298.51mg/g) > GACO383 (209.64 mg/g) and p nitro phenol adsorption capacity varies in the order GACZC1073 (490.20 mg/g) > GACNZnO1073 (471.70 mg/g) > GACOZC1073 (377.36 mg/g) > GACONZnO1273 (344.83 mg/g) > GAC383 (340.14 mg/g) > GACO383 (224.22 mg/g).
- GACZC1073 shows highest phenol adsorption (408.16 mg/g) and GACZC 1073 has higher *p*-nitrophenol adsorption (490.20 mg/g).
- GACNZnO1073 shows maximum methylene blue (MB) adsorption capacity 261.1 mg/g.
- Carbon GACOZC1073, GACONZnO1273, GACZC1073 and GACNZnO1273 shows more than 50% efficient to adsorption of trace elements from the water sample tested.
- GACZC1073 is 30.61% more efficient towards phenol, 44.12% more efficient to remove *p* –nitrophenol & 30.85 % are more efficient to adsorption of methylene blue compared to native carbon GAC383.
- GACNZnO1273 is 22.82% more efficient for phenol adsorption, 38.68% are more efficient for *p* –nitrophenol removal & 31.82 % are more efficient for methylene blue adsorption than GAC383.

- GACOZC1073 is 42.39% are more efficient towards phenol removal, 68.22% are more efficient to remove p –nitrophenol & 51.18% are more efficient for methylene blue adsorption compared to oxidised carbon GACO383.
- GACONZnO1273 is 45.43% are more efficient for phenol adsorption, 53.72% are more efficient for p -nitrophenol removal and 50.52% are more efficient for methylene blue adsorption than GACO383.

Future Scope of the Study

Study of adsorption, desorption and regeneration of the new carbons (GACZC, GACOZC, GACNZnO, GACONZnO) in a pilot - plant / filtration system / modelling simulation for process optimisation and validation. Development of a carbon based drinking water purification system for house hold applications. Optimisation studies of best among the series for the specific adsorption removal of heavy and trace metals (Li, Mg, Al, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Ba, Tl & Pb) from contaminated water.

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PUBLICATIONS

- Adsorption of *p* nitrophenol on coconut shell granular activated carbon: Isotherms, kinetics and thermodynamics *V Sivanandan Achari*, *S Jayasree & A S Rajalakshmi*
- 2. Adsorption of p-nitrophenol on ZnO Incorporated Activated Carbons: Isotherms, Kinetics and Surface Area Jayasree S., Achari V. S.

Adsorption of *p*-nitrophenol on coconut shell granular activated carbon: Isotherms, kinetics and thermodynamics

V Sivanandan Achari*, S Jayasree & A S Rajalakshmi

School of Environmental Studies

Cochin University of Science and Technology, Kochi 682 022, Kerala, India E-mail: vsachari@gmail.com

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Adsorption of *p*-nitrophenol by modified granular activated carbons based on coconut shell from aqueous solutions has been studied under laboratory conditions. Four granular activated carbons GAC383 (native form), GAC0383 (its nitric acid oxidised form), GACZC1073 (native form incorporated with Zn^{2+} ions and activated at 1073) and GAC0ZC1073 (oxidised form impregnated with $ZnCl_2$) have been used. Batch experiments have been carried out with variants being concentration, time, temperature and equilibrium conditions. Pseudo first, second order kinetic models, intraparticle diffusion models and Elovich kinetic model are applied to study the respective kinetics. Pseudo second order rate equations are found to be best suited for the adsorption systems. Equilibrium isotherm for concentration range (25-3000 mg/L) is analysed by Langmuir (L) and John - SivanandanAchari (J-SA) isotherm models. GACZC1073 has higher adsorption capacity (490.2 mg/g) than GAC0383 (224.2 mg/g). The temperature on the adsorption of *p*- nitrophenol is studied at different temperatures. The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy are calculated using Van't Hoff equation. It is inferred that, the adsorption of *p*-nitrophenol on new modified carbons is endothermic and occurs through physisorption. This study reveals that Zn^{2+} ions impregnated activated carbon GACZC1073 has more adsorption efficiency evidenced by a high adsorption of rate α and surface diffusion K_{idl} promoted by extra adsorption sites generated during activation.

Keywords: Adsorption, Adsorption kinetics, Granular Activated Carbon, John–Sivanandan Achari (J–SA) Isotherm, *p*-nitrophenol

Adsorption kinetics, equilibrium isotherm and thermodynamic studies are very important for the optimization of adsorption process for the design of unit operation¹. Adsorption kinetics involves the determination of the rate at which pollutants are removed from solution media onto carbon surface. Also it controls the residence time of the solute and hence its uptake at the solid-solution interfaces².

Studies on adsorption isotherms are essential to understand how adsorbate interact with carbon granules and are critical in optimizing the use of adsorbent³. To design an adsorption reactor system. heat change of adsorption process is also important. Hence, study of the prominent thermodynamic parameters of the adsorption process such as enthalpy, entropy and free energy change are mostly done in adsorption science⁴. In this regard, adosrption of *p*-nitrophenol by modified granular activated carbons based on coconut shell from aqueous solutions had been studied under laboratory conditions. Four granular activated carbons GAC383 (native form), GACO383 (its nitric acid oxidised form),

GACZC1073 (native form incorporated with Zn^{2+} ions and activated at 1073) and GACOZC1073 (oxidised form impregnated with Zn^{2+} ions) were used. Batch experiments were carried out as a function of concentration time, temperature and equilibrium conditions. The main objective of this work is to make an attempt to evaluate the relative adsorption potential of coconut shell based granular activated carbons (GAC383, GACO383, GACZC1073 and GACOZC1073) newly developed under a set of activation conditions using *p*-nitrophenol as adsorbate.

Experimental Section

Commercially available coconut shell based granular activated carbon (manufactured by Indo German Carbon Industry, Cochin, India) was used as the basic carbon source for the preparation of new carbon series⁵. One kilogram of this carbon washed with NaOH and HCl to remove impurities and neutralize to neutral *p*H 7.0 and dried at 110°C and marked as GAC383. This was then oxidised by 12.9% HNO₃ washed with distilled water and dried at 110°C

and labelled as GACO383. About 10 g of GAC383 mixed with 50 mL water containing 0.035 g $ZnCl_2$ ($Zn^{2+} = 0.017g$) and activated under steam at 1073K in a temperature controlled furnace. The carbon was then dried in oven and the product was designated as GACZC1073. The same procedure was followed for GACO383 and the sample was marked as GACOZC1073. These four carbons were further used for the study of adsorption kinetics, isotherm and thermodynamic studies.

Selection of granular activated carbon for the adsorption process is largely dependent due to favourable physico chemical characteristics such as porosity, surface area, surface functional groups, surface morphology, crystallinity etc. The textural properties of the carbon materials are given in Table 1. Evaluation of physical charateristics such as pore volume and surface area were undertaken by using nitrogen adsorption-desorption isotherm at liquid nitrogen 77K using Micromeritics (Tristar 3000 V6. 07A). Surface functional groups were quantitatively measured using Boehm titration method. The elemental composition [C, H, N & O] of the modified granular activated carbons were evaluated by using Elemental Vario EL III. The surface morphology was evaluated by using Scanning Electron Microscope (SEM) Jeol Model JSM-6390LV and High Resolution Transmission Electron Microscope (HRTEM) Jeol /JEM 2100.

The batch experiments of the adsorption kinetics and isotherms were conducted at a temperature of 30° C in a 100 mL screw cap conical flask. 1.0 g/L adsorbent dosage was weighed and placed in the flask containing 50 mL solution of *p*-nitrophenol of a desired concentration ranging from 25-3000 mg/L and temperature ranging from 10 to 50°C. The adsorption kinetics were studied using initial concentration of *p*-nitrophenol 250 mg/L in a temperature controlled bath shaker. For isotherm study shaking time was fixed as 480 minute based on preliminary studies conducted for the determination of equilibration time. After shaking, the suspension was filtered using Whatmann No.1 filter paper. The concentration of the filtrate was measured using a UV-Visible Spectrophotometer at 317 nm.

Adsorption kinetic studies were undertaken using *p*-nitrophenol and the time dependent data were used to test different kinetic models such as pseudo first, Ho second, intraparticle diffusion and Elovich models⁶. Equilibrium data were applied to different isotherm models such as Langmuir isotherm and John – Sivanandan Achari (J- SA)⁷⁻⁹ isotherm to calculate the adsorption capacity and other structural constants. The thermodynamic parameters such as enthalpy, entropy and Gibbs free energy (Δ H, Δ S and Δ G) were calculated from the Langmuir isotherms parameter (K_L) by using the Van't Hoff Equation¹⁰.

Results and Discussion

Characterisation of modified GACs

The physico chemical characteristics of modified granular activated carbons (GAC383, GACO383, GACZC1073 and GACOZC1073) are listed in Table 1. The granular activated carbon impregnated with Zn²⁺ ions and activated at high temperature shows high basic groups, high carbon content, large micropore volume and surface area compared to other carbons. Granular carbons having very high carbon content is expected to have high surface area. It is known that the Zn^{2+} ions incorporated into the interior of GAC inhibits the expected contraction during activation temperature, which implies that Zn²⁺ may act as a template for creation of micro porosity¹¹. In this, carbon GACZC1073 has higher micropore volume and micro porous surface area. GACOZC1073 shows higher BET surface area and

Table 1	— Physic	co – chem	nical chara	cterization	of modifi	ied granu	ılar activ	vated car	bon (GAC)	based on co	oconut shell	
Carbon	Carboxylic(meq/g)	Lactones(meq/g)	Phenolic(meq/g)	Base (meq/g)	C%	%Н	N%	%0	V_{t} (Cm ³ g ⁻¹)	V_{mic} ($Cm^{3}g^{-1}$)	$\frac{SA_{BET}}{(m^2/g)}$	$\begin{array}{c} SA_{mi} \\ (m^2/g) \end{array}$
GAC383	0.40	0.17	0.45	0.50	89.43	0.60	0.36	9.6	0.573	0.351	996.8	588.7
GACO383	1.38	1.34	2.10	0.20	65.10	2.61	0.58	31.7	0.526	0.297	974.3	540.6
GACZC1073	0.39	0.10	0.20	0.90	94.47	0.09	0.31	5.1	0.569	0.378	1083.6	767.0
GACOZC1073	0.23	0.94	0.17	0.43	84.07	0.52	0.59	14.8	0.604	0.221	1101.8	349.4

lower micro pore volume and micro pore surface area that is because oxidation/ activation enlarge the pore structure. Granular activated carbon oxidized with nitric acid (GACO383) shows high oxygen content, less percentage of carbon and enhances the acidic functional groups. The SEM (Fig. 1) and TEM (Fig. 2) images showed that GACZC1073 is highly microporous evidenced by the porosity (0.378 cm³/g) and surface area (767 m²/g) value determined by N₂ gas adsorption at 77K.

Adsorption kinetic study

The adsorption kinetic study of *p*-nitrophenol on four carbons (GAC383, GACO383, GACZC1073 and GACOZC1073) was undertaken using initial concentration (250 mg/L) at a temperature 30°C. Figure 3 shows the *p*-nitrophenol uptake behaviour as a function of time. Among these four carbons Zn^{2+}



Fig. 1 — Scanning electron microgrpahs of GACZC1073 at $100\mu m$ magnification

impregnated granular activated carbon activated at 1073K (GACZC1073) shows maximum adsorption capacity (229.5 mg/g) for an initial concentration of 250 mg/L *p*-nitrophenol used for kinetic study (Table 2). These time dependent data are applied in



Fig. 2 — Transmission electron microscopy of GACZC1073



Fig. 3 — Effect of contact time on the adsorption of p-nitrophenol on granular activated carbon (GAC) based on coconut shell

Kinetic Models	Parameters	Carbon						
		GAC383	GACO383	GACZC1073	GACOZC1073			
Experimental value	q _e exp (mg/g)	213.4	129.3	229.5	181.6			
Pseudo first order	$q_e cal (mg/g) \ K_1 (min^{-1}) \ R^2$	151.3 0.007 0.98	84.2 0.006 0.93	129.3 0.006 0.87	151.5 0.0103 0.98			
Pseudo second order	$q_e cal (mg/g)$ $K_2 * 10^5 (gmg^{-1}min^{-1})$ R^2	228.8 9.20 0.99	136.8 15.6 0.99	258.6 11.30 0.99	199.2 10.40 0.99			
Intraparticle diffusion Model	$\begin{array}{c} K_{id1} \ (mgg^{-1}min^{-1/2}) \\ C_1 \\ R^2 \\ K_{id2} \ (mgg^{-1}min^{-1/2}) \end{array}$	16.80 -2.21 0.97 5.34	12.89 -15.83 0.97 2.99	26.56 -35.02 0.95 4.18	8.77 28.67 0.89 4.91			
Elovich Kinetic Model	$\begin{array}{c} C_2 \\ R^2 \\ \alpha (mgg^{-1}min^{-1}) \\ \beta (gmg^{-1}) \\ R^2 \\ R^2 \end{array}$	97.64 0.99 12.76 0.0233 0.99 0.2267	62.04 0.99 10.75 0.0397 0.97	133.47 0.96 18.24 0.0226 0.94 0.4943	80.75 0.95 11.64 0.0276 0.97 0.1926			
	$E_a(kcal/mol)$	0.2267	0.1792	0.4943	0.1926			

Table 2 — Kinetic Parameters for the adsorption of *p*-nitrophenol on granular activated carbon (GAC) based on coconut shell

different kinetic models such as Pseudo first order, Ho second order, Weber intra particle diffusion model and Elovich model to identify the mechanism of adsorption on modified carbons.

Pseudo first order model

Among the common kinetic models known to study adsorption,

Lagergen model is the simplest one followed for solute adsorption. This model is expressed in a linear form¹².

$$ln(q_e - q_t) = lnq_e - K_t \qquad \dots (1)$$

where K_1 (min⁻¹) is the pseudo-first order rate constant, t (min) the contact time, q_t and q_e are the amount of nitrophenol adsorbed at any time t and at equilibrium respectively for the granular activated carbon under study. The constants are given in Table 2.

Ho second order kinetic model

Ho presented a sorption based pseudo-second order rate law expression for the reaction rate dependence on the adsorption capacity on solid phase but not the concentration of adsorbate. The model is represented in the following form¹³.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad \dots (2)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), *t* is the reaction time (min), q_t is the amount of adsorbate adsorbed at time *t* (mg/g), K_2 is the equilibrium rate constant of pseudo second order adsorption (g/mgmin). This model is used to express the kinetics of *p*-nitrophenol adsorption on the new carbons and the graph shown in Fig. 4.



Fig. 4 — Pseudo second order kinetic model for the adsorption of p-nitrophenol on granular activated carbon (GAC) based on coconut shell

Intraparticle diffusion model

Weber and Morris¹⁴ used intraparticle diffusion model to predict the rate controlling step of an adsorption process. When mass transfer is the controlling step, it is important to identify the diffusion mechanism. According to intraparticle diffusion model, the initial rate of diffusion is given by the following Equation:

$$q_t = K_{id} t^{0.5} + C$$
 ... (3)

where q_t (mg/g) is the amount of *p*- nitrophenol adsorbed at any time *t* (min), K_{id} (mgg⁻¹min^{-1/2}) is the intra particle diffusion constant and *C* is the boundary layer thickness from the slope and intercept respectively, the plot of q_t vs. square root of time in min shown in Fig. 5, for the new granular activated carbons.

Elovich kinetic model

The simplest form of Elovich model¹⁵ is represented by

$$q_t = \frac{1}{\beta} (\ln \alpha \beta) + \frac{1}{\beta} \ln t \qquad \dots (4)$$

The α (mg g⁻¹ min⁻¹) is the initial rate constant and β (g mg⁻¹) is related to the extent of surface coverage and activation energy of adsorption, can be determined respectively from the intercept and slope of the plot q_t vs. *lnt*. Activation energy (E_a) for the adsorption of *p*-nitrophenol on these modified carbons is obtained using Arrhenius equation based on Elovich constant (β), from a linear plot of *log* β against *1*/*T* for the temperature ranges from 283 to 323K.

The kinetic parameters for the adsorption of *p*- nitrophenol on modified granular activated



Fig. 5 — Intrapartcile diffusion model for the adsorption of p-nitrophenol on granular activated carbon (GAC) based on coconut shell

carbons are calculated and listed in Table 2. The amount adsorbed $(q_e exp)$ determined from the batch kinetic study is more comparable with q_e calculated $(q_e cal)$ obtained from the pseudo second order kinetic model whose correlation coefficient (R^2 =0.99) was found to be high compared to the first order model applied (R^2 ranges 0.87-0.98). This means the adsorption of *p*-nitrophenol on these modified GAC follows Ho second order kinetic model¹⁶ which implies adsorption is controlled by the square of unoccupied sites on granular activated carbons. To determine the adsorption mechanism, the intraparticle diffusion model by Weber is applied on this time dependent adsorption data. Figure 5 shows two straight line portions on plotting the data. The first stage is attributed to surface diffusion and the second stage is due to pore diffusion. The K_{id1} (ranges 8.77-26.56 mgg⁻¹min^{-1/2}) is higher than the K_{id2} (ranges 2.99-5.34 mgg⁻¹min^{-1/2}) for all carbons indicating that pore diffusion is a slow step (Table 2). This reveals that the adsorption mechanism of *p*-nitrophenol on the new carbons also follow intraparticle diffusion model. As regards to Elovich model tested, GACZC1073 shows higher initial adsorption rate (α) compared to other carbons. The activation energy (E_a) calculated ranges 0.17-0.49 kcal/mol (is less than 4.0 kcal/mol) indicate that the surface diffusion¹⁷ has a major role on adsorption. Zn²⁺ ions impregnation increases adsorption sites on the surface of granular activated carbon. Hence, enhances the overall adsorption efficiency.

Adsorption Isotherm and thermodynamic study

Figure 6 depicts the isotherm plot for p- nitrophenol over the new GAC's, in which the



Fig. 6 — General isotherm plot for the adsorption of p-nitrophenol on granular activated carbons based on coconut shell

amount of *p*- nitrophenol adsorbed per gram of adsorbent (q_e) is plotted against the equilibration concentration (C_e) . The isotherm has a steep phase in the beginning followed by saturation at higher initial concentration typical for type I microporous materials as per IUPAC (2015) classification¹⁸. The equilibrium data are further processed to fit the standard adsorption isotherm models of Langmuir and John – Sivanandan Achari (*J-SA*) Isotherm models.

Langmuir isotherm is a mathematical construct to evaluate the adsorption efficiency of activated carbon (Fig. 7). The form of the model is¹⁹

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad \dots (5)$$

 K_L (Lmg⁻¹) is adsorption energy and q_{max} (mg/g) is monolayer adsorption capacity.

John – Sivanandan Achari (J-SA) Isotherm is an emperical isotherm²⁰⁻²² and the equation can be expressed as

$$\log \log C_e = C + n \log q_e \qquad \dots (6)$$

C and n are the *J-SA* isotherm constants; n is referred as adsorbability constants and is a measure of adsorption efficiency.

Monolayer adsorption capacity increases according to the order GACZC1073 (490.2 mg/g) > GACOZC1073 (377.4 mg/g) > GAC383 (340.1 mg/g) > GACO383 (224.2 mg/g), that indicates granular activated carbon incorporated with Zn^{2+} ions and activated / carbonized at 1073K has the highest adsorption efficiency among the group selected for isotherm study. The J-SA plot Fig. 8 shows a straight line with single phase adsorption and the q_m (*J-SA*) and monolayer adsorption capacity $q_{max}(L)$ of



Fig. 7 — Langmuir isotherm for the adsorption of *p*-nitrophenol on granular activated carbons based on coconut shell

Langmuir model (Fig. 7) are comparable for all GAC's as listed in Table 3 indicating that these modified carbon are microporous and belongs to type I category according to classification by John and Achari $(2002)^{23}$.

Thermodynamic parameters

The mechanism of adsorption of *p*- nitrophenol on the above carbon is elucidated by different thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). These parameters were calculated from the Langmuir isotherm constants (K_L) adopting the Van't Hoff's Equation (7 and 8). The temperature effect on the adsorption of *p*- nitrophenol was studied at 5 different temperatures (10, 20, 30, 40 and 50°C) as shown in Figs 9 and 10.

$$\Delta G = -RT \ln K_L \qquad \dots (1)$$

$$lnK_{L} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad \dots \tag{8}$$



Fig. 8 — John – Sivanandan Achari isotherm for the adsorption of p-nitrophenol on granular activated carbons based on coconut shell

The values of ΔS and ΔH are calculated from the intercept and slope of the plot $ln K_L$ versus 1/T for p-nitrophenol adsorption on different GAC and are given in Table 4. The positive value of ΔH indicates that adsorption of p- nitrophenol on GAC were



Fig. 9 — Plot of lnK_L versus 1/T for the estimation of thermodynamic parameters for the adsorption of *p*-nitrophenol on GACO383 based on coconut shell



Fig. 10 — Plot of lnK_L versus 1/T for the estimation of thermodynamic parameters for the adsorption of *p*-nitrophenol on GACZC1073based on coconut shell

Table 3 — Equilibrium adsorption isotherm parameters for the adsorption of *p*-nitrophenol on granular activated carbon (GAC) based on coconut shell

Isotherm Models	Parameters	Granular Activated Carbon (GAC)					
		GAC383	GACO383	GACZC1073	GACOZC1073		
Langmuir Model	$q_{max}(L) (mg/g)$	340.1	224.2	490.2	377.3		
	$K_L(L/mg^1)$	9.0	2.2	9.7	5.2		
	$a_L(L/mg^1)$	0.026	0.010	0.019	0.014		
	\mathbf{R}^2	0.99	0.99	0.99	0.99		
John SivanandanAchari	q _m (J-SA)(mg/g)	349.95	238.78	509.45	389.13		
(J-SA) isotherm	С	1.20	0.3580	1.28	0.945		
	n	0.718	0.417	0.711	0.615		
	\mathbb{R}^2	0.99	0.98	0.99	0.99		

Table 4 — Thermodynamic Parameters for the adsorption of <i>p</i> -nitrophenol on granular activated carbon (GAC) based on coconut shell									
Carbon		1	ΔH	ΔS					
	283	293	303	313	323	(KJmol ⁻¹)	$(\text{Jmol}^{-1}\text{K}^{-1})$		
GAC383	-4.78	-5.17	-5.54	-5.83	-6.36	6.02	38.18		
GACO383	-1.70	-1.85	-2.02	-2.18	-2.36	2.96	16.45		
GACZC1073	-4.14	-4.99	-5.71	-6.44	-7.19	17.16	75.44		
GACOZC1073	-3.31	-3.72	-4.20	-4.68	-5.52	11.85	53.26		

endothermic in nature. The adsorption occurs by endothermic process. Increasing temperature enhances the rate of diffusion of the adsorbate molecule across the external boundary layer and in the internal pores of the adsorbate particle, due to the decrease in the viscosity of the solution 24 . The magnitude of the standard enthalpy change, gives an idea for adsorption is physical or chemical in nature on carbon surfaces. The ΔH for all the new GAC is less than 20 KJ/mol which indicates that adsorption of *p*-nitrophenol on new modified GAC follows physisorption mechanism. The positive value of entropy change (ΔS) reflects good affinity towards the GAC and the increasing randomness at the solidsolution interface during the adsorption reaction. The negative ΔG confirms the feasibility and spontaneity of the adsorption process. From these data, we ascertain that the adsorption process is more favourable at higher temperature (323K), due to endothermic nature of the adsorption system.

Conclusion

impregnated activated Zinc ions carbon (GACZC1073) based on Indian coconut shell shows higher adsorption efficiency to remove *p*-nitrophenol compared to other granular activated carbons. Kinetic studies showed that adsorption of *p*-nitrophenol followed pseudo-second order model. Two phases in the intraparticle diffusion suggest that the adsorption process proceeds by surface adsorption and intraparticle diffusion, the particle diffusion is a slow step. Adsorption of p-nitrophenol on GAC shows good agreement between Langmuir and John-Sivanandan Achari isotherm plot and it indicate the development of microporosity during Zn^{2+} activation. The adsorption capacity of the carbon studied for the present communication can be arranged in the following order GACZC1073 (490.2 mg/g) > GACOZC1073 (377.4 mg/g) > GAC383 (340.1 mg/g) > GACO383 (224.2 mg/g). Thermodynamic parameters such as enthalpy change, free energy change and entropy change showed that the adsorption process of p-nitrophenol is endothermic and spontaneous.

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478

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Adsorption of *p*-nitrophenol on ZnO Incorporated Activated Carbons: Isotherms, Kinetics and Surface Area

Jayasree S., Achari V. S.

School of Environmental Studies, Cochin University of Science and Technology, Cochin-682022. Jayasreeprageesh@gmail.com, vsachari@gmail.com

ABSTRACT

The removal of p - nitrophenol (4- nitrophenol) by modified granular activated carbons (GAC) from aqueous solutions has been studied under laboratory conditions. Four coconut shell based granular activated carbons viz; GAC383 (native form), GAC0383 (its nitric acid oxidised form), GACZnO1273 (GAC383 incorporated with ZnO) and GACOZnO1273 (GACO383 incorporated with ZnO and activated 1273) are used. Batch experiments were carried out as a function of initial concentration and contact time to test their adsorption efficiency. The time dependent experimental data obtained was analysed using known kinetic models: pseudo first order, pseudo second order and intraparticle diffusion models to examine the mechanism of adsorption. Pseudo second order rate equations have been best description followed in the adsorption kinetics. Equilibrium isotherm is also studied in batch reactors for p-nitrophenol GAC system with concentration range (25-3000 mg/l). Langmuir, Freundlich and John -Sivanandan Achari isotherm models are used to study adsorption system. Carbon incorporated with zinc oxide and steam activated at 1273K (GACZnO1273) has a higher adsorption capacity of 471.7mg/g. The oxidized carbon GACO383 has lower adsorption efficiency (224.2mg/g). Respective monolayers (q_m) used to determine the surface area of the granular activated carbons from p nitrophenol uptake.

KEYWORDS: granular activated carbon, p - nitrophenol, kinetic models, adsorption isotherm, John - Sivanandan achari isotherm.

INTRODUCTION

Phenols are known as one of the most toxic types of organic compounds used in various chemical industries such as pharmaceuticals, petrochemicals, coke oven, insecticide manufacturing and steel foundry [1]. They are carcinogenic and toxic in nature to bring danger to the human, flora and fauna in the biosphere. Hence, it has been included in Environmental Protection Agency (EPA) list of priority pollutants[2]. Phenols and p nitro phenol are common derivative found in wastewaters by the above industries, cause hazards to human environment. They cause unpleasant epileptic quality to drinking water. Ingestion cause many injuries to humans leading to damage of haemoglobin. BIS (Bureau of Indian Standard) maintain a desirable limit of 0.001mg/l for drinking water. This indicates the need of treatment for nitrophenol rich wastewaters prior to disposal into natural environment to protect natural fresh water sources.

Among the various treatment technologies, granular Activated carbon (GAC) adsorption is a safe and affordable method to treat phenol rich wastewater preferably in the tertiary stages of the effluent treatment. Metal ion impregnated GAC have more adsorption efficiency compared to its native form of activated carbon [3]. Optimization of adsorption process thereafter for the design of unit operations, the adsorption kinetics and equilibrium isotherm studies are very important. In this regard, the main objective of this work is an attempt to evaluate the relative adsorption potential of coconut shell based granular activated carbons (GAC383, GACO383, GACZnO1273 and GACOZnO1273) newly developed under a set of activation conditions. Equilibrium and kinetic adsorption behaviour of these carbons are done using nitrophenol from aqueous phase in bench scale batch reactors.

EXPERIMENTAL

Coconut shell based granular activated carbons (manufactured by Indo German carbon industry, Cochin, India) have been used as the starting material. The native carbon was washed with distilled water and then dried at 110^oC, marked as GAC383. This was then oxidized using 12.9% HNO₃,

washed and dried at 110° C, this new carbon marked as GACO383 ^[4]. About 10g of GAC383 mixed with 50ml water containing 0.025g ZnO (Zn²⁺= 0.0168g) and activated under steam at 1273K in a temperature controlled furnace. The carbon was then dried in oven and the product is represented GACZnO1273. Similarly, about 10g of GACO383 mixed with 50ml water containing 0.025g ZnO (Zn²⁺= 0.0168g) and activated at 1273K in a temperature controlled furnace, marked as GACOZnO1273. Adsorption kinetic studies were done 50ml of nitrophenol solution having concentration of 250 mg/l mixed with 0.05g of carbon. The remaining concentration (qt) was determined at different time intervals (10, 20, 30, 40, 60, 120, 240, 360 and 480minutes) by analyzing in a spectrophotometer at 317nm. These data are further processed for pseudo first, pseudo second and intraparticle diffusion models. Equilibrium adsorption studies were under varying initial concentrations (25 3000mg/l)^[5]. Adsorption equilibration data are further subjected to fit Langmuir, Freundlich and John - Sivanandan Achari isotherm models. Respective monolayers (qm) used to determine the surface area of the granular activated carbons from p nitrophenol uptake.

RESULTS AND DISCUSSION

Adsorption Kinetics

The adsorption kinetics of nitrophenol on specially modified carbons were studied using initial concentration of nitrophenol 250 mg/l at 30° C (Figure1). Among the carbons GACZnO1273 shows maximum adsorption 226 mg/l at equilibration time 8hr. Kinetie studies of nitrophenol GAC system provide insight into chemical property changes in tune with time measured as its reaction rate. It can come out with knowledge on involvement of GAC surface – chemistry and rate of removal of p nitrophenol. The time dependent experimental data of kinetics was analysed using different kinetic models: pseudo first order, pseudo second order and intra particle diffusion models to examine the mechanism of adsorption.

The kinetic models are;

Lagergren pseudo first order model

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \tag{1}$$

Ho second order kinetic model

$$\frac{t}{q_t} = \frac{1}{K_2 q_g^2} + \frac{t}{q_g}$$
(2)

Intra particle diffusion model

$$q_t = K_{id} t^{0.5} + C (3)$$

Where t (min) the contact time, q_t and q_e are the amount of nitrophenol adsorbed at any time t and at equilibrium respectively, K_1 (1/min) is the pseudo –first order rate constant, K_2 (g/mgmin) is the pseudo – second order rate constant and K_{id} (mg/g/min^{1/2}) is the intra particle diffusion constant.



Figure 1: Effect of contact time on the adsorption of nitrophenol on modified granular activated carbons.



Figure 2: Equilibrium adsorption isotherms of nitrophenol on modified granular activated carbons

The respective kinetic parameters are calculated (Table 1). It is seen that pseudo second order model (eqn 2) adequately describes the adsorption of nitrophenol on the new granular activated carbons with a good correlation ($R^2 = 0.99$). The q_e (q_e exp) experimental are extremely compatible with q_e calculated (q_e cal)obtained by the (eqn 2). This indicates, nitrophenol adsorption on new carbons follows pseudo second order kinetic model. That is, the adsorption is controlled by the square of unoccupied sites on granular carbon. In the case of intra particle diffusion model the plot did not pass through the origin it indicates that the intraparticle diffusion is not only rate controlling step in the adsorption process.

Table 1 Comparison of the pseudo first, second order and intra particle diffusion model of adsorption of nitrophenol											
Sample	q _e exp	Pseudo second order kinetics			Pseudo first order Kinetics			Intraparticle diffusion model			
	_	q _e cal	K ₂	R ²	q _e cal	\mathbf{K}_1	\mathbb{R}^2	Kid	R ²		
GAC383	213.4	228.8	9.2*10 ⁻⁵	0.99	151.3	0.0069	0.98	5.3	0.99		
GACO383	129.3	136.8	0.00016	0.99	84.3	0.0057	0.93	2.9	0.98		
GACZnO1273	226.7	241.6	6.7*10 ⁻⁵	0.99	149.0	0.0067	0.95	4.5	0.98		
GACOZnO1273	188.1	207.8	1.3*10-4	0.99	122.2	0.0074	0.95	4.1	0.98		

Adsorption Isotherms

Langmuir isotherm:

Isotherm plot for nitrophenol removal by the new GAC (Figure 2) reveals that the adsorptive capacity increases according to the order GACZnO1273 (473.6mg/g) > GACOZnO1273 (353.3mg/g) > GAC383 (341mg/gl) > GACO383 (220.4mg/g), that indicates granular activated carbon incorporated with zinc oxide and activated / carbonized at 873K have more adsorption efficiency among the group highlighted. The equilibrium data are further processed to fit the standard adsorption isotherm models of Langmuir, Freundlich and John Sivanandan Achari, the constants are evaluated and presented in Table 2.

$$\frac{C_e}{q_e} = \frac{1}{\kappa_L} + \frac{\alpha_L}{\kappa_L} C_e \tag{4}$$

 K_L – adsorption energy, $K_L/a_L(q_{max})$ – monolayer adsorption capacity.

Freundlich isotherm:
$$logq_{e} = logK_{F} + 1/nlogC_{e}$$
 (5)
K_F – adsorption capacity and 1/n – process intensity.

John - Sivanandan Achari Isotherm [J-SA] [4, 6, 7]:

$$loglogC_e = C + nlogq_e \tag{6}$$

Adsorbent	Langmuir isotherm				Freu	J-SA				
	q _{max} (mg/g)	K _L (L/ mg)	R ²	SA (m ² /g)	K _F (mg/g)	1/n	R ²	q Jmax	R ²	SA (m²/g)
GAC383	340.1	9.1	0.99	773.1	56.9	0.2569	0.90	366.3	0.98	1158.4
GACO383	224.2	2.2	0.99	509.6	19.3	0.3363	0.93	242.9	0.98	768.0
GACZnO1273	471.7	7.7	0.99	1072.2	66.1	0.2731	0.93	478.6	0.98	1087.9
GACOZnO1273	344.8	5.9	0.99	783.7	49.2	0.2722	0.95	343.48	0.97	780.6

It is found that Carbon GACZnO1273 has monolayer- coverage (q_{max}) value of 471.7 mg/g. This is higher compared to the respective values for GAC383, GACO383 and GACOZnO1273. GACO383 carbon has more surface acidity. Being nitrophenol is acidic, more repulsive interaction limit adsorption of nitrophenol. However, this carbon on activation with ZnO at 1273K has showed on improved uptake of 347 mg/g. Freundlich parameter 1/n < 1.0 for GAC indicated the occurrence of a favourable and efficient adsorption condition. Subsequently, based on adsorption monolayer capacity (q_{max}) surface areas of the GAC are determined and presented in Table 2.

CONCLUSION

The results indicated that the specially modified granular active carbons have significant adsorptive properties on activation with ZnO under steam. Metal oxide incorporated carbon activated at 873K (GACZnO1273) shows maximum nitrophenol adsorption capacity 471.7 mg/g at equilibration time of 8hr. Pseudo second order model have high R² values (0.99) in all the cases of carbons. Best fit were given by Langmuir isotherm model (R²-0.99) for the adsorption of nitrophenol over Freundlich isotherm model (R²-0.90-0.95). Agreement of Langmuir and John Sivanandan Achari isotherm with single phase adsorption and comparable magnitude for critical constant indicate that the carbon materials newly prepared by incorporated Zn²⁺ ions are micro porous.

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