ECOTOXIC METAL RECORDS AND ITS DEGREE OF GEOCHEMICAL SYMPHONY IN THE NICHE OF COCHIN ESTUARINE SYSTEM- *A THERAPTIC PERSPECTIVE*

Thesis submitted to
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for the degree of
Doctor of Philosophy
in
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Under the Faculty of Marine Sciences

by

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Dedicated to the Almighty,
parents,teachers and dear ones…

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Certificate

This is to certify that the thesis entitled **"Ecotoxic Metal Records and its Degree of Geochemical Symphony in the Niche of Cochin Estuarine System- *A Theraptic Perspective*"** to be submitted by Mr. Pratheesh V.B, is an authentic record of research work carried out by him under my guidance and supervision in partial fulfillment of the requirement of the degree of Doctor of Philosophy in Environmental Chemistry of Cochin University of Science and Technology, under the faculty of Marine Sciences.

Dr.Sujatha C.H.
(Supervising Guide)

Kochi - 682016
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Declaration

I, **Pratheesh.V.B**, do hereby declare that the thesis entitled **"Ecotoxic Metal Records and its Degree of Geochemical Symphony in the Niche of Cochin Estuarine System-** ***A Theraptic Perspective*****"** is a genuine record of research work done by me under the supervision of **Dr. Sujatha C.H**, Asst. Professor, Department of Chemical and Oceanography, Cochin University of Science and Technology, Kochi, Kerala, India has not been previously formed the basis for the award of any degree, diploma, associate-ship, fellowship or other similar title of any University or institution.

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Words of Gratitude…

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Preface

Water is the elixir of life and is one of the world’s inevitable resources. The larger part of an organism's body is water and a major geological agent changing Earth's surface through erosion by water and ice. Pure water is an animated fluid, while polluted water is a real curse for human beings. The increase of population and exploitation of natural resources for his own benefit, man has behaved in a wild manner by creating pollution hazard not only to aquatic life but also to his own life. The discharge of heavy metals, one of the severe toxicant, into aquatic ecosystems has become a matter of concern in India over the last few decades. In industry, heavy metals are unavoidable chemical constituent and also comprise the main part of the effluent. Banks of lakes and rivers are densely populated areas which contains large amount of metals along with other industrial effluents and the metal concentrations are even able to oscillate in wide ranges. One important fact in varying the concentration in water is the binding capacity of metals on to sediments and in turn releases into the aquatic phases. The heavy metal load of sediments often reaches such high levels that a sudden desorption would be a great danger. Therefore, sorptional processes influence the change in water quality to a great extent.

The metal pollutants of environmental concern include Pb, Cr, Hg, U, Se, Zn, As, Cd, Cu and Ni. These toxicants may be derived from mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives. Heavy metals such as Zn, Pb and Cr have a number of applications in basic engineering works, paper and pulp industries, leather tanning, Organo chemicals, petrochemicals, fertilizers, etc. These toxic chemicals and heavy metals flow into the ocean when industrial, agricultural, and human wastes run off are deliberately discharged into rivers and eventually empty into the sea. These pollutants cause disease, genetic mutations, birth defects, reproductive difficulties, behavioural changes, and death in many marine organisms. In many cases, animals near the top of the food chain are most affected because of a process called biomagnification. Biomagnification refers to the process whereby certain substances such as heavy metals or pesticides move up the food chain, work their way into rivers or lakes, and are eaten by aquatic organisms such as fish, which in turn are eaten by large birds, animals or humans. The substances become concentrated in tissues or internal organs as they move up the chain. With the rise of pollution, the harmful poisons consumed by the lowest trophic level increases and tend to concentrate as they move from one trophic level to the next. Since man is in the top of the trophic level, gets most of this poisonous material into his body and in this way humans gets intoxicated through biomagnification.

Monitoring and systematic gathering of information on heavy metal levels in the environment are essential components of any pollution abatement. The establishment of such a system often presupposes the existence of minimum pollution standards and regulations. There is a conspicuous lack of data on the nature and extent of metal pollution either at local or regional levels, particularly to assist in the understanding of metal cycling in the environment. No systematic continuos monitoring study of a particular aquatic system viz, Cochin estuarine system, were carried out to examine the dynamics of the fragile ecosystems. Therefore the present monograph initiates this attempt by estimating the concentration of toxic heavy metals in the aqueous and sediment phases.

The contamination of heavy metals in the environment is of great concern due to its potential impact on human and animal health. Environmental remediation deals with the removal of pollution or contaminants from soil, groundwater, sediment, or surface water for the general protection of human health and the environment. Remediation process is a subject of concern to an array of regulatory requirements and monitoring programme which could be based on the assessment of human health and ecological risks. Just like disease is a concern to living organisms, pollution is the causative agent for both chronic and acute toxicity which inturn creates several diseases in the environment through biomagnification. Hence remedial or therapeutic approaches are needed to mitigate the problem. The word 'therapy' implies the treatment of any disease by any and all means like drug therapy, physical therapy and massage therapy and the word 'therapeutic' is the art of motivated treatment based on logical or illogical premises. To make a distinct from the word 'therapeutic' and also for the term 'environmental remedial approach', the word 'Theraptic' is used in the present monograph.

The heavy metal contamination in the environment may lead to circumstances like bioaccumulation and inturn biomagnification. Hence cheaper and effective technologies are needed to protect the precious natural resources and biological lives. A suitable technique is the one which meets the technical and environmental criteria for dealing with a particular remediation problem and should be site-specific due to spatial and climatic variations and it may not economically feasible everywhere. The search for newer technologies for the environmental therapy, involving the removal of toxic metals from wastewaters has directed attention to adsorption, based on metal binding capacities of various adsorbent materials. Therefore, the present study aim to identify and evaluate the most current mathematical formulations describing sorption processes. Although vast amount of research has been carried out in the area of metal removal by adsorption process using activated carbon few specific research data are available in different scientific institutions. The present work highlights the seasonal and spatial variations in the distribution of some selected heavy metals among various geochemical phases of Cochin Estuarine system and also looked into an environmental theraptic/remedial approach by adsorption technique using activated charcoal and chitosan, to reduce and thereby controlling metallic pollution.

The thesis has been addressed in seven chapters with further subdivisions. The first chapter is introductory, stating the necessity of reducing or preventing water pollution due to the hazardous impact on environment and health of living organisms and drawing it from a careful review of literature relevant to the present study. It provides a constricted description about the study area, geology, and general hydrology and also bears the major objectives and scope of the present study. The second chapter describes the study area and the methodology adopted for the research. The bimonthly data of eight stations on various components are condensed to seasonal averages of the years 2007 and 2008 in order to establish reliable trends. Statistical quality analysis was carried out and interpreted the interrelation among different parameters. Chapter three deal with the data handling, quantification, spatial and seasonal representation of various hydrographical parameters and its interpretations based on assorted statistical quality controls. Fourth chapter covers the distribution of metals in the selected sampling stations; the spatio-temporal variations of metals and their statistical treatment.

Fifth Chapter depicts the significance, types and factors affecting adsorption of metal ions from aqueous solution, characteristics and properties of selected adsorbents like activated charcoal and chitosan. Remedial/theraptic approach for the removal of selected heavy metals is methodically described in the sixth chapter by taking sorptional study using activated charcoal and chitosan. Batch adsorption experiments, kinetic and thermodynamic study of the adsorption of metal (Cd, Cu, Ni, Pb & Zn) ions were initially and elaborately studied with activated charcoal as adsorbent. Desorption study of metals from activated charcoal was also included in the sorptional experiments. The sorptional behaviour of a cheaper, natural organic biopolymer adsorbent, Chitosan was also asserted by quantifying its adsorption capacity and removal efficiency with Zinc ion. The sorptional capacity of sediment itself was examined by adopting station-4 sediment as an adsorbent, to make out the adsorption-desorption mechanism in the environment. Finally, the salient features of overall research work is summarised in chapter seven.

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CONTENTS

Chapter -1

Chapter -2

Chapter -3

Chapter -4

Chapter -5

Chapter -7

List of Tables

List of Figures

Abbreviations

AAS	Atomic Absorption Spectrometer
Ac.C	Activated Charcoal
APDC	Ammonium Pyrrollidine Dithocarbamate
B_n	Geochemical background value
CCA	Chromated copper arsenate
C_{metal}	Concentrations of heavy metal
$C_{normaliser}$	Concentrations of normaliser
CES	Cochin Estuarine System
CF	Contamination Factor
cm	Centimeter
C_n	Measured concentration
CV	Coefficient of Variation
DDDC	Diethylammonium Diethyldithiocarbamate
EC	Electrical Conductivity
EF	Enrichment factor
G	Gibbs free enenrgy
g	Gram
I_{geo}	Geoaccumulation index
K_d	Distribution coefficient
kg	Kilogram
LOD	Limit of detection
mgpl	Milli gram per litre
ml	Milli litre
M	mass
NF	Normalisation factor
^{o}C	Degree celcius
PC	Principal components
PCA	Principal Component Analysis
PLI	Pollution Load Index

Chapter 1

INTRODUCTION

1.1 Water and Aquatic Systems

Water is essential to life and key to economic development and prosperity. The quality of water varies greatly around the world, with many regions facing severe shortages. Water scarcity not only threatens mankind but also the peaceful coexistence of nations. Sustainable management of water and aquatic ecosystems should therefore be given top priority worldwide. Water is a very important substance, as it makes up the larger part of an organism's body. The atoms-hydrogen and oxygen like other substance on earth, is a major geologic agent of change for modifying Earth's surface through erosion by water and ice. Water is the only common substance that occurs naturally on earth in three different physical states. The solid state, ice, is characterized by a rigid crystalline structure occurring at or below 0°C and occupying a definite volume (found as glaciers and ice caps, as snow, hail, and frost, and as clouds formed of ice crystals). Liquid water covers three-fourths of Earth's surface in the form of swamps, lakes, rivers, and oceans as well as found as rain clouds, dew, and ground water. The gaseous state of water (water vapour) neither occupies a definite volume nor is rigid because it takes on the exact shape and volume of its container. Water vapour (liquid water molecules suspended in the air) occurs in steam, humidity, fog, and clouds. Because of their polar covalent bonds and the asymmetrical bent arrangement, water molecules have a tendency to orient themselves in an electric field, with the positively charged hydrogen toward the negative pole and the negatively charged oxygen toward the positive pole. This attributes to have a large dielectric constant, which is responsible for making water an excellent solvent and can be reclaimed indefinitely as per the requirement. Water has one of the highest specific heats of any naturally occurring substance and hence it is often cooler around an ocean or large lake during summer and remains cooler longer than the land. Similarly regions around large bodies of water are warmer in winter as the water is slower to cool. Water has extremely high surface tension like Mercury. One of the most important characteristics of water is that it is almost the universal solvent, with extra ordinary abilities to dissolve other substances. Hence as water flows through soil or vegetation or a region of anthropogenic activities, changes its characteristics as it dissolves the various solutes.

Comprising over 70% of the Earth's surface, water is certainly the most precious natural resource that exists on our planet. Water resources can be classified as salt water and freshwater. The remaining unfrozen fresh water is mainly found as groundwater, with only a small fraction present above ground or in the air. Salt water contains great amounts of dissolved salt, whereas freshwater has a concentration of less than 1%. Only freshwater can be applied as drinking water and most of these are stored in glaciers and icecaps, mainly in the Polar Regions and in Greenland, and it is unavailable. Of all the water on earth, 97% of the water on the Earth is salt water, and only 3% is fresh water of which slightly over two thirds is frozen in glaciers and polar ice caps (Figure: 1.1).

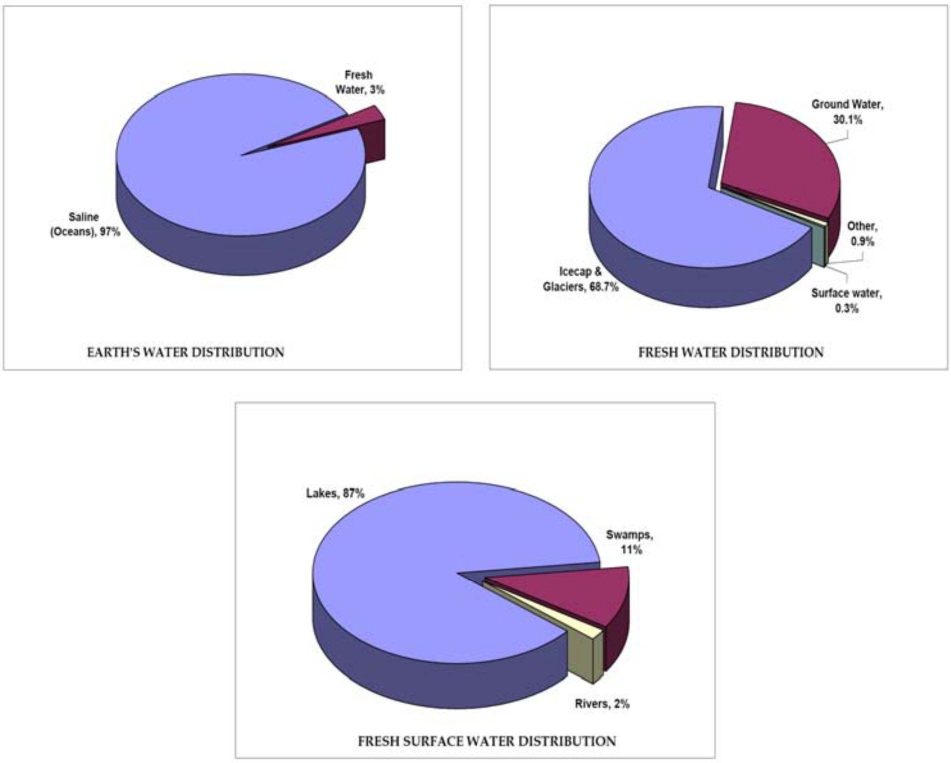

Figure 1.1: Graphical Distribution of location of water on Earth

On land water can be found as Surface water in streams, lakes, wetlands and reservoirs. Rainwater that infiltrates into the soil and stored in pores is categorized as groundwater. The layer that consists mainly of groundwater is called the saturation layer. The water content of an aquifer normally depends on the grain sizes. This means that the rate of extraction may be limited by poor permeability. In the water cycle, some of the precipitation sinks into the ground and goes into watersheds, aquifers and springs. The amount of water that seeps into the ground depends on how steep the land is and is present under ground. When the water seeps down, it will reach a layer of ground that already has water in it. That is the saturated zone. The highest point in the saturated zone is called the water table. (Figure: 1.2) The water table can raise and lower depending on seasons and rainfall. When rain falls the saturation layer will grow wider as a result of an expanding amount of groundwater. Groundwater flows through layers of sand, clay, rock, and gravel and thus sanitizes the water to some extent.

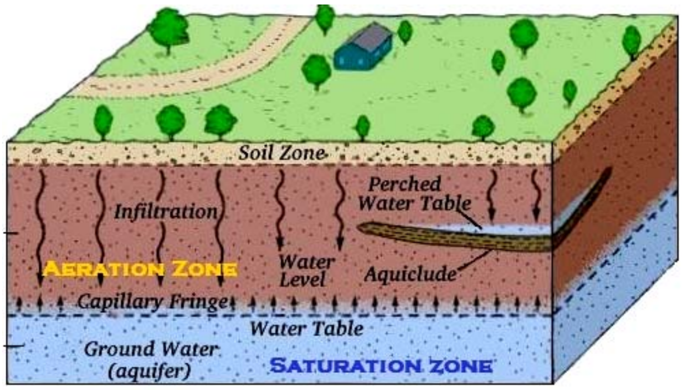

Figure 1. 2: Water table

The elements present in the aquatic environment are broadly classified into the dissolved gases, micronutrients, the major elements and the minor and trace elements. Almost all elements present in the earth's crust are found in various natural waters in different concentrations depending on the source and environmental interactions. The physical, chemical, biological and geological interactions taking place in the environment can influence the composition of natural water. The composition is also affected by the type and amount of soluble products of rock weathering and by the terrain traversed by that water. A major element is often defined as an element that occurs in the Earth's crust in an average concentration greater than 1.0 wt %. This definition restricts the number of elements to eight: oxygen, silicon, aluminium, iron, calcium, magnesium, sodium, and potassium in decreasing abundance. Most of the major cations and a fraction of the anions in the oceans originate from weathering of igneous silicates whereas most of the anions have come from the volatiles. Minor elements usually have the concentration 0.1 to 1% and a trace element usually accounts less than 0.1%. The major ions are conservative, which means that their concentrations in water bear a constant ratio to one another.

They contribute significantly to the observed salinity of water. Mineral salts and organic materials can dissolve in water and is the ideal medium for transporting products of geochemical weathering as well as life-sustaining minerals and nutrients into and through animal and plant bodies (Ball, 1999).

The increasing population along with the associated developmental activity has played havoc with freshwater sources in the world. The estimated utilizable freshwater resources of the country - both surface and groundwater includes circa 1086 km^3 and is expected to be able to meet the demands up to the year 2050. The water quality of the surface water sources is, however a cause of grave concern as in most of the rivers and lakes it does not even meet the aesthetic quality standards. The quality of aquatic resources is a cause of vital concern for providing food, silage, fuel and water for domestic, irrigation and industrial purposes and there is an urgent need for maintaining and improvising the strategy by implementing various conservation programmes. Steps were taken mainly due to their degradation and shrinkage, encroachment, weed infestation, catchments erosion, surface runoff transporting pesticides/fertilizer residue and discharge of raw domestic sewage and effluents which results in the deterioration of water quality, prolific weed growth, decline in biodiversity and other associated problems. Water demand already exceeds supply at an unprecedented rate; many more areas are expected to experience this imbalance in the near future. Subsequently, we are slowly but surely harming our planet to the point where organisms are dying at an alarming rate. Civilizations have flourished and collapsed as a result of changing water supplies. Life on the Earth would be non-existent without water. Although humans recognize this fact, we disregard it by polluting the water resources.

1.2 Aquatic Pollution and its Impacts

Pollution is derived from Latin word "polluere" which means to defile. It's an undesirable change in the physical, chemical or biological characteristics of our air, land and water that can harmfully affect human life or that of other species, our industrial processes, living conditions and cultural assets. According to Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), Pollution of the marine environment is defined as the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) which results in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water and reduction of amenities. In the last few years, there has been a momentous increase in population all over the world, and there exists a rising global concern over pollution. This has been convoyed by rigorous urbanization, increase in industrial activities and greater exploitation and mistreatment of cultivable land. These changes have aggravated an enormous increase in the quantity of discharge and the array of pollutants that could reach the river water causing detrimental effects on fish and fisheries. Water-borne diseases and water related health problems are mostly due to inadequate and incompetent management of water resources. It is reported that there exists a large amount of circumstantial evidence to indicate a decline in the population level of aquatic biota (Houlahan et al., 2000), impairment in growth (Alvarez and Fuiman, 2005) and to show an increase in disturbed behaviour deformities (Klump et al., 2002) and various diseases in aquatic organisms (Zelikoff et al., 2002). Sujatha et al., (2000) investigated and observed the problem of hydride forming toxic metals in the surfacial sediments of a tropical estuary.

Pollution of water restricts its use for human need or natural functions in the ecosystem. Environmental hazards in lakes, rivers and coastal waters are often a result of human pollution of nutrients or toxic substances. Since the nature is very complex it is hard to understand and calculate how toxic substances will spread in the ecosystem and their impacts. The common water pollutants can be segregated as natural, agricultural, municipal and industrial pollutants. Physical pollutants to lakes and streams include materials such as particles of soil that are eroded from the landscape or washed from paved areas by flowing water. Once in a lake or stream, some particles settle out of the water to become bottom sediments. Natural water pollutants could include all the natural phenomena that happen from time to time such as volcanic eruptions, earthquakes that cause major upheavals in the ocean floor and storms that cause flash floods.

The source of the major pollutants in water can also be categorized into four- Sediment, chemicals, Oxygen depleting nutrients, and Biological (bacterial) pollutants. Insecticides/herbicides are among the most widely used toxic chemicals for various purposes in industry, forestry, gardens, agriculture and household. Water often serves as the sink for these chemicals after their application in the different fields. These pollutants are often not entirely specific for their target organisms. Their universal presence in the environment can affect non-target species, such as aquatic biota and plants. Pesticides are the only toxic chemicals deliberately released into the environment in large amounts.

Sediments which act as the sink and reservoir play key role in the pollution of aquatic systems. Sediment is defined as minerals or organic solid matter that is either blown or washed into water bodies. Once the sediment is eroded, it is transported easily by runoff. Sources include construction sites, agricultural practices, logging, flooding, and runoff from urban areas. Contaminants such as pesticides, heavy metals and toxins can be transported by sediment. Sediment pollution is very detrimental. These sediments provide a history book of our environmental sins and these records are the most prevalent and easiest to interpret stratigraphically. Many deep lake basins are natural traps for sediment because the energy levels within them are seldom high enough to transport the materials once it has settled to the lake bottom. According to the function of various processes like flow rates, topography and climate lake basins can typically be divided into three zones: an erosion zone, a transportation zone, and an accumulation zone. It is the accumulation zone that is least affected by wind-driven turbulence and other processes, allowing for the accumulation of even fine-grained sediments and re-suspended material. Eventually sediments in the accumulation zone provide the most complete, continuous, and reliable record of past environmental change. These alterations could have devastating effects on aquatic ecosystems. According to a 1992 EPA report sediment is the leading cause of surface water pollution (Pratheesh et al., 2008). It is important to stop erosion of soil and place buffers between open ground and waterways to limit this type of pollution. Chemicals such as pesticides, herbicides, vehicle fluids, and industrial waste often do not break down easily and can spend a long time in the environment affecting the health of many organisms. Some chemicals also have the tendency of "bioaccumulation" on the food chain and accumulate until they reach toxic levels (Pratheesh et al., 2008).

Regardless of the type or source of a pollutant entering a lake or stream, the overall consequences to the environment may be the same—be it the degradation caused by soil erosion that eliminates the habitat of a stream organism, or the discharge of a chemical that interferes with a species' reproductive cycle. The effects of water pollution are not only devastating to people but also to animals, fish, and birds. The solution to water pollution is the elimination of pollutants at their source. This can be accomplished by reducing the use of polluting chemicals in the home and industry, by treating point sources to remove pollutants, and by each individual being more mindful of how human activities affect the landscape and the aquatic environment. Virtually all types of water pollution are harmful to the health of humans and animals after long-term exposure. Although human beings recognise this fact, we disregard it by polluting the water resources.

1.3 Metals in Aquatic System

Pollution of the aquatic environment by inorganic chemicals has been considered a major threat to the aquatic organisms. The agricultural drainage water containing pesticides and fertilizers and effluents of industrial activities and runoffs in addition to sewage effluents supply the water bodies and sediment with huge quantities of inorganic anions and heavy metals (ECDG, 2002). The pollution of aquatic ecosystems by heavy metals has assumed serious proportions due to their toxicity and accumulative behaviour. When released into the aquatic environment, many anthropogenic chemicals bind or adsorb onto particulate matter. Depending on the river morphology and hydrological conditions, suspended particles with associated contaminants can settle along the watercourse and become part of the bottom sediments, often for many kilometres downstream from the chemical sources (Vigano et al., 2003). Of the effective pollutants, the heavy metals have the drastic environmental impact on all organisms. The most anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal (Santos et al., 2005).

Metal contamination in aquatic system is one of the largest threats to environmental quality and human health. In aquatic system, metals are present as dissolved ions, colloids, suspended solid forms. The ecological impact of metals depends on their form in water, capacity of complexation, sedimentation and bioaccumulation. Metal ions can be incorporated into food chains and concentrated in aquatic organisms to a level that affects their physiological state. The metal concentration in water depends on the redox conditions, pH and ionic strengths. The metals may be categorised as heavy metals and trace metals. A heavy metal is a member of a loosely-defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Generally, heavy metals have specific gravity above 5 g/cm^3, which is 5 times than that of the water (Hawkes, 1997). There are 35 metals that are concern because of occupational or residential exposure; 23 of these are the heavy elements or heavy metals: antimony(Sb), arsenic(As), bismuth(Bi), Cadmium(Cd), cerium(Ce), chromium(Cr), cobalt(Co), copper(Cu), gallium(Ga), gold(Au), iron(Fe), lead(Pb), manganese(Mn), mercury(Hg), nickel(Ni), platinum(Pt), silver(Ag), tellurium(Te), thallium(Tl), tin(Sn), uranium(U), vanadium(V), and zinc(Zn) (Lide, 1992). Some trace metals are adsorbed on surface of suspended material or may be incorporated into the lattice site of minerals such as iron and Mn oxides or in organic mater (Rognerud et al., 2000). Some well-known toxic metallic elements (Glanze, 1996) with a specific gravity that is 5 or more times that of water are As, 5.7; Cd, 8.65; Fe, 7.9; Pb, 11.34; and Hg, 13.546. Cd, Pb, and Hg are highly toxic at relatively low concentrations, can accumulate in body tissues over long periods of time, and are nonessential for human health. Table 1.1 lists metals according to their toxicities (Wood, 1974).

Heavy metals enter the aquatic environment through the earth crust which has led to steady state, back ground level in aquatic environment. Metals are introduced to the ocean by river runoff, wind, hydrothermal venting and anthropogenic activities. Rivers and small streams are a major source of particulate and dissolved metals both of which are mobilised during the weathering of granitic and basaltic crust (Jerome et al., 2008). In addition to the geological weathering, human activities such as Municipal, industrial wastes, beside the atmospheric route have also introduced large quantities of heavy metals to localized area (Figure: 1.3). Once, heavy metals in the aquatic environment, can exist in colloidal, particulate and dissolved phases; Metal ion forms (i)aqua complexes $[M\ (H_2O)n]^{+}_{m}$,where the water itself act as ligands and (ii) Ligands containing electron pair donor atoms such as Inorganic anion ligands and organic ligands replaces the coordinated water in the aqua metal complexes. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. The primary anthropogenic sources of heavy metals are point sources such as mines, foundries, smelters, and coal-burning power plants, as well as diffuse sources such as combustion by-products and vehicle emissions. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings.

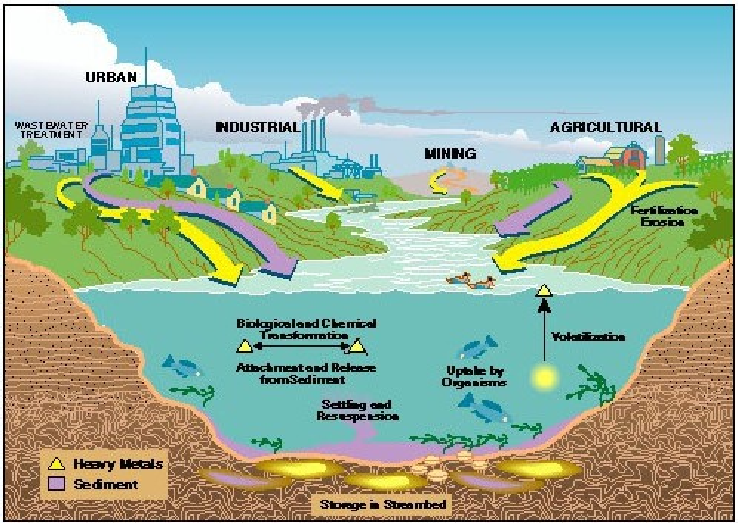

Figure 1.3: Source and sink of Heavy metals

Table 1.1: Classification of metals according to their toxicity and availability in hydrologic environment (Wood, 1974).

Non toxic	Low toxicity		Medium to high toxicity		
Alminium	Barium	*Rhenium*	*Actinium*	Nickel	*Tungsten*
Bismuth	*Cerium*	*Rhodium*	Antimony	*Niobium*	Uranium
Calcium	*Dysprosium*	*Samarium*	Beryllium	*Osmium*	Vanadium
Cesium	*Erbium*	Scandium	Boron	Palladium	Zinc
Iron	*Europium*	*Terbium*	Cadmium	Platinum	*Zirconium*
Lithium	*Gadolinium*	Thulium	Chromium	Polonium	
Magnesium	*Gallium*	*Tin*	Cobalt	*Radium*	
Manganese	Germanium	*Yttrium*	Copper	*Ruthenium*	
Molybdenum	*Gold*	*Ytterbium*	*Hafnium*	Silver	
Potassium	*Holmium*		Indium	*Tantalum*	
Strontium	*Neodymium*		*Iridium*	Thallium	
Rubidium	*Praseodymium*		Lead	Thorium	
Sodium	*Promethium*		Mercury	*Titanium*	
Metals that normally do not exist as dissolved species in natural waters or are very rare in crustal rocks are in italics.					

The commonly encountered toxic heavy metals are As, Pb, Hg, Cd, Fe and Al. As these heavy metals cannot be degraded or destroyed, they are persistent in all parts of the environment. Humans also affect the natural geological and biological redistribution of heavy metals by altering the chemical form of heavy metals released to the environment. Such alterations often affect a heavy metal's toxicity by allowing it to bioaccumulate in plants and animals, bioconcentrate in the food chain, or attack specific organs of the body. The three heavy metals commonly cited as being of the greatest public health concern are Cd, Pb, and Hg. There is no biological need for any of these three heavy metals. Cd has many commercial applications, including electroplating and the manufacture of batteries. Exposure to Cd can occur in the workplace or from contaminated foodstuffs and can result in emphysema, renal failure, cardiovascular disease, and perhaps cancer. Man discovered lead more than 8,500 years ago, and over time have used it in artwork, plumbing, gasoline, batteries, and paint. Modern-day exposure to Pb occurs in the workplace or through the ingestion of Pb-contaminated items such as paint chips. The primary adverse health effect from exposure to Pb is permanent neurological impairment (particularly in children). Other adverse health effects associated with Pb include sterility in males and nephrotoxicity. Mercury is equally toxic. Depending on its chemical form (elemental, inorganic, or organic) mercury is able to cause a myriad of adverse health effects including neurotoxicity (elemental mercury, methyl mercury), nephrotoxicity (elemental mercury, mercuric salts such as mercuric chloride), teratogenicity (methyl mercury), and death (elemental mercury, methyl mercury). The major source of human exposure to mercury compounds is through the consumption of seafood that contains high levels of organic mercury compounds.

Toxic metals, including heavy metals, are individual metals and metal compounds that have been shown to negatively affect people's health. In very small amounts many of these metals are necessary to support life. However, in larger amounts, they become toxic. They may build up in biological systems and become a significant health hazard" (OSHA, 2004). Certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., Fe, Cu, Mn, and Zn). These elements, or some form of them, are commonly found in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products (IOSHIC, 1999). The environmental impact of trace metals are more or less depend on the different physical and chemical species which are present than that on the total metal concentration (Sibley and Morgan, 1975). Trace metals are metals in extremely small quantities that reside in or are present in animal and plant cells and tissue. They are a necessary part of good nutrition; although they can be toxic if ingested in excess quantities. Trace metals include Fe, Mg, Li, Zn, Cu, Cr, Ni, Co, V, As, molybdenum(Mo), Mn, and selenium(Se). Trace metals such as Zn, Cu and Fe play a biochemical role in the life processes of all aquatic plants and animals; therefore, they are essential in the aquatic environment in trace amounts.

The impact of heavy metals wastes into aquatic environment may result in physical, chemical and biological responses and these can be separated into two categories-Effects of the environment on the metal and Effects of the metal on the environment. Water bodies contaminated by heavy metals may lead to bioaccumulation in the food chain of an estuarine environment. Normally, such contaminants are transported from its sources through river system and deposited downstream. Most of the pollutants could be mixed and became suspended solid and bottom sediment through sedimentation and hence estuary is a potential sink for these pollutants for a long period of time (Morrisey et al., 2003). Sediment is the most important reservoir or sink of metals and other pollutants. Toxic metals released into aquatic systems are generally bound to particulate matter, which eventually settles and becomes incorporated into sediments. However, change in environmental conditions might cause some of the sediment-bound metals to be remobilized and to be released back into the waters, thereby exposing the aquatic biota to possible deleterious consequences. Besides the physical, chemical and biological characteristics of the water and the sediment, the chemical partitioning of heavy metals between different sediment forms is very important in determining the bioavailability of heavy metals.

Metal fractions have varying mobility, biological availability and chemical behaviour. Thus it is necessary to identify and quantify the metal forms in order to assess the environmental impact of contaminated sediments. It has been recognized that aquatic sediments absorb persistent and toxic chemicals to levels many times higher than the water column concentration (Casper et al., 2004). The variability of metals in fine sediments is controlled more by hydraulic than geochemical activity by which, the sediments are deposited and transported (Marcus, 1996). The transition metals are present in sediment as insoluble hydroxides, carbonates and sulphides. $Fe(OH)_3$ and MnO_2 also influence the heavy metal deposition and distribution of sediments (Jenne, 1976). Hence metals in suspended and bed sediments are more sensitive than the metals in dissolved form and their level of contamination in an aquatic system (Turner and Millward, 2002). Metals associated with the aqueous phase of soils are subject to movement with soil water, and may be transported through the vadose zone (the region between the earth's surface and the water table) to ground water. Metals, unlike the hazardous organics, cannot be degraded. Some metals, such as Cr, As, Se, and Hg can be transformed to other oxidation states in soil, reducing their mobility and toxicity. Immobilization of metals, by mechanisms of adsorption and precipitation, will prevent movement of the metals to ground water. Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility.

In sediments, metals are found in one or more of several pools of the soil, as described by Shuman (1991):

1. dissolved in the soil solution;
2. occupying exchange sites on inorganic soil constituents;
3. specifically adsorbed on inorganic soil constituents;
4. associated with insoluble soil organic matter;
5. precipitated as pure or mixed solids;
6. present in the structure of secondary minerals; and/or
7. Present in the structure of primary minerals.

In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. Multiphase equilibria must be considered when defining metal behaviour in soils (Figure 1.4). Metals in the soil solution are subject to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization, a potentially important mechanism for Hg, Se, and As. At the same time metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions (Mattigod et al., 1981). The ability to predict the concentration of a given metal in the soil solution depends on the accuracy with which the multiphase equilibria can be determined or calculated. Metals exist in the soil solution as either free (uncomplexed) metal ions (e.g., Cd^{2+}, Zn^{2+}, Cr^{3+}), in various soluble complexes with inorganic or organic ligands (e.g., $CdSO_4^o$,$ZnCl^+$, $CdCl_3^-$), or associated with mobile inorganic and organic colloidal material. A complex is defined as a unit in which a central metal ion is bonded by a number of associated atoms or molecules in a defined geometric pattern, e.g$ZnSO_4$, $CdHCO_3^+$, $Cr(OH)_4^-$ .The associated atoms or molecules are termed ligands. In the above examples, SO_4^{2-}, HCO_3^-, and OH^- are ligand. The total concentration of a metal, Me_T, in the soil solution is the sum of the free ion concentration $[Me_{z+}]$, the concentration of soluble organic and inorganic metal complexes, and the concentration of metals associated with mobile colloidal material.

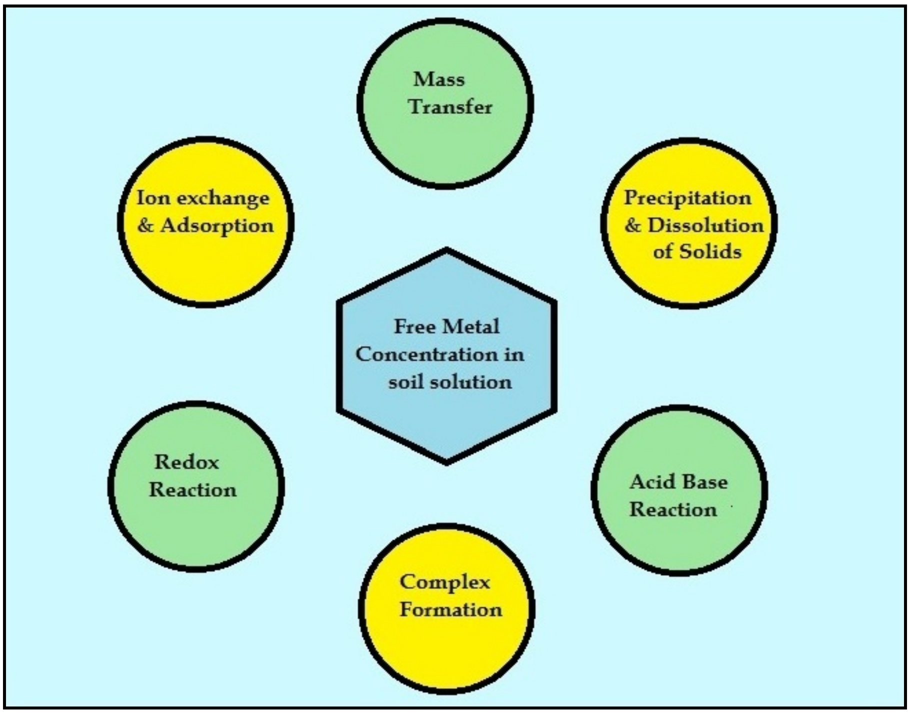

Figure 1.4: Principal controls on free metal concentrations in soils solution. (Mattigod et al., 1981)

1.4 Cochin Estuarine System (CES)

The word "estuary" is derived from the Latin word aestuarium meaning tidal inlet of the sea, which in itself is derived from the term aestus, meaning tide. There have been many definitions proposed to describe an estuary. The most widely accepted definition is: "a semi-enclosed coastal body of water, which has a free connection with the open sea, and within which sea water is measurably diluted with freshwater derived from land drainage." An estuary is a partly enclosed coastal body of water with one or more rivers or streams flowing into it, and with a free connection to the open sea (Pritchard, 1967). Estuaries form a transition zone between river environments and ocean environments and are subject to both marine influences, such as tides, waves, and the influx of saline water; and riverine influences, such as flows of fresh water and sediment. The inflow of both seawater and freshwater provide high levels of nutrients in both the water column and sediment, making estuaries among the most productive natural habitats in the world. Estuaries are a dynamic ecosystem with a connection to the open sea through which seawater enters accordingly to the rhythm of the tides. The seawater entering the estuary is diluted by the freshwater flowing from rivers and streams. The pattern of dilution varies in different estuaries (McLusky and Elliott, 2004) and is dependent on the volume of freshwater, tidal amplitude range, and the extent of evaporation from the water within the estuary.

Estuaries are amongst the most heavily populated areas throughout the world, with about 60% of the world's population living along estuaries and the coast. As a result, estuaries are suffering degradation by many factors, including sedimentation from soil erosion from deforestation, overgrazing, and other poor farming practices; overfishing; drainage and filling of wetlands; eutrophication due to excessive nutrients from sewage and animal wastes; pollutants including heavy metals, PCBs, radionuclide's and hydrocarbons from sewage inputs; and damming for flood control or water diversion (Wolanski, 2007). Estuary variables consist mainly of fluctuations in dissolved oxygen, salinity and sediment load within the water. There is extreme spatial unevenness in salinity, with a range of near 0 at the river end to 34 ‰ at the estuary mouth. At any one point the salinity will vary considerably over time and seasons, making it a harsh environment for organisms. Estuaries tend to be naturally eutrophic because land runoff discharges nutrients into estuaries. With human activities, land run-off also now includes the many chemicals used as fertilizers in agriculture as well as waste from livestock and humans. Excess oxygen depleting chemicals in the water can Pb to hypoxia and the creation of dead zones (Gerlach, 1975). It can result in reductions in water quality, fish, and other animal populations. Every estuary is unique. There are, however, some general trends, which make it possible to predict the nature of the estuarine environments, the circulation pattern and various processes and interactions taking place in estuaries. From pre-historic times, the banks of rivers and estuaries have been the centres of civilization, because of the favourable features such as the profuse vegetation, fertile soil, access to navigational facilities etc. that have catalysed the flourishing of human habitats in those regions. The growing up of large cities nearby estuaries has in many cases caused environmental disturbances, particularly due to the discharge of domestic and industrial waste.

Cochin (9°45′N and 76°17′E) or as it is now officially called Kochi is a city situated in the South-western part of India in the state of Kerala. It is a corporation of multiple cities that are situated around the inlet of the Cochin estuary also known as the Vembanad Lake. It is situated on the coast of Arabian Sea and since the 13th century it's an important economic centre in this area. After Bombay it is the second city on the western coast of India and also possesses the second harbour of the western coast (Figure 1.5). There are three main Islands of Cochin viz., Vypeen, Vallarpadam and Bolghatty connected through Goshree Bridge, apart from many smaller islands scattered along the coast. The Bolghatty palace is situated in the island amidst 15 acres of lush green lawns built by the Dutch. The total area of the Island is about 2.61 sq. km.

Figure 1.5: Satellite picture showing Cochin Estuarine System

The Cochin Estuarine System (CES), approximately around 320 km^2 in area, consisting of Vembanad Lake and the surrounding islands with six rivers flowing in to the estuary, is a very important and integral part of the estuarine ecosystem in Kerala (southwest coast of India). It is used extensively for fishing, transport of goods and also used as a dumping ground for industrial and domestic wastes. The estuarine system extends between 9^0 40′12″ and 10^{0}10′46″North and 76^0 09′52″ and 76^0 23′57″East with its northern boundary at Azheekodu and southern boundary at Thanneermukham bund. Two large rivers (Periyar and Muvattupuzha) discharge into this estuary. The Thanneermukham bund regulates flow from the other four rivers i.e., Meenachil, Manimala, Achankovil and Pamba. The major sources of sediments to the Cochin harbour are the two large rivers -Muvattupuzha and Periyar and the four other rivers to a lesser extend.

Muvattupuzha River:

The name Muvattupuzha is made up of three Malayalam words: 'Moonu', which stands for 'three', 'aaru' - small river, and 'puzha', which also means river. 'Aaru' is a word that is usually used for rivers in the southern half of Kerala, while the term 'puzha' is used in the northern parts. The three rivers are the Kothamangalam River or Kothayaar, Kaliyar and Thodupuzhayaar, which merge to form a single river. Thus it is called centre point of confluence of three rivers or Thriveni Sangamam in Malayalam. The joined single river then flow towards south-west as a single river to the vembanad estuary near Vaikkom. Finally, it merges with the Arabian Sea. The Kothamangalam river originates from Vanchimala and flows in a west-north-west direction for about 25 km and then turn right angle near Kothamangalam town and flows in a south-south west direction for about 10 km and joins Kaliyar river The Kaliyar river originates near Painavu in Idukki district and flows in a north west direction for about 25 km with the name Velurpuzha and then takes the name Kaliyar river. Kannadi River joins the Kaliyar near Venmattam. One of the major tributaries of Kaliyar River is Karimannur River. Kaliyar River changes its trend near Naduvakad and flows in a westerly direction for about 20 km till the confluence of Thodupuzha River. The Thodupuzha River originates from Tangakkanam hills and its main tributaries are Valiathodu, Nach and Idakkaipuzha River. The Thodupuzha River flows in a north-western direction through Thodupuzha town till it joins with Kaliyar near Muvattupuzha town. Both Kothamangalam and Kaliyar rivers join near Muvattupuzha town and forms the Muvattupuzha River, which initially takes an overall westerly direction till it reaches Kadamattom and thereafter flows towards south with a meandering course till it reaches Thalayolaparambu. Muvattupuzha River is one of the major perennial rivers in central Kerala. It originates from the Western Ghats and drains mainly through highly lateralised crystalline rocks. The Muvattupuzha river basin is bounded by the Periyar river basin in the north and the Meenachil river basin in the south.

Periyar River:

The name 'Periyar' has sprouted from the words Periya Ar, meaning the biggest river. The river Periyar, the longest river of the state is considered to be the lifeline of Central Kerala. It originates from the Sivagiri peaks (1800m MSL) of Sundaramala in Tamil Nadu. The total length is about 300 Kms (244Kms in Kerala) with a catchment area of 5396 Sq Kms (5284 Sq. Kms in Kerala). Average annual rainfall is 3200mm. The total annual flow is estimated to be 11607cubic meters. During its journey to Arabian Sea at Cochin the river is enriched with water of minor tributaries like Muthayar, Perunthuraiar, Chinnar, Cheruthony, Kattappanayar and Edamalayar at different junctures. After about 48Km it receives the Mullayar and then turns west to flow into the Periyar lake at Thekkady. From there it flows on and passes Vandiperiyar and after receiving River Perumthurai and River Kattappana, reaches the Idukki catchment. Afterwards, Idamalayar joins Periyar near Neriamangalam. After Neriamangalam the river flows into the Periyar Barrage and then on to the Bhoothathankettu dam. The river then meanders through Malayattoor, Kalady and Aluva. At Aluva, the river bifurcates into the Mangalapuzha branch and the Marthanadavarma branch. The former joins river Chalakudy and finally drains into the Lakshadweep Sea and the latter bisects the industrial belt at Eloor before discharging into the backwaters adjoining the Arabian Sea. Periyar has been performing a pivotal role in shaping the economic prospects of Kerala, as it helps in power generation, domestic water supply, irrigation, tourism, industrial production, collection of various inorganic resources and fisheries. However, as in the case of many other inland water bodies, River Periyar is gradually undergoing eco-degradation throughout its course of flow due to various anthropogenic stresses, which include indiscriminate deforestation, domestic-agricultural- industrial water pollution, excessive exploitation of resources, large scale sand mining, various interferences in the flow of water etc.

CES has four connections with the Arabian Sea. The northerly connection, Azhikod, is at the mouth of the Periyar River. This connection takes care of half the discharge by the Periyar River, but has no real influence of tidal inflow (Chandramohan, 2002). The other half flows to the more southern gull near Cochin. This is also the approach channel for the harbour of Cochin. In the southern part of the Periyar river is a bund preventing salt water intrusion upstream in the Periyar. So during dry season the total volume of water is being diverted through the northern entrance. The inlet near Cochin discharges half of the discharge of the Periyar River and almost the whole discharge for the other five rivers, the Muvattupuzha, the Meenachil, the Manimala, the Pamba and the Achakoil, who let out their water on the Vembanad Lake.

Extensive studies have been carried out in Cochin backwaters especially on the physical, chemical and biological aspects and impacts due to dredging. These problems were discussed by Gopinathan and Qasim (1971); Anto et al., (1977); Sundaresan, (1989) and Rasheed et al., (1995). The intensity of research effort expended in elucidating the physical, biological and chemical characteristics of the Cochin estuarine system during the last three decades is indicative of the economic and social importance. Many hazardous substances including heavy metals, discharged into the aquatic environment are known to accumulate in the estuarine sediments. Venugopal et. al. (1982) studied the levels of Cu, Mn, Co, Ni and Zn in the sediments of the northern limb of Cochin backwaters, which runs through the industrial belt. All the metals showed some degree of variations over the area studied. Nair et. al. (1990) found that the metal concentration in recently deposited sediments show varying and different behaviour was being influenced by natural as well as anthropogenic factors. For Cochin backwaters, seasonal hydrographic changes play a predominant role in regulating metals in sediments. Generally, post monsoon is associated with build up of metals, which become enriched in the accumulative phases of the sedimentary material. Terrestrial transport appears to occur mostly during monsoon, which is associated with higher river discharge and bed-load movements. The distribution pattern of chromium and strontium (Jayasree and Nair, 1995) were positively correlated to hydrographic features and sediment grain size.

The climate of Kerala, as per Koppen's classification, (Peel et al., 2007) is tropical monsoon with seasonally excessive rainfall and hot summer except over Thiruvananthapuram district, where the climates as tropical savana with seasonally dry and hot summer weather. The entire state is classified as one meteorological sub division for climatologically purposes. The year may be divided into four seasons: Winter (January and February), Summer (March to May), a Monsoon (rainy) season (June to September), and a Post-monsoon period (October to December). The present work mainly focuses on the Cochin estuarine system. The Station-1, Muvattupuzha River was taken as the reference site and various hydrographical parameters of all stations were compared with this. Water samples and sediments from seven stations were collected bimonthly from the period January 2007 to December 2008. Sediment Samples from station 4 (CH-MJ) was collected in October 2010, for the recent quantification of selected metals and for adsorption studies.

1.5 Objectives & Scope of Study

The West Coast of India is having a special significance in the marine research because of the contributions from the monsoon season to the productivity. The tropical Cochin Estuarine System is one of the most productive and positive estuary in the West Coast of India. This water body is considered to be the nursery of shrimps, which considerably support the Indian exports. The prime importance of the Cochin Estuarine System in the national scenario can be seen from the research considerations it has attracted. For the last few decades the Cochin Estuarine System was subjected to thorough study in different disciplines and parameters. The works so far reported include the biological, physical, geological and chemical studies. The introduction of a multitude of industries on the banks of the river and at estuary and exhaustive urbanisation has led to considerable contamination of the estuarine system because of the discharge of wastes in to this system. The focus of research, so, is now on the impact of these contaminants to the system.

The research work was carried out in the Cochin estuarine system including the riverine zones- Periyar and Muvattupuzha. Metal distribution along with other physico-chemical parameters of the selected stations in the Cochin Estuarine System is considerably influenced by the tropical features of the location and by human activities. The industrial units located along the banks of the river discharge treated and untreated effluents into the river. The present study intends to re-look the physico-chemical parameters and metal distribution of samples corresponding to the three prominent seasons (Pre-Monsoon, Monsoon, and Post Monsoon) with the adoption of statistical methods. Pollution by heavy metals is a severe threat to aquatic ecosystem due to its toxic nature even at low concentrations. They are major pollutants in marine, ground, industrial and even treated wastewaters and tend to accumulate in living organisms causing rigorous problems to ecosystem. Natural processes and regardless human activities have polluted and reduced the quality of water resources. Groundwater and superficial water have been contaminated in various ways. Wastewater generally contains toxic inorganic and organic pollutants. Inorganic pollutants consist of mineral acids, inorganic salts, finely divided metal trace elements, cyanides, nutrients and organo-metallic compounds.

Sediment acts the reservoir or sink of metals and other pollutants. Toxic metals released into aquatic systems are generally bound to particulate matter, which eventually settles and becomes incorporated into sediments. However, change in environmental conditions might cause some of the sediment-bound metals to be remobilized and to be released back into the waters, thereby exposing the aquatic biota to possible deleterious consequences. Besides the physical, chemical and biological characteristics of the water and the sediment, the chemical partitioning of heavy metals between different sediment forms is very important in determining the bioavailability of heavy metals. Metal fractions have varying mobility, biological availability and chemical behaviour. Thus it is necessary to identify and quantify the metals in order to assess the environmental impact of contaminated sediments.

The determination and removal of trace elements (toxic or otherwise) in sediments is critical for monitoring crop growth and the possible contamination of the food chain. The increasing stringent environmental regulation and enforcement of discharge limits require effective decontamination and purification method. Since it is important to eliminate or reduce the concentration of heavy metals in the aquatic ecosystems, various processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, reverse osmosis, and electro-dialysis. However, the application of some of these methods may be impractical due to economic constraints or may be insufficient to meet strict regulatory requirements and may generate hazardous products or products which are difficult to treat. Many physico-chemical methods have been proposed for their removal from contaminated water or sediments. From the analytical point of view, it is known that solid phase extraction (adsorption) is a better technique based on the use of the sorbent that retains analytes. The adsorption process, proved its advantage over the other processes because of its cost effectiveness and the high-quality of the treated effluent it produces. Activated carbon is widely used as an adsorbent and is particularly considered to be a competitive and effective process for the removal of heavy metals at trace quantities due to its high adsorption capacity. But the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon. The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently.

Numerous studies were carried out in the distribution of toxic heavy metals in sediment samples of Cochin estuarine system. But little effort has been yet made in the approach of remediation. So the present study is an attempt to remove or decrease the concentration of selected metals in the sediments of Cochin Estuarine System.

The main objectives of the present study are:

- To evaluate the hydrographical parameters of water samples including metal distribution from selected stations of CES.
- To evaluate the sediment characteristics and metal distribution of selected stations.
- To quantify and study the seasonal and spatial distribution of heavy metals in sediments.
- Adsorption study and the formulation of adsorption isotherms for selected metals.
- Kinetic study of adsorption of metal ions at varying concentration, pH and particle size.

A proper management of aquatic systems is need of the day, because of the role they play in maintaining the life on the earth. A clear understanding of the chemical character and the dynamics can lead to the development of models, which can predict the requirements for such a management. The attempts have been to quantify a potential remedial approach and bring it into a model for the sustainable maintenance of the system.

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Chapter 2

STUDY AREA AND ANALYTICAL METHODOLOGY

Contents

2.1 Description of Study Area

Kerala is a green state from the south most point of India to 560 kilometres up north. Kerala, surrounded with two natural boundaries- the Arabian Sea and the Western Ghats, has developed in a unique manner due to the moderate climate and the heavy rains during the southwest monsoon. This southwest monsoon is from June until August and comes with a lot of heavy showers. The backwaters of Kerala are unique to Kerala and are found equivalent to flooded polders of Holland in Europe. The Kerala Backwaters are a network of lakes, canals and estuaries and the deltas of 44 rivers that all drain into the Arabian Sea. Most of these rivers rise in the Western Ghats which have high rainfall all year. The Cochin backwaters are the largest of the backwaters on the Kerala coast. The hydrography of these backwaters is controlled mainly by discharges from Periyar, Muvattupuzha and Chitrapuzha rivers and also by tidal action through the Cochin bar mouth. Saline water intrusion to the southern parts of the estuary is regulated by a saltwater barrier the Thanneermukkam bund.

Kochi (Cochin), the Queen of Arabian Sea, is the commercial capital and the most cosmopolitan capital of Kerala. The origin of the name

"Kochi" is thought to be from the Malayalam word kochu azhi, meaning 'small lagoon'. Yet another presumption is that Kochi is derived from the word Kaci meaning 'harbour'. Accounts by Italian explorers Nicolo Conti (15th century), and Fra Paoline in the 17th century say that it was called 'Kochchi', named after the river connecting the backwaters to the sea (Dinesh Mani, 2005). After the arrival of the Portuguese, and later the British, the name Cochin stuck as the official appellation. The city reverted to a closer anglicisation of its original Malayalam name, Kochi, in 1996. However, it is still widely referred to as Cochin, with the city corporation retaining its name as Corporation of Cochin. Kochi is the landing point for all visitors visiting Kerala and was a major centre of commerce and trade with the Arabs, Chinese, Portuguese, Dutch and the British in the past. With one of the finest natural harbours in the world and strategically located on the East-West sea trade route from Europe to Australia, this harbour city makes an important geographical location for the present research work. The harbour is partly located in Ernakulam and also some terminals are on Willingdon Island. The Cochin Estuarine System, one of the largest tropical estuaries in the Kerala State extends between 9^0 40′12″ and $10^0$10′46″North and 76^0 09′52″ and 76^0 23′57″East. It has a length of about 70 km and width lies between a few hundred meters to about 6 km. The CES covers approximately an area of 300 km^2 and are highly dependent on the river basins draining into them.

A major port at Cochin, (Cochin Port Trust) and 14 minor ports and fishing harbours are situated in this coastal zone. Utilizing the dredged material from the shipping channel, the land area in the vicinity of the Cochin port has been considerably enlarged; Wellington Island, Raman Thuruth (Candle Island), Marine drive, Vallarpadam etc. In addition to the ports mentioned above, a series of fishing harbours and fish landing centres are established along this coast. Vallarpadam Island where the International Container Transhipment Terminal (ICTT) is located (Figure: 2.1) is connected to Vypin Island, Bolghatty Island and with Ernakulam city.

ICTT is the largest and India's first global hub terminal and became India's gatewatey to International markets, competing with other transhipment ports in the region. Most of the industries of Kerala are situated at Eloor-Edayar- Ambalamugal area which is in and around to the river side. In addition to this, the bulk of the state's wood and clay based industries, fish processing plants, boat building yards, coir industries etc. are situated in and around the Cochin estuary area are the major industrial areas located in the coastal zone. Major industries Fertilizer and Chemicals Travancore Ltd. (FACT), Hindustan Insecticides Ltd. (HIL), Indian Rare Earths (IRE), Merchem, Sud chemie, Cochin Minerals and Rutiles Ltd. (CMRL), Binani Zinc Ltd. (BZL), Travancore Cochin Chemicals, BPCL Kochi Refinery, Hindustan Organic Chemicals (HOC), Cochin Shipyard are all located in Kochi availing the advantage of the Cochin port and ICTT facilities.

Figure 2.1: Map showing ICTT, Vallarpadam

The total rainfall over this region is about 320cm, of which nearly 75% occurs during monsoon season, which is from June to September. Several rivers and tributaries are flows into the Cochin estuary that may varies drastically with season. Of the total river discharge into the estuary, 33% of the discharge contributes from river Periyar. The percentage contribution from Muvattupuzha, Achenkovil, Pampa, Meenachil and

Manimala rivers were 24.2, 5.8, 19.7, 8.3 and 8.8 respectively (Srinivas, 2000). Due to heavy industrialisation, the northern part of the CES has been identified as severely polluted with respect to trace metals (Nair et al., 1990) The geochemistry of the sediments in the CES and the adjoining aquatic environment have been influenced by both natural and anthropogenic pollution loads (Sujatha et al., (1999); Balachandran et al., (2003); Arun, (2005); Martin et al., (2008)) and therefore there is an urgent need to the wise use of this aquatic system.

Based on the specific geographical features, water flow regimes and anthropogenic activities, eight stations were selected (Figure. 2.2). The sample collections were made out bimonthly during the same period of two years (2007 & 2008) to understand the impact of anthropogenically polluted sites of the estuary and seasonal variation. Samplings were done on February, April, June, August, October and December on both the years. Samples were categorised as per the climatic conditions into 3–Pre Monsoon (February & April), Monsoon (June & August) and Post Monsoon (October & December). The details of the sampling locations are given in the Table 2.1

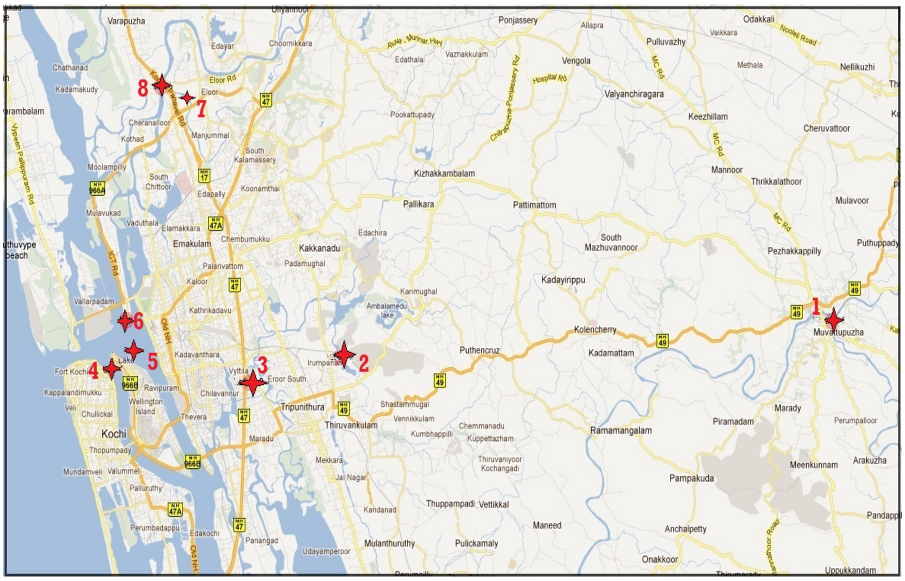

Figure 2.2: Map of Cochin Estuary System showing the location of Sampling Stations

Table 2.1: Details of the sampling locations

Station No:	Station Name	Depth (M)	Latitude (N)	Longitude (E)
1	Muvattupuzha river	5-10	09° 59' 09''	76° 35' 01''
2	Chitrapuzha river	0.5- 1	09° 57' 38''	76° 22' 10''
3	Champakara Canal	1.5-2.5	09° 57' 22''	76° 19' 34''
4	Cochin Harbour-- Mooring Jetty	0.5-1	09° 58' 04''	76° 15' 29''
5	Cochin Harbour-- Embarkation Jetty	2-4	09° 58' 12''	76° 15' 42''
6	Bolghatty	3-7	09° 59' 01''	76° 15' 59''
7	Cheranellore-Manjummel	0.5-1	10° 04' 01''	76° 17' 33''
8	Cheranellore Ferry	1-5	10° 04' 22''	76° 16' 56''

Station-1: Muvattupuzha River (Thriveni Sangamam)

Station-1 was chosen as the Muvattupuzha River and considered as a less polluted reference site, with the other sites under consideration. This station is the upstream of CES and also frees from industrial pollution and is therefore regarded as a reference site (Figure:2.3). Muvattupuzha River is about 121 km long and has a dendritic drainage pattern . Muvattupuzha river formed by the confluence of three tributaries, viz. Kothamangalam, Kaliyar and Thodupuzha rivers, is practically free from Pollution but slowly is changing, due to the growth of small towns on the river's banks as well as industrial endeavours. Samples - water and sediments were collected from the Thriveni Sangamam. During the period from January to May, this river maintains a constant flow probably due to tailrace water from Idukki hydroelectric power station.

Figure 2.3: Station-1, Muvattupuzha River

Station-2: Chitrapuzha River

Station 2 was selected as the area nearer to the Chitrapuzha Bridge, the downstream of Chitrapuzha River, which hosts diverse aquatic organisms and many areas have been transformed into breeding pools so as to increase fish production for commercial exploitation. Chitrapuzha River originates as a small stream from the upper reaches of high ranges in the eastern boundary of Kerala, passes through the valley and finally joints in the Cochin backwaters. Numerous industrial units including a diesel power project, fertilizer manufacturing unit and a petrochemical unit are located along the banks of the Chitrapuzha River (Figure:2.4). Effluents from these industrial units along with agricultural and other anthropogenic effluents find their way into Chitrapuzha River ultimately into Cochin backwaters. The lower reaches of this river became part of National water ways in 1993 and is now mainly used for transporting chemicals from Cochin port to the industrial units located on the banks of the river. The river Chitrapuzha is thus of considerable social and economic importance. During the present study, due to some renovation work near to the bridge, the river flow was almost restricted and the water level was very low. Also the sediment samples were not collected on these periods as it may not give an accurate representation of the environment.

Figure 2.4: Station-2, Chitrapuzha River

Station-3: Champakara Canal

The Champakara Canal of length 21.5Kms, starts from the Cochin Port confluence with the West Coast Canal and ends at the railway bridge near to Fertilizers and Chemicals Travancore Limited, boat basin at Ambalamugal. The point near to the Champakara fish market area was chosen as Station 3 (Figure:2.5). This is one among the site which is highly polluted due to slaughtering, urban domestic and sewage wastes.

Figure 2.5: Station-3, Champakara Canal

Station-4: Cochin Harbour- Mooring Jetty (CH-MJ)

Cochin harbour is one of the finest natural harbours in the world, and the only all weather harbour on the west coast, south of Bombay, affords a safe anchorage to ships. Willingdon Island is a man made one which was formed with materials dredged while deepening the Cochin Port and channel. The harbour situated on the Willingdon Island is an artificial Island tucked inside the backwaters.

Figure 2.6: Station-4, Cochin Harbour- Mooring Jetty

Station-5: Cochin Harbour- Embarkation Jetty (CH-EJ)

Embarkation jetty is located at the North End of Cochin Harbour, situated on the Wellington Island. Station 4 & 5 considered for this work was on the north and south end of the Cochin harbour where ship activities, dredging etc functions intensively. These two sites (Figure:2.6 and Figure:2.7) on either side of the Willingdon Island were assumed to be polluted sites of the stations under study.

Figure 2.7: Station-5, Cochin Harbour- Embarkation Jetty (CH-EJ)

Station-6: Bolghatty

Samples were collected from the area near to boat jetty in front of Bolghatty palace (Figure:2.8). The palace was built by the Dutch during their reign of the Kingdom of Kochi. The palace is today a heritage hotel, managed by the Kerala State Tourism Department. The island also has a golf course. Bolghatty Island has a local name Mulavukad. This island is on the western side of Ernakulam. This sampling station confluence the merits of both the Arabian Sea and the Cochin estuary.

Figure 2.8: Station-6, Bolghatty

Station-7: Cheranellore-Manjummel

Station 7 was selected as the spot on one of the streams of Periyar River nearer to Cheranellore-Manjummel bank where the domestic activities are high and close to the industrial belt. The width of the stream in this area is small and turbulence is minimum and almost stagnant (Figure:2.9). This point is a narrow stream of Periyar river and neighbouring a Petrochemical industry.

Figure 2.9: Station-7, Cheranellore-Manjummel

Station-8: Cheranellore Ferry

Station 8 was opted as Cheranellore Ferry, the area near to the Varapuzha Bridge where the two streams of River Periyar merges (Figure:2.10). The pollution load index of this area is very high as it is the downstream of Periyar which floods across the industrial locale of Edayar and Aluva to Arabian Sea.

Figure 2.10: Station-8, Cheranellore Ferry

2.2 Sample Collection & Preservation:

Fundamental to water-quality sampling is the fact that the analytical results can be no better than the sample on which the analysis was performed. Sample collection must be proper, so that the quality and integrity of the sample is ensured up to the time that it is delivered to the analyzing laboratory. Sample collection and preservation were done as per standard methods (APHA, (1998); Grasshoff, (1999)). Surface sample were collected approximately 10 cm below the water surface and bottom samples were collected approximately 25 cm above the sediments. All the sample collecting equipments- scoops, bags and containers were acid washed and rinsed thoroughly with distilled water. Surface water samples were collected using a thoroughly cleaned acid washed plastic bucket and transferred to 5 litre clean pre washed plastic cans with tight fitting plug, which are rinsed initially with a portion of sample. Bottom samples were taken using Niskin sampler. The depth of water level at Stations 2, 4 and 7 was very low and hence bottom sample collection was not carried out as it may not represent the homogeneity of the sample. Colour and odour were noted first and pH was noted using pH meter. Water for determination of Dissolved Oxygen (DO) was collected first. Samples were siphoned off in a

DO bottle, and adding Winkler A and B on the spot fix them for DO. All the samples were transported to the laboratory without any alteration and were refrigerated. The samples for trace metal analysis were acidified using Nitric Acid to pH 2.5 and preserved at about 4°C. The surface sediment samples were collected from each station using a plastic scoop in labelled plastic bags and were frozen.

2.3 Analytical Methodology:

2.3.1 Hydrographical Parameters

The analytical methodologies for the present evaluation were selected according to the recommendations given by "Standard methods for the examination of Water and Waste Waters" by APHA, (1999). The chemicals and water used for the entire analysis are Analar (A.R), high purity grade and Milli Q water. The following hydrographical parameters were analysed.

1. ***Temperature***: A sensitive thermometer was inserted into the water sample and temperature was allowed to become constant and reading noted.
2. ***pH***: pH was determined using ELICO L 120 pH meter. The pH values were determined using a digital direct readout pH meter, which is a combination of glass and AgCl electrodes. The instrument should be calibrated using a standard buffer solutions having pH 4, 7 and 9. After calibration the electrodes are washed with distilled water, blot dried and immersed in the sample for recording pH.
3. ***Electrical Conductivity (EC) and Total Dissolved Solids (TDS)***: EC and TDS were measured using ELICO CM 183 EC-TDS analyzer.

4. **Salinity**: Salinity of water samples was estimated by Mohr-Knudsen method (Muller, 1999). The end point is the formation of red silver chromate.

   Procedure:-To a known amount of the sample, 1ml of potassium chromate indicator solution is added and titrated against standard $AgNO_3$ solution. $AgNO_3$ is standardized with NaCl solution using potassium chromate as indicator

   Concentration of chloride in mgpl = [A x B x 35.45 x 1000]/Volume of sample, ml

   A = Volume of $AgNO_3$
   B = Normality of $AgNO_3$
   Chlorinity = Chlorosity / density
   Salinity = 1.8065 X Chlorinity

5. **Dissolved Oxygen**: Modified Winkler method was used for the estimation of dissolved oxygen (Hansen et al., 1999). The oxygen present in the sample was immediately fixed with Winkler A (Mn^{2+}Solution) and Winkler B (alkaline KI). After acidification, the iodine released was estimated by using sodium thio sulphate and starch as indicator.

   Procedure: Thiosulphate solution was standardized by a known value of 0.01N KIO_3 solution, when the solution became pale yellow; 1ml of starch solution was added. The endpoint is the disappearance of blue colour. Add 1ml 1:1 H_2SO_4 to the alkali fixed sample solution to dissolve the brown precipitate. Titrate with the known volume of solution against standard thiosulphate solution using starch as indicator. From the normality of the sample solution its strength can be calculated. From the value amount of O_2 per litre of the solution, and then the amount of dissolved oxygen in mgpl of the solution was determined.

DO, mgpl= N X 8 X 1000, where N = Normality of the sample solution

6. Nitrite and Phosphate: Nitrite and phosphate were determined spectrophotometrically using ELICO 520 spectrophotometer. Nitrite was converted to an azo dye with sulphanilamide and NED. Formation of phosphomolybdate complex using ascorbic acid as reductant was used for phosphate determination (Grasshoff, 1999). Phosphate was also estimated spectrophotometrically using UV-Visible Genesys spectrophotometer.

2.3.2 Metals

Water Samples:

For trace metal analysis, extreme care was taken in sampling and sub - sampling. Water samples were collected in acid -washed polythene cans and kept in iceboxes. Known volumes of samples were filtered through pre –weighted Millipore filter paper (0.45µm) and the filtrate was acidified to pH 2.5 using concentrated hydrochloric acid (APHA, 1995). Since the metal quantity is very less pre-concentration of the water sample is required. The dissolved metals were extracted using Ammonium Pyrrollidine Dithocarbamate (APDC) and Diethylammonium Diethyldithiocarbamate (DDDC) at pH 4.5 and brought back to aqueous layer by back-extraction with concentrated nitric acid and made up to 20 ml with Milli -Q water.

Procedure: Transfer 1 litre of the sample to a separating funnel after adjusting the pH to about 4.5 by addition of 10 ml of aqueous solution of 10% di-ammonium hydrogen citrate buffer and pure ammonia. Add 5 ml each of APDC and DDDC followed by 50 ml of chloroform (Danielsson et al., 1982). Shake the mixture for 2 minutes and allow separating the phases for about 15 minutes. Drain the organic layer to a 250 ml separating funnel. Ensure the chloroform layer is completely free from water. Continue the extraction by addition of another 30 ml of chloroform to the funnel and shake again for 2 minutes. Repeat once again with 20 ml of $CHCl_3$.

combined three portions and add 2 ml conc. HNO_3 by micropipette. After mixing for 1 minute let the funnel stands for 15 minutes, to decompose the metal carbamates. Add 5 – 8 ml of Milli Q water and shake for 2 minutes to ensure complete back extraction. After the phase has separated the chloroform layer is discarded. The acid phase containing the back extracted metal is drained into 25 ml beaker and separating funnel is rinsed with 2 ml of 1M HNO_3 and quantitatively transferred to a suitable bottle. The trace metal concentration is determined using Atomic Absorption Spectrometer (AAS).

Sediment Samples:

Even though the trace element concentration in soils and sediments are normally much higher than those for water samples, many precautionary steps taken relating to sample container preparations and sampling of waters are equally applicable to soil and sediments. Soil composition may vary greatly over a small area. Samples have to be taken from a number of locations to obtain a suitable average composition studies, the source of contamination and its mobility within the soil should be taken into account. Sediment samples were collected at all stations with a Van Veen grab. Sediments were scooped carefully from the middle portion without being disturbed, using a clean plastic spoon, to pre -cleaned plastic containers and were kept in iceboxes and then transferred to freezer until analysis was carried out. The sample, after drying were finely powdered using a mortar.

The samples were homogenised by cone and quarter method. This technique involves pouring the sample into a cone, flattening the cone, dividing the flattened cone into four equal divisions (quartering), and then removing 2 opposite quarters. The remaining two quarters are re-piled into a cone and the process is repeated until the desired sample size is obtained. The use of the cone and quarter method to homogenize a sample involves the removal of the first quarter and re-piling it into a cone followed by the subsequent re-piling of the opposite quarter and then the remaining two quarters to reform a single cone (Raab et al., 1990). This process is repeated several times until sample homogeneity is achieved. The homogenised sediment sample were accurately weighed and digested with a mixture of HCl-HF -$HClO_4$- HNO_3, evaporating to dryness each time until the digestion was complete and brought into solution in 2ml of ultra pure HNO_3 and made upto 100 ml centrifuged and transferred to a clean dried plastic bottle. The solution is then analyzed using ICP OES, Perkin Elmer, Optima DV 2100.

Instrumentation:

The instruments used for the metal analysis are Atomic Absorption Spectrometer (AAS) and Inductively Coupled Plasma –Optical Emission Spectrometer (ICP OES). For water samples, AAS was used for the metal determination and for sediments both AAS and ICP were used. Metal concentration obtained with both techniques was compared and found with in the agreeable reproducibility. In the case of Sediments, sample digestion and preparation was carried out in the Chemical Oceanography Department of CUSAT and subsequent analysis in ICP OES at R&D Department of Binani Zinc Ltd.,Aluva, India.

Atomic Absorption Spectrometer:

Instrument Model: Perkin Elmer AAnalyst 100 (Figure: 2.11)

Figure 2.11: Perkin Elmer AAS-AAnalyst100

Atomic-absorption spectroscopy uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption according to the Beer-Lambert law. Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration. The Schematic representation of the working of AAS is given in Figure: 2.12

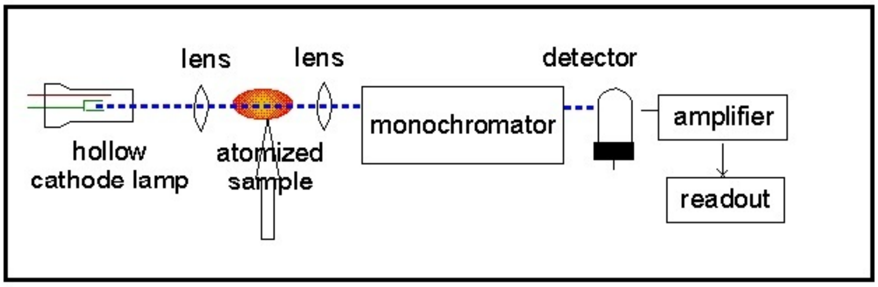

Figure 2.12: Schematic representation of AAS

Inductively coupled plasma optical emission spectroscopy (ICP-OES):

Instrument Model: Perkin Elmer Optima 2100 DV

The ICP is a high-temperature, optically thin source that allows extended dynamic-range measurements on a multi-element basis. The extended dynamic range allows for the analysis of ppb to percent level analytes in a single run. The multi-element capability is well suited for the demands of most environmental laboratories, providing a greater level of productivity than traditional single-element determinations by atomic absorption spectroscopy. The Optima 2100 DV (Figure:2.13) is a simultaneous hybrid, allowing for simultaneous background correction, full data reprocessing, interference correction and unmatched wavelength stability. The software data acquisition algorithms in the Optima 2100 DV allows more rapid data acquisition and to allow the environmental user to achieve the required sensitivity in a relatively short amount of time.

Figure 2.13: ICP OES Optima2100DV instrument

In inductively coupled plasma-optical emission spectrometry, the sample is usually conveyed into the instrument as a stream of liquid sample. Inside the instrument, the liquid is converted into an aerosol through a process known as nebulisation. The sample aerosol is then transported to the plasma where it is desolvated, vaporised, atomized, and excited and/or ionized by the plasma. The excited atoms and ions emit their characteristic radiation which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration information for the analyst. A representation of the layout (Charles and Kenneth, 1997) of a typical ICP-OES instrument is shown in Figure:2.14. Two multi element standards containing 100 ppm and 500 ppm of Cd, Cu, Fe, Ni, Pb, Zn were prepared from a 1000 ppm multi element standard (PerkinElmer Part Number N930-0281) in 2% v/v Nitric acid (suprapure grade). The operating conditions and parameters are given in the Table 2.2 and 2.3.

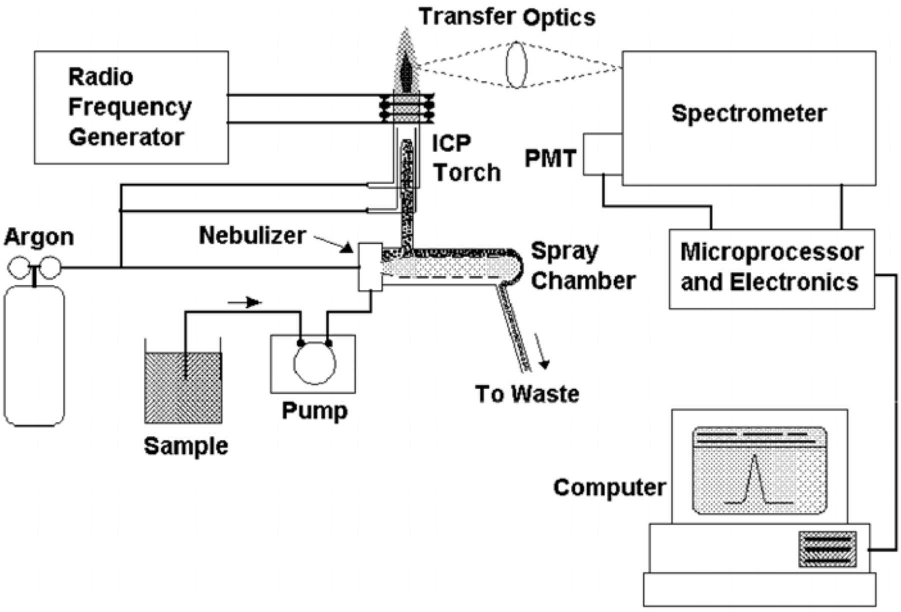

Figure 2.14: Schematic layout of ICP-OES instrument

Table 2.2: Instrument set up & Operating parameter for ICP OES

Parameter	Settings
RF Power	1450 W
Nebulizer Flow	0.8 L/min
Auxiliary Flow	0.4 L/min
Plasma Flow	17 L/min
Sample Flow	1.5 mL/min
Source Equilibration Time	15 seconds
Background Correction	Manual selection of points
Measurement Processing Mode	Peak Area/ Ht
Auto Integration	1-5 seconds (min-max)
Read Delay	60 seconds
Replicates	3
Sample introduction	2 ml per minute
Torch Type	Radial, Axial, Att. Radial, Att. axial

Table 2.3: Wavelengths and Viewing Modes for Each Element

Element	Wavelength (nm)	Survey Lower	Survey Upper	Points/ Peak	Viewing Mode
Cd	228.802	228.651	228.958	7	Axial
Cu	327.393	327.285	327.505	7	Axial
Fe	259.939	259.821	260.057	7	Axial
Ni	221.648	221.547	221.749	7	Axial
Pb	220.353	220.255	220.451	7	Axial
Zn	206.200	206.014	206.385	7	Axial

Wavelength and limit of detection (LOD):

The LOD was determined by running a method blank 10 times and the 2 mgpl control standard 10 times on the raw intensity mode on the polychromator. The formula used for the determination of the LOD gave better than 99% confidence level. The formula to calculate the LOD is as follows:

$$\text{LOD} = \frac{3\sigma \text{ Blank intensity x Standard Concentration}}{\text{Standard Intensity} - \text{Blank Intensity}}$$

Calibration/Standardisation of AAS & ICP OES:

AAS:

The AAS instrument was calibrated using standards of Merck. These standards were diluted to provide calibration standards over the calibration range. It was then standardised with the Standard Reference Material, SRM 1643e, traceable to National Institute of Standards & Technology (NIST). SRM 1643e is intended primarily used for evaluating the procedure used in the determination of trace elements in fresh water. This SRM simulates the elemental composition of fresh water with Nitric acid at a concentration of 0.8 molar in order to stabilize the trace elements.

The percentage accuracy of metal analysis using AAS and recovery of analyte concentrations for SRM 1643e were presented in Table 2.4. The analysis of SRM has yielded a competitive result with the certified values.

ICP OES:

The ICP-OES instrument was calibrated using standards of Merck. These standards were diluted to provide calibration standards over the calibration range. The calibration range included a calibration blank and a minimum of 4 calibration standards. After the instrument was calibrated, the correlation coefficients were checked to be better than 0.999. This was the accepted criterion of the calibration. After the calibration, a two-point standardisation was performed using a calibration blank and the highest concentration standard for the particular determinant and the acceptance criteria for the standardization factor were between 0.8 and 1.2. The method blanks and extract solutions were analysed and no concentration above the LOD was allowed to be present. The calibration was verified using a NIST certified Standard Reference Material, SRM 2709.

SRM 2709 is an agricultural soil that was oven-dried, sieved, radiation sterilized, and blended to achieve a high degree of homogeneity. The U.S. Geological Survey (USGS), under contract to NIST, collected and processed the material for SRM 2709. The soil was collected from a ploughed field, in the central California San Joaquin Valley, at Longitude 120° 15′ and Latitude 36° 30′. The certified elements for SRM 2709 are included in Table 2.5. The values are based on measurements using one definitive method or two or more independent and reliable analytical methods. The percentage accuracy of metal analysis using ICP OES and recovery of analyte concentrations for SRM 2709, San Joaquin Soil is presented in Table 2.5. The analysis of NIST SRM 2709 has yielded a very good result with the certified values. Recoveries were calculated as the percent of certified elemental concentration extracted from the standard soil.

Table 2.4: Percentage accuracy of metal analysis using AAS and recovery for NIST SRM 1643e

Metal	NIST SRM 1643e Certified Value in µg/l	Replicate			Mean	SD	CV %	Recovery %
		# 1	#2	#3				
Cd	6.568 ± 0.073	6.658	6.487	6.695	6.61	0.11	1.7	100.7
Cu	22.76 ± 0.31	22.56	22.01	21.98	22.2	0.33	1.5	97.5
Fe	98.10 ± 1.4	95.36	94.69	96.35	95.47	0.84	0.9	97.3
Ni	62.41 ± 0.69	59.36	60.11	59.17	59.5	0.50	0.8	95.4
Pb	19.63 ± 0.21	15.87	16.87	14.98	15.9	0.95	5.9	81.0
Zn	78.50 ± 2.2	76.55	74.98	77.21	76.2	1.15	1.5	97.1

Table 2.5: Percentage accuracy of metal analysis using ICP OES & Absolute recovery for NIST SRM 2709

Metal	NIST SRM 2709 Certified Value in mg/kg	Replicate			Mean	SD	CV %	Recovery %
		# 1	#2	#3				
Cd	0.38 + 0.01	0.37	0.35	0.34	0.35	0.01	4.2	92.3
Cu	34.6 + 0.7	33.4	33.0	32.9	33.1	0.24	0.7	95.6
Fe(%)	3.50 + 0.11	3.61	3.49	3.70	3.60	0.10	2.9	102.8
Ni	88.0 + 5	78.2	79.9	79.3	79.1	0.88	1.1	89.9
Pb	18.9 + 0.5	15.9	15.1	15.0	15.3	0.49	3.2	81.1
Zn	106 + 0.3	103.0	103.6	102.9	103.1	0.38	0.4	97.3

2.3.3 Sediment Characteristics:

2.3.3.1 Texture Analysis

Soil texture refers to sand, silt and clay composition. Soil content affects soil behaviour, including the retention capacity for nutrients and water. Sand and silt are the products of physical weathering, while clay is the product of chemical weathering. Clay content has retention capacity for nutrients and water. Clay soils resist wind and water erosion better than silty and sandy soils, because the particles are more tightly joined to each other. In medium-textured soils, clay is often trans-located downward through the soil profile and accumulates in the subsoil (Figure:2.15). Texture analysis of the sediment was done based on Stoke's law using the method of Krumbein and Pettijohn, (1938).

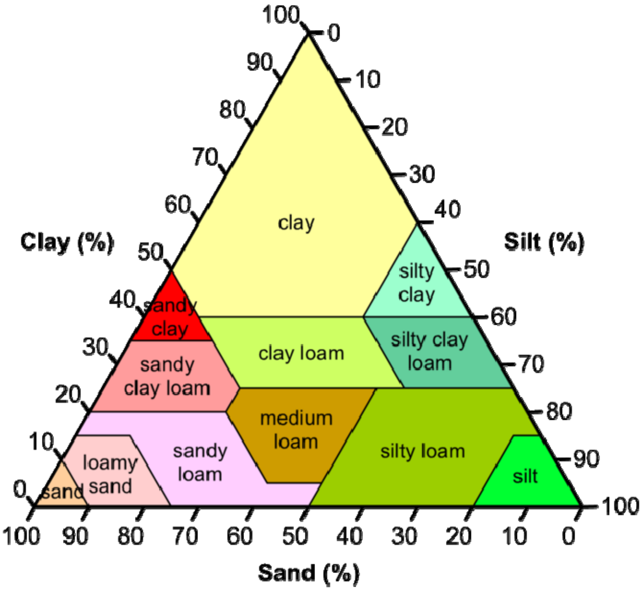

Figure 2.15: Soil Composition

Procedure: About 40g of sediment was treated with 10ml of 1N HCl to it. Stir well to remove carbonates. After washing, the residue was treated with 30 ml of 15% H_2O_2, till effervescence ceases and kept overnight to remove organic matter. The solution was slightly warmed to remove excess H_2O_2 and washed with milli Q water and dried below 60ºC in air oven. To 10g of the dried sediment, 7.5g Sodium hexa meta phosphate and 200 ml of milli Q were added and kept overnight. The sample was passed through a sieve of mesh size 63µm pouring a water through a funnel into a 1000ml measuring cylinder and the volume was made up to 1000ml. The residue left in the sieve (sand fraction) was gravimetrically estimated. 20ml of the sample from 10 cm depth was pipetted out from the cylinder after

60 minutes and was dried in the previously weighed beaker and it corresponds to clay fraction. The balance in the fraction after subtracting the sand and clay was taken as silt. After oven drying, the weight of material in the beaker was calculated. The percentage of sand, clay and silt were calculated using the formula.

Sand (%) = [(Weight retained in the mesh)/10] x 100
Silt (%) = [(Dif. Wt. – 0.15)/ (20 x10)] 1000 x 100
Where Dif. Wt: = beaker weight after drying – empty beaker weight
Clay (%) = 100-(Sand% + Silt %)

2.3.3.2 Total Organic Carbon

Total organic carbon was estimated on dry sediments by the procedure of El Wakeel and Riley modified by Gaudette et al., (1974).

Procedure: About 0.2g dry sediment was weighed and transferred to 500ml dry conical flask .10 ml of potassium dichromate and 20 ml conc. Sulphuric acid are added and kept for half an hour. Added 170 ml water and 10 ml phosphoric acid followed by 10g sodium fluoride. Then 15 drops of ferroin indicator was added and titrated against standard ferrous ammonium sulphate. End point was the appearance of red colour.

TOC(%) = 10(1-T/S)(1N)(0.003)(100/W)
Where T = Titre value of the sample; S= Titre value of blank; W= Weight in grams of sample; N= Normality of potassium dichromate.

2.4 Data Analysis

To study the dependence of metal on each of the hydrographic parameters and their relative significance in the prediction of equation, multiple regression analysis was employed. Variations of the data were studied by calculating Standard deviation, Coefficient of Variation, Correlation and Multiple Regression. Statistical parameters were calculated employing the statistical software SPSS v10 for windows. The annual mean, standard deviation and percentage coefficient of variation for all the parameters recorded were computed along with minimum and maximum values to get an idea of the spread of the data. Both spatial and temporal variations were significant. The spatial variations are discussed mainly on the basis of annual mean concentrations recorded at each Station. Correlation study was carried out to find out the influence of various hydrographical parameters on the distribution of dissolved and particulate metals. The seasonal and annual mean values are represented graphically to bring out seasonal and spatial variations. Multiple regression analysis was performed on the total metal concentrations to assess the role of different parameters in determining distribution pattern of heavy metals. An attempt was also made to quantify the natural and anthropogenic contribution of heavy metals to the sediment. The experimental data obtained for the present work were used to differentiate the seasonal changes of various parameters along the study area. In the absence of a sequential extraction of metals in sediments, statistical procedures can be used for making inferences on the important pathways of elemental deposition (Isaac et al., 2005). This was attained by adopting different environmental techniques of reaching Metal Normalisation, Enrichment factor and using Principal Component Analysis.

2.4.1 Standard Deviation (SD):

Standard deviation is a widely used measurement of variability or diversity used in statistics and probability theory. It shows how much variation or "dispersion" there is from the average (mean, or expected value). A low standard deviation indicates that the data points tend to be very close to the mean, whereas high standard deviation indicates that the data are spread out over a large range of values.

2.4.2 Coefficient of Variation (CV):

The coefficient of variation (CV) is defined as the ratio of the standard deviation to the mean: A statistical measure of the dispersion of data points in a data series around the mean. The coefficient of variation represents the ratio of the standard deviation to the mean, and it is a useful statistic for comparing the degree of variation from one data series to another, even if the means are drastically different from each other. The coefficient of variation is a dimensionless number. So for comparison between data sets with different units or widely different means, one should use the coefficient of variation instead of the standard deviation.

2.4.3 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) is an exploratory tool designed by Karl Pearson in 1901 to identify unknown trends in a multidimensional data set. PCA is a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences. PCA was employed to deduce the geochemical processes in these ecosystems. Varimax orthogonal rotation was applied in order to identify the variables that are more significant for each factor based on the significance of their correlations that are expressed as factor loadings (Buckley et al., 1995; Davis, 2002).Since patterns in data can be hard to find in data of high dimension, where the luxury of graphical representation is not available, PCA is a powerful tool for analysing data.

2.4.4 Assessment of metal contamination

2.4.4.1 Metal Normalisation

Total soil concentration data are required to evaluate soil quality and the ability of soils to support life. However to determine the source and dispersion of contaminants, an accurate depiction of spatial distributions, normalised data are required. Normalisation means the concentration of each metal in the sample is divided by the concentration of the same metal in the reference material. The significance of normalisation is to check the similarity of pattern for many elements supporting homogeneity. In the present study, metals are normalised with the concentration of metals in reference station-Muvattupuzha (Station-1).

2.4.4.2 Enrichment Factor (EF)

A common approach to estimate how much a soil sample is contaminated (naturally and anthropogenically) with the heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above uncontaminated background levels. The assessment of metal and level of contamination in soils require pre-anthropogenic knowledge of metal concentrations to act as pristine values. Pollution will be measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material. The EF method normalises the measured heavy metal content with respect to a sample reference such as Al, Fe or Zn. A number of different enrichment calculation methods and different reference materials have been reported by Abrahim and Parker, (2008); Charkravarty and Patgiri (2009); Harikumar and Jisha (2010); Sekabira, (2010). In this study, EFs were computed by normalising with Fe (Blomqvist et al., 1992). Iron is conservative during diagenesis (Berner, 1980) and its geochemistry is similar to that of many trace metals both in oxic and anoxic environments. Natural concentrations of Fe in sediments are more uniform than Al and beyond the influence of humans, justify its use as a normaliser (Daskalakis and O'Connor, 1995). An EF value less than 1.5 suggests that the trace metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002 and Feng et al., 2004). However, an EF value greater than 1.5 suggests that a significant portion of the trace metal is delivered from non-crustal materials or non-natural weathering processes and that the trace metals are provided by other sources (Feng et al., 2004).

In this study, the degree of anthropogenic pollution was established by adapting Enrichment factor ratios (EF) used by Huu et al., (2010) and Sutherland et al., (2000).

The EF of a heavy metal in sediment can be calculated using the following formula (Huu, 2010)

$$\mathrm{EF} = \frac{C_{\mathbf{metal}} / C_{\mathbf{normaliser}} \text{ of Sample}}{C_{\mathbf{metal}} / C_{\mathbf{normaliser}} \text{ of Reference}}$$

Where, C_{metal} and $C_{normaliser}$ are the concentrations of heavy metal and the normaliser in soil (Fein the present study) and in unpolluted control as Reference. As the EF values increase, the contributions of the anthropogenic origins also increase.

Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure and to assess the degree of anthropogenic influence (Emmanuel and Edward, 2010). Five contamination categories are recognized on the basis of the enrichment factor as follows (Sutherland et al., 2000)

$\mathrm{EF} < 2$: Deficiently to minimal enrichment
$2 \leq \mathrm{EF} < 5$: Moderate enrichment
$5 \leq \mathrm{EF} < 20$: Significant enrichment
$20 \leq \mathrm{EF} < 40$: Very high enrichment
$\mathrm{EF} \geq 40$: Extremely high enrichment

2.4.4.3 Contamination Factor (CF)

The level of contamination of soil by metal is expressed in terms of a contamination factor (CF) calculated as:

$$\mathbf{CF} = C_n/B_n$$

Where C_n = measured concentration of sample and Bn =geochemical background value. The contamination factor CF < 1 refers to low contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ indicates considerable contamination and $CF > 6$ indicates very high contamination.

2.4.4.4 Pollution Load Index (PLI)

Each site was evaluated for the extent of metal pollution by employing the method based on the pollution load index (PLI) developed by Thomilson et al. in 1980, as follows:

$$\mathbf{PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots CF_n)^{1/n}}$$

where n is the number of metals studied and CF is the contamination factor. The PLI provides simple but comparative means for assessing a site quality, where a value of $PLI < 1$ denote perfection; $PLI = 1$ denotes that only baseline levels of pollutants are present and $PLI > 1$ would indicate deterioration of site quality. (Thomilson et al., 1980).

This type of measure has however been defined by some authors in several ways, for example, as the numerical sum of eight specific contamination factors (Hakanson, 1980), whereas, Abrahim (2005) assessed the site quality as the arithmetic mean of the analysed pollutants. In this study, PLI is calculated based on Mmolawa et al., (2011), taking the geometric mean of the studied pollutants as this method tends to reduce the outliers, which might bias the reported results.

2.4.4.5 Geoaccumulation index (I_{geo})

Enrichment of metal concentration above baseline concentrations was calculated using the method proposed by Muller, (1969), termed the geoaccumulation index (I_{geo}). To quantify the degree of anthropogenic contamination and to compare different metals that appear in different ranges of concentration in lake sediments, an approach to indexing geoaccumulation, I_{geo}, was used. A quantitative check of metal pollution in aquatic sediments was proposed by Müller and Suess, (1979) as equation and is called the Index of Geoaccumulation, that is, the enrichment on geological substrate:

$$I_{geo} = \log_2 (C_n/1.5 \times B_n)$$

Where C_n = measured concentration of sample, and B_n =geochemical background value.

The factor 1.5 is introduced in this equation to minimise the effect of possible variations in the background values, B_n which may be attributed to lithogenic variations of trace metals in soils. The geoaccumulation index compares the measured concentration of the element in the fine-grained sediment fraction C_n with the geochemical background value B_n. The index of geoaccumulation consists of seven grades, whereby the highest grade (6) reflects 100-fold enrichment above background values. Förstner et al. listed geoaccumulation classes (Förstner et al., 1993) and the corresponding contamination intensity for different indices (Gulfem and Turgut, 1999) , which is shown in Table 2.6.

Table 2.6: Geoaccumulation index classification (Förstner et al., 1993).

Sediment geoaccumulation index, I_{geo}	**I_{geo} Class**	**Contamination intensity**
>5	6	Very strong
>4-5	5	Strong to very strong
>3-4	4	Strong
>2-3	3	Moderate to strong
>1-2	2	Moderate
>0-1	1	Uncontaminated to moderate
<0	0	Practically uncontaminated

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Chapter 3

GENERAL HYDROGRAPHY AND SEDIMENT CHARACTERISTICS

Contents

3.1 Introduction

The study of the hydrographical parameters of the estuarine environment is of great importance to characterise the general features, distribution pattern and relative abundance of metals. These studies are also significant with regards to water management and pollution control. The hydrographical conditions in an estuary mainly depend on the intrusion of sea water and the influx of fresh water from rivers. The coagulation and precipitation of dissolved solids and evaporation of water also have profound effect on the hydrographical conditions of an estuary. Hydrographic parameters of an estuary undergo considerable tidal and seasonal variations. As a consequence of marked seasonal fluctuations in meteorological features viz., temperature, rainfall etc., large scale variations of different physicochemical properties are observed in estuarine ecosystems. Role of hydrographic features to the development of fishery in estuarine and coastal waters is well established. The demand for water has already increased manifold over the years due to urbanization, agriculture expansion, increasing population, rapid industrialization and economic development. At present, changes in cropping pattern and land-use pattern, over-exploitation of water storage and changes in irrigation and drainage are modifying the hydrological cycle in many climate regions and river basins of India. An assessment of the availability of water resources in the context of future national requirements and expected impacts of climate change and its variability is critical for relevant national and regional long term development strategies and sustainable development. The physicochemical characteristics have always been the major constraints that affect the water resources adversely. Physical parameters reflect the aesthetic acceptability of water for drinking and domestic purposes. The physical parameters include colour, odour, taste, temperature, turbidity, conductivity and suspended solids. Seasonal variations in the hydrographical parameters showed marked changes in the chemical constituents. Atmospheric temperature, as well as rainfalls showed marked seasonal variation. The estuary experiences three seasons- Monsoon, with maximum rainfall, Post Monsoon characterised by scarce rainfall and atmospheric cooling, Pre Monsoon denoting warm weather season. The estuary is influenced by semidiurnal tides with two floods and two ebb periods of unequal heights within a tidal day. The highest high tide variations were also owing to the change in seawater intrusion and freshwater discharges from the adjoining areas. The tidal height in CES was about one meter.

3.2 Hydrographical Parameters

The important hydrographic parameters such as pH, temperature, Salinity, DO, Conductivity, Phosphate and Nitrite etc. play a significant role in the distribution of trace metals and nutrients in the aquatic system. The determination of the above parameters was also carried out along with trace metal analysis in the present study and the results obtained are outlined in the following sections. Surface water and bottom water samples from each station are designated ‘S’ and ‘B’ followed by the station number. The depth of water is very low in the stations 2, 4 & 7 and hence the bottom water samples were not collected from these stations, as it may not be an accurate representative sample. The average value of both the years under study was taken into consideration for each parameter. The Station-wise seasonal variations on Temperature, pH, Salinity, DO, Conductivity, TDS, Phosphate, Nitrite and Sulphate in surface and bottom waters are in Tables: 3.1 to 3.8. Seasonal and spatial variations of each parameter are depicted in Figures: 3.1 to 3.8.

3.2.1 Rainfall

The average rainfall in the Cochin estuary is about 3.2m, which exhibits considerable variations from year to year. Approximately 75% of the total rainfall occurs during the monsoon period which starts from late May or early June to September. With the onset of monsoon and within the course of a few weeks, the hydrographic conditions in the estuary undergoes remarkable changes due to the influx of freshwater as the system rapidly changes from marine to brackish water condition and similar observation reported by earlier workers (Menon et al., 2000). The early morning drizzling in the Cochin estuarine area was noted by many meteorologists because of the proximity of industrial area and the influence of Arabian sea which results high humidity (>75%).

Monthly rainfall ranged between 2 mm (March to May) and 150-248 mm (July & August). A seasonal pattern in precipitation became apparent; heavier precipitation occurred during south west monsoon (May–August) and north-east monsoon (September–December) there was little precipitation (2-15) during January–April. 90% of precipitation occurred during the monsoon and rest fall on the post monsoon and April is always characterized by a summer precipitation.

3.2.2 Temperature

Temperature is an important factor that can modify both physical and ecological properties of aquatic environment. The ideal temperature range is 20°C-25°C and acceptable value is between 2°C-30°C. Water temperature regulates ecosystem functioning both directly through physiological effects on organisms, and indirectly, as a consequence of habitat loss (ANZECC, 2000). Photosynthesis and aerobic respiration, and the growth, reproduction, metabolism and the mobility of organisms are all affected by changes in water temperature.

Aquatic organisms can only survive within a particular temperature range (Hoegh, 1999) Unnatural changes in water temperature impact indirectly upon biota through loss of supporting habitat such as coral reefs (Ward et al., 1998), by changing the solubility of oxygen and calcium carbonate in water, or by influencing the extent to which metal contaminants (Luoma, 1983) and other toxicants are assimilated by physiological processes. Over normal temperature ranges, biologic activity doubles for each 10 degree rise in temperature. The major seasonal cause of water temperature change is due to the change in solar insolation in addition to currents and local hydrodynamics. Also, temperature in surface waters varies during the day and tends to be highest in the late afternoon as the sun sets. Large temperature differences between surface and bottom waters are indicative of stratification and small temperature differences are indicative of de-stratification. Hydrogen sulphide gas may come from the lakes and rivers, when the water column loses stratification, and temperature differences between surface and bottom waters approach zero. Influx of freshwater through the rivers and intrusion of sea water through the Bar-mouth reaches have profound influence on the distribution of temperature in backwater system (Pillai et al., 1975) apart from local phenomena such as mixing of heated waste water, heat production during biochemical oxidation etc.

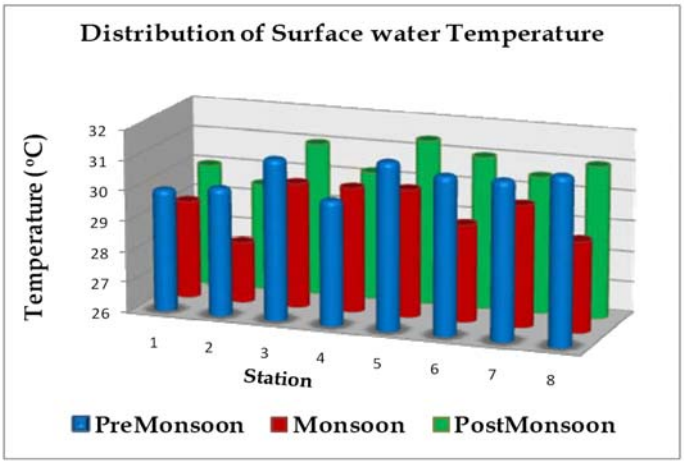
Seasonal and station-wise variation of temperature of surface and bottom water is given in Fig: 3.1 and Table: 3.1. Temperature shows maximum values in the surface and bottom water during Pre Monsoon and low values during Monsoon in the Cochin estuarine System. The surface temperatures ranged between 28.0 to 31.5 ^{0}C and bottom temperatures from 28 to 30.8 ^{o}C. The seasonal variations of surface temperature of water does not exactly corresponds to similar variations in atmospheric temperature indicating that the heat exchange with atmosphere is not the only factor affecting the surface temperature in estuaries. Station-wise statistical summary of temperature is given in Table: 3.2

Table 3.1: Station-wise seasonal variations of Temperature in Degree Celsius

Station	**Surface water – Temperature (^{o}C)**			**Bottom water -Temperature (^{o}C)**		
	Pre Mon.	**Monsoon**	**Post Mon.**	**Pre Mon.**	**Monsoon**	**Post Mon.**
1	30.0	29.2	30.0	28.8	28.2	28.2
2	30.2	28.0	29.5	--	--	--
3	31.3	30.1	31.0	30.2	29.5	30.0
4	30.1	30.1	30.2	--	--	--
5	31.5	30.2	31.4	31.2	29.0	30.5
6	31.2	29.2	31.0	30.5	28.4	30.5
7	31.2	30.0	30.5	--	--	--
8	31.5	29.0	31.0	31.0	28.0	30.8

Table 3.2: Station-wise statistical summary of temperature

Station	**Surface water – Temperature (^{o}C)**					**Bottom water -Temperature (^{o}C)**				
	Min	**Max**	**Mean**	**SD**	**CV %**	**Min**	**Max**	**Mean**	**SD**	**CV %**
1	29.2	30.0	29.7	0.46	1.6	28.2	28.8	28.4	0.35	1.2
2	28.0	30.2	29.2	1.12	3.8	--	--	--	--	--
3	30.1	31.3	30.8	0.62	2.0	29.5	30.2	29.9	0.36	1.2
4	30.1	30.2	30.1	0.06	0.2	--	--	--	--	--
5	30.2	31.5	31.0	0.72	2.3	29.0	31.2	30.2	1.12	3.7
6	29.2	31.2	30.5	1.10	3.6	28.4	30.5	29.8	1.21	4.1
7	30.0	31.2	30.6	0.60	2.0	--	--	--	--	--
8	29.0	31.5	30.5	1.32	4.3	28.0	31.0	29.9	1.68	5.6



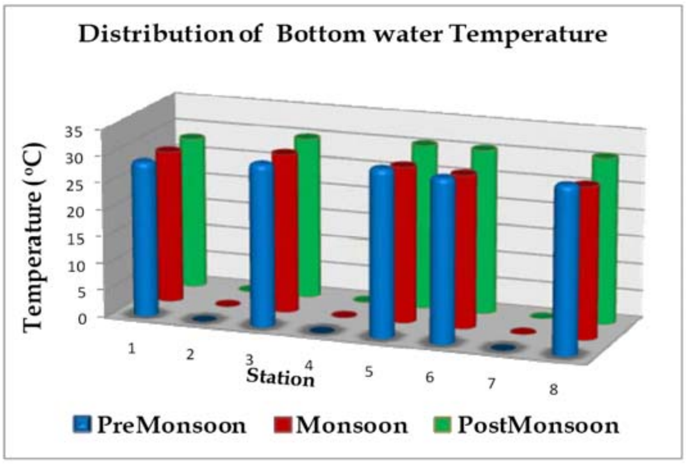


Figure 3.1: Seasonal & Spatial variation of Temperature in Surface & Bottom waters

3.2.3 pH

pH is a measure of acidity or alkalinity of water on a log scale from 0 (extremely acidic) through 7 (neutral) to 14 (extremely alkaline). It is the negative base-10 log of the hydrogen ion (H^+) activity in moles per litre. Hydrogen ions predominate in water with pH less than 7; hydroxyl ions (OH^-) predominate in water with pH greater than 7. The primary concern with pH is its direct relationship to the toxicity of ammonia and nitrite. Each pH integer above the neutral 7 reflects a tenfold increase in such toxicities. The pH levels in a given pond can fluctuate daily and is determined by complex relationships between carbon dioxide, hardness, alkalinity, photosynthesis, and respiration.

The pH of marine waters is close to 8.2, whereas most natural freshwaters have pH values in the range from 6.5 to 8.0. Most waters have some capacity to resist pH change through the effects of the carbonate-buffer system. In this system, hydroxyl ions produced during the hydrolysis of bicarbonate neutralise H^+ ions, and maintain pH at a near constant level. Bicarbonate ions (HCO_3^-) are acquired from the weathering of silicate or carbonate minerals as rainwater passes through the soil zone. Most aquatic organisms and some bacterial processes require that pH be in a specified range. For example, the activity of nitrifying bacteria is optimal over a narrow pH range from 7 to 8.5 (Henriksen and Kemp, 1988). If pH changes above or below the preferred range of an organism (including microbes), physiological processes may be adversely affected (ANZECC, 2000) especially true for most organisms if the ambient pH drops to below 7 or rises to above 9. Physical damage to the gills, skin and eyes can also occur when pH is sub-optimal for fish, and skin damage increases susceptibility to fungal infections such as red spot disease. pH is driven more frequently to greater extremes under eutrophic conditions, allowing algal species with tolerance to extreme pH levels to grow and dominate communities, and to potentially form algal blooms (Hinga, 2002). Changes in pH can also have indirect impacts on aquatic organisms. For example, changes in pH can alter the biological availability of metals, the speciation of nutrients and the toxicities of ammonium, aluminium and cyanide (ANZECC, 2000). Increases in pH can also cause the electrostatic forces that bind viruses to particles to be overcome, thus facilitating their release to the water column (Miller, 2001). pH is important in calcium carbonate solubility (calcite or aragonite), which is important for shell-forming organisms. Shell growth (i.e. calcification) is inhibited if water becomes too acidic.

Seasonal and spatial variation of pH in surface and bottom water samples for all the stations are given in Table: 3.3. For Surface water, pH values in the present study ranged from 6.7 to 8.41, 6.33 to 7.92 and 5.77 to 7.04 during Pre-Monsoon, Monsoon and Post-Monsoon respectively. For bottom water, pH values ranged from 6.65 to 7.52, 6.31 to 7.64 and 6.03 to 7.07 during Pre-Monsoon, Monsoon and Post-Monsoon respectively. (Figure: 3.2). Station-wise statistical summary of pH is given in Table: 3.4

The highest pH value of 8.41 for surface water was observed at station-7 and the lowest value of 5.77 was recorded at station-2. The highest and lowest values were noted during the precipitation time (October, June and Aug) this indicated that highly acidic effluents were discharged during the rain fall time and then the pH indicated a recovery in pre monsoon. The water flow in station-7 was almost stagnant and this station is highly influenced by the anthropogenic activities including laundries. The station-2, Chitrapuzha River carries the effluents of the neighbouring fertilizer and petroleum refining industry and the comparatively low pH in this region enhanced the concentration of sulphide and nitrite in surface water of this station in all seasons. In the case of bottom water samples, the highest value of 7.94 was recorded at Station-6 and the lowest value of 6.03 was recorded at Station-3. The pH value in estuary (7.5 to 8.0) usually indicates the presence of carbonates of calcium and magnesium. These substantiate the dominance of bicarbonate, sodium and chloride towards downstream as compared to upstream. There exist transitions of pH from acidic state in riverine sites to alkaline state in estuarine sites, which can be explained by the utilization and release of dissolved oxygen during the biological processes occurring in the estuary (Nasnolkar et al., 1996). In post Monsoon, pH showed a lower value than the other two seasons, due to river discharges and mixing of surface runoff with tidal activity.

Table 3.3: Station-wise seasonal variations of pH

Station	Surface water – pH			Bottom water -pH		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	6.72	6.33	6.31	6.67	6.31	6.20
2	7.02	6.39	5.77	--	--	--
3	6.70	6.93	6.02	6.93	6.77	6.03
4	7.49	7.62	6.61	--	--	--
5	7.52	7.80	7.04	7.52	7.64	7.07
6	7.42	7.92	7.45	7.42	7.24	7.06
7	8.41	7.25	6.44	--	--	--
8	6.82	7.05	6.33	6.65	6.79	6.52

Table 3.4: Station-wise statistical summary of pH

Station	Surface water – pH					Bottom water -pH				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	6.31	6.72	6.45	0.23	3.6	6.20	6.67	6.39	0.25	3.8
2	5.77	7.02	6.39	0.63	9.8	--	--	--	--	--
3	6.02	6.93	6.55	0.47	7.2	6.03	6.93	6.58	0.48	7.3
4	6.61	7.62	7.24	0.55	7.6	--	--	--	--	--
5	7.04	7.80	7.45	0.38	5.2	7.07	7.64	7.41	0.30	4.1
6	7.42	7.92	7.60	0.28	3.7	7.06	7.42	7.24	0.18	2.5
7	6.44	8.41	7.37	0.99	13.4	--	--	--	--	--
8	6.33	7.05	6.73	0.37	5.5	6.52	6.79	6.65	0.14	2.0

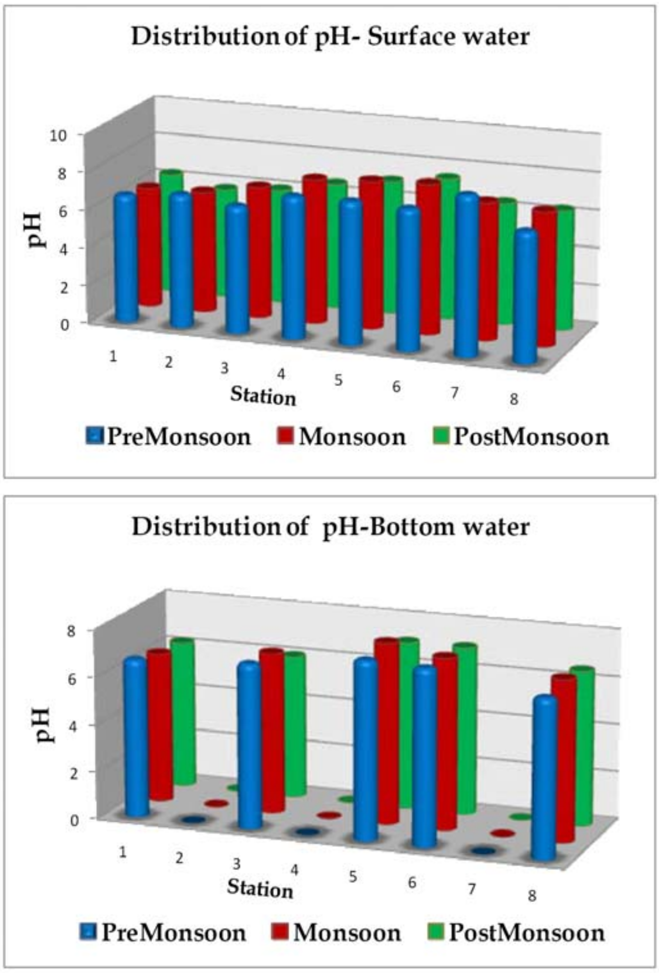


Figure 3.2: Seasonal & Spatial variation of pH in Surface & Bottom water

3.2.4 Salinity

Salinity distribution provides information on the amount of seawater intrusion into the estuary and also the distances up to which the seawater penetrates into the rivers. Absolute (or ideal) salinity is the mass fraction of salts in seawater (Fofonoff, 1985). In practical terms, salinity is expressed as PSU (practical salinity units) which are based on water temperature and conductivity measurements. Salinity used to be expressed in parts per thousand (ppt). For oceanic seawater, ppt and psu are very close.

Salinity of estuaries usually increases away from a freshwater source such as a river, although evaporation sometimes causes the salinity at the head of the estuary to exceed seawater. The vertical salinity structure and the nature of salinity variation along the estuary (i.e. how rapidly salinity varies in the vertical and horizontal) are the defining features of the salinity structure of coastal waterways. Salinity is a dynamic indicator of the nature of the exchange system. The salinity of the water within the estuary tells us how much fresh water has mixed with sea water. It's an important determinant of the mixing regime because of the density variation associated with salinity variation; salinity stratification tends to inhibit vertical mixing in an estuary; which can have important implications for dissolved oxygen concentrations. The circulation with estuaries and coastal regions can derive from or be strongly influenced by the density variation associated with salinity. In effect, dense saline water tends to flow under fresh water. The stratification recorded might play an important role in the settling of detritus and hence in the metal fluxes. Thus salinity plays a dominant role in influencing metal concentrations in water and sediments and its distribution strongly depends on seawater intrusion through the bar-mouth and on the influx of river water. Salinity of estuarine waters has been considered as an index of the estuarine mixing processes and tidal effects.

Most aquatic organisms function optimally within a narrow range of salinity. When salinity changes to above or below this range, an organism may lose the ability to regulate its internal ion concentration. Organism dies due to the direct physiological effects or it becomes more vulnerable to biotic pressures such as predation, competition, disease or parasitism. Consequently, shifting salinity distributions can affect the distributions of macro benthos (Boesch, 1977) as well as those of rooted vegetation and sessile organisms (Alber, 2002). The nature of the longitudinal salinity gradient is an important factor in the successful recruitment of larval and juvenile fish (Bulger et al., 1993). Salinity is an important control on the types of pathogenic organisms and invasive species that can occur in a coastal waterway and on the activity of nitrifying and denitrifying bacteria (Rysgaard et al., 1999). As a general rule, widely-varying salinity regimes tend to select for a low-abundance and low-diversity suite of species, which are adapted to a broad range of ionic concentrations.

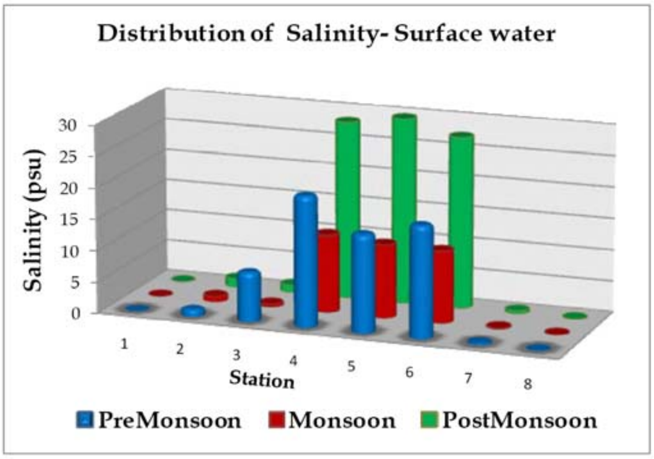
Seasonal and spatial variation of Salinity in surface and bottom water samples for all the stations are given in Table: 3.5. Daily variations of water salinity in the Cochin estuarine system are influenced by the diurnal tidal cycle. Surface salinity values were found to be lower than that of bottom in most of the Stations (Figure: 3.3). Stratification of the backwaters as depicted by a distinct high salinity bottom layer as a result of the influx of seawater during the monsoon season has been previously observed and reported by Ramamirtham & Jayaraman (1963). Station-wise statistical summary of Salinity is given in Table: 3.6. Like temperature, salinity always shows an inverse relation. During post monsoon period due to lower tidal effects and freshwater inflow did not allow salinity of this canal water to rise even after rainy season. This is confirmed by high dilution factor during these post monsoon months. The salinity was highest during pre monsoon season, which gradually declined to almost zero during monsoon. The influx of highly saline water and low discharge of fresh water by rivers caused high salinity during Pre-Monsoon and Post-Monsoon seasons. The estuary was virtually completely inundated with freshwater as a result of the high volumes of river and runoff discharged during the monsoon season. Salinities increased during the relatively dry post-monsoon season to levels approaching those prevailing during the pre-monsoon season. Low salinity during Monsoon is due to the heavy rains that caused large freshwater influx into the system, while the differences in the surface and bottom salinity is due to the out flowing riverine water giving a two layered structure (Dehadrai and Bhargava, 1972). Similar results were reported by Nasnolkar et al., (1996). Riverine Stations showed comparatively lower salinity than others. This indicates the freshwater influx either through Muvattupuzha River or Vembanad Lake. Other Stations 3, 4, 5 and 6 close to the river mouth are much high saline in nature. This can be attributed to the sea water intrusion from Arabian Sea to the river water. During Pre-Monsoon, increased tidal activity brings a vertical mixing; as a result the salinity increases from 0.08 to 18.55 psu in the studied sites. The salinity variation may be caused by semi-diurnal mixed tides as observed by earlier reporters (Srinivas et al., 2003; Martin et al., 2008).

Table 3.5: Station-wise seasonal variations of Salinity

Station	Surface water-Salinity (psu)			Bottom water Salinity (psu)		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	0.06	0.04	0.06	0.17	0.03	0.07
2	1.16	0.87	1.34	--	--	--
3	8.01	0.50	1.19	7.83	0.50	1.84
4	20.90	12.43	28.36	--	--	--
5	15.67	11.79	29.67	16.55	14.19	29.88
6	17.89	11.61	27.47	18.55	16.05	21.92
7	0.34	0.16	0.48	--	--	--
8	0.08	0.05	0.09	2.75	0.07	1.16

Table 3.6: Station-wise statistical summary of Salinity

Station	Surface water-Salinity (psu)					Bottom water Salinity (psu)				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	0.04	0.06	0.05	0.01	22.5	0.03	0.17	0.09	0.07	81.0
2	0.87	1.34	1.12	0.24	21.1	--	--	--	--	--
3	0.50	8.01	3.23	4.15	128.4	0.50	7.83	3.39	3.90	115.1
4	12.43	28.36	20.56	7.97	38.8	--	--	--	--	--
5	11.79	29.67	19.04	9.41	49.4	14.19	29.88	20.21	8.46	41.9
6	11.61	27.47	18.99	7.99	42.1	16.05	21.92	18.84	2.95	15.6
7	0.16	0.48	0.33	0.16	49.1	--	--	--	--	--
8	0.05	0.09	0.07	0.02	28.4	0.07	2.75	1.33	1.35	101.6



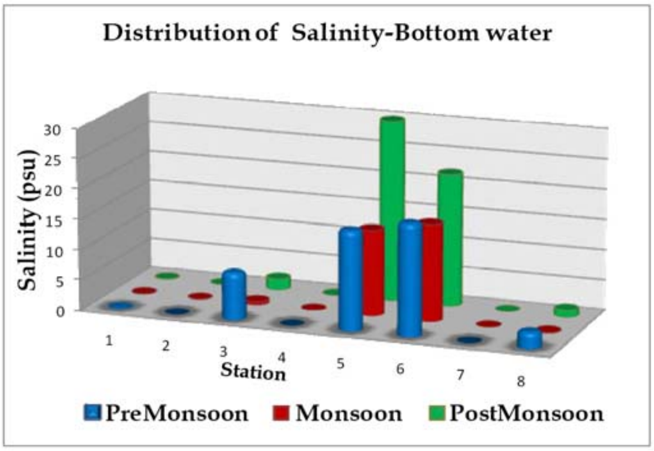


Figure 3.3: Seasonal & Spatial variation of Salinity in Surface & Bottom water

3.2.5 Dissolved Oxygen

Dissolved Oxygen (DO) is one of the most important water quality parameters concerning fish and other aquatic life. It is a measure of the amount of oxygen dissolved in the water that is available for aquatic life and is typically measured in Parts per million (ppm). DO is necessary to sustain aquatic biota and it also provides a self purification capacity to water. Biodegradation of dissolved, suspended and deposited organic materials depends on oxygen, as also on the respiration of aquatic biota. If the river is heavily loaded with organic materials, the amount of oxygen consumed may be more than what can be absorbed through water-air interface so that the oxygen content quickly falls.

DO values infer to the amount of oxygen contained in water, and define the living conditions for oxygen-requiring (aerobic) aquatic organisms. Oxygen has limited solubility in water, usually ranging from 6 to 14 ppm (Connell and Miller, 1984). DO concentrations reflect an equilibrium between oxygen-producing processes (photosynthesis) and oxygen-consuming processes (e.g. aerobic respiration, nitrification, chemical oxidation), and the rates at which DO is added to and removed from the system by atmospheric exchange (aeration and degassing) and hydrodynamic processes (Connell and Miller, 1984). Oxygen solubility varies inversely with salinity, water temperature and atmospheric and hydrostatic pressure. Dissolved oxygen consumption and production are influenced by plant and algal biomass, light intensity and water temperature (because they influence photosynthesis), and are subject to diurnal and seasonal variation. Dissolved oxygen is provided from plants during the photosynthesis process, diffusion of oxygen at the air-water interface, wind or wave action, and cascading or splashing water. Hence DO levels fluctuate with the time of day and the activities in water. DO concentrations naturally vary over a twenty-four hour period due to tidal exchange, and because of the net production of oxygen by plants & algae during the day time. During the night time, plants stop producing oxygen in the photosynthesis process and actually start using up oxygen. Fish and aquatic life activity such as feeding also uses up dissolved oxygen in the water. Another large dissolved oxygen user is bacteria. During the decomposition process, bacteria use oxygen to breakdown organic material. During a plant or algae die off, decomposition rates greatly increase and so does the demand for oxygen. This can drastically drop the dissolved oxygen rates and cause fish die off.

Highly productive systems are expected to have large diurnal DO ranges. Nutrient enrichment stimulates plant and algal growth (and algal blooms) and often results in a mass influx of particulate organic matter to the sediments (Eutrophication). The decomposition of this labile organic matter by aerobic micro organisms leads to a rapid acceleration of oxygen consumption, and potential depletion of oxygen in bottom waters. Stratification can isolate bottom waters from oxygen enriching processes and can give rise to anoxic and hypoxic events. Discharges of wastes rich in organic carbon from various industries and fish processing units can substantially reduce dissolved oxygen concentrations. Most aquatic organisms require oxygen in specified concentration ranges for respiration and efficient metabolism, and DO concentration changes above or below this range can have adverse physiological effects.

Seasonal and spatial variation of DO in surface and bottom water samples for all the stations are given in Table: 3.7. The distribution of dissolved oxygen was found to be greatly related to salinity and has an inverse relation with it. For Surface water, DO values range from 1.92 to 5.77 ppm, 1.3 to 4.84 ppm and 2.9 to 5.10 ppm during Pre-Monsoon, Monsoon and Post-Monsoon respectively. For Bottom water, DO values range from 1.28 to 4.27 ppm, 0.9 to 4.25 ppm and 1.98 to 5.49 ppm during Pre-Monsoon, Monsoon and Post-Monsoon respectively (Figure: 3.4). Station-wise statistical summary of Salinity is given in Table: 3.8 DO values showed a decreasing trend during Monsoon which arises from the consumption of oxygen for the oxidation of organic matter which reaches the estuary by land run off. The sewage from the Kochi city and the neighbouring areas and the heavy load of organic material find their way into Kochi backwaters and are responsible for the decrease in dissolved oxygen. Oxygen levels also can be reduced through over fertilization of water plants by run-off from farm fields containing phosphates and nitrates (the ingredients in fertilizers). Under these conditions, the numbers and size of water plants increase. When these plants die, they become food for bacteria, which in turn multiply and use large amounts of oxygen and depleting all the oxygen. Station 1, which is a riverine site, has the highest DO value. Station 8, which is also riverine, shows comparatively higher DO values than the estuarine sites. The lower DO values in the estuarine sites may be attributed to the low solubility of oxygen in saline waters and supports with the earlier studies conducted by Sankaranarayanan and Panampunnayil (1979). The lower oxygen content of bottom waters compared to surface waters is due to greater salinity, greater degree of respiration and bacterial oxidation of organic matter at the bottom. It is also attributed to the fact that air is easily exchanged with surface water with less penetration to bottom layers. A greater photosynthetic activity on the surface also contributes to greater dissolved oxygen content on surface waters.

Table 3.7: Station-wise seasonal variations of Dissolved Oxygen

Station	Surface water-DO(ppm)			Bottom water-DO(ppm)		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	5.77	4.84	4.37	4.27	4.25	5.49
2	4.33	3.98	3.87	--	--	--
3	2.99	3.99	4.99	2.35	0.90	2.80
4	3.21	1.50	4.44	--	--	--
5	4.70	1.85	5.10	2.99	1.55	4.73
6	1.92	1.50	2.90	2.14	1.35	1.98
7	3.36	2.89	3.56	--	--	--
8	2.99	1.30	3.64	1.28	1.25	3.00

Table 3.8: Station-wise statistical summary of Dissolved Oxygen

Station	Surface water-DO(ppm)					Bottom water-DO(ppm)				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	4.37	5.77	4.99	0.71	14.3	4.25	5.49	4.67	0.71	15.2
2	3.87	4.33	4.06	0.24	5.9	--	--	--	--	--
3	2.99	4.99	3.99	1.00	25.1	0.90	2.80	2.02	0.99	49.2
4	1.50	4.44	3.05	1.48	48.4	--	--	--	--	--
5	1.85	5.10	3.88	1.77	45.6	1.55	4.73	3.09	1.59	51.5
6	1.50	2.90	2.11	0.72	34.1	1.35	2.14	1.82	0.42	22.9
7	2.89	3.56	3.27	0.34	10.5	--	--	--	--	--
8	1.30	3.64	2.64	1.21	45.7	1.25	3.00	1.84	1.00	54.3

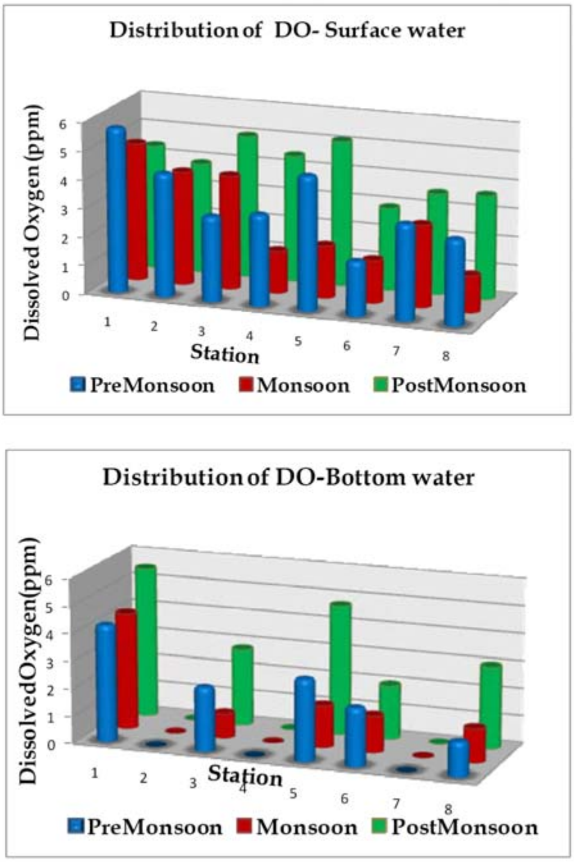


Figure 3.4: Seasonal & Spatial variation of Dissolved Oxygen in Surface & Bottom water

3.2.6 Electrical Conductivity

Electrical conductivity (EC) is a measure of how well a solution conducts electricity and is correlated with salt content. Conductivity is typically reported in units of µS/cm (micro siemens per centimetre). Freshwater fish generally thrive over a wide range of electrical conductivity. Some minimum salt content is desirable to help fish maintain their osmotic balance. The upper range varies with fish species (Nathan and Thomforde, 1980).

Electrical conductivity (EC) of water is a direct function of its total dissolved salts (Harilal et al., 2004). Hence it is an index to represent the total concentration of soluble salts in water (Purandara et al., 2003).

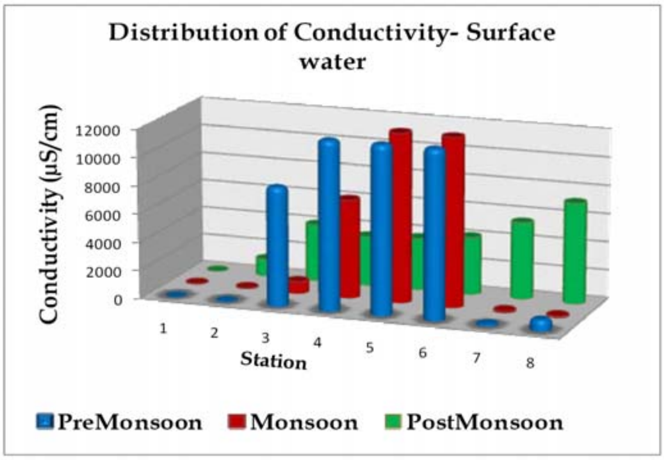
Seasonal and spatial variation of Conductivity in surface and bottom water samples for all the stations are given in Table: 3.9. Varying conductivity values were shown by the above stations (Figure: 3.5). Station-wise statistical summary of Conductivity is given in Table: 3.10. Riverine stations (1, 2, 7 and 8) showed very low values which is in agreement with salinity values. Estuarine stations (3, 4, 5 and 6) which are highly saline showed very high conductivity values and total dissolved solids. In surface and bottom water, highest conductivity value was recorded at station 6 during Monsoon period.

Table 3.9: Station-wise seasonal variations of Conductivity

Station	Surface water-Conductivity(μS/cm)			Bottom water-Conductivity(μS/cm)		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	28	43	14	183	43	12
2	48	70	1212	--	--	--
3	8430	849	4035	8385	884	3025
4	18440	7002	3510	--	--	--
5	16655	18501	3700	16580	22502	3500
6	15127	18550	4100	17300	24500	4300
7	171	115	5465	--	--	--
8	818	110	7170	3425	168	2080

Table 3.10: Station-wise statistical summary of Conductivity

Station	Surface water-Conductivity(μS/cm)					Bottom water-Conductivity(μS/cm)				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	14	43	28	15	51.2	12	183	79	91	114.8
2	48	1212	443	666	150.2	--	--	--	--	--
3	849	8430	4438	3807	85.8	884	8385	4098	3864	94.3
4	3510	18440	9651	7809	80.9	--	--	--	--	--
5	3700	18501	12952	8065	62.3	3500	22502	14194	9723	68.5
6	4100	18550	12592	7551	60.0	4300	24500	15367	10238	66.6
7	115	5465	1917	3073	160.3	--	--	--	--	--
8	110	7170	2699	3888	144.0	168	3425	1891	1637	86.6



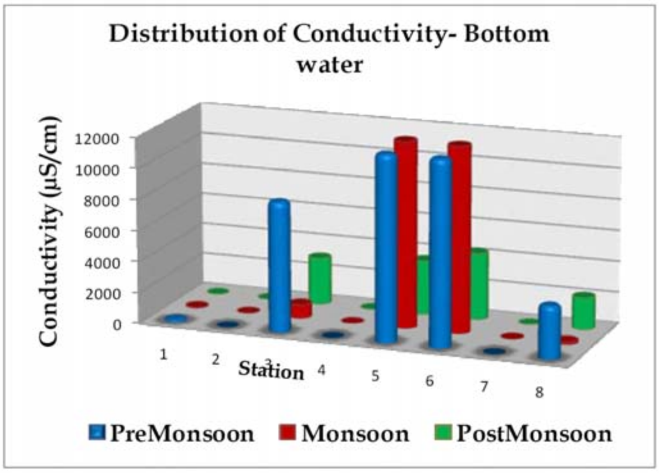


Figure 3.5: Seasonal & Spatial variation of Conductivity in Surface & Bottom water

3.2.7 Phosphate

Phosphorus is present in estuaries in various inorganic and organic forms in dissolved, colloidal or particulate state. Dissolved inorganic phosphate exists in different forms like $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} and their relative concentrations in aquatic system are pH dependent. Phosphorous is necessary to all living organism as it is the constituent of ATP present in the nucleic acid as phosphate groups of nucleotides. The main sources of phosphates are excreta, food wastes and synthetic detergents which contributes a major part and high value of phosphate causes eutrophication. Rivers are the major source of phosphorus input to estuaries. The riverine influx of phosphorus in estuaries may be substantially modified by precipitation or dissolution causing changes in the concentration of phosphorus (Fox et al., 1985). The weathering of insoluble calcium and ferric phosphate rocks and land drainage especially from agricultural run off delivers phosphorus to estuaries (Martin, 1970). The external sources bringing phosphorus to estuaries are from domestic sewage and industrial effluent particularly from fertilizer plants producing phosphatic fertilizers.

Seasonal and spatial variation of Phosphate in surface and bottom water samples for all the stations are given in Table: 3.11. Phosphate concentration in the Surface water ranges from 0.029 to 2.132ppm, 0.072 to 1.528ppm and 0.003 to 3.7 ppm in the Pre-Monsoon, Monsoon and Post-Monsoon period respectively. In bottom water phosphate concentration varies from 0.086 to 2.005ppm, 0.039 to 1.147 ppm and 0.016 to 0.412ppm in the Pre-Monsoon, Monsoon and Post-Monsoon period respectively. (Figure: 3.6. Station-wise statistical summary of Phosphate is given in Table: 3.12. Higher value of phosphate in both surface and bottom water was recorded at station-3 in the Post-Monsoon Season and this may be due to the contamination of water with phosphatic fertiliser during the tenure of sampling. Dilution of estuarine water with rainwater accounts for comparatively lower concentration in the monsoon months and liberation of phosphate from the bottom mud is responsible for the higher concentration during summer months (Arun, 2005). It was observed that generally Phosphates were more enriched at the surface than in the bottom and often these nutrients available in the water column were not fully utilized by the phytoplankton and high concentration were detected in the surface column and similar results was also reported by Gopinathan et al., (2001).

Phosphate distribution in Cochin estuary shows a marked seasonal variation. Several workers have reported high concentration of dissolved phosphate in Cochin estuary during Pre-Monsoon period which exceed the limit of water pollution standards and low values during Monsoon period, (Lakshmanan et aI., 1987; Anirudhan, 1988; Babu, 1999).

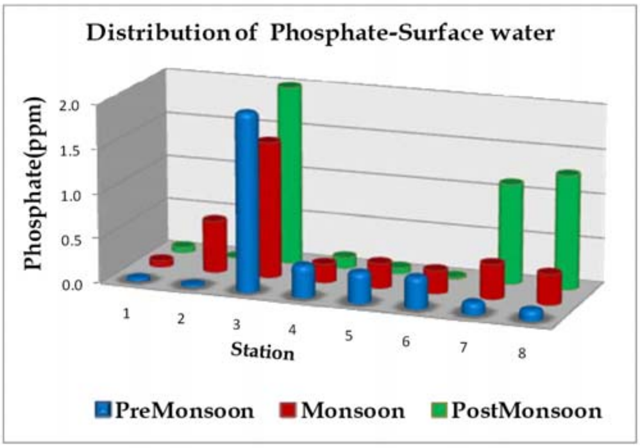
The low values observed during monsoon period was explained as due to the combined effect of dilution of Cochin estuarine water by riverine fresh water containing low phosphate content and the removal by adsorption caused by the influx of silt laden fresh water. Increased riverine discharge during monsoon periods results in low salinity & pH and high dissolved oxygen favouring the removal of phosphorus from the overlying waters by sedimenting particles. Other workers have also reported that the removal of phosphate from the overlying water by suspended sediments is enhanced by low salinity, low pH and high dissolved oxygen (Nagarajaiah and Gupta, 1983; Babu, 1999).

Table 3.11: Station-wise seasonal variations of Phosphate

Station	Surface water-Phosphate(ppm)			Bottom water-Phosphate(ppm)		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	0.041	0.072	0.062	0.086	0.039	0.049
2	0.029	0.582	0.003	--	--	--
3	2.132	1.528	3.700	2.005	1.147	4.412
4	0.364	0.214	0.123	--	--	--
5	0.346	0.283	0.066	0.358	0.194	0.016
6	0.356	0.263	0.021	0.364	0.23	0.222
7	0.136	0.393	1.127	--	--	--
8	0.118	0.346	1.283	0.227	0.424	1.139

Table 3.12: Station-wise statistical summary of Phosphate

Station	Surface water-Phosphate(ppm)					Bottom water-Phosphate(ppm)				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	0.041	0.072	0.058	0.016	27.1	0.039	0.086	0.058	0.025	42.7
2	0.003	0.582	0.205	0.327	159.8	--	--	--	--	--
3	1.528	3.700	2.453	1.121	45.7	1.147	4.412	2.521	1.693	67.1
4	0.123	0.364	0.234	0.122	52.1	--	--	--	--	--
5	0.066	0.346	0.232	0.147	63.4	0.016	0.358	0.189	0.171	90.3
6	0.021	0.356	0.213	0.173	81.1	0.222	0.364	0.272	0.080	29.3
7	0.136	1.127	0.552	0.514	93.2	--	--	--	--	--
8	0.118	1.283	0.582	0.617	106.0	0.227	1.139	0.597	0.480	80.4



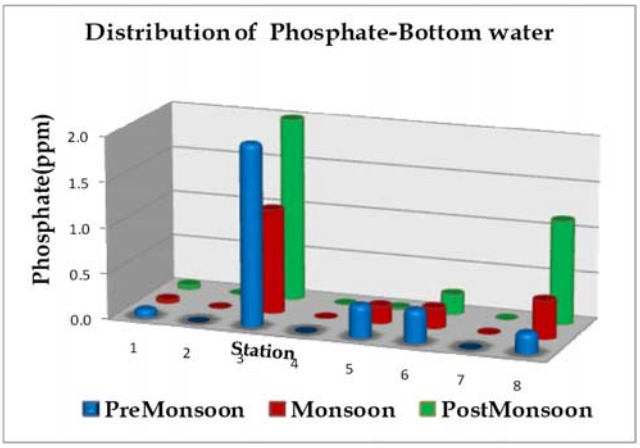


Figure 3.6: Seasonal & Spatial variation of Phosphate in Surface & Bottom water

3.2.7 Nitrite

Nitrogen exists in nine oxidation states (from +5 to -3), all of which have significant roles in the marine environment. The hydrosphere contains about 23 x 10^{12} tons of nitrogen in soluble form which represent only about 0.5% of the total available nitrogen on the globe. Nitrate and nitrite constitute about 65% of the soluble form of nitrogen (Martin, 1970). The concentrations of various forms of nitrogen in an estuary at a given time is controlled by factors like input rates, the inter conversion reactions occurring within the water column, incoming tides, freshwater discharge, denitrification, deposition etc.

Nitrite (nitrogen with oxidation number of +3) is formed during the oxidation of ammonia to nitrate and during reduction of nitrate to ammonia. Nitrites can enter the aquatic system through effluents from industries using nitrites as corrosion inhibitors (Owens, 1978) and certain biologically purified wastes which may also contain large amounts of nitrites. In most estuaries except which are subjected to discharge of sewage and industrial effluents, nitrite concentration seldom exceeds 10% of the total oxidised nitrogen (Head, 1985). Levels of nitrite concentration in estuaries range between 0.5 to 6.0 μg N per litre and is usually very high when compared to sea water in which it is <0.1 μg N per litre. Sarala Devi et al., (1983) reported that nitrite concentration of some estuaries in Kerala ranges between 0.05 to 2.16 μg N per litre.

Seasonal and spatial variation of Nitrite in surface and bottom water samples for all the stations are given in Table: 3.13. Concentration of nitrite in surface water was lower compared to that of phosphate and the values ranged from 0.015 to 0.319 ppm, 0.014 to 0.253 ppm and 0.002 to 0.043 ppm during the Pre-Monsoon, Monsoon and Post-Monsoon period respectively (Figure: 3.7). Station-wise statistical summary of Nitrite is given in Table: 3.14

The lower values of nitrite in any season may be explained by the fact that nitrite is an essential nutrient required for phytoplankton growth and expected photosynthesis to be high in the photic zone due to the utilization of this nutrient for oxidation of organic matter. The CES is facing major threat from eutrophication and luxuriant growth of aquatic weeds, due to the excessive nutrients received either from natural or other artificial sources like sewage disposal sites.

Table 3.13: Station-wise seasonal variations of Nitrite

Station	Surface water-Nitrite (ppm)			Bottom water-Nitrite (ppm)		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	0.083	0.253	0.022	0.060	0.243	0.026
2	0.136	0.028	0.014	--	--	--
3	0.319	0.021	0.036	0.301	0.028	0.020
4	0.091	0.028	0.002	--	--	--
5	0.098	0.204	0.016	0.120	0.047	0.005
6	0.116	0.057	0.009	0.053	0.029	0.014
7	0.015	0.014	0.019	--	--	--
8	0.110	0.103	0.043	0.016	0.001	0.042

Table 3.14: Station-wise statistical summary of Nitrite

Station	Surface water-Nitrite (ppm)					Bottom water-Nitrite (ppm)				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	0.022	0.253	0.119	0.120	100.3	0.026	0.243	0.110	0.117	106.4
2	0.014	0.136	0.059	0.067	112.5	--	--	--	--	--
3	0.021	0.319	0.125	0.168	134.0	0.020	0.301	0.116	0.160	137.5
4	0.002	0.091	0.040	0.046	113.5	--	--	--	--	--
5	0.016	0.204	0.106	0.094	88.9	0.005	0.120	0.057	0.058	101.5
6	0.009	0.116	0.061	0.054	88.3	0.014	0.053	0.032	0.020	61.5
7	0.014	0.019	0.016	0.003	16.5	--	--	--	--	--
8	0.043	0.110	0.085	0.037	43.2	0.001	0.042	0.020	0.021	105.5

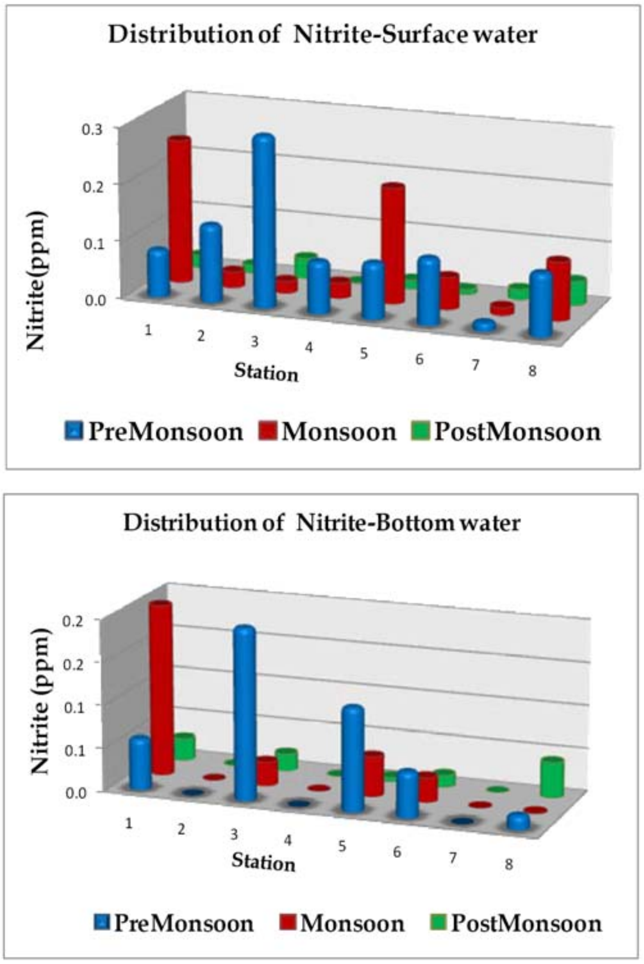


Figure 3.7: Seasonal & Spatial variation of Nitrite in Surface & Bottom water

3.2.8 Sulphate

Sulphate in aquatic system might be highly inflated by river discharges. Many workers reported conservative behaviour for sulphate in various aquatic systems. Gupta and Naik, (1981) suggested that sulphate behaved in a purely conservative manner in Mandovi and Zuari river systems. In the Cochin Estuarine System, Nify, (2009) and Beenamma, (1993) studied the various Sulphur species in the water and sediments and found that sulphate showed deviation from conservative behaviour.

The seasonal distributions of dissolved sulphate in surface and bottom water samples are presented in Figure: 3.8. The concentration of sulphate in Pre monsoon varied from 3.8 to 2469 mgpl in surface and from 0.70 to 60.3 mgpl at the bottom. In monsoon, the values ranged from 7.6 to 590 mgpl at the surface and from 0.18 to 17.8 mgpl at the bottom. In Post monsoon, sulphate concentration varied from 44.1 to 1987 mgpl in surface and from 0.9 to 44 mgpl in bottom. Seasonal and spatial variation of Conductivity in surface and bottom water samples for all the stations are given in Table: 3.15. The concentration of sulphate is found to be higher at stations closer to the bar mouth. Station-wise statistical summary of Sulphate is given in Table: 3.16

The highest sulphate concentration was recorded at station 6 for surface water (2469 mgpl) where the salinity is 17.89 psu. Station 1 which lies in the riverine zone recorded lowest values. Highest values were recorded in the Pre monsoon season and the lowest in the monsoon season. There was no distinct relation observed in sulphate content of surface and bottom and varied spatially and seasonally. The occurrence of sulphate ions is in the form of dissolved sodium sulphate, calcium sulphate and magnesium sulphate and the main source of sulphate ions was probably from industrial effluent, discharged unit and river discharges. Sulphate concentration showed deviation from conservative behaviour in certain stations and this could be due to the change in the pattern of biogeochemical activities of sulphate in the estuary. The distribution pattern of sulphate showed a general decreasing trend towards the upstream. The highest values for sulphate observed in station 5 & 6 are due to the nearby marine conditions. Lowest sulphate concentrations were recorded at station 1 which is the farthest from bar mouth. This station is in the Muvattupuzha River and is characterized by low sea water influx.

Table 3.15: Station-wise seasonal variations of Sulphate

Station	Surface water-Sulphate (ppm)			Bottom water-Sulphate (ppm)		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	3.8	7.6	55.8	0.7	0.2	0.9
2	47.7	7.7	44.1	--	--	--
3	1333	118	852	17.6	4.0	25.6
4	799	479	1115	--	--	--
5	2200	590	1434	60	18	44
6	2469	275	1987	25	14	38
7	257	30	136	--	--	--
8	328	23	305	36	2	24

Table 3.16: Station-wise statistical summary of Sulphate

Station	Surface water-Sulphate (ppm)					Bottom water-Sulphate (ppm)				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	3.78	55.80	22.38	29.00	129.60	0.18	0.90	0.60	0.37	62.45
2	7.74	47.70	33.18	22.11	66.62	--	--	--	--	--
3	118	1333	768	612	80	4	26	16	11	70
4	479	1115	798	318	40	--	--	--	--	--
5	590	2200	1408	805	57	18	60	41	21	53
6	275	2469	1577	1153	73	14	38	26	12	49
7	30	257	141	114	81	--	--	--	--	--

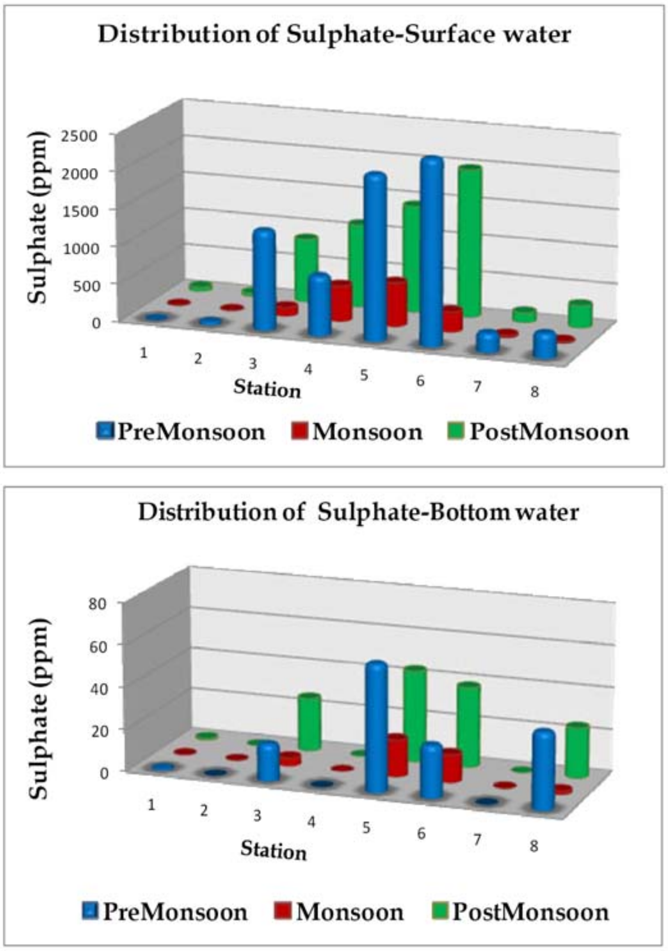


Figure 3.8: Seasonal & Spatial variation of Sulphate in Surface & Bottom water

3.3 Sediment Characteristics

Environmental quality is an important global issue. Wastes from industry and agriculture impair not only the water quality, but also the sediment quality in the receiving river systems. Sediments play a key role in regulation of the chemical environment of estuaries because of their sorptional characteristics. The affinity of the sediments for the chemical species present in the bottom waters leads to a high concentration of the entity in the bed. However this uptake is primarily in the surface layer of the sediment, and penetration deeper in to the bed is slow. Therefore, if re-suspension or erosion occurs, the material will get re-suspended in the water. Sediments, especially clay and silt, are associated with the transport of many pollutants. The impaired sediments also accumulate on the channel bed with time, and later become a major source of pollution through re-suspension. The nature and extent of fluctuation in the composition of sediments can indicate the balance between the erosion and depositional forces of the ecosystem. The supply and sources of these materials and the sites of the deposition mainly depends on the system, river discharge, currents, wave action and tidal regime.

The sediments of CES serve as a receptacle for the effluents of the several industrial and manufacturing units, domestic sewage from Kochi city and from a string of smaller townships. Enormous quantities of waste water discharged daily into this water body are not flushed out, leading to stagnation and build up of pollution with high concentration of ammonia, phosphates etc. Sediment texture (particle-size), Total organic content and metals were determined for each sample in order to characterize the sediment and to help clarify the difference between site metal concentrations. The distribution of metals and its statistical analysis was studied in detail and is given in the chapter-4.

3.3.1 Texture analysis

Texture analyses of the sediments in the CES exhibited varying types of combinations- mixture of sand (Stations 1 and 2), clay/silt (Stations 3, 4 & 5) in all the three seasons (Figure: 3.9 a,b,& c). Colour and Grain size of the sediments varied temporally and spatially (Table: 3.17).

Samples of Station 1 & 2 were almost sandy in nature and no fine grained material was observed in monsoon season of the study period. Monsoonal floods flushed away all accumulated material exposing the gravel underneath.

Station 2, Chitrapuzha, an effluent discharge area and consists of a collection of organic debris which is dark green and black in nature, this could be attributed to the settlement and decay of organic material.

Station 3 was characterized by sediment having light black shade with variation in the grain size. Samples are sandy in nature in all three seasons. But in Post Monsoon clayey nature was observed due to reduced water flow.

Station 4 was mostly clayey in nature but in monsoons an occurrence of silt was noted due to the settling of sediment. The estuarine sediment collected from Stations 5 and 6 are largely affected by dredging activities and leaching due to seasonal changes. They were dark brown to red in colour. Dredging changed the sediment size character totally into fine sandy and silty in the Pre monsoon. While monsoon and post monsoon was characterized by slit and clay with dark brown clay type sediment. In post-monsoon, Station 6 is sandy in nature having little silt and clay.

Station 7 & 8 riverine in character, was sand dominated and indicates high energy zone association with high turbulence in Pre monsoon but had clayey/silty nature in monsoon and Post-monsoon because of the heavy loading of these materials in the rainy season. Such difference in texture type is mainly due to the transport of sediments from one place to another and reversal exchange with the tidal currents (Sankaranarayanan et al., 1986).

Table 3.17: Texture analysis of sediments

Station	Season	Sand %	Silt %	Clay %
1	Pre Monsoon	97.03	0.98	1.99
	Monsoon	97.45	0.39	2.16
	Post Monsoon	97.03	0.80	2.17
2	Pre Monsoon	87.55	3.89	8.56
	Monsoon	92.56	1.89	5.55
	Post Monsoon	89.45	2.78	7.77
3	Pre Monsoon	69.22	8.24	22.54
	Monsoon	71.23	7.56	21.21
	Post Monsoon	87.55	3.89	8.56
4	Pre Monsoon	20.52	5.66	73.82
	Monsoon	42.29	38.72	18.99
	Post Monsoon	22.54	5.01	72.45
5	Pre Monsoon	21.22	73.12	5.66
	Monsoon	34.63	43.39	21.98
	Post Monsoon	35.93	42.52	21.55
6	Pre Monsoon	5.45	78.54	16.01
	Monsoon	19.10	53.59	27.31
	Post Monsoon	94.35	0.08	5.57
7	Pre Monsoon	89.25	5.75	5.00
	Monsoon	84.85	8.76	6.39
	Post Monsoon	53.02	23.04	23.94
8	Pre Monsoon	85.91	6.77	7.32
	Monsoon	15.58	57.39	27.03
	Post Monsoon	38.12	36.38	25.50

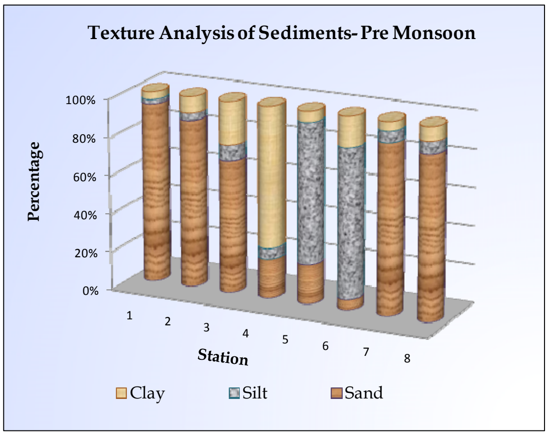


Figure 3.9a: Texture analysis of sediment in Pre monsoon Season

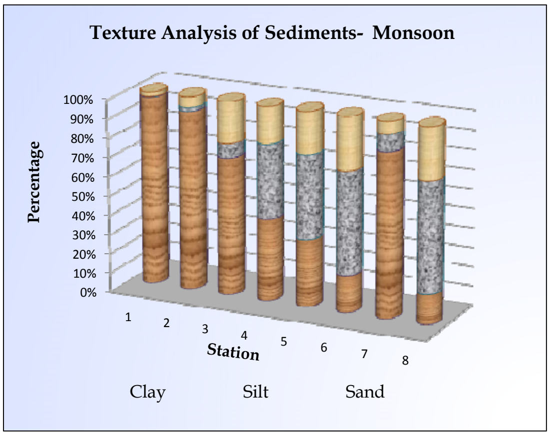


Figure 3.9b: Texture analysis of sediment in Monsoon Season

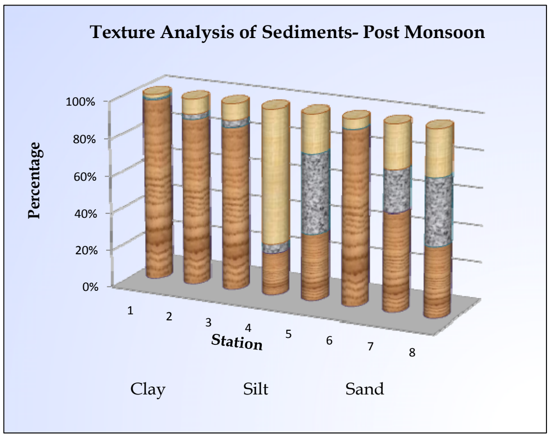


Figure 3.9c: Texture analysis of sediment in Post Monsoon Season

3.3.2 Total Organic Carbon

Total Organic Carbon (TOC) refers to the amount of organic matter conserved within the sediment. The amount of organic matter found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of organic matter are degraded by microbial processes during burial. The spatial statistical summaries of TOC in different seasons are ascribed in the Table: 3.18. Station-wise statistical summary of TOC is given in Table: 3.19

The organic carbon value varies from 0.15 to 2.19 %, 0.09 to 1.8 % and 0.36 to 3.45 % during Pre-monsoon, Monsoon and Post-monsoon respectively (Figure: 3.10). The highest values reported at Stations 4 & 6 during Post monsoon and lowest value at Station 8 during Monsoon could be attributed to the settling of the terrigenous organic matter in the non-monsoonal months derived from land during monsoon to the water zone. However these values fairly agree with the earlier reports from Cochin estuary (Bhosle et al., 1977; Sankaranaryanan and Panampunnayil, 1979). The seasonal variation in the organic carbon content in the sediments may be related to the planktonic activity in the overlying water, the humic material brought from land and also to the oxidation of organic matter by the organisms living in the bottom (Qasim and Sankaranarayanan, 1969; Rajagopal and Reddy, 1984).

Table 3.18: Station wise summary data of TOC

Stations	**Total Organic Carbon (%)**		
	Pre Monsoon	**Monsoon**	**Post Monsoon**
1	0.16	0.73	0.36
2	0.15	0.54	0.45
3	2.91	0.46	1.54
4	1.87	1.8	3.43
5	1.98	1.76	0.42
6	2.61	0.61	3.45
7	0.28	0.54	0.10
8	1.54	0.09	1.16

Table 3.19: Station-wise statistical summary of TOC in Sediments

Station	Min	Max	Mean	SD	CV %
1	0.16	0.73	0.42	0.29	69.4
2	0.15	0.54	0.38	0.20	53.7
3	0.46	2.91	1.64	1.23	75.0
4	1.80	3.43	2.37	0.92	38.9
5	0.42	1.98	1.39	0.84	60.9
6	0.61	3.45	2.22	1.46	65.6
7	0.10	0.54	0.31	0.22	72.1
8	0.09	1.54	0.93	0.75	80.8

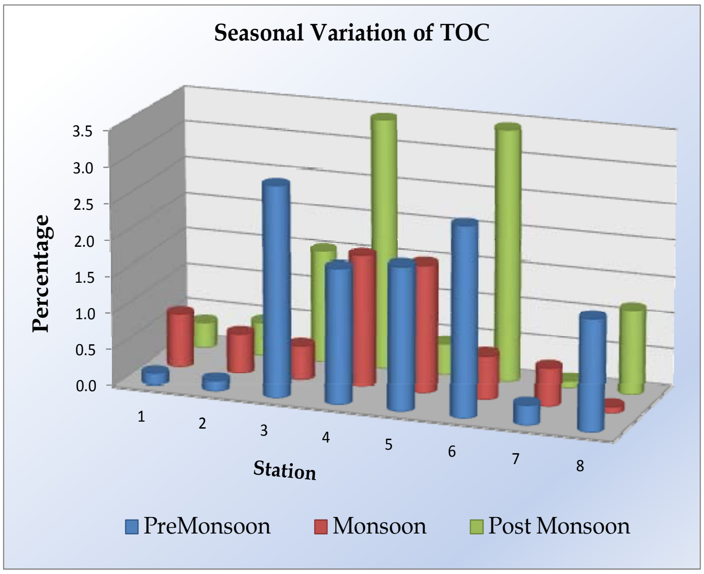


Figure 3.10: Seasonal & Spatial variation of TOC in sediment

Investigations on the organic matter in sediments indicate the extent of biological activity and indirectly the fertility of overlying sea water as well as the pollution status of the waters (Alagarsamy, 1991). Organic carbon is observed to be gradually increasing from upstream towards the downstream. The upstream region of the CES is mainly characterised by low productivity, weak tidal currents, high oxygen, and sandy-silt sediment. However, during Monsoon, high values of organic carbon were observed in the Stations 4 & 5. This can be attributed to the flooding of the estuary with the freshwater from the watershed which carries a lot of land derived organic matter. Though the conditions are not favourable for the accumulation of organic matter in sediments the effect of land drainage and the possible organic supply from tributaries in the upstream region, account for high organic carbon in these sediments. Shirodkar and Kamat, (1988) while working in the Mandovi estuary also observed high values of Organic Carbon in the upstream during the Monsoon.

According to Svedrup et al., (1942), "an abundant supply of organic matter in the column of water, a relatively rapid accumulation of fine grained inorganic matter and low oxygen content of the waters immediately above the bottom sediments would favour high organic matter in the bottom sediments". Emery, (1956) points out that water temperature is an important factor determining the degree of accumulation of organic matter. The relatively high content of organic matter in sediments is attributed to the factors like availability of low oxygen in the environment, and presence of fine clay sediments.

3.3.4 pH

The spatial statistical summaries of sediment pH in different seasons are ascribed in the Table: 3.20. The pH value varies from 6.11-7.08, 6.15-7.69 and 6.25-8.07 during Pre-monsoon, Monsoon and Post-monsoon respectively (Figure: 3.11). The highest values reported at Stations 6 during Post monsoon and lowest value at Station 2 during Pre Monsoon season. Station-wise statistical summary of TOC is given in Table: 3.21

Table 3.20: Station wise summary data of sediment pH

Stations	pH		
	Pre Mon.	Monsoon	Post Mon.
1	6.44	7.22	6.31
2	6.11	7.14	6.25
3	6.17	7.44	7.09
4	6.22	7.05	7.76
5	6.54	7.69	6.71
6	7.08	765	8.07
7	6.87	7.10	7.05
8	7.44	7.98	8.42

Table 3.21: Station-wise statistical summary of Sediment pH

Station	Min	Max	Mean	SD	CV %
1	6.15	6.44	6.30	0.15	2.3
2	6.11	7.14	6.50	0.56	8.6
3	6.17	7.44	6.90	0.66	9.5
4	6.22	7.76	7.01	0.77	11.0
5	6.54	7.69	6.98	0.62	8.9
6	7.08	8.07	7.60	0.50	6.5
7	6.81	7.11	6.99	0.16	2.3
8	7.42	8.42	7.94	0.50	6.3

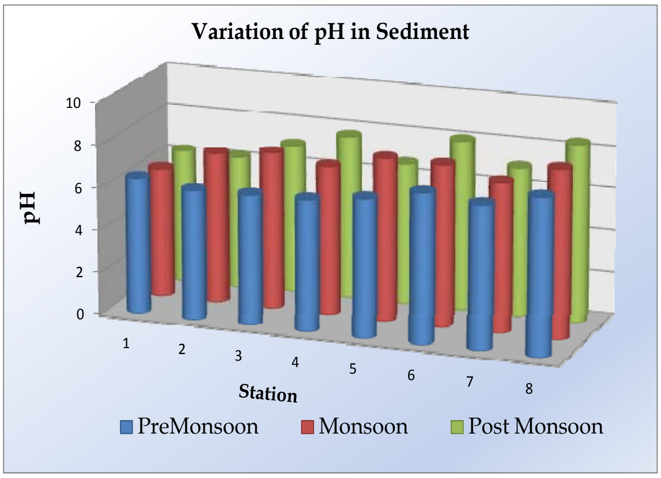


Figure 3.11: Seasonal & Spatial variation of sediment pH

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Chapter 4

HEAVY METAL DISPERSION RECORD IN WATER AND SEDIMENT

Contents

4.1 Introduction

Pollution of the natural environment by heavy metals is a worldwide problem as these metals are indestructible and have toxic effects on living organisms when they exceed a certain concentration limit. This chapter presents the seasonal and spatial variations of heavy metals in dissolved water phase and sediment compartments of the study area. The data is statistically analysed to bring out the significance of hydrographic parameters in the seasonal and spatial variations. The study of the distribution of heavy metals in the dissolved and sediment phases is very important to understand their role in various biogeochemical processes occurring in estuary and tidal rivers. Measurement of the total concentration of metals in soils is useful for determining the vertical and horizontal extent of contamination and for measuring any net change (leaching to ground water, surface runoff, erosion) in sediment metal concentration over time. Multiple regression analysis was carried out to distinguish the role of different parameters in the distribution of trace metals in the sediments in addition to quantification of enrichment. The quantification of enrichment of heavy metals in the sediments is estimated by calculating the Enrichment Factor. In estuarine waters, the different processes controlling metal distribution tend to be superimposed. Inputs can be from rivers, sediments, atmospheric and degradation of materials formed in situ; removal can be by biological uptake, sorption in or on to the sedimentary particles both organic or inorganic and flushing with ocean and coastal waters. Further, knowledge on the distribution and concentration of heavy metals in estuarine waters would help to detect the sources of pollution in the aquatic systems. Many investigations on the trace metals in Cochin estuary were done (Shibu et al., 1990; Babukutty, 1991; Ouseph, 1992).

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, Zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, conversion-coating, anodizing-cleaning, milling, and etching. Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic containing wastes; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium. All of these generators produce a large quantity of wastewaters, residues, and sludge that can be categorised as hazardous wastes requiring extensive waste treatment. As many of these sources of toxic metals are included in the selected stations, the toxic metals such as Cd, Cu, Ni, Pb and Zn were given importance and selected for the present study. Also the remedial approach by adsorption was found to be effective on these metals. Iron were also selected as it’s a metal conservative in nature and used for the assessment of metal contamination by computing the Normalisation factor, Enrichment Factor, Pollution load index and Geoaccumulation index.

Toxicity profile

Heavy metals are generally considered to be those whose density exceeds 5 gm per cubic centimetre. A large number of elements fall into this category, but the ones listed in Table 4.1.a are those of relevance in the selected geographic area of the present work. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. The Maximum Contamination Level, MCL (the highest level of a contaminant that is allowed in drinking water) standards, for those heavy metals, established by USEPA are summarized in Table 4.1.a. (Babel and Kurniawan, 2003)

Table 4.1.a: The MCL standards for the selected heavy metals (Babel and Kurniawan, 2003).

Heavy metal	Toxicities	MCL (µg/L)
Cadmium	Kidney damage, renal disorder, human carcinogen	10
Copper	Liver damage, Wilson disease, Insomnia	250
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	200
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, & nervous system	6
Zinc	Depression, lethargy, neurological signs & increased thirst	800

The metals and organic chemicals selected for analysis are contaminants known to bio-accumulate in sediments. There are no absolute chemical concentrations that correspond to sediment toxicity, but "Effects Range Low" (ERL) and "Effects Range Median" (ERM) values are used as guidelines in assessing sediment contamination. ERM is the median concentration of a contaminant observed to have adverse biological effects in the literature studies examined by Long et al., 1995. ERM and ERL Guidance Values in Sediments (Long et al., 1995) is detailed given in Table 4.1.b A more protective indicator of contaminant concentration is the ERL criteria, which is the 10th percentile concentration of a contaminant represented by studies demonstrating adverse biological effects in the literature. Ecological effects are not likely to occur at contaminant concentrations below the ERL criterion (USEPA, 2004). The qualitative ratings for the sample sites based on ERM and ERL criteria are given below:

Good : No ERM concentrations are exceeded, and less than five ERL concentrations are exceeded.

Fair : Five or more ERL concentrations are exceeded.

Poor : An ERM concentration is exceeded for one or more Contaminants.

Table 4.1.b: ERM and ERL Guidance Values in Sediments
(Long et al., 1995)

Metal	ERL mg/kg	ERM mg/kg
Cadmium	1.2	9.6
Copper	34	270
Nickel	21	52
Lead	47	218
Zinc	150	410

4.2 Distribution of Heavy Metals

Human activities can increase metal concentrations to higher than background levels. Anthropogenic sources of metals include industrial and municipal waste products, urban and agricultural runoff, fine sediments eroded from catchments, atmospheric deposition, Chromated copper arsenate (CCA) treated wood walkways, antifouling paints from ships (mainly tin and copper), metals from pipes in sewage treatment plants and drainage from acid sulphate soils and mine sites. CCA is chemical wood preservative containing chromium, copper and arsenic and is used in pressure treated wood to protect wood from rotting due to insects and microbial agents. Mine drainage, in particular, can significantly increase the concentrations of some metals. Metal contamination tends to be localised to areas situated in close proximity to mine sites, industrial installations and large cities.

Metals are partitioned amongst soluble phases, suspended and bottom sediments and biota in aquatic systems. The major pathways of metal partitioning include adsorption, complexation, precipitation and biological uptake. Adsorption is usually the predominant process because metals have strong affinities for iron and manganese oxy-hydroxides, particulate organic matter, and to lesser extent clay minerals. Consequently, metals tend to accumulate in bottom sediments. The soluble phase represents the principal source of bio-available metals. The dissolved fraction is favoured under conditions of low pH, low particulate loads and high concentrations of dissolved organic matter. Low pH is particularly important because (i) the solubility of metal hydroxides increases as pH decreases (ii) the adsorption capacity of solid surfaces decreases; and (iii) H+ ions compete with metals for coordination sites on organic molecules.

All sediments naturally contain trace levels of metals. The presence of metals in sediments is, therefore not indicative of contamination. The concentration of metals in uncontaminated sediment is primarily related to the geology of the parent material from which the soil was formed. The average concentration of select metals in soils is listed in Table 4.2. Depending on the local geology, the concentration of metals in a soil may exceed the ranges listed in Table 4.2. Use of common ranges or average concentration of trace metals in soils as an indicator of whether a soil is contaminated is not appropriate since the native concentration of metals in a specific soil may fall out of the listed ranges. Only by direct analysis of uncontaminated soils can background the levels of metals. Concentrations of metals in water and sediment were determined by AAS and inductively coupled plasma–Optical Emission spectrometer with 3 replicate analyses and the average value is presented in the table. The repeatability of the test was ensured and the instruments are also validated with the Standard Reference Material with appreciable good recovery.

Table 4.2: Content of various metals in soils (Lindsay, 1979)

Metals Selected	Average for Soil (mg/Kg)	Common Range for Soil (mg/Kg)
Al	71,000	10,000-300,000
Cd	0.06	0.01-0.70
Cr	100	1-1,000
Cu	30	2-100
Fe	38,000	7,000-550,000
Mn	600	20-3,000
Ni	40	5-500
Pb	10	2-200
Zn	50	10-300

There have been a number of studies on the distribution of heavy metals in sediments of Cochin estuary. Some of the earlier investigations carried out in the heavy metal distribution in the sediments of Cochin estuary were Murty and Veerayya, (1981), Venugopal et al., (1982), Ouseph (1987), Nair et al., (1990) and Jayasree and Nair, (1995).

In the present research work eight stations were selected and samplings were conducted bimonthly in the year 2007& 2008. Surface water, bottom water and sediment samples were collected from these stations and sub-sampled as per the standard procedure. The bottom water samples were not available in stations 2, 4 & 7, since the depths of these stations are very low. Also sampling couldn't carried out at station 2 in the second year as the river flow on this point was foiled due to some restoration work under and near the banks the Chitrapuzha river. The metal concentrations in water samples and sediment extracts were determined using two different analysers, namely a Atomic Absorption Spectrometer (AAS), Perkin Elmer-AAnalyst 100 and a Perkin Elmer Optima 2100 DV Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).The use of two different instruments managed by two different laboratory assures high quality control. Moreover, the AAS is most suitable for very dilute solutions and the ICP-OES the most suitable for more concentrated solutions. Blanks and reference material was used. Standard reference material (SRM) for soils used were the SRM 2709 (National Institute of Standards & Technology, 2003), whereas the SRM used for water analysis were the SRM 1643e (National Institute of Standards & Technology, 2004). Quantification of metal ion was based upon calibration curves of standard solutions. These calibrated curves were determined several times during the period of analysis.

4.3 Distribution of Heavy Metals in Aqueous and Sediment Phase

The station-wise overall distribution of selected metals for the study, in the aqueous phase (surface and bottom water) is given in Table 4.3.a & 4.3.b. Station-wise distribution of selected metals in the sediment phase is given in Table 4.4.a. The distribution of metals in surface water, bottom water and sediment is given in Figure: 4.1 to 4.3. The observed order of metal concentration found in surface and bottom water was Fe > Zn > Cu > Pb > Ni > Cd and for sediment the order observed was Fe > Zn > Cu > Ni > Pb > Cd.

Table: 4.3.a Station-wise overall distribution of metals in surface water (in µg/L); ***n=96***

Table 4.3.a: Station-wise overall distribution of metals in surface water (in µg/L); **n=96**

Station	Cd µg/L	Cu µg/L	Fe µg/L	Ni µg/L	Pb µg/L	Zn µg/L
1	0.206	5.21	87.8	1.94	1.90	15.42
2	0.462	4.16	562.4	2.48	2.51	10.35
3	0.449	4.95	143.0	2.04	1.97	31.65
4	0.642	8.95	366.6	2.45	3.03	21.44
5	0.455	7.62	246.5	1.87	2.65	17.20
6	0.515	4.61	244.3	3.42	2.15	12.06
7	0.353	10.59	231.4	1.58	2.62	13.09
8	0.704	4.83	135.6	2.77	2.55	30.70

Table 4.3.b: Station-wise overall distribution of metals in Bottom water (in µg/L); **n=60**

Station	Cd µg/L	Cu µg/L	Fe µg/L	Ni µg/L	Pb µg/L	Zn µg/L
1	0.101	4.95	159.3	2.29	2.16	18.97
2	--	--	--	--	--	--
3	0.227	6.39	355.5	2.40	2.77	24.33
4	--	--	--	--	--	--
5	0.315	11.19	313.4	1.81	4.82	20.13
6	0.375	6.87	293.8	2.03	3.57	20.04
7	--	--	--	--	--	--
8	0.641	4.35	160.1	1.84	4.01	39.88

Table 4.4.a: Station-wise overall distribution of metals in sediment (in mg/kg); n=96

Station	Cd mg/kg	Cu mg/kg	Fe mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
1	0.646	18.05	25570	28.96	6.14	29.32
2	0.570	22.41	34585	13.92	6.36	35.74
3	1.960	26.55	27581	36.32	12.71	101.90
4	2.056	32.04	31879	47.27	10.13	190.11
5	2.034	43.55	25536	38.66	12.86	207.63
6	4.614	56.29	33957	60.70	14.12	260.34
7	2.428	55.21	35825	22.78	13.19	147.77
8	7.043	126.25	43421	39.22	31.41	248.79

Based on the EPA's sediment contamination assessment criteria, the ecological condition of the sediments from the selected areas was good in the period 2007-08; with three stations (Staions-5, 6 & 8) exceeding 4 ERL values and hence these station are in the borderline. Table: 4.4.b provides a comparison of annual mean metal concentrations to the ERM and ERL criteria The Values exceeding the ERL are typed in the cell highlighted with light red colour and with bold red text. None of the values exceeds the ERM criteria.

Table 4.4.b: Comparison of annual mean concentration of metal in sediments to the ERL and ERM values

Station	Cd mg/kg	Cu mg/kg	Fe mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
ERL	1.2	34	--	21	47	150
ERM	9.6	270	--	52	218	410
1	0.646	18.05	25570	**28.96**	6.14	29.32
2	0.570	22.41	34585	13.92	6.36	35.74
3	**1.960**	26.55	27581	**36.32**	12.71	101.9
4	**2.056**	32.04	31879	**47.27**	10.13	**190.11**
5	**2.034**	**43.55**	25536	**38.66**	12.86	**207.63**
6	**4.614**	**56.29**	33957	**60.7**	14.12	**260.34**
7	**2.428**	**55.21**	35825	**22.78**	13.19	147.77
8	**7.043**	**126.25**	43421	**39.22**	31.41	**248.79**

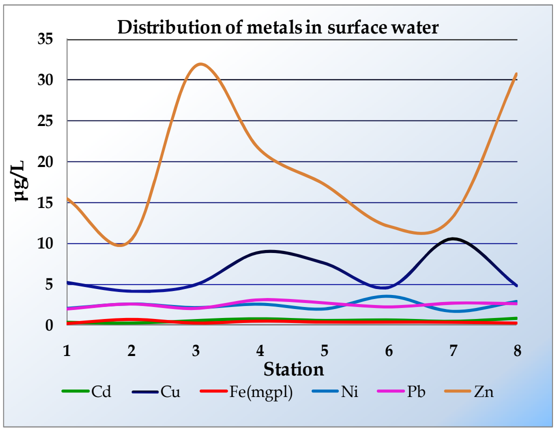


Figure 4.1: Distribution of metals in Surface water

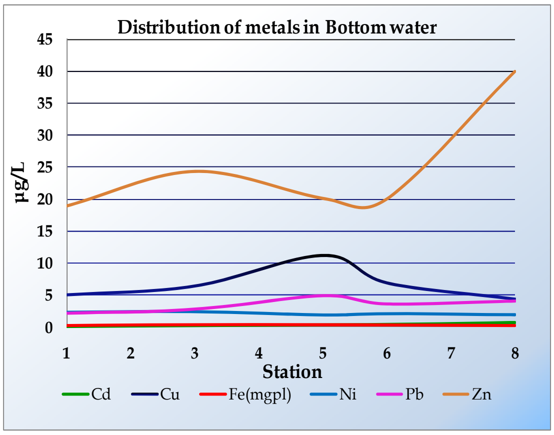


Figure 4.2: Distribution of metals in Bottom water

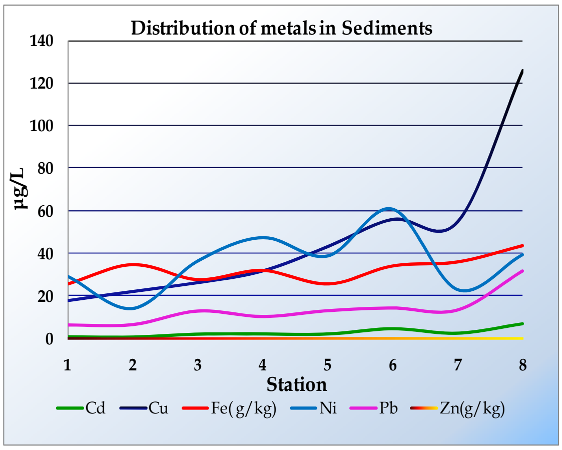


Figure 4.3: Distribution of metals in Sediment

A detailed discussion of the metal records with statistical computation was carried out for each metal. The variation of concentration of each metal with respect to the season and location are discussed as follows.

(i) Cadmium:

General Characteristics

Cadmium is a soft, silver white electropositive metal. Cadmium is element 48 and a member of Group IIB in the periodic table. The density of the metal is 8.6 g/cm^3 (at 20°C) and has a melting point of 320.9°C. The metal is not abundant in the environment and is found together with zinc-containing ores. Like zinc, the metal occurs in the divalent form. The most commonly found cadmium compound is CdS. Cadmium easily forms complexes with ammonia and cyanide, $\mathrm{Cd}\left(\mathrm{NH}_3\right)_6^{4-}$ and $\mathrm{Cd}\left(\mathrm{CN}\right)_4^{2-}$ and can also form organic complexes. Although cadmium oxidises easily, it is very resistant to rusting (Berman, 1980; Friberg et al., 1979). Cadmium crustal abundance is circa 0.2 mg/kg and is closely related to the Zinc-Lead and Zinc-Lead-Copper carrying ores. The percentages of cadmium present in these ores differ significantly, but it is in the range of 0.02-1.4%. The principle mineral for cadmium is hexagonal CdS (Greenockite). In unpolluted areas that have higher than normal cadmium levels, the source will most likely be of the weathering of parent rocks (Fergusson, 1990).

Cadmium is mainly used in the production of alloys (especially low melting point alloys) and is also used in electroplating industries. Its resistance to rust makes it a very good metal to electroplate other metals that are susceptible to rust. Cadmium is much better than zinc (galvanised) in this regard. Cadmium is also used in the production in nickel-cadmium batteries. Cadmium sulphides are commonly used as pigment in the manufacture of paints and plastics, and Cadmium Stearate is used as a stabiliser in plastics. Possible pollution sources are zinc and lead mining practices, phosphate fertiliser, sewage sludge, industrial wastes and atmospheric deposits. Phosphate fertiliser can have high concentrations of cadmium depending on the composition of the parent rock used; with long term fertilisation the concentration of cadmium can be elevated. (Alloway, 1990; Fergusson, 1990).

Cadmium may give rise to both acute and chronic poisoning. The main symptoms are nausea, vomiting, abdominal cramps and headaches. The dose that will give rise to vomiting is in the order of 15 mgpl in water and for protein-containing food somewhat higher concentrations. The chronic effects of cadmium exposure are kidney and liver damage, anaemia, hypertension and negative effects on bone formation. Cadmium is also classified as a carcinogen, teratogen and a mutagen (Berman, 1980).

Results & Discussion

Station wise and seasonal wise distribution of Cd in aqueous and sediment phase is given in Table 4.5 & 4.6. The station wise statistical summary showing the minimum and maximum values, mean, standard deviation and Percentage Coefficient of Variation (%CV) of cadmium in aqueous and sediment phase are furnished in Tables 4.7 & 4.8.

Table 4.5: Station wise seasonal distribution of Cd in Water

Station	Cd(µg/L) in Surface water			Cd(µg/L) in Bottom water		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	0.098	0.078	0.441	0.101	0.099	0.254
2	0.052	0.658	0.675	--	--	--
3	0.247	0.525	0.575	0.227	0.425	0.575
4	0.449	0.632	0.845	--	--	--
5	0.238	0.526	0.600	0.315	0.442	0.450
6	0.285	0.659	0.601	0.375	0.687	0.700
7	0.383	0.325	0.350	--	--	--
8	0.717	0.585	0.809	0.641	0.659	0.725

Table 4.6: Station wise seasonal distribution of Cd in Sediment

Station	Cd (in mg/kg)		
	Pre Monsoon	Monsoon	Post Monsoon
1	0.385	1.028	0.526
2	0.480	0.948	0.282
3	1.681	1.981	2.217
4	1.560	3.464	1.145
5	0.996	2.239	2.867
6	2.896	2.967	7.980
7	1.299	2.124	3.862
8	7.221	9.184	4.723

Table 4.7: Station-wise statistical summary of Cd in Water

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	0.078	0.441	0.206	0.204	99.2	0.099	0.254	0.151	0.089	58.8
2	0.052	0.675	0.462	0.355	76.8	--	--	--	--	--
3	0.247	0.575	0.449	0.177	39.4	0.227	0.575	0.409	0.175	42.7
4	0.449	0.845	0.642	0.198	30.9	--	--	--	--	--
5	0.238	0.600	0.455	0.191	42.1	0.315	0.450	0.402	0.076	18.8
6	0.285	0.659	0.515	0.201	39.0	0.375	0.700	0.587	0.184	31.3
7	0.325	0.383	0.353	0.029	8.2	--	--	--	--	--
8	0.585	0.809	0.704	0.113	16.0	0.641	0.725	0.675	0.044	6.6

Table 4.8: Station-wise statistical summary of Cd in Sediment

Station	Min	Max	Mean	SD	CV %
1	0.385	1.028	0.646	0.34	52.2
2	0.282	0.948	0.570	0.34	59.9
3	1.681	2.217	1.960	0.27	13.7
4	1.145	3.464	2.056	1.24	60.2
5	0.996	2.867	2.034	0.95	46.8
6	2.896	7.980	4.614	2.92	63.2
7	1.299	3.862	2.428	1.31	53.9
8	*4.723*	*9.184*	*7.043*	*2.24*	*31.7*

For surface water, the concentration of Cd varies from 0.052-0.717 µg/L, 0.158-0.659 µg/L and 0.175-0.845 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The maximum concentration was found in station-4 during Post Monsoon. This may be due to the shipping activities of Cochin Port mooring jetty. The concentration of Cd in bottom water ranges from 0.101 - 0.641 µg/L, 0.099-0.687 µg/L and 0.254-0.725 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration was recorded at station 2 & 4 respectively in surface water and the same for bottom waters at station 1 & 8 respectively. The station-wise annual mean concentration varies from 0.128 - 0.704 µg/L for surface water and 0.151 - 0.675 µg/L for Bottom water. In both surface and bottom water, maximum Cd concentration was recorded in the Post Monsoon season. Also surface water showed higher value than that of the bottom water in all stations. In sediment, the concentration ranges from 0.385-7.221 mg/kg, 0.948-9.184 mg/kg, and 0.282- 7.980 mg/kg during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration (0.570 & 7.043 mg/kg) of Cd in sediment was recorded at station 2 & 8 respectively. The seasonal variation of Cd is instanced in Figure: 4.4. The higher value of Cd was recorded in the Post Monsoon season at station-6. The high value may be due to the intrusion of sea water at Bolghatty, the bar mouth of Cochin.

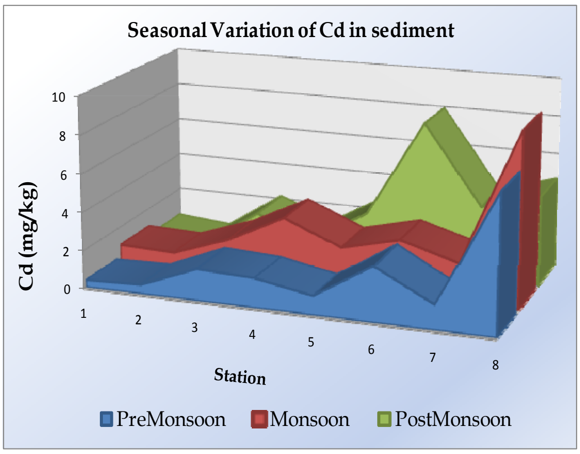


Figure 4.4: Seasonal Variation of Cd in Sediment

Station-wise seasonal mean variation of Cd in Surface, Bottom water and Sediment are illustrated in Figure: 4.5.

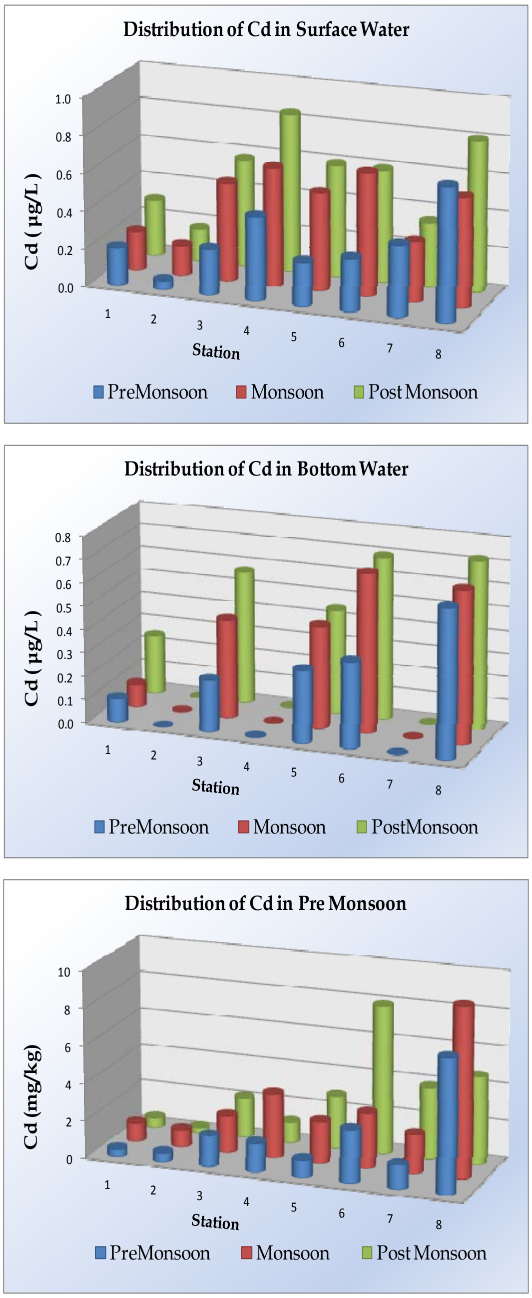


Figure 4.5: Station-wise seasonal mean variation of Cd in Surface water, Bottom water and Sediment

The concentration levels in the estuarine Zone were in agreement with earlier studies of Nair et al., (1990), Shibu et al., (1990) , Babukutty, (1991) and Jospeh, (2002) in the Cochin estuary.

Generally solubility of cadmium increases when the pH of the soil decreases. As with all cationic metals, the Cd chemistry in the soil environment, to a great extent, is controlled by pH. Cadmium forms soluble complexes with inorganic and organic ligands, in particular with Chloride. The formation of these complexes will increase the Cd mobility in soils. On the other hand, under neutral and reducing conditions, the element is relatively immobile. Under acidic conditions Cd solubility increases and very little adsorption of Cd by soil colloids, hydrous oxides, and organic matter takes place. At pH values greater than 6, cadmium is adsorbed by the soil solid phase or is precipitated, and the solution concentrations of cadmium are greatly reduced. The property of being quite soluble makes it much easier to be bio-available for plants and living organisms. The key factor that plays a role in the mobility of cadmium is the cation exchange capacity. This parameter is the most important factor for adsorption of cadmium and others to a much lesser degree. Another factor that has an affect on the adsorption of cadmium is the ionic strength; an increase in ionic strength decreases the amount of cadmium adsorbed (Morillo, 2002).

The concentration of Cd in all the season increases, as the flow of water from upstream advances the Arabian Sea. The trend of Salinity also increases to downstream of the study areas (Figure: 4.6). Except in station 1 & 8, as salinity increases Cd concentration in aqueous phase (both surface & bottom) also increases. The moderately high value in station 1 & 8 may be due to the local input of contaminated wastewater from the pesticides used in agricultural sectors and industrial effluents. As pointed out by Zwolsman et al., (1993), cadmium bound to suspended matter is desorbed (partially) when river water mixes with seawater. Speciation studies suggest that desorption of particulate cadmium during estuarine mixing is due to the formation of chlorocomplexes (Turner et al., 1981; Windom et al., 1991; Dai et al., 1995).

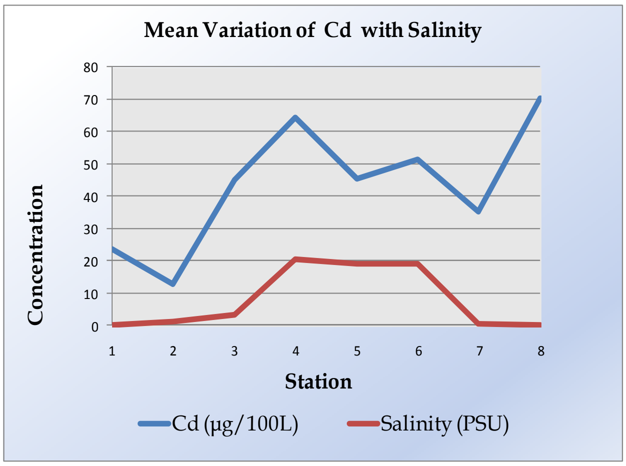


Figure 4.6: Mean variation of Cd concentration with Salinity

(ii) Copper (Cu)

General Characteristics

Copper is one of the most important metals to man. It is element 29 and a member of Group IB of the periodic table. The metal's atomic weight is 63.54 and has a melting point of 1083°C and a density of 8.96 g/cm^3 (at 20°C). Copper in nature usually occurs in +1 or +2 oxidation states. In the +2 form its properties are very similar to that of Zn^{2+}, Mg^{2+} and $Fe^{2+.}$ Copper reacts with halogens, but not with non-oxidising acids. Copper is readily dissolved with nitric and concentrated sulphuric acid. It can also be dissolved in ammonium and sodium cyanide in the presence of oxygen (Alloway, 1990; Cotton and Wilkinson, 1962). Copper is found in nature as mainly sulphides, sulphates and carbonates. The major mineral that contains copper is chalcopyrite ($CuFeS_2$), which constitutes 34% copper. It is widely dispersed in rocks and is concentrated in large Cu ore deposits. By estimation, copper's average concentration in the earth crust is 24-55 mg/kg and is ranked as being the 26th most abundant metal (Adriano, 1986; Bowen, 1979; Cox and Nriagu, 1979).

The metal is a very good conductor of heat and electricity and widely used in the production of electrical wires and alloys. The element is also widely used in agriculture through bactericides, fungicides and algaecides in water purification processes. The major contributors of possible pollution are thus the industrial processes and agriculture (Adriano, 1986). The major impact of copper on plants is the reduction on growth, poorly developed root system and reduced branching of branches. Copper is also part of the essential required by plants and animals elements and is part of all materials analysed. Elevated concentrations of copper have been found in epilepsy sufferers, but there is still no agreement that it causes the condition. Excessive levels of ingested copper can lead to chronic and acute poisoning.

Results & Discussion

Station wise and seasonal wise distribution of Cu in aqueous and sediment phase is given in Table 4.9 & 4.10. The station wise statistical summary showing the minimum and maximum values, mean, standard deviation and Percentage Coefficient of Variation (%CV) of Copper in aqueous and sediment phase are furnished in Tables 4.11 & 4.12.

Table 4.9: Station wise seasonal distribution of Cu in Water

Station	Cu(µg/L) in Surface water			Cu(µg/L) in Bottom water		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	3.01	5.89	6.73	2.64	8.80	3.43
2	2.25	5.66	4.58	--	--	--
3	3.02	5.84	6.00	3.31	8.11	7.75
4	3.06	9.88	13.93	--	--	--
5	3.82	7.86	11.18	2.17	10.64	20.75
6	1.77	6.21	5.85	2.15	9.08	9.38
7	3.20	9.20	19.38	--	--	--
8	3.81	10.69	11.35	2.11	9.35	1.60

Table 4.10: Station wise seasonal distribution of Cu in Sediment

Station	Cu (in mg/kg)		
	Pre Monsoon	Monsoon	Post Monsoon
1	22.15	22.18	9.81
2	17.13	34.59	15.50
3	26.12	31.21	22.30
4	24.98	40.53	30.62
5	37.41	54.36	38.88
6	66.02	33.76	69.08
7	52.64	77.43	35.57
8	130.78	154.46	93.52

Table 4.11: Station-wise statistical summary of Cu in Water

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	3.01	6.73	5.21	1.95	37.4	2.64	8.80	4.95	3.35	67.7
2	2.25	5.66	4.16	1.74	41.9	--	--	--	--	--
3	3.02	6.00	4.95	1.68	33.8	3.31	8.11	6.39	2.68	41.9
4	3.06	13.93	8.95	5.49	61.3	--	--	--	--	--
5	3.82	11.18	7.62	3.68	48.3	2.17	20.75	11.19	9.30	83.2
6	1.77	6.21	4.61	2.47	53.6	2.15	9.38	6.87	4.09	59.6
7	3.20	19.38	10.59	8.18	77.2	--	--	--	--	--
8	3.81	11.35	8.62	4.18	48.5	1.60	9.35	4.35	4.34	99.6

Table 4.12: Station-wise statistical summary of Cu in Sediment

Station	Min	Max	Mean	SD	CV %
1	9.81	22.18	18.05	7.14	39.5
2	15.50	34.59	22.41	10.59	47.2
3	22.30	31.21	26.55	4.47	16.8
4	24.98	40.53	32.04	7.87	24.6
5	37.41	54.36	43.55	9.39	21.6
6	33.76	69.08	56.29	19.57	34.8
7	35.57	77.43	55.21	21.05	38.1
8	93.52	154.46	126.25	30.72	24.3

For surface water, the concentration of Cu varies from 1.77-3.82 µg/L, 5.67-10.69 µg/L and 4.58-19.34 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The maximum concentration was found in station-7 during Post Monsoon. This may be due to the stagnant wastewater discharges and also due to the human activities at this station. The concentration of Cu in bottom water ranges from 2.11-3.31 µg/L, 8.11-10.64 µg/L and 1.60-20.75 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration was recorded at station 2 & 7 respectively in surface water and the same for bottom waters at station 8 & 5 respectively. The station-wise annual mean concentration varies from 4.16 – 10.59 µg/L for surface water and 4.35-11.19 µg/L for Bottom water. The maximum Cu concentration was recorded in the Post Monsoon season in all stations, while the maximum concentration for bottom water was recorded in monsoon season. Also bottom water showed higher Cu concentration than that of the surface water in all stations. In sediment, the Cu concentration ranges from 17.13-130.78 mg/kg, 22.18-154.46 mg/kg, and 9.81-93.52 mg/kg during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration (22.41 & 126.25 mg/kg) of Cu in sediment was recorded at station 1 & 8 respectively. The seasonal variation of Cu is illustrated in Figure: 4.7.

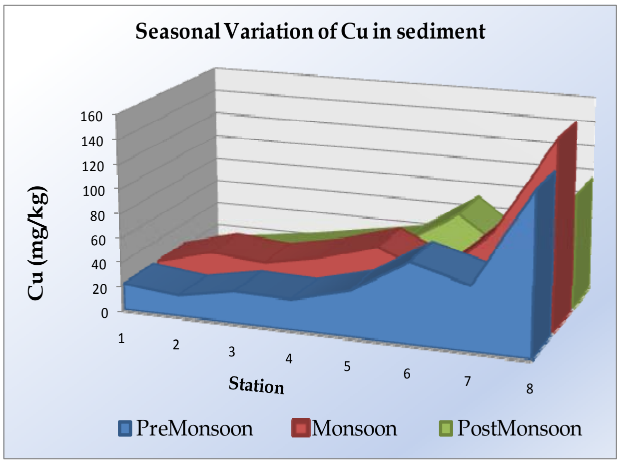


Figure 4.7: Seasonal Variation of Cu in Sediment

Station-wise seasonal mean variation of Cu in Surface, Bottom water and Sediment are illustrated in Figure: 4.8.

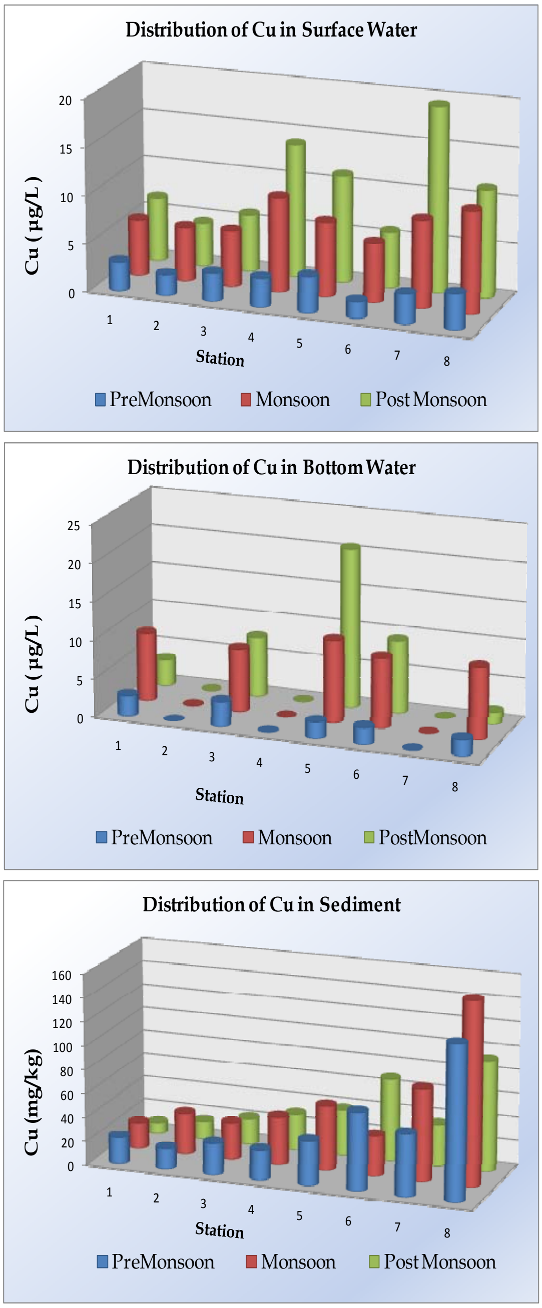


Figure 4.8: Station-wise seasonal mean variation of Cu in Surface, Bottom water and Sediment

Copper in soil is very strongly adsorbed and is one of the most immobile metals found in soil. Factors that influence the adsorption of copper are: Organic matter, manganese and iron oxides and the type of clay present in the soil. The solubility, mobility and bioavailability of copper are very much dependent on the pH of the soil. Copper availability is the highest at lower pH values and is at an optimum at pH values lower than 5. When Cu^{2+} and Cd^{2+} mobility is compared, it is seen that Cd shows a much better mobility than Cu in the soil profile (Locascio, 1978).Copper is retained in sediments through exchange and specific adsorption mechanisms. At concentrations typically found in native soils, Cu precipitates are unstable. This may not be the case in waste-soil systems and precipitation may be an important mechanism of retention (Cavallaro and McBride, 1978). Copper, however, has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase Cu mobility in soils.

(iii) Iron (Fe)

General Characteristics

Iron is element 26 and a member of Group VIII in the Periodic Table. The metal has an atomic weight of 55.85, a density of 7.9 g/cm^3 (at 20°C) and a melting point of 1535°C. The oxidation states Fe occurs in nature are: +II, +III, +IV and +VI. The +II (Fe^{2+} ferrous) and +III (Fe^{3+} ferric) states are the most abundant of the mentioned states. Iron is the fourth most abundant metal in the earth's crust with an average concentration of 50 000 mg/kg. Abundant iron minerals in nature are: Hematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($Fe_2O_3.H_2O$) and siderite ($FeCO_3$). Iron occurs also in clay particles in the oxide form and is very important in the adsorption qualities of the soil (Greenwood and Earnshaw, 1984). Ferrous chloride and ferrous sulphate are water-soluble and iron carbonate, iron oxide, iron hydroxide and sulphides have limited solubility in water. The metal oxidises readily in the presence of oxygen and moisture (rusting) (Alloway, 1990; Davies, 1980).

Iron is used in the production of many alloys. Iron compounds are widely used as catalysts, pigments in paints and electronic products. Iron is mainly used in the production of steel with treatment with coal, phosphorous, silica, and sulphur. Other elements that are used in this process are chromium, nickel, manganese and molybdenum. Iron salts are also used as a flocculent in water purification process. Iron is also the main part of haemoglobin that is primarily used for the transfer of oxygen in the human body. Iron is used in medicine and as a dietary supplement. The main pollution sources of iron are mining (acid mine drainage) and industries converting iron into other products (Davies, 1980).

Iron is an important micronutrient in humans and animals for the production of haemoglobin. A deficiency of this element will cause insufficient oxygen transportation in the body. Iron, however, can also be toxic in all forms and at moderate concentrations fatal poisoning is not uncommon. The amount of iron poisoning increased with the increased use of Fe in medicine. Severe poisoning will occur with amounts of 0.5 g especially in children. Symptoms of poisoning usually occur 1 to 2 hours after ingestion and include vomiting and ulceration of the gastric tract. Frequently the stool and vomit may become bloody from bleeding ulcers. It is also documented that iron is a carcinogen and with localised exposure can cause sarcomas (Berman, 1980; MacKinnon and Bancewicz, 1973).

Results & Discussion:

Station wise and seasonal wise distribution of Fe in aqueous and sediment phase is given in Table 4.13 & 4.14. The station wise statistical summary showing the minimum and maximum values, mean, standard deviation and Percentage Coefficient of Variation (%CV) of Iron in aqueous and sediment phase are furnished in Tables 4.15 & 4.16.

Table 4.13: Station wise seasonal distribution of Fe in Water

Station	Fe (µg/L) in Surface water			Fe (µg/L) in Bottom water		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	145.5	67.0	51.0	136.2	108.0	233.6
2	216.9	852.8	617.5	--	--	--
3	145.0	127.5	156.5	192.0	206.3	668.4
4	153.2	742.5	204.0	--	--	--
5	156.2	390.0	193.3	134.3	319.0	487.0
6	94.7	314.5	323.6	142.6	293.5	445.3
7	152.5	197.0	344.6	--	--	--
8	123.3	183.3	100.2	130.7	165.5	184.2

Table 4.14: Station wise seasonal distribution of Fe in Sediment

Station	Fe (in g/kg)		
	Pre Monsoon	Monsoon	Post Monsoon
1	27.34	25.83	23.54
2	30.08	37.67	36.00
3	26.92	29.48	26.35
4	29.40	39.70	26.53
5	27.46	33.42	15.72
6	30.62	29.67	41.58
7	23.92	24.30	59.26
8	49.75	38.78	41.73

Table 4.15: Station-wise statistical summary of Fe in Water

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	51.0	145.5	87.8	50.6	57.6	108.0	233.6	159.3	65.9	41.4
2	216.9	852.8	562.4	321.5	57.2	--	--	--	--	--
3	127.5	156.5	143.0	14.6	10.2	192.0	668.4	355.5	271.1	76.2
4	153.2	742.5	366.6	326.6	89.1	--	--	--	--	--
5	156.2	390.0	246.5	125.7	51.0	134.3	487.0	313.4	176.4	56.3
6	94.7	323.6	244.3	129.6	53.1	142.6	445.3	293.8	151.3	51.5
7	152.5	344.6	231.4	100.5	43.4	--	--	--	--	--
8	100.2	183.3	135.6	42.9	31.6	130.7	184.2	160.1	27.2	17.0

Table 4.16: Station-wise statistical summary of Fe in Sediment

Station	Min	Max	Mean	SD	CV %
1	23.54	27.34	25.57	1.91	7.5
2	30.08	37.67	34.59	3.99	11.5
3	26.35	29.48	27.58	1.67	6.0
4	26.53	39.70	31.88	6.92	21.7
5	15.72	33.42	25.54	9.01	35.3
6	29.67	41.58	33.96	6.62	19.5
7	23.92	59.26	35.82	20.29	56.6
8	*38.78*	*49.75*	*43.42*	*5.68*	*13.1*

For surface water, the concentration of Fe varies from 94.7-216.9 µg/L, 67-852.8 µg/L and 51-617.5 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The concentration of Fe in bottom water ranges from 130.7-192 µg/L, 108-319 µg/L and 184.2-668.4 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration was recorded at station 1 & 2 respectively in surface water and the same for bottom waters at station 1 & 3 respectively. The station-wise annual mean concentration varies from 87.8-562.4µg/L for surface water and 159.3-355.5 µg/L for Bottom water. According to the study conducted in Chitrapuzha River by P.V Jospeh, (2002) concentration of iron varied 3.33- 404.58 µg/L in the surface and from 2.46 - 449.36 µg/L in the bottom waters. For Surface water, the maximum Fe concentration was recorded in the Monsoon season in all stations, while the maximum concentration for bottom water was recorded in Post monsoon season. Also bottom water showed higher Fe concentration than that of the surface water in all stations. In sediment, the Fe concentration ranges from 23.92 -49.75g/kg, 24.30-39.70 g/kg, and 15.73-59.26 g/kg during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration (25.54 & 43.42 g/kg) of Fe in sediment was recorded at station 5 & 7 respectively. The seasonal variation of Fe is illustrated in Figure: 4.9. An increased concentration of Fe in station-8 was observed in all season due to the effluent discharge and land runoff from the various industrial units. In Station-7, high concentration of Fe in post monsoon season might be due to the anthropogenic activities and also due to settling of waste/sludge after the monsoon season, in the almost stagnant Periyar side stream.

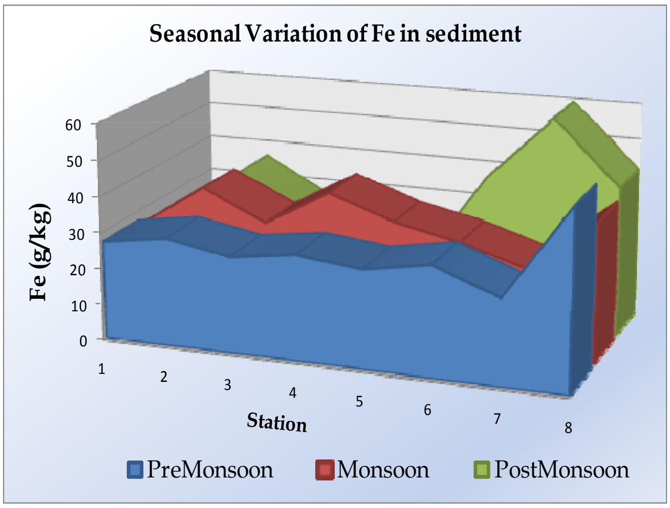


Figure 4.9: Seasonal Variation of Fe in Sediment

Station-wise seasonal mean variation of Fe in Surface, Bottom water and Sediment are illustrated in Figure: 4.10.

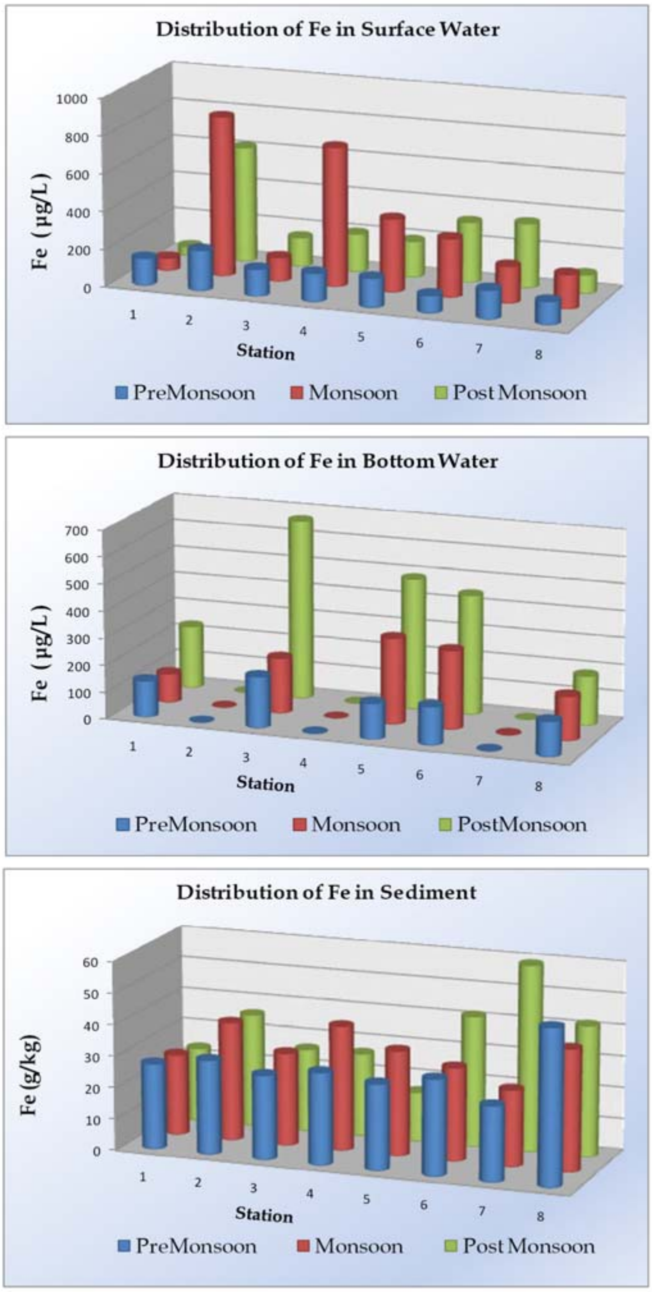


Figure 4.10: Station-wise seasonal mean variation of Fein Surface, Bottom water and Sediment

The factors that play a role in the mobility of iron are Redox potential, pH and chelation. Inorganic iron compounds can be hydrolysed to form Fe^{3+}, $FeOH^{2+}$ $Fe(OH)_2^+$, $Fe(OH)_{3(aq)}$ and $Fe(OH)_4^-$. The Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^+$ forms are predominantly found in soil or solutions of low pH (acidic).Whereas the $Fe(OH)_{3(aq)}$ and $Fe(OH)_4^-$ will be found in pH conditions higher than 7. Bacterial conversion of Fe can produce soluble forms of iron in water (Davies, 1980; Hesse, 1962).The following equation indicates that with the oxidation of Fe(II) to Fe(III) contributes to the lowering of pH:

$$Fe^{2+} + 3H_2O \rightarrow Fe\ (OH)_3 + 3H^+ + e^-$$

(iv) Nickel (Ni)

General characteristics

Nickel is element 28 and in part of Group VIII in the periodic table. It has an atomic weight of 58.71, a density of 8.9 g/cm^3 (at 20°C) and a melting point of 1453°C. Nickel is a hard, silver-white, malleable metal with good electrical conductor characteristics. The metal generally occurs in the oxidation states of 0, +I, +II, +III and +IV. The most common and important oxidation states of nickel found in are the 0 and II states and these are also the most stable nickel compounds. Ni is soluble in dilute nitric acid and to a small extent in sulphuric and hydrochloric acids. However, it is not soluble in NH_4OH. (Adriano, 1986; Friberg et al., 1979).The nickel concentration in the earth's crust is on average 80 mg/kg. The nickel content varies considerably in the different types of rocks. The most important compounds of Ni are: Nickel sulphide (NiS) and Nickel Arsenate. In nature the mineral containing nickel is laterite, it is a nickel oxide that is generally mined in open-pit mines (Adriano, 1986).

Nickel is used in the manufacture processes of alloys (mainly stainless steel), electroplating, Ni-Cd batteries and electronic components. Nickel is highly corrosion resistant and this gives the alloys produced from nickel the same properties. These alloys are widely used in a number of fields. Nickel is also used in lesser amounts in jewellery, coins, tools and medical equipment. The main sources of possible nickel pollutions are industries refining nickel into alloys, sewage sludge and phosphate fertilisers (Ni content in phosphate rocks) (Alloway, 1990; Adriano, 1986).

In studies performed to investigate the toxicity of the metal, it was found that it is toxic to animals, humans and plants. Exposure to nickel has many localised effects and the main studied compound is nickel carbonyl. The main localised effect is dermatitis which can also be caused through ingestion of nickel. Other characteristics of nickel are that it has carcinogenic and teratogenic properties and contact with it must rather be avoided. (Friberg et al., 1979).

Results & Discussion

Station wise and seasonal wise distribution of Ni in aqueous and sediment phase is given in Table 4.17 & 4.18. The station wise statistical summary showing the minimum and maximum values, mean, standard deviation and Percentage Coefficient of Variation (%CV) of Nickel in aqueous and sediment phase are furnished in Tables 4.19 & 4.20.

Table 4.17: Station wise seasonal distribution of Ni in Water

Station	Ni (µg/L) in Surface water			Ni (µg/L) in Bottom water		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	1.49	3.91	0.43	1.63	3.25	1.98
2	1.60	3.69	2.15	--	--	--
3	2.06	2.53	1.53	2.10	2.48	2.63
4	1.49	3.48	2.40	--	--	--
5	1.66	3.19	0.78	1.81	2.69	0.93
6	1.27	2.85	6.13	1.03	4.03	1.05
7	0.75	2.70	1.30	--	--	--
8	2.06	3.41	2.84	0.99	4.01	0.53

Table 4.18: Station wise seasonal distribution of Ni in Sediment

Station	Ni (in mg/kg)		
	Pre Monsoon	Monsoon	Post Monsoon
1	46.08	32.72	8.07
2	12.10	28.64	1.01
3	40.80	36.14	32.04
4	41.78	56.30	43.75
5	39.15	50.19	26.65
6	35.51	43.56	103.03
7	30.83	22.97	14.53
8	58.19	53.78	5.69

Table 4.19: Station-wise statistical summary of Ni in Water

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	0.43	3.91	1.94	1.79	92.0	1.63	3.25	2.29	0.85	37.3
2	1.60	3.69	2.48	1.08	43.7	--	--	--	--	--
3	1.53	2.53	2.04	0.50	24.6	2.10	2.63	2.40	0.27	11.3
4	1.49	3.48	2.45	1.00	40.6	--	--	--	--	--
5	0.78	3.19	1.87	1.22	65.2	0.93	2.69	1.81	0.88	48.8
6	1.27	6.13	3.42	2.47	72.4	1.03	4.03	2.03	1.72	84.8
7	0.75	2.70	1.58	1.00	63.3	--	--	--	--	--
8	2.06	3.41	2.77	0.68	24.5	0.53	4.01	1.84	1.89	102.7

Table 4.20: Station-wise statistical summary of Ni in Sediment

Station	Min	Max	Mean	SD	CV %
1	8.07	46.08	28.96	19.28	66.6
2	1.01	28.64	13.92	13.90	99.9
3	32.04	40.80	36.32	4.38	12.1
4	41.78	56.30	47.27	7.88	16.7
5	26.65	50.19	38.66	11.78	30.5
6	35.51	103.03	60.70	36.88	60.8
7	14.53	30.83	22.78	8.15	35.8
8	5.69	58.19	39.22	29.12	74.3

For surface water, the concentration of Ni varies from 0.75-2.06µg/L, 2.53-3.91 µg/L and 0.43-6.13 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The maximum concentration was found in station-6 during Post Monsoon. This may be due to the intrusion of sea water to Cochin bar mouth. The concentration of Ni in bottom water ranges from 0.99-2.10 µg/L, 2.48-4.03µg/L and 0.53-2.63 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration was recorded at station 7 & 6 respectively in surface water and the same for bottom waters at station 5 & 3 respectively. The station-wise annual mean concentration varies from 1.58-3.42 µg/L for surface water and 1.81-2.40 µg/L for Bottom water. In both surface (except in station-6) and bottom water, maximum Ni concentration was recorded in the Monsoon season. Also surface water showed higher value than that of the bottom water in the up streams, but towards the downstream as salinity increases the Ni concentration in bottom water showed a lesser value than that of the surface water. In sediment, the concentration ranges from 12.10-58.19 mg/kg, 22.97-56.30 mg/kg, and 1.01-103.03 mg/kg during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration

(13.92-60.70 mg/kg) of Ni in sediment was recorded at station 2 & 6 respectively. The seasonal variation of Ni is instanced in Figure: 4.11. In all season and stations (except in station-6), Monsoon season registers higher concentration of Ni. But in station-6 the higher value was observed in Post monsoon season. Nickel does not form insoluble precipitates in unpolluted soils and retention for Ni is, therefore, exclusively through adsorption mechanisms. Nickel will adsorb to clays, iron and manganese oxides, and organic matter and is thus removed from the soil solution. The formation of complexes of Ni with both inorganic and organic ligands will increase Ni mobility in soils. In retention studies, it was shown that the retention of Ni increases with the increase of pH (above 7). The mobility of Ni increases when the pH decreases and the pH also contribute to the precipitation of the nickel compounds formed under the different pH conditions (Adriano, 1986; Harter, 1983).

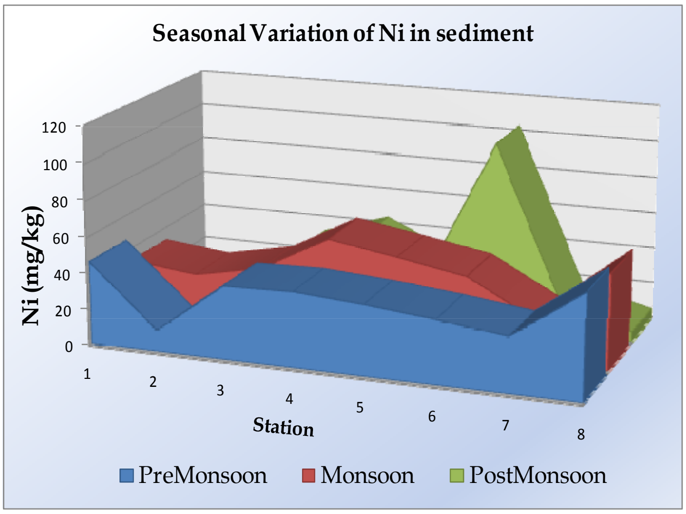
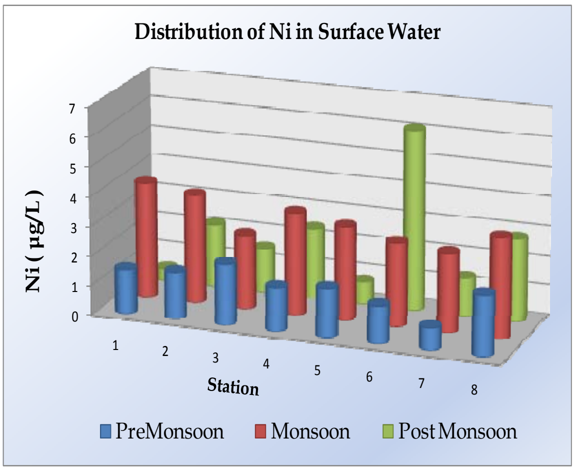
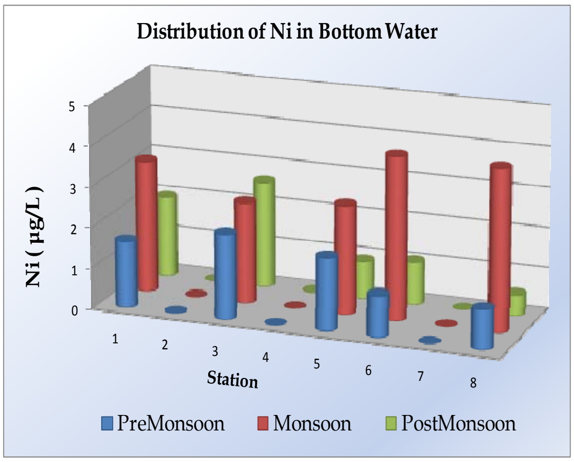


Figure 4.11: Seasonal Variation of Ni in Sediment

Station-wise seasonal mean variation of Ni in Surface, Bottom water and Sediment are illustrated in Figure 4.12.





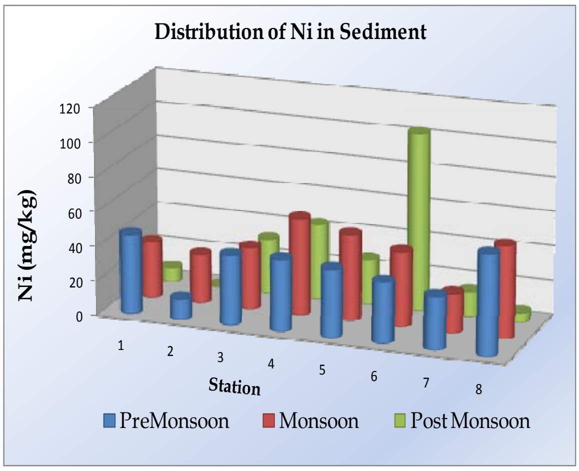


Figure 4.12: Station-wise seasonal mean variation of Ni in Surface water, Bottom water and Sediment

(v) Lead (Pb)

General Characteristics

Lead is element 82 and is a member of Group IV-A in the periodic table. The metal has an atomic weight of 207.19, a density of 11.35 g/cm^3 (at 20°C) and a melting point of 327.5°C. Pb is a soft malleable metal, and has poor electrical conductivity. Lead is widely found in the environment and is the most abundant heavy metal with atomic weight of more than 60. The average concentration of lead in the earth's crust is between 13 to 16 mg/kg. There are over 200 minerals that contain Pb, but the most economically important is anglesite ($PbSO_4$). Lead is present in rocks at varying amounts and it can displace elements from the rock matrix such as calcium, sodium, strontium, barium and potassium through the closely related properties. (Swaine, 1978; Nriagu, 1972). Pb generally occurs in the +II or +IV oxidation states and is slowly soluble in acids. The chloride and bromide salts are not soluble in water and the carbonate ($PbCO_3$) and hydroxide ($Pb(OH)_2$) salts are almost insoluble. In contrast, the nitrate ($PbNO_3$) and acetate forms are very soluble in cold water (Adriano, 1986; Friberg et al., 1979).

The main users of lead are in the construction and automotive industries. Other uses of lead are as a shielding agent for radioactive material, batteries, soldering products and fuel additive. Lead arsenate used to be widely used in pesticides, but it has been banned for this use. Possible pollution contributions will be for industrial wastes and also in diffuse pollution from the combustion of leaded furnace fuels used in the industries (Adriano, 1986; Friberg et al., 1979).

The most common form of lead poisoning is gastrointestinal colic. It can be the cause of long or short-term exposure to lead. The symptoms are usually: Discolouration of the skin, slow pulse and increase in blood pressure. Under chronic effects it is common to find anaemia with liver, kidney, nervous system, endocrine organ and cardiovascular damage. The carcinogenic, teratogenic and genetic effects are also widely published in the literature (Berman, 1980; Friberg et al., 1979).

Results & Discussion

Station wise and seasonal wise distribution of Pb in aqueous and sediment phase is given in Table 4.21 & 4.22. The station wise statistical summary showing the minimum and maximum values, mean, standard deviation and Percentage Coefficient of Variation (%CV) of Lead in aqueous and sediment phase are furnished in Tables 4.23 & 4.24.

Table 4.21: Station wise seasonal distribution of Pb in Water

Station	Pb (µg/L) in Surface water			Pb (µg/L) in Bottom water		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	2.19	3.25	0.25	2.02	4.12	0.35
2	2.44	2.98	2.11	--	--	--
3	2.67	1.25	1.98	2.10	2.69	3.51
4	3.35	3.25	2.49	--	--	--
5	3.16	0.55	4.25	3.97	5.75	4.75
6	2.75	0.73	2.98	2.36	5.58	2.78
7	2.52	1.68	3.65	--	--	--
8	2.76	1.79	3.11	2.37	6.32	3.33

Table 4.22: Station wise seasonal distribution of Pb in Sediment

Station	Pb (in mg/kg)		
	Pre Monsoon	Monsoon	Post Monsoon
1	5.41	6.70	6.32
2	6.04	4.18	8.85
3	10.96	10.64	16.54
4	7.05	13.08	10.26
5	7.50	12.82	18.25
6	14.11	11.05	17.21
7	5.35	14.51	19.73
8	36.80	20.82	36.61

Table 4.23: Station-wise statistical summary of Pb in Water

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	0.25	3.25	1.90	1.52	80.2	0.35	4.12	2.16	1.89	87.3
2	2.11	2.98	2.51	0.44	17.5	--	--	--	--	--
3	1.25	2.67	1.97	0.71	36.1	2.10	3.51	2.77	0.71	25.6
4	2.49	3.35	3.03	0.47	15.5	--	--	--	--	--
5	0.55	4.25	2.65	1.90	71.7	3.97	5.75	4.82	0.89	18.6
6	0.73	2.98	2.15	1.24	57.5	2.36	5.58	3.57	1.75	49.0
7	1.68	3.65	2.62	0.99	37.7	--	--	--	--	--
8	1.79	3.11	2.55	0.68	26.8	2.37	6.32	4.01	2.06	51.5

Table 4.24: Station-wise statistical summary of Pb in Sediment

Station	Min	Max	Mean	SD	CV %
1	5.41	6.70	6.14	0.66	10.8
2	4.18	8.85	6.36	2.35	37.0
3	10.64	16.54	12.71	3.32	26.1
4	7.05	13.08	10.13	3.02	29.8
5	7.50	18.25	12.86	5.38	41.8
6	11.05	17.21	14.12	3.08	21.8
7	5.35	19.73	13.19	7.28	55.1
8	20.82	36.80	31.41	9.17	29.2

For surface water, the concentration of Pb varies from 2.19-3.35 µg/L, 0.55-3.25 µg/L and 0.25-4.25 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The maximum concentration was found in station-8 during Monsoon. This may be due to contamination from the land runoff and from the effluent discharges from the industries on the bank of Periyar. The concentration of Pb in bottom water ranges from 2.02-3.97 µg/L, 2.69-6.32 µg/L and 0.35-4.75 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration was recorded at station 1 & 4 respectively in surface water and the same for bottom waters at station 1 & 5 respectively. The station-wise annual mean concentration varies from 1.90-3.03 µg/L for surface water and 2.16-482 µg/L for Bottom water. Bottom water showed slight higher value than that of the surface water in almost all station and in all seasons. In sediment, the concentration ranges from 5.35-36.80 mg/kg, 4.18-20.82 mg/kg, and 6.32-36.61 mg/kg during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration (6.36 & 31.41 mg/kg) of Pb in sediment was recorded at station 2 & 8 respectively. The seasonal variation of Pb is instanced in Figure: 4.13. In Pre monsoon and Post Monsoon season, Pb in the sediment sample was found to be higher, where as in Monsoon period comparatively less value was recorded at station-8. The concentration of Pb in bottom water recorded a higher value in Monsoon than that in Pre monsoon and Monsoon season. This indicates the leaching out of Pb from the sediment sample and hence lesser value observed for sediments in Monsoon.

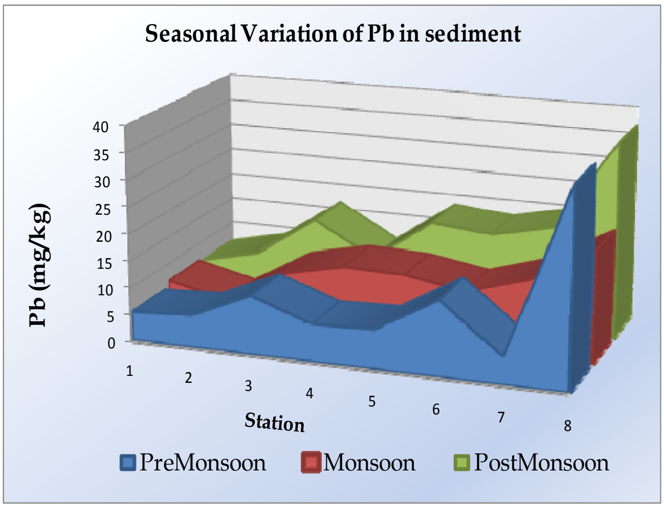


Figure 4.13: Seasonal Variation of Pb in Sediment

Station-wise seasonal mean variation of Pb in Surface, Bottom water and Sediment are illustrated in Figure: 4.14.

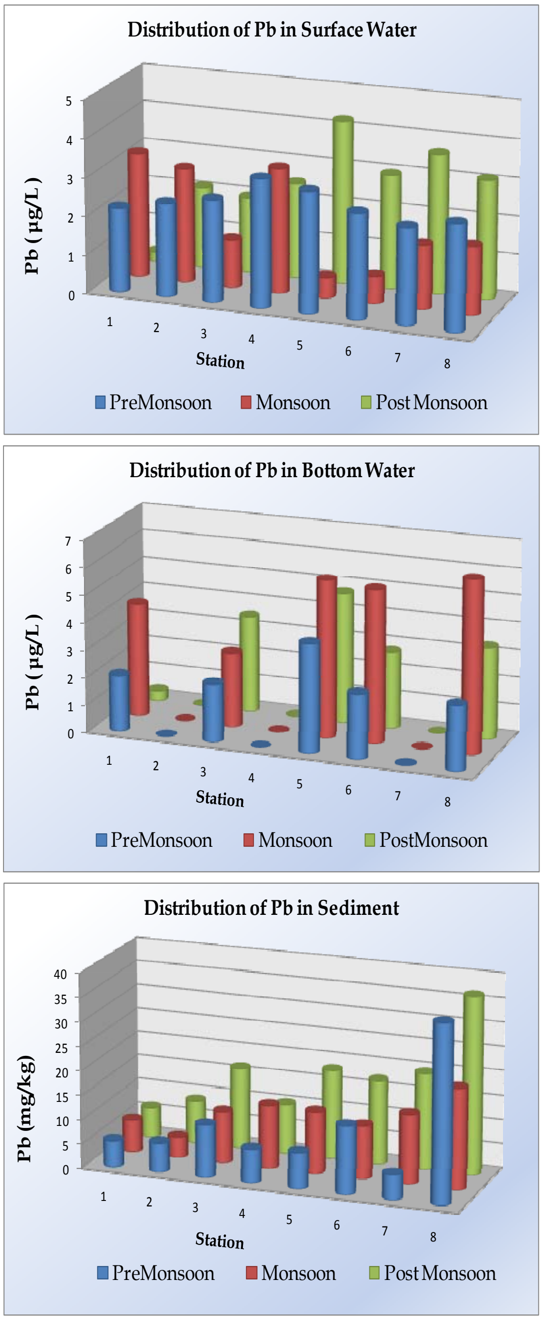


Figure 4.14: Station-wise seasonal mean variation of Pb in Surface water, Bottom water and Sediment

Under pH conditions of between 5-8.5 lead is present mainly in the carbonate form, between pH 8.5-12.5 it was found that it is in the hydroxide form. With pH values above 12.5 hydroxide complexes are formed which are very soluble in water. The pH also influences the chemical form and stability of Pb. The main factor in adsorption is the clay content in the soil. Soluble lead in the soil reacts with clays, phosphates, sulphates, carbonates, hydroxides, and organic matter such that Pb solubility is greatly reduced. Lead has a strong affinity for organic ligands and the formation of such complexes may greatly increase the mobility of Pb in soil. (Kotuby-Amacher and Gambrell, 1988).

(v) Zinc (Zn)

General Characteristics

Zinc is element 30 and a member of Group IIB in the periodic table. Zn has an atomic weight of 65.37, a density of 7.133 g/cm^3 (at 20°C) and a melting point of 419.7°C. The metal occurs mainly in the divalent state (Zn^{2+})in nature and is soluble in acidic and neutral conditions. Zinc is found in at least 80 minerals in nature, but the most important of these minerals are the sulphides (Sphalerite and Wurtzite) and their weathering products. Zinc in soil concentration is reported to be about 70 mg/kg and is present in all rock types. It is also commonly known that this metal can easily be incorporated in the rock structure. (Adriano, 1986; Friberg et al., 1979). Under alkaline conditions the Zn precipitates in the hydroxide form. The divalent ion is known to form complexes in water solution, for example, $Zn(CN)_4^{2-}$ and $Zn(NH_3)_4^{2-}$ (Shamberger and Oehme, 1979).

The metal is mainly used in the electroplating industries where metal that is not corrosion resistant is coated with zinc. This process is known as galvanising and is used on metal that may be used outdoors. Other uses of zinc include: pigment in paints, a micronutrient in fertilisers, batteries, and hardening agents in concrete and cement. Smaller amounts are also used in the manufacture of disinfectant solutions and cosmetic products. The main contributors to possible pollution are industrial wastes, over fertilisation and sewage sludge (Adriano, 1986; Friberg et al., 1979).

Zinc is an essential element in humans and animals and is required in various enzymatic reactions. A deficiency in zinc can easily occur and is well documented. Ingesting large quantities of zinc will cause gastrointestinal disturbances, which in turn promote vomiting and diarrhoea. The toxicity of zinc compared to other metals is very low and can be seen as non-toxic in moderate amounts. Compounds of the carbamate ester are highly toxic and this is in agreement with the characteristics of the compounds. Carcinogenic, mutagenic and teratogenic characteristics are common with high level, long-term exposure. Zinc has a relatively high toxicity to fish and other aquatic life. (Friberg et al., 1979).

Results & Discussion

Station wise and seasonal wise distribution of Zn in aqueous and sediment phase is given in Table 4.25 & 4.26. The station wise statistical summary showing the minimum and maximum values, mean, standard deviation and Percentage Coefficient of Variation (%CV) of Zinc in aqueous and sediment phase are furnished in Tables 4.27 & 4.28.

Table 4.25: Station wise seasonal distribution of Zn in Water

Station	Zn (µg/L) in Surface water			Zn (µg/L) in Bottom water		
	Pre Mon.	Monsoon	Post Mon.	Pre Mon.	Monsoon	Post Mon.
1	12.23	12.82	21.20	13.66	17.86	25.40
2	12.45	8.14	10.47	--	--	--
3	24.73	9.55	60.68	21.86	17.67	33.47
4	20.81	16.02	27.50	--	--	--
5	14.19	11.19	26.21	16.85	15.23	28.31
6	8.39	10.55	17.24	14.44	26.45	19.24
7	17.97	13.74	7.56	--	--	--
8	34.11	13.14	44.85	38.14	30.49	51.02

Table 4.26: Station wise seasonal distribution of Zn in Sediment

Station	Zn (in mg/kg)		
	Pre Monsoon	Monsoon	Post Monsoon
1	40.16	25.94	21.84
2	23.65	71.36	12.20
3	128.89	79.38	97.43
4	242.99	251.68	75.66
5	254.42	178.32	190.14
6	233.29	163.60	384.14
7	105.55	198.43	139.35
8	338.62	253.48	154.27

Table 4.27: Station-wise statistical summary of Zn in Water

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	12.23	21.20	15.42	5.02	32.5	13.66	25.40	18.97	5.95	31.4
2	8.14	12.45	10.35	2.16	20.8	--	--	--	--	--
3	9.55	60.68	31.65	26.26	82.9	17.67	33.47	24.33	8.18	33.6
4	16.02	27.50	21.44	5.77	26.9	--	--	--	--	--
5	11.19	26.21	17.20	7.95	46.2	15.23	28.31	20.13	7.13	35.4
6	8.39	17.24	12.06	4.61	38.2	14.44	26.45	20.04	6.05	30.2
7	7.56	17.97	13.09	5.24	40.0	--	--	--	--	--
8	13.14	44.85	30.70	16.13	52.5	30.49	51.02	39.88	10.38	26.0

Table 4.28: Station-wise statistical summary of Zn in Sediment

Station	Min	Max	Mean	SD	CV %
1	21.84	40.16	29.32	9.61	32.8
2	12.20	71.36	35.74	31.37	87.8
3	79.38	128.89	101.90	25.06	24.6
4	75.66	251.68	190.11	99.21	52.2
5	178.32	254.42	207.63	40.95	19.7
6	163.60	384.14	260.34	112.73	43.3
7	105.55	198.43	147.77	47.01	31.8
8	154.27	338.62	248.79	92.26	37.1

For surface water, the concentration of Zn varies from 8.39-34.11 µg/L, 8.14-16.02 µg/L and 7.56-60.68 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The maximum concentration was found in station-3 during Post Monsoon. This may be due to contamination from the waste water discharges and waste from the slaughtering units near to the Champakkara canal. The concentration of Zn in bottom water ranges from 13.66-38.14 µg/L, 15.23-30.49 µg/L and 19.23-51.02 µg/L during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration was recorded at station 2 & 3 respectively in surface water and the same for bottom waters at station 1 & 8 respectively. The station-wise annual mean concentration varies from 10.35-31.65 µg/L for surface water and 18.97-39.88 µg/L for Bottom water. Surface water showed slightly lesser value than that of the bottom water in almost all station and in all seasons. In sediment, the concentration ranges from 23.65-338.62 mg/kg, 2594-253.48 mg/kg, and 1220-384.14mg/kg during Pre Monsoon, Monsoon and Post Monsoon respectively. The lowest and highest annual mean concentration (35.74 & 260.34 mg/kg) of Zn in sediment was recorded at station 2 & 6 respectively. The seasonal variation of Zn is illustrated in Figure: 4.15.

It was observed that the concentration of Zn in sediment showed increasing trend from station 1 to 8. As expected, the less polluted reference station- Muvattupuzha records the low Zn value in all the three season. In station 2, 3 & 7, Zn concentration was found to be almost in the same range in all the three season, even-though there was an increasing station-wise trend. In Pre monsoon and Monsoon season, high concentration of Zn in sediment was recorded at Station-4 and comparatively low value in Post monsoon season. In station-6, Post monsoon season showed high value of Zn where as in station-8 Pre-monsoon season showed high Zn value.

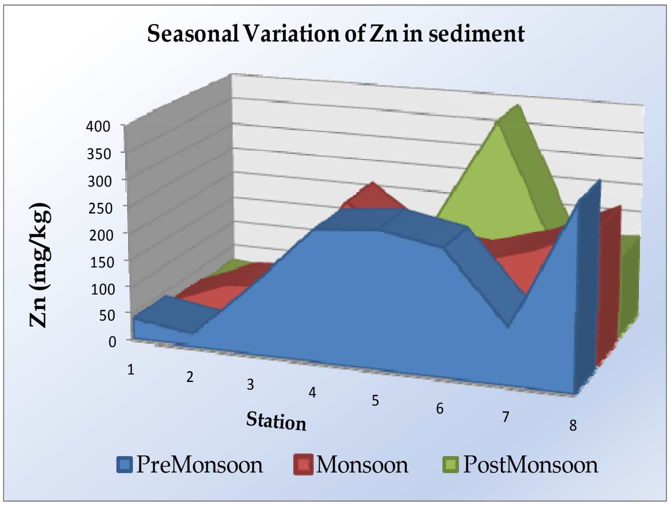


Figure 4.15: Seasonal Variation of Zn in Sediment

Station-wise seasonal mean variation of Zn in Surface, Bottom water and Sediment are illustrated in Figure: 4.16.

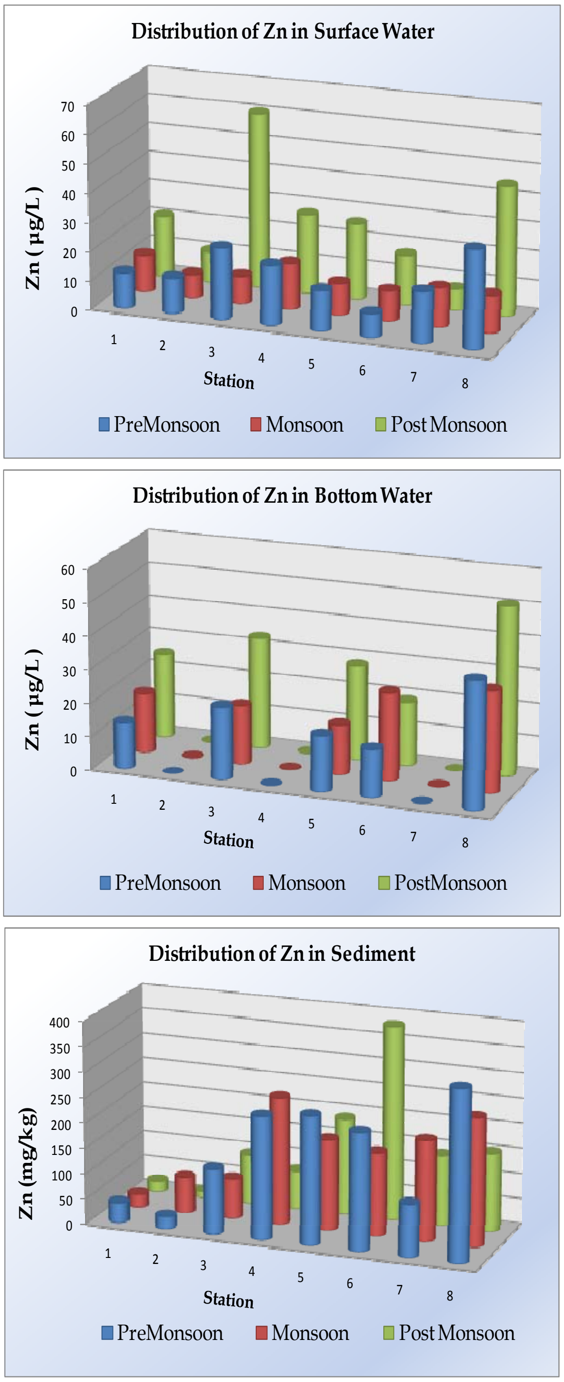


Figure 4.16: **Station-wise seasonal mean variation of Zn in Surface water, Bottom water and Sediment**

Zn is very soluble in acidic soil conditions and this solubility also makes it very bio-available for plants. A very small fraction of zinc adsorbed onto the clay particles is not mobilised, but can be dissolved in acid for analytical purposes. In soil with high organic matter, it can help the adsorption process through the formation of Organo-metal complexes, which are less soluble in water (Alloway, 1990; Adriano, 1986). Zn is readily adsorbed by clay minerals, carbonates, or hydrous oxides. Studies conducted by Hickey and Kittrick, (1984), Kuo et al., (1983), and Tessier et al., (1980) found that the greatest percent of the total Zn in polluted soils and sediments was associated with Fe and Mn oxides. Precipitation is not a major mechanism of retention of Zn in soils because of the relatively high solubility of Zn compounds. Precipitation may become a more important mechanism of Zn retention in sediment-waste systems. As with all cationic metals, Zn adsorption increases with pH. Zn hydrolyses at pH more than 7 and these hydrolysed species are strongly adsorbed to soil surfaces. Zn forms complexes with inorganic and organic ligands that will affect its adsorption reactions with the soil surface.

4.3 Sediment /Water Distribution Coefficient (K_d) of Metals

The accumulation of metals from the overlying water to sediment is dependent on number of external environmental factors such as pH, ionic strength, anthropogenic input, the type and concentration of organic and inorganic ligands and available surface area for adsorption caused by the variation in grain size distribution. Increased concentration of heavy metals and organic matter will tend to be associated with fine grained sediments because of their high surface to volume ratio and adsorption abilities. The effect of heavy metal contamination in sediments may be either acute or chronic on benthic organisms and can adversely impact water supply via borehole abstraction and associated groundwater activities. The heavy metal enrichment at some sites along the rivers reflects the effects of agricultural activities, sewage treatment plant effluents, collectors, discharges and industrial activities.

The metal partition coefficient for the sediment and the overlying bottom water sample gives the information for the remediation of metal pollution. In natural media, metal contaminants undergo reactions with ligands in water and with surface sites on the solid materials with which the water is in contact. Reactions in which the metal is bound to the solid matrix are referred to as sorption reactions and cationic exchange reactions. The metal that is bound to the sediment is said to be sorbed. The "distribution coefficient" (K_d) is the "soil-water" partitioning coefficient. K_d(L/kg) is the ratio of sorbed metal concentration (expressed in mg metal per kg sorbing material) to the dissolved metal concentration (expressed in mg metal per L of solution) at equilibrium.

$$K_d = \frac{\text{Metal concentration in sediment } \left(\text{mg / kg}\right)}{\text{Metal concentration in Bottom water } \left(\text{mg / L}\right)}$$

During transport of metals in soils and surface water systems, metal sorption to the solid matrix results in a reduction in the dissolved concentration of metal and this affects the overall rate of metal transport. For a particular metal, K_d values in soil are dependent upon various geochemical characteristics of the soil and its pore water. Likewise for water systems– the K_d for a particular metal depends on the nature of suspended solids or sediment and key geochemical parameters of the water. Geochemical parameters that have the greatest influence on the magnitude of K_d include the pH of the system and the nature and concentration of sorbents associated with the soil or surface water. The partition/distribution coefficient are measures of how hydrophilic ("water loving") or hydrophobic ("water fearing") a chemical substance is. The hydrophobic nature of a compound can gives an indication of how easily a compound might be taken up in water from the sediments to pollute waterways, and its toxicity to animals and aquatic life. Distribution coefficients may be measured or predicted for compounds currently causing problems or with foresight to gauge the structural modifications necessary to make a compound environmentally friendlier in the research phase.

The values of K_d below about 0.1 L/kg are indicative of high mobility, and variation of ten fold around this value, and especially lower, will not have a large effect on assessment results because the element is essentially as mobile as water. For high K_d values, in the order of 10^4 L/kg and above the element can be considered essentially immobile for a specific assessment period.

The distribution coefficient for each metal in three seasons were calculated and given in the Table: 4.29. The variations of distribution coefficient in all the 3 seasons for each metal were depicted in Figure 4.17.

Table 4.29: Distribution coefficients (K_d) for Cd, Cu, Fe, Ni, Pb & Zn

Station	K_d for Cd			K_d for Cu			K_d for Fe		
	Pre Mon.	Mon.	Post Mon.	Pre Mon.	Mon.	Post Mon.	Pre Mon.	Mon	Post Mon.
1	3815	10380	2071	8408	2521	2864	200735	239149	100784
2	9201	6002	1614	7614	6109	3387	138700	44180	58306
3	7411	4662	3856	7896	3847	2878	140215	142914	39421
4	3473	5482	1355	8151	4104	2199	191879	53464	130102
5	3163	5067	6372	17237	5110	1874	204550	104772	32284
6	7725	4319	11400	30758	3720	7369	214674	101098	93386
7	3392	6536	11036	16454	8416	1836	156788	123347	171985
8	11265	13936	6514	62126	16520	58450	380788	234333	226550

Station	K_d for Ni			K_d for Pb			K_d for Zn		
	Pre Mon.	Mon.	Post Mon.	Pre Mon.	Mon.	Post Mon.	Pre Mon.	Mon	Post Mon.
1	28211	10066	4086	2675	1625	18063	2940	1453	860
2	7565	7767	470	2473	1403	4194	1900	8766	1165
3	19447	14601	12204	5214	3956	4711	5895	4492	2911
4	28133	16201	18229	2106	4024	4122	11677	15710	2751
5	21675	18676	28816	1891	2229	3842	15102	11709	6716
6	34639	10823	98128	5981	1979	6189	16156	6185	19969
7	40845	8508	11175	2120	8634	5404	5874	14442	18435
8	59076	13402	10736	15559	3294	10992	8878	8313	3024

Station 1 showed high value of distribution coefficient for Cd & Fe, during monsoon season in comparison with Pre monsoon and Post monsoon season. So water of this station was found to have comparatively less concentration than that in the other season. In station 6, high distribution coefficient for Cd, Ni & Zn was observed in the Post monsoon season. In all seasons, stations 2, 3, 4 & 7 showed a same trend of sediment to water ratio for all the metals under study. Except Zn, all the other metals showed high distribution coefficient in the Pre monsoon season at station 8. The variation in partition coefficient was shown by the estuarine station 4, 5 and 6 because of the varied texture of the sediments in these stations. Sand dominated in the sediments of station1, 2 & 3 in all the seasons but clay and silt dominated in the sediments of stations 4, 5 and 6.

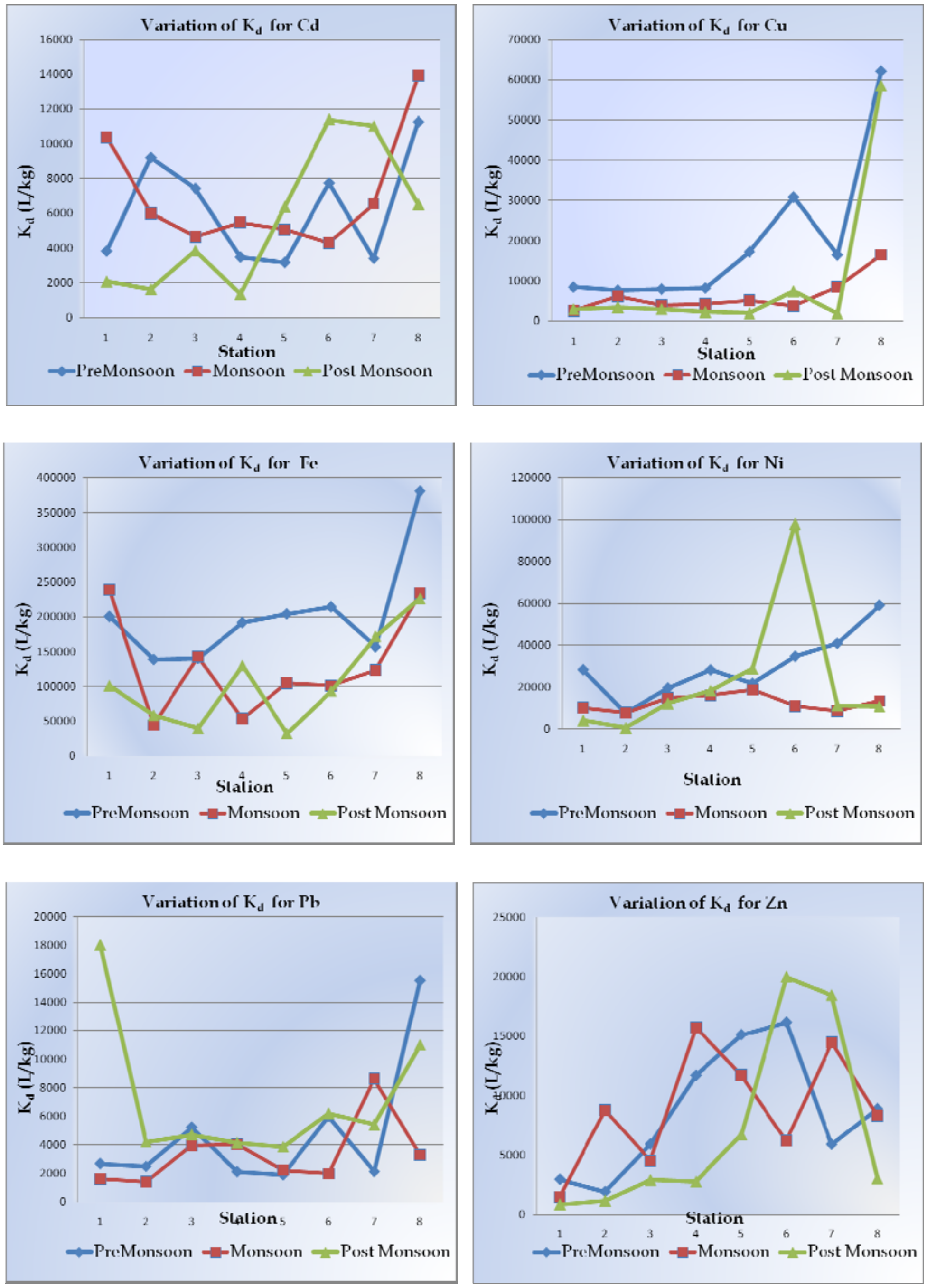


Figure 4.17: Seasonwise variation of Distribution Coeffcient.

4.4 Statistical Approach

4.4.1 Correlation Study of metals

In order to have an overview about the parameters which influence the distribution model of total metals during different seasons, a number of sediment parameters were examined. These factors exhibited considerable seasonal and spatial variations due to changes in environmental conditions from estuarine to riverine environments. The sediment parameters considered were sediment organic carbon, Salinity of water, sediment texture (Sand, silt and Clay), total Cd, Cu, Fe, Ni, Pb and Zn. Statistical tests were then performed to establish the inter-metal relationships, and classify metals. Multiple regression analysis was performed on the total metal concentrations considering these variables as independent. The regression models were generally found fit for all metals. Correlation analysis of heavy metals, salinity, TOC and sediment texture (sand, silt and clay) of eight stations are shown in the Table: 4.30. Correlation coefficient greater than 0.8, that is of high correlation are highlighted in the table. The scatter diagrams representing the correlation study of the metals with high correlation value are depicted in the Figure: 4.18.Analysis was done using software SPSS 10.

Only Cd, Ni &Zn in sediment samples showed positive correlation with the salinity of the overlying water of the sediment. The correlation between metals and sediment fractions indicates their physical behaviour towards the texture. All metals are positively correlated with silt & clay i.e.; fine fractions of the sediments and all the metal showed negative correlation with sandy fraction of the sediment. Except Fe all the other five metals have more positive correlation with silt fraction than that of the clay fraction. Zn recorded high correlation with the silt fraction of the sediment. Cd, Ni & Zn showed positive correlation with Organic Carbon. High correlation between Ni and TOC indicates the accumulation of this metal with organically bounded carbon in the sediments. Cd showed high correlation with Cu, Pb, Zn & pH with values

0.94, 0.94, 0.81 & 0.97 respectively. Also Cu showed high positive correlation with Fe & Zn (0.80& 0.97). Inter-elemental association was also evaluated by correlation coefficient (r) and the results are presented in Table: 4.30 and indicates that some elemental pairs, for example Cd/Cu (r = 0.94), Cd/Fe (r=0.74), Fe/Cu(r=080), Ni/Cd (r=0.53), Pb/Cd (r=0.94), Pb/Fe(r=0.72), Zn/Cd(r=0.81), Zn/Cu(r=0.70), Zn/Ni(r=0.77), Zn/Pb(r=0.68) etc, have strong correlations with each other. On the other hand, pairs such as Ni/Pb(r=0.31), Zn/Fe (r=0.43) are moderately significant, whereas the rest of metal pairs show no significant correlation with each other. Strong correlations signify that each paired elements have common contamination sources. Physico-chemical properties and metal speciation study were however not performed in the present study, to help in ascertaining these results.

Table 4.30: Correlation coefficient values of metals in sediments

	Cd	Cu	Fe	Ni	Pb	Zn	pH	Salinity	TOC	Sand	Silt	Clay
Cd	1.00											
Cu	0.94	1.00										
Fe	0.74	0.80	1.00									
Ni	0.53	0.27	0.00	1.00								
Pb	0.94	0.97	0.72	0.31	1.00							
Zn	0.81	0.70	0.43	0.77	0.68	1.00						
pH	0.97	0.88	0.69	0.63	0.88	0.91	1.00					
Salinity	0.08	-0.10	-0.27	0.74	-0.09	0.61	0.26	1.00				
TOC	0.25	-0.02	-0.14	0.88	0.07	0.60	0.42	0.83	1.00			
Sand	-0.52	-0.40	-0.15	-0.76	-0.42	-0.89	-0.66	-0.85	-0.76	1.00		
Silt	0.58	0.50	0.11	0.64	0.48	0.85	0.67	0.68	0.46	-0.82	1.00	
Clay	0.17	0.07	0.11	0.50	0.12	0.45	0.30	0.61	0.73	-0.70	0.15	1.00

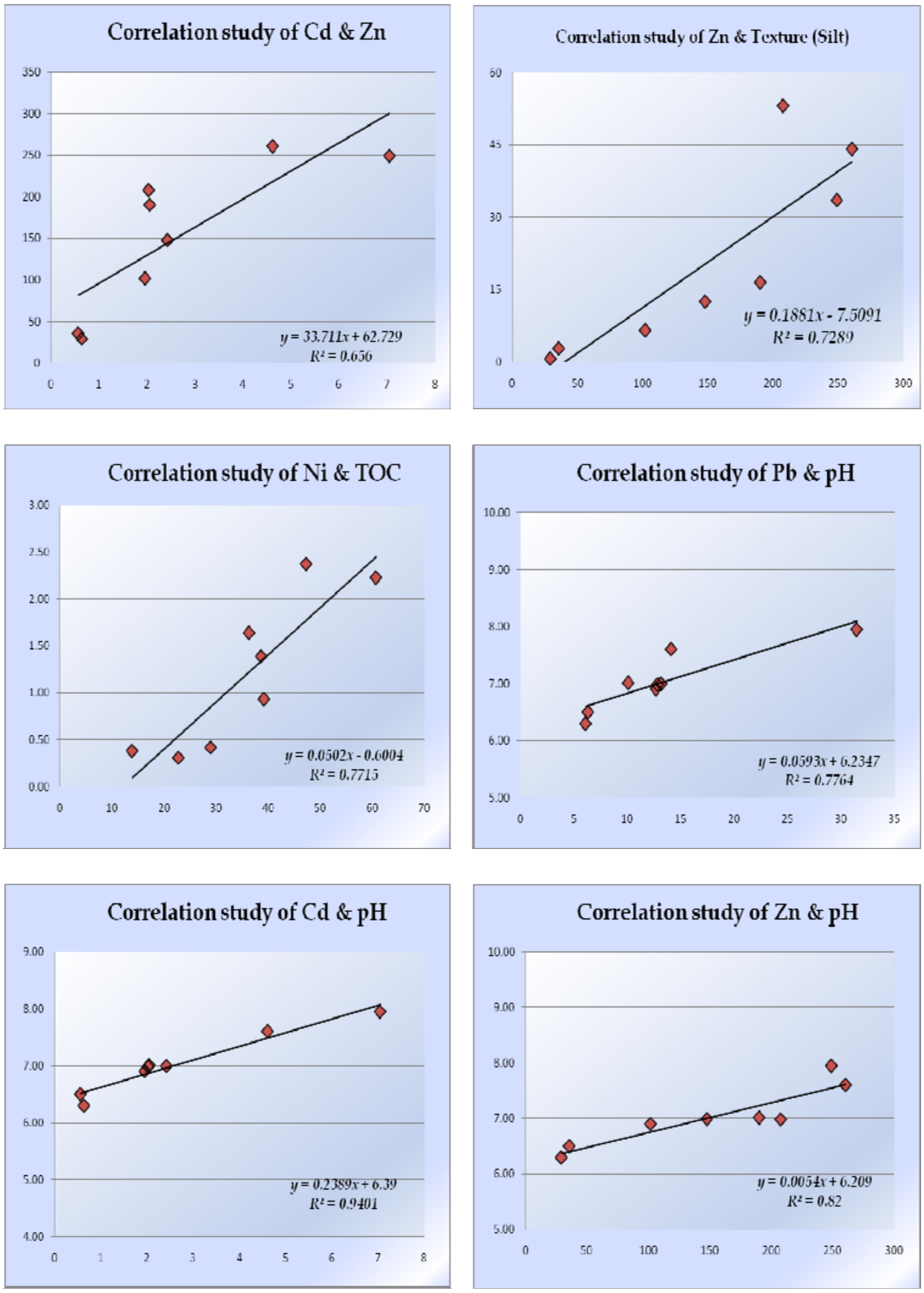


Figure 4.18a : Scatter diagram representing the correlation of metals in sediment

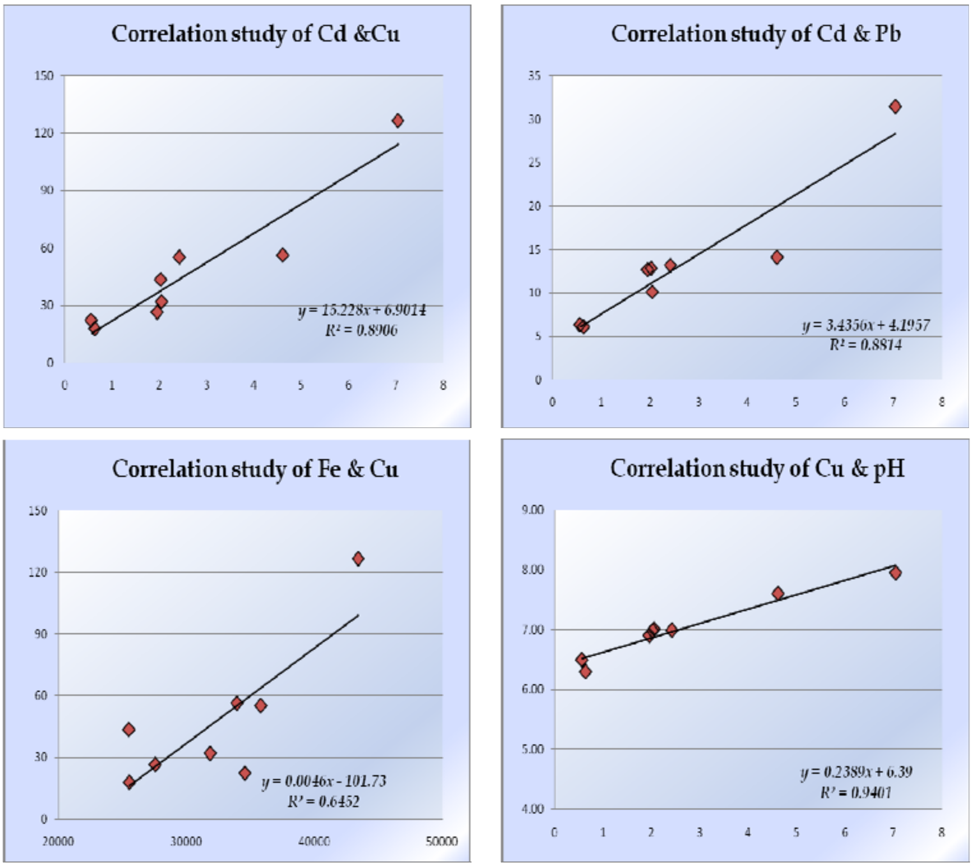


Figure 4.18b: Scatter diagram representing the correlation of metals in sediment

4.2.2 Principal Component Analysis (PCA)

The objective of the technique is to establish a linear relationship between different variables and reduce them into fewer important components that can adequately explain most of the variance In the data set In practice, the technique consists of the determination of the covariance or correlation matrix of the normalised variables, followed by the calculation of the eigenvector matrix which represents the magnitude and directions of variables in space, and the eigen values which represents their corresponding variances. PCA is a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences. Since patterns in data can be hard to find in data of high dimension, where the luxury of graphical representation is not available, PCA is a powerful tool for analysing data. PCA was performed to establish possible factors that contribute towards the metal concentrations and source apportionment. The number of significant principal components (PC) was selected on the basis of Varimax orthogonal rotation with Kaiser Normalisation with Eigen value greater than 1 (Buckley et al., 1995 and Davis, 2002). Seasonal variations of the physical and chemical parameters in the surface, bottom waters and sediment samples were considered in this analysis. The normalised data was then subjected to principal component analysis using STATISTIXL 2007. The PC analysis of water and sediments in the present geographic area of study and in other hot spot area were performed and the outcome of the PC analysis is more or less similar to others (Ratheesh et al., 2010; Deepulal, 2011; Selvam et al., 2011). The rotated component matrix for water sample and sediment are given in Table 4.31& 4.32 and illustrated in Figure: 4.19, 4.20 & 4.21.

Table 4.31: Factor analysis showing contribution of statistically dominant variables measured in Surface & Bottom water

Variable	Surface Water				Bottom Water		
	PC 1	**PC 2**	**PC 3**	**PC 4**	**PC 1**	**PC 2**	**PC 3**
Cd	0.08	-0.85	-0.40	-0.31	0.39	-0.58	-0.38
Cu	0.41	0.82	-0.19	-0.28	-0.90	0.29	-0.10
Fe	0.29	-0.03	-0.65	0.65	-0.66	0.49	0.56
Ni	0.41	-0.67	0.34	0.49	0.56	0.74	0.28
Pb	0.60	0.62	-0.13	0.39	-0.79	-0.53	0.01
Zn	-0.24	0.16	0.82	-0.03	0.33	-0.82	0.39
pH	0.90	0.14	0.04	-0.29	-0.98	-0.13	-0.14
Salinity	0.89	-0.22	-0.06	-0.23	-0.96	0.03	-0.18
DO	-0.71	0.04	-0.51	-0.36	0.32	0.50	-0.74
Conducitivity	0.87	-0.25	0.11	-0.32	-0.94	0.01	-0.09
Eigenvalue	3.70	2.37	1.69	1.35	5.30	2.42	1.30
% of total Variance.	36.97	23.74	16.94	13.49	53.04	24.21	13.03
Cumilative %	36.97	60.71	77.65	91.14	53.04	77.25	90.28

Table 4.32: Factor analysis showing contribution of statistically dominant variables measured in Sediment

Variable	PC 1	PC 2
Cd	0.86	-0.48
Cu	0.74	-0.66
Fe	0.49	-0.72
Ni	0.78	0.44
Pb	0.75	-0.61
Zn	0.98	0.04
pH	0.94	-0.31
TOC	0.63	0.68
Sand	-0.88	-0.40
Silt	0.80	0.16
Clay	0.51	0.49
Salinity	0.57	0.79
Eigenvalue	6.91	3.36
% of Variance.	57.58	28.03
Cumilative %	57.58	85.62

PCA of surface water showed that four components accounts for 91.1 % of the total variance. First component, which accounted for 36.96% of the total variance, is characterized by very high positive loadings on pH, Salinity and Conductivity and strong negative loadings on DO. Component 2 accounted for 23.74% of the total variance and is characterized by very high positive loadings of Cu and Pb and strong negative loadings on Cd and Ni. Component 3 accounted for 16.9% of the total variance and characterized by high positive loadings on Zn and negative loadings on Fe. Component 4 accounted for 13.49% of the total variance and is characterized by positive loadings on Fe and Ni.

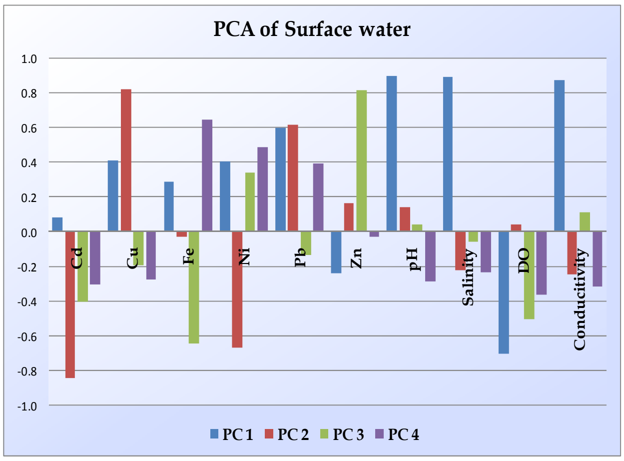


Figure 4.19: Factor loadings for the parameters in Surface water

PCA of bottom water showed that three components accounts for 90.3 % of the total variance. First component, which accounted for 53.03% of the total variance, is characterized by positive loadings on Ni and strong negative loadings on Cu, Pb, pH, Salinity and Conductivity. Component 2 accounted for 24.21% of the total variance and is characterized by very high positive loadings of Ni and strong negative loadings on Cd and Zn. Component 3 accounted for 13.03% of the total variance and characterized by high positive loadings on Fe and negative loadings on DO.

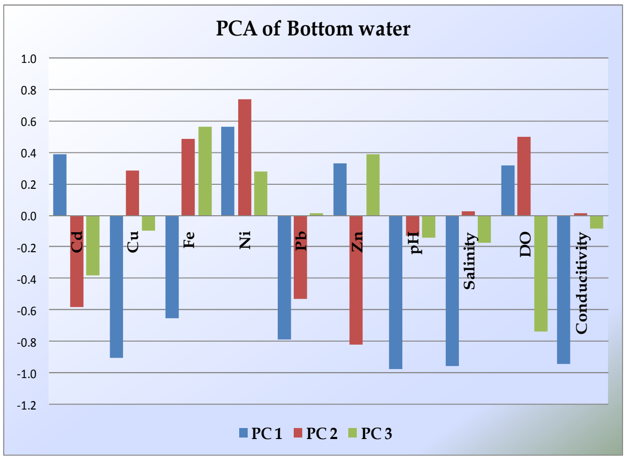


Figure 4.20: Factor loadings for the parameters in Bottom water

PCA of sediment showed that two components accounts for 85.6 % of the total variance. First component, which accounted for 57.58% of the total variance, is characterized by very high positive loadings on every variable except a strong negative loading on sand fraction of sediment. Component 2 accounted for 28.03% of the total variance and is characterized by very high positive loadings of elements like Ni, TOC, salinity, Silt and clay fractions of sediment and strong negative loadings on Sand sediment fraction, Cu, Fe, Cd and Pb.

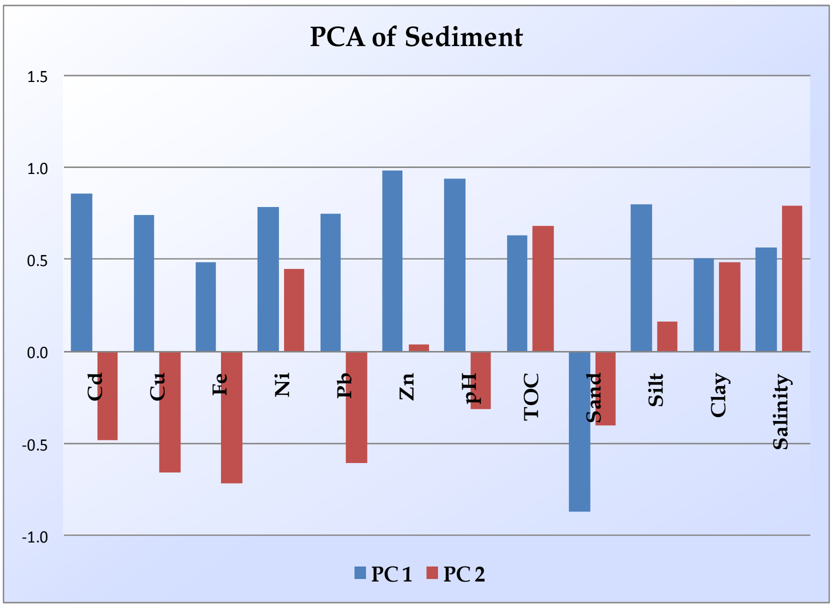


Figure 4.21: Factor loadings for the parameters in sediment

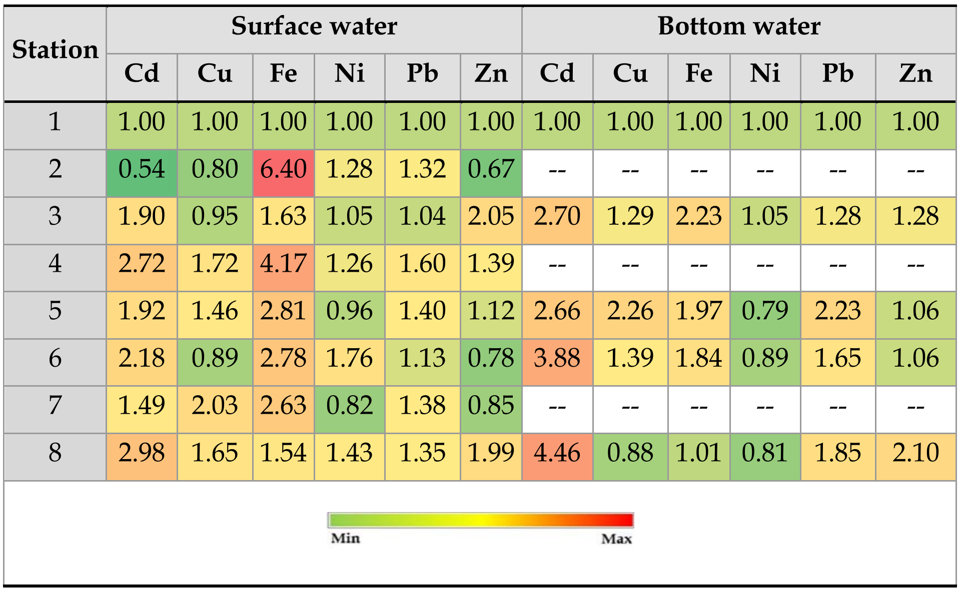
4.5 Assessment of Metal Contamination

The intensity and severity of metal contamination can be assessed by calculating various statistical parameters like Normalisation Factor, Enrichment Factor, Contamination Factor, Pollution Load Index, and Geo-accumulation Index.

4.5.1 Metal Normalisation

Normalisation means the concentration of each metal in the sample is divided by the concentration of the same metal in the reference material. In the present study, samples from station-1 are considered as reference site and the metal concentration of this site is used for the Normalisation. The normalised mean concentrations of metals in the water and sediment samples were given in the Table 4.33 & 4.34. The Normalisation factor (NF) <1 refers to a low contamination with respect to the reference site, 1<NF<3 means moderate contamination, 3<NF<6 indicates severe contamination and NF>6 indicates extreme contamination. In surface water, Fe showed severe and extreme contamination at station 4 & 2 respectively. In bottom water, Cd showed moderate contamination at station-6 & 8. In sediments, the metals that showed extreme contamination are Cd (at station 6& 8), Cu (at station-8), Pb (at station-8) and Zn (at stations-4, 5, 6 & 8).The metals that show moderate contaminations in sediments are Cd (at stations-3, 4, 5 &7), Cu (at stations 6 &7) and Zn (at station-3).

Table 4.33: Mean normalised concentration of metals in Surface &Bottom water



Station	Surface water						Bottom water					
	Cd	Cu	Fe	Ni	Pb	Zn	Cd	Cu	Fe	Ni	Pb	Zn
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.54	0.80	6.40	1.28	1.32	0.67	--	--	--	--	--	--
3	1.90	0.95	1.63	1.05	1.04	2.05	2.70	1.29	2.23	1.05	1.28	1.28
4	2.72	1.72	4.17	1.26	1.60	1.39	--	--	--	--	--	--
5	1.92	1.46	2.81	0.96	1.40	1.12	2.66	2.26	1.97	0.79	2.23	1.06
6	2.18	0.89	2.78	1.76	1.13	0.78	3.88	1.39	1.84	0.89	1.65	1.06
7	1.49	2.03	2.63	0.82	1.38	0.85	--	--	--	--	--	--
8	2.98	1.65	1.54	1.43	1.35	1.99	4.46	0.88	1.01	0.81	1.85	2.10

Table 4.34: Mean normalised concentration of metals in Sediment

Station	Cd mg/kg	Cu mg/kg	Fe mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
1	1.00	1.00	1.00	1.00	1.00	1.00
2	0.88	1.24	1.35	0.48	1.04	1.22
3	3.03	1.47	1.08	1.25	2.07	3.48
4	3.18	1.78	1.25	1.63	1.65	6.48
5	3.15	2.41	1.00	1.33	2.09	7.08
6	7.14	3.12	1.33	2.10	2.30	8.88
7	3.76	3.06	1.40	0.79	2.15	5.04
8	10.90	6.99	1.70	1.35	5.12	8.49

Min Max

4.5.2 Enrichment Factor

A general approach for the estimation of sediment contamination of heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations with uncontaminated/less contaminated background levels. If EF < 2, means minimum enrichment, 2 ≤ EF < 5 refers to moderate enrichment, 5 ≤ EF < 20 refers to significant enrichment, 20 ≤ EF < 40 corresponds to very high enrichment and when EF ≥ 40 refers to extremely high enrichment.

The EF of a heavy metal in sediment can be calculated using the following formula

$$EF = \frac{C_{\textbf{metal}} \ / C_{\textbf{normaliser}} \text{ of Sample}}{C_{\textbf{metal}} \ / C_{\textbf{normaliser}} \text{ of Reference}}$$

Where, C_{metal} and $C_{normaliser}$ are the concentrations of heavy metal and the normaliser in soil (Fe in the present study) and in unpolluted control as Reference (station-1). As the EF values increase, the contributions of the anthropogenic origins also increase. Iron is conservative even after the chemical and physical changes undergone by sediment after its initial deposition and its geochemistry is similar to that of many trace metals. The Enrichment Factor calculated for each metal in sediment samples are given in the Table 4.35.

Table 4.35: Distribution of EF for metals in Sediments

Station	Cd mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
2	0.65	0.92	0.36	0.77	0.90
3	2.81	1.36	1.16	1.92	3.22
4	2.55	1.42	1.31	1.32	5.20
5	3.15	2.42	1.34	2.10	7.09
6	5.38	2.35	1.58	1.73	6.69
7	2.68	2.18	0.56	1.53	3.60
8	6.42	4.12	0.80	3.01	5.00

4.5.3 Contamination Factor(CF)

The level of contamination of soil by metal is expressed in terms of a contamination factor (CF) calculated as:

$$CF = C_n / B_n$$

Where C_n = measured concentration of sample and B_n =geochemical background value. The contamination factor, $CF < 1$ refers to low contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ indicates considerable contamination and $CF > 6$ indicates very high contamination. Contamination factors of various metals in the sediment samples are presented in Table: 4.36. Based on the calculation of contamination factor CF values, extreme contamination of sites was showed due to metals- Cd (at stations- 6 & 8), Cu (at station 8) and Zn (at stations-4, 5, 6 & 8).

Table 4.36: Distribution of CF for metals in sediment

Station	Cd mg/kg	Cu mg/kg	Fe mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
2	0.88	1.24	1.35	0.48	1.04	1.22
3	3.03	1.47	1.08	1.25	2.07	3.48
4	3.18	1.78	1.25	1.63	1.65	6.48
5	3.15	2.41	0.99	1.33	2.09	7.08
6	7.14	3.12	1.33	2.10	2.30	8.88
7	3.76	3.06	1.40	0.79	2.15	5.04
8	10.90	6.99	1.70	1.35	5.12	8.49

4.5.4 Pollution Load Index (PLI)

To effectively compare whether the eight stations suffer contamination or not, the pollution load index (PLI) was used. The PLI is aimed at providing a measure of the degree of overall contamination at a sampling site.

$$\mathbf{PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots CF_n)^{1/n}}$$

where n is the number of metals studied (six metals in the present study) and CF is the contamination factor. The Contamination Factor, CF for each metal in given in the Table: 4.36. The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1 denote perfection; PLI = 1 present that only baseline levels of pollutants are present and PLI > 1 would indicate deterioration of site quality.

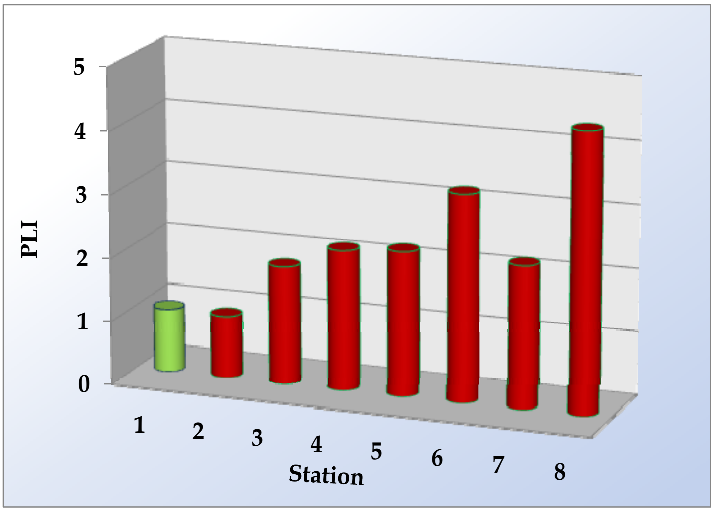


Figure 4.22: Pollution Load Index for the six metals studied

The PLI values for stations 1 to 8 are 1.00, 0.98, 1.88, 2.23, 2.31, 3.29, 2.27 and 4.44 respectively. Based on the results presented in Figure: 4.22, the overall degree of contamination by the 6 metals is of the order station-8 > 6 > 5 > 7 > 4 > 3 >1 >2. Stations 6 & 8 showed strong signs of pollution or deterioration of site quality, whereas Station-2 is almost at baseline level. Relatively high PLI values at Stations 6 & 8 and, to some degree, stations-5, 7, 4 & 3 suggest input from anthropogenic sources attributed to increased human and industrial activities.

4.5.5 Geo accumulation Index

A quantitative test of metal pollution in the sediments was calculated using the Index of Geo-accumulation, and is given by:

$$\mathbf{I_{geo} = log_2 (C_n/1.5 \times B_n)}$$

Where C_n = measured concentration of sample, and B_n =geochemical background value (Station-1 in the present study).

The factor 1.5 in this equation is to minimise the effect of possible variations in the background values, B_n which may be attributed to lithogenic variations of trace metals in soils. The geo-accumulation index compares the measured concentration of the element in the fine-grained sediment fraction C_n with the geochemical background value B_n. The calculated geo-accumulation (I_{geo}) values are presented in the Table: 4.37. Geo-accumulation index value <1 indicates a practically uncontaminated nature, >0-1 refers to Uncontaminated to moderate, >1-2 refers moderate, >2-3 indicates moderate to strong, >3-4 strong, >4-5refers to strong to very strong and >5 refers to very strong contamination. Based on the I_{geo} values, a moderate to strong contamination was observed for metals Cd (at station 6 & 8), Cu (at station-8) and Zn (at stations 4, 5, 6 & 8).

Table 4.37: Description of I_{geo} values of metals in sediment

Station	Cd mg/kg	Cu mg/kg	Fe mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
1	**-0.58**	**-0.58**	**-0.58**	**-0.58**	**-0.58**	**-0.58**
2	**-0.77**	**-0.27**	**-0.15**	**-1.64**	**-0.53**	**-0.30**
3	**1.02**	**-0.03**	**-0.48**	**-0.26**	**0.46**	**1.21**
4	**1.09**	**0.24**	**-0.27**	**0.12**	**0.14**	**2.11**
5	**1.07**	**0.69**	**-0.59**	**-0.17**	**0.48**	**2.24**
6	**2.25**	**1.06**	**-0.18**	**0.48**	**0.62**	**2.57**
7	**1.33**	**1.03**	**-0.10**	**-0.93**	**0.52**	**1.75**
8	**2.86**	**2.22**	**0.18**	**-0.15**	**1.77**	**2.50**

Min Max

4.6 Conclusion

Samples-surface water, bottom water and sediment were analysed by the appropriate analytical technique and the results are tabulated and graphically represented. The data analysis of the observed findings was carried out discussed the abnormalities and source of the metal contamination. The sediment to water (bottom water) distribution coefficient of metals was also determined. Statistical study like multiple regression analysis and Principal component analysis of data was effectively performed. The metal contamination assessment were done with the methods like Normalisation factor (NF), Contamination factor (CF), Enrichment factor (EF), Pollution Load Index (PLI) and Geo-accumulation Index (I_{geo}).As revealed from the four metal contamination assessment methods; I_{geo}, PLI, CF and to a less degree, EF, sediments of stations 4, 5, 6 & 8 are pollution impacted, as compared to stations-1, 2 & 7. None of the sampling sites exceed more than five ERL's, but three stations exceed more than four ERL's values indicating these stations are in the borderline of metal contamination. Finally, the majority of the metals seem to be correlated. This correlation however does not conclusively show that they share a common source. The study indicates that their observed distributions are also closely related to sediment texture and organic content. Complete physico-chemical properties of sediments and metal speciation study were however not performed in the present study, to help in ascertaining precisely the results obtained.

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Chapter 5

SORPTIONAL SPECIALITIES AND SIGNIFICANCE

Contents

5.1 Introduction & Scope

Water is the resource that covers almost three-quarters of the planet, and upon which all life depends. Throughout the history of the natural world, water sources have been the centres of life, providing habitat and sustenance for animals and plants alike. Heavy metal pollution is a quickly growing problem for our oceans, lakes, and rivers. Right now it is one among the prevalent pollution problems. Heavy metals are important in many respects but the toxic effects, when unduly exposed to them could be potentially life threatening hence, cannot be neglected. While these metals are in many ways indispensable, good precaution and adequate occupational hygiene should be taken in handling them. Although metal poisoning could be clinically diagnosed and medically treated, the best option is to prevent heavy metal pollution and the subsequent human poisoning.

The presence of large quantities of toxic metals such as mercury, lead, Cadmium, zinc or others, poses serious health risks to humans, and this threat puts the scientific community under pressure to develop new methods to detect and eliminate toxic contaminants from wastewaters in efficient and economically viable ways. There exist various processes for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, reverse osmosis, and electro-dialysis. Many physico-chemical methods have been proposed for their removal from contaminated water or sediments. The solid phase extraction (adsorption) is a better technique based on the use of the sorbent that retains analytes. The adsorption process, proved its advantage over the other processes because of its cost effectiveness and the high-quality of the treated effluent it produces. Activated charcoal is widely used as an adsorbent and is particularly considered to be a competitive and effective process for the removal of heavy metals at trace quantities due to its high adsorption capacity. But the use of activated charcoal is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon. The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently. In the present work, adsorption study of heavy metals onto activated charcoal was studied experimentally in batch process.

In a batch treatment process using powdered activated charcoal, adsorption of impurities from a liquid is essentially an equilibrium phenomenon. The first step of the process involves migration or diffusion of the impurities into the porous cavities within the carbon particles. Once inside the pore structure, the impurity molecules are attracted to the internal pore surfaces by weak electrostatic forces known as van der Waals' forces. This "physical adsorption" of impurity molecules onto the internal surface of the pore structure is the most common type of adsorption and is reversible. Physical adsorption can be an advantage in some separation scenarios in which the adsorbed material is the desired product. After adsorption, a change in processing conditions may cause the product to desorb from the carbon. In some cases, the adsorbed material may interact with active sites on the carbon pore surfaces and form chemical bonds with the surface. This process is called chemisorption and is considered irreversible.

Powdered activated charcoal usually works well in applications involving removal of trace contaminants from liquids. Evaluating the economics of the process requires answering two questions: will activated charcoal adsorb the impurity to an acceptable level and what is the cost? Most organic chemical impurities are adsorbed on activated charcoal to some extent. The present study focussed to determine how well activated charcoal will remove heavy metal ions from aqueous solution at varying condition and the factors affecting the removal of metals. In most of the cases, there are numerous types of impurities present at different concentration levels. All of these impurities are competing with each other in the adsorption process. Since different impurity types are adsorbed at different rates and in different amounts, it is very important that adsorption study to be conducted at normal and drastic environmental conditions.

5.1.1 Adsorption

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. When two non-miscible phases (solid and liquid or solid and gas etc.) are brought into contact, it is observed that the concentration of one phase is greater at the interphase than in the bulk. The tendency of accumulation of molecules to take at a surface is called adsorption. Thus the adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. Conversely, a concentration decrease may sometimes be observed, which is called negative adsorption. Adsorption process involves two components Adsorbent and Adsorbate. Adsorbent is the substance on the surface of which adsorption takes place. Adsorbate is the substance which is being adsorbed on the surface of adsorbent. Adsorbate gets adsorbed. Adsorbate + Adsorbent give rise to Adsorption

Adsorption has been applied as a general term to include many one or a group of effects taking place at the contact surface between two different phases. In a specific case it may be a capillary effect, or an adsorption, or a chemical change. Or it may be a combination of two or more of these. The term "Adsorption" as at present used, indicates simply that the action taking place, which is always a change in concentration, is limited roughly to the surface, and is relatively small in amount. In view of the fact that the term is used to include so many effects that may differ entirely in their nature, such as the formation of a film of liquid or gas on any solid, the accumulation of any dissolved substance on the surface of any solid, liquid, or gas in contact with its solution, etc. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). The process of adsorption arises due to presence of unbalanced or residual forces at the surface of liquid or solid phase. These unbalanced residual forces have tendency to attract and retain the molecular species with which it comes in contact with the surface (Figure: 5.1)

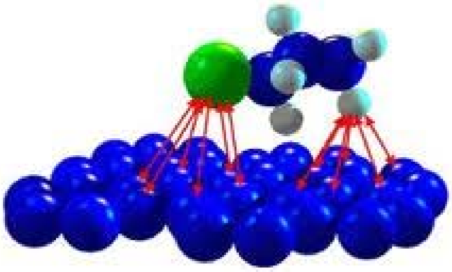


Figure 5.1: Adsorbate molecules gets attached to the surface molecule of the adsorbent

The equation which is generally used for the adsorption isotherm, and which has been found to hold for a good many individual cases, is

$X/M = kC^n$

in which, X is the amount adsorbed, M is the mass of the adsorbing substance, C is the concentration of the adsorbed substance, 'k' and 'n' are constants depending on the materials used. 'n' may be positive or negative, whole or fractional. The equation as given does not include the surface factor at all, in spite of the fact that adsorption is defined as a "change in concentration of the adsorbed substance at the surface of contact." Its omission is brought about chiefly by two factors, the necessity of using very large surfaces in order to get a measurable effect, and the practical difficulties involved in the subjection of a large, known surface to adsorption. The solid materials ordinarily used for an adsorbing surface are in a finely divided condition in order to increase the surface as much as possible, without at the same time increasing the bulk of the material used. With material of this kind it is very probable that the relation between surface and weight is constant. That is, two grams of finely ground charcoal, clay, or silica, have a surface double that of one gram of the same sample of material. In order for this to hold exactly, it is necessary to assume that the particles of the portions of the adsorbing substance used are all of the same mean size. In effect then, the term "M," in the equation given above is a relative measure of the surface involved. If adsorption is considered as a purely physical effect, then a change in concentration without chemical reaction occurring, and produce it upon a known surface, and with a known concentration of a solute, the adsorption per unit surface should be a constant quantity. Since the same materials are used, "k" and "n" should have constant values, and if "C" is also kept constant, X/M or X/S should give a constant value (S, represents the surface).

5.1.2 Types of adsorption

Adsorption can be classified into two categories depending upon the concentration and the nature of force existing between adsorbate molecule and adsorbent.

a) Depending upon the concentration:

In adsorption the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase. If the concentration of adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called Positive Adsorption. If the concentration of the adsorbate is less than its concentration in the bulk then it is called negative adsorption. Example: When a concentrated solution of KCl is shaken with blood charcoal, it shows positive adsorption, while with a dilute solution of KCl, it shows negative adsorption.

b) Depending upon the nature of force existing between adsorbate molecule and adsorbent:

Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vander waal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. The adsorption at surface or interface is largely as a result of binding forces between atoms, molecules and ions of adsorbate and surface. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into three types: Physical Adsorption, Chemical Adsorption and Persorption. The main difference between the physisorption and chemisorption are the nature of force existing between the adsorbate and adsorbent. Physisorption takes place at low temperature with low enthalpy of adsorption, whereas chemisorption takes place at high temperatures and its enthalpy of adsorption is very high. Physisorption is not specific and the process is reversible by heating or decreasing the pressure, while chemisorption is highly specific and is an irreversible process.

Physical adsorption or Physisorption

When the force of attraction existing between adsorbate and adsorbent are weak Vander waal forces, comprised of London dispersion force and classical electrostatic forces, the process is called Physical Adsorption or Physisorption. In this process, the electron distributions of adsorbate molecule undergo some distortions in mutual proximity, however the electrons maintain their association with the original nuclei. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. $\Delta H_{adsorption}$ is 20-40KJ/mol.It takes place at low temperature below boiling point of adsorbate. As the temperature increases, the process of Physisorption decreases.

Chemical Adsorption or Chemisorption

When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical Adsorption or Chemisorption. Chemisorption takes place with formation of uni-layer of adsorbate on adsorbent. It has high enthalpy of adsorption. It has high enthalpy of adsorption compared to physisorption. i.e. $\Delta H_{adsorption}$ is 200-400KJ/mol. It can take place at all temperature. With the increases in temperature, chemisorption first increases and then decreases.

Persorption

It is another type of novel phenomenon in which a given molecule is encaged between the vacant spaces simply by mechanical effect rather than being held by the usual valence bond forces. For example water molecule in Zeolites which are not held by ordinary valence bonds but merely fit into the vacant spaces in the lattice of aluminium, silicon and metal atoms. On dehydration, the water is removed and the spaces can be filled by other molecules. Dehydrated Zeolites are a good sorbing agent which takes up vapours of water, methyl and ethyl alcohols, while benzene and ether and acetone vapours are not sorbed. To distinguish it from other types of adsorption, Mc Bain (1909) suggested the term Persorption for this type of adsorption. However, the term 'Cage Adsorption' seems to be more appropriate as it differs from true solid solution only in respect that it is not completely uniform throughout the solid. Persorption is operative in highly active charcoal and silica gel.

5.1.3 Factors affecting the extent of adsorption

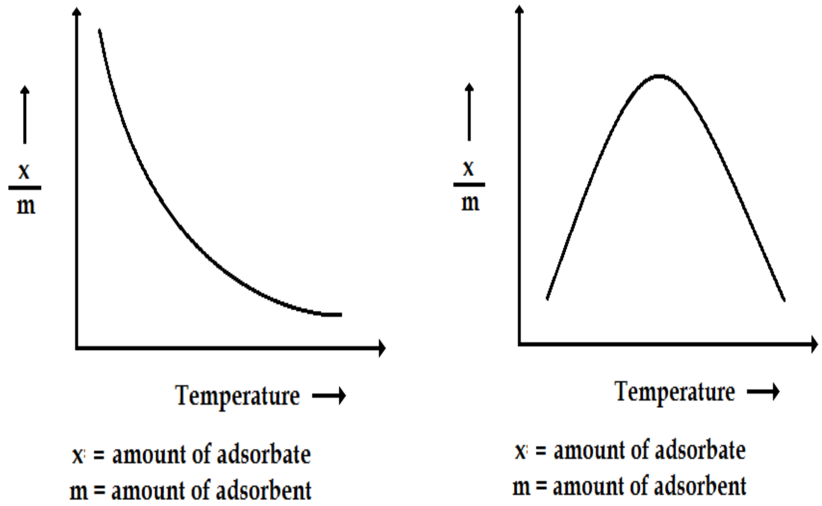
The factors which affect extent of adsorption are (i) Temperature, (ii) Pressure (iii) Surface area of the adsorbent and (iv) Activation of adsorbent.

(i) Temperature

Adsorption increases at low temperature conditions. Adsorption process is exothermic in nature. As adsorption is accompanied by evolution of heat, so according to the Le-Chatelier's principle, the magnitude of adsorption should decrease with rise in temperature.

$$\mathbf{A+B \Leftrightarrow AB + Heat}$$

The relationship between the extent of adsorption and temperature at any constant pressure is called adsorption isobar. A physical adsorption isobar shows a decrease in x/m (where 'm' is the mass of the adsorbent and 'x' that of adsorbate) as the temperature rises. The isobar of chemisorption shows an increase in the beginning and then decrease as the temperature rises. The variation of extend of sorption-physisorption and chemisorption with temperature is given in Figure: 5.2.



Effect of temperature on Physisorption **Effect of temperature on Chemisorption**

Figure 5.2: Variation of Physisorption & Chemisorption with Temperature

(ii) Pressure

With the increases in pressure, adsorption increases up to a certain extent till saturation level is achieved. After saturation level is achieved no more adsorption takes place no matter how high the pressure is applied.

(iii) Surface Area of adsorbent

As adsorption is a surface phenomenon, surface area offered by adsorbent becomes important factor for consideration. Larger sizes imply a greater adsorption capacity.

(iv) Activation of Adsorbent

Activation of adsorbent surface is done so as to provide more number of vacant sites on surface of adsorbent. This can be done by breaking solid crystal in small pieces, heating charcoal at high temperature, breaking lump of solid into powder or other methods suitable for particular adsorbent. The surface of activated charcoal is only slight polarity and hence non-polar substances will be more easily picked up by the carbon than polar ones.

5.1.4 Adsorption from Solution

The adsorption at solid –liquid interface is a complicated process by a large number of factors. Both adsorbate-adsorbent interactions and those between the components in solution as well as the surface structure of the adsorbent are important in determining the extent of adsorption. The adsorption of solute at solid-liquid interface is a consequence of free energy of the surface. When a solution is placed in contact with a solid, the solute molecules accumulate on the surface of the solid and the free (surface) energy of the solid is decreased. It follows, from the general consideration, which a particular solute which lowers the surface tension of solution will accumulate more on the surface of the solid and there will be a greater proportion of solute to solvent at the interface than in the bulk of solution. Substances which reduce the surface tension are said to be surface active agent. On the other hand, if the solute bring about an increase of surface tension of solution, its accumulation on the surface will be less than in the bulk. This type of behaviour is termed as negative adsorption. The exact relationship between adsorption and surface tension was given by J.W. Gibbs and is known as "Gibbs Adsorption equation". Glasston (1946) derived the equation on the basis of chemical potential (μ). In the presence of two phases (α and β), the surface (surface phase) is located in between the phase α and phase β. Experimentally, it is difficult to determine the exact structure of an inhomogeneous surface phase that is contact with a bulk liquid phase containing more than one solute (Hiemenz et al., 1997). In-homogeneity of the surface phase is a result of variation of mole ratios (Shchukin et al., 2001).

A model proposed by Josiah Willard Gibbs proposed that the surface phase as an idealized model that had zero thickness. In reality, although the bulk regions of α and β phases are constant, the concentrations of components in the interfacial region will gradually vary from the bulk concentration of α to the bulk concentration of β over the distance x. This is in contrast to the idealized Gibbs model where the distance x takes on the value of zero. The Figure: 5.3 illustrate the differences between the real and idealized models.

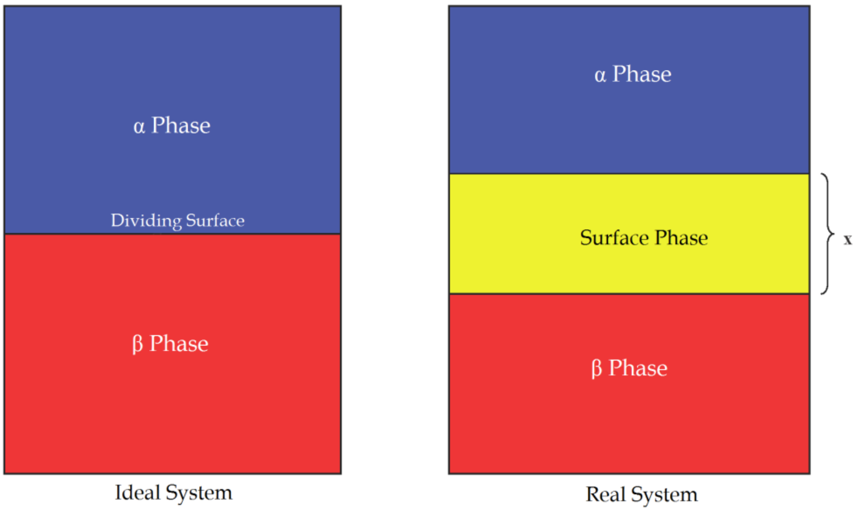


Figure 5.3: Comparison between the real and idealized models of the surface

In the idealized model, the chemical components of the α and β bulk phases remain unchanged except when approaching the dividing surface (Chattoraj and Birdi, 1984). The total moles of any component (Examples: water, ethylene glycol etc.) remains constant in the bulk phases but varies in the surface phase for the real system model as shown in Figure: 5.4.

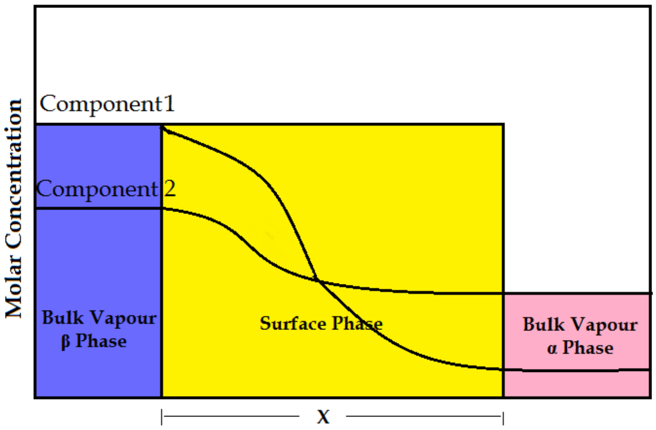


Figure 5.4: Variation in the concentration of components in the Surface phase of the real model

In the real system, however, the total mole of a component varies depending on the arbitrary placement of the dividing surface. The quantitative measure of adsorption of the i^{th} component is captured by the surface excess quantity (Shchukin et al., 2001). The surface excess represents the difference between the total moles of the i^{th} component in a system and the moles of the i^{th} component in a particular phase (either α or β) and is represented by:

$$\Gamma_i = \frac{n_i^{Total} - n_i^{\alpha} - n_i^{\beta}}{A}$$

where Γ_i is the surface excess of the i^{th} component, n are the moles, α and β are the phases, and A is the area of the dividing surface.

Γ represents excess of solute per unit area of the surface over what would be present if the bulk concentration prevailed all the way to the surface, it can be positive, negative or zero. It has units of mol/m^2.

For a two-phase system consisting of the α and β phase in equilibrium with a surface s dividing the phases, the total Gibbs free energy of a system can be written as:

$$G = G^{\alpha} + G^{\beta} + G^{S}$$

where G is the Gibbs free energy.

The equation of the Gibbs Adsorption Isotherm can be derived from the "particularization to the thermodynamics of the Euler theorem on homogeneous first-order forms" (Callen, 1985). The Gibbs free energy of each phase α, phase β and the surface phase can be represented by the equation:

$$G = U + pV - TS + \sum_{i-1}^{k} \mu_i n_i$$

where U is the internal energy, p is the pressure, V is the volume, T is the temperature, S is the entropy, and μ_i is the chemical potential of the i-th component.

By taking the total derivative of the Euler form of the Gibbs equation for the phase, β phase and the surface phase:

$$\mathrm{d}G = \sum_{\alpha,\beta,S} \left(\mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T + \sum_{i=1}^{k} \mu_i \,\mathrm{d}n_i + \sum_{i=1}^{k} \mathrm{n}_i \,\mathrm{d}\mu_i \right) + A\mathrm{d}\gamma + \gamma \mathrm{d}A,$$

where A is the cross sectional area of the diving surface, and γ is the surface tension.

For reversible processes, the first law of thermodynamics requires that:

$$\mathrm{d}U = \delta q + \delta w,$$

where q is the heat energy and w is the work.

$$\delta q + \delta w = \sum_{\alpha,\beta,S} \left(T\mathrm{d}S - p\mathrm{d}V - \delta w_{\text{non-pV}} \right).$$

Substituting the above equation into the total derivative of the Gibbs energy equation and by utilizing the result γdA is equated to the non-pressure volume work when surface energy is considered:

$$\mathrm{d}G = \sum_{\alpha,\beta,S} \left(V\mathrm{d}p - S\mathrm{d}T + \sum_{i=1}^{k} \mu_i \,\mathrm{d}n_i + \sum_{i=1}^{k} \mathrm{n}_i \,\mathrm{d}\mu_i \right) + A\mathrm{d}\gamma,$$

by utilizing the Gibbs-Duhem equation of:

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_{i=1}^{k} \mu_i \,\mathrm{d}n_i.$$

The equation relating the α phase, β phase and the surface phase becomes:

$$\sum_{i=1}^{k} \mathrm{n}_i^{\alpha} \,\mathrm{d}\mu_i + \sum_{i=1}^{k} \mathrm{n}_i^{\beta} \,\mathrm{d}\mu_i + \sum_{i=1}^{k} \mathrm{n}_i^{S} \,\mathrm{d}\mu_i + A\mathrm{d}\gamma = 0.$$

When considering the bulk phases (α phase, β phase), at equilibrium at constant temperature and pressure the Gibbs Duhem equation requires that:

$$\sum_{i=1}^{k} \mathbf{n}_i{}^{\alpha} \, \mathbf{d}\mu_i = \sum_{i=1}^{k} \mathbf{n}_i{}^{\beta} \, \mathbf{d}\mu_i = 0.$$

The resulting equation is the Gibbs adsorption isotherm equation:

$$\sum_{i=1}^{k} \mathbf{n}_i{}^{\mathbf{S}} \, \mathbf{d}\mu_i + A\mathbf{d}\gamma = 0.$$

The Gibbs adsorption isotherm is an equation which could be considered an adsorption isotherm that connects surface tension of a solution with the concentration of the solute. For a binary system containing two components the Gibbs Adsorption Equation in terms of surface excess is:

$$-\mathbf{d}\gamma = \Gamma_1 \mathbf{d}\mu_1 + \Gamma_2 \mathbf{d}\mu_2.$$

A theoretical analysis of adsorption from solution leading to a suitable equation of the adsorption process is much more difficult than for adsorption from the gaseous phase, mainly for two reasons: Firstly, the thermal motion of molecules in the liquid phase their mutual interaction and phase behaviour of liquid are much less understood then the corresponding properties of gases. Secondly, in adsorption from solution at least two components compete for the available surface of the adsorbent.

One of the fundamental problems in solution adsorption is the nature of the adsorbed phase. The properties of adsorbed phase depend especially on the porosity and the chemical nature of the adsorbents, the concentration of solution, and miscibility of the components. According to Kiselev et al., (1956) and Dzhigit et al., (1947) these factors determine whether monomolecular or multi molecular adsorption will occur or whether process similar to capillary condensation of gases will takes place. The state of adsorbed phase has also been investigated by many other authors

Electrolytes may be adsorbed in two basically different ways. In the first, only one of the two ions is preferentially adsorbed on the solid surface. This mode of adsorption is known as ionic adsorption. In the second mode - molecular adsorption, either both kinds of ions are adsorbed on the surface to the same extent or the non dissociated molecule is adsorbed. The second also includes the adsorption at non-electrolytes. In the ionic adsorption the originally neutral adsorbent may gain surface electric charge by the adsorption of an ion, a different ion may pass into the solution in exchange for it or when anions are adsorbed, H^+ ion, formed by hydrolysis, may be adsorbed simultaneously. The first is an instance of exchange adsorption and the second one of hydrolytic adsorption. In both, the adsorbent remains electro-neutral or retains its original charge.

5.1.5 Adsorption Isotherm

If the temperature is kept constant, then for a given adsorbent-adsorbate system depends on the equilibrium pressure, and the equilibrium can be represented as

$$x/m = f(P) \quad [T=\text{Constant}]$$

Such equilibrium is called an adsorption isotherm. Adsorption is usually described by isotherms which show how much solute can be adsorbed by the adsorbent at a given temperature. An adsorption isotherm relates the concentration of solute on the surface of the adsorbent to the concentration of the solute in the fluid with which the adsorbent is in contact. These values are usually determined experimentally, but there are also models to predict them, both for single metal adsorption and multi component adsorption. Although the Langmuir and the Freundlich adsorption isotherms are the two well established types of adsorption isotherms for single metal adsorption, there are other equations which model adsorption equilibrium. Table 5.1 shows the other main equations. The adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. It can give useful information regarding the adsorbate, the adsorbent, and the adsorption process. It helps in the determination of the surface area of the adsorbent, the volume of the pores, and their size distribution, the heat of adsorption, and the relative absorbability of a solid, gas or a vapour on a given adsorbent.

The more important adsorption isotherms are the Langmuir, the Freundlich, the Temkin, the Brunauer-Emmett-Teller (BET), and the Dubinin equations. The first three isotherm equations are very important for chemisorption, although the Langmuir and Freundlich isotherms are equally important for physisorption. There are three possible theoretical approaches for deriving adsorption isotherms:

- The kinetic approach
- The statistical approach
- The thermodynamic approach

In the kinetic approach, the condition of the equilibrium is that the rate of adsorption is equal to the rate of desorption at equilibrium. Equating the two rates in an isotherm equation can be obtained. In the statistical approach, the equilibrium constant is represented by a ratio of partition functions of vacant sites, adsorbed molecules, and the gas-phase molecules. The isotherm equation can be obtained by equating this ratio to the corresponding ratio of concentrations; this approach has the advantage that it gives numerical value to the constants that cannot be evaluated by the kinetic approach. The equilibrium can also be approached thermodynamically, using either the conditions that the work done in transferring an infinitesimal amount of gas from the gas phase to the surface at constant temperature is zero, or alternatively the Gibbs adsorption equation. In this manuscript, mainly two adsorption isotherm equations are concentrated and experimental data was verified with these isotherms.

Langmuir Adsorption isotherm

The Langmuir isotherm equation is the first theoretically developed adsorption isotherm. Many of the equations proposed later and which fit the experimental results over a wide range are either based on this equation, or these equations have been developed using the Langmuir concept. The equation has also been derived using thermodynamic and statistical approaches but we shall discuss the commonly used kinetic approach for its derivation. Langmuir derived this equation based on certain assumptions. More important of these assumptions are

- The adsorbed entitles (atoms or molecules or ions) are attached to the surface at definite localized sites.
- Each site accommodates one and only one adsorbed entity.
- The energy state of each adsorbed entity is the same at all sites on the surface independent of the presence or absence of other absorbed entities at neighbouring sites. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

Thus, the Langmuir model assumes that the surface is perfectly smooth and homogenous and that the lateral interactions between the adsorbed entities are negligible. For liquids (adsorbate) adsorbed on solids (adsorbent), the Langmuir isotherm can be expressed by

$$q= \frac{q_{max}\ k.C}{1+kc}$$

Where q is the substance amount of adsorbate adsorbed per gram of the adsorbent. q_{max} is the maximal substance amount of adsorbate per gram of the adsorbent. The constant, k is called the adsorption constant and C is the concentration of adsorbate in liquid.

The Langmuir isotherm model was used to evaluate the adsorption equilibrium data. The linear form of the Langmuir equation is given by,

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m} C_{eq} + \frac{1}{q_m K_L}$$

Table 5.1: Equations of some Isotherm model for adsorption Equilibrium.

Isotherm	**Equation**	**Observations**
Freundlich	$q_e = a_F C_{eq}^{b_F}$	a_F and b_F are empirical parameters. b_F is usually <1 (Gerente *et al.*, 2007).
Langmuir	$q_e = \frac{q_{e,\max} b C_{eq}}{1 + b C_{eq}}$	$q_{e,max}$ is the maximum adsorption capacity and b is a constant (Gerente *et al.*, 2007).
BET	$q_e = \frac{q_{e,\max} K_b C_{eq}}{(C_s - C_{eq})\left[1 + (K_b - 1)\frac{C_{eq}}{C_s}\right]}$	$q_{e,max}$ is the maximum adsorption capacity, K_b is a dimensionless constant; C_s is the concentration at which all sites are saturated. This model is valid for multiply layers on a homogeneous surface (Do, 1998).
Redlich – Peterson	$q_e = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{b_R}}$	K_R and a_R are constants. The exponent b_R lies between 0 and 1 (Gerente *et al.*, 2007).
Temkin	$q_e = \frac{RT}{b_T} \ln(A_T C_{eq})$	R is the universal gas constant, T is absolute temperature, A_T and b_T are constants (Gerente *et al.*, 2007).
Dubinin – Radushkevich	$q_e = q_D \exp(-B_D \varepsilon^2)$ $\varepsilon = RT \ln\left(\frac{P}{P_o}\right)$	q_D is the Dubinin–Radushkevich monolayer capacity, B_D is a constant related to the mean free energy of sorption per mole of the sorbate, ε is the Polyani potential which is related to equilibrium concentration, P is the pressure of adsorbed species and P_o is the saturated vapour pressure (Do, 1998).

The applicability of the Langmuir isotherm equation to the experimental data was carried out by a large number of workers, but deviations were often noticed. According to the Langmuir isotherm equation, the plot of C_{eq}/q_{eq} against C_{eq} should be linear. When the experimental data was subjected to these criteria, only few data conformed to Langmuir model. Numerical values of q_e, max, the maximum adsorbable concentration of metallic ions, and K_L, the Langmuir adsorption equilibrium constant were determined from the slope and intercept of the linear form of the Langmuir isotherm, and by non-linear fitting of the Langmuir equation. According to Hall et al., (1966), the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, expressed by Equation, Separation factor $R_L = 1/(1 + K_LC_e)$

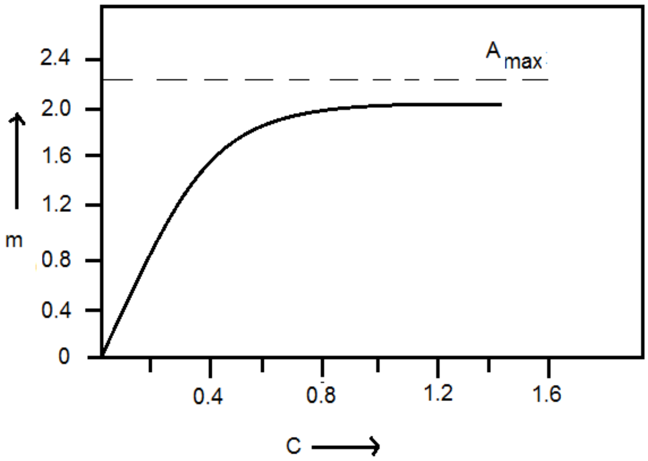


Figure 5.5: Langmuir Adsorption Isotherm

Furthermore, the Langmuir theory requires the heat of adsorption to be independent of the surface coverage while direct determinations of heat of adsorption are found to decrease invariably with increasing surface coverage. Thus, although Langmuir isotherm equation is of limited significance for interpretation of the adsorption data because of its idealized character, the equation remains of basic importance for expressing dynamic adsorption equilibrium. Furthermore, it has provided a good basis for the derivation of other more complex models. The assumptions that the adsorption sites on solid surfaces are energetically homogenous and that there are no lateral interactions between the adsorbed molecules are the weak points of the Langmuir model.

Freundlich adsorption Isotherm

The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as (Najua et al., 2008):

$$q_e = K_f\ C_e^{1/n}$$

Where q_e is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at equilibrium. K_f and n are the empirical constants dependent on several factors and n is greater than one. This equation is conveniently used in linear form by taking the logarithmic of both sides of the above equation.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

A plot of ln q_e against ln C_e yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants n and K can be determined from the slope and the intercept respectively.

Types of Adsorption Isotherm:

Five different types of adsorption isotherm and their characteristics are explained below.

(i) Type I Adsorption Isotherm:

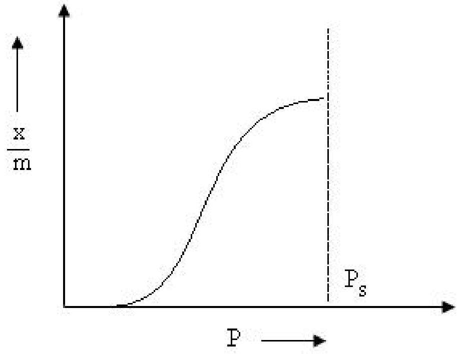


Figure 5.6: Type I Adsorption Isotherm

- The graph in Figure:5.6 depict Monolayer adsorption.
- This graph can be easily explained using Langmuir Adsorption Isotherm.
- Examples of Type-I adsorption are Adsorption of Nitrogen (N_2) or Hydrogen (H) on charcoal at temperature near to -180^{0}C.

(ii) Type II Adsorption Isotherm:

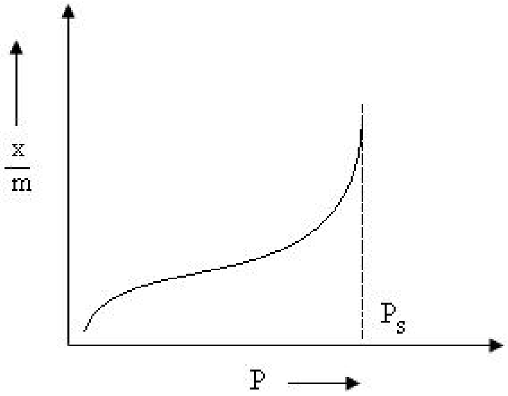


Figure 5.7: Type II Adsorption Isotherm

- Type II Adsorption Isotherm represented in Figure:5.7 show large deviation from Langmuir model of adsorption.
- The intermediate flat region in the isotherm corresponds to monolayer formation.
- Examples of Type-II adsorption are Nitrogen (N_2 (g)) adsorbed at -195^{0}C on Iron (Fe) catalyst and Nitrogen (N_2 (g)) adsorbed at -195^{0}C on silica gel.

(iii) Type III Adsorption Isotherm:

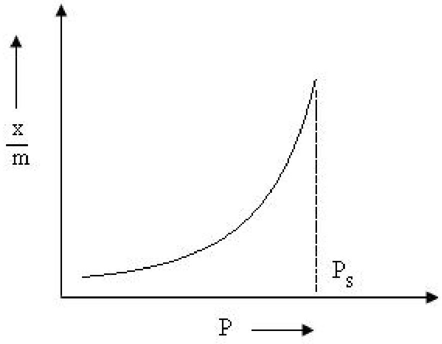


Figure 5.8: Type III Adsorption Isotherm

- Type III Adsorption Isotherm depicted in Figure:5.8 also show large deviation from Langmuir model.
- In BET equation value if C <<< 1 Type III Adsorption Isotherm obtained.
- This isotherm explains the formation of multilayer.
- There is no flattish portion in the curve which indicates that monolayer formation is missing.
- Examples of Type III Adsorption Isotherm are Bromine (Br_2) at 79^{0}C on silica gel or Iodine (I_2) at 79^{0}C on silica gel.

(iv) Type IV Adsorption Isotherm:

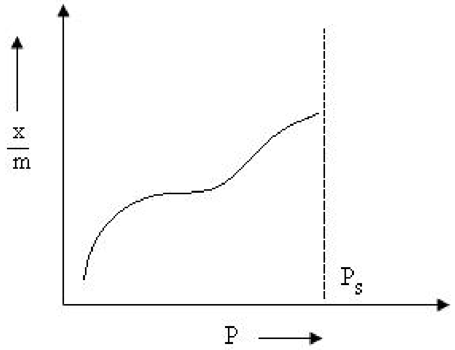


Figure 5.9: Type IV Adsorption Isotherm

- At lower pressure region of graph in Figure:5.9 are quite similar to Type II. This explains formation of monolayer followed by multilayer.
- The saturation level reaches at a pressure below the saturation vapour pressure .This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure (P_S) of the gas.
- Examples of Type IV Adsorption Isotherm are of adsorption of Benzene on Iron Oxide (Fe_2O_3) at 50^0C and adsorption of Benzene on silica gel at 50^0C.

(v) Type V Adsorption Isotherm:

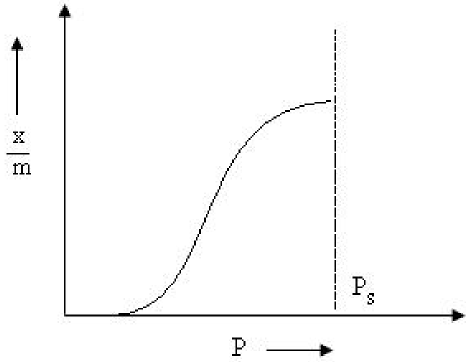


Figure 5.10: Type V Adsorption Isotherm

- Explanation of Type V graph in Figure:5.10 are similar to Type IV.
- Example of Type V Adsorption Isotherm is adsorption of Water (vapours) at 100^0C on charcoal.
- Type IV and V shows phenomenon of capillary condensation of gas.

5.1.6 Adsorption Mechanism of metal ion

An activated carbon in contact with a metal salt solution is a two-phase system consisting of a solid phase, which is the activated carbon surface, and a liquid phase which is the salt solution. The solution contains varying amounts of different metal ion species and their complexes so that the interface between the two phases will behave as an electrical double layer and determine the adsorption processes taking place in the system. The adsorptive removal capacity of an activated carbon for metal cations from the aqueous solutions generally depends on the physicochemical characteristics of the carbon surface, which include the surface area, pore-size distribution, electrokinetic properties, and the chemical structure of the carbon surface, as well as on the nature of the metal ions in the solution.

Activated carbon surfaces are almost invariably associated with a certain amount of chemisorbed oxygen and hydrogen. These hetero-atoms are derived from the source raw material and become a part of the chemical structure as a result of imperfect carbonization, or they become chemically bonded to the carbon surface during activation or subsequent treatments. In addition, the activated carbons may also become associated with atoms of nitrogen, halogens, and sulphur, but only on treatment with suitable reagents. These hetero-atoms are present on the carbon surface in the form of carbon-oxygen, carbon-hydrogen. Carbon-nitrogen and carbon-sulphur surface compounds, also called surface complexes or surface groups. However, carbon-oxygen surface groups are by far the most important chemical structures that are present on all activated carbons and influence the adsorption characteristics under all practical situations.

In the solution phase, the metal salt undergoes ionization and hydrolysis, which results in the formation of free and complex cationic and anionic species. However, the prevalence of any one or several cations or anions depends upon the concentration and the pH of the solution. For example, for a divalent metal salt MCl_2, the ionization of the salt produces M^{2+} cations, while its hydrolysis can produce $(MOH)^+$, $M(OH)_2$ aq. $M\left(OH\right)_3^-$ and $M\left(OH\right)_4^{2-}$ ions. In addition, small amounts of polynuclear species such as $M_2\left(OH\right)_3^+$ and $M_4\left(OH\right)_4^{4+}$ may also be formed at higher concentrations of the salt in the solution and at suitable pH values.

The most important parameters that influence and determine the adsorption of metals from aqueous solutions are the carbon-oxygen surface functional group present on the activated carbon surface and the pH of the solution. These two parameters determine the nature and the concentration of the charge on the activated carbon surface and the amount and the concentration of the ionic species in the solution. Electrokinetic studies have shown that the nature and the concentration of the carbon surface charge can be modified by changing the pH of the solution. For each carbon there is a pH value where the carbon surface corresponds to zero point charge (pH_{ZPC}). The carbon surface has a positive charge below zero point charge (ZPC) and a negative charge above ZPC up to a certain range of pH of the solution.

The origin of the positive charge has been attributed to the presence of the basic surface groups, the excessive protonation of the surface at low pH values of the solution, and to graphene layers that act as Lewis bases, resulting in the formation of acceptor-donor complexes with water molecules. However, the information regarding the relative contribution of basic oxides and graphene layers has not been very well elucidated in the literature. Radovic (2004) has rightly pointed out that the repulsive electrostatic interactions between the adsorbate metal ions and the graphenes layers are more "detrimental for adsorbent effectiveness" than the repulsion from the basic surface oxygen groups. The negative charge on the carbon surface at higher pH values (>pH = ZPC) is due to the ionization of the acidic surface oxygen groups.

The above description of the activated carbon solution system makes it easier to visualize the mechanisms involved in the adsorptive removal of metals from aqueous solutions by activated carbons. When in solution the acidic surface oxygen groups present on the activated carbon surface undergo ionization producing H^+ ions, the degree of ionization depending upon the pH of the solution. The degree of ionization is very low at pH values lower than ZPC and is very high when the pH of the solution is above ZPC.

The H^+ ions are directed toward the liquid phase, leaving the carbon surface with negatively-charged sites. This results in attractive electrostatic interactions between the negatively-charged surface sites, and the positively-charged metal cations in the solution. When the activated carbon surface is given an oxidative treatment, the number and the concentration of the acidic surface groups and hence those of the negatively charged sites increase, resulting in higher attractive interactions and an increase in the adsorption of metal cations. Similarly, when these acidic surface groups are removed from the carbon surface by degassing, the attractive electrostatic interactions as well as the adsorption decrease, the decrease in adsorption depending upon the decrease in the number of acidic groups eliminated from the carbon surface.

Bansal and coworkers (Goyal et al.,2001; Chang, C. and Ku,1998; Aggarwal et al., 1999; Bansal et al., 2002) carried out systematic studies on the adsorptive removal of several metal cations on different granulated and fibrous activated carbons by enhancing and removing gradually the amounts of acidic carbon-oxygen surface groups. These workers found even a linear relationship between the amount of metal ion adsorbed and the surface acidity of the given carbon. In the case of heat-treated carbons, Biniak et al.(2001) while studying the adsorption of copper, have suggested that the mechanism could involve dipole-dipole (π-d) interactions between the graphene layers and the metal ionic species.

A surface complexation model is often used to describe adsorption behaviour (Sposito, 1989). Several types of surface complexes can form between a metal and adsorbent surface functional groups and are defined by the extent of bonding between the metal ion and the surface (Figure:5.11). Metals in a diffuse ion association or in an outer sphere complex are surrounded by waters of hydration and are not directly bonded to the adsorbent surface. These ions accumulate at the interface of the charged surfaces in response to electrostatic forces. These reactions are rapid and reversible with only a weak dependence on the electron configuration of the surface group and the adsorbed ion. These two metal-surface interactions have also been termed exchange reactions because the introduction of other cations into the system, in sufficient concentration, causes the replacement or exchange of the original cations. Metals associated with exchange sites may, depending on the environment, be relatively mobile. Exchangeable metals may be the most significant reserve of potentially mobile metals in soil (Silveira and Sommers, 1977; Latterell et al., 1978).

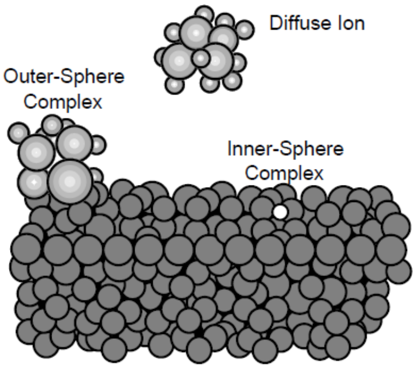


Figure 5.11: The three mechanism of cation adsorption on siloxane surface (Sposito,1989)

With inner sphere complexation, the metal is bound directly to the adsorbent surface; no waters of hydration are involved. It is distinguished from the exchangeable state by having ionic or covalent character to the binding between the metal and the surface. A much higher bonding energy is involved than in exchange reactions, and the bonding depends on the electron configuration of both the surface group and the metal. This adsorption mechanism is often termed specific adsorption. The term specific implies that there are differences in the energy of adsorption among cations, such that other ions, including major cations, Na, Ca, Mg, do not effectively compete for specific surface sites. Specifically adsorbed metal cations are relatively immobile and unaffected by high concentrations of the major cations due to large differences in their energies of adsorption.

At low concentrations, metals are adsorbed by the specific adsorption sites. These adsorbed metals are not removed by the input of major cations. With increasing concentration of the metal, the specific sites become saturated and the exchange sites are filled (Hendrickson and Corey, 1981; Lehmann and Harter, 1984; Garcia-Miragaya et al., 1986; O'Connor et al., 1984;). Metals associated with these non specific sites are exchangeable with other metal cations and are thus potentially mobile.

5.2 Adsorbent: Properties and Classification

5.2.1 Introduction

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Adsorption occurs when the attractive forces at the adsorbent surface overcome the attractive forces of the liquid. Adsorption can perform many separations that are impossible or impractical by conventional techniques, such as distillation, absorption, and even membrane-based systems. Lately, applications for adsorption have expanded rapidly because of sharply rising environmental or quality requirements. Likewise, advances in adsorbent technology have made it possible to meet many of those demands. Recently developed adsorbents are now available "off-the-shelf," and in most cases they can perform satisfactorily. Nevertheless, new adsorbents are constantly being synthesized that have dramatically improved properties which translate into better performance. There exist hundreds, if not thousands, of different applications of adsorption (Park and Yang, 2005), but we are looking at adsorbent selection rather than process selection.

5.2.2 Selection of Adsorbent

The most important attributes of an adsorbent for any application are: adsorption capacity, selectivity, regenerability, kinetics, compatibility, and cost. Rarely will a single adsorbent be optimal in all these respects. Frequently it will be possible to narrow the choice to one or two classes of adsorbents, but that still commonly leaves a vast array of possibilities (Kent S. Knaebel, 2010).

Adsorption capacity (or "loading") is the most important characteristic of an adsorbent. Simply stated, it is the amount of adsorbate taken up by the adsorbent, per unit mass (or volume) of the adsorbent. The adsorption capacity (mg/g) is affected by the physical and chemical characteristics of the adsorbent (surface area, pore size, diameter, chemical composition) and adsorbate (molecular size, vapour pressure and boiling point, liquid density, molecular polarity, chemical composition), the concentration of the adsorbate in the liquid phase (solution), the characteristics of the phase (pH, temperature, pressure, humidity), the contact time and the data are plotted as an isotherm (loading versus concentration at constant temperature). Surface area is a relative term, usually measured by inferring the monolayer coverage within an adsorbent of a substance with known density and molecular dimensions. The pore size distribution is a related property that indicates the fraction of the space within a particle occupied by micro pores, meso pores and macro pores. Pore dimensions intuitively correlate with both capacity and kinetics, but the exact dependence is subtle. The Iodine Number is a rough measure of capacity for small molecules and correlates with surface area. The Molasses Number was developed for decolourisation of cane sugar, and relates to adsorption of large molecules from a liquid. Figure 5.12 shows the pore size distributions of some common adsorbents.

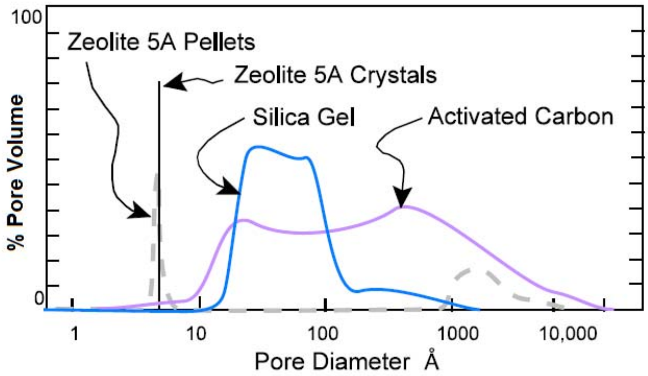


Figure 5.12: Pore size distribution of some common adsorbentsv (Kent S. Knaebel, 2010).

Selectivity is the ratio of the capacity of one component to that of another at a given fluid concentration. That ratio generally approaches a constant value as concentration drops towards zero. All cyclic adsorption applications rely on **Regenerability**, so that the adsorbent can operate in sequential cycles with uniform performance. This means each adsorbable component (adsorptive or adsorbate) must be relatively weakly adsorbed (or physisorbed). The heat of adsorption provides a measure of the energy required for regeneration, and in that regard low values are desirable. Regeneration might be accomplished by a thermal swing, pressure swing, chemical (e.g., by displacement, elution, or supercritical extraction), or sometimes by a combination of those. Displacement would involve introducing a species that adsorbs more strongly than the adsorbate of interest, while elution would entail dissolving the adsorbed material by a solvent that is weakly adsorbed if at all.

Mass transfer kinetics is a catch-all term related to intra-particle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process. **Compatibility** covers various possible modes of chemical and physical attack that could reduce the life expectancy of the adsorbent, such as biological fouling or attrition. **Cost** is perhaps the most subtle characteristic to understand because it may vary from week to week even for the same exact material.

5.2.3 Adsorbent Classification

Most minerals and many synthetic inorganic materials have been tried as adsorbents. Some of them are alumina, silica, and zeolite. A wide variety of organic materials have been used as for "sorption," besides activated charcoal or charcoal. Some might function as solid "absorbents" rather than adsorbents. Among these are cellulose (the most abundant biopolymer in nature), chitin (the second most abundant biopolymer in nature), collagen, wool, starch-polyacrylamide gels (which absorb many times their own weight of water at ambient temperature, but release most of it by gentle heating), polysaccharrides derived from corn, and miscellaneous forms of biomass (e.g., residue from crop harvests).

5.2.3.1 Inorganic Materials

Most minerals and many synthetic inorganic materials have been tried as adsorbents. Some have been successful, despite being poor adsorbents, simply because they were so inexpensive. Others have turned out to be immensely effective adsorbents. Conversely, some inorganic materials may act more as "absorbents" than adsorbents, but have applications from drying to recovery of PCBs. Many other inorganic adsorbents have been developed recently, such as pillared clays, aluminophosphates, and mesoporous adsorbents, which have not yet achieved that level of prominence. The inorganic adsorbents covered below are commercial products, and are frequently encountered (Kent S. Knaebel, 2010).

(i) Alumina

Activated alumina is produced from hydrated alumina, Al_2O_3 A $_n$ H_2O, where n=1 or 3, by dehydration (calcining) under carefully controlled conditions to get n=0.5. It is a white or tan, opaque material that has a chalky appearance. Stable crystalline forms are usually not thought of as adsorbents due to their low surface areas. Conversely, transitional forms, such as gamma and eta alumina, have defect spinel forms which lead to higher concentrations of surface acid sites. Corresponding effective surface areas are from 200 to 400 m^2/g. Common forms are balls 1 to 8 mm dia., granules, extrudates (pellets) 2 to 4 mm dia., and powder. The two widest uses of activated alumina are as a catalyst (or catalyst support) and as a desiccant. Ancillary uses as an adsorbent are for removal of: oxygenates and mercaptans from hydrocarbon feed streams, fluoride ions from water, HCl from hydrogen in catalytic reforming, and others. Pre-treatment, for most gas-phase applications, requires heating to about 250°C.

(ii) Silica

Silicas are generally clear or faintly tinted, and transparent or translucent. Some silica gels, however, are manufactured with alumina blended in, and this yields an appearance of alumina, viz., opaque and white or tan. Several forms are available that encompass diverse types of silica gel, porous boro-silicate glass, and aerogels. Effective surface areas range from 300 to 900 m^2/g, depending on the density, with more dense materials having finer pores and larger surface areas. Common forms are beads 1 to 3 mm dia., granules, extrudates (pellets) 2 to 4 mm dia., and powder. The widest uses of silica gel and porous glass are as a desiccant. Ancillary uses as an adsorbent are for separation of hydrocarbons, dewpoint reduction for natural gas, and drying of liquid hydrocarbons. Pretreatment, for gas-phase applications (especially as a desiccant), requires heating to about 200°C.

(iii) Zeolites

Most zeolites are aluminosilicates which could be thought of as stoichiometric blends of the two previous adsorbents, silica and alumina (Kent S. Knaebel, 2010). Thus, they are generally white, opaque and chalk-like in appearance. One would think that given their make-up, all zeolites would be hydrophilic. Accordingly, most that have significant alumina content are hydrophilic, while those that are predominately silica are hydrophobic. Internally, zeolites are inherently crystalline and exhibit micropores within those crystals that have uniform dimensions. The micropores are so small and uniform that they commonly can distinguish nearly identically sized molecules. As a result they have been called "molecular sieves." Frequently there is water of hydration within the crystals, and in order to balance the charges, cations are associated with the alumina. The common empirical formula for a zeolite containing a single cation, M, of valence, n, is: $M_2/n\ CAl_2O_3\ C_x\ Sit\ C_y\ H_2O$, where x is the silica-to-alumina ratio (generally 1 to 5), and y is the molar water of hydration.

5.2.3.2 Organic Materials

These include adsorbents that are based on organic material, whether synthetic or naturally occurring. A wide variety of organic materials have been used as for "sorption," besides activated charcoal or charcoal. Some might function as solid "absorbents" rather than adsorbents. Among these are cellulose (the most abundant biopolymer in nature), chitin (the second most abundant biopolymer in nature), collagen, wool, starch-polyacrylamide gels (which absorb many times their own weight of water at ambient temperature, but release most of it by gentle heating), poly saccharrides derived from corn, and miscellaneous forms of biomass (e.g., residue from crop harvests). Some of these may have niches, but none would be considered a general purpose adsorbent.

(i) Polymers

Polymeric adsorbents tend to be opaque spherical beads, but the colour depends strongly on the product. Most commonly they are white or tan, but some are brown, orange, or black. The first materials were originally the inert particles that would otherwise have been further treated to make macroporous or macroreticular ion exchange resins. As such, they were typically polystyrene/divinylbenzene copolymers having a spherical shape and high pore volume. Some are still that sort of by-product, but most are manufactured separately, with high performance in adsorption as their purpose. Internally, the polymer beads contain "microbeads" that are joined together at a few points each, creating a macropore structure. Each micro bead is usually comprised of a gel, but may be made porous.

In addition, some polymeric adsorbents are activated via pyrolysis, in much the same way as carbon (yielding the black materials alluded to above), yet the particles retain their strength and spherical shape. The effective surface area is usually smaller than for activated charcoal, e.g., 5 to 800 m^2/g. The corresponding pore diameters ranged from about 20 to 2,000 D, or from 3 to 2000 D if activated. The available forms are fairly limited: beads of 0.3 to 1 mm dia., usually in a relatively narrow range. Chitin and chitosan are some examples of biopolymer and are nitrogenous polysaccharides that are made up of Acetylglucosamine and glucosamine unit, which can be used as an adsorbent.

(ii) Activated carbon

Although the choices among zeolites are immense, activated carbons are even more diverse. The base materials that comprise activated carbons include: wood, coal, peat, coconut shells, saran, recycled tires, and others. Activation produces a distribution of internal pores, and affects the carbon surface (e.g., graphitic versus oxidized), generally to enhance its adsorptive capacity. Thus, by varying activation conditions, differences of the internal surfaces can be induced, even for materials that appear to be identical. The microscopic structure (pore size distribution and surface area), surface qualities, and chemical composition all strongly affect adsorption characteristics, and they therefore affect the performance parameters like capacity, selectivity, regenerability, kinetics, compatibility, and cost. Effective surface areas generally range from 300 to 1,500 m^2/g, depending on the base material, activation method, density, etc., although some made from petroleum coke exceed 3,000 m^2/g. Surface areas are treated about the same as engine horsepower or displacement are for automobiles: those with the largest tend to imply that they are the best.

In the present study for the removal of heavy metals was carried out using synthetic and natural organic adsorbents. The adsorbents selected were Activated Charcoal extra pure food grade and Chitosan. About 100g of Adsorbent was procured from an ISO 9001:2008 certified manufacturers of Laboratory and industrial chemicals- NICE Chemicals, Edapally, Kochi. Chitosan was procured from India Sea foods, Kochi. The specification of the selected adsorbent activated charcoal is given in specification.

5.3 Activated Charcoal as Adsorbent

5.3.1 Definition

Activated charcoal (Ac.C) is a solid, porous, black carbonaceous material and tasteless. Marsh (1984) and Jian (1997) defined Ac.C as a porous carbon material, usually chars, which have been subjected to reaction with gases during or after carbonization in order to increase porosity. AC is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface (Figure: 13). Ac.C is an organic material that has an essentially graphitic structure. The main features common to all AC are; graphite like planes which show varying degrees of disorientation and the resulting spaces between these planes which constitute porosity, and the unit built of condensed aromatic rings are referred to as Basic Structure Units (BSU) (Benaddi, 2000).

Benaddi (2000) also stated that AC.C is predominantly an amorphous solid with a large internal surface area and pore volume. Cokes, chars and activated charcoal are frequently termed amorphous carbon.

Activated Charcoal or Activated carbons form a large and important class of porous solids having found a wide range of technological applications. As a consequence, the porous structures of these materials and their adsorption of gases, vapours, and liquids have been extensively studied. The activated charcoal processing method involved two types of activation, physical and chemical activation. The development of porosity in activated charcoals can be achieved by physical activation, i.e., by reaction of the carbon with oxidizing gases (steam, carbon dioxide, and air) and by chemical activation. i.e. by reaction of carbon precursors with reagents, such as Phosphoric acid and Zinc Chloride.

5.3.2 Properties

Activated charcoal (Ac.C) powder was introduced in the early twentieth century. Ac.C powder is a natural substance. It was used at that time to remove colour from sugar and to improve the taste and smell of water. Also called activated absorbent charcoal and medicinal charcoal, Ac.C powder is still used today, primarily for health care purposes. Though this black powder is quite fine in texture, Ac.C powder has significant binding power, making it an effective absorber of toxins and other substances that need to be removed from the body or the environment. Ac.C contains: (a) bulk atoms that are neutral, (b) surface atoms that are the real adsorption atoms and (c) corner atoms that are very reactive and even react with metals.

The adsorption capacity depends as much on the characteristics of the charcoal (primarily its porous texture and the chemical properties of its surface) as on those of the aqueous solution (primarily pH and ionic strength). Both natural and residual waters contain micro-organisms that can be adsorbed on charcoal during water treatment. This process can give rise to the formation of bacteria colonies on the Ac.C (Camper et al., 1986), due to: (1) the adsorptive properties of charcoal, which produce an increase in the concentration of nutrients and oxygen as well as the removal of disinfectant compounds; (2) the porous structure of the charcoal particles, which provides the bacteria with a protective environment; and (3) the presence of a large variety of functional groups on the surface of the charcoal, which enhances the adhesion of the micro organisms. In general, bacteria attached to the charcoal particles are very resistant to disinfectants.

The properties of Ac.C are categorized into two categories: physical and activity properties. Its physical properties are more important in the industrial industry due to how it is classified; commercially made Ac.C is separated into several categories, defined by their physical attributes. Therefore its physical properties have more importance over any activity attributes. Ac.C's physical properties involve its porosity and chemical makeup. Ac.C is very porous; its surface area is nearly 1500 m^2/g, equalling one tablespoon. Its surface makeup is described as being sponge-like, riveted with microscopic holes and crevices similar to sand paper. The physical structure of Ac.C is only viewable with a microscope, however, due to the small surface area of the holes and rivets. It appears smooth and granite like when observed by the naked eye.

Figure 5.13: Photograph of activated Charcoal procured for the study

Ac.C binds to surfaces by attracting dissimilar bonds within its structure, which is commonly referred to as Van der Waals force. This is how Ac.C commonly binds to other surfaces. However, due to the properties of Ac.C, it only binds with certain chemicals, such as ammonia, inorganic compounds, alcohols, and iodine. Iodine is typically used when binding Ac.C. Iodine is often used because it is easily absorbed by Ac.C, and is the basis for determining its capacity for storing charcoal molecules. Comparing the amount of iodine held within the charcoal's structure helps determine its porosity as well.

5.3.3 Preparation

The preparation involves two main steps: the carbonization of the carbonaceous raw material at temperatures below 800 °C in an inert atmosphere and the activation of the carbonized product (Roop and Meenakshi, 2005). Thus, all carbonaceous materials can be converted into Ac.C, although the properties of the final product will be different, depending on the nature of the raw material used, the nature of the activating agent, and the conditions of the carbonization and activation processes. During the carbonization process, most of the non-carbon elements such as oxygen, hydrogen, and nitrogen are eliminated as volatile gaseous species by the pyrolytic decomposition of the starting material. The residual elementary carbon atoms group themselves into stacks of flat, aromatic sheets cross-linked in a random manner. These aromatic sheets are irregularly arranged, which leaves free interstices. These interstices give rise to pores, which make Ac.C an excellent adsorbent. During carbonization these pores are filled with the tarry matter or the products of decomposition or at least blocked partially by disorganized carbon. This pore structure in carbonized char is further developed and enhanced during the activation process, which converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various sizes and shapes, giving rise to an extended and extremely high surface area of the product. The activation of the char is usually carried out in an atmosphere of air, CO_2, or steam in the temperature range of 800 °C to 900°C. This results in the oxidation of some of the regions within the char in preference to others, so that as combustion proceeds, a preferential etching takes place. This results in the development of a large internal surface, which in some cases may be as high as 2500 m^2/g. Common forms are beads 1 to 3 mm dia., granules, extrudates (pellets) 2 to 4 mm dia., and powder. Generally, the raw materials for the production of Ac.C are those with high carbon but low inorganic contents such as wood, lignite, peat and coal (Lua and Guo, 2001). Beside that, lot of agricultural waste and by product have successfully converted to Ac.C for examples macadamia nutshell (Ahmadpour and Do, 1996), and peach stones (Arriagada, et al., 1997).

5.3.4 Chemical composition and structure

Ac.C has a microcrystalline structure. But this microcrystalline structure differs from that of graphite with respect to interlayer spacing, which is 0.335 nm in the case of graphite and ranges between 0.34 and 0.35 nm in Ac.C. The orientation of the stacks of aromatic sheets is also different, being less ordered in Ac.C. ESR studies have shown that the aromatic sheets in Ac.C contain free radical structure or structure with unpaired electrons. These unpaired electrons are resonance stabilized and trapped during the carbonization process, due to the breaking of bonds at the edges of the aromatic sheets, and thus, they create edge carbon atoms. These edge carbon atoms have unsaturated valencies and can, therefore, interact with heteroatoms such as oxygen, hydrogen, nitrogen, and sulphur, giving rise to different types of surface groups. The elemental composition of a typical Ac.C has been found to be 88% C, 0.5% H, 0.5% N, 1.0% S, and 6 to 7% O, with the balance representing inorganic ash constituents. The oxygen content of an Ac.C can vary, however, depending on the type of the source raw material and the conditions of the activation process.

The structure developed is a function of the carbonisation and activation temperatures. In terms of pore structure, the adsorbent pores can be divided into three basic classes: (1) macropores (> 1000Å), (2) transitional or mesopores and (3) micropores (<10Å). The macropores do not add appreciably to the surface area of the carbon, but provide a passageway to the particle interior and the micropores. The micropores are developed primarily during charcoal activation and result in the large surface area for adsorption to occur.

5.3.5 Application

Some typical applications are: water and wastewater treatment to remove hazardous organic compounds or those that impart odour or taste, cleanup of off-gases containing volatile organic compounds (especially solvents which might be recovered, and odoriferous chemicals which are merely trapped), upgrading methane from substandard natural gas wells, food decolourisation, and pharmaceutical purification. Impregnated Ac.C is widely used in gas masks and to remove other specific contaminants in gas or water. Impregnates include sulphuric acid (for ammonia or mercury), iron oxide (for hydrogen sulphide or mercaptans), zinc oxide (for hydrogen cyanide), and a combination of heavy metal salts (for phosgene, arsine, and nerve gases). Pre-treatment for gas-phase applications is often performed as the last step of manufacture, due to the large quantities employed because it would be impractical to do on-site and requires heating to about 200°C. It is a popular ingredient in colon cleanses products and some nutritional products. While no major problems have been reported, the long-term safety of using nutritional products containing Ac.C powder has not been determined.

5.4 Chitosan as Adsorbent

5.4.1 Structure & properties

Chitin and chitosan, the naturally abundant and renewable polymers have excellent properties such as, biodegradability, bio-compatibility, non-toxicity, and adsorption. Most of the naturally occurring polysaccharides e.g., cellulose, dextrin, pectin, alginic acid, agar, agarose, and carragenas are natural and acidic in nature, whereas chitin and chitosan are examples of highly basic polysaccharides. Their properties include solubility in various media, solution, viscosity, polyelectrolyte behaviour, polyoxysalt formation, ability to form films, metal chelations, optical, and structural characteristics (Peter et al., 2000; Pradip et al., 2004).

Chitin is the second most abundant polymer in nature. Chitin occurs in nature as ordered crystalline micro fibrils forming structural components in the exoskeleton of arthropods (Rinaudo, 2006), its major source being the seafood crustacean (crab, shrimp, prawn, and lobster shells) that are usually disposed as waste material. Depending on its source, three different crystalline polymorphic forms of chitin have been identified: α-chitin (shrimp and crab shells), β-chitin (squid pen), and γ-chitin (stomach cuticles of cephalopoda) (Jang et al., 2004).the structure of chitin and chitosan is given in Figure: 5.14 & 5.15.

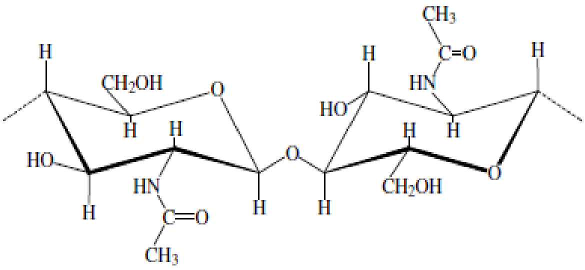


Figure 5.14: Structure of Chitin

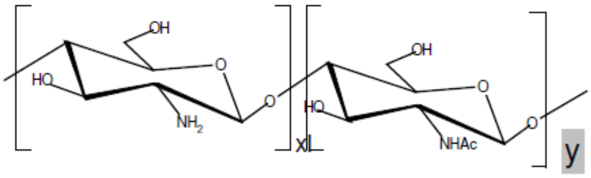


Figure 5.15: Structure of Chitosan

Chitosan is obtained by deacetylation of chitin, which is extracted from the shells of shrimps, crabs and other crustaceans (Figure: 5.16). Chitosan chelates five to six times greater amounts of metals than chitin (Yang et al., 1984) Chitosan has many useful features e.g. hydrophilicity, biocompatibility, biodegradability, anti-bacterial property and remarkable affinity for many proteins (Ravi Kumar, 1999). This polymer is a well known sorbent, effective in the uptake of metal ions, since the amine groups on the chitosan chain can serve as chelation sites for metals. The mechanism by which metal ions are bound by chitosan probably involves attachment of these ions to $-NH_2$ groups. Because of this difference, it may be suitable for scavenging important heavy metal ions and complexes that cannot be adequately treated by other natural polymers (Randall, 1979; Ruey-Shin Juang, 1997). Guibal et al (1995) studied the enhancement of metal ion sorption performances of chitosan. Chitosan displayed a surface controlled sorption mechanism, indicating a monolayer sorption with interactions between the sorbed molecules and heterogeneous distribution of sorption energies. Chitosan interaction with metal ions has also been studied by Schmuhl et al (2001).

Figure 5.16: Photograph of Chitosan used for the study

The chemical properties of chitosan include the following: Linear polymine, Reactive amino groups, Reactive hydroxyl groups available and Chelates many transitional metal ions. The following are the biological properties of chitosan: Biocompatible, Binds to mammalian and microbial cells aggressively, Regenerative effect on connective gum tissue, Accelerates the formation of osteoblast responsible for bone formation, Hemostatic, Fungistatic, Spermicidal, Antitumor, Anticholesteremic, Accelerates bone formation, Central nervous system depressant and Immuno-adjuvant.

5.4.2 Characteristics

Chitosan is a semicrystalline polymer in the solid state (Rinaudo, 2006). Chitosan has been shown to be biologically renewable, biodegradable, biocompatible, non antigenic, non-toxic and biofunctional (Malafaya et al., 2007). The main parameters for its characterization are the deacetylation degree (DD), the crystallinity, and the polymer molecular weight (Guibal, 2004). These parameters may affect its conformation in solution, and its physico-chemical and biological properties (Sorlier et al., 2001). The deacetylation degree controls the fraction of free amino groups that will be available for interactions with metals ions. Infra-red spectroscopy and NMR analysis are the most common methods to evaluate the deacetylation degree. Infrared spectra of chitosan are usually obtained with a frequency range of 4000–400cm^{-1} and the degree of deacetylation (DD) is given by equation (Domszy and Roberts, 1985),

$$\mathrm{DD} = 100 - \left[\frac{A_{1654}}{A_{3450}} \times 100 / 1.33\right]$$

5.4.3 Preparation

Chitin and chitosan are naturally abundant and renewable polymers having properties such as, biodegradability, bio-compatibility, non-toxicity, and adsorption. These are natural resources and are the waste products of the crabbing and shrimp canning industry.

Chitosan is obtained by deacetylation of chitin, which is extracted from the shells of shrimps, crabs and other crustaceans and some fungi. Chitin is a white, hard, inelastic, nitrogenous polysaccharide found in the exoskeleton as well as in the internal structure of invertebrates. The waste of these natural polymers is a major source of surface pollution in coastal areas. The production of chitosan from crustacean shells obtained as a food industry waste is economically feasible, especially if it includes the recovery of carotenoids.

The processing of chitin shells mainly involves the removal of proteins and the dissolution of calcium carbonate that is present in crab shells in high concentrations. The resulting chitin is deacetylated in 40% sodium hydroxide at 120 °C for 1 to 3 hour. This treatment produces 70% deacetylated chitosan. The following four steps in chronological order of the process are needed to produce chitosan from crustacean shells: (i) Deproteinisation, (ii) Demineralization (iii) Decolouration, and (iv) Deacetylation. The flowchart of preparation of chitin is given in Figure: 5.17.

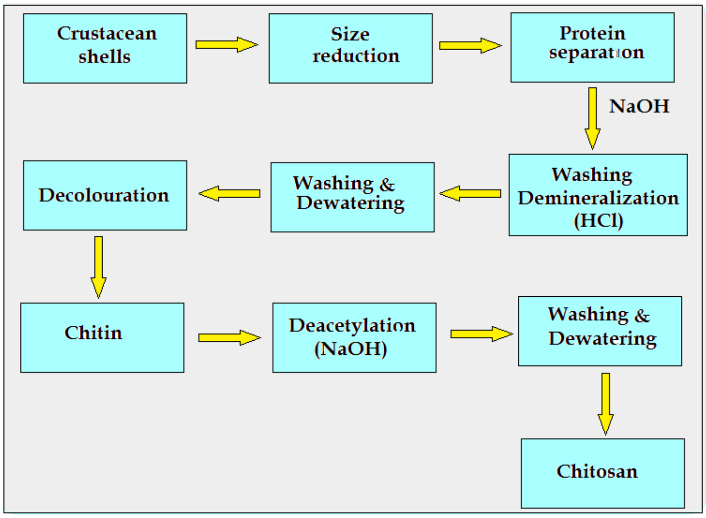


Figure 5.17: Flowchart of the preparation of Chitosan from Crustacean shell

5.4.4 Application of chitosan:

Chitosan has a wide range of applications which depend on its physical, chemical, and biological properties. The principal areas are agriculture, drinking water and waste water treatment, food and beverages, cosmetics and toiletries, biomedics and pharmaceutics, fibres and textiles, and paper technology (Rinaudo, 2006; Ravi Kumar, 2000). Due to its physical and chemical properties, chitosan is being used in a vast array of widely different products and applications, ranging from pharmaceutical and cosmetic products to water treatment and plant protection. In different applications, different properties of chitosan are required. These properties change with, e.g., degree of acetylation and molecular weight as well. Due to its polycationic nature, chitosan can be used as flocculating agent. It can also act as chelating agent, and heavy metals trapper. Weltroswki et al. (1996) used chitosan N-benzyl sulphonate derivatives as sorbents for removal of metal ions in acidic medium.

5.5 Characterisation of Activated Charcoal

5.5.1 Introduction

Characterization for Ac.C is very important in order to classified Ac.C for specific uses. Basically, Ac.C characterized by physical properties and chemical properties. As Guo and Lua (2002) mentioned that the characteristics of activated charcoal depends on the physical and chemical properties of the raw materials as well as activation method used. Physical properties of Ac.C, such as ash content and moisture content can affect the use of a granular Ac.C and render them either suitable or unsuitable for specific applications. While the specific surface area of activated charcoal and surface chemistry is classified as chemical properties. The characterisation of activated charcoal was carried out and the results are tabulated in the Table: 5.2

5.5.2 pH

1.0g of the activated charcoal was shaken for 30 minutes with 20 ml of doubly distilled water and filtered. The pH of the filtrate was measured with Metrohm pH meter. The filtrate showed a value of pH 8.5.

5.5.3 Moisture Content

Activated charcoal is generally quantified on a moisture free basis. Unless packaged in airtight containers, some activated carbons when stored under humid conditions will adsorb considerable moisture over a period of month. They may adsorb as much as 25 to 30% moisture and still appear dry. For many purposes, this moisture content does not affect the adsorptive power, but obviously it dilutes the carbon. Therefore, an additional weight of moist carbon is needed to provide the required dry weight.

5.5.4 Ash content

The ash content of a carbon is the residue that remains when the carbonaceous materials is burned off. As activated charcoal contain inorganic constituents derived from the source materials and from activating agents added during manufacture, the total amount of inorganic constituents will vary from one grade of carbon to another. The inorganic constituents in a charcoal are usually reported as being in the form in which they appear when the carbon is ashed. Ash content can lead to increase hydrophilicity and can have catalytic effects, causing restructuring process during regeneration of used activated carbon. The inorganic material contained in activated charcoal is measured as ash content, generally in the range between 2 and 10% (Yang, 2003).

To determine the content of ash, 2 grams of powdered charcoal was accurately weighed and placed in a porcelain crucible and heated in air in a muffle furnace until the carbon has been completely burned. The temperature should be below 600°C to minimize volatilization of inorganic constituents, and also to leave the ash in a suitable condition for further examination. The ratio of difference in weight to the initial weight taken multiplied by 100 gives the ash content of the Ac.C.

5.5.5 Surface functional group

The selectivity of activated carbons for adsorption is depended upon their surface chemistry, as well as their pore size distribution (Radovic, 2001). Normally, the adsorptive surface of activated carbon is approximately neutral such as that polar and ionic species are less readily adsorbed than organic molecules.

Various surface functional groups containing oxygen, nitrogen and other hetero-atoms have been identified on activated carbon. It because activated carbons have a large porosity and numerous disordered spaces, this makes heteroatom are readily combined on the surface during manufacturing processes (carbonisation and activation). Hetero-atoms are incorporated into the network and are also bound to the periphery of the planes. The hetero-atoms bound to the surfaces assume the character of the functional groups typically found in aromatic compounds, and react in similar ways with many reagents. These surface groups play a key role in the surface chemistry of activated carbon (Qi and Yang, 2003).

There are numerous methods of determining surface functional groups and attempts have been made to study the surface groups by spectroscopic methods, for examples by infrared(IR). Figure 5.18 presents several IR- active functional groups that may be found at the edges of and within graphene layers after the oxidative treatment of active carbon.(a) aromatic c=c stretching;(b)and (c) carboxyl-carbonates; (d) carboxylic acid; (e)lactone(4-membered ring);(f)lactone (5- membered ring); (g) ether brigde; (h) cyclic ether; (i) cyclic anhydride (5-membered ring); (j) cyclic anhydride (6-membered ring); (k) quinine; (l)phenol;(m)alcohol;and(n) ketene.

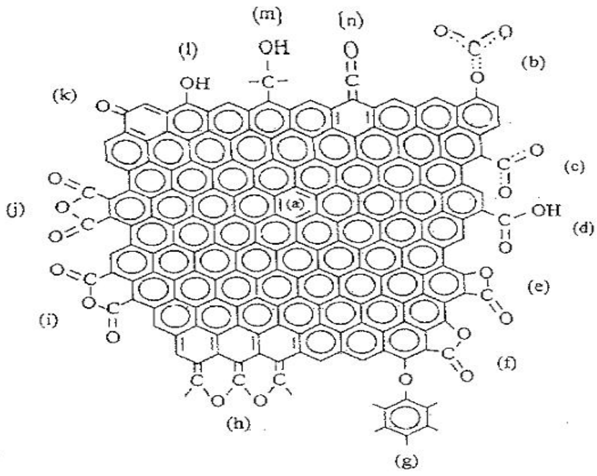


Figure 5.18: IR- active functionalities on carbon surfaces

5.5.6 Surface area

Generally, the larger the specific surface area of the adsorbent, the better its adsorption performance will be (Guo and Lua, 2003). The most widely used commercial active carbons have a specific surface area of the order of 600- 1200 m^2/g. The pore volume limits the size of the molecules that can be adsorbed whilst the surface area limits the amount of material which can be adsorbed, assuming a suitable molecular size. The adsorptive capacity of adsorbent is related to its internal surface area and pore volume.

5.5.7 Porosity study

The porous structure of activated charcoal can be characterized by various techniques such as adsorption of gases (N_2, Ar, Kr & CO_2) or vapours (benzene, water), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image of the activated charcoal used for the present is taken from the Regional Research Laboratory, Thiruvanthapuram. Figure 5.19 depicts the SEM picture of the activated charcoal used for the study.

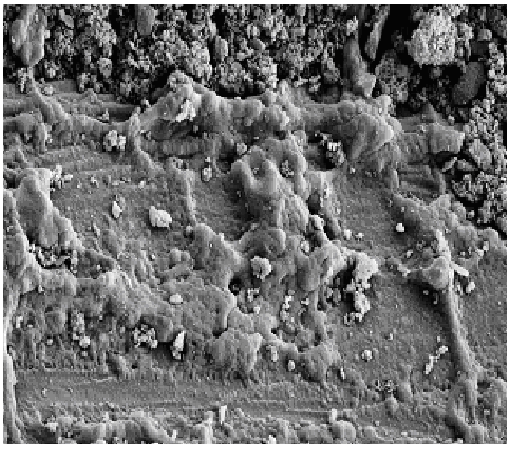


Figure 5.19: SEM image (Mag: X 5000) of activated Charcoal

5.5.8 Bulk and Tap density

Bulk and tap densities of the activated charcoal were measured according to ASTM standard method No. D 2854-70. An empty cylinder of known volume was weighed. It was then filled with activated charcoal and weighed again. During tap density measurement, the cylinder was tapped mechanically while being filled. The value of bulk and tap densities were obtained by dividing weight by volume of the cylinder.

Table 5.2 : Experimentally determined values of different parameters of activated charcoal

Parameter	Value
pH	6.8
Moisture content	3.5%
Carbon Content	74%
Bulk Density	0.531 gm/cm^3
Tap Density	0.687 gm/cm^3
Total surface area	850 m^2/gm
Particle Size	5.5 ±0.2 micron
Iodine Adsorption	700 mg/gm

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Chapter 6

SORPTIONAL BEHAVIOUR OF METAL IONS

Contents

6.1 Introduction

A number of researches have been reported in the literatures using coconut shell and palm kernel shell as raw materials. Table: 6.1 summarises various works with reference to the raw materials using, methods and their application of Ac.C produced. By now, a lot of research has been done on Ac.C in the removal of pollutants from water and is one of the fastest growing areas is in environmental applications such as wastewater treatment. In the treatment of wastewater, it is used for purification, decolourisation and the removal of toxic organics and heavy metal ions (Kim et al., 2003). Recently in most of the countries, many researchers have been focused more on the removal of heavy metal ions such as Cu (Kim et al., 2003), Zn and Cr (Monser and Adhoum, 2002) and Hg (Budinova et al., 2008). But only few works have been done on the removal of metals like Pb, Ni and Cd using activated charcoal. The facts and info about sorption study was hardly observed in the removal of heavy metals using activated charcoal in Cochin Estuarine System.

Table 6.1: Summary of prior work on activated charcoal

Authors	Year	Raw material	Method	Application
Lua and Guo	2001	Oil palm stones	CO_2 activation	SO_2 removal
Hu and Srivinasan	2001	Coconut shell & palm shell	$ZnCl_2$ & CO_2 activation	Phenol, methylene blue
Guo and Lua	2003	Palm shell	H_3PO_4	Ammonia Adsorption
Mozammel et al.	2002	Coconut shell	$ZnCl_2$ activation	Iodine
Hu et al.	2001	Coconut shell and palm seed	$ZnCl_2$ activation	Phenol and dye
Daud and Ali	2004	Palm shell & coconut shell	Physical activation(N_2gas)	Nitrogen Adsorption
Theivarasu et al	2010	cocoa shell	CO_2 activation	Rhodamine-B

The growth of the activated carbon market in the last two decades in the most industrialized region will very probably continue in the near future as more developing areas of the world will realise the importance of controlling water and air pollution. This demand can be satisfied considering the large number of raw material available for the production of Ac.C, the variety of activation processes described, and the available forms of Ac.C. Thus, the continuous research has to be implemented to develop the high quality of Ac.C for specific uses.

The adsorption of heavy metals like Cd, Cu, Fe, Ni, Pb & Zn ions on solids from solutions are significant for three important reasons. (i) The adsorption on solids could be used for the enrichment and pre-concentration of ions in electrolytic solution, (ii) the adsorption process finds its uses in glass manufacture, laser technology and in electrical, chemical and nuclear industries and finally (iii) the most important of all its use for waste disposal of radioactive materials. The adsorption of uranium, thorium, cerium and strontium on activated carbon has been subject of many studies in the past (Hilpert et al., 1985). Little data are available for the adsorption of Cd, Cu, Fe, Ni, Pb & Zn ions on activated charcoal. So the present work describes the investigations of the adsorption of Cd, Cu, Fe, Ni, Pb & Zn ions on activated charcoal. Many investigations are carried out using activated charcoal as adsorbent for the removal of dyes (Yavuz and Aydin, 2006), Tri halo Methane (Robert, 2006), estrogens (Rowsell et al., 2009) and hydrogen sulphide (Cheerawit et al., 2010).

Activated charcoal (Ac.C) was opted as the adsorbent and it is a material with an exceptionally high surface area such that one gram of activated carbon has a surface area of approximately 500 m^2 (for comparison, a tennis court is about 260 m^2). The three main physical carbon types are granular, powder and extruded (pellet). Ac.C is frequently used in everyday life, in: industry, food production, medicine, pharmacy, military, etc. In pharmacy, Ac.C is considered to be the most effective single agent available as an emergency decontaminant in the gastrointestinal tract. It is used after a person swallows or absorbs almost any toxic drug or chemical.

6.2 Adsorption Study of Heavy Metals

6.2.1 Adsorbent

Two organic adsorbents were selected for the present sorption study. They are-

a) Activated Charcoal (Ac.C) powder, Merck, Product Number: 102184.

b) Chitosan, a linear polymer produced commercially by deacetylation of chitin.

6.2.2 Adsorbate

- Cadmium Standard solution: 1000 mgpl Cd CertiPUR®, Traceable to SRM from NIST $Cd(NO_3)_2$ in HNO_3 0.5 mol/l
- Copper standard solution: 1000 mgpl Cu CertiPUR®, Traceable to SRM from NIST $Cu(NO_3)_2$ in HNO_3 0.5 mol/l.

- Nickel standard solution: 1000 mgpl Ni CertiPUR®, Traceable to SRM from NIST $Ni(NO_3)_2$ in HNO_3 0.5 mol/l
- Lead standard solution: 1000 mgpl Pb CertiPUR®, Traceable to SRM from NIST $Pb(NO_3)_2$ in HNO_3 0.5 mol/l
- Zinc standard solution: 1000 mgpl Zn CertiPUR®, Traceable to SRM from NIST $Zn(NO_3)_2$ in HNO_3 0.5 mol/l

6.2.3 Analysis

Glassware needed for the adsorption study was Erlenmeyer's flasks (100 ml), funnels, pipettes, Whatman Filterpaper No: 40, rubber stoppers, activated charcoal and standard metal ion solutions. Calibrated glassware and Milli Q water was used in the entire course of the study. The concentrations of metal ions in the solutions before and after equilibrium were determined by Perkin Elmer Optima 2100 DV Inductively Coupled Plasma-Optical Emission Spectrometry. The pH of solution was measured with a Metrohm pH meter. The shaking was carried out in an automatic shaker with temperature control.

6.2.4 Batch Equilibrium Experiment

Adsorption from solution is customarily conducted either as a column or as a batch operation. In the former instance the solution is allowed to percolate through a column usually held in a vertical position such as is the common practice with ion exchange columns. In a batch operation, a quantity of adsorbent is mixed all at once with a quantity of solution and the system kept in agitation for a convenient period of time. Separation of the resultant solution is accomplished by filtering, centrifuging, or decanting. It should be possible to characterize a solution adsorbent system by either column or batch technique and arrive at the same result since the physical and/or chemical forces applicable in each case must be identical. Furthermore, the results obtained from a batch experiment should be somewhat more reliable because of several reasons.

Among the most serious objections to column experiments are: (1) The overall complexity and expense of experimental equipment; (2) the inherent difficulties associated with maintaining a constant flow rate; (3) the difficulty of assuring a constant temperature throughout the column; (4) the appreciable probability of channelling within the packed column; (5) the variability in the results associated with classification by particle size during settling of the column; (6) the errors inherent in any of the various methods of settling of the column; and (7) the relatively large expenditure both in time and manpower required for a column experiment.

6.3 Adsorption of Heavy metal on Activated Charcoal

Batch adsorption Experiment

Batch adsorption experiments were performed by contacting 0.1g of the selected adsorbent- activated charcoal, with 50ml of the aqueous solution of different initial concentrations (10 to 50 mgpl) taken in six different Erlenmeyer flasks at natural solution (natural solution means the actual solution in which it was prepared by dissolving the standard solution in MilliQ water) pH(6.2). The experiments were performed in wrist action shaker for a period of 1 hour at 120 rpm using 100 ml Erlenmeyer flasks containing 20 ml of different metal ion (Cd, Cu, Ni, Pb & Zn) concentrations. The adsorption measurements were carried out at various intervals of shaking time and also at varying temperatures (30, 40, 50 & 60 degree Celsius). Continuous mixing was provided during the experimental period with a constant agitation speed of 120 rpm for better mass transfer with high interfacial area of contact. The samples were taken at the intervals 5, 10, 15, 30, 45 & 60 minutes after mixing the activated charcoal with the metal ion solution. The remaining concentration of metal ion concentration in each sample after adsorption at different time intervals were collected after filtering the adsorbent with Whatman filter paper No. 40 to make it adsorbent free. First 2-3 ml portion of filtrate was discarded because of the adsorption of metal ions solution by filter paper and then about 10-15ml of the solution was transferred into a vial for metal analysis in ICP OES. Control flasks without the adsorbents are also prepared simultaneously. Concentrations of the metal ions were then corrected for adsorption loss of metal ions on the walls of filter paper and glassware by running the control flask as a blank. Blanks were prepared for each experimental parameter: pH, contact time, solution temperature, metal ion concentration and adsorbent dose. The prepared blanks were treated exactly the same way the samples were treated. For pH, contact time, adsorbent dose and temperature blanks were subjected to their average values. During the analysis, blank measurement was made before each sample measurement. The actual concentration of non adsorbed metal ions, C_t, was calculated using the equation: $C_t=C_m-C_{blank}$.

The amount of metal ion adsorbed per gram of the charcoal 'q'$_i$ in each flask was calculated using the equation:

$$q_i = \frac{\left(C_i^0 - C_i^1\right)V}{m}$$

where C_i^0 , C_i^1 are the concentrations of metal ion before and after adsorption respectively. V is the volume of the liquid phase in the mixture charcoal – metal ion solution, m is the mass of the (adsorbent) charcoal (in grams), i=1-6 is the number of flask corresponding to different shaking time intervals. In the above equation, V is the same for i=1-6, and also the mass of the charcoal (m) taken was 2g in all cases.

6.4 Adsorption Modelling

The assumptions associated with the Langmuir isotherm restricts to only for monolayer. Adsorption cannot proceed beyond monolayer coverage and all adsorption sites are equivalent. The Freundlich model, on the other hand, assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. From the various models of adsorption isotherm, two equilibrium models, namely

Langmuir and Freundlich isotherm models (Do, 1998) are used in this study to analyze the equilibrium experimental data. Initial concentration of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II)ions are varied from 5 to 50 mgpl while the weight of activated charcoal and pH are kept constant. The adsorption capacity of the activated charcoal increases with increase of initial metal ion concentration from 10 to 50 mgpl.

The equilibrium adsorption data were fitted to Freundlich and Langmuir isotherm equations. The adsorption data at equilibrium for a wide range of adsorbate concentrations are well described by the Langmuir and Freundlich models. The Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. It was also assumed that the adsorbed layer is one molecule in thickness and those sites are equal, resulting in equal energies and enthalpies of adsorption. The strength of the intermolecular attractive forces is believed to fall of rapidly with distance. For liquids (adsorbate) adsorbed on solids (adsorbent), the Langmuir isotherm can be expressed by

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Rearranging the above equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$$

where C_e is the equilibrium aqueous metal ions concentration (mgpl), q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium, q_m and K_L are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption respectively. Webi and Chakravort (1974) proposed that the Langmuir constant, K_L, can be expressed in term of a dimensionless constant, Separation Factor (R_L) and can be expressed as

$$R_L = \frac{1}{1 + K_L C_0}$$

where K_L is the Langmuir constant and C_0 (mgpl) is the initial concentration of the adsorbate. The smaller R_L value indicates a highly favourable adsorption. The magnitude of R_L value gives an idea about the nature of adsorption equilibrium: the process is non-spontaneous when R_L is greater than one; favourable when R_L lies between 0 and 1; and irreversible when R_L is zero (Mckay et al., 1982).

The applicability of the Freundlich sorption isotherm was also analyzed, using the same set of experimental data, by plotting log(q_e) versus log(C_e). Freundlich isotherm predicts that the maximum concentration on the adsorbent will increase as long as there is an increase of concentration in liquid. Such an isotherm is another form of Langmuir isotherm which was stated for amorphous surface. The amount adsorbed is summation of the adsorption of all sites, each having bond energy. Equation of Freundlich isotherm (Do, 1998) is as follows

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

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (µg/g) at equilibrium, C_e is the equilibrium concentration of heavy metal ion (mgpl); K_F is the Freundlich constant [(µg/g)(L/mg)$^{(1/n)}$] and gives the capacity of the adsorbent and n_F is the Freundlich exponent and presents an indication of the favourability (Pollard et al., 1991). The Freundlich equation (Freundlich, 1906) known is the linear form the above equation and is given as:

$$\log q_e = \log K_F \frac{1}{n_F} \log C_e$$

Separation Factor (R_L) and can be expressed as

$$R_L = \frac{1}{1+K_F C_0}$$

where K_F is the Freundlich constant and C_0 (mgpl) is the initial concentration of the adsorbate. The process is non-spontaneous when R_L is greater than one; favourable when R_L lies between 0 and 1; and irreversible when it is zero.

χ^2 Analysis

Pearson's chi-squared test (χ2), also known as the chi-squared goodness-of-fit test or chi-squared test for independence is a statistical hypothesis test in which the sampling distribution of the test statistic is a chi-squared distribution when the null hypothesis is true, or any in which this is asymptotically true. A test of independence assesses whether paired observations on two variables, expressed in a contingency table, are dependent on each other. The chi-squared statistic is calculated by finding the difference between each observed and theoretical frequency for each possible outcome, squaring them, dividing each by the theoretical frequency, and taking the sum of the results. A second important part of determining the test statistic is to define the degrees of freedom of the test: this is essentially the number of observed frequencies adjusted for the effect of using some of those observations to define the theoretical frequencies (Greenwood and Nikulin, 1996).

To identify the suitable isotherm for adsorption of metal ions onto activated charcoal, the χ analysis were carried out. The mathematical statement for χ,

$$\chi^2 = \Sigma \frac{\left(f_0 - f_e \right)^2}{f_e}$$

Where

χ2 is the Pearson's cumulative test statistic, which asymptotically approaches a χ2 distribution

f_o is the observed frequency,

f_e is an expected (theoretical) frequency, asserted by the null hypothesis.

The observed frequencies are found by looking at the cross tabulation and the expected frequencies are obtained by using the following formula:

$$f_e = \frac{(\text{Marginal row total})\ \text{X}\ (\text{Marginal column total})}{\text{N}}$$

6.4.1 Effect of variable parameters: Effect of adsorbent dosage

The dependence of heavy metal adsorption on Ac.C was determined keeping the other factors like initial concentration, pH, shaking time fixed while the dosage of Ac.C was varied. Different doses of the adsorbent (Ac.C) was mixed with the metal ion solution and the mixture was agitated in a mechanical shaker for 1 hour. It was found that adsorption of all the selected metals ions was amplified on increasing the dosage of Ac.C. The effect of adsorbent dosage on adsorption of the metal ion on Ac.C was studied by varying the adsorbent concentration (25-150 mg/50 ml) for initial nickel ion concentration of 20 mgpl. The percentage of adsorption increased with increase in the Ac.C concentration (Figure: 6.1). This was attributed to increased adsorbent surface area and availability of more adsorption sites (Edwin, 2008, Kadirvelu K and Namasivayam, 2007).

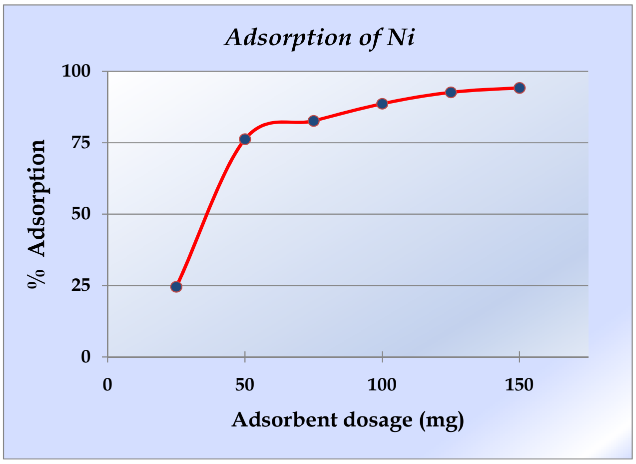

Figure 6.1 : Effect of adsorbent dosage on Ni $^{2+}$ adsorption
(Conditions: Adsorbate conc.:20 mgpl, pH:6,
Temp:303K & time :60 min.)

6.4.2 Effect of Contact time

The effect of period of contact between the adsorbent and adsorbate on the removal of the metal ions in a single cycle was determined by keeping particle size, initial concentration, dosage, pH, and temperature constant. The adsorption of metal ions (Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} & Zn^{2+}) on activated charcoal were studied as a function of shaking time for different intervals of time. Figure: 6.2 showed the variation of Ni ion adsorbed on Ac.C with the increase in shaking time. It was observed that it attains a steady state or equilibrium in 40-45 minutes at varying initial metal ion concentration at 30^0C (303K). These plots indicate that the remaining concentration of metal ions becomes asymptotic to the time axis, such that there are no appreciable changes in the remaining metal ion concentration beyond duration of 45 minutes. To ensure enough time to reach equilibrium, 60 minutes of contact was used throughout the batch experiments.

6.4.3 Effect of adsorbate concentration

The adsorption experiment of metal ions on the activated charcoal was conducted at various concentrations (10, 20, 30, 40 and 50 mgpl) for a shaking period of 60 minutes, keeping other factors constant. To study the effect of adsorbate concentration, adsorption studies was conducted with varying concentration with specific intervals of time, such that temperature (303K), pH ($6.0\underline{+}0.2$), shaking time (60 minutes) and adsorbent concentration (0.1g/50ml). The effect of initial concentration of adsorbate ion is depicted in Figure: 6.2. It was found that the percent adsorption decreased with increase in initial adsorbate concentration, but the actual amount of metal ion adsorbed per unit mass of adsorbent increased with increase in metal ion concentration. It means that the adsorption is highly dependent on initial concentration of metal ion. It is because of that at lower concentration, the ratio of the initial number of metal ion to the available surface area is low, subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of metal ion is dependent upon initial concentration (Vijayakumaran, 2009; Edwin, 2008).

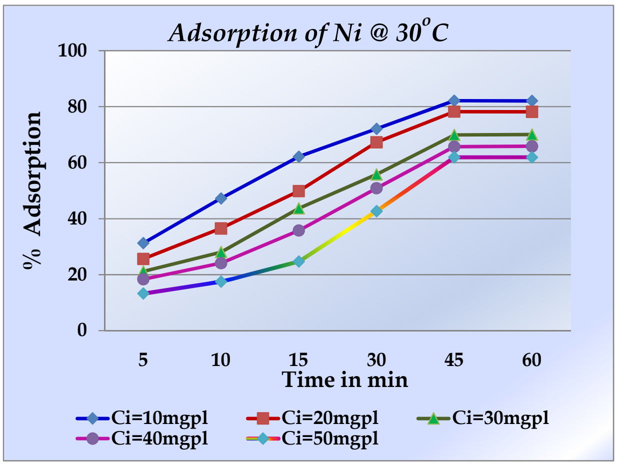

Figure 6.2: Effect of adsorbate concentration on Ni adsorption
(Conditions: Adsorbent Dosage: 0.1g/50ml, pH:6,
Temp:303K & time: 60 min.)

6.4.4 Effect of pH on adsorption

Adsorption experiments were carried out at a range of varying pH of the solution i.e. 3-10. The acidic and alkaline pH of the medium was maintained by adding the required amounts of hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, and temperature were kept constant while carrying out the experiments. The effect of pH on the adsorption was studied while the initial concentration of metal ion (C_i), shaking time, temperature and amount of adsorbent (Ac.C) were fixed. For all the five metal cations, increase in solution pH throughout the range studied resulted in increased adsorption. This trend is in agreement with the fact that the metal ions are adsorbed by ion- exchange mechanism (Edwin, 2008).

As the solution pH is lowered, concentration of H^+ ions will increase proportionally which will effectively compete with metal cations for active adsorption sites on carbon surface, thereby reducing the available sites for metal cations. At lower pH values, the carbon will have a net positive charge. Higher uptakes obtained at lower pH may be due to the electrostatic attractions between negatively charged functional groups associated with the metal ion and positively charged adsorbent surface. Hydrogen ion also acts as bridging ligands between the adsorbent wall and the metal ion (Zawani et al., 2009). The reduction in adsorption capacity of metal ion on adsorbent with increasing pH can be attributed to change in surface characteristics and charge. Thus pH of the aqueous solution is an important operational parameter in the adsorption process. This is because it affects the solubility of the metal ions concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of adsorbate during reaction (Amuda et al., 2007).

In order to find out the optimum pH for maximum removal of adsorbate, experiments were carried out with solutions of same metal ion concentration but adjusted to different initial pH values (with HNO_3 or NaOH). Measurements were carried out below which chemical precipitation of metal hydroxides do not occur. These values have been estimated by Edwin (2008) and was found to be as 7.8 for $Ni(OH)_2$; 2.5 for $Fe(OH)_3$; and 7.5 for $Cu(OH)_2$. The conditions set for the determination of effect of pH on adsorption of metals are as follows: shaking time: 1 hour, Initial adsorbate concentration: 20mgpl, Adsorbent dose:0.1g/50ml and temperature : 303K.The pH corresponding to maximum adsorption of heavy metal ion were determined and the optimum pH range for Ni(II), Cu(II), Cd(II), Pb(II) and Zn(II) found to be between 3.0 to 10.0 At pH values less than ~3, very less sorption has been observed for all metal ions. The lack of sorption at low pH could be attributed to the hydrogen ions competing with the metal ions for sorption/ exchange sites. The pH dependence on the adsorption of the metals selected for the study is depicted in Figure: 6.3

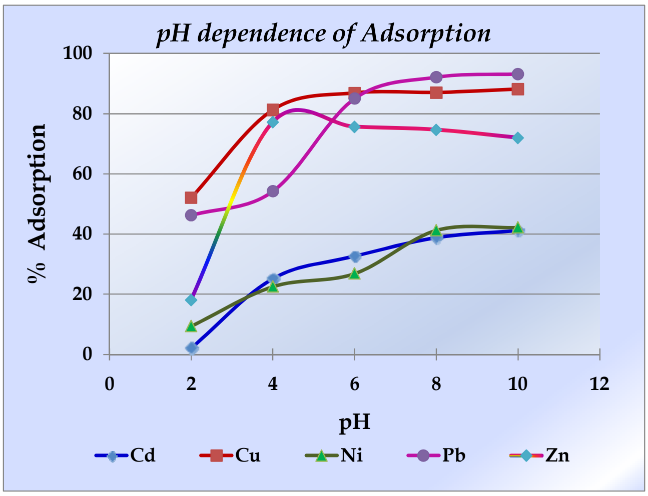

Figure 6.3: Effect of pH on the adsorption of metals on Activated charcoal (Conditions: Adsorbent dosage=0.1g/50ml, C_i= 20 mgpl, Temp:303K & time 60 min.)

6.4.5 Effect of Temperature on adsorption

The adsorption experiments were performed at four different temperatures viz., 30, 40, 50 and 60 °C in a thermostat controlled shaker machine (Remi, India). The constancy of the temperature was maintained with an accuracy of ±0.5 °C. For all the systems increase in temperature resulted in greater adsorption. The increased adsorption at higher temperatures can be due to one or more of the following reasons. On increasing the temperature, acceleration of some originally slow step(s) takes place (Khalid et al., 1998), creation of some new activation sites on the adsorbent surface (Khalid et al., 1999), and decrease in the size of the adsorbing species (Johnson, 1990). This could well occur due to progressive desolvation of the adsorbing ion as the solution temperature increases. The temperature dependence of the adsorption of metal ion on activated charcoal is shown in Figure: 6.4, plotting the quantity of metal ion adsorbed (q) against time (t) at different temperatures. The experimental result shows that the amount of metal ion adsorbed on activated charcoal increased with increasing adsorption temperature.

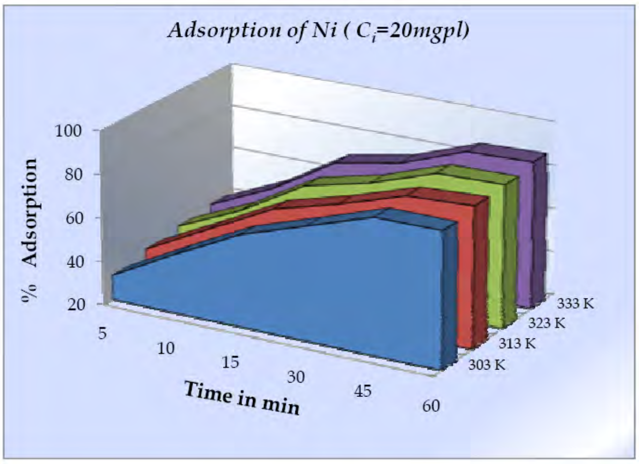

Figure 6.4: Effect of temperature on Ni^{2+} adsorption on to Ac.C. (Conditions: Adsorbent conc. : 0.1g/50ml, adsorbate conc. :20 mgpl &time: 60 min.)

6.5 Thermodynamic Modelling

Thermodynamic parameters such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) can be estimated from equilibrium constants determined at different temperatures. Thermodynamic parameters were calculated at pH 6.0$\pm$0.2 at different temperatures (303, 313, 323 & 333K) and varying initial metal ion concentrations (10, 20, 30, 40 & 50 mgpl). The Gibbs free energy change of the sorption process is given by the following equation (Mohapatra et al., 2009).

$$\Delta G^0 = -RT \ln K_c$$

$$K_c = q_e / C_e$$

where, K_c is the equilibrium constant, which is determined as the ratio of q_e to $C_{e.}$, R is the universal gas constant (8.314 J/mol K) and T is temperature (K). The values of ΔH^0 and ΔS^0 were determined from the Van't Hoff equation as given below.

$$\log\ K_c = \frac{\Delta S^0}{(2.303R)} - \frac{\Delta H^0}{2.303RT}$$

The effect of increase in temperature on the adsorption of metal ions at the charcoal-solution interface has been studied in the temperature range of 303-333 K. The value of equilibrium constant, K_c at different concentrations and temperature is described in Table: 6.2. It was observed that the equilibrium constant, K_c decreases with increase in the initial Ni ion concentration at all temperature range of the study. The value of K_c was also found to increase with the increase in temperature (Edwin, 2008; Vijayakumaran, 2009).

Table 6.2: Equilibrium constant K_c at different concentrations & temperature

Temp(K)	C_i (mgpl)	C_e (mgpl)	q_e (mg/g)	K_c
303	10	1.790	8.210	4.586
	20	4.356	15.644	3.591
	30	8.988	21.012	2.338
	40	13.666	26.334	1.927
	50	19.029	30.971	1.628
313	10	1.552	8.448	5.443
	20	3.845	16.155	4.202
	30	8.398	21.602	2.572
	40	13.178	26.822	2.035
	50	18.547	31.453	1.696
323	10	1.465	8.535	5.824
	20	3.602	16.398	4.553
	30	7.721	22.279	2.885
	40	12.789	27.211	2.128
	50	18.163	31.838	1.753
333	10	1.261	8.739	6.928
	20	3.315	16.686	5.034
	30	7.427	22.573	3.039
	40	12.458	27.542	2.211
	50	17.612	32.388	1.839

Graphs plotted for each temperature range (303K, 323K, 323K, 333K) between log K_c and 1/T was found to be linear. From the slopes and intercepts of the plots between log K_c and 1/T, ΔH^0 and ΔS^0 were calculated with Vant' Hoff plots (Figure :6.5) and the parameters are given in Table: 6.3 Heat of adsorption and entropy values are comparable with other studies using activated charcoal and other natural adsorbents (Edwin, 2008; Vijayakumaran, 2009).

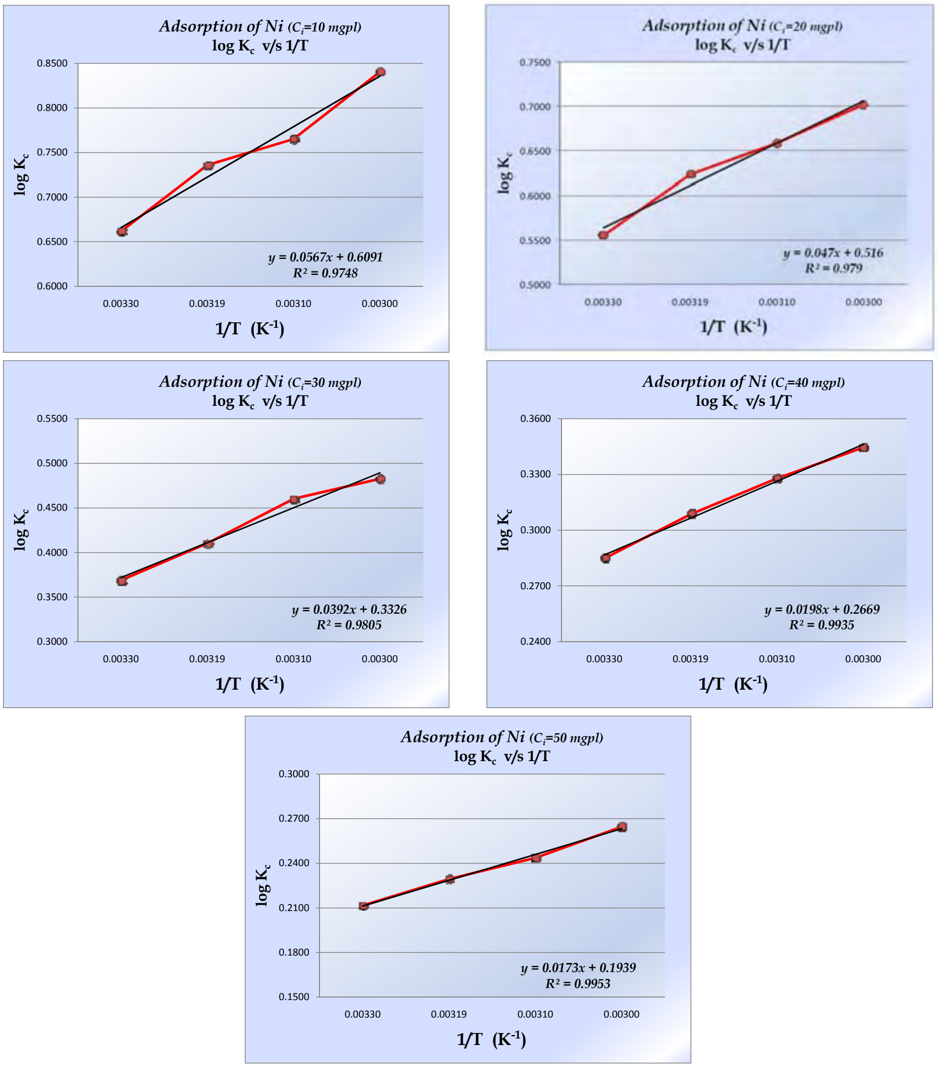

Figure 6.5: (Plot of log K_c versus (1/T) for C_i = 10 to 50 mgpl

Table 6.3: Equilibrium constant and thermodynamic parameters for the adsorption of Ni ions

Initial Concn C_i (mgpl)	K_c				ΔG^0				ΔH^0	ΔS^0
	303 K	313 K	323K	333K	303 K	313 K	323K	333K		
10	4.586	5.443	5.824	6.928	-3.84	-4.41	-4.73	-5.36	-0.33	11.66
20	3.585	4.202	4.553	5.034	-3.22	-3.74	-4.07	-4.47	-0.28	9.86
30	2.338	2.572	2.885	3.039	-2.14	-2.46	-2.85	-3.08	-0.23	6.37
40	1.927	2.035	2.128	2.211	-1.65	-1.85	-2.03	-2.20	-0.12	5.11
50	1.628	1.696	1.753	1.839	-1.23	-1.37	-1.51	-1.69	-0.10	3.71

(Shaking time: 60min, Activated charcoal dose=0.1g/50ml,pH=6.0)

The negative values of the standard free energy change (ΔG^0) for this reaction suggests that the adsorptive nature is spontaneous (Manju et al., 1999). The negative ΔG^0 value obtained confirmed that the feasibility of the adsorption process and the spontaneous nature of the adsorption. The positive ΔS^0 values reflect that significant change occurs in the internal structure of adsorbent during adsorption of metal ions. The positive value suggests a high degree of disorderliness at the solid-solution interface during the adsorption process of Cu (II) by activated charcoal (Pragnesh et al., 2009). It also reflects the affinity of the adsorbent for Cu (II) and suggests some structural changes in adsorbate and adsorbent. The adsorbed solvent (water) molecules, which are displaced by the adsorbed species, gain more translational entropy than is lost by the adsorbate ions. Furthermore, before the adsorption process takes place the adsorbate ions are heavily solvated (the system is more ordered) and this order is lost when the ions are adsorbed on the surface, due to the release of solvated water molecules (Edwin, 2008). Enhancement of adsorption capacity of activated charcoal at higher temperatures may be attributed to the enlargement of the pore size and/or activation of the adsorbent surface and increase in the mobility of the metal ions.

The value of ΔH° of any adsorption process can be positive or negative. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of metal ion adsorption increases, this rules out the possibility of chemisorptions. However, the very low ΔH° value depicts metal ion is physisorbed onto adsorbent (Vijayakumaran, 2009; Arivoli, 2007; Singh et al., 1994). Negative value of ΔH indicates the exothermic nature of the process. This is also confirms the possibility of physical adsorption as with the increase in temperature of the system (Zawani et al., 2009). The positive value of ΔH° was also observed indicating that the adsorption is endothermic and irreversible, probably due to non polar interactions (Stephan et al., 2002).

6.6 Kinetic Modelling

Chemical kinetics is the area of chemistry concerned with speed, or rates, at which a chemical reaction occurs. The kinetic is the movement or change in concentration of reactant or product with time; therefore, kinetic refers to the rate of the reaction, or the reaction rate (Chang, 2008). Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. Adsorption is a time-dependent process and is significant to know the rate of adsorption for design and evaluate the adsorbent in removing the metals. In many cases, the adsorption kinetics based on the overall adsorption rate by the adsorbents is described by the first order Lagergren model and pseudo second-order.

Zero-order adsorption:

Adsorptions whose order is zero are rare. The rate law of zero order is

$$\text{Rate} = \frac{dq}{dT}$$

$$\frac{dq}{dT} = k_{\mathbf{ads}}(q_t - q_e)^o$$

$$= k_{ads}$$

where q_t, and q_e are amounts of metal ion adsorbed at time t and at equilibrium, respectively, and k_{ads} denote the adsorption rate constant. Thus, the rate of zero order adsorption is a constant, independent of amounts of metal ion adsorbed. Using the calculus with integration by applying the initial conditions q = 0 at t = 0 and $q = q_t$; at t = t,

$$(q_e - q_t) = q_e - k_{ads}t$$

The plot of log $(q_e\text{-}q_t)$ versus t will give a straight line and the value of adsorption rate constant k_{ads} can be obtained from the slope of the graph.

First-order adsorption:

A first-order adsorption is an adsorption whose rate depends on the amounts of maximum adsorption raised to the first power. First order rate expression of Lagergren (Zawani et al., 2009; Annadurai and Krishnan, 1997) is given as:

The rate is

$$\frac{dq}{dT} = k_{\mathbf{ads}}(q_e - q_t)$$

where qt, and qe are amounts of metal ion adsorbed(mg/g), at time t and at equilibrium, respectively, and k_1 is the rate constant of first order adsorption (min^{-1}). After definite integration by applying the initial conditions q = 0 at t = 0 and q = q_t at t = t, the above equation becomes

$$\log(q_e - q_t) = \log q_e - (k_1 t/2.303)$$

The plot of log (q_e-q_t) versus t will give a straight line and the value of adsorption rate constant k_1 can be obtained from the slope of the graph.

Second- order adsorption:

Adsorption process, whose rate depends on the concentration of one reactant raised to the second power. The rate is

$$\frac{dq}{dT} = K_2(q_e - q_t)^2$$

Using the calculus the following is the expression for the second order adsorptions:

$$\frac{1}{q_e - q_t} = \frac{1}{q_t} + k_2 t$$

Where, k_2 is the pseudo-second-order rate constant of adsorption (g $mg^{-1}min^{-1}$). The linearised integrated form of the above equation is given as:

$$\frac{1}{q_t} = \frac{1}{k_2\, q^2_t} + \frac{t}{q_e}$$

If the pseudo second-order kinetics is applicable to the system, then the plot of (t/q_t) versus t will give a linear relationship with ($1/ q_e$) and ($1/ k_2 q^2_t$) as slope and intercept, respectively. The pseudo second-order kinetics model has been successfully applied to several biosorption systems as reported by McKay et al., (1999) and Otero et al., (2003). Activated charcoal was used to evaluate various kinetic parameter with which pH of the solution is adjusted to the value at which maximum sorption of respective metal ion takes place. The metal ion solution (20mgpl, 50ml) was shaken with 50 mg of the adsorbent, activated charcoal in stoppered Erlenmeyer flasks at the desired temperatures (303 K, 313 K, 323 K and 333 K) and at different time intervals at increments of 5 min up to 15minutes and then at an increment of 15 minutes from15-60minutes. The supernatant liquid was removed immediately after each prescribed time interval and filtered and transferred to clean metal free vials. The metal ion concentration was then evaluated using ICP OES. In the present study, in order to validate the adsorption kinetics and to understand the sorption behaviour Ac.C, adsorption of Ni^{2+} has been carried out. The adsorption of Ni^{2+} from an aqueous solution follows reversible first order kinetics, when a single species considered on a heterogeneous surface. The heterogeneous equilibrium between the Ni^{2+} solution and the activated charcoal have expressed

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Where, k_1 is the forward rate constant and k_2 is the backward rate constant. A represents Ni^{2+} remaining in the aqueous solution and B represents nickel ion adsorbed on the surface of activated charcoal. Ion exchange of metal ions from the liquid phase on to the solid phase can be considered as a reversible reaction with two phases. Therefore, a simple first order kinetic model is used to establish the rate of reaction (Gozen et al., 1997). The kinetic study data of Ni ion adsorption at different temperatures is given in Table: 6.4 and it was observed that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant. At equilibrium, the rate is the ratio of the concentration of adsorbate in adsorbent and concentration of adsorbate in aqueous solution given by K_c. The results indicates that K_c , k_1 and k_2 values and increases with increase in temperature. The results observed are comparable with other adsorption kinetic studies (Kalpana et al.,2007; Pragnesh et al.,2009). The rate constant of adsorption process carried out for different initial adsorbate concentrations and for different operation temperatures are determined in three types of adsorptions; zero order adsorption, first order adsorption, and second order adsorption and found to have greater R^2 values for first order mechanism (Srivastava et al., 1997).

Table 6.4: Kinetic parameters for the adsorption of Ni^{2+} at different temperatures.

Initial Ni Conc. C_i	Temp (K)	K_c (min^{-1})	k_1 (min^{-1})	k_2 (min^{-1})
20 mgpl	303	3.585	0.4394	0.3546
	313	4.202	0.4590	0.3879
	323	4.553	0.4622	0.4257
	333	5.034	0.5101	0.4301

6.7 Results and Discussion

6.7.1 Adsorption study of Cd^{2+}

The properties of Cd are similar to those of Zn that the two elements invariably occur together. There are no important minerals of Cd and is only about one thousandth as abundant, as Zn. The principle source of Cd is the flue dust from the purification of Zn by distillation. In its compound state the usual oxidation state of Cd is +2. It exists in aqueous solution as colourless Cd^{2+} ions. Cd exposure causes both acute and chronic type of poisoning.

Batch Adsorption Study

A known quantity of activated charcoal (0.1g/50ml) was added to the Erlenmeyer flask containing Cd(II) solution of strength predetermined with ICP OES. The flask was placed in a constant temperature bath and stirred with the help of a stirrer until equilibrium was attained. Initial adsorption studies were conducted to ascertain the conditions of shaking time and pH for the maximum adsorption of Cd on activated charcoal from aqueous solution at different temperatures (303, 313, 323, and 333K) with the interval of 5°C up to first 15minutes and then of 15minutes interval from 15 to 60 minutes. The studies confirmed that the equilibrium is attained within 45 minutes and maximum adsorption of Cd occurred at pH-6.2 with the adsorbate concentration 20.147 mgpl and adsorbent dosage of 0.1g/50ml. The effect of Cd ion concentration on its adsorption on activated charcoal was studied in varying metal ion concentration range (10.002, 15.011, 20.147, 25.009, and 30.001 mgpl).

Adsorption Isotherm:

The experimental data analysed according to the linear form of the Langmuir and Freundlich isotherms. The Langmuir isotherm represented by the following equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$$

where C_e is the equilibrium aqueous metal ions concentration (mgpl), q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium, q_m and K_L are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption respectively.

The initial Cd ion concentration, equilibrium concentration, amount adsorbed, percentage adsorption, at different are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption respectively. The initial Cd ion concentration, equilibrium concentration, amount adsorbed, percentage adsorption, at different concentration and temperature was calculated and given in Table: 6.5. The plots of C_e /q_e versus C_e at different temperatures are found to be linear with the slope

$(1/q_m)$ and intercept $(1/q_mK_L)$, indicating the applicability of the Langmuir model (Figure: 6.6). The value of q_m and K_L was then calculated from the slope and the intercept.

Table 6.5: Equilibrium parameters of Cd^{2+} adsorption

Temp (K)	C_i (mgpl)	C_e (mgpl)	q_e (mg/g)	% Adsorption	C_e/q_e	log C_e	log q_e
303	10.002	3.254	3.374	67.47	0.964	0.5124	0.5281
	15.011	5.014	4.999	66.60	1.003	0.7002	0.6988
	20.147	7.014	6.567	65.19	1.068	0.8460	0.8173
	25.009	9.124	7.943	63.52	1.149	0.9602	0.9000
	30.001	11.326	9.338	62.25	1.213	1.0541	0.9702
313	10.002	3.158	3.422	68.43	0.923	0.4994	0.5343
	15.011	5.001	5.005	66.68	0.999	0.6991	0.6994
	20.147	7.101	6.523	64.75	1.089	0.8513	0.8144
	25.009	9.112	7.949	63.57	1.146	0.9596	0.9003
	30.001	11.215	9.393	62.62	1.194	1.0498	0.9728
323	10.002	3.064	3.469	69.37	0.883	0.4863	0.5402
	15.011	4.914	5.049	67.26	0.973	0.6914	0.7032
	20.147	7.098	6.525	64.77	1.088	0.8511	0.8145
	25.009	9.055	7.977	63.79	1.135	0.9569	0.9018
	30.001	11.114	9.444	62.95	1.177	1.0459	0.9751
333	10.002	2.954	3.524	70.47	0.838	0.4704	0.5470
	15.011	4.815	5.098	67.92	0.944	0.6826	0.7074
	20.147	6.987	6.580	65.32	1.062	0.8443	0.8182
	25.009	8.945	8.032	64.23	1.114	0.9516	0.9048
	30.001	11.098	9.452	63.01	1.174	1.0452	0.9755

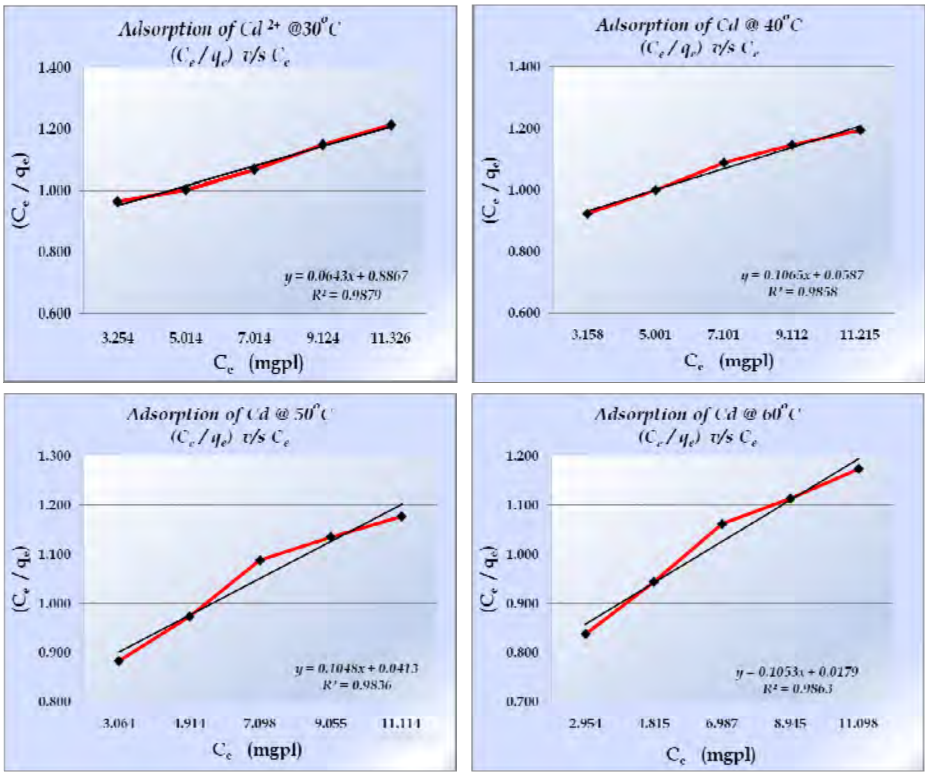

Figure 6.6: Langmuir isotherm of Cd^{2+} adsorption at different temperatures.

The statistical significance of the correlation coefficient (R^2) for C_e/q_e versus C_e is the criteria by which the fitting of the data to Langmuir isotherm. It explains monolayer coverage of adsorbate at the outer surface of the adsorbent. The parameters q_m and K_L have been calculated and the results are represented in Table: 6.6. It was observed that the Langmuir isotherm fits well with the experimental data.

Table 6.6: Langmuir isotherms Parameters for the adsorption of Cd^{2+}onto Ac.C at different temperatures

Temp	Langmuir Constants			
(K)	q_m	K_L	R^2	χ^2
303	15.58	0.072	0.9921	0.5822
313	9.39	1.814	0.9858	0.5577
323	9.54	2.538	0.9836	0.5321
333	9.50	5.883	0.9863	0.5023

The Freundlich equation have also employed for the adsorption of Cd^{2+} on the adsorbent. The linear form of Freundlich isotherm have represented as

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e$$

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (μg/g) at equilibrium, C_e is the equilibrium concentration of heavy metal ion (mgpl); K_F is the Freundlich constant $[(\mu g/g)(L/mg)^{(1/n)}]$ and gives the capacity of the adsorbent and n_F is the Freundlich exponent and presents an indication of the favourability. The linear plots of log q_e versus log C_e at different temperature shows that the adsorption of Cd^{2+} follows the Freundlich isotherm (Figure:6.7). The values of K_f and n were calculated from the slope and intercept of the log q_e versus log C_e plot and is given in the Table: 6.7. The magnitude of K_F and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity. Freundlich constants calculated shows the increase of negative charge on the surface, that enhances the electrostatic force like Van der Waal's between the carbon surface and metal ion, which inturn increases the adsorption of metal ion. The intensity of adsorption is an indicative of the bond energies between Cd^{2+} and adsorbent and the possibility of slight chemisorptions rather than physisorption. The values of n are greater than one indicating the adsorption is favourable. The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa. Higher the K_F value, the greater is the adsorption intensity.

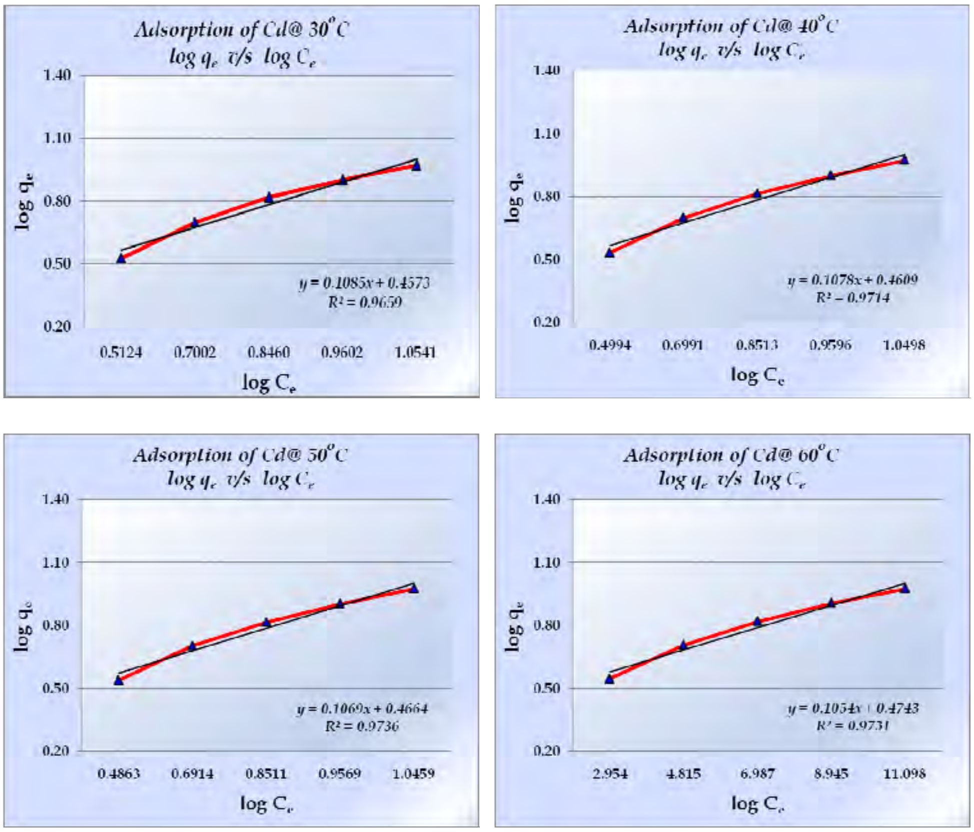

Figure 6.7: Freundlich isotherm of Cd^{2+} adsorption at different temperature

Table 6.7: Freundlich Isotherms parameters for the adsorption of Cd^{2+}onto Ac.C at different temperatures

Temp (K)	Freundlich Constants			
	n_F	K_F	R^2	χ^2
303	9.21	2.86	0.9686	0.0030
313	9.28	2.88	0.9738	0.0045
323	9.35	2.92	0.9758	0.0068
333	9.48	2.97	0.9754	0.0101

Chi-squared test or χ^2 test:

Pearson's chi-squared test or also known as χ^2 test is the goodness-of-fit test or chi-squared test for independence. The test is most often used in the context of linear models like linear regression, analysis of variance. The χ^2 values for Langmuir and Freundlich isotherm are computed and included in the Table: 6.6 & 6.8. If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a larger number. Therefore, it is necessary to analyse the data set using the non-linear Chi-square test to confirm the best-fit isotherm for the sorption process. The χ^2 values of both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and relatively better fit is observed with Langmuir model as its χ^2 value is less than that of Freundlich model. The Langmuir isotherm is more widely used and provides information on the monolayer adsorption capacity in contrast to the Freundlich model.

Table 6.8: Separation Factor ($R_{L)}$ for the adsorption of Cd^{2+} at different temperatures

Cd^{2+} conc. mgpl	Separation Factor,R_L			
	303K	**313K**	**323K**	***333K***
10.002	0.5808	0.0522	0.0379	0.0167
15.011	0.4801	0.0354	0.0256	0.0112
20.147	0.4076	0.0266	0.0193	0.0084
25.009	0.3566	0.0216	0.0155	0.0068
30.001	0.3160	0.0180	0.0130	0.0056

The Separation Factor (R_L) values of Langmuir isotherms at different temperatures are quantified (Table: 6.8) and according to this, Langmuir model was found to be fit better since the R_L values are comparably less. The value of correlation co-efficient that was used as a main criterion for judging the fitness of the adsorption data. K_L values of each metal ion at different temperature also having an augmented trend in Langmuir model than that in the other model. A comparison of the coefficient of regression (R^2) and χ^2 for the two isotherms indicate the best fitment of the experimental data with the Langmuir model. In all the systems studied, R_L values were comprised between 0 and 1 indicating favourable adsorption of all the metal ions on the selected adsorbent activated charcoal.

It was observed that there was a gain in percentage adsorption with the increase of temperature (Michael et al., 2005). Figure: 6.8 show the temperature dependence of Cd removal using activated charcoal.

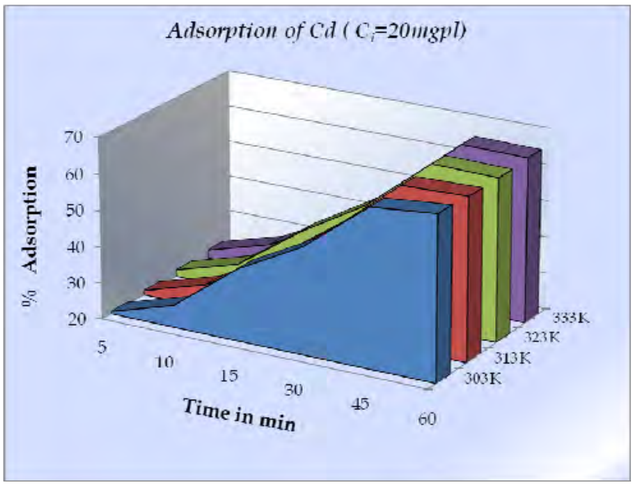

Figure 6.8: Effect of temperature on Cd^{2+} adsorption on to Ac.C.
(Conditions: Adsorbent dosage=0.1g/50ml, C_i= 20.147 mgpl, Temp:303K & time 60 min.)

Kinetic Study

The kinetics data of Cd^{2+} ion adsorption on activated charcoal is given in Table: 6.9. The data was found to fit the first order kinetic equations. The value of log (q_e-q_t) versus time plotted for different temperatures are shown in Figures 6.9 to 6.12. The rate constant of the forward reaction can calculated from the slope of the above plot. The rate constant of the backward reaction, k_2 was calculated using equilibrium constant, K_c and rate of forward reaction,k_1. The rate of forward reaction was found to be greater than the rate of backward reaction at all temperatures and for all initial Cd ion concentration and these values are also given in Table: 6.9. The reaction follows a first order rate law about thirty minutes and attained equilibrium there after.

Table 6.9: Kinetics data of Cd^{2+}adsorption at various temperatures & Initial adsorbate ion concentrations

Temp (K)	C_i (mgpl)	q_e (mg/g)	k_1 (min^{-1})	k_2 (min^{-1})	K_c (min^{-1})
303	10.002	3.374	0.327	0.638	0.964
	15.011	4.999	0.320	0.683	1.003
	20.147	6.567	0.352	0.716	1.068
	25.009	7.943	0.292	0.857	1.149
	30.001	9.338	0.275	0.938	1.213
313	10.002	3.422	0.314	0.609	0.923
	15.011	5.005	0.323	0.676	0.999
	20.147	6.523	0.345	0.744	1.089
	25.009	7.949	0.296	0.850	1.146
	30.001	9.393	0.276	0.918	1.194
323	10.002	3.469	0.311	0.572	0.883
	15.011	5.049	0.311	0.662	0.973
	20.147	6.525	0.368	0.719	1.088
	25.009	7.977	0.297	0.838	1.135
	30.001	9.444	0.297	0.880	1.177
333	10.002	3.524	0.297	0.541	0.838
	15.011	5.098	0.311	0.634	0.944
	20.147	6.580	0.345	0.716	1.062
	25.009	8.032	0.297	0.817	1.114
	30.001	9.452	0.283	0.891	1.174

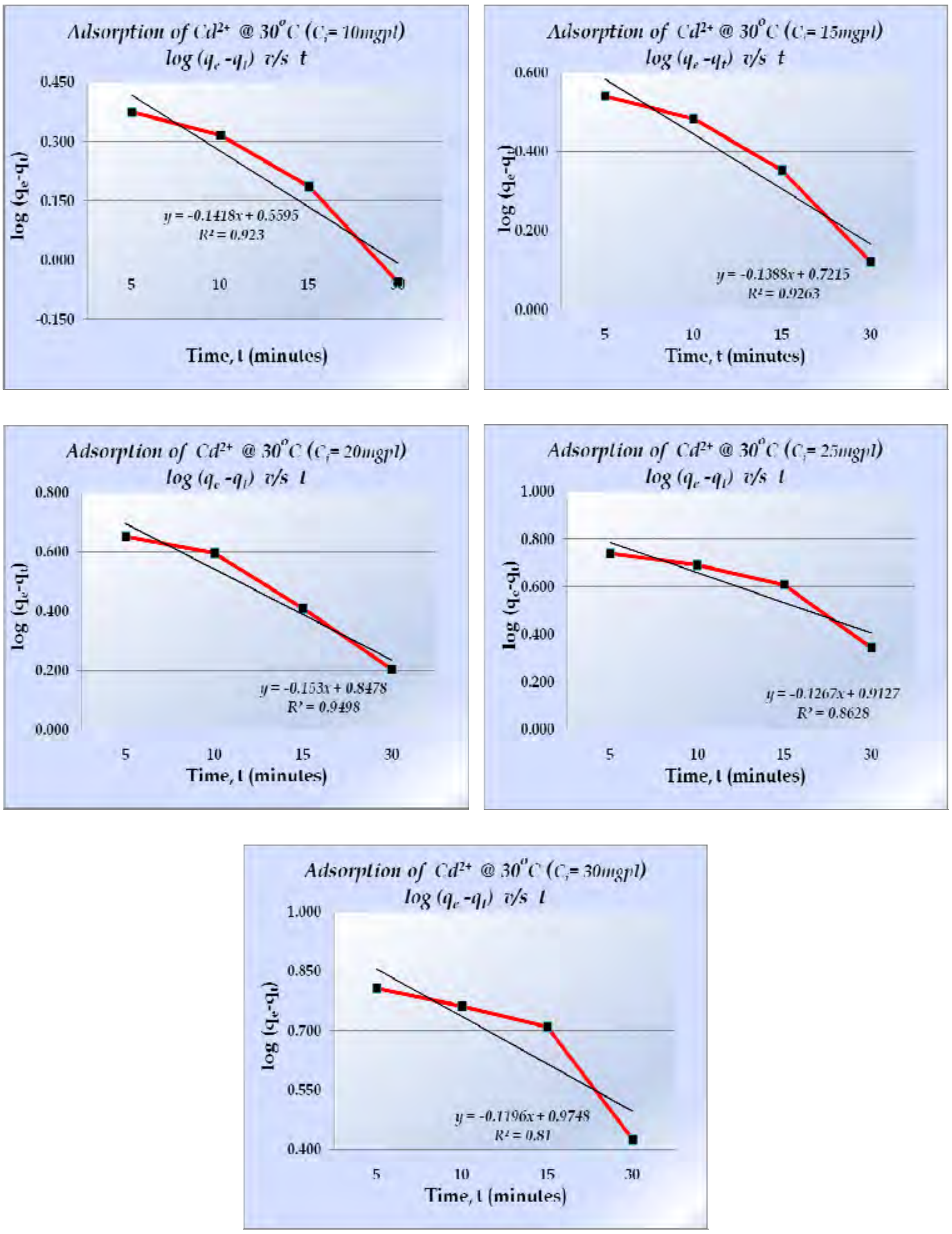

Figure 6.9: Kinetic study plot of Cd^{2+} adsorption at various Concentrations (Temp: 303K)

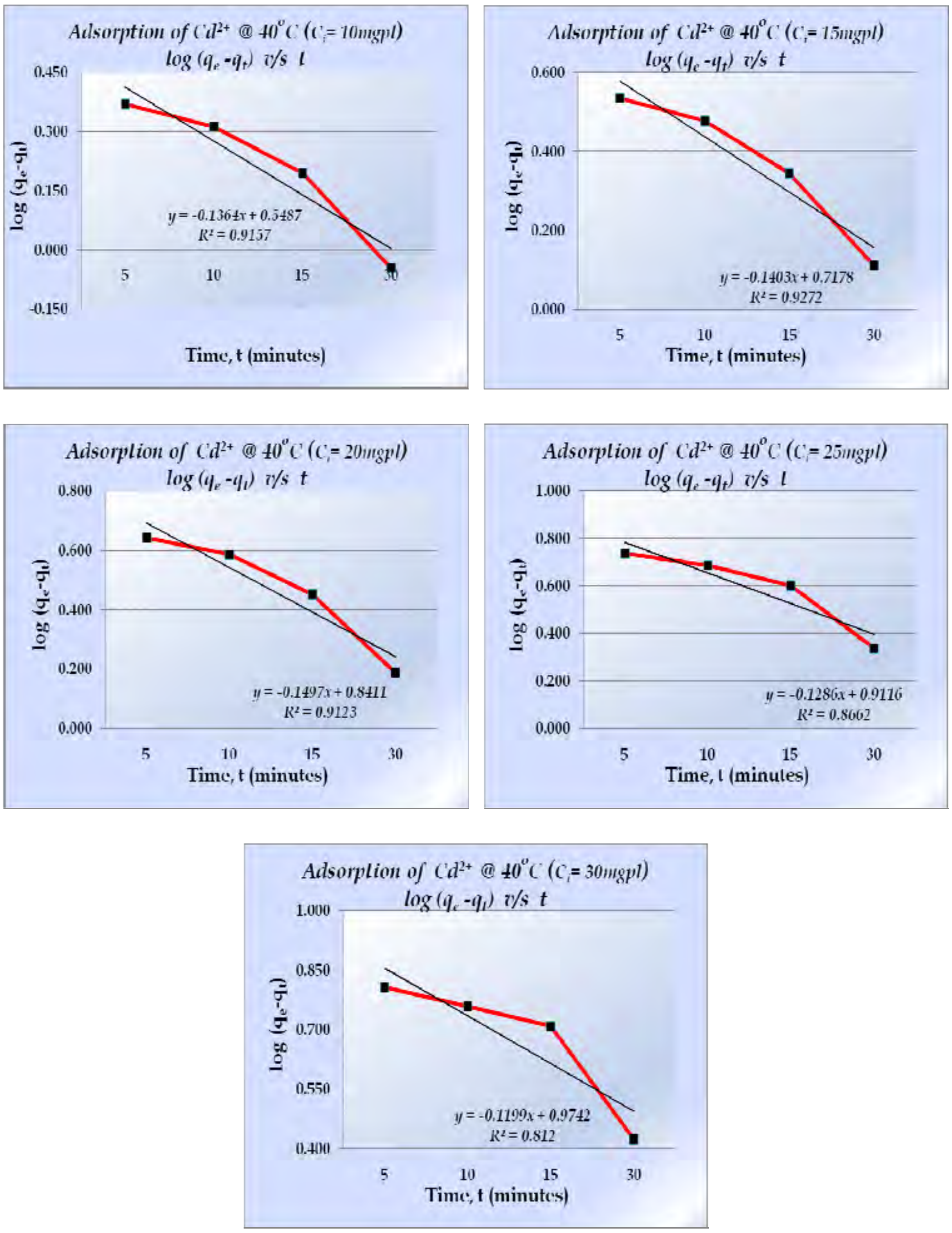

Figure 6.10: Kinetic study plot of Cd^{2+} adsorption at various Concentrations (Temp: 313K)

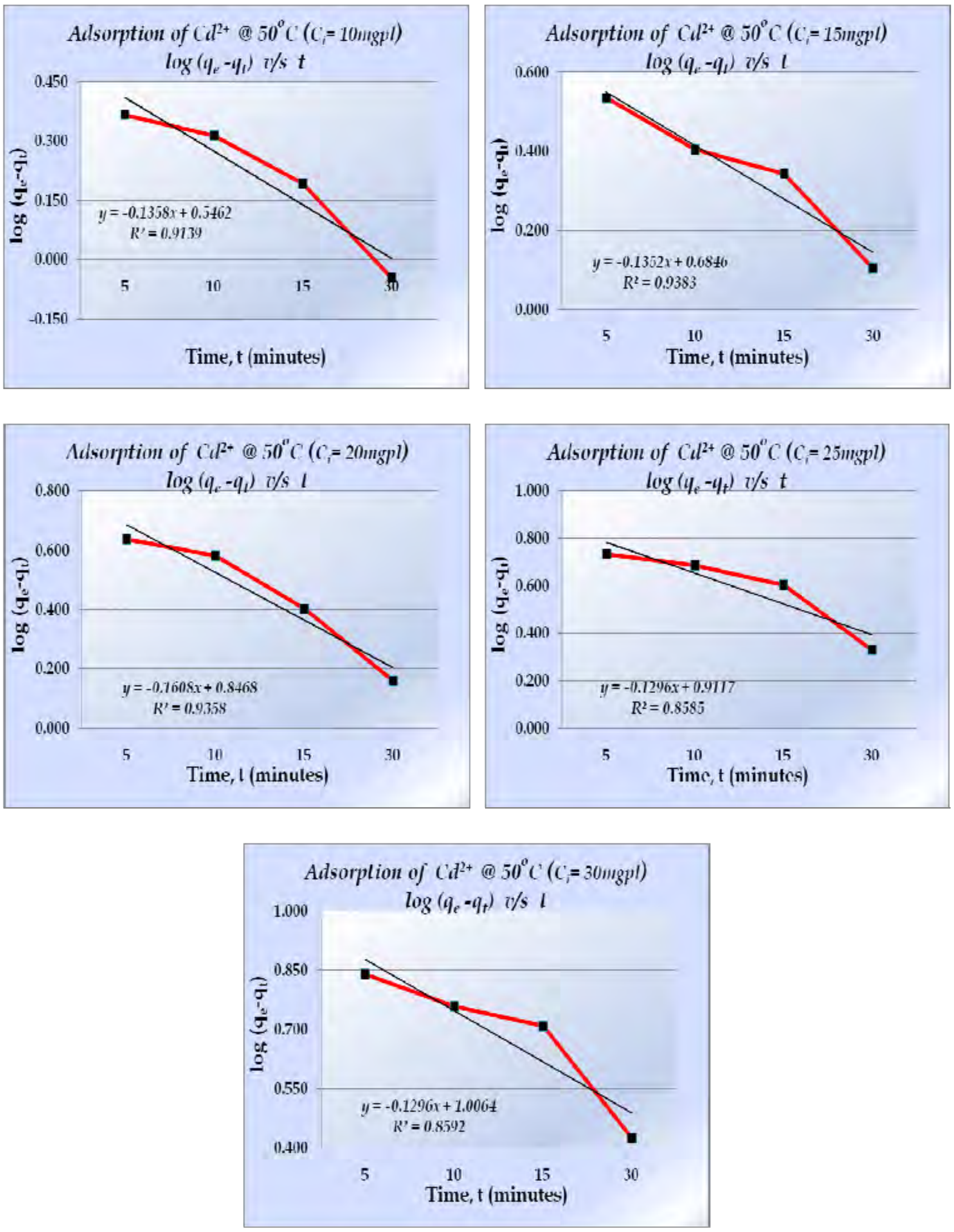

Figure 6.11: Kinetic study plot of Cd^{2+} adsorption at various Concentrations (Temp: 323K)

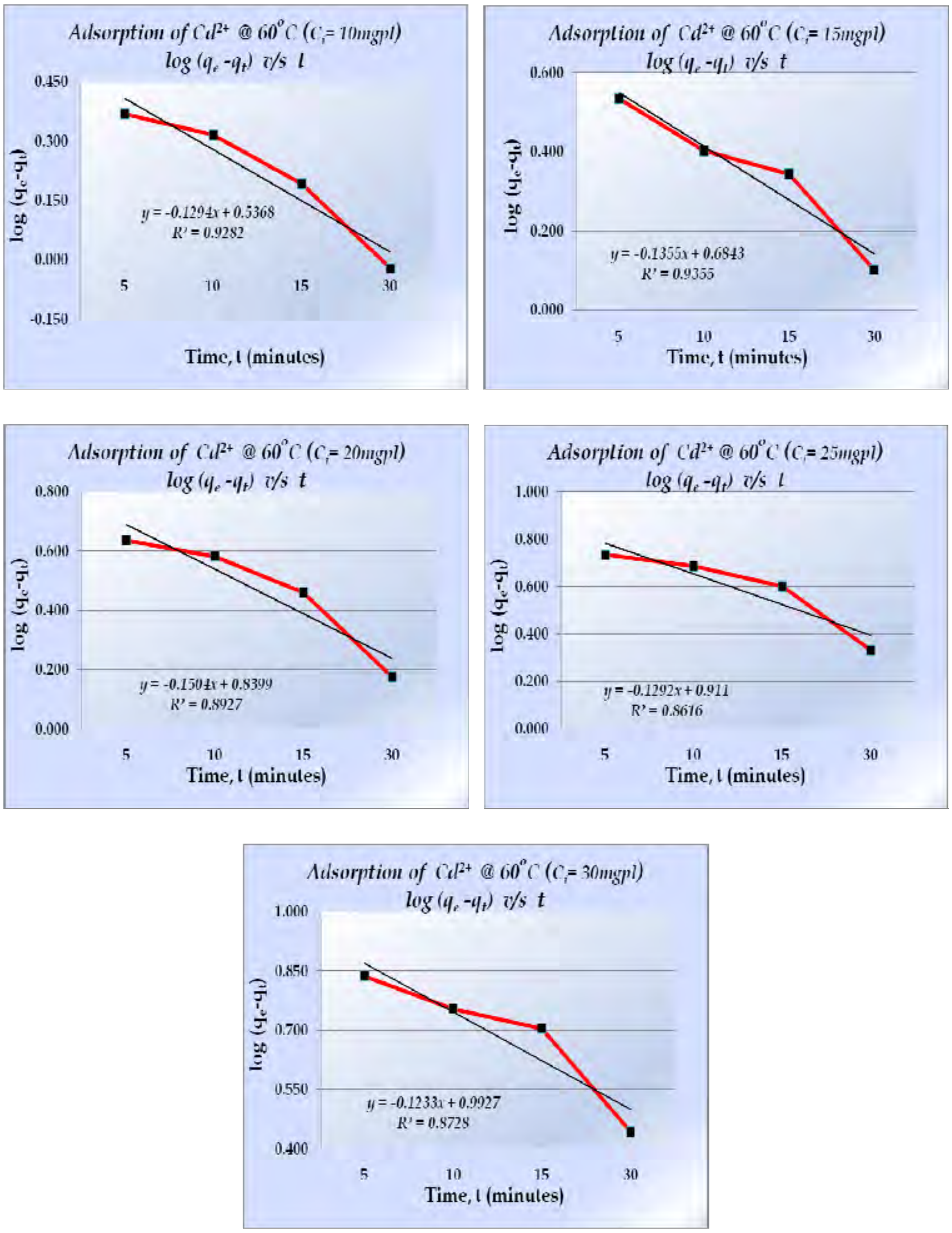

Figure 6.12: Kinetic study plot of Cd^{2+} adsorption at various Concentrations (Temp: 333K)

6.7.2 Adsorption study of Cu^{2+}

Cu is also the member of Iron family and it is one of the first metals known to man, occurring in the glacial drift as dark brown, heavy nuggets, Further it is in crystalline form reddish metal, cubic, oxidation slate +2 and +4. It is toxic and damages the liver.

Batch Adsorption Study

The dosage of activated charcoal was optimised by the preliminary studies and the amount of activated charcoal (0.1g/50ml) was added to the Cu^{2+} solution of strength predetermined with ICP OES and the flask was placed in a constant temperature bath and stirred with the help of a stirrer until equilibrium was attained. The experiment was conducted at varying Cu^{2+} concentrations (10, 15, 20, 25& 30mgpl) at different temperatures (303, 313, 323, and 333K). Adsorption of Cu was fount to more as compared to Ni, Zn and Cd. It is due to the outer most shells $3d^{10}$, $4s^2$. Due to the half filled orbital in Cu, it has high affinity towards carbon surface.

Adsorption Isotherm

The experimental data analysed according to the linear form of the Langmuir and Freundlich isotherms. The initial Cu ion concentration, equilibrium concentration, amount adsorbed, percentage adsorption, at different concentration and temperature is given in Table:6.10. The plots of C_e / q_e versus C_e at different temperatures are found to be linear with the slope ($1/ q_m$) and intercept ($1/q_mK_L$), indicating the applicability of the Langmuir model (Figure: 6.13). The value of q_m and K_L was then calculated from the slope and the intercept. The parameters of q_m, K_L and other statistical parameters was then computed and the results are represented in Table: 6.11. It was observed that the Langmuir isotherm was well fitted with the experimental data.

Table 6.10: Equilibrium parameters of Cu^{2+} adsorption

Temp (K)	C_i (mgpl)	C_e (mgpl)	q_e (mg/g)	% Adsorption	C_e/q_e	log C_e	log q_e
303	10.112	2.478	3.817	75.49	0.649	0.3941	0.5817
	14.987	4.689	5.149	68.71	0.911	0.6711	0.7117
	20.221	7.845	6.188	61.20	1.268	0.8946	0.7916
	25.005	11.321	6.842	54.73	1.655	1.0539	0.8352
	30.098	14.556	7.771	51.64	1.873	1.1630	0.8905
313	10.112	2.254	3.929	77.71	0.574	0.3530	0.5943
	14.987	4.218	5.385	71.86	0.783	0.6251	0.7311
	20.221	7.284	6.469	63.98	1.126	0.8624	0.8108
	25.005	10.928	7.039	56.30	1.553	1.0385	0.8475
	30.098	14.285	7.907	52.54	1.807	1.1549	0.8980
323	10.112	2.032	4.040	79.91	0.503	0.3079	0.6064
	14.987	4.002	5.493	73.30	0.729	0.6023	0.7398
	20.221	7.049	6.586	65.14	1.070	0.8481	0.8186
	25.005	10.445	7.280	58.23	1.435	1.0189	0.8621
	30.098	14.063	8.018	53.28	1.754	1.1481	0.9041
333	10.112	1.984	4.064	80.38	0.488	0.2975	0.6090
	14.987	3.858	5.565	74.26	0.693	0.5864	0.7454
	20.221	6.854	6.684	66.10	1.026	0.8359	0.8250
	25.005	9.545	7.730	61.83	1.235	0.9798	0.8882
	30.098	13.135	8.482	56.36	1.549	1.1184	0.9285

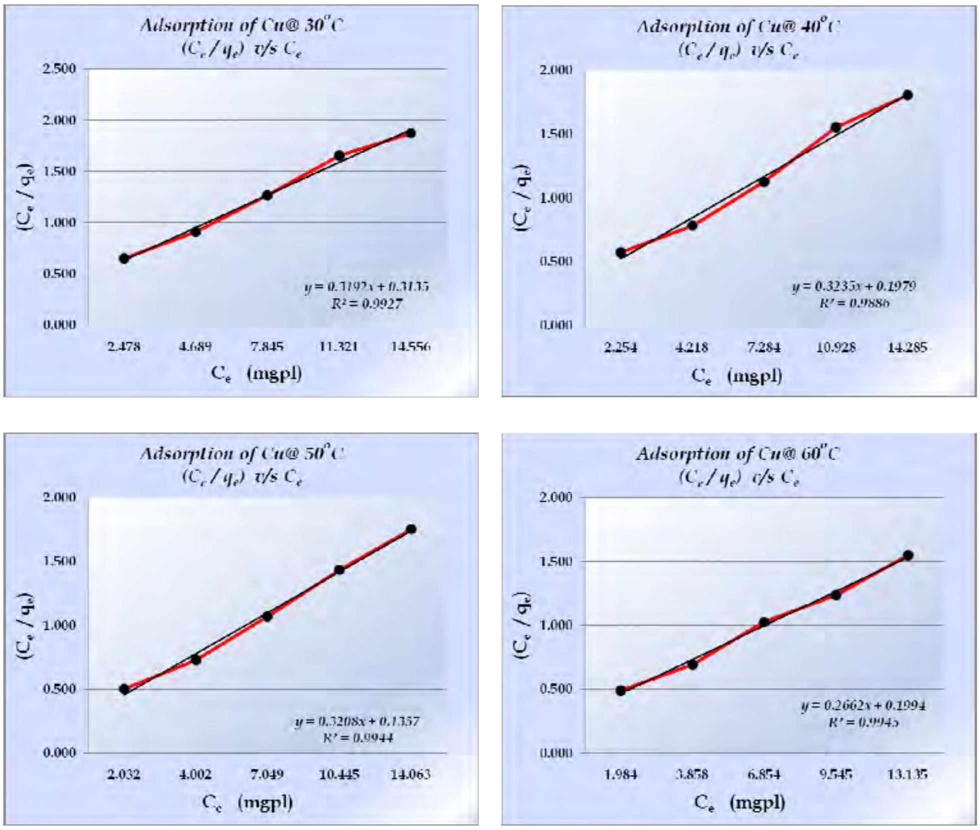

Figure 6.13: Langmuir isotherm of Cu^{2+} adsorption at different temperatures.

Table 6.11: Langmuir isotherms parameters for Cu^{2+} adsorption at different temperatures

Temp	**Langmuir Constants**			
(K)	**q_m**	**K_L**	**R^2**	**χ^2**
303	3.13	1.018	0.9927	0.2479
313	3.09	1.635	0.9886	0.2128
323	3.12	2.364	0.9944	0.1900
333	3.76	2.385	0.9945	0.2150

From the results, it is clear that the value of adsorption efficiency q_m decreases and adsorption energy K_L of the charcoal increases on increasing the temperature. The maximum adsorption, q_m corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The separation factor (R_L) was calculated and the values were found to be between 0 and 1 and confirming that the favourable status of the adsorption.

The kinetic data was also applied in the linear model of Freundlich equation. The linear form of Freundlich isotherm is represented as

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e$$

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (µg/g) at equilibrium, C_e is the equilibrium concentration of heavy metal ion (mgpl); K_F is the Freundlich constant [(µg/g) (L/mg)$^{(1/n)}$] and gives the capacity of the adsorbent and n_F is the Freundlich exponent and presents an indication of the favourability. Graphs was plotted with log q_e versus log C_e at different temperature and showed that the adsorption of Cu^{2+} follows the Langmuir isotherm (Figure: 6.14). The values of K_f and n were calculated from the slope and intercept of the log q_e versus log C_e plot and is given in the Table: 6.12. The magnitude of K_F and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity.

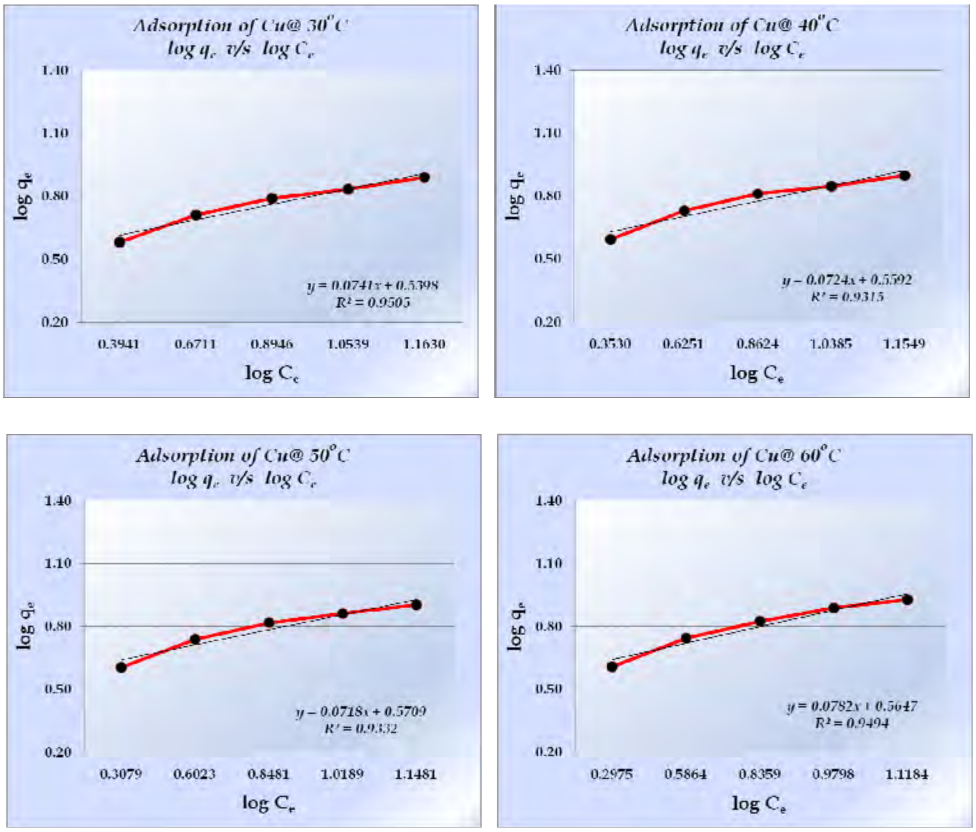

Figure 6.14: Freundlich isotherm of Cu^{2+} adsorption at different temperatures.

Table 6.12: Freundlich isotherms parameters for Cu^{2+} adsorption at different temperatures

Temp (K)	Freundlich Constants			
	n_F	K_F	R^2	χ^2
303	13.50	3.47	0.9505	0.0885
313	13.81	3.62	0.9315	0.1200
323	13.93	3.72	0.9332	0.1541
333	12.79	3.67	0.9494	0.1442

The χ^2 values for Langmuir and Freundlich isotherm are computed and included in the Table: 6.11 & 6.12. The χ^2 values for both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and relatively better fit is observed with Langmuir model as its R^2 value is more compared with the Freundlich model.

Table 6.13: Separation Factor ($R_{L)}$ for the adsorption of Cu^{2+} at different temperatures

Cu^{2+} conc. mgpl	Separation Factor,R_L			
	303K	**313K**	**323K**	***333K***
10.112	0.0885	0.0570	0.0402	0.0690
14.987	0.0615	0.0392	0.0275	0.0476
20.221	0.0463	0.0294	0.0205	0.0357
25.005	0.0378	0.0239	0.0166	0.0291
30.098	0.0316	0.0199	0.0139	0.0243

The Separation Factor (R_L) values of Langmuir isotherms at different temperatures are given in Table: 6.13 and according to this, Langmuir model was found to be fit better since the R_L values in all the systems studied are comparably less indicating favourable adsorption of all the metal ions on the selected adsorbent activated charcoal. The value of correlation co-efficient that was used as a main criterion for judging the fitness of the adsorption data showed. R^2 values of each metal ion at different temperature also showed higher value in Langmuir model than that in the other model. The statistical parameters also indicated the best fitment of the experimental data with the Langmuir model. It was found that the percentage adsorption increases with temperature. Figure: 6.15 shows the temperature dependence of removal Cu^{2+} ion solution of strength 20mgpl, using activated charcoal.

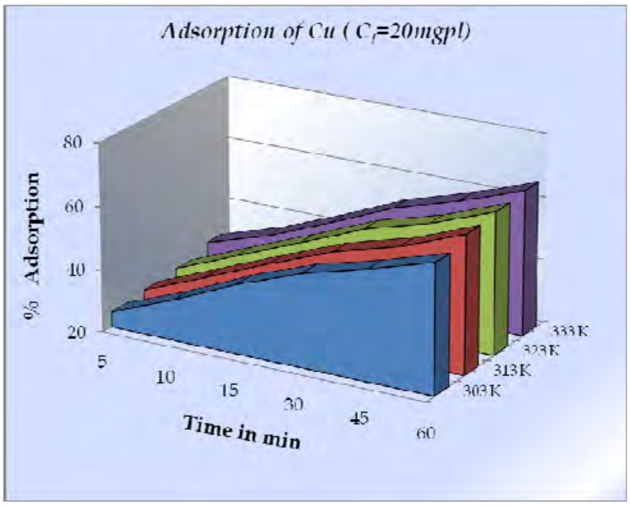

Figure 6.15: Effect of temperature on Cu^{2+} adsorption on to Ac.C.
(Conditions: Adsorbent dosage=0.1g/50ml, C_i= 20.221 mgpl, Temp:303K & time 60 min.)

Kinetic study

The data of kinetics of Cu^{2+} ion adsorption on activated charcoal is given in Table: 6.14. The data was found to fit the first order kinetic equations. The value of log (q_e-q_t) versus time plotted for different temperatures are shown in Figures 6.16 to 6.19. The reaction follows a first order rate kinetics to about thirty minutes and then after equilibrium has been established. The rate constant of the forward reaction can be calculated from the slope of the log (q_e-q_t) versus time plot. The rate constant of the backward reaction, k_2 is calculated using equilibrium constant, K_c and rate of forward reaction, k_1. The rate of forward reaction was found to be greater than the rate of backward reaction and the values are given in Table: 6.14.

Table 6.14: Kinetics data of Cu^{2+}adsorption at various temperatures & Initial adsorbate ion concentrations

Temp (K)	C_i (mgpl)	q_e (mg/g)	k_1 (min^{-1})	k_2 (min^{-1})	K_c (min^{-1})
303	10.112	3.817	0.385	0.265	0.649
	14.987	5.149	0.442	0.468	0.911
	20.221	6.188	0.380	0.888	1.268
	25.005	6.842	0.495	1.159	1.655
	30.098	7.771	0.371	1.502	1.873
313	10.112	3.929	0.378	0.196	0.574
	14.987	5.385	0.396	0.387	0.783
	20.221	6.469	0.343	0.783	1.126
	25.005	7.039	0.465	1.087	1.553
	30.098	7.907	0.380	1.427	1.807
323	10.112	4.040	0.371	0.132	0.503
	14.987	5.493	0.375	0.353	0.729
	20.221	6.586	0.348	0.723	1.070
	25.005	7.280	0.431	1.004	1.435
	30.098	8.018	0.387	1.367	1.754
333	10.112	4.064	0.401	0.087	0.488
	14.987	5.565	0.371	0.323	0.693
	20.221	6.684	0.334	0.692	1.026
	25.005	7.730	0.380	0.855	1.235
	30.098	8.482	0.348	1.201	1.549

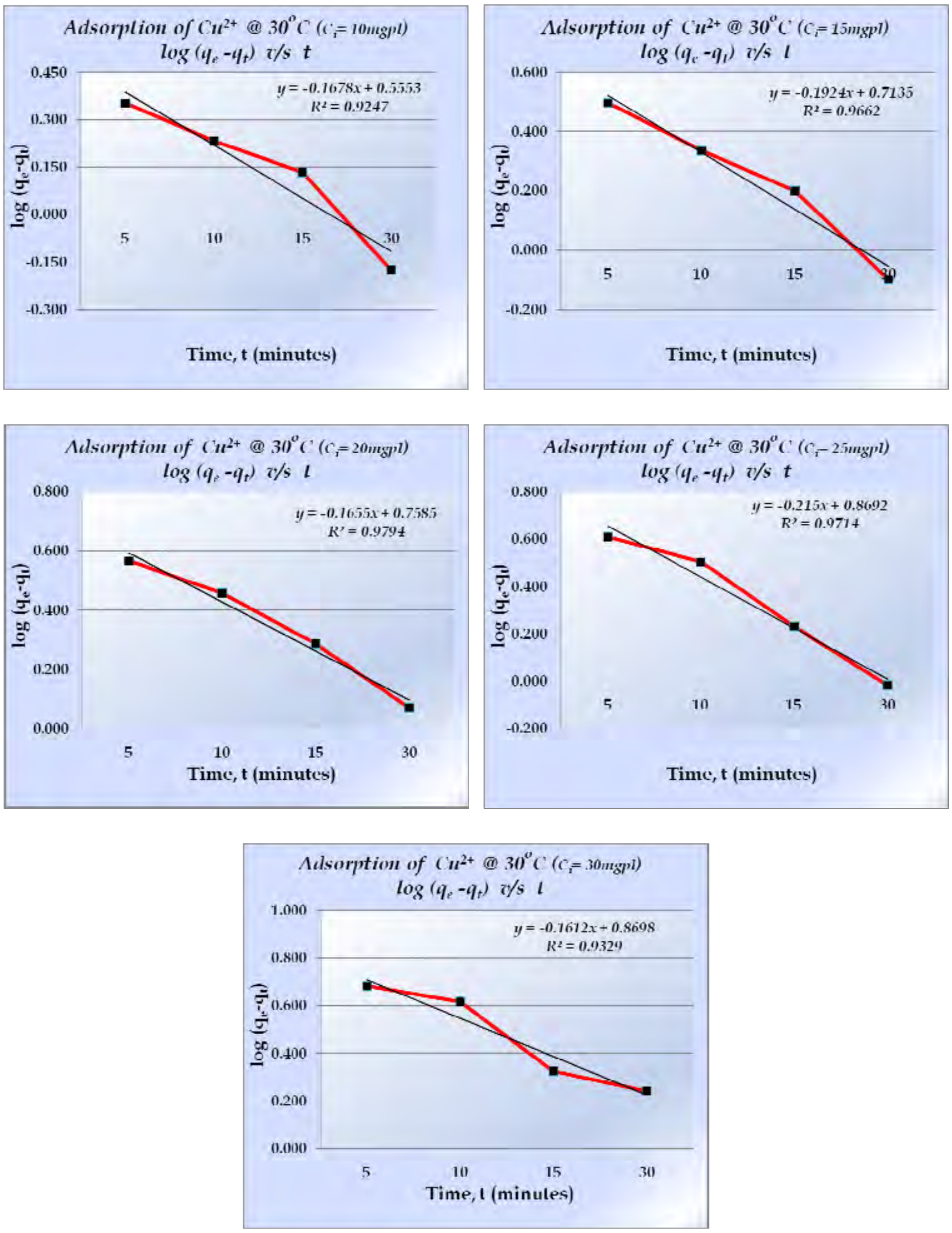

Figure 6.16: **Kinetic study plot of Cu^{2+} adsorption at various Concentrations (Temp:303K)**

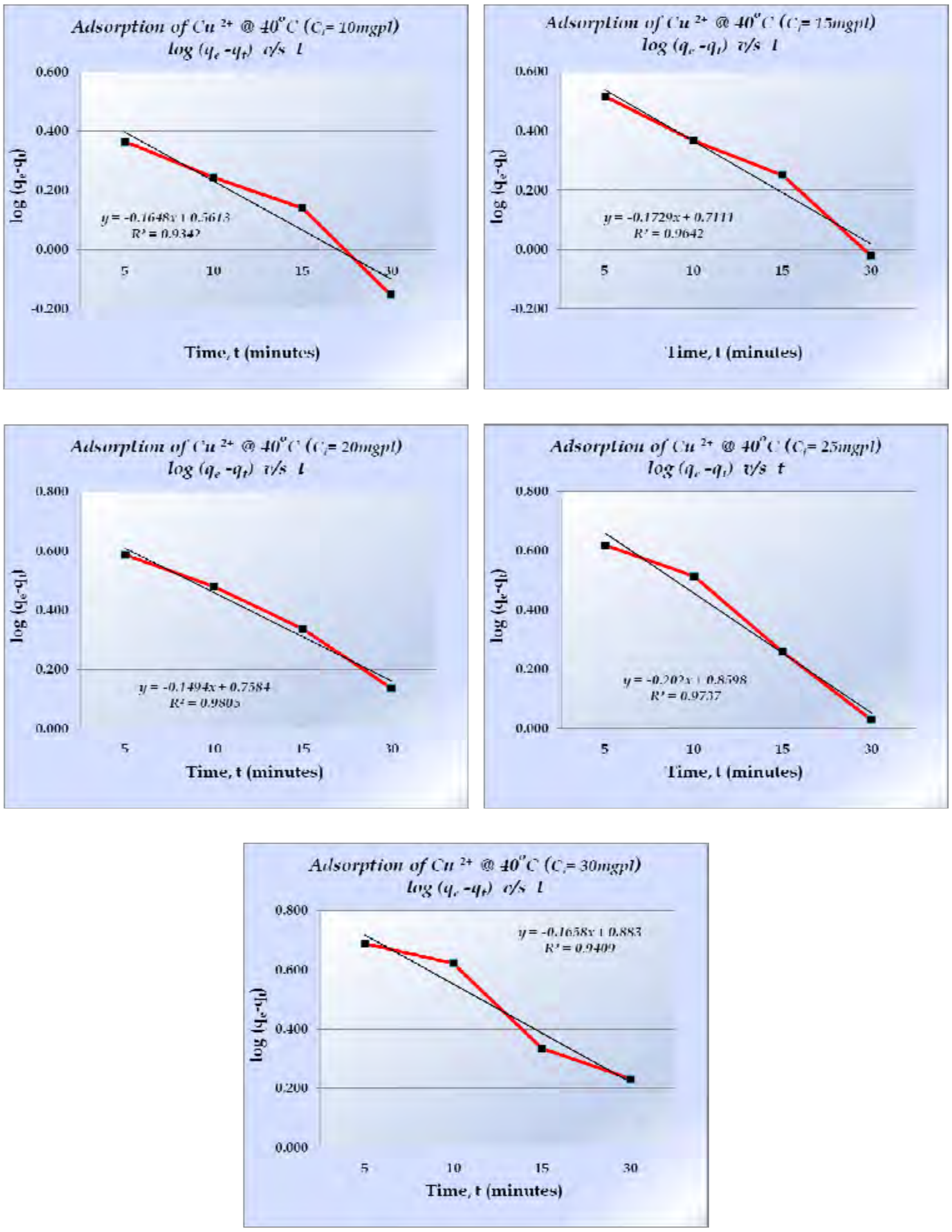

Figure 6.17: **Kinetic study plot of Cu^{2+} adsorption at various Concentrations (Temp: 313K)**

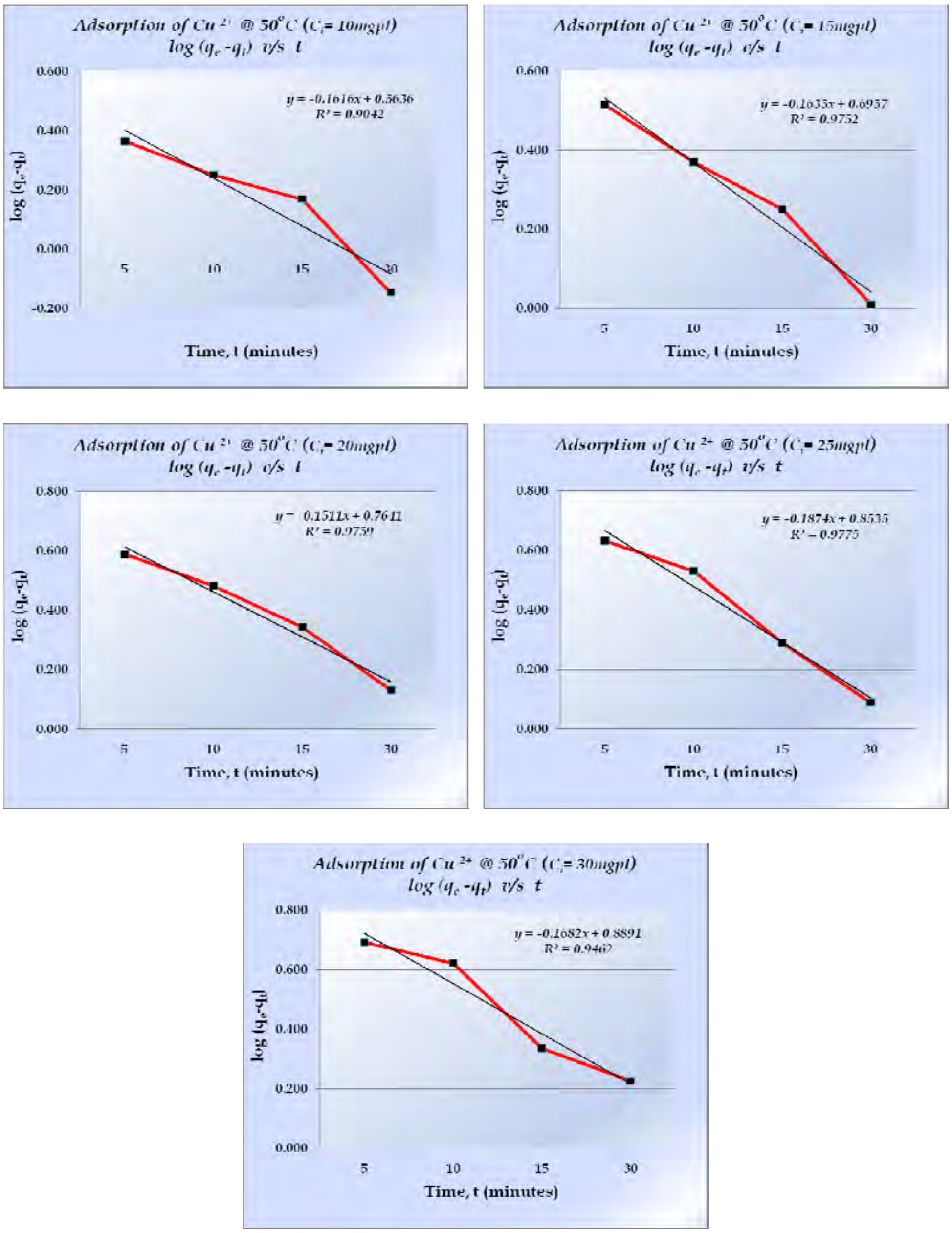

Figure 6.18: Kinetic study plot of Cu^{2+} adsorption at various Concentrations (Temp: 323K)

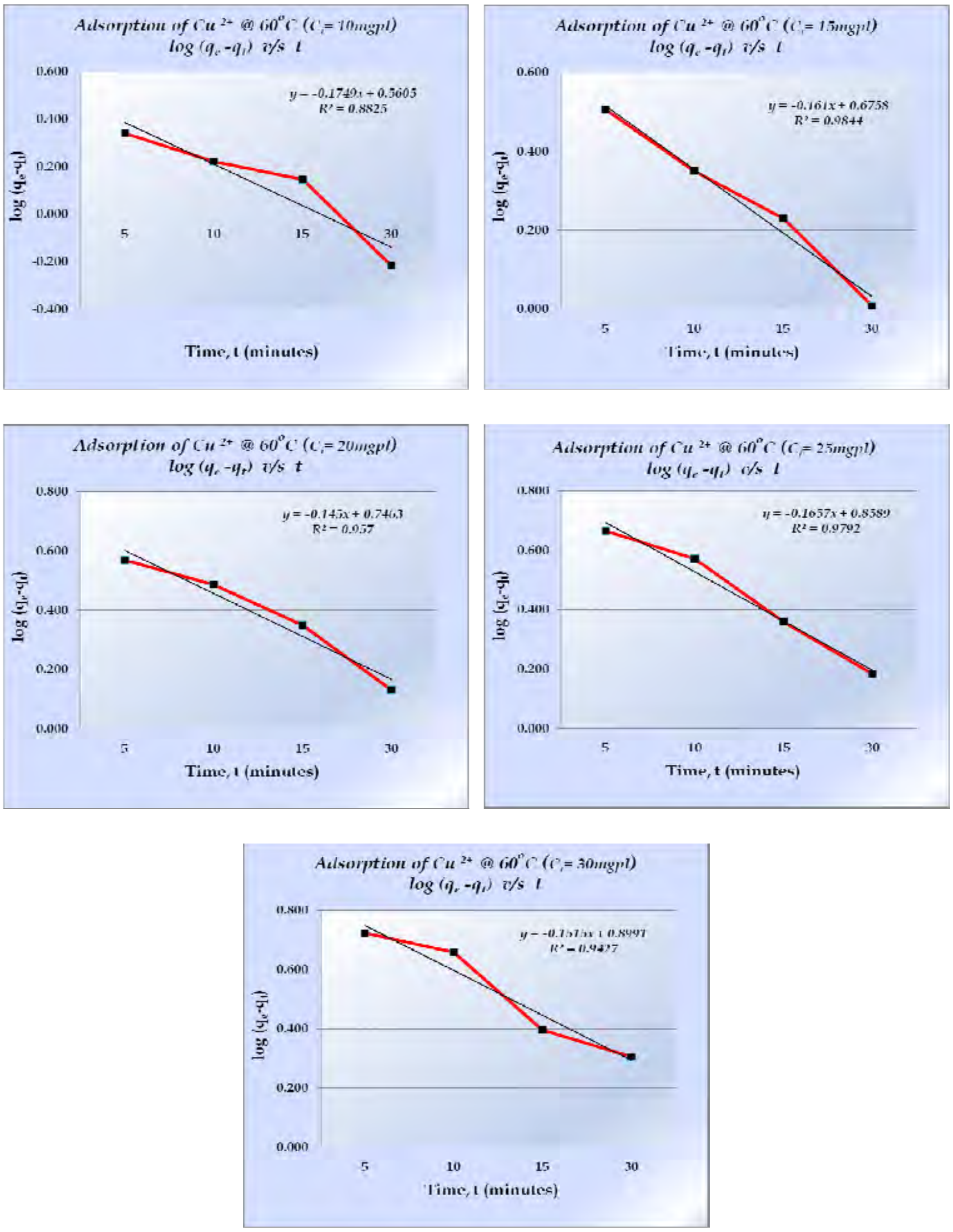

Figure 6.19: Kinetic study plot of Cu^{2+} adsorption at various Concentrations (Temp: 333K)

6.7.3 Adsorption study of Ni^{2+}

Ni is the member of Iron family and has properties similar to that of Cobalt. It's a silver coloured white malleable metal and can exist in +1, +2, +3 oxidation states, but the chemistry of Ni compounds is usually found that of the +2 state. Even though metallic Ni is found to be non toxic, its gaseous form like Nickel Carbonyl is very toxic.

Batch Adsorption Study

Batch adsorption experiments were carried out using an Erlenmeyer flask of 250 ml capacity. Predetermined amount of activated charcoal (0.1g/50ml) was added to the Ni(II) solution of strength predetermined with ICP OES and the flask was placed in a constant temperature bath and stirred with the help of a stirrer until equilibrium was attained. At the end of adsorption process, adsorbent particles were filtered through Whatman No: 40 papers and the equilibrium concentration of Ni^{2+} in the supernatant was then analysed in ICP OES. The experiment was conducted at varying Ni^{2+} concentrations (10, 20, 30, 40 & 50 mgpl) at different temperatures (303, 313, 323, and 333K). The pH of solution was adjusted to 6.0 using dilute NaOH and H_2SO_4 in equilibrium study.

Adsorption Isotherm

The experimental data analysed according to the linear form of the Langmuir and Freundlich isotherms. The Langmuir isotherm represented by the following equation

$$\frac{C_e}{q_e}=\frac{C_e}{q_m}+\frac{1}{q_m K_L}$$

where C_e is the equilibrium aqueous metal ions concentration (mgpl), q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium, q_m and K_L are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption respectively. The initial Ni ion concentration, equilibrium concentration, amount adsorbed, percentage adsorption, at different concentration and temperature is given in Table: 6.15. The plots of C_e / q_e versus C_e at different temperatures are found to be linear with the slope ($1/ q_m$) and intercept ($1/q_mK_L$), indicating the applicability of the Langmuir model (Figure: 6.20). The value of q_m and K_L was then calculated from the slope and the intercept. The parameters q_m and K_L have been calculated and the results are represented in Table: 6.16. It was observed that the Langmuir isotherm fits well with the experimental data.

Table 6.15: Equilibrium parameters of Ni^{2+} adsorption

Temp (K)	C_i (mgpl)	C_e (mgpl)	q_e (mg/g)	% Adsorption	C_e/q_e	log C_e	log q_e
303	10	1.552	8.448	84.48	0.184	0.1909	0.9268
	20	3.845	16.155	80.78	0.238	0.5849	1.2083
	30	8.398	21.602	72.01	0.389	0.9242	1.3345
	40	13.178	26.822	67.06	0.491	1.1198	1.4285
	50	18.547	31.453	62.91	0.590	1.2683	1.4977
313	10	1.552	8.448	84.48	0.184	0.1909	0.9268
	20	3.845	16.155	80.78	0.238	0.5849	1.2083
	30	8.398	21.602	72.01	0.389	0.9242	1.3345
	40	13.178	26.822	67.06	0.491	1.1198	1.4285
	50	18.547	31.453	62.91	0.590	1.2683	1.4977
323	10	1.465	8.535	85.35	0.172	0.1660	0.9312
	20	3.602	16.398	81.99	0.220	0.5565	1.2148
	30	7.721	22.279	74.26	0.347	0.8877	1.3479
	40	12.789	27.211	68.03	0.470	1.1068	1.4347
	50	18.163	31.838	63.68	0.570	1.2592	1.5029
333	10	1.261	8.739	87.39	0.144	0.1009	0.9414
	20	3.315	16.686	83.43	0.199	0.5204	1.2223
	30	7.427	22.573	75.24	0.329	0.8708	1.3536
	40	12.458	27.542	68.86	0.452	1.0954	1.4400
	50	17.612	32.388	64.78	0.544	1.2458	1.5104

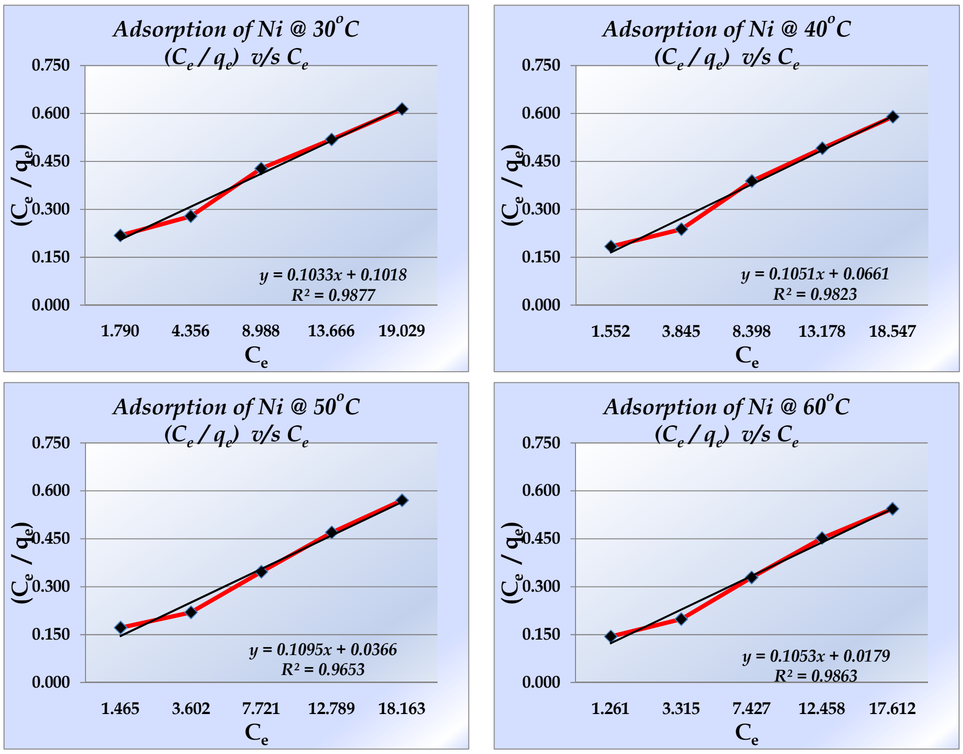

Figure 6.20: Langmuir isotherm of Ni^{2+} adsorption at different temperatures.

The statistical significance of the correlation coefficient (R^2) for C_e / q_e versus C_e is the criteria by which the fitting of the data to Langmuir isotherm. It demonstrates monolayer coverage of adsorbate at the outer surface of the adsorbent. The parameters q_m and K_L have been calculated and the results are represented in Table: 6.16. It was observed that the Langmuir isotherm fits well with the experimental data.

Table 6.16: Langmuir isotherms Parameters for the adsorption of Ni^{2+}onto Ac.C at different temperatures

Temp	Langmuir Constants			
(K)	q_m	K_L	R^2	χ^2
303	9.68	1.015	0.9877	0.3332
313	9.51	1.590	0.9823	0.3025
323	9.13	2.992	0.9653	0.2642
333	8.97	9.612	0.9863	0.2279

From the results, it is clear that the value of adsorption efficiency q_m decreases and adsorption energy K_L of the charcoal increases on increasing the temperature. From the data the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface (Vijayakumaran et al., 2009).The trend shows that the adsorbent prefers to bind acidic ions and that speciation predominates on adsorbent characteristics, when ion exchange is the predominant mechanism. The separation factor (R_L) was calculated and the values were found to be between 0 and 1 and confirming that the favourable status of the adsorption (Rajalakshmi et al., 2009; Edwin, 2008).

The Freundlich equation have also employed for the adsorption of Ni^{2+} on the adsorbent. The linear form of Freundlich isotherm have represented as

$$\log q_e = \log K_F + \frac{1}{n_F} \log Ce$$

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (µg/g) at equilibrium, C_e is the equilibrium concentration of heavy metal ion (mgpl); K_F is the Freundlich constant $[(\mu g/g)(L/mg)^{(1/n)}]$ and gives the capacity of the adsorbent and n_F is the Freundlich exponent and presents an indication of the favourability. Linear plots of log q_e versus log C_e at different temperature showed that the adsorption of Ni^{2+} follows the Freundlich isotherm (Figure: 6.21). The values of K_f and n were calculated from the slope and intercept of the log q_e versus log C_e plot and is given in the Table: 6.17. The magnitude of K_F and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity. Freundlich constants calculated shows the increase of negative charge on the surface that enhances the electrostatic force like Van der Waal's between the carbon surface and metal ion, which increases the adsorption of nickel ion.

The intensity of adsorption is an indicative of the bond energies between Ni^{2+} and adsorbent and the possibility of slight chemisorptions rather than physisorption. The values of n are greater than one indicating the adsorption is favourable. The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa. Higher the K_F value, the greater is the adsorption intensity.

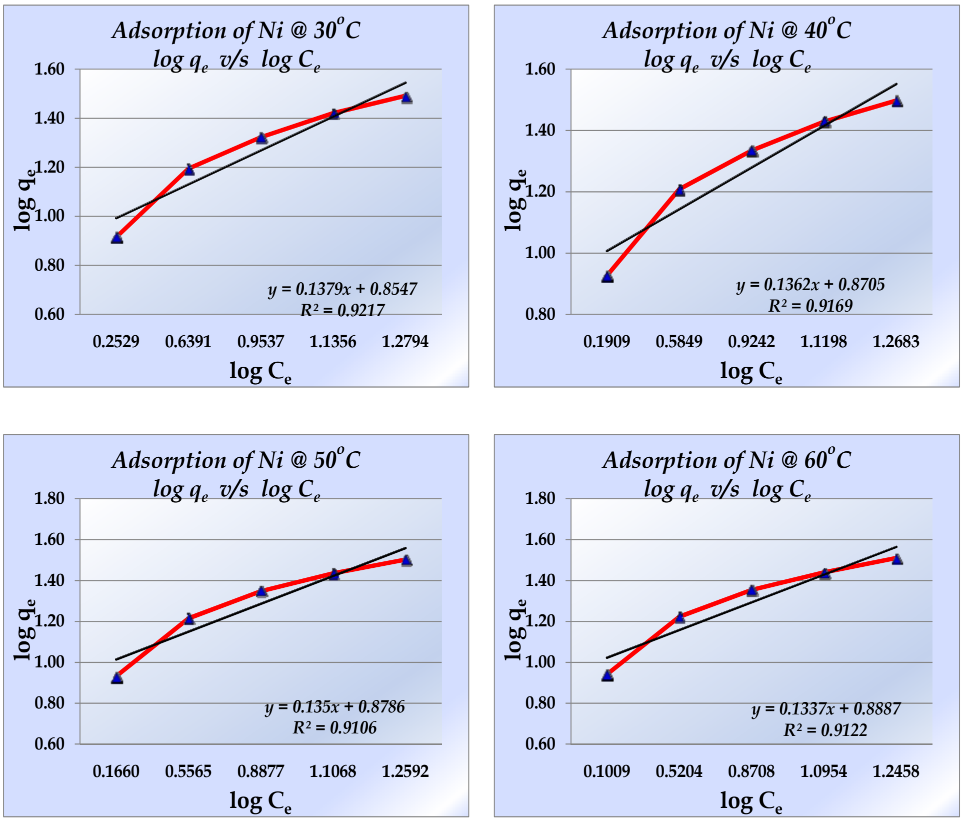

Figure 6.21: Freundlich isotherm of Ni^{2+} adsorption at different temperature

Table 6.17: Freundlich Isotherms parameters for the adsorption of Ni^{2+}onto Ac.C at different temperatures

Temp (K)	Freundlich Constants			
	n_F	K_F	R^2	χ^2
303	7.25	7.155	0.9218	0.2514
313	7.30	7.369	0.9116	0.3017
323	7.41	7.561	0.9106	0.3885
333	7.48	7.739	0.9122	0.5112

χ^2 test is most often used in the context of linear models like linear regression, analysis of variance. The χ^2 values for Langmuir and Freundlich isotherm are computed and included in the Table: 6.16 & 6.17. If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a larger number. Therefore, it is necessary to analyze the data set using the non-linear Chi-square test to confirm the best-fit isotherm for the sorption process. The χ^2 values of both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and relatively better fit is observed with Langmuir model as its χ^2 value is less than that of Freundlich model. The Langmuir isotherm is more widely used and provides information on the monolayer adsorption capacity in contrast to the Freundlich model.

Table 6.18: Dimensionless Separation Factor(R_L) for the adsorption of Ni^{2+} at different temperatures

Ni conc. mgpl	Separation Factor,R_L			
	303K	313K	323K	*333K*
10.002	0.0897	0.0592	0.0323	0.0103
20.011	0.0470	0.0305	0.0164	0.0052
30.004	0.0318	0.0205	0.0110	0.0035
40.014	0.0240	0.0155	0.0083	0.0026
50.001	0.0193	0.0124	0.0066	0.0021

The Separation Factor (R_L) values of Langmuir isotherms at different temperatures are quantified (Table: 6.18) and according to this, Langmuir model was found to be fit better since the R_L values are comparably less. The value of correlation co-efficient that was used as a main criterion for judging the fitness of the adsorption data showed. R^2 values of each metal ion at different temperature also showed an augmented trend in Langmuir model than that in the other model. The statistical parameters are indicating the best fitment of the experimental data with the Langmuir model. In all the systems studied, R_L values were comprised between 0 and 1 indicating favourable adsorption of all the metal ions on the selected adsorbent activated charcoal.

The temperature dependence of the adsorption of Ni ion on activated charcoal is shown in Figure: 6.22, plotting the percentage adsorption against time (t) at different temperatures. The experimental result shows that the amount of metal ion adsorbed on activated charcoal increased with increasing adsorption temperature.

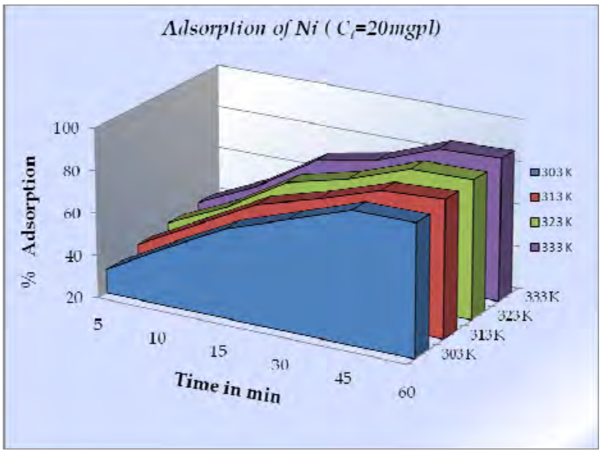

Figure 6.22: Effect of temperature on Ni^{2+} adsorption on to Ac.C. (Conditions: Adsorbent dosage=50mg/50ml, C_i= 10.001 mgpl, Temp:303K & time 60 min.)

Kinetic study

The kinetics data of Ni^{2+} ion adsorption on activated charcoal is given in Table: 6.19. The data was found to fit the first order kinetic equations. The value of log (q_e-q_t) versus time plotted for different temperatures are shown in Figures 6.23 to 6.26. The rate constant of the forward reaction can be calculated from the slope of the above plot. The rate constant of the backward reaction, k_2 is calculated using equilibrium constant, K_c and rate of forward reaction,k_1. The rate of forward reaction was found to be greater than the rate of backward reaction and the values are given in Table: 6.19. The reaction follows a first order rate law about thirty minutes and then after equilibrium has been established which means adsorption increases on boosting the shaking time and attains a constant value after thirty minutes.

Table 6.19: Kinetics data of Ni^{2+}adsorption at various temperatures & Initial adsorbate ion concentrations

Temp (K)	C_i (mgpl)	q_e (mg/g)	k_1 (min^{-1})	k_2 (min^{-1})	K_c (min^{-1})
303	10	8.448	0.544	0.360	0.184
	20	16.155	0.510	0.272	0.238
	30	21.602	0.417	0.028	0.389
	40	26.822	0.379	0.112	0.491
	50	31.453	0.296	0.294	0.590
313	10	8.448	0.286	0.102	0.184
	20	16.155	0.189	0.049	0.238
	30	21.602	0.184	0.205	0.389
	40	26.822	0.174	0.317	0.491
	50	31.453	0.110	0.479	0.590
323	10	8.535	0.300	0.128	0.172
	20	16.398	0.191	0.028	0.220
	30	22.279	0.172	0.175	0.347
	40	27.211	0.140	0.330	0.470
	50	31.838	0.110	0.460	0.570
333	10	8.739	0.308	0.164	0.144
	20	16.686	0.179	0.020	0.199
	30	22.573	0.170	0.159	0.329
	40	27.542	0.161	0.291	0.452
	50	32.388	0.137	0.407	0.544

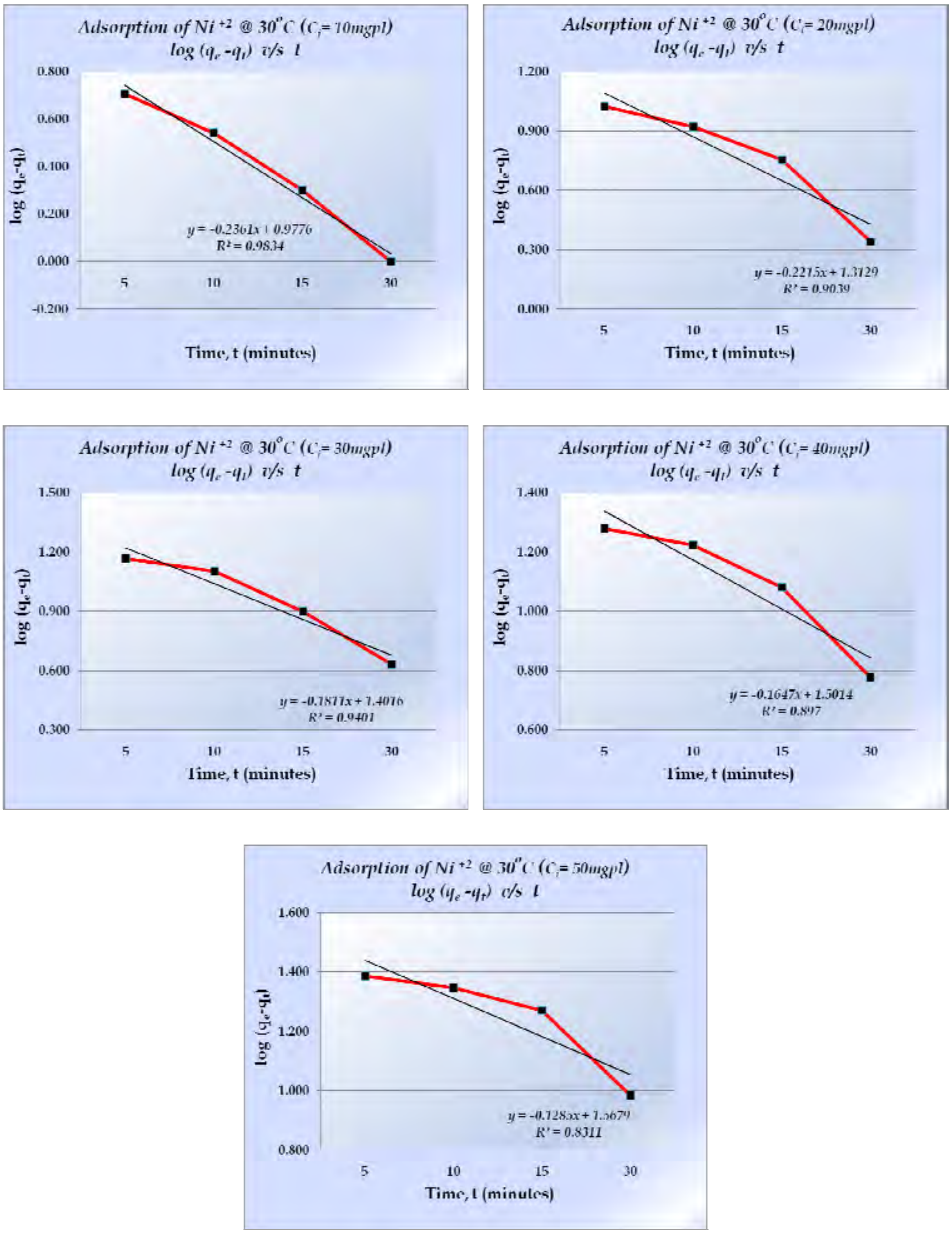

Figure 6.23: Kinetic study plot of Ni^{2+} adsorption at various Concentrations (Temp : 303K)

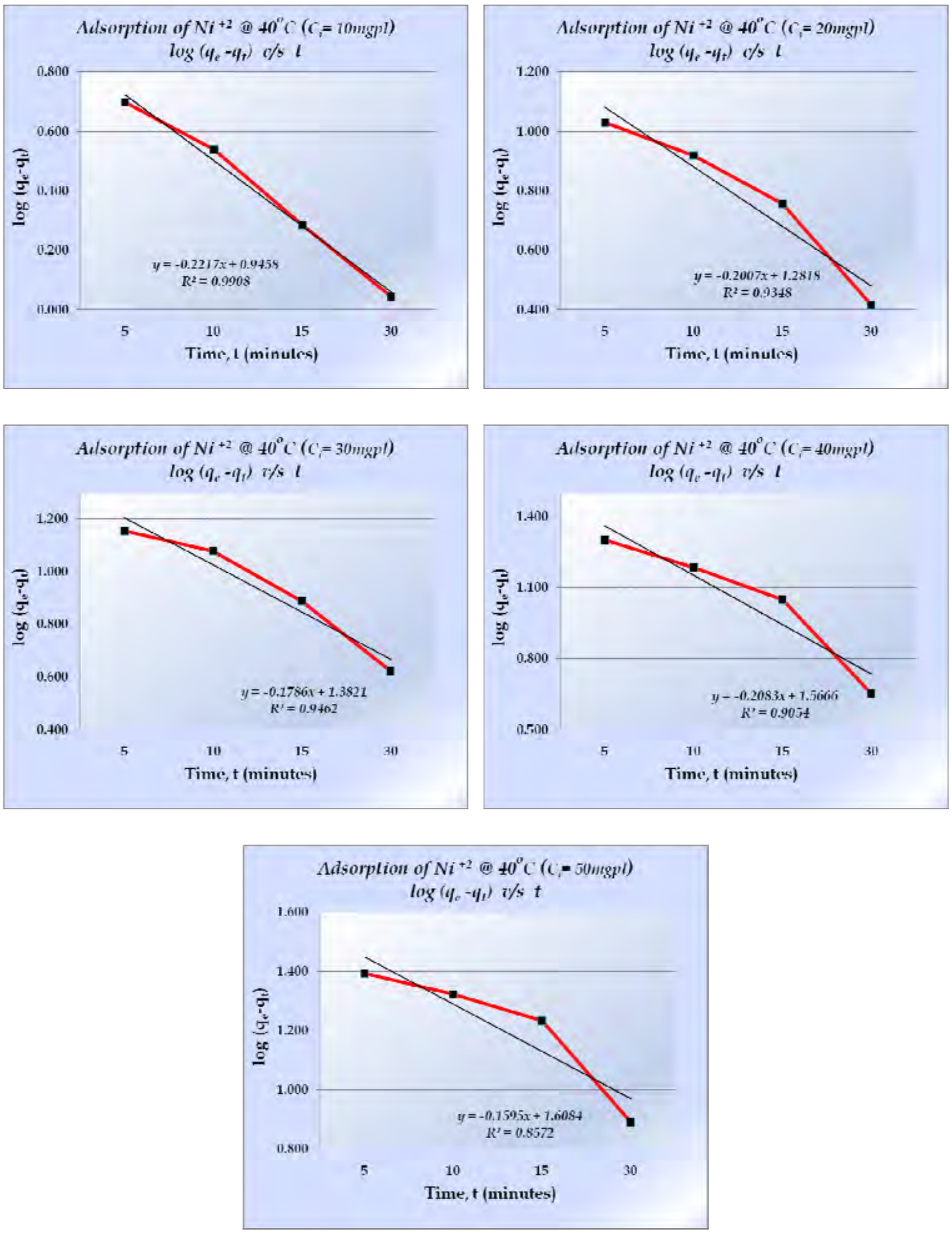

Figure 6.24: Kinetic study plot of Ni^{2+} adsorption at various Concentrations (Temp:313K)

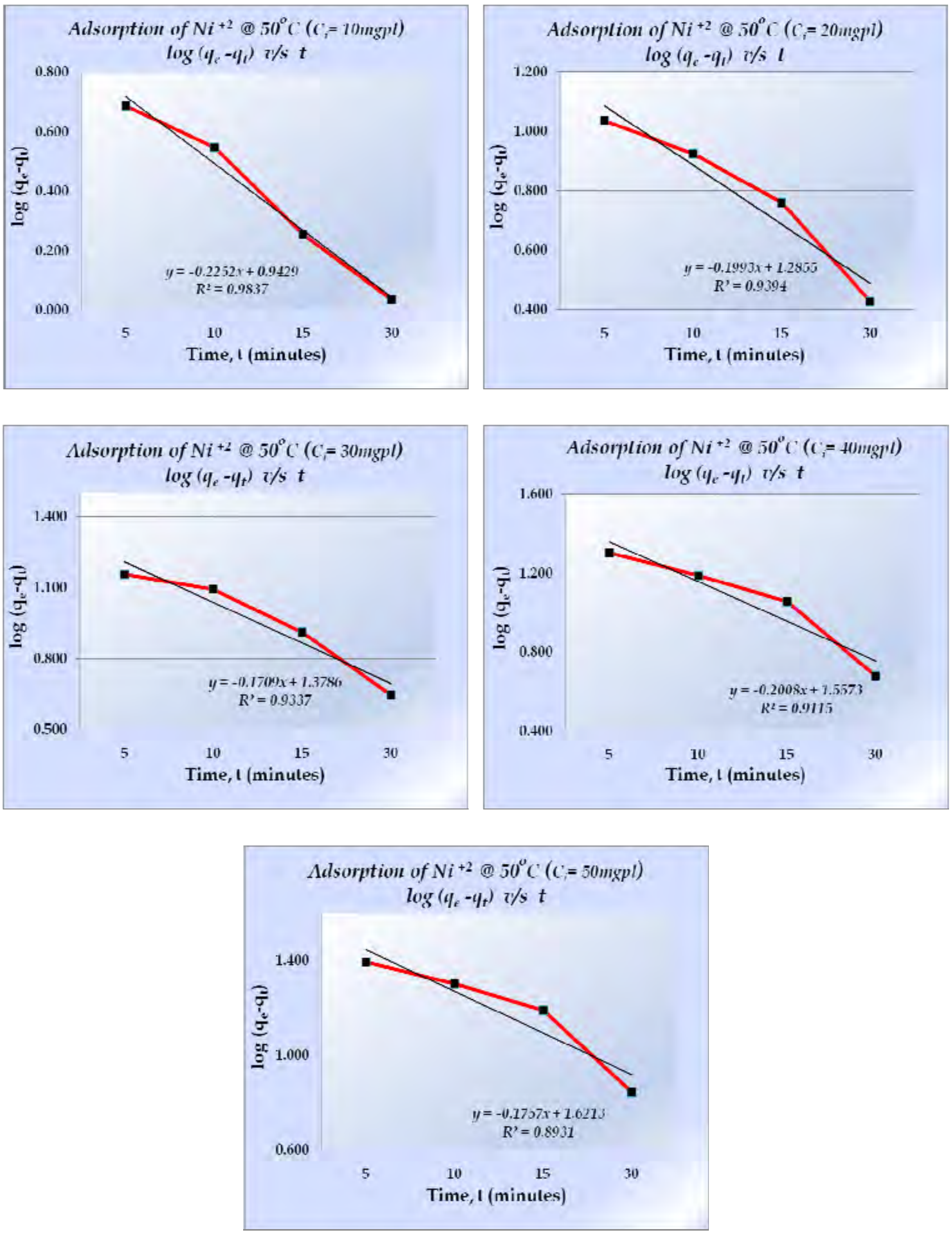

Figure 6.25: Kinetic study plot of Ni^{2+} adsorption at Various Concentrations (Temp:323K)

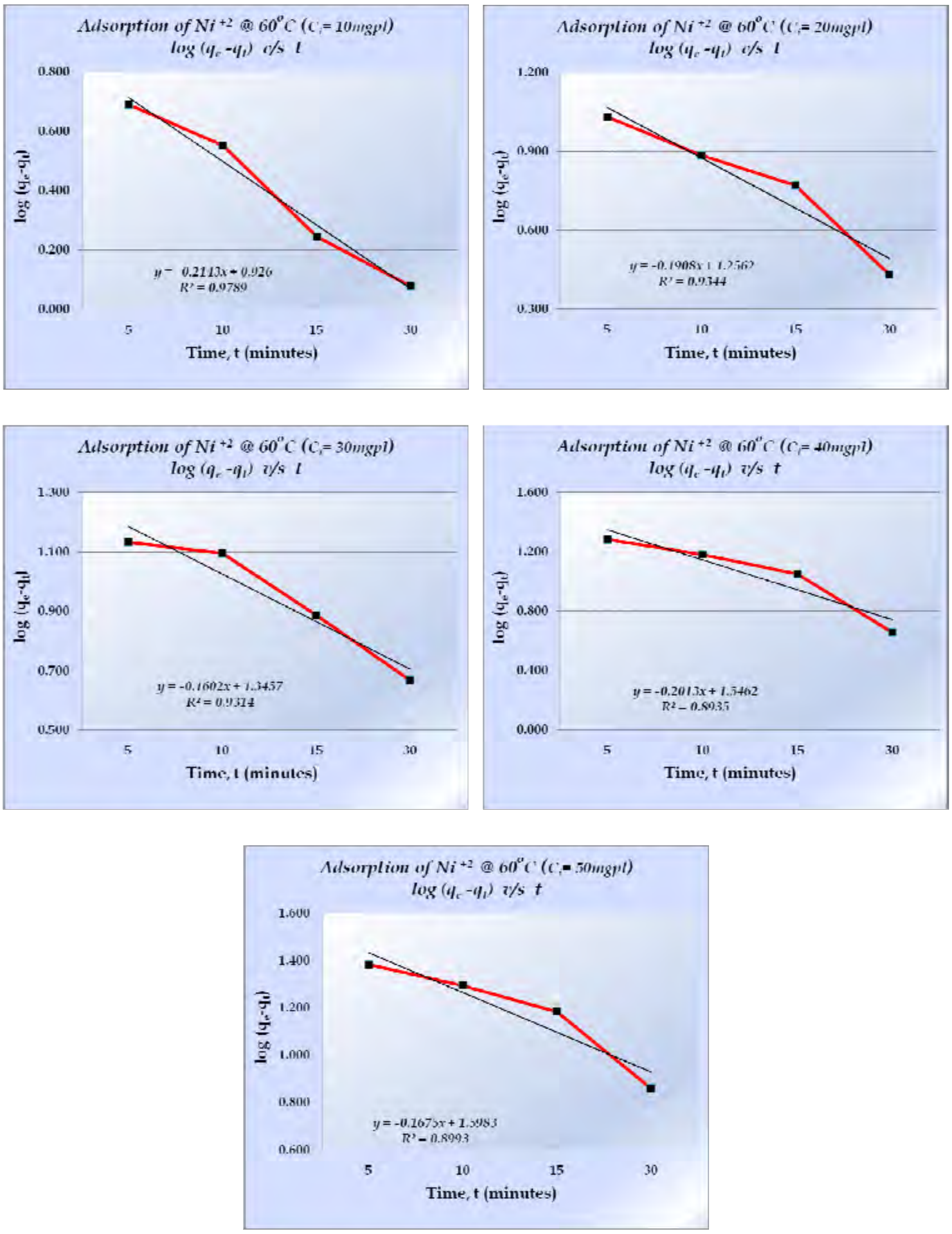

Figure 6.26: Kinetic study plot of Ni^{2+} adsorption at Various Concentrations (Temp:333K)

6.7.4 Adsorption study of Pb^{2+}

The element lead is member of the carbon family. It is the most metallic of the group IV element like Tin, it shows oxidation state of +2 and +4 hut the +4 state is more highly oxidizing.

Batch Adsorption Study

The effect of adsorbent dose on Pb^{2+} ion removal was studied by agitating 50ml of 20, 30, 40, 50 and 60 mgpl of Pb^{2+}, adjusted to an initial pH of 5.0ml and containing different doses of adsorbent (10-150mg/50ml) for a time period greater than their respective equilibrium times. The effects of pH, time, temperature, initial concentration, adsorbent dosage on Pb^{2+} ion removal was studied by using 50ml above mentioned known concentrations of standard metal ion solution adjusted to an initial pH of 2, 3, 5, 4, 6, 8, 9 and 10 mixed with different dosage of carbon and agitated for 60min.

Adsorption Isotherm

The experimental data analysed according to the linear form of the Langmuir and Freundlich isotherms. The initial Pb^{2+} concentration, equilibrium concentration, amount adsorbed, percentage adsorption, at different concentration and temperature is given in Table: 6.20. The plots of C_e /q_e versus C_e at different temperatures are found to be linear with the slope (1/ q_m) and intercept (1/q_mK_L), indicating the applicability of the Langmuir model (Figure: 6.27). The value of q_m and K_L was then calculated from the slope and the intercept. It was observed that the Langmuir isotherm fits well with the experimental data. The parameters R^2, q_m and K_L have been calculated and the results are represented in Table: 6.21. It was observed that the Langmuir isotherm fits well with the experimental data.

Table 6.20: Equilibrium parameters of Pb^{2+} adsorption

Temp (K)	C_i (mgpl)	C_e (mgpl)	q_e (mg/g)	% Adsorption	C_e/q_e	log C_e	log q_e
303	20.013	2.254	17.759	88.74	0.127	0.3530	1.2494
	30.154	5.245	24.909	82.61	0.211	0.7197	1.3964
	40.112	10.660	29.452	73.42	0.362	1.0277	1.4691
	50.084	16.756	33.328	66.54	0.503	1.2242	1.5228
	60.015	21.075	38.940	64.88	0.541	1.3238	1.5904
313	20.013	2.115	17.898	89.43	0.118	0.3253	1.2528
	30.154	5.201	24.953	82.75	0.208	0.7161	1.3971
	40.112	10.580	29.532	73.62	0.358	1.0245	1.4703
	50.084	16.625	33.459	66.81	0.497	1.2208	1.5245
	60.015	20.985	39.030	65.03	0.538	1.3219	1.5914
323	20.013	2.084	17.929	89.59	0.116	0.3189	1.2536
	30.154	5.150	25.004	82.92	0.206	0.7118	1.3980
	40.112	10.384	29.728	74.11	0.349	1.0164	1.4732
	50.084	16.316	33.768	67.42	0.483	1.2126	1.5285
	60.015	20.145	39.870	66.43	0.505	1.3042	1.6006
333	20.013	2.049	17.964	89.76	0.114	0.3115	1.2544
	30.154	5.089	25.065	83.12	0.203	0.7066	1.3991
	40.112	10.121	29.991	74.77	0.337	1.0052	1.4770
	50.084	16.280	33.804	67.49	0.482	1.2117	1.5290
	60.015	19.856	40.159	66.91	0.494	1.2979	1.6038

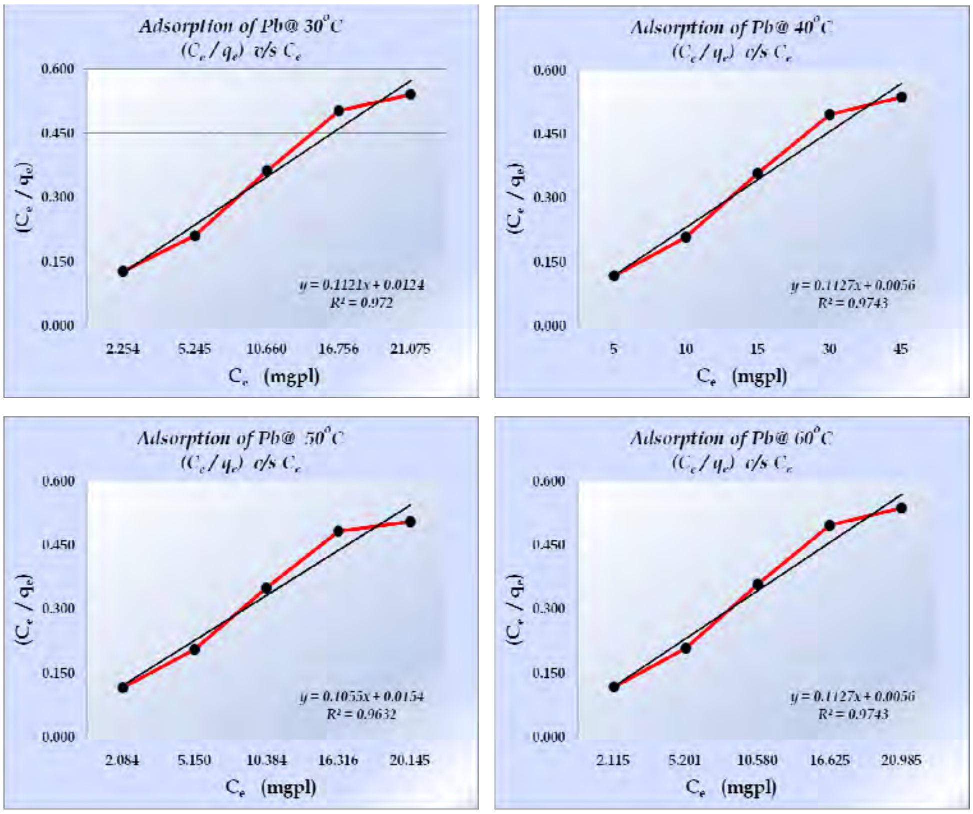

Figure 6.27: Langmuir isotherm of Pb^{2+} adsorption at different temperatures.

Table 6.21: Langmuir isotherms Parameters for Pb^{2+} adsorption at different temperatures

Temp	Langmuir Constants			
(K)	q_m	K_L	R^2	χ^2
303	8.92	8.968	0.9720	0.0795
313	8.87	20.125	0.9743	0.0758
323	9.48	6.851	0.9632	0.0780
333	8.87	20.125	0.9743	0.0773

The equilibrium data was also applied on the Freundlich isotherm equation. The linear plots of log q_e versus log C_e at different temperature show that the adsorption of Pb^{2+} also follows the Freundlich isotherm (Figure: 6.28). The values of K_f and n were calculated from the slope and intercept of the log q_e versus log C_e plot and is given in the Table:6.22 . The magnitude of K_F and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity.

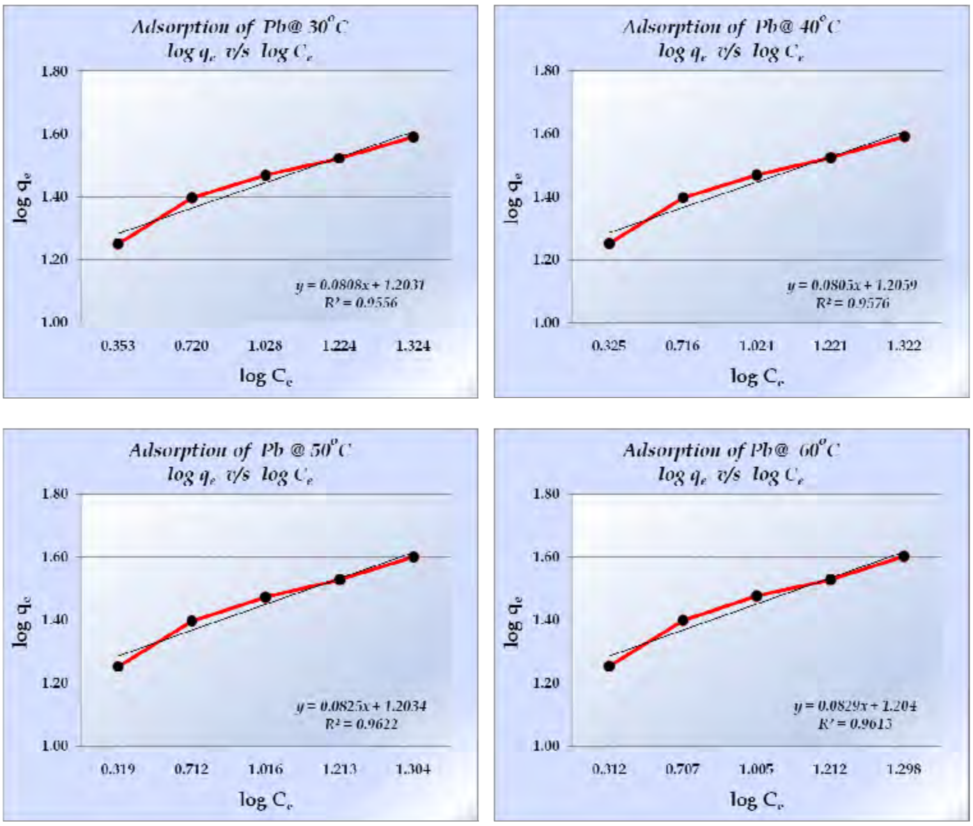

Figure 6.28: Freundlich isotherm of Pb^{2+} adsorption at different temperature

Table 6.22: Freundlich Isotherms parameters for Pb^{2+} adsorption

Temp (K)	Freundlich Constants			
	n_F	K_F	R^2	χ^2
303	12.38	9.03	0.9556	0.3069
313	12.42	16.07	0.9576	0.3365
323	12.12	15.97	0.9622	0.3342
333	12.06	16.00	0.9613	0.3403

The χ^2 values for Langmuir and Freundlich isotherm are computed and included in the Table: 6.21 & 6.22. If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a larger number. The χ^2 values of both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and relatively better fit is observed with Langmuir model as its χ^2 value is less than that of Freundlich model. The Langmuir isotherm is more widely used and provides information on the monolayer adsorption capacity in contrast to the Freundlich model.

Table 6.23: Separation Factor ($R_{L)}$ for the adsorption of Pb^{2+} at different temperatures

Pb^{2+} conc. mgpl	Separation Factor, R_L			
	303K	313K	323K	*333K*
20.013	0.0055	0.0025	0.0072	0.0025
30.154	0.0037	0.0016	0.0048	0.0016
40.112	0.0028	0.0012	0.0036	0.0012
50.084	0.0022	0.0010	0.0029	0.0010
60.015	0.0019	0.0008	0.0024	0.0008

The Separation Factor (R_L) values of Langmuir isotherms at different temperatures are quantified (Table: 6.23) and the values were found to be between 0 and 1 and confirming that the favourable status of the adsorption. According to this, Langmuir model was found to be fit better since the R_L values are comparably less. The value of correlation co-efficient that was used as a main criterion for judging the fitness of the adsorption data showed. R^2 values of each metal ion at different temperature also showed an increased drift in Langmuir model than that in the other model. The statistical parameters are indicating the best fitting of the experimental data with the Langmuir model. In all the systems studied, R_L values were comprised between 0 and 1 indicating favourable adsorption of all the metal ions on the selected adsorbent activated charcoal.

Equilibrium studies revealed as in the case of adsorption of other metal ions, the effective adsorption increases with the increase in temperature (Michael et al., 2005). The effect of temperature on the adsorption of Pb^{2+}on activated charcoal is given in Figure: 6.29.

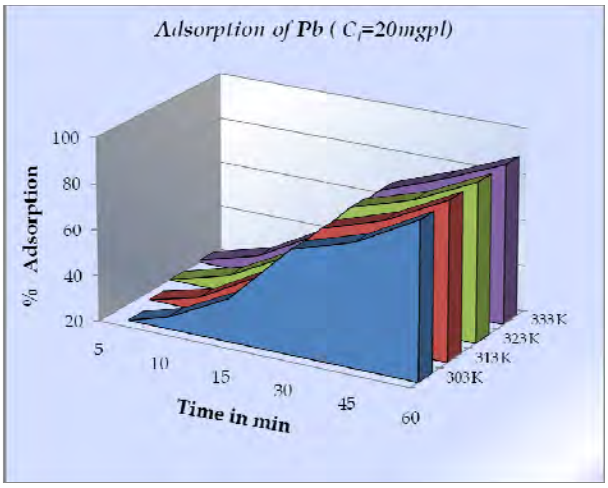

Figure 6.29: Effect of temperature on Pb^{2+} adsorption
(Conditions: Adsorbent dosage=0.1g/50ml,
C_i= 20.013 mgpl, Temp:303K & time 60 min.)

Kinetic Study

The kinetics data of Pb^{2+} ion adsorption on activated charcoal is given in Table: 6.24. The data was found to fit the first order kinetic equations. The value of log (q_e-q_t) versus time plotted for different temperatures are shown in Figures 6.30 to 6.33. The rate constant of the forward reaction can calculated from the slope of the above plot. The rate constant of the backward reaction, k_2 is calculated using equilibrium constant, K_c and rate of forward reaction,k_1. The rate of forward reaction was found to be greater than the rate of backward reaction and the values are given in Table: 6.24. The reaction follows a first order rate law about thirty minutes and there after equilibrium has been established which means adsorption increases with an increase in shaking time and attains a constant value after 45 minutes.

Table 6.24: Kinetics data of Pb^{2+}adsorption at various temperatures & Initial adsorbate ion concentrations

Temp (K)	C_i (mgpl)	q_e (mg/g)	k_1 (min^{-1})	k_2 (min^{-1})	K_c (min^{-1})
303	20.013	17.759	0.362	0.235	0.127
	30.154	24.909	0.348	0.137	0.211
	40.112	29.452	0.415	0.054	0.362
	50.084	33.328	0.344	0.159	0.503
	60.015	38.940	0.371	0.170	0.541
313	20.013	17.898	0.367	0.249	0.118
	30.154	24.953	0.354	0.145	0.208
	40.112	29.532	0.409	0.051	0.358
	50.084	33.459	0.344	0.153	0.497
	60.015	39.030	0.371	0.166	0.538
323	20.013	17.929	0.383	0.266	0.116
	30.154	25.004	0.361	0.155	0.206
	40.112	29.728	0.404	0.055	0.349
	50.084	33.768	0.392	0.091	0.483
	60.015	39.870	0.294	0.211	0.505
333	20.013	17.964	0.376	0.262	0.114
	30.154	25.065	0.365	0.162	0.203
	40.112	29.991	0.409	0.072	0.337
	50.084	33.804	0.358	0.124	0.482
	60.015	40.159	0.304	0.191	0.494

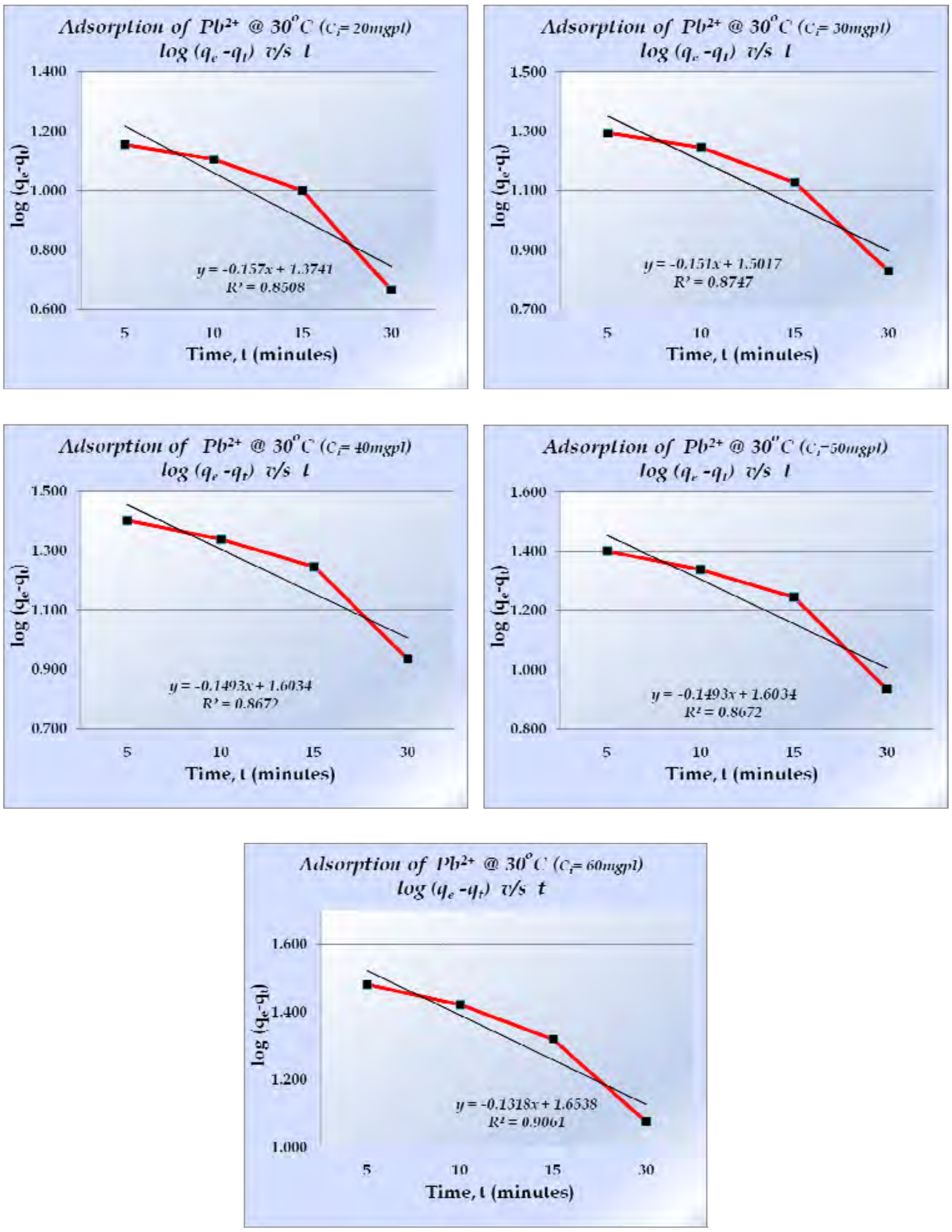

Figure 6.30: Kinetic study plot of Pb^{2+} adsorption at various Concentrations (Temp: 303K)

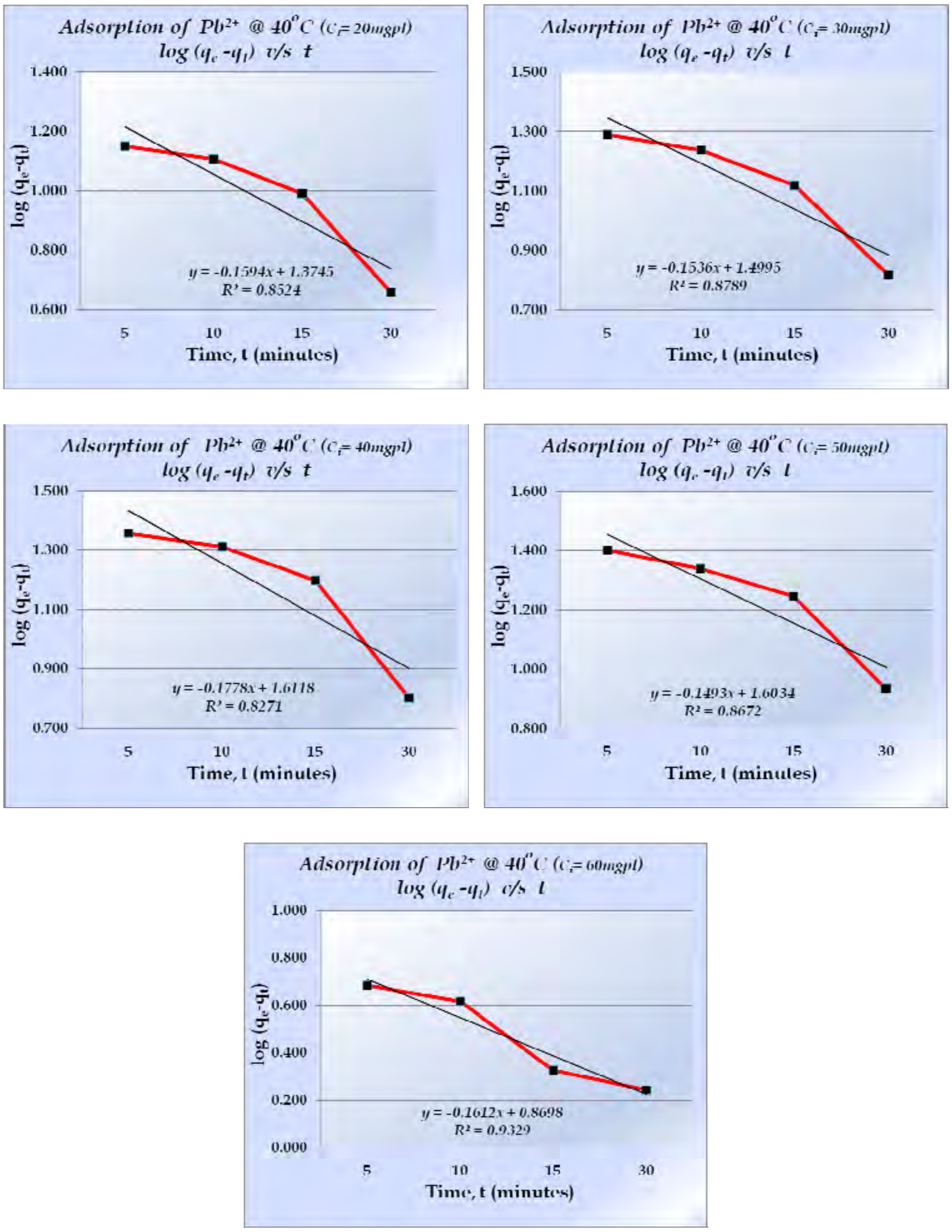

Figure 6.31: Kinetic study plot of Pb^{2+} adsorption at various Concentrations (Temp: 313K)

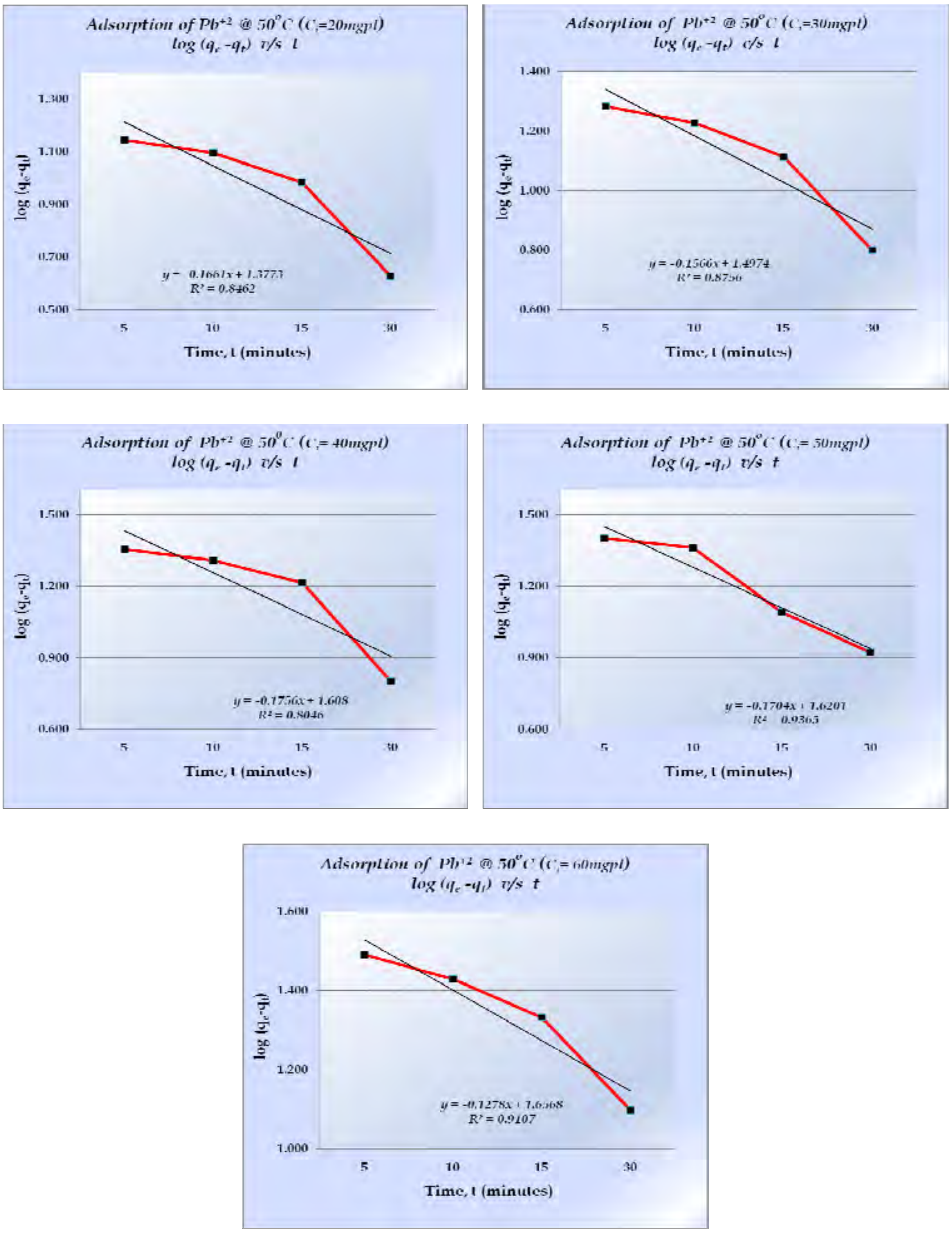

Figure 6.32: Kinetic study plot of Pb^{2+} adsorption at various Concentrations (Temp: 323K)

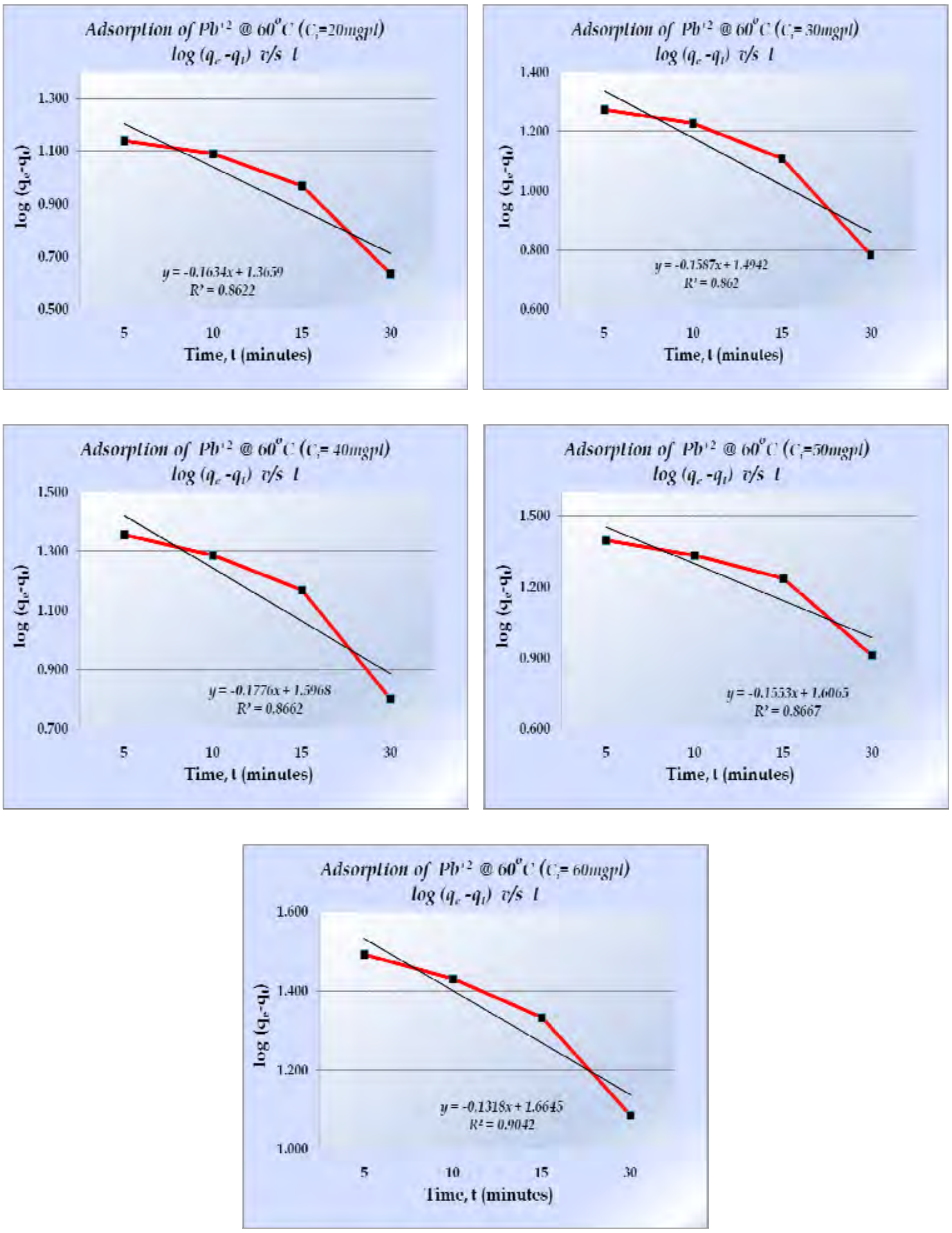

Figure 6.33: Kinetic study plot of Pb^{2+} adsorption at various Concentrations (Temp: 333K)

6.7.5 Adsorption study of Zn^{2+}

Zn is a silvery metal of hexagonal crystal structure. Zn is in group II of the periodic table. Zn was in use as a constituent of brass perhaps 2000 years before and on ancient method of brass production involved heating chunk of Cu with Zinc Carbonate and a reducing agent such as charcoal. Zn metal exists in +2 oxidation state. The presence of moisture in air may lead to corrosion. Zn compound may contain significant amount of Cd and lead but also it is very toxic particularly a larger dose of $ZnCl_2$ which leads to the damage of the mucous membranes and respiratory tract.

Batch Adsorption Study

Batch adsorption experiments were carried out using an Erlenmeyer flask of 250 ml capacity. Activated charcoal (50mg/50ml) was added to flask containing Zn (II) solution of strength predetermined with ICP OES and the flask was placed in a constant temperature bath and stirred with the help of a stirrer until equilibrium was attained. The adsorbent particles were filtered and transferred to vials and the equilibrium concentration of Zn^{2+} in the supernatant was then analysed in ICP OES. The experiment was conducted at varying Zn^{2+} concentrations (10, 15, 20, 25 & 30 mgpl) at different temperatures (303, 313, 323, and 333K). The pH of solution was adjusted to 70±0.2 in equilibrium study.

Adsorption Isotherm

The experimental data analysed according to the linear form of the Langmuir and Freundlich isotherms. The initial Zn ion concentration, equilibrium concentration, amount adsorbed, percentage adsorption, at different concentration and temperature is given in Table: 6.25. The plots of C_e/q_e versus C_e at different temperatures are found to be linear with the slope ($1/q_m$) and intercept ($1/q_mK_L$), indicating the applicability of the Langmuir model (Figure: 6.34). The value of q_m and K_L was then calculated from the slope and the intercept. The parameters q_m and K_L have been calculated and the results are represented in Table: 6.26. It was observed that the Langmuir isotherm fits well with the experimental data. The similar adsorption of Zn ion agreeing Langmuir equation was also observed sorption study using maize cob (Igwe et al., 2007).

Table 6.25: Equilibrium parameters of Zn^{2+} adsorption

Temp (K)	C_i (mgpl)	C_e (mgpl)	q_e (mg/g)	% Adsorption	C_e/q_e	log C_e	log q_e
303	10.054	1.685	8.369	83.24	0.201	0.2266	0.9227
	15.112	3.289	11.823	78.24	0.278	0.5171	1.0727
	20.005	5.354	14.651	73.24	0.365	0.7287	1.1659
	25.148	8.042	17.106	68.02	0.470	0.9054	1.2331
	30.025	11.587	18.438	61.41	0.628	1.0640	1.2657
313	10.054	1.601	8.453	84.08	0.189	0.2044	0.9270
	15.112	3.192	11.920	78.88	0.268	0.5041	1.0763
	20.005	5.281	14.724	73.60	0.359	0.7227	1.1680
	25.148	7.914	17.234	68.53	0.459	0.8984	1.2364
	30.025	11.445	18.580	61.88	0.616	1.0586	1.2691
323	10.054	1.514	8.540	84.94	0.177	0.1801	0.9315
	15.112	3.002	12.110	80.13	0.248	0.4774	1.0831
	20.005	5.117	14.888	74.42	0.344	0.7090	1.1728
	25.148	7.811	17.337	68.94	0.451	0.8927	1.2390
	30.025	11.288	18.737	62.41	0.602	1.0526	1.2727
333	10.054	1.381	8.673	86.26	0.159	0.1402	0.9382
	15.112	2.814	12.298	81.38	0.229	0.4493	1.0898
	20.005	5.007	14.998	74.97	0.334	0.6996	1.1760
	25.148	7.716	17.432	69.32	0.443	0.8874	1.2413
	30.025	11.038	18.987	63.24	0.581	1.0429	1.2785

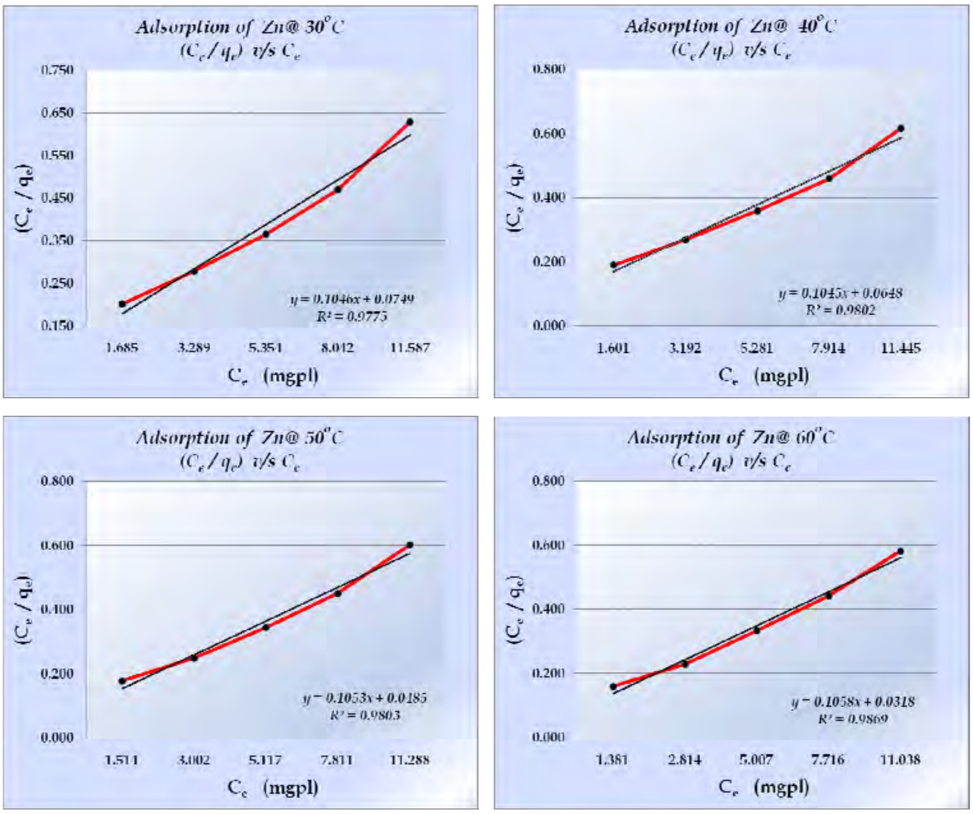

Figure 6.34: Langmuir isotherm of Zn^{2+} adsorption at different temperatures.

Table 6.26: Langmuir isotherms Parameters for Zn^{2+} adsorption at different temperatures

Temp	Langmuir Constants			
(K)	q_m	K_L	R^2	χ^2
303	9.56	1.397	0.9775	0.1122
313	9.57	1.613	0.9802	0.1067
323	9.50	2.171	0.9803	0.0996
333	9.45	3.327	0.9869	0.0906

The equilibrium data was also applied on the Freundlich isotherm equation. The linear plots of log q_e versus log C_e at different temperatures show that the adsorption of Zn^{2+} also follows the Freundlich isotherm

(Figure: 6.35). The values of K_f and n were calculated from the slope and intercept of the log q_e versus log C_e plot and is given in the Table: 6.27. The magnitude of K_F and n shows easy separation of heavy metal ion from aqueous medium and high adsorption capacity.

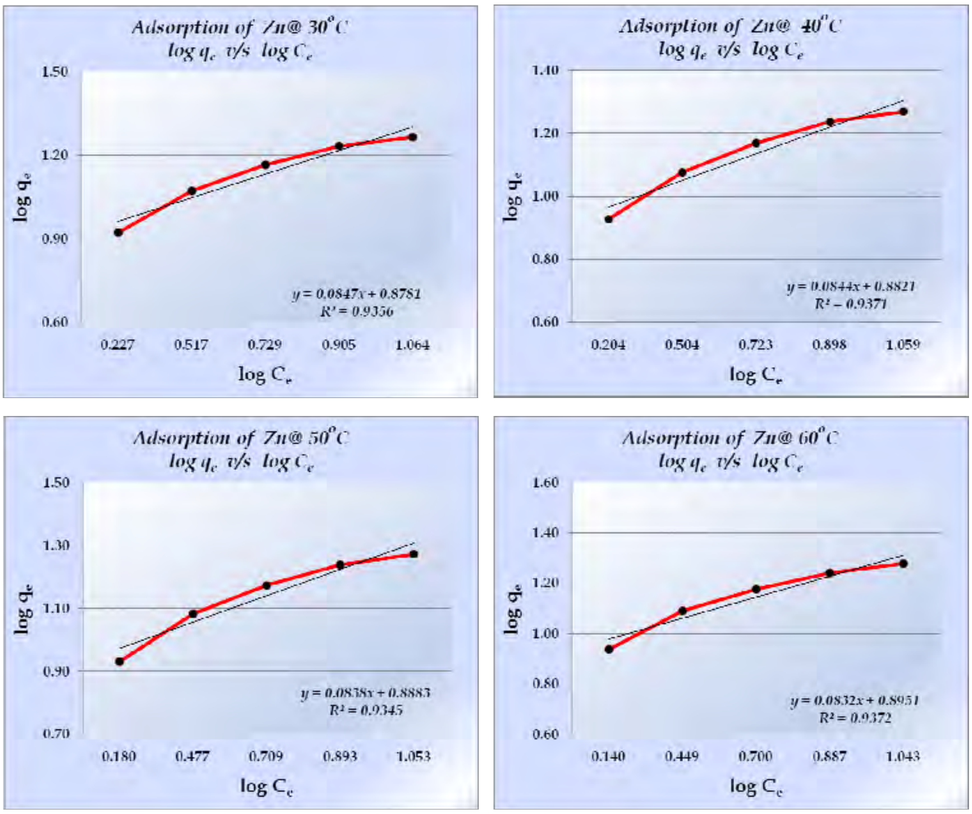

Figure: 6.35: Freundlich isotherm of Zn^{2+} adsorption at different temperatures.

Table 6.27: Freundlich Isotherms parameters for Zn^{2+} adsorption

Temp (K)	Freundlich Constants			
	n_F	K_F	R^2	χ^2
303	11.81	7.55	0.9356	0.2591
313	11.85	7.62	0.9371	0.2866
323	11.93	7.73	0.9345	0.3247
333	12.02	7.85	0.9372	0.3901

The χ^2 values for Langmuir and Freundlich isotherm are computed and included in the Table: 6.26 & 6.27. The χ^2 values of both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and relatively better fit is observed with Langmuir model as its χ^2 value is less than that of Freundlich model. The Langmuir isotherm is more widely used and provides information on the monolayer adsorption capacity in contrast to the Freundlich model.

Table 6.28: Separation Factor (R_L) for the adsorption of Zn^{2+} at different temperatures

Zn^{2+} conc. mgpl	Separation Factor, R_L			
	303K	313K	323K	333K
10.054	0.0665	0.0581	0.0438	0.0290
15.112	0.0452	0.0394	0.0296	0.0195
20.005	0.0346	0.0301	0.0225	0.0148
25.148	0.0277	0.0241	0.0180	0.0118
30.025	0.0233	0.0202	0.0151	0.0099

The Separation Factor (R_L) values of Langmuir isotherms at different temperatures are quantified (Table: 6.28) and the values were found to be between 0 and 1 and confirming that the favourable status of the adsorption. According to this, Langmuir model was found to be fit better since the R_L values are comparably less. The statistical parameters are indicating the best fitment of the experimental data with the Langmuir model. In all the systems studied, R_L values were comprised between 0 and 1 indicating favourable adsorption of all the metal ions on the selected adsorbent activated charcoal. The correlation co-efficient value was used as a main criterion for judging the fitness of the adsorption data showed. R^2 values of each metal ion at different temperature also showed an increased drift in Langmuir model than that in the other model.

Equilibrium studies revealed as in the case of adsorption of other metal ions, the effective adsorption increases as temperature increases. The effect of temperature on the adsorption of Zn^{2+} on activated charcoal is given in Figure: 6.36.

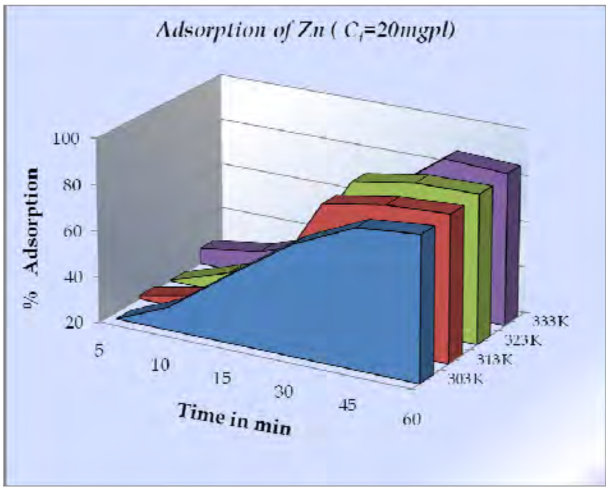

Figure 6.36: Effect of temperature on Zn^{2+} adsorption
(Conditions: Adsorbent dosage=50mg/50ml,
C_i= 20.005 mgpl, Temp:303K & time 60 min.)

Kinetic Study

The kinetic data of Zn^{2+} ion adsorption on activated charcoal is given in Table: 6.29. The data was found to fit the first order kinetic equations. The value of log (q_e-q_t) versus time plotted for different temperatures are shown in Figures: 6.37 to 6.40. The rate constant of the backward reaction, k_2 is calculated using equilibrium constant, K_c and rate of forward reaction, k_1. The reaction follows a first order rate law about thirty minutes and then after equilibrium has been established which means adsorption increases with an increase in shaking time and attains a constant value after thirty minutes.

Table 6.29: Kinetics data of Zn^{2+}adsorption at various temperatures& Initial adsorbate ion concentrations

Temp (K)	C_i (mgpl)	q_e (mg/g)	k_1 (min^{-1})	k_2 (min^{-1})	K_c (min^{-1})
303	10.054	1.685	0.484	0.283	0.201
	15.112	3.289	0.558	0.279	0.278
	20.005	5.354	0.508	0.142	0.365
	25.148	8.042	0.533	0.063	0.470
	30.025	11.587	0.573	0.055	0.628
313	10.054	1.601	0.484	0.294	0.189
	15.112	3.192	0.558	0.290	0.268
	20.005	5.281	0.508	0.149	0.359
	25.148	7.914	0.533	0.073	0.459
	30.025	11.445	0.573	0.043	0.616
323	10.054	1.514	0.542	0.365	0.177
	15.112	3.002	0.604	0.356	0.248
	20.005	5.117	0.546	0.203	0.344
	25.148	7.811	0.512	0.062	0.451
	30.025	11.288	0.531	0.072	0.602
333	10.054	1.381	0.639	0.480	0.159
	15.112	2.814	0.563	0.334	0.229
	20.005	5.007	0.508	0.174	0.334
	25.148	7.716	0.533	0.090	0.443
	30.025	11.038	0.573	0.008	0.581

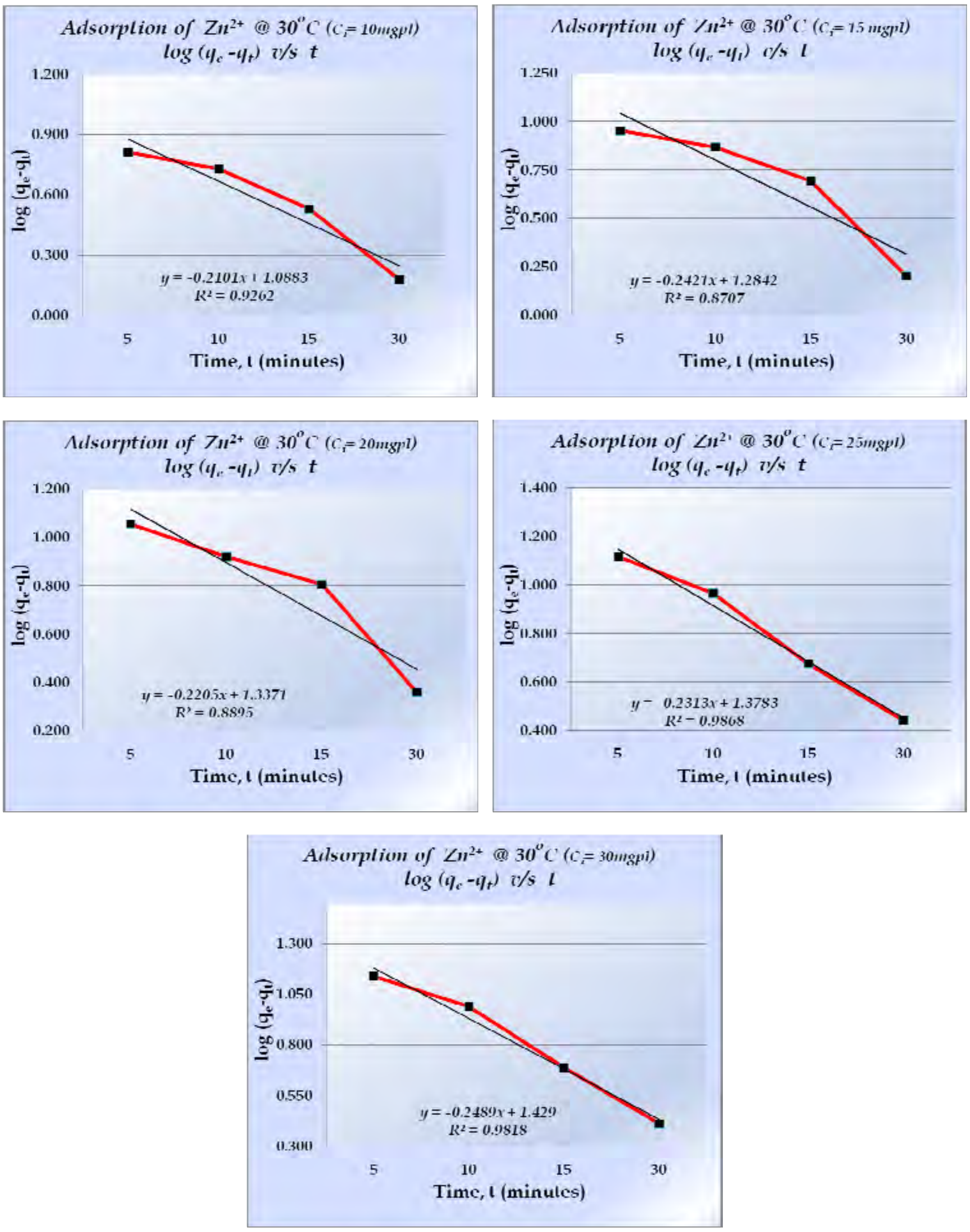

Figure 6.37: Kinetic study plot of Zn^{2+} adsorption at various Concentrations (Temp: 303K)

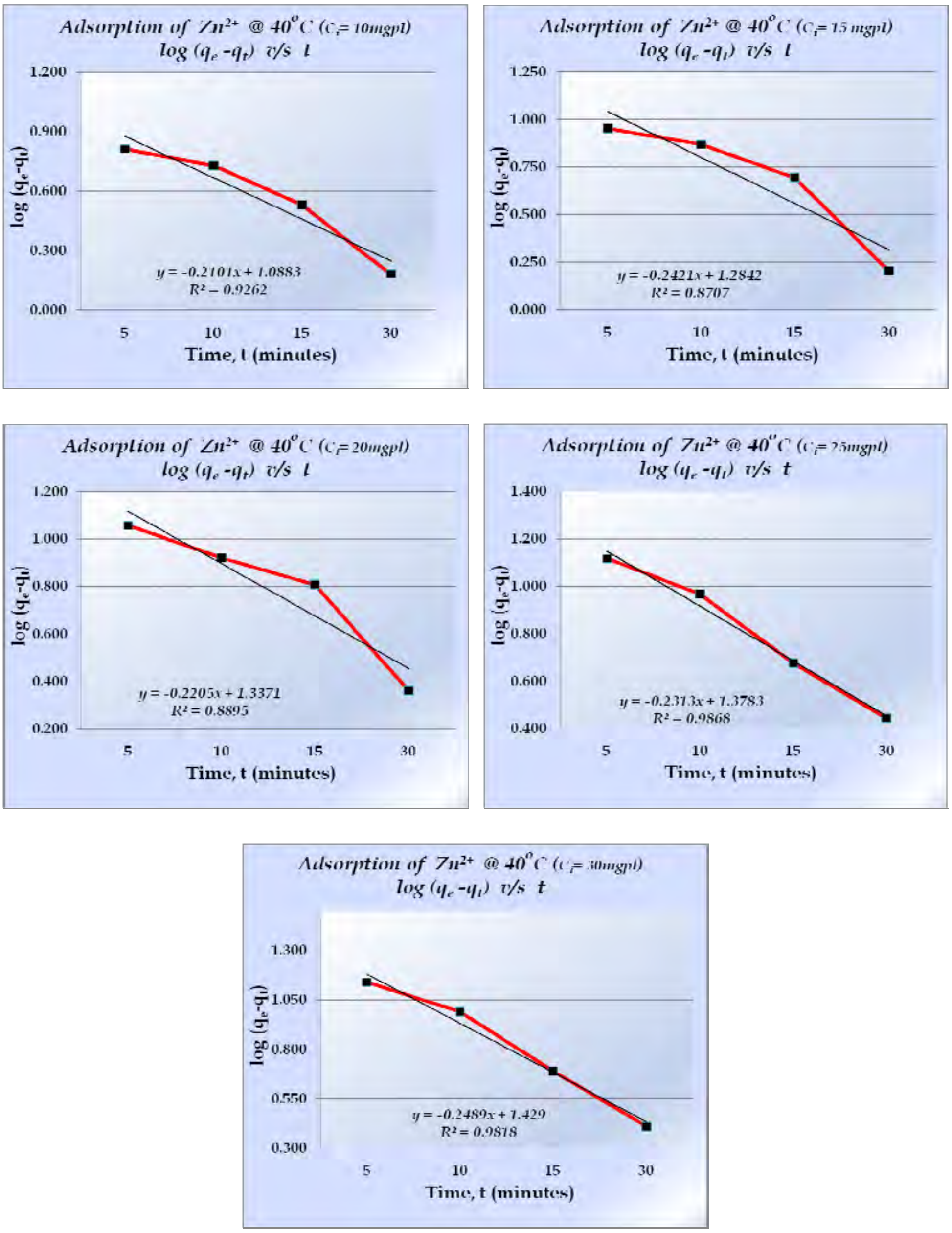

Figure 6.38: Kinetic study plot of Zn^{2+} adsorption at various Concentrations (Temp: 313K)

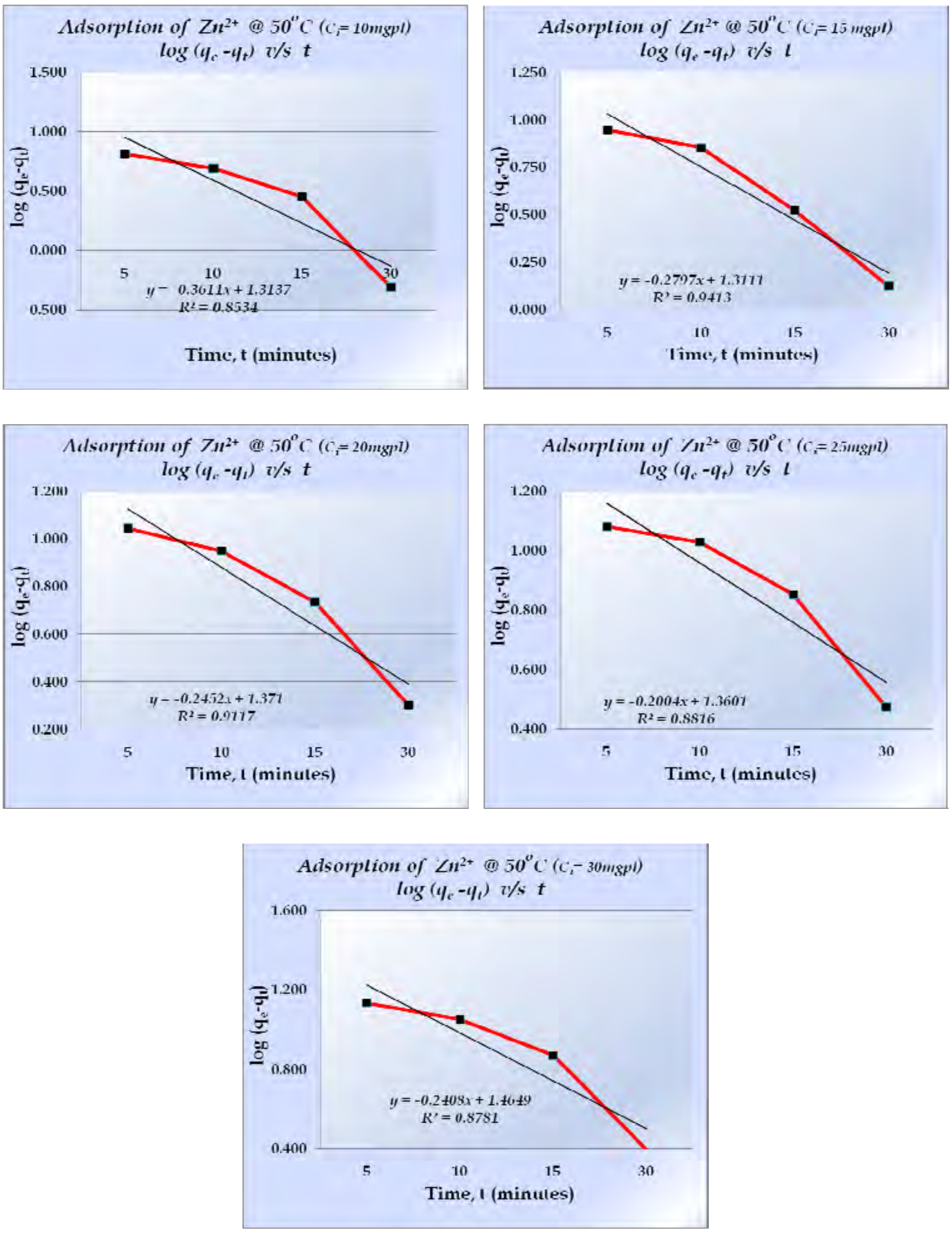

Figure 6.39: Kinetic study plot of Zn $^{2+}$ adsorption at various Concentrations (Temp: 323K)

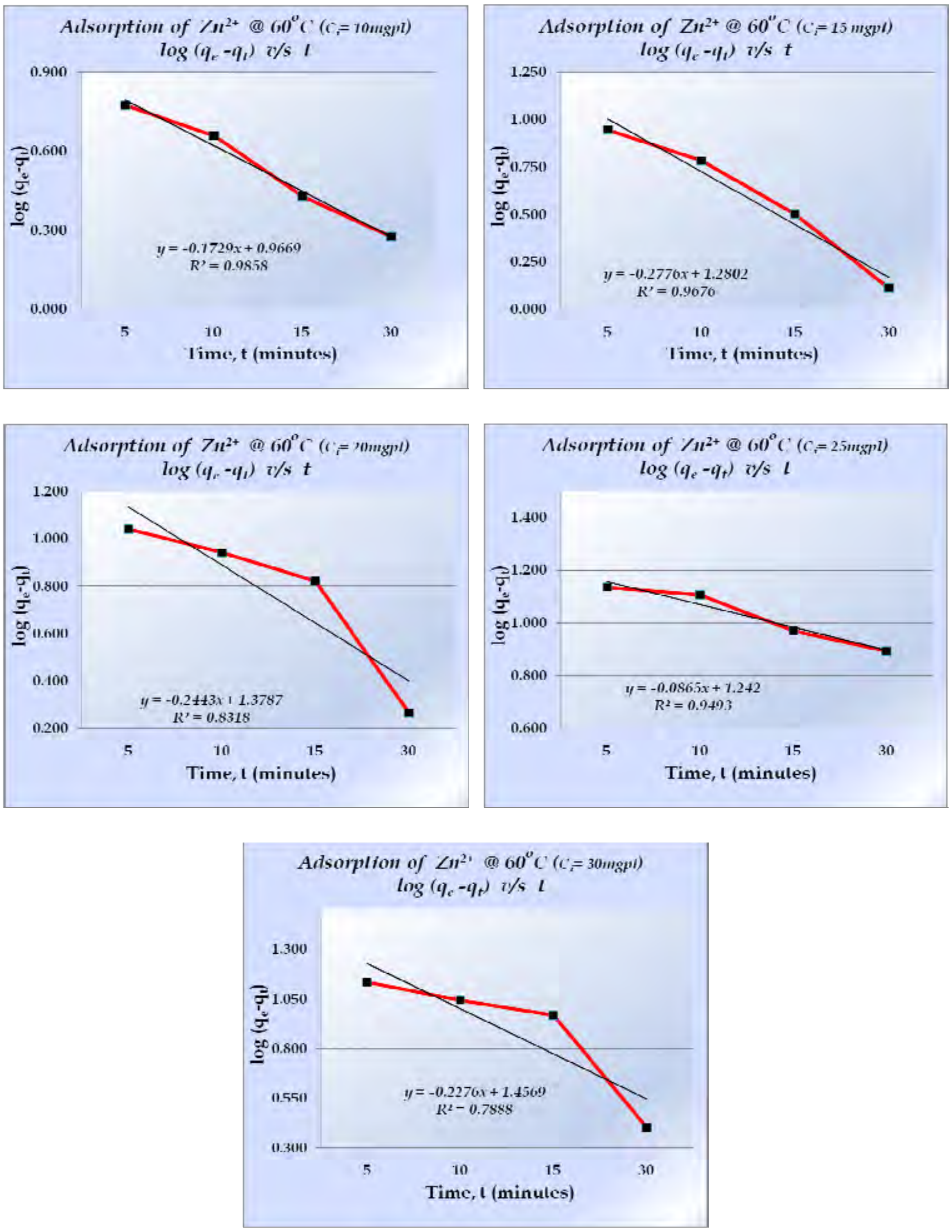

Figure 6.40: Kinetic study plot of Zn^{2+} adsorption at various Concentrations (Temp: 333K)

6.8 Desorption of metals from Activated charcoal

6.8.1 Introduction

Desorption studies are often performed to determine the reversibility of the sorption reactions. This gives an idea of the strength of the association of the metal with the adsorbent surface. It helps to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. It also gives the feasibility of recovering both the adsorbed species and the adsorbent and to clarify the nature of adsorption processes. If the adsorbed metal ions can be desorbed using neutral pH water, then the attachment of the metal ion of the adsorbent is by weak bonds. Sulphuric acid or alkaline water desorb the metal ions then the adsorption is by ion exchange (Namasivayam et al.,1996).

6.8.2 Experimental Details

After adsorption experiments using the selected adsorbent (activated charcoal), and adsorbate doses, the adsorbate loaded adsorbents i.e. activated charcoal with metal ions; were separated and washed gently with several portions of distilled water to remove any unadsorbed species. For this, activated charcoal after adsorption study was separated and filtered and washed thrice separately with each 10 ml of Milli Q water. The samples were then air-dried and agitated with 0.1M solutions of HCl, HNO_3, acetic acid and water for a period of 6 hours at room temperature. The metal-activated charcoal and reagent mixture was then filtered with Whatman No: 40 filter paper and the filtrate was analysed for metal ions and the amounts of desorbed species were determined using ICP OES by procedure as described earlier. The initial concentration of the metal ion was taken as the amount of metal ion adsorbed on the activated charcoal in adsorption study. The % desorption of metal ions was computed and given in Table:6.30.

Table 6.30: Comparative results of desorption study

Metal ion	% Desorption with			
	H_2O	CH_3COOH	HNO_3	HCl
Cd^{2+}	24.65	50.36	81.21	89.56
Cu^{2+}	29.81	48.63	79.98	89.23
Ni^{2+}	25.23	50.21	80.33	92.11
Pb^{2+}	30.22	49.56	84.65	91.22
Zn^{2+}	28.25	44.22	85.22	92.64

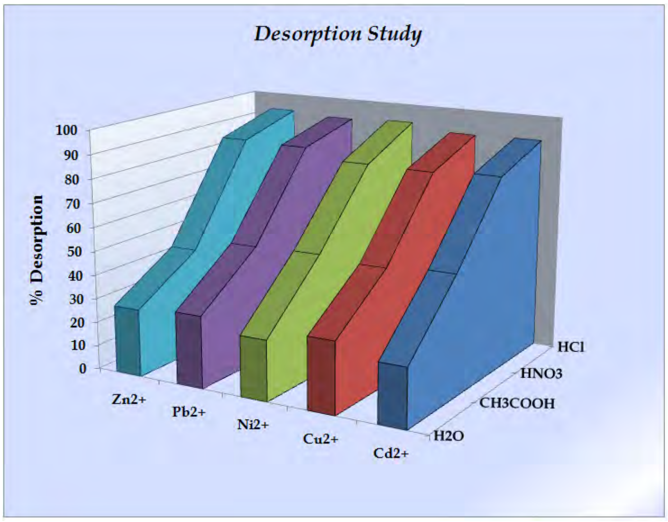

Figure 6.41: Desorption study using various reagents

6.8.3 Conclusion

The results indicated that hydrochloric acid was found to be a better reagent for desorption, because circa 90% removal of adsorbed metal ions. The effect of various reagents used for the desorption study is given in Figure: 6.41. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the effect of pH dependence studied. The hydrogen ions from HCl easily displace Pb(II) ion adsorbed to carbon during the desorption process. Desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through by physisorption (Dipa et al., 2002). Desorption studies conducted by Edwin (2008) also inferred that HCl was an effective reagent in the regeneration of activated charcoal when used as an adsorbent for the removal of Cu, Ni and Fe ions. The effectiveness of hydrochloric acid as a reagent in the adsorption studies was also confirmed in the desorption study carried out by Sudha et al.(2007). Similar results were obtained in the case of desorption of Pb(II) ion from activated carbon prepared from coir pith Eichrronia and activated carbon cloths(Shekinah et al., 2002).

6.9 Adsorption of heavy metals on Chitosan

6.9.1 Introduction

The adsorption study was also performed with chitosan as adsorbent for the removal of Zn from solution. Zinc is an essential heavy metal for human body and other living organism, but in excess concentration it may be very much toxic. Exposure to the high concentration of Zn for a longer time may affect the physiological functions of the body. A larger dose of $ZnCl_2$ may be toxic leads to the damage of the mucous membranes and respiratory tract. Food poisoning through galvanized Zn container has occurred involving in several cases of vomiting, diarrhoea, and abdominal cramps. Among the studied metals, the Zn was found to be in higher concentration and is in the delimitation of the threshold limit. Chitosan is a naturally abundant renewable polymer, having excellent properties such as, biodegradability, bio-compatibility, non-toxicity, and adsorption.

6.9.2 Batch Equilibrium Experiment

Batch experiments were carried out at three different temperatures (303K, 313K & 323K) using a mechanical shaker with temperature control and shaking speed of 120 rpm for 30 minutes. At the end of this time, the suspension was filtered, and the filtrate was collected to determine the ion concentration were determined using an ICP OES. Adsorption studies for

Zn (II) was carried out at the optimum initial pH value of 6.0+0.1with two different adsorbate concentrations of 3 to 12 mgpl with chitosan particle size of 0.2-0.45mm dosage taken as 10mg/50ml adsorbate solution. All the experiments were performed in duplicates for the reliability of the results.

6.9.3 Effect of pH

The influence of pH on the metallic ion adsorption capacity of the chitosan, experiments was conducted at different initial pH values. The sorption characteristics of chitosan determined at pH 5, 6, 7 and 8 against time is illustrated in Figure: 6.42. High pH values were not considered owing to avoid precipitation. Adsorption experiments were performed by mixing 10mg of chitosan with 50ml of 12mgpl Zn^{2+} ion in five different Erlenmeyer flask containing varying pH. Batch experiments were carried out at room temperature using an agitation speed of 120 rpm for 30 minutes. At the end of this time, the suspension was filtered, and the filtrate was collected to determine the ion concentration. The adsorption process is strongly pH dependent, since the properties of both the chitosan surface and the solution composition (metal ion speciation) changes with pH. The number of active sites on the surface of the adsorbent may change with varying pH (Gonzalez, et al., 1990). Table: 6.31 explain the details of the concentrations of Zn (II) in solution at definite time intervals at four pH levels. The rate of adsorption showed a maximum when the pH is 6.0. The sorption rate is lower at alkaline ranges. Low pH would favour protonation of the amino sites on the surface, resulting in a reversal of charge leading to a reduction in the chelating ability of chitosan (Schmuhl, 2001). At alkaline range, the formation of $Zn (OH)_2$ complexes prevents further adsorption of Zn (II).

Table 6.31: Effect of pH on Zn2+ adsorption on Chitosan

Time (min)	pH=5		pH=6		pH=7		pH=8	
	C (mgpl)	q (mg/g)	C (mgpl)	q (mg/g)	C (mgpl)	q (mg/g)	C (mgpl)	q (mg/g)
2	11.84	0.85	11.88	0.65	11.78	1.15	11.85	0.80
4	8.74	16.35	8.65	16.80	9.01	15.00	9.12	14.45
8	4.98	35.15	4.56	37.25	6.85	25.80	7.65	21.80
16	4.56	37.25	4.11	39.50	6.21	29.00	7.23	23.90
30	4.25	38.80	3.87	40.70	6.02	29.95	7.12	24.45

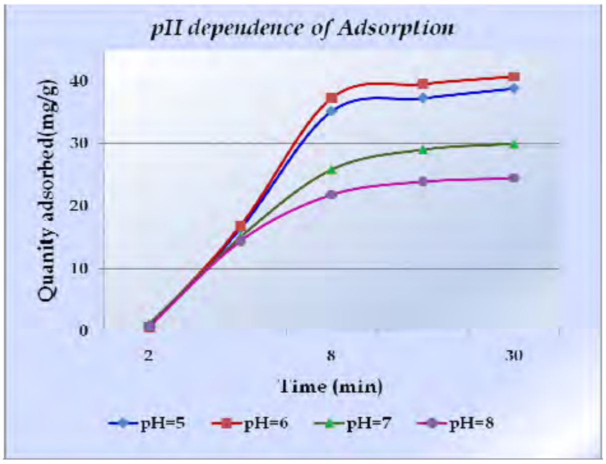

Figure 6.42: Dependence of pH on chitosan adsorption

6.9.4 Adsorption Isotherm

The experimental data analysed according to the linear form of the Langmuir and Freundlich isotherms. The Langmuir isotherm represented by the following equation

$$\frac{C_e}{q_e}=\frac{C_e}{q_m}+\frac{1}{q_m K_L}$$

Where C_e is the equilibrium metal ion concentration (mgpl), q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium, q_m and K_L

are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption respectively.

The initial Zn^{2+} concentration, equilibrium concentration, amount adsorbed, percentage adsorption, at different concentration and temperature is given in Table: 6.32. The plots of C_e /q_e versus C_e at different temperatures are found to be linear with the slope (1/ q_m) and intercept (1/$q_m K_L$), indicating the applicability of the Langmuir model (Figure: 6.43). The value of q_m and K_L was then calculated from the slope and the intercept. The parameters R^2, q_m and K_L have been calculated and the results are represented in Table: 6.33. It was found that the adsorption isotherm for the Zn-chitosan system could be represented well by the Freundlich isotherm.

Table 6.32: Equilibrium parameters of Zn^{2+} adsorption using chitosan as adsorbent

Temp (K)	C_i (mgpl)	C_e (mgpl)	q_e (mg/g)	% Adsorption	C_e/q_e	log C_e	log q_e
303	3.101	1.214	0.206	60.85	5.8940	0.0842	-0.6862
	6.025	2.629	0.334	56.37	7.8600	0.4198	-0.4756
	9.117	4.112	0.472	54.90	8.7100	0.6141	-0.3260
	12.008	6.885	0.721	42.66	9.5540	0.8379	-0.1423
313	3.101	1.145	0.297	63.08	3.8500	0.0588	-0.5267
	6.025	2.398	0.355	60.20	6.7600	0.3798	-0.4501
	9.117	4.489	0.526	50.76	8.5400	0.6521	-0.2793
	12.008	5.369	0.614	55.29	8.7500	0.7299	-0.2121
323	3.101	1.087	0.319	64.95	3.4100	0.0362	-0.4965
	6.025	1.912	0.410	68.27	4.6580	0.2815	-0.3867
	9.117	3.689	0.676	59.54	5.4580	0.5669	-0.1701
	12.008	6.178	0.783	48.55	7.8890	0.7908	-0.1062

Table 6.33: Langmuir & Freundlich Isotherms parameters for Zn^{2+} adsorption on to Chitosan

Temp (K)	Langmuir Constants				Freundlich Constants			
	q_m	K_L	R^2	χ^2	n_F	K_F	R^2	χ^2
303	0.85	0.234	0.9490	1.7039	5.61	0.14	0.9960	0.4194
313	0.61	0.577	0.8811	0.5950	8.97	0.20	0.9691	0.4319
323	0.70	0.793	0.9471	0.8168	7.20	0.23	0.9611	0.6129

The Langmuir plots showed the increase in the rate of adsorption when the temperature of the system is increased. The enhanced adsorptive nature of chitosan at higher temperature is due to the enlargement in the internal pores of the adsorbent to trap in more Zn ions on its surface. The C_e values of adsorbate in solution are higher at lower temperatures and they decrease with increasing temperature indicating greater adsorption at higher temperatures. The trend shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism. To confirm the adsorbability of the process, the separation factor (R_L) has calculated and presented in Table: 6.34. The values were found to be between 0 and 1 and confirm the favouring of adsorption process.

The Freundlich equation have also employed for the adsorption of Zn^{2+} on the Chitosan. The linear form of Freundlich isotherm have represented as

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e$$

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (µg/g) at equilibrium, C_e is the equilibrium concentration of heavy metal ion (mgpl); K_F is the Freundlich constant [(µg/g)(L/mg)$^{(1/n)}$] and gives the capacity of the adsorbent and n_F is the Freundlich exponent and presents an indication of the favourability. The linear plot of log q_e versus log C_e at different temperature shows that the adsorption of Zn^{2+} follows the Freundlich isotherm (Figure:6.44).

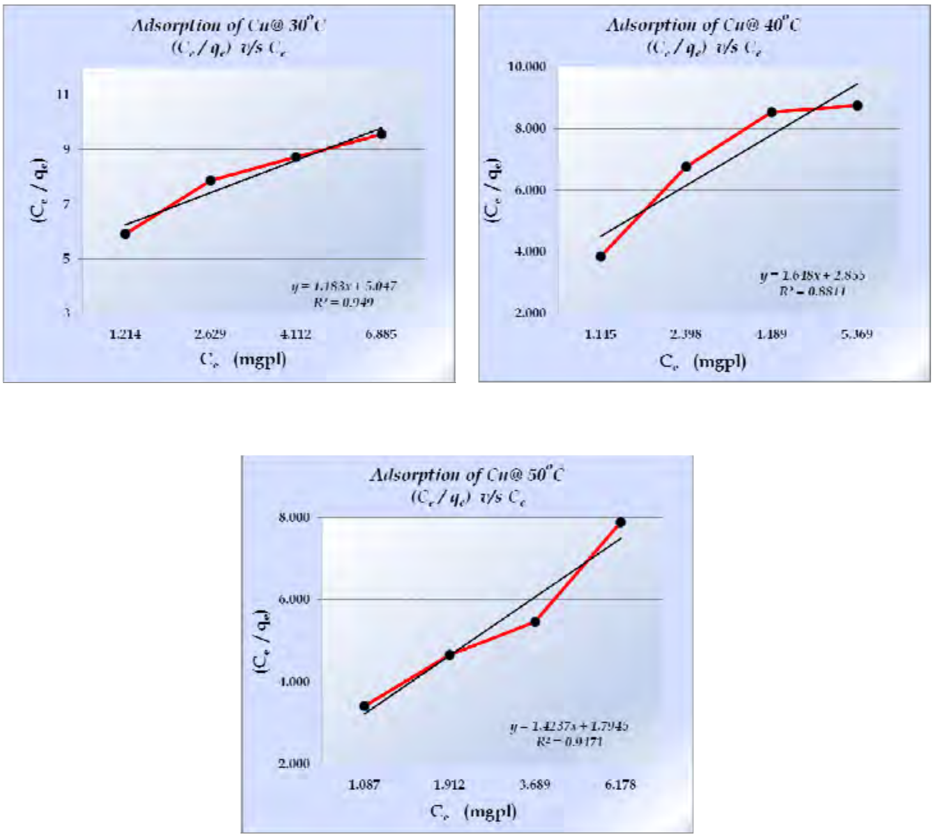

Figure 6.43: **Langmuir isotherm of Zn^{2+} adsorption on to chitosan at different temperatures.**

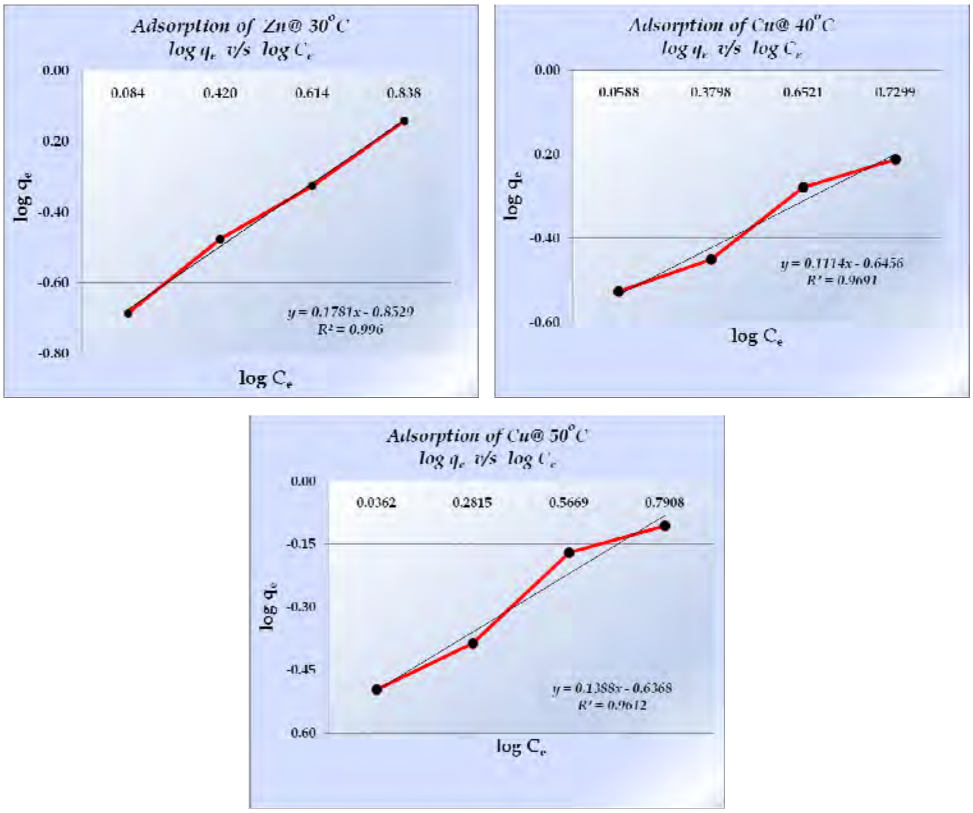

Figure 6.44: Freundlich isotherm of Zn^{2+} adsorption on to chitosan at different temperatures.

The values of K_f and n were calculated from the slope and intercept of the log q_e versus log C_e plot and is given in the Table: 6.33. The magnitude of K_F and n shows easy separation of heavy metal ion from water and high adsorption capacity. The intensity of adsorption is an indicative of the bond energies between Zn^{2+} and adsorbent and the possibility of slight chemisorptions rather than physisorption. The values of n are greater than one indicating the adsorption is favourable. The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration; but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa. The K_F, which is a measure of adsorption capacity, increased with temperature. The magnitude of the exponent, n gives an indication of the favourability and capacity of the adsorbent/ adsorbate system. Treyb al (1980) has reported that 'n' values between 1 and 10 represent favourable adsorption conditions. Higher the K_F value, the greater is the adsorption intensity.

Chi-squared test or χ^2 test

Pearson's chi-squared test is the goodness-of-fit test for independence. The test is most often used in the context of linear models like linear regression, analysis of variance. The χ^2 values for Langmuir and Freundlich isotherm are computed and included in the Table: 6.33. If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a larger number. The χ^2 values of both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and a relatively better fit is observed with Freundlich model as its χ^2 value is less than that of Langmuir model.

Table 6.34: Separation Factor (R_L) for the adsorption of Zn^{2+} on to chitosan at different temperatures

Zn conc. mgpl	Separation Factor,R_L		
	303K	313K	323K
3.101	0.5791	0.3584	0.2890
6.025	0.4146	0.2233	0.1730
9.117	0.3188	0.1597	0.1215
12.008	0.2621	0.1261	0.0950

Table 6.35: Comparative statistical data for Langmuir and Freundlich isotherm model

Temp (K)	R^2		χ^2	
	Langmuir	Freundlich	Langmuir	Freundlich
303	0.9490	0.9960	1.7039	0.4194
313	0.8811	0.9691	0.5950	0.4319
323	0.9471	0.9611	0.8168	0.6129

The value of correlation co-efficient that was used as a main criterion for judging the fitness of the adsorption data showed. R^2 values of each metal ion at different temperature also showed an increased trend in Freundlich model than that in the other model. A comparison of the coefficient of regression (R^2) and χ^2 for the two isotherms is shown on Table: 6.35. These statistical parameters are indicating the best fitting of the experimental data with the Freundlich model. In all the Zn-chitosan systems studied, R_L values were comprised between 0 and 1 indicating favourable adsorption of all the metal ions on the cheap natural adsorbent, Chitosan.

6.9.5 Conclusion

The study showed that the solution pH strongly affects the adsorption capacity of chitosan. It was observed that the greatest adsorption of Zn (II) occurs at pH6$\pm$0.1. From this study, the results outweighs that adsorption increases with the increase of temperature and decreases with the increase in adsorbate concentration. The enhanced adsorptive nature of chitosan at higher temperature is due to the protrusion in the internal pores of chitosan. The optimum contact period of 90 minutes is required for the maximum removal of Zn (II) by chitosan. The adsorption mechanism obeys both Freundlich and Langmuir equations indicating beneficial adsorption occurring through a monolayer mechanism involving physisorption and/or chemisorption. But the experiment data fits well with the Freundlich model based on the computed statistical parameters. The percentage removal of Zn ions at 30^0C in the Zn -chitosan system was found to be less (60.85%) and comparable that with the adsorption onto activated charcoal (83.24%). The result showed the Chitosan can be replaced for activated charcoal as it is economically cheap and readily available.

6.10 Adsorption of metal ions on sediment

6.10.1 Introduction

Sediments show strong tendency to accumulate contaminant, especially heavy metals, and analysis of these sediments thus constitutes a rapid means of obtaining time integrated information concerning a range of limnological variables (Carral et. al., 1995). Comparison of heavy metals distribution with grain size allowed the identification of the area where the sediment fine fraction appears affected by heavy metal anthropogenic contamination (Leoni and Sartori, 1996).

It has been shown that the presence of heavy metals is affected by the particle composition of sediments (Asami and Sampei, 1979; Thome and Nickless, 1981). In sediments of polluted streams the largest amounts of heavy metals are associated with organic matter (humic and fulvic acids, colloids, synthetic organic substances), the fine-grained sediment fraction (clay, silt and fine sand) and Fe/Mn hydrous oxides, or are precipitated as hydroxides, sulphites or carbonates (Forstner, 1981). The heavy metal concentration generally increased with the decreasing particle size of the sediments. The general trend is an increase in the presence of heavy metals with decreasing particle size. The fraction 0-75 has the highest concentrations and this fraction of the sediment is very important because it is considered to be the potential mobile fraction of the sediment under the normal conditions of a river system.

The particle-size distribution (PSD) also known as grain size distribution of a powder, or granular material, or particles dispersed in fluid, is a list of values or a mathematical function that defines the relative amounts of particles present, sorted according to size(Jillavenkatesa et al., 2001). Grain size distribution is one of the most important characteristics of sediment. This is true because grain size is a powerful tool for describing a site's geomorphic setting, interpreting the geomorphic significance of fluid dynamics in the natural environment, and distinguishing local versus regional sediment transport mechanisms as well as because grain size is a dominant controlling factor in sediment geochemistry. Cations derived from mineral weathering and pollution sources are preferentially adsorbed onto clay, which has the highest surface area to volume ratio of any particle size class.

Sieve analysis was used to determine the particle size of sediment. This continues to be used for many measurements because of its simplicity, cheapness, and ease of interpretation. Methods may be simple shaking of the sample in sieves until the amount retained becomes more or less constant. Alternatively, the sample may be washed through with a non-reacting liquid (usually water) or blown through with an air current. The grain size distribution of a sediment sample is determined by any one of a number of techniques or combination of techniques depending on the range of sizes present in a sample. For this procedure, "fines" are any particle smaller than 63.5 microns. Sand is 63.5 microns to 2 mm in diameter. Gravel is larger than 2 mm.

The bulk sediment samples were subjected to grain size analysis by combination of wet sieving (Krumbein and Pettijohn, 1938).

6.10.2 Materials & Methods

Duplicate sediment samples were collected from the Station 4 (Cochin Harbour- Mooring Jetty) during Post monsoon period, October, 2010. The samples from these stations were opted for the adsorption study.

The sample was powdered using a mortar and a particle size was determined. The sample was washed till a pH of 7.0 was obtained, filtered and dried in an air oven at 100ºC for 24 hours. Sample pH and organic carbon were analysed according to the procedure mentioned in Chapter 2. The sediments were air-dried and fractionated into selected particle size fraction (< 1000 µm (sand), <125 µm (silt), and < 63 µm (fine/clay)) by sieving. A weighed amount of the dried sample from each fraction was subjected to tri-acid digestion for wet chemical analysis. Metal ions Cd, Cu, Ni, Pb & Zn ions was analysed by ICP OES. The sediment as such (< 2000 µm) and the fractions of the sieved sediments were analysed for heavy metals according to the procedure described in the section 2.3. The standard solution of the above mentioned metal ions were used as the heavy metal sources or the adsorptive solution for the sorption study.

The particle size distributions of the sample are shown in Table: 6.36. About 70%of the station-4 sediment fraction was clayey in nature and was observed that metal ions were present mainly in particles of < 63 µm in size. The organic content of the sediment was of the order of 0.25-4.78%.

Table 6.36: Textural characteristics of sediment sample of station-4

Station ID	**pH**	**TOC (%)**	**% Fraction**		
			Sand (<1000 µm)	**Silt (<125 µm)**	**Clay (<63 µm)**
4	6.89	4.26	18.11	11.25	70.64
4	6.58	4.78	19.19	10.48	70.33

The extractable heavy metal ions present in each fraction was analysed and tabulated in the Table 6.37. It was observed that the metal ion concentration was found to be more in the fraction <63 µm. This may be due to the strong association with organic carbon in the clayey fraction. The amount of extractable metal was in the order Zn>Ni>Cu>Pb>Cd. The extracted amount did not give the total amount but it was expected to include the more soluble forms of the metals. The amount of each metal extracted was higher in the finer fractions of the sediment. The smaller particles would definitely have greater total surface area and thus provide more extractable amount of the metals. Similar correlations between metal concentrations and particle size have been shown for riverine sediments (Marcus, 1987; Forstner, 1982).

Table 6.37: Heavy metal distribution in each particle size fraction of sediments of Station-4

Metal ion	**Conc. in normal Sediment (mg/kg)**	**Concentration in the fraction (mg/kg)**		
		Sand (<1000µm)	**Silt (<125 µm)**	**Clay (<63 µm)**
Cd	1.731	0.224	0.480	1.028
Cu	39.187	10.733	15.690	12.765
Ni	51.35	13.572	17.943	19.83
Pb	18.047	4.613	5.949	7.486
Zn	318.34	69.741	117.958	130.64

6.10.3 Adsorption of Zinc ion on sediment

The adsorption of heavy metal ion on sediment fractions was studied by taking Zn ion solution as adsorbate solution. Zn is an essential heavy metal for human body and other living organism, but in excess concentration it may be very much toxic. Exposure to the high concentration of Zn for a longer time may affect the physiological functions of the body. A larger dose of $ZnCl_2$ may be toxic leads to the damage of the mucous membranes and respiratory tract. Food poisoning through galvanized Zn container has occurred involving in several cases of vomiting, diarrhoea, and abdominal cramps. Among the studied metals the Zn was found to be in higher concentration and is in the delimitation of the threshold limit. The adsorption parameters of different fractions of the sediment were studied and it was found that the adsorption strongly depends on the particle size of the sediment.

Batch Adsorption Experiment

A known quantity of the three fractions of sediment sample (0.1g/50ml) was added to three separate Erlenmeyer flask containing 50 mgpl, Zn (II) solution of strength predetermined with ICP OES. The contents were stirred at 120 rpm for desired period of time at room temperature (30^0C). The flask was placed in a constant temperature bath and stirred with the help of a stirrer until equilibrium was attained. Initial adsorption studies were conducted to ascertain the conditions of shaking time and pH for the maximum adsorption of Cd on the sediment fractions from aqueous solution. In order to determine the equilibrium time for the adsorption process, adsorption experiments were performed for the uptake of metal ions for different duration of contact times for a fixed adsorbent dose of 0.1g/50ml and with an optimum initial metal ion concentration of (50-50mgpl) for the three particle size of adsorbent (<1000 µm, <125 µm and<63 µm) at a pH 7.0. The solution pH for the experiments was chosen as close to that encountered in the river water. The background metal level in the various fractions of the sediments was determined and compared to the amount of adsorbate added for the adsorption tests. The studies confirmed that the equilibrium is attained within 45 minutes and maximum adsorption of Zn occurred with sediment clayey fraction of sediment having particle size <63 µm with the different concentration of adsorbate concentration 10-30 mgpl and adsorbent dosage of 0.1g/50ml.

Adsorption Isotherm

The experimental data analysed according to the linear form of the Langmuir and Freundlich isotherms. The Langmuir isotherm represented by the following equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$$

Where C_e is the equilibrium aqueous metal ions concentration (mgpl), q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium, q_m and K_L is Langmuir constants related to the maximum adsorption capacity and the energy of adsorption respectively.

The initial Zn^{2+} concentration, equilibrium concentration, amount adsorbed, percentage adsorption, at different concentration and temperature is given in Table: 6.38. The plots of C_e /q_e versus C_e at different temperatures are found to be linear with the slope (1/ q_m) and intercept ($1/q_mK_L$), indicating the applicability of the Langmuir model (Figure: 6.45). The value of q_m and K_L was then calculated from the slope and the intercept.

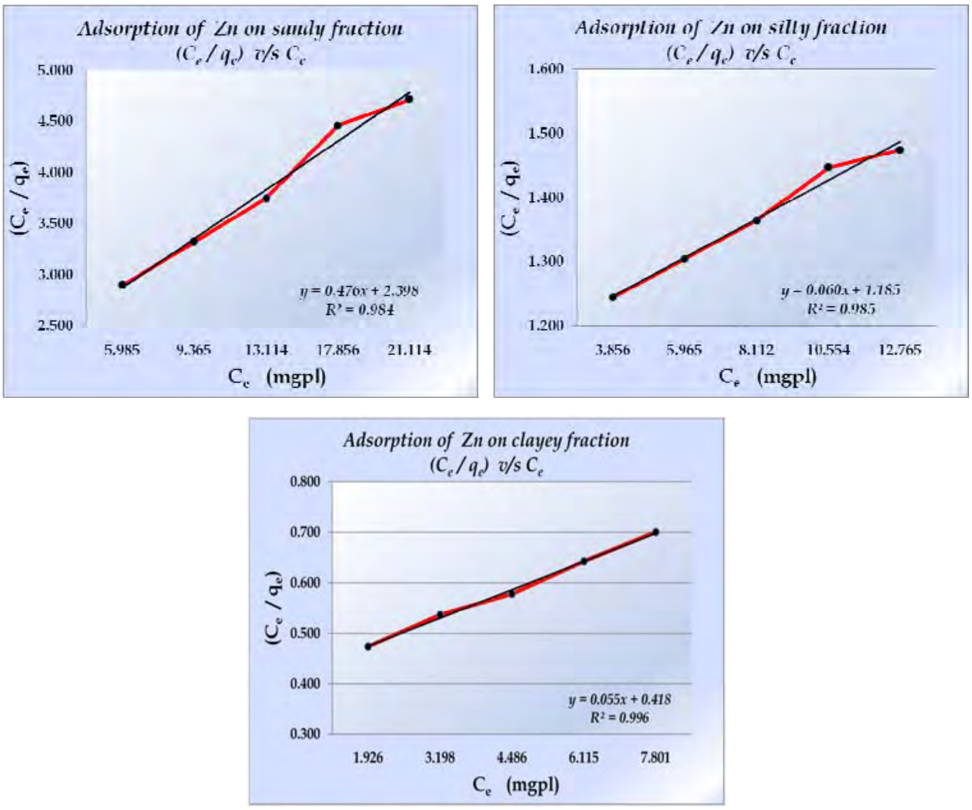

Figure 6.45: Langmuir isotherm of Zn^{2+} adsorption on various fractions of sediment.

The parameters R^2, q_m and K_L have been calculated and the results are represented in Table: 6.39. The statistical significance of the correlation coefficient (R^2) for C_e/q_e versus C_e is the criteria by which the fitting of the data to Langmuir isotherm. It explains monolayer coverage of adsorbate at the outer surface of the adsorbent. It was found that the adsorption isotherm for the Zn-Sediment system could be represented well by the Langmuir isotherm.

Table 6.38: Equilibrium parameters of Zn^{2+} adsorption using sediment as adsorbent

Sediment size	**Initial conc C_i of Zn (mgpl)**	**Equi.Conc of Zn, C_e (mgpl)**	**q_e (mg/g)**	**% Removal**	**C_e/q_e**	**log C_e**	**log q_e**
<1000 µm	10.115	5.985	2.065	40.83	2.8983	0.7771	0.3149
	15.006	9.365	2.821	37.59	3.3203	0.9715	0.4503
	20.112	13.114	3.499	34.80	3.7479	1.1177	0.5439
	25.869	17.856	4.007	30.98	4.4568	1.2518	0.6028
	30.078	21.114	4.482	29.80	4.7108	1.3246	0.6515
<125 µm	10.115	3.856	3.099	61.65	1.2443	0.5861	0.4912
	15.006	5.965	4.574	60.53	1.3043	0.7756	0.6602
	20.112	8.112	5.947	59.45	1.3642	0.9091	0.7743
	25.869	10.554	7.297	58.03	1.4463	1.0234	0.8632
	30.078	12.765	8.657	57.56	1.4746	1.1060	0.9373
<63 µm	10.115	1.926	4.064	80.84	0.4739	0.2847	0.6090
	15.006	3.198	5.957	78.84	0.5368	0.5049	0.7750
	20.112	4.486	7.760	77.58	0.5781	0.6519	0.8898
	25.869	6.115	9.517	75.68	0.6426	0.7864	0.9785
	30.078	7.801	11.139	74.06	0.7004	0.8922	1.0468

Table 6.39: Langmuir Isotherms parameters for Zn^{2+} adsorption on to station-4 sediment

Sediment size	Langmuir Constants			
	q_m	K_L	R^2	χ^2
<1000 µm	2.10	0.199	0.9844	0.9761
<125 µm	16.58	0.051	0.9852	0.7367
<63 µm	17.89	0.133	0.9964	0.3113

The Freundlich equation have also employed for the adsorption of Cd^{2+} on the adsorbent. The linear form of Freundlich isotherm have represented as

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e$$

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (µg/g) at equilibrium, C_e is the equilibrium concentration of heavy metal ion (mgpl); K_F is the Freundlich constant [(µg/g) (L/mg) $^{(1/n)}$] and gives the capacity of the adsorbent and n_F is the Freundlich exponent and presents an indication of the favourability. The linear plots of log q_e versus log C_e at different temperature show that the adsorption of Cd^{2+} follows the Freundlich isotherm (Figure: 6.46). The values of K_F and n were calculated from the slope and intercept of the log q_e versus log C_e plot and is given in the Table: 6.40. The magnitude of K_F and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity. Freundlich constants calculated shows the increase of negative charge on the surface that enhances the electrostatic force like Van der Waal's between the carbon surface and metal ion, which increases the adsorption of metal ion. The values of n are greater than one indicating the adsorption is favourable. The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa. Higher the K_F value, the greater is the adsorption intensity.

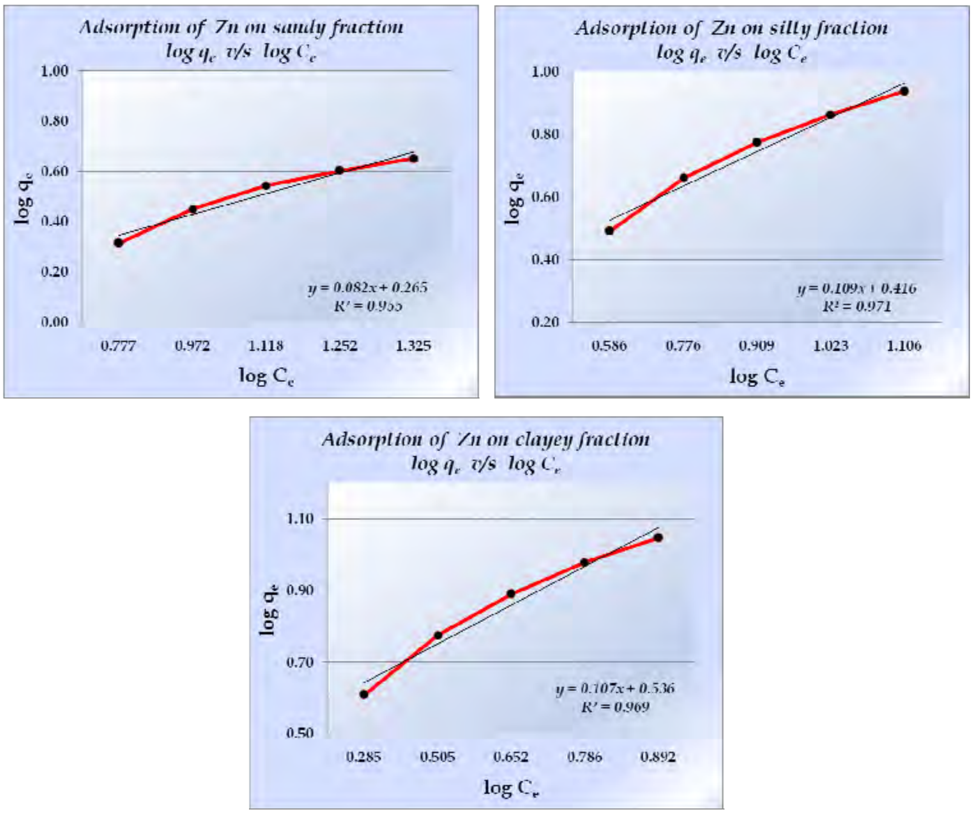

Figure 6.46: Freundlich isotherm of Zn^{2+} adsorption on various fractions of sediment.

Table 6.40: Freundlich Isotherms parameters for Zn^{2+} adsorption on to station-4 sediment

Sediment size	**Freundlich Constants**			
	n_F	K_F	R^2	χ^2
<1000 µm	12.11	9.02	0.9551	0.0066
<125 µm	9.13	2.61	0.9719	0.0001
<63 µm	9.27	3.44	0.9699	0.0588

The χ^2 values for Langmuir and Freundlich isotherm are computed and included in the Table: 6.39 & 6.40. If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a larger number. The χ^2 values of both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and relatively better fit is observed with Freundlich model as its χ^2 value is less than that of Langmuir model. But the R^2 value was found to less for Langmuir isotherm and hence considered as the best line fitting. The Langmuir isotherm is more widely used and provides information on the monolayer adsorption capacity in contrast to the Freundlich model. Similar studies were also reported by Mohapatra et al. (2009) and Jain (2001).

Table 6.41 Separation Factor ($R_{L)}$ for the adsorption of Zn^{2+} for different textures of sediment

Zn^{2+} conc. mgpl	Separation Factor,R_L		
	<1000 μm	**<125** μm	**<63** μm
10.115	0.3324	0.6604	0.4270
15.006	0.2513	0.5672	0.3314
20.112	0.2003	0.4944	0.2725
25.869	0.1630	0.4319	0.2295
30.078	0.1434	0.3954	0.1997

The Separation Factor (R_L) values of Langmuir isotherms at different temperatures are quantified (Table: 6.41) and according to this, Langmuir model was found to be fit better since the R_L values are comparably less. The value of correlation co-efficient that was used as a main criterion for judging the fitness of the adsorption data showed.R^2 values of each metal. A comparison of the coefficient of regression (R^2) and χ^2 for the two isotherms indicate the best fitment of the experimental data with the Langmuir model. Also in the Zn-sediment systems studied, R_L values were comprised between 0 and 1 indicating favourable adsorption of all the metal ions on the sediment adsorbent.

6.10.4 Conclusion

The present study has shown the potentiality of freshly deposited sediments to reduce or control metal pollution which may enter a river system through the disposal of municipal and industrial effluents. The Zn ions have more affinity for the clay and silt fraction of the sediment. It was observed from the present study that an adsorption increases as the particle size of the sediment decreases and showed a decrement with the increase in adsorbate concentration. The optimum contact period of 90 minutes is required for the maximum removal of Zn (II) by the sediment selected. The adsorption mechanism obeys both Freundlich and Langmuir equations indicating beneficial adsorption occurring through a monolayer mechanism involving physisorption and/or chemisorption. But the experiment data fits well with the Langmuir model based on the statistical parameters computed. The percentage removal of Zn ions at 30^{0}C in the Zn -sediment system was found to be high in clayey fraction (80.8%) than sandy (40.8%) and silt (61.7%) fraction. The removal efficiency of Zn ion using the finer fraction of the sediment was found to be comparable that with the adsorption onto activated charcoal (83.24%).This showed that that the sediment can adsorb more quantity of metal ions when it is in the environment indicating that the sediment itself can act as adsorbent in the favourable condition. Adsorption/ desorption equilibria and complexation with fulvic and humic acids present in the sediment also play an important role on speciation and further studies are needed to better understand processes affecting the sorption of metal ions in natural systems.

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Chapter 7

SUMMARY

The overall research programme encompasses the distinct features of hydrography of the CES in three prominent seasons, along with the spatial and seasonal distribution pattern of heavy metals with physicochemical parameters. The results showed that the heavy metals present in the water and sediment have strong correlation with pH, nutrients, texture and organic carbon. Among the studied heavy metals Pb, Cd and Zn are of major concern, which occasionally may be associated with adverse biological effects based on the comparison with sediment quality guidelines. Statistical studies like Principal component analysis (PCA) and correlation analysis were used to find out the relationships between the various hydrographical parameters.

Station-1 was selected as a controlled site and the rest are the hot spot polluting area of CES with varying salinity, nutrients level, electrical conductivity, texture, organic carbon, heavy metals and other organic toxicants. These were well established with the various metal contamination assessment indicators like Normalisation factor (NF), Contamination factor (CF), Enrichment factor (EF), Pollution Load Index (PLI) and Geo-accumulation Index (I_{geo}). From these results it was inferred that the sediments of stations, Cochin Harbour-Mooring jetty, Embarkation jetty, Bolghatty and Cheranellore Ferry (Stations 4, 5, 6 & 8) are under the threat of pollution when compared to the stations, Muvattupuzha and Cheranellore- manjummel (stations 1 & 7).

The preliminary investigation and the dispersion records of various toxic heavy metals of the selected eight stations showed that the metal contamination level is in the borderline of threshold limit. This report motivated and paved the way for working out to explicate a prominent, eco-friendly theraptic or remedial approach to reduce/control the pollution abatement divulging the idea of sorption technique. The word 'therapy' implies the treatment of any disease by any and all means like drug therapy, physical therapy and massage therapy and the word 'therapeutic' is the art of motivated treatment based on logical or illogical premises. To make a distinct from the word 'therapeutic' and also for the term 'environmental remedial approach', the word 'Theraptic' is used in the present monograph. The exploration for novel technologies in the environmental therapy of removal of toxic metals from wastewaters, has directed attention to sorptional techniques, based on metal binding capacities of various adsorbent materials.

Heavy metals are dangerous because they tend to bio-accumulate and increases the concentration of a metal or chemical in a biological organism over time, compared to the concentration in the environment. This process of bioaccumulation leads to biomagnification by which tissue concentrations of toxicants in organisms at one trophic level exceed tissue concentrations in organisms at the next lower trophic level in a food chain. Since man is in the top of the trophic level, gets most of these toxic heavy metals into his body and consecutively human's gets intoxicated through biomagnification. Hence the remediation or therapy of polluted environment is extremely vital for the aquatic organisms and inturn for human beings, as a preventative measure for chronic and acute diseases.

In the current study, sorptional technique as a theraptic scheme to lessen the metallic toxicants of environment was attempted in batch experiments with adsorbents- activated charcoal and chitosan. In light of the objective of Chapter five of this monograph to investigate the ability of the adsorbents like activated charcoal and Chitosan to adsorb some heavy metals like Cd, Cu, Ni, Pb and Zn ions in the solution, it was observed from the Tables 6.5, 6.10, 6.15, 6.20 and 6.25 the percentage of heavy metals adsorbed on charcoal at 30^0C and under same conditions decreases in the order Pb> Ni> Zn> Cu>Cd. Sorption experimental data obtained with the selected metals was in agreement with both Langmuir and Freundlich isotherm. The adsorption capacity and metal removal efficiency of chitosan was studied with the adsorption of Zn ion. Chitosan also meets the requirements of a good adsorbent but its efficiency was less compared to activated charcoal.

In order to make out the sorption mechanism involved in the sediment-water system, adsorption study was carried out with Zn ions by taking station-4 sediment as an adsorbent. It was observed from the study that the adsorption capacity of particular sediment will be more with its finer fractions. Hence texture of the sediment plays a key role in the sorption process in an environment. The adsorption mechanism and kinetics studies in-vitro was to some extent similar to in-vivo conditions with the limitations that, the conditions and phenomenon persisting in the environment like turbulence, sediment transport mechanism, effects and competency of other ions in the system are not taken into account in the current laboratory study. In the aquatic niche, sediment undergoes adsorption-desorption process depending upon the favourable environmental condition. If the environmental condition is pertinent for an adsorption process, then the metal ions in the water may preferably adsorbed onto the sediment and inturn desorption process occurs with the release of metals from the sediment to water. Hence the water-sediment system always will be reverting with the adsorption and desorption process for attaining an equilibrium. The adsorption process depends on the sorptional capacity of the sediment, adsorbate concentration, pH of the solution and more over the particle size of the adsorbent.

Among the adsorbents selected for this study, experimental data obtained with the activated charcoal and the natural sediment

(sediment of station 4), clearly fits with the Langmuir equation where as the Chitosan follows a Freundlich model. It was observed that the maximum efficiency in removing the metal ion was found to be on using activated charcoal as adsorbent. Based on the outcomes of this adsorption study, it could be applied in the environmental niche for outbreak of any sudden misshapen and leads to over discharge of industrial wastes. Besides for the pollution abatement, the outcomes of this adsorption study showed that activated charcoal could be well suited for pharmaceutical field of research to reduce or divert effect of intoxication due to heavy metals. Hence the activated charcoal equally finds relevance in the therapeutic field for the intoxication due to heavy metals in humans and in environment.

It can be concluded that the sorptional technique can be used as a theraptic/remedial approach for the removal of heavy metals from aquatic environment via protecting the aquatic life to control biomagnification. This theraptic procedure to environment using adsorption also proved its advantage over other remedial processes because of its cost effectiveness and easy, hassle-free process. As per the study, the activated charcoal can be thus best used an adsorbent in the removal of metal ions. The study showed that the Chitosan could also be used as an alternative adsorbent due to its low costs, non persistent nature, and sorptional efficiency and hence it is affordable for the industries to mitigate the pollution due to toxic metals in a large scale. Chitosan is a cheaper adsorbent as it is a processed product of a food waste, but the availability of this degradable adsorbent is less that that of charcoal. Among the adsorbents selected, synergism or antagonism effects between themselves also contribute. Hence further research would open to widen the horizon of this overwhelming subject.

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Season & Station wise distribution of Cd ion (mg/kg) in Sediments

Station	Pre Monsoon			Monsoon			Post Monsoon		
	2007	2008	Avg	2007	2008	Avg	2007	2008	Avg
1	0.461	0.309	0.385	1.674	0.382	1.028	0.604	0.448	0.526
2	0.564	0.396	0.480	0.948	*	0.948	0.282	*	0.282
3	0.496	2.867	1.681	3.414	0.549	1.981	0.738	3.697	2.217
4	2.225	0.894	1.560	4.981	1.948	3.464	0.706	1.584	1.145
5	1.220	0.772	0.996	2.720	1.759	2.239	2.866	2.868	2.867
6	2.737	3.055	2.896	2.812	3.122	2.967	9.180	6.780	7.980
7	0.998	1.599	1.299	4.075	0.173	2.124	2.898	4.827	3.862
8	4.882	9.560	7.221	2.858	15.510	9.184	5.298	4.148	4.723

Season & Station wise distribution of Cu ion (mg/kg) in Sediments

Station	Pre Monsoon			Monsoon			Post Monsoon		
	2007	2008	Avg	2007	2008	Avg	2007	2008	Avg
1	32.16	12.15	22.15	22.49	21.87	22.18	10.49	9.13	9.81
2	12.08	22.17	17.13	34.59	*	34.59	15.50	*	15.50
3	27.02	25.22	26.12	49.77	12.65	31.21	12.70	31.91	22.30
4	28.01	21.94	24.98	55.69	25.37	40.53	20.65	40.60	30.62
5	31.15	43.66	37.41	53.05	55.67	54.36	57.18	20.59	38.88
6	72.07	59.97	66.02	27.08	40.44	33.76	94.26	43.90	69.08
7	48.30	56.98	52.64	71.90	82.96	77.43	34.17	36.98	35.57
8	113.9	147.7	130.8	114.3	194.6	154.5	30.58	156.5	93.5

Season & Station wise distribution of Fe ion (mg/kg) in Sediments

Station	Pre Monsoon			Monsoon			Post Monsoon		
	2007	2008	Avg	2007	2008	Avg	2007	2008	Avg
1	36070	18610	27340	23022	28635	25828	28775	18312	23543
2	29423	30739	30081	37675	*	37675	36001	*	36001
3	26487	27346	26916	26259	32693	29476	26840	25860	26350
4	31931	26878	29405	35955	43440	39697	19411	33658	26534
5	32809	22117	27463	32789	34056	33422	16534	14912	15723
6	38820	22420	30620	35025	24320	29672	39169	43991	41580
7	27434	20402	23918	22548	26051	24299	89029	29486	59257
8	40454	59046	49750	40052	37513	38782	29004	54457	41731

Season & Station wise distribution of Ni ion (mg/kg) in Sediments

Station	Pre Monsoon			Monsoon			Post Monsoon		
	2007	2008	Avg	2007	2008	Avg	2007	2008	Avg
1	66.63	25.52	46.08	29.78	35.65	32.72	ND	8.07	8.07
2	8.33	15.87	12.10	28.64	*	28.64	1.01	*	1.01
3	27.59	54.01	40.80	27.60	44.68	36.14	ND	32.04	32.04
4	38.78	44.77	41.78	47.24	65.36	56.30	ND	43.75	43.75
5	39.18	39.11	39.15	42.02	58.36	50.19	45.13	8.18	26.65
6	49.83	21.18	35.51	41.47	45.65	43.56	125.23	80.84	103.03
7	33.00	28.65	30.83	26.26	19.68	22.97	24.68	4.37	14.53
8	41.33	75.05	58.19	47.30	60.25	53.78	ND	5.69	5.69

Season & Station wise distribution of Pb ion (mg/kg) in Sediments

Station	Pre Monsoon			Monsoon			Post Monsoon		
	2007	2008	Avg	2007	2008	Avg	2007	2008	Avg
1	8.76	2.05	5.41	7.74	5.65	6.70	6.04	6.60	6.32
2	5.32	6.76	6.04	4.18	*	4.18	8.85	*	8.85
3	6.97	14.95	10.96	12.96	8.32	10.64	8.94	24.13	16.54
4	7.93	6.17	7.05	16.51	9.65	13.08	9.34	11.19	10.26
5	7.92	7.08	7.50	13.66	11.98	12.82	18.69	17.81	18.25
6	8.11	20.12	14.11	13.64	8.45	11.05	23.17	11.24	17.21
7	4.52	6.19	5.35	20.36	8.65	14.51	18.36	21.09	19.73
8	14.97	58.62	36.80	23.22	18.41	20.82	44.56	28.65	36.61

Season & Station wise distribution of Zn ion (mg/kg) in Sediments

Station	Pre Monsoon			Monsoon			Post Monsoon		
	2007	2008	Avg	2007	2008	Avg	2007	2008	Avg
1	71.8	8.5	40.2	42.2	9.7	25.9	27.4	16.3	21.8
2	19.6	27.7	23.7	71.4	*	71.4	12.2	*	12.2
3	69.6	188.2	128.9	80.4	78.4	79.4	23.2	171.6	97.4
4	300.1	185.9	243.0	258.0	245.4	251.7	61.7	89.7	75.7
5	235.2	273.6	254.4	167.3	189.3	178.3	280.1	100.2	190.1
6	214.7	251.9	233.3	179.6	147.6	163.6	696.7	71.6	384.1
7	110.6	100.5	105.6	211.4	185.5	198.4	178.4	100.3	139.3
8	375.0	302.2	338.6	228.4	278.6	253.5	119.3	189.3	154.3

Adsorption of Cd^{2+} on Ac.C at 303K

Initial conc Ci of Cd (mgpl)	Shaking time in min	Conc of Cd, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.002	5	7.987	1.008	20.15	2.367	0.3741
	10	7.387	1.308	26.14	2.067	0.3152
	15	6.321	1.841	36.80	1.534	0.1857
	30	5.014	2.494	49.87	0.880	-0.0555
	45	3.295	3.354	67.06	0.021	-1.6882
	60	3.254	3.374	67.47	0.000	
15.011	5	11.955	1.528	20.36	3.471	0.5404
	10	11.101	1.955	26.05	3.044	0.4834
	15	9.521	2.745	36.57	2.254	0.3529
	30	7.658	3.677	48.98	1.322	0.1212
	45	5.114	4.949	65.93	0.050	-1.3010
	60	5.014	4.999	66.60	0.000	
20.147	5	15.987	2.080	20.65	4.487	0.6519
	10	14.900	2.624	26.04	3.943	0.5958
	15	12.147	4.000	39.71	2.567	0.4093
	30	10.214	4.967	49.30	1.600	0.2041
	45	7.354	6.397	63.50	0.170	-0.7696
	60	7.014	6.567	65.19	0.000	
25.009	5	20.098	2.456	19.64	5.487	0.7393
	10	18.951	3.029	24.22	4.914	0.6914
	15	17.248	3.881	31.03	4.062	0.6087
	30	13.547	5.731	45.83	2.212	0.3447
	45	9.211	7.899	63.17	0.043	-1.3615
	60	9.124	7.943	63.52	0.000	
30.001	5	24.141	2.930	19.53	6.408	0.8067
	10	22.879	3.561	23.74	5.777	0.7617
	15	21.568	4.217	28.11	5.121	0.7094
	30	16.654	6.674	44.49	2.664	0.4255
	45	11.451	9.275	61.83	0.063	-1.2041
	60	11.326	9.338	62.25	0.000	

Adsorption of Cd^{2+} on Ac.C at 313K

Initial conc Ci of Cd (mgpl)	Shaking time in min	Conc of Cd, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.002	5	7.842	1.080	21.60	2.342	0.3696
	10	7.265	1.369	27.36	2.054	0.3125
	15	6.287	1.858	37.14	1.565	0.1944
	30	4.958	2.522	50.43	0.900	-0.0458
	45	3.198	3.402	68.03	0.020	-1.6990
	60	3.158	3.422	68.43	0.000	--
15.011	5	11.857	1.577	21.01	3.428	0.5350
	10	11.002	2.005	26.71	3.001	0.4772
	15	9.425	2.793	37.21	2.212	0.3448
	30	7.587	3.712	49.46	1.293	0.1116
	45	5.025	4.993	66.52	0.012	-1.9136
	60	5.001	5.005	66.68	0.000	--
20.147	5	15.879	2.134	21.18	4.389	0.6424
	10	14.801	2.673	26.53	3.850	0.5855
	15	12.754	3.697	36.70	2.827	0.4512
	30	10.185	4.981	49.45	1.542	0.1881
	45	7.186	6.481	64.33	0.043	-1.3716
	60	7.101	6.523	64.75	0.000	--
25.009	5	19.998	2.506	20.04	5.443	0.7358
	10	18.847	3.081	24.64	4.867	0.6873
	15	17.098	3.956	31.63	3.993	0.6013
	30	13.445	5.782	46.24	2.167	0.3358
	45	9.125	7.942	63.51	0.006	-2.1871
	60	9.112	7.949	63.57	0.000	--
30.001	5	24.025	2.988	19.92	6.405	0.8065
	10	22.699	3.651	24.34	5.742	0.7591
	15	21.425	4.288	28.59	5.105	0.7080
	30	16.521	6.740	44.93	2.653	0.4237
	45	11.321	9.340	62.26	0.053	-1.2757
	60	11.215	9.393	62.62	0.000	--

Adsorption of Cd^{2+} on Ac.C at 323K

Initial conc C_i of Cd (mgpl)	Shaking time in min	Conc of Cd, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.002	5	7.714	1.144	22.88	2.325	0.3664
	10	7.185	1.409	28.16	2.061	0.3140
	15	6.177	1.913	38.24	1.557	0.1921
	30	4.865	2.569	51.36	0.901	-0.0455
	45	3.099	3.452	69.02	0.017	-1.7607
	60	3.064	3.469	69.37	0.000	--
15.011	5	11.765	1.623	21.62	3.426	0.5347
	10	9.987	2.512	33.47	2.537	0.4042
	15	9.324	2.844	37.89	2.205	0.3434
	30	7.458	3.777	50.32	1.272	0.1045
	45	4.987	5.012	66.78	0.037	-1.4377
	60	4.914	5.049	67.26	0.000	--
20.147	5	15.755	2.196	21.80	4.329	0.6363
	10	14.712	2.718	26.98	3.807	0.5806
	15	12.145	4.001	39.72	2.524	0.4020
	30	9.987	5.080	50.43	1.445	0.1597
	45	7.014	6.567	65.19	-0.042	--
	60	7.098	6.525	64.77	0.000	--
25.009	5	19.887	2.561	20.48	5.416	0.7337
	10	18.751	3.129	25.02	4.848	0.6856
	15	17.062	3.973	31.78	4.004	0.6024
	30	13.326	5.842	46.72	2.136	0.3295
	45	9.014	7.998	63.96	-0.021	--!
	60	9.055	7.977	63.79	0.000	--!
30.001	5	24.935	2.533	16.89	6.911	0.8395
	10	22.569	3.716	24.77	5.728	0.7580
	15	21.325	4.338	28.92	5.106	0.7080
	30	16.425	6.788	45.25	2.656	0.4241
	45	11.225	9.388	62.58	0.055	-1.2557
	60	11.114	9.444	62.95	0.000	--!

Adsorption of Cd^{2+} on Ac.C at 333K

Initial conc C_i of Cd (mgpl)	Shaking time in min	Conc of Cd, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.002	5	7.624	1.189	23.78	2.335	0.3266
	10	7.087	1.458	29.14	2.067	0.3197
	15	6.065	1.969	39.36	1.556	0.3524
	30	4.856	2.573	51.45	0.951	0.2918
	45	2.999	3.502	70.02	0.023	0.2754
	60	2.954	3.524	70.47	0.000	--
15.011	5	11.661	1.675	22.32	3.423	0.5344
	10	9.863	2.574	34.30	2.524	0.4020
	15	9.231	2.890	38.51	2.208	0.3440
	30	7.346	3.833	51.06	1.265	0.1022
	45	4.879	5.066	67.50	0.032	-1.4949
	60	4.815	5.098	67.92	0.000	--
20.147	5	15.654	2.247	22.30	4.334	0.6368
	10	14.629	2.759	27.39	3.821	0.5822
	15	12.757	3.695	36.68	2.885	0.4601
	30	9.987	5.080	50.43	1.500	0.1761
	45	6.924	6.612	65.63	-0.031	--
	60	6.987	6.580	65.32	0.000	--
25.009	5	19.776	2.617	20.93	5.415	0.7336
	10	18.654	3.178	25.41	4.855	0.6861
	15	16.925	4.042	32.32	3.990	0.6010
	30	13.235	5.887	47.08	2.145	0.3314
	45	8.911	8.049	64.37	-0.017	--
	60	8.945	8.032	64.23	0.000	--
30.001	5	24.832	2.585	17.23	6.867	0.8368
	10	22.451	3.775	25.17	5.677	0.7541
	15	21.225	4.388	29.25	5.064	0.7045
	30	16.634	6.684	44.56	2.768	0.4422
	45	11.130	9.436	62.90	0.016	-1.7986
	60	11.098	9.452	63.01	0.000	--

Adsorption of Cu^{2+} on Ac.C at 303K

Initial conc C_i of Cu (mgpl)	Shaking time in min	Conc of Cu, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.112	5	6.976	1.568	31.01	2.249	0.3520
	10	5.890	2.111	41.75	1.706	0.2320
	15	5.196	2.458	48.62	1.359	0.1332
	30	3.816	3.148	62.26	0.669	-0.1746
	45	3.016	3.548	70.17	0.269	-0.5702
	60	2.478	3.817	75.49	0.000	--
14.987	5	10.959	2.014	26.88	3.135	0.4962
	10	9.013	2.987	39.86	2.162	0.3349
	15	7.851	3.568	47.61	1.581	0.1989
	30	6.279	4.354	58.10	0.795	-0.0996
	45	5.203	4.892	65.28	0.257	-0.5901
	60	4.689	5.149	68.71	0.000	--
20.221	5	15.199	2.511	24.84	3.677	0.5655
	10	13.571	3.325	32.89	2.863	0.4568
	15	11.713	4.254	42.08	1.934	0.2865
	30	10.199	5.011	49.56	1.177	0.0708
	45	9.091	5.565	55.04	0.623	-0.2055
	60	7.845	6.188	61.20	0.000	--
25.005	5	19.457	2.774	22.19	4.068	0.6094
	10	17.693	3.656	29.24	3.186	0.5032
	15	14.719	5.143	41.14	1.699	0.2302
	30	13.247	5.879	47.02	0.963	-0.0164
	45	12.355	6.325	50.59	0.517	-0.2865
	60	11.321	6.842	54.73	0.000	--
30.098	5	24.186	2.956	19.64	4.815	0.6826
	10	22.826	3.636	24.16	4.135	0.6165
	15	18.794	5.652	37.56	2.119	0.3261
	30	18.048	6.025	40.04	1.746	0.2420
	45	16.092	7.003	46.53	0.768	-0.1146
	60	14.556	7.771	51.64	0.000	--

Adsorption of Cu^{2+} on Ac.C at 313K

Initial conc C_i of Cu (mgpl)	Shaking time in min	Conc of Cu, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.112	5	6.876	1.618	32.00	2.311	0.3638
	10	5.758	2.177	43.06	1.752	0.2435
	15	5.021	2.546	50.35	1.384	0.1410
	30	3.665	3.224	63.76	0.706	-0.1515
	45	2.987	3.563	70.46	0.367	-0.4359
	60	2.254	3.929	77.71	0.000	--
14.987	5	10.789	2.099	28.01	3.286	0.5166
	10	8.889	3.049	40.69	2.336	0.3684
	15	7.785	3.601	48.05	1.784	0.2513
	30	6.125	4.431	59.13	0.954	-0.0207
	45	5.119	4.934	65.84	0.451	-0.3463
	60	4.218	5.385	71.86	0.000	--
20.221	5	15.003	2.609	25.80	3.860	0.5865
	10	13.325	3.448	34.10	3.021	0.4801
	15	11.625	4.298	42.51	2.171	0.3366
	30	10.022	5.100	50.44	1.369	0.1364
	45	8.885	5.668	56.06	0.801	-0.0966
	60	7.284	6.469	63.98	0.000	--
25.005	5	19.221	2.892	23.13	4.147	0.6177
	10	17.458	3.774	30.18	3.265	0.5139
	15	14.556	5.225	41.79	1.814	0.2586
	30	13.069	5.968	47.73	1.071	0.0296
	45	12.115	6.445	51.55	0.594	-0.2266
	60	10.928	7.039	56.30	0.000	--
30.098	5	24.025	3.037	20.18	4.870	0.6875
	10	22.660	3.719	24.71	4.188	0.6220
	15	18.602	5.748	38.20	2.159	0.3342
	30	17.689	6.205	41.23	1.702	0.2310
	45	15.886	7.106	47.22	0.801	-0.0966
	60	14.285	7.907	52.54	0.000	--

Adsorption of Cu^{2+} on Ac.C at 323K

Initial conc C_i of Cu (mgpl)	Shaking time in min	Conc of Cu, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.112	5	6.662	1.725	34.12	2.315	0.3646
	10	5.598	2.257	44.64	1.783	0.2512
	15	4.986	2.563	50.69	1.477	0.1694
	30	3.458	3.327	65.80	0.713	-0.1469
	45	2.785	3.664	72.46	0.377	-0.4242
	60	2.032	4.040	79.91	0.000	--
14.987	5	10.556	2.216	29.57	3.277	0.5155
	10	8.698	3.145	41.96	2.348	0.3707
	15	7.569	3.709	49.50	1.784	0.2513
	30	6.050	4.469	59.63	1.024	0.0103
	45	4.896	5.046	67.33	0.447	-0.3497
	60	4.002	5.493	73.30	0.000	--
20.221	5	14.812	2.705	26.75	3.882	0.5890
	10	13.112	3.555	35.16	3.032	0.4817
	15	11.458	4.382	43.34	2.205	0.3433
	30	9.756	5.233	51.75	1.354	0.1315
	45	8.596	5.813	57.49	0.774	-0.1115
	60	7.049	6.586	65.14	0.000	--
25.005	5	19.025	2.990	23.92	4.290	0.6325
	10	17.225	3.890	31.11	3.390	0.5302
	15	14.336	5.335	42.67	1.946	0.2890
	30	12.895	6.055	48.43	1.225	0.0881
	45	11.989	6.508	52.05	0.772	-0.1124
	60	10.445	7.280	58.23	0.000	--
30.098	5	23.886	3.106	20.64	4.912	0.6912
	10	22.425	3.837	25.49	4.181	0.6213
	15	18.396	5.851	38.88	2.167	0.3358
	30	17.425	6.337	42.11	1.681	0.2256
	45	15.598	7.250	48.18	0.768	-0.1148
	60	14.063	8.018	53.28	0.000	--

Adsorption of Cu^{2+} on Ac.C at 333K

Initial conc C_i of Cu (mgpl)	Shaking time in min	Conc of Cu, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.112	5	6.369	1.872	37.02	2.193	0.3409
	10	5.321	2.396	47.38	1.669	0.2223
	15	4.785	2.664	52.68	1.401	0.1463
	30	3.198	3.457	68.37	0.607	-0.2168
	45	2.525	3.794	75.03	0.271	-0.5678
	60	1.984	4.064	80.38	0.000	--
14.987	5	10.256	2.366	31.57	3.199	0.5050
	10	8.332	3.328	44.41	2.237	0.3497
	15	7.254	3.867	51.60	1.698	0.2299
	30	5.896	4.546	60.66	1.019	0.0082
	45	4.633	5.177	69.09	0.387	-0.4120
	60	3.858	5.565	74.26	0.000	--
20.221	5	14.256	2.983	29.50	3.701	0.5683
	10	12.986	3.618	35.78	3.066	0.4866
	15	11.325	4.448	43.99	2.236	0.3494
	30	9.556	5.333	52.74	1.351	0.1307
	45	8.326	5.948	58.82	0.736	-0.1331
	60	6.854	6.684	66.10	0.000	--
25.005	5	18.789	3.108	24.86	4.622	0.6648
	10	17.002	4.002	32.01	3.729	0.5715
	15	14.112	5.447	43.56	2.284	0.3586
	30	12.596	6.205	49.63	1.526	0.1834
	45	11.636	6.685	53.47	1.046	0.0193
	60	9.545	7.730	61.83	0.000	--
30.098	5	23.689	3.205	21.29	5.277	0.7224
	10	22.236	3.931	26.12	4.551	0.6581
	15	18.112	5.993	39.82	2.489	0.3959
	30	17.169	6.465	42.96	2.017	0.3047
	45	15.325	7.387	49.08	1.095	0.0394
	60	13.135	8.482	56.36	0.000	--

Adsorption of Ni^{2+} on Ac.C at 303K

Initial conc C_i of Ni (mgpl)	Shaking time in min	Conc of Ni, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.005	5	6.875	3.126	31.26	5.084	0.7062
	10	5.278	4.722	47.22	3.488	0.5426
	15	3.787	6.214	62.14	1.996	0.3002
	30	2.790	7.210	72.10	1.000	-0.0001
	45	1.786	8.214	82.14	-0.005	--
	60	1.790	8.210	82.10	0.000	--
20.008	5	14.880	5.121	25.60	10.524	1.0222
	10	12.699	7.301	36.51	8.343	0.9213
	15	10.025	9.975	49.87	5.669	0.7535
	30	6.543	13.458	67.29	2.187	0.3397
	45	4.362	15.638	78.19	0.006	-2.2218
	60	4.356	15.644	78.22	0.000	--
30.018	5	23.659	6.341	21.14	14.671	1.1665
	10	21.588	8.412	28.04	12.600	1.1004
	15	16.898	13.103	43.68	7.910	0.8982
	30	13.255	16.745	55.82	4.267	0.6301
	45	9.025	20.976	69.92	0.037	-1.4353
	60	8.988	21.012	70.04	0.000	--
40.105	5	32.660	7.340	18.35	18.994	1.2786
	10	30.365	9.635	24.09	16.700	1.2227
	15	25.699	14.301	35.75	12.033	1.0804
	30	19.652	20.348	50.87	5.987	0.7772
	45	13.712	26.288	65.72	0.046	-1.3335
	60	13.666	26.334	65.84	0.000	--
50.011	5	43.366	6.634	13.27	24.337	1.3863
	10	41.257	8.744	17.49	22.228	1.3469
	15	37.659	12.341	24.68	18.630	1.2702
	30	28.658	21.342	42.68	9.629	0.9836
	45	19.021	30.979	61.96	-0.008	--
	60	19.029	30.971	61.94	0.000	--

Adsorption of Ni^{2+} on Ac.C at 313K

Initial conc C_i of Ni (mgpl)	Shaking time in min	Conc of Ni, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	Log (qe-qt)
10.005	5	6.541	3.459	34.59	4.989	0.6980
	10	5.014	4.986	49.86	3.462	0.5393
	15	3.478	6.522	65.22	1.926	0.2847
	30	2.658	7.342	73.42	1.106	0.0438
	45	1.701	8.299	82.99	0.149	-0.8268
	60	1.552	8.448	84.48	0.000	--
20.008	5	14.554	5.446	27.23	10.709	1.0297
	10	12.145	7.855	39.28	8.300	0.9191
	15	9.546	10.454	52.27	5.701	0.7560
	30	6.445	13.555	67.78	2.600	0.4150
	45	4.012	15.988	79.94	0.167	-0.7762
	60	3.845	16.155	80.78	0.000	--
30.018	5	22.658	7.342	24.47	14.260	1.1541
	10	20.365	9.635	32.12	11.967	1.0780
	15	16.124	13.876	46.25	7.726	0.8880
	30	12.587	17.413	58.04	4.189	0.6221
	45	8.419	21.581	71.94	0.021	-1.6819
	60	8.398	21.602	72.01	0.000	--
40.105	5	33.141	6.859	17.15	19.963	1.3002
	10	28.456	11.544	28.86	15.278	1.1841
	15	24.356	15.644	39.11	11.178	1.0484
	30	17.658	22.342	55.86	4.480	0.6513
	45	13.457	26.543	66.36	0.279	-0.5544
	60	13.178	26.822	67.06	0.000	--
50.011	5	43.254	6.746	13.49	24.707	1.3928
	10	39.541	10.459	20.92	20.994	1.3221
	15	35.652	14.348	28.70	17.105	1.2331
	30	26.325	23.675	47.35	7.778	0.8909
	45	18.985	31.015	62.03	0.438	-0.3585
	60	18.547	31.453	62.91	0.000	--

Adsorption of Ni^{2+} on Ac.C at 323K

Initial conc C_i of Ni (mgpl)	Shaking time in min	Conc of Ni, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.005	5	6.325	3.675	36.75	4.860	0.6866
	10	4.987	5.013	50.13	3.522	0.5467
	15	3.254	6.746	67.46	1.789	0.2525
	30	2.547	7.453	74.53	1.082	0.0341
	45	1.512	8.488	84.88	0.047	-1.3316
	60	1.465	8.535	85.35	0.000	--
20.008	5	14.487	5.513	27.57	10.885	1.0368
	10	12.014	7.986	39.93	8.412	0.9249
	15	9.356	10.644	53.22	5.754	0.7600
	30	6.278	13.722	68.61	2.676	0.4275
	45	3.854	16.146	80.73	0.252	-0.5986
	60	3.602	16.398	81.99	0.000	--
30.018	5	22.014	7.986	26.62	14.293	1.1551
	10	20.101	9.899	33.00	12.380	1.0927
	15	15.875	14.125	47.08	8.154	0.9113
	30	12.145	17.855	59.52	4.424	0.6458
	45	8.001	21.999	73.33	0.280	-0.5535
	60	7.721	22.279	74.26	0.000	--
40.105	5	32.875	7.125	17.81	20.086	1.3029
	10	28.145	11.855	29.64	15.356	1.1863
	15	24.124	15.876	39.69	11.335	1.0544
	30	17.548	22.452	56.13	4.759	0.6775
	45	12.812	27.188	67.97	0.023	-1.6383
	60	12.789	27.211	68.03	0.000	--
50.011	5	42.879	7.121	14.24	24.717	1.3930
	10	38.140	11.860	23.72	19.978	1.3005
	15	33.658	16.342	32.68	15.496	1.1902
	30	25.145	24.855	49.71	6.982	0.8440
	45	18.215	31.785	63.57	0.052	-1.2798
	60	18.163	31.838	63.68	0.000	--

Adsorption of Ni^{2+} on Ac.C at 333K

Initial conc C_i of Ni (mgpl)	Shaking time in min	Conc of Ni, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.005	5	6.154	3.846	38.46	4.893	0.6895
	10	4.814	5.186	51.86	3.553	0.5505
	15	3.014	6.986	69.86	1.753	0.2437
	30	2.457	7.543	75.43	1.196	0.0776
	45	1.358	8.642	86.42	0.097	-1.0150
	60	1.261	8.739	87.39	0.000	--
20.008	5	14.014	5.986	29.93	10.700	1.0294
	10	10.987	9.013	45.07	7.673	0.8849
	15	9.214	10.786	53.93	5.900	0.7708
	30	6.014	13.986	69.93	2.700	0.4313
	45	3.452	16.548	82.74	0.137	-0.8617
	60	3.315	16.686	83.43	0.000	--
30.018	5	20.987	9.013	30.04	13.560	1.1323
	10	19.856	10.144	33.81	12.429	1.0944
	15	15.121	14.879	49.60	7.694	0.8862
	30	12.078	17.922	59.74	4.651	0.6676
	45	7.658	22.342	74.47	0.231	-0.6362
	60	7.427	22.573	75.24	0.000	--
40.105	5	31.658	8.342	20.86	19.200	1.2833
	10	27.654	12.346	30.87	15.196	1.1817
	15	23.688	16.312	40.78	11.230	1.0504
	30	16.987	23.013	57.53	4.529	0.6560
	45	12.547	27.453	68.63	0.089	-1.0506
	60	12.458	27.542	68.86	0.000	--
50.011	5	41.689	8.311	16.62	24.077	1.3816
	10	37.254	12.746	25.49	19.642	1.2932
	15	32.874	17.126	34.25	15.262	1.1836
	30	24.854	25.146	50.29	7.242	0.8599
	45	18.012	31.988	63.98	0.400	-0.3979
	60	17.612	32.388	64.78	0.000	--

Adsorption of Pb^{2+} on Ac.C at 303K

Initial conc C_i of Pb (mgpl)	Shaking time in min	Conc of Pb, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
20.013	5	16.536	3.477	17.37	14.282	1.1548
	10	14.996	5.017	25.07	12.742	1.1052
	15	12.251	7.762	38.78	9.997	0.9999
	30	6.895	13.118	65.55	4.641	0.6666
	45	5.213	14.800	73.95	2.959	0.4712
	60	2.254	17.759	88.74	0.000	--
30.154	5	24.896	5.258	17.44	19.651	1.2934
	10	22.865	7.289	24.17	17.620	1.2460
	15	18.663	11.491	38.11	13.418	1.1277
	30	11.996	18.158	60.22	6.751	0.8294
	45	7.965	22.189	73.59	2.720	0.4346
	60	5.245	24.909	82.61	0.000	--
40.112	5	33.665	6.447	16.07	23.005	1.3618
	10	31.452	8.660	21.59	20.792	1.3179
	15	25.365	14.747	36.76	14.705	1.1675
	30	17.125	22.987	57.31	6.465	0.8106
	45	13.896	26.216	65.36	3.236	0.5100
	60	10.660	29.452	73.42	0.000	--
50.084	5	41.968	8.116	16.20	25.212	1.4016
	10	38.562	11.522	23.01	21.806	1.3386
	15	34.356	15.728	31.40	17.600	1.2455
	30	25.365	24.719	49.36	8.609	0.9350
	45	20.962	29.122	58.15	4.206	0.6239
	60	16.756	33.328	66.54	0.000	--
60.015	5	51.652	8.363	13.93	30.577	1.4854
	10	47.552	12.463	20.77	26.477	1.4229
	15	42.025	17.990	29.98	20.950	1.3212
	30	32.992	27.023	45.03	11.917	1.0762
	45	25.458	34.557	57.58	4.383	0.6418
	60	21.075	38.940	64.88	0.000	--

Adsorption of Pb^{2+} on Ac.C at 313K

Initial conc C_i of Pb (mgpl)	Shaking time in min	Conc of Pb, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
20.013	5	16.238	3.775	18.86	14.123	1.1499
	10	14.895	5.118	25.57	12.780	1.1065
	15	11.895	8.118	40.56	9.780	0.9903
	30	6.658	13.355	66.73	4.543	0.6573
	45	4.896	15.117	75.54	2.781	0.4442
	60	2.115	17.898	89.43	0.000	--
30.154	5	24.665	5.489	18.20	19.464	1.2892
	10	22.465	7.689	25.50	17.264	1.2371
	15	18.336	11.818	39.19	13.135	1.1184
	30	11.758	18.396	61.01	6.557	0.8167
	45	7.698	22.456	74.47	2.497	0.3974
	60	5.201	24.953	82.75	0.000	--
40.112	5	33.332	6.780	16.90	22.752	1.3570
	10	31.080	9.032	22.52	20.500	1.3118
	15	26.365	13.747	34.27	15.785	1.1982
	30	16.923	23.189	57.81	6.343	0.8023
	45	13.556	26.556	66.20	2.976	0.4736
	60	10.580	29.532	73.62	0.000	--
50.084	5	41.789	8.295	16.56	25.164	1.4008
	10	38.265	11.819	23.60	21.640	1.3353
	15	33.965	16.119	32.18	17.340	1.2390
	30	25.001	25.083	50.08	8.376	0.9230
	45	20.651	29.433	58.77	4.026	0.6049
	60	16.625	33.459	66.81	0.000	--
60.015	5	51.259	8.756	14.59	30.274	1.4811
	10	47.353	12.662	21.10	26.368	1.4211
	15	41.865	18.150	30.24	20.880	1.3197
	30	32.885	27.130	45.21	11.900	1.0755
	45	25.322	34.693	57.81	4.337	0.6372
	60	20.985	39.030	65.03	0.000	--

Adsorption of Pb^{2+} on Ac.C at 323K

Initial conc C_i of Pb (mgpl)	Shaking time in min	Conc of Pb, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
20.013	5	16.001	4.012	20.05	13.917	1.1435
	10	14.526	5.487	27.42	12.442	1.0949
	15	11.689	8.324	41.59	9.605	0.9825
	30	6.325	13.688	68.40	4.241	0.6275
	45	4.658	15.355	76.73	2.574	0.4106
	60	2.084	17.929	89.59	0.000	--
30.154	5	24.365	5.789	19.20	19.215	1.2836
	10	22.025	8.129	26.96	16.875	1.2272
	15	18.111	12.043	39.94	12.961	1.1126
	30	11.456	18.698	62.01	6.306	0.7998
	45	7.425	22.729	75.38	2.275	0.3570
	60	5.150	25.004	82.92	0.000	--
40.112	5	32.995	7.117	17.74	22.611	1.3543
	10	30.689	9.423	23.49	20.305	1.3076
	15	30.785	13.356	23.25	16.372	1.2141
	30	16.698	23.414	58.37	6.314	0.8003
	45	13.254	26.858	66.96	2.870	0.4579
	60	10.384	29.728	74.11	0.000	--
50.084	5	41.456	8.628	17.23	25.140	1.4004
	10	39.335	10.749	21.46	23.019	1.3621
	15	28.659	21.425	42.78	12.343	1.0914
	30	24.685	25.399	50.71	8.369	0.9227
	45	20.225	29.859	59.62	3.909	0.5921
	60	16.316	33.768	67.42	0.000	--
60.015	5	51.112	8.903	14.83	30.967	1.4909
	10	46.996	13.019	21.69	26.851	1.4290
	15	41.625	18.390	30.64	21.480	1.3320
	30	32.652	27.363	45.59	12.507	1.0972
	45	22.569	37.446	62.39	2.424	0.3845
	60	20.145	39.870	66.43	0.000	--

Adsorption of Pb^{2+} on Ac.C at 333K

Initial conc C_i of Pb (mgpl)	Shaking time in min	Conc of Pb, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
20.013	5	15.802	4.211	21.04	13.753	1.1384
	10	14.328	5.685	28.41	12.279	1.0892
	15	11.348	8.665	43.30	9.299	0.9684
	30	6.355	13.658	68.25	4.306	0.6341
	45	4.355	15.658	78.24	2.306	0.3629
	60	2.049	17.964	89.76	0.000	--
30.154	5	23.829	6.325	20.98	18.740	1.2728
	10	21.918	8.236	27.31	16.829	1.2261
	15	17.898	12.256	40.64	12.809	1.1075
	30	11.159	18.995	62.99	6.070	0.7832
	45	7.257	22.897	75.93	2.168	0.3361
	60	5.089	25.065	83.12	0.000	--
40.112	5	32.743	7.369	18.37	22.622	1.3545
	10	29.447	10.665	26.59	19.326	1.2861
	15	24.876	15.236	37.98	14.755	1.1689
	30	16.454	23.658	58.98	6.333	0.8016
	45	12.987	27.125	67.62	2.866	0.4573
	60	10.121	29.991	74.77	0.000	--
50.084	5	41.188	8.897	17.76	24.908	1.3963
	10	37.724	12.360	24.68	21.444	1.3313
	15	33.426	16.658	33.26	17.146	1.2342
	30	24.425	25.659	51.23	8.145	0.9109
	45	19.826	30.258	60.41	3.546	0.5497
	60	16.280	33.804	67.49	0.000	--
60.015	5	50.903	9.112	15.18	31.047	1.4920
	10	46.790	13.225	22.04	26.934	1.4303
	15	41.346	18.669	31.11	21.490	1.3322
	30	32.030	27.985	46.63	12.174	1.0854
	45	22.119	37.896	63.14	2.263	0.3547
	60	19.856	40.159	66.91	0.000	--

Adsorption of Zn^{2+} on Ac.C at 303K

Initial conc C_i of Zn (mgpl)	Shaking time in min	Conc of Zn, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.054	5	8.198	1.856	18.46	6.513	0.8138
	10	7.042	3.012	29.96	5.357	0.7289
	15	5.069	4.985	49.58	3.384	0.5294
	30	3.198	6.856	68.19	1.513	0.1798
	45	1.943	8.111	80.67	0.258	-0.5884
	60	1.685	8.369	83.24	0.000	--
15.112	5	12.244	2.868	18.98	8.955	0.9521
	10	10.667	4.445	29.41	7.378	0.8679
	15	8.218	6.894	45.62	4.929	0.6928
	30	4.887	10.225	67.66	1.598	0.2036
	45	4.256	10.856	71.84	0.967	-0.0146
	60	3.289	11.823	78.24	0.000	--
20.005	5	16.751	3.254	16.27	11.397	1.0568
	10	13.680	6.325	31.62	8.326	0.9204
	15	11.749	8.256	41.27	6.395	0.8058
	30	7.644	12.361	61.79	2.290	0.3598
	45	5.780	14.225	71.11	0.426	-0.3706
	60	5.354	14.651	73.24	0.000	--
25.148	5	21.127	4.021	15.99	13.085	1.1168
	10	17.279	7.869	31.29	9.237	0.9655
	15	12.783	12.365	49.17	4.741	0.6759
	30	10.812	14.337	57.01	2.770	0.4424
	45	8.783	16.365	65.07	0.741	-0.1302
	60	8.042	17.106	68.02	0.000	--
30.025	5	25.360	4.665	15.54	13.773	1.1390
	10	21.366	8.659	28.84	9.779	0.9903
	15	16.456	13.569	45.19	4.869	0.6875
	30	14.159	15.866	52.84	2.572	0.4103
	45	13.769	16.256	54.14	2.182	0.3389
	60	11.587	18.438	61.41	0.000	--

Adsorption of Zn^{2+} on Ac.C at 313K

Initial conc C_i of Zn (mgpl)	Shaking time in min	Conc of Zn, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.054	5	7.885	2.169	21.57	6.284	0.7982
	10	7.326	3.115	27.14	5.338	0.7274
	15	6.623	4.896	34.13	3.557	0.5511
	30	2.214	7.840	77.98	0.613	-0.2125
	45	1.746	8.308	82.63	0.145	-0.8386
	60	1.601	8.453	84.08	0.000	--
15.112	5	12.001	3.111	20.59	8.809	0.9449
	10	11.185	4.865	25.99	7.055	0.8485
	15	10.214	6.356	32.41	5.564	0.7454
	30	4.625	10.487	69.40	1.433	0.1562
	45	4.025	11.087	73.37	0.833	-0.0794
	60	3.192	11.920	78.88	0.000	--
20.005	5	16.553	3.452	17.26	11.272	1.0520
	10	15.158	5.654	24.23	9.070	0.9576
	15	13.856	8.025	30.74	6.699	0.8260
	30	7.335	12.670	63.33	2.054	0.3126
	45	5.452	14.553	72.75	0.171	-0.7670
	60	5.281	14.724	73.60	0.000	--
25.148	5	20.010	5.138	20.43	12.096	1.0826
	10	19.885	6.356	20.93	10.878	1.0365
	15	17.774	7.885	29.32	9.349	0.9708
	30	16.563	8.585	34.14	8.649	0.9370
	45	8.552	16.596	65.99	0.638	-0.1952
	60	7.914	17.234	68.53	0.000	--
30.025	5	25.112	4.913	16.36	13.667	1.1357
	10	23.856	6.169	20.55	12.411	1.0938
	15	22.325	7.700	25.65	10.880	1.0366
	30	13.956	16.069	53.52	2.511	0.3998
	45	13.659	16.366	54.51	2.214	0.3452
	60	11.445	18.580	61.88	0.000	--

Adsorption of Zn^{2+} on Ac.C at 323K

Initial conc C_i of Zn (mgpl)	Shaking time in min	Conc of Zn, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.054	5	8.012	2.042	20.31	6.498	0.8128
	10	7.112	3.650	29.26	4.890	0.6893
	15	6.235	5.698	37.98	2.842	0.4536
	30	2.001	8.053	80.10	0.487	-0.3125
	45	1.552	8.502	84.56	0.038	-1.4202
	60	1.514	8.540	84.94	0.000	--
15.112	5	11.856	3.256	21.55	8.854	0.9471
	10	10.886	4.985	27.96	7.125	0.8528
	15	10.110	8.781	33.10	3.329	0.5223
	30	4.335	10.777	71.31	1.333	0.1248
	45	3.885	11.227	74.29	0.883	-0.0540
	60	3.002	12.110	80.13	0.000	--
20.005	5	16.235	3.770	18.85	11.118	1.0460
	10	14.886	5.965	25.59	8.923	0.9505
	15	15.564	9.460	22.20	5.428	0.7346
	30	7.115	12.890	64.43	1.998	0.3006
	45	5.223	14.782	73.89	0.106	-0.9747
	60	5.117	14.888	74.42	0.000	--
25.148	5	19.885	5.263	20.93	12.074	1.0819
	10	18.665	6.632	25.78	10.705	1.0296
	15	17.251	10.225	31.40	7.112	0.8520
	30	16.356	14.365	34.96	2.972	0.4730
	45	8.239	16.909	67.24	0.428	-0.3686
	60	7.811	17.337	68.94	0.000	--
30.025	5	24.956	5.069	16.88	13.668	1.1357
	10	23.569	7.456	21.50	11.281	1.0524
	15	19.560	11.337	34.86	7.401	0.8693
	30	13.765	16.260	54.16	2.477	0.3939
	45	13.441	16.584	55.23	2.153	0.3331
	60	11.288	18.737	62.41	0.000	--

Adsorption of Zn^{2+} on Ac.C at 333K

Initial conc C_i of Zn (mgpl)	Shaking time in min	Conc of Zn, C (mgpl)	q(mg/g)	% Removal	qe-qt (mg/g)	log (qe-qt)
10.054	5	7.336	2.718	27.03	5.955	0.7749
	10	6.965	4.112	30.72	4.561	0.6591
	15	6.003	5.984	40.29	2.689	0.4296
	30	3.265	6.789	67.53	1.884	0.2751
	45	1.236	8.818	87.71	-0.145	--
	60	1.381	8.673	86.26	0.000	--
15.112	5	11.635	3.477	23.01	8.821	0.9455
	10	10.663	6.235	29.44	6.063	0.7827
	15	8.225	9.112	45.57	3.186	0.5032
	30	4.112	11.000	72.79	1.298	0.1133
	45	3.662	11.450	75.77	0.848	-0.0716
	60	2.814	12.298	81.38	0.000	--
20.005	5	16.005	4.000	20.00	10.998	1.0413
	10	12.651	6.256	36.76	8.742	0.9416
	15	10.665	8.365	46.69	6.633	0.8217
	30	6.856	13.149	65.73	1.849	0.2669
	45	5.001	15.004	75.00	-0.006	--
	60	5.007	14.998	74.97	0.000	--
25.148	5	21.365	3.783	15.04	13.649	1.1351
	10	18.869	4.658	32.97	12.774	1.1063
	15	15.365	8.115	45.85	9.317	0.9693
	30	15.524	9.624	63.25	7.808	0.8925
	45	7.869	17.279	68.71	0.153	-0.8153
	60	7.716	17.432	69.32	0.000	--
30.025	5	24.689	5.336	17.77	13.651	1.1352
	10	22.145	7.880	26.25	11.107	1.0456
	15	20.336	9.689	32.27	9.298	0.9684
	30	13.562	16.463	54.83	2.524	0.4021
	45	13.225	16.800	55.95	2.187	0.3398
	60	11.038	18.987	63.24	0.000	--

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1. **Pratheesh.V.B**, Nify Benny & Sujatha. C.H, (2009). Isolation, Stabilization and Characterization of Xanthophyll from Marigold Flower- Tagetes Erecta-L, Modern Applied Sciences Vol-3(2):19-28
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8. **Pratheesh.V.B** and Sujatha.C.H (2013). Evaluation of Distribution Coefficient of Heavy Metals in the Riverine and Estuarine Systems of Kochi, Kerala. Toxicological and Environmental Chemistry.(on peer review)

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CORRIGENDUM

A few format errors in the Reference citation and slight divergence/ imperfection in the statements crafted lacking facts in the explanation. The assertions are rectified in this corrigendum.

Chapter: 1, Page: 4, Paragraph: 2, Line: 9

Natural water may be considered to be composed of dissolved gases, micronutrients, major and minor elements and trace metals. Almost all elements present in the earth's crust are found in various natural waters in different concentrations depending on the source and environmental interactions.

Chapter: 1, Page: 6, Paragraph: 2 (full Para)

Pollution is the introduction of contaminants into the natural environment that causes adverse change. Pollution is often classified as point source or nonpoint source pollution. Water pollution is the contamination of water bodies like lakes, rivers, oceans, aquifers and groundwater and takes place when pollutants are released directly or indirectly into water bodies without sufficient treatment to remove harmful compounds. Water is referred to as polluted when it is messed up by anthropogenic contaminants and either does not support as potable water and/or undergoes a distinct change in its capacity to support its constituent biotic communities, such as fish. Surface water seeps through the soil and becomes groundwater. Groundwater aquifers are susceptible to contamination from sources that may not directly affect surface water bodies and can be contaminated through various sources like pesticides, sewage, nutrients, synthetic organics and acidification. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water.

Chapter: 1, Page: 7, Paragraph: 3, Line: 2

Sediments can be defined as a naturally occurring material or organic solid matter that is broken down by processes of weathering and erosion, and is subsequently transported by the action of wind, water, or ice, and/or by the force of gravity acting on the particle itself.

Chapter: 1, Page: 9, Paragraph: 1, Line: 10

Depending on the river morphology and hydrological conditions, suspended particles with associated contaminants can settle along the watercourse and become part of the bottom sediments, often for many kilometres downstream from the chemical sources (Vigano et al., 2003). Heavy metal pollution is a major threat to the environment due to the bioaccumulation and biomagnifications, causing heavier exposure for some organisms than is present in the environment alone. The most anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal (Santos et al., 2005).

Chapter: 1, Page: 12, Paragraph: 1, Line: 1

The commonly encountered toxic metals are As, Pb, Hg, Cd, Fe and Al. As these heavy metals cannot be degraded or destroyed, they are persistent in all parts of the environment. Arsenic toxicity produces various systemic complications like skin lesions, lung and liver diseases and other diseases like polyneuropathy, peripheral vascular disease, hypertension and ischeamic heart disease, diabetes mellitus, non-pitting oedema of feet/hands, weakness and anaemia (Guha, 2008).

Iron has an essential role as a constituent of enzymes, and in fresh waters, it's an important nutrient for algae and other organisms. But an increasing load of iron may significantly change both the structure and function of lotic ecosystems. The direct and indirect effects of iron contamination decrease the species diversity and abundance of aquatic organism (Vuori.K, 1995).

Aluminium and silicon are the most abundant elements in nature and are known as water quality parameters. However, Aluminium toxicity has been linked with a variety of neurological and behavioural disorders (A.S.Prasad, 1976). Humans also affect the natural geological and biological redistribution of heavy metals by altering the chemical form of heavy metals released to the environment.

Chapter: 1, Page: 22, Paragraph: 2, Line: 3

These problems were discussed by Gopinathan and Qasim (1971); Anto et al., (1977); Sundaresan, (1989) and Rasheed and Balachand (1995).

Chapter: 1, Page: 24, Paragraph: 2, Line: 2

Metal distribution along with the physico-chemical parameters in the Cochin estuarine systems are considerably influenced by the tropical features and human activities. Studies conducted by Ratheesh Kumar C.S et. al. (2010) and G.D Martin (2012) showed the adverse effects of pollution by anthropogenic activities.

Chapter: 1, Page: 30, Reference section.

[40] G. D.Martin, Rejomon George, P. Shaiju, . R.Muraleedharan, S. M. Nair, and N. Chandramohanakumar (2012). Toxic Metals Enrichment in the Surficial Sediments of a Eutrophic Tropical Estuary (Cochin Backwaters, Southwest Coast of India). The Scientific World Journal.Vol:2012.

[41] Ratheesh Kumar, C. S., Joseph, M. M., Gireesh Kumar, T. R., Renjith, K.R., Manju, M. N. and Chandramohanakumar, N.(2010). Spatial Variability and Contamination of Heavy Metals in the Inter-tidal Systems of a Tropical Environment. Int. J. Environ. Res., 4(4):691-700.

[42] D.N. Guha Mazumder.2008.Chronic arsenic toxicity & human health, Indian J Med Res 128, pp 436-447

[43] Vuori.K (1995). Direct and indirect effects of iron on river ecosystems. Ann. Zool. Fennici. Vol: 32.pp 317-329.

[44] A.S. Prasad. 1976. “Trace elements in human health and disease,” Vol II, pp. 1-474, Academic Press, Inc., NY, USA.

Chapter: 3, Page: 91, Paragraph: 1, Line: 1

The lower values of nitrite in any season may also be explained by the fact that nitrite is an essential nutrient required for phytoplankton growth and expected photosynthesis to be high in the photic zone due to the utilization of this nutrient for oxidation of organic matter. The CES is facing major threat from eutrophication and luxuriant growth of aquatic weeds, due to the excessive nutrients received either from natural or other artificial sources like sewage disposal sites. Agricultural runoff has been identified as one of the most significant contributors of nitrate /nitrite loadings to a water body (Smith et al., 1987).The decrease in agricultural land usage also may be the cause of decreasing trend in nitrate/nitrite concentrations.

Chapter: 3, Page: 108, Reference section.

[46] Smith, R. A., R. B. Alexander, and M. Wolman. 1987. Water quality trends in the nation's rivers. Science 235:1607-1615.

Chapter: 4, Page: 122, Paragraph: 1, Line: 20

The high value may be due to the intrusion of sea water at Bolghatty, the bar mouth of Cochin. Cadmium ion may release from the sediments deposited near to station-6 transported by the runoff of monsoon season. Cd ion present in the industrial effluents may get sorbed into sediments, as it has the capacity to adsorb metals (Strawn, 1999) under preferable conditions. In monsoon, metal-sorbed sediments get transported by the runoff and get deposited in the downstream of river Periyar or in the inner Cochin estuary by the counter current of intruded sea water. The intrusion of seawater increases salinity and thereby ionic strength. Ionic strength and pH have great influence on desorption of cadmium ion from sediments. The desorption of cadmium ions from sediments increases with the increase of ionic strength of solution and increases with the decrease of pH (Songhu Y, 2000).

Chapter: 4, Page: 176, Reference section.

[44] Strawn, Daniel G., and Donald L. Sparks.(1999). Sorption kinetics of trace elements in soils and soil materials. Fate and transport of heavy metals in the Vadose Zone. Lewis Publishers, Chelsea.

[45] Songhu Yuan 1, Zhimin Xi, Yi Jiang, Jinzhong Wan, Chan Wu, Zhonghua Zheng, Xiaohua Lu. (2007). Desorption of copper and cadmium from soils enhanced by organic acids. Environmental Science Research Institute, Huazhong University of Science and Technology.

Chapter: 5, Page: 201, Paragraph: 1, Line: 9

In addition, small amounts of polynuclear species such as $M_2(OH)_3^+$ and $M_4(OH)_4^{4+}$ may also be formed at higher concentrations of the salt in the solution and at suitable pH values (R.C Bansal and M. Goyal, 2010).

Chapter: 5, Page: 230, Reference section.

[53] Roop Chand Bansal and Meenakshi Goyal. 2010. Activated Carbon Adsorption, Taylor & Francis group, CRC Press.

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