STUDIES ON THE TREATMENT OF EFFLUENTS FROM NATURAL RUBBER PROCESSING UNITS

A Thesis submitted to
the Cochin **University of Science and Technology**
in partial fulfilment of the requirements
for the award of the degree of
DOCTOR OF PHILOSOPHY
in the Faculty of Technology

by

G. MADHU

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 022, INDIA

JANUARY 1994

CERTIFICATE

This is to certify that the thesis entitled "STUDIES ON THE TREATMENT OF EFFLUENTS FROM NATURAL RUBBER PROCESSING UNITS" being submitted by Shri G.MADHU in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy is a record of the bona fide research work carried out by him in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology under my supervision and guidance. No part of the work presented in this thesis has formed the basis of the award of any other degree, diploma or other similar title from any other institution.

Dr.K.E. George
(Supervising Teacher)
Reader
Department of Polymer Science
and Rubber Technology
Cochin University of
Science and Technology

Cochin 682022
24th January 1994

DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the supervision of Dr.K.E. George, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology. No part of this thesis has been presented for any other degree or diploma from any other institution.

Cochin 682022
Madhu
24th January 1994
G. Madhu

ACKNOWLEDGEMENT

I wish to express my profound gratitude to Dr.K.E. George, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology for his valuable guidance and encouragement throughout the course of the research work.

I am greatly indebted to Dr.D.Joseph Francis, Professor and Head, Department of Polymer Science and Rubber Technology for his valuable suggestions and for providing the necessary laboratory facilities.

I am grateful to my present employer, Fertilisers and Chemicals Travancore Ltd., Udyogamandal for permitting me to carry out the studies.

I wish to express my sincere thanks to the management and staff of Meenachil Rubber Marketing and Processing Co-operative Society Ltd., Palai for providing the necessary help in carrying out the investigations.

Finally I thank Mr.K.P.Sibiraj for neatly typing this thesis.

G. Madhu

ERRATA

Page No.	Line No.	May be corrected From	To
2	13	Organic compound	Organic compounds
18	4	Of from 1 million micron	from 1 million micron
18	21	odourous	Odorous
21	1	from 60 to 70	60 to 70
26	10	higher the volume	higher than the --
29	16	Envrionment	Environment
30		Kjeldhal	kjeldahl
31	24	an anaerobic	the anaerobic
36	8	was	were
67	5	2B.1.2	2B.1.1
103	10	nitrogen efficiencies	nitrogen removal -
106	12	-do-	-do-
122	21	(30)	delete (30)
123	13	those	that
131	7	paramound	paramount
145	9	850 NTU	680 NTU
209	Table 4.5	Sample Nos.1 and 2 may be added.	
227	5	(17)	(13)
268	17	Simpler and products	Simpler end produc
273	14	delete the portion "which makes has a number of advantages"	

Page Nos.279 and 280 to be interchanged.

Certified that the corrections suggested by the examiners have been incorporated.

Dr. K.E. George
Supervising Teacher

PREFACE

Agriculture and agro-based industries have played an important role in the development of human civilization. Most of these industries cause environmental pollution. Natural rubber processing industry with a variety of products is no exception in this regard. Natural rubber is harvested from Hevea trees in the form of a liquid called latex which contains 30-40 per cent rubber hydrocarbon and small quantities of carbohydrates, lipids, proteins etc. The rubber hydrocarbons are separated by acid coagulation for the preparation of ribbed sheets, crepe and crumb. It is also processed in the form of latex concentrate by centrifugation and creaming. More than 90 per cent of the latex concentrate is obtained by centrifuging ammoniated field latex. In the above processes, large quantity of water is used. The wash water loaded with organic compounds mentioned above and organic and inorganic acids used in the process go to form the effluents causing environmental pollution.

The pollution problems in rubber processing units caught the attention of researchers in Malaysia in the early seventies and a few systems have been developed for the treatment of rubber processing effluents. The growing environmental awareness among the people and the introduction of various environmental legislations have forced the rubber processing units in India, mostly situated in the South Indian states of Kerala, Tamilnadu and Karnataka, to adopt some kind of effluent treatment systems. But the absence of simple, economic and effective methods of effluent treatment causes hardships to these units in the small-scale sector. The present study was undertaken to evaluate the effectiveness of a few physico-chemical and biological methods for the treatment of effluents from natural rubber processing units.

The overall objective of this study is to evaluate the effectiveness of certain physico-chemical and biological methods for the treatment of effluents from natural rubber processing units. A survey of the chemical characteristics of the effluents discharged from rubber processing units showed that the effluents from latex concentration units were the most polluting. Hence the effluent samples from a centrifuge latex concentration unit were used for the tre ty studies. The treatment methods evaluated ir this study were tried successfully for waste waters fror process industries like distilleries, textile mills, food processing etc. An attempt has been made to extend these methods for the treatment of effluents from a latex concentration unit under Indian conditions.

CONTENTS

Chapter 1

INTRODUCTION

1.1 GENERAL

Natural rubber is one of the most versatile plant products of mother nature. The name 'rubber' is derived from the quality of the material in rubbing black lead pencil marks out of paper. This important material has a variety of uses in our everyday life. Even before the advent of technology for the manufacture of modern rubber products, it was in use in some form or other. In the last 150 years, the demand for natural rubber has increased considerably due to the several developments that has taken place in the production, processing, compounding and use of this product.

Natural rubber is obtained from the latex of various plants. Eventhough the latex of about 2000 species of plants contain rubber as a constituent, only a few of them have been exploited for the commercial production of rubber. Among them, Hevea brasiliensis is the main source of natural rubber today. India is among the major rubber growing nations in the world. The other producers of natural rubber are Malaysia, Indonesia, Thailand and

Srilanka. In India, rubber has been traditionally grown in the high lands of Southwest, predominantly in Kerala and in some parts of Tamil Nadu and Karnataka.

The crops harvested from rubber plantations consist of 75 per cent field latex and 25% field coagulum generally termed as scrap rubber. The field latex and field coagulum harvested from plantations are not generally used as such for the manufacture of rubber goods. This necessitates the processing of crops into forms that allow easy storage, transportation and utilisation by manufacturing industries (1). During the processing of natural rubber latex large quantity of water is used. The waste water loaded with organic compound and organic and inorganic acids used in the process form the effluents causing environmental pollution.

1.2 COMPOSITION OF NATURAL RUBBER LATEX

NR latex is mainly obtained as a white fluid from the bark of *Hevea brasiliensis* by the process of tapping. The rubber content of latex varies between 25 and 40 per cent by weight and this variation is owing to factors such as type of tree, tapping intensity, soil conditions and the season. In addition to the rubber hydrocarbon, a large number of non-rubber constituents are also present in latex. The rubber hydrocarbon in latex is predominantly cis-1,4 polyisoprene and it occurs as molecular aggregates in the form of discrete particles which are usually spherical with diameter ranging from about 0.02 to 3 microns (2).

Hevea latex is a hydrosol or a weak lyophillic negatively charged colloidal system of spherical or pear shaped rubber globules dispersed in an aqueous serum. The dispersed rubber particles are strongly protected by a complex film made of protein, neutral lipid and phospho lipid (3). Excluding rubber and water, the substances present in latex are proteins, lipids, quebrachitol and inorganic salts. The total protein content (4) is about 1-2 per cent of which 20 per cent is absorbed on the surface of the rubber particles and the rest is dissolved or dispersed in the serum. The lipids consist of fats, waxes, sterol esters, and phospholipids and its total content is about 0.9 per cent. The total concentration of inorganic materials is about 0.5 per cent, the main constituents being salts of potassium, magnesium, copper, iron, sodium, calcium and phosphorous.

1.3 PROCESSING OF NR LATEX AND EFFLUENT GENERATION

Field latex and field coagulum obtained from rubber plantations are highly susceptible to degradation caused by oxidation and microbial contamination (5). Hence natural rubber latex is processed into forms that allow easy storage and marketing.

Field latex can be processed into the following forms (6):

a) Ribbed smoked sheet or air dried sheet
b) Preserved latex and latex concentrate
c) Pale latex crepe and
d) Technically specified block rubber or crumb rubber

Similarly field coagulum is processed into crepe rubber and crumb rubber. The crepe rubber produced from field coagulum can be classified into three grades namely estate brown crepe (EBC), remilled crepe and flat bark crepe depending on the quality of the coagulum used. The processing methods of all these grades are almost the same.

During the processing of natural rubber, large quantity of water is used for various purposes such as dilution of latex, cleaning of various utensils used, washing, cooling etc. The quantity of water used and the volume and characteristics of wastewater generated during processing vary depending upon the type of natural rubber processed and product produced (7). A brief description of the various processing methods and sources of effluents are given in the following sections.

a) Ribbed Smoked Sheets

Fig.1.1 illustrates the process of making ribbed sheets from latex. Latex collected from the field is first sieved to remove foreign materials. It is then bulked to have uniform property and diluted to a standard dry rubber content (DRC) of 12.5 per cent to improve the quality of coagulum. Dry rubber content usually expressed as a percentage may be defined as the 'real' rubber content of latex if all the serum were removed (8). Chemicals like sodium bisulphite and para nitro phenol are added to prevent decolourisation. They also act as preservative. The latex is then coagulated using formic acid or acetic acid. After completion of coagulation, the serum is drained out and the coagulum is obtained in the form of blocks. Washed coagulum is then rolled to sheets using a pair of plain rolls and another set of grooved ones. The

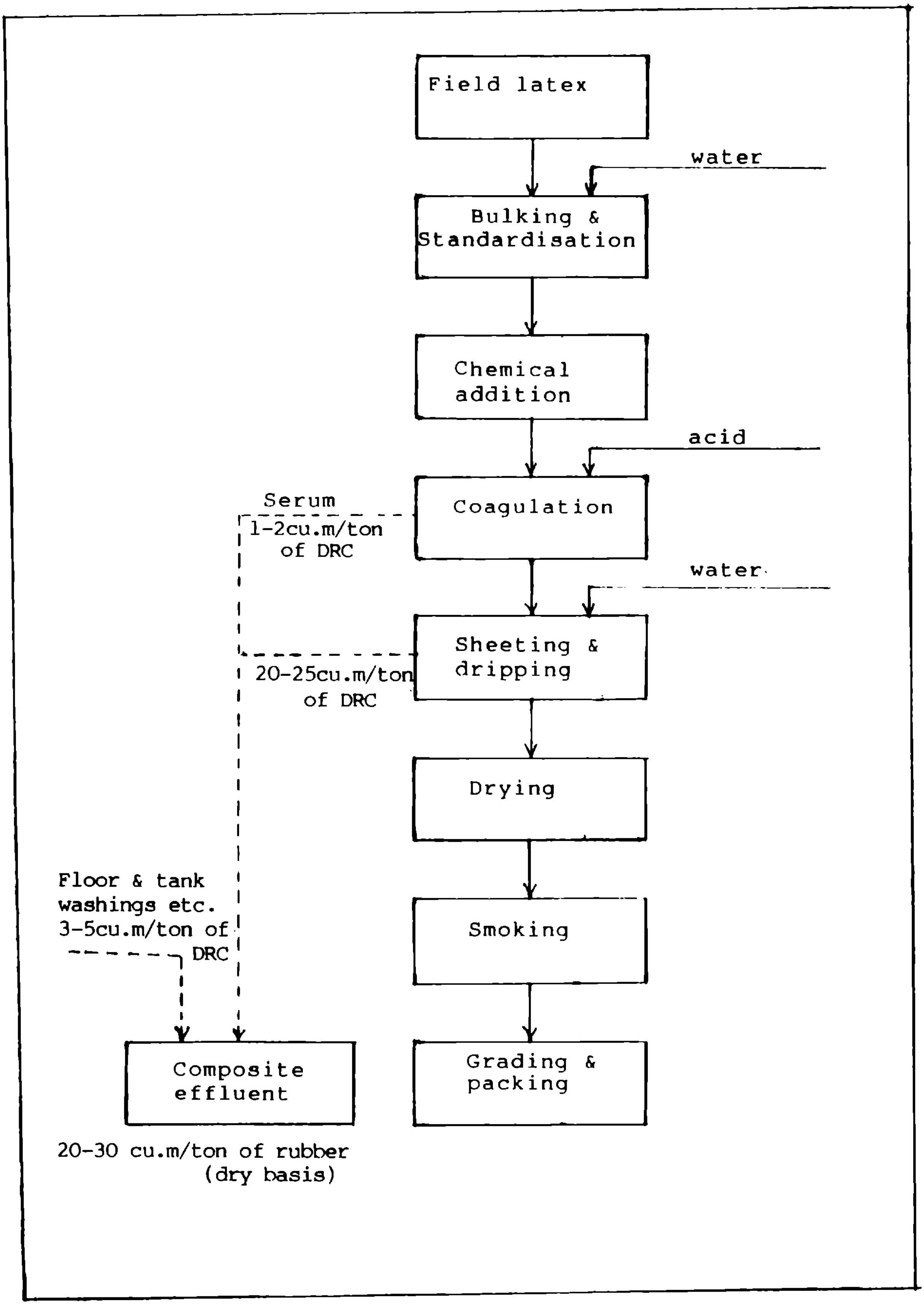


FIG.1.1 PROCESS FLOW SHEET FOR RIBBED SMOKED SHEET MANUFACTURE.

sheets are then allowed to drip in shade and smoked in smoke houses for producing ribbed smoked sheet.

Water is used in the process for diluting the latex and for washing the coagulum during sheeting operations. This water forms part of the effluent. The water consumption is estimated to be in the range of 20-30 litre/kg. of DRC.

b) Preserved Latex and Latex Concentrate

The field latex if kept as harvested will coagulate within 6-12 hours of its collection. Micro-organisms like bacteria and yeast contaminate the latex as it comes out of the tree. They metabolise the non-rubber constituents of the latex and produce volatile fatty acids such as formic, acetic and propionic acids which lead to coagulation of latex (10). Hence preservatives are added to latex to keep it for longer periods (10,11). Among the various chemicals used as preservatives, ammonia is of prime importance. The latex from the field is sieved and bulked and ammonia is bubbled through it so as to get a concentration of 0.7 to 1.0 per cent by volume of latex. Ammonia inhibits bacterial growth, acts as an alkaline buffer and raise the pH and neutralise the free acid formed in latex (12). It inactivates some metal ions which tend to coagulate latex by forming insoluble compounds or complexes with them.

Preserved field latex is unsuitable for most latex applications as its rubber content is low. For most product manufacture, a latex of 60 per cent minimum dry rubber content is essential. The important methods for the concentration of preserved field latex are (i) creaming, (ii) centrifuging. These methods involve partial removal of non-rubber constituents and the particle size distribution of the concentrate differs from that of the initial latex as a proportion of the smaller particles are eliminated in the serum. At present, more than 90 per cent of the latex concentrate is obtained by centrifuging.

1. Centrifuging

In the centrifuging process, the centrifugal force brings about separation of rubber particles. The ammoniated field latex is subjected to strong centrifugal force in a bowl rotating at a speed of around 6000 rpm whereby individual rubber particles tend to separate into a layer surrounding the axis of rotation leaving behind an outer layer (skim) having a comparatively lower rubber

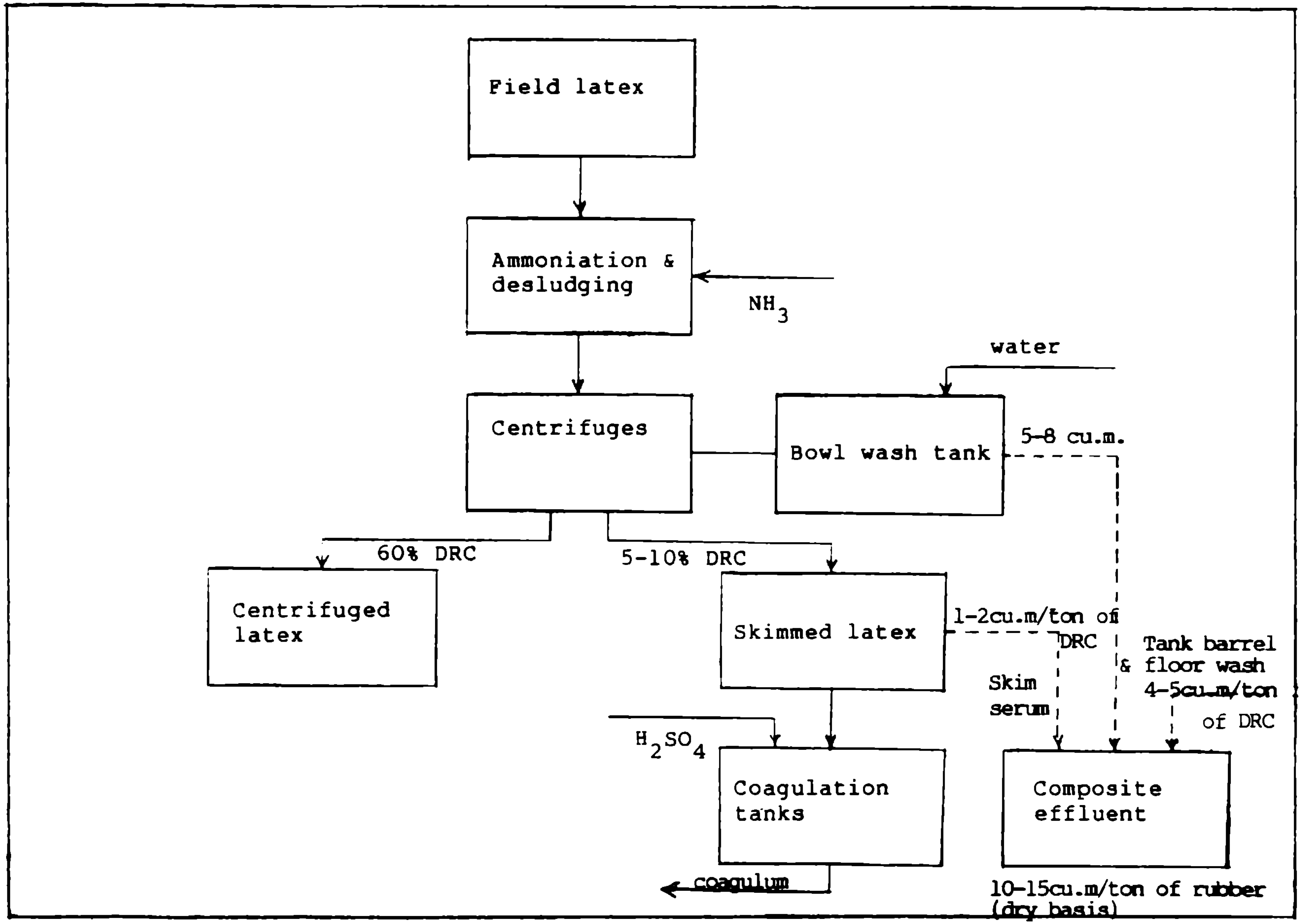


FIG.1.2 PROCESS FLOW SHEET OF A CENTRIFUGE LATEX CONCENTRATE UNIT.

content. The DRC of the centrifuged latex is around 60 per cent. About 85 to 90 per cent of the total rubber in the field latex will be separated into the concentrated fraction. 10-15 per cent rubber will be lost into the skim fraction. The volume of the skim latex will be approximately equal to that of the concentrated fraction. To recover the rubber in skim latex, it is coagulated with sulphuric acid and the serum left out is drained off.

The water requirement in centrifuging process is in the range of 10-15 litres per kg of dry rubber. The water requirement is for cleaning the latex storage tanks once a week, washing the barrels, washing the bowls of the centrifuging machine twice in a shift and coagulation of skim latex. All the water used in the process comes out as effluent apart from the skim serum. The flow diagram of the process with effluent generation is shown in Fig.1.2.

2. Creaming

In the creaming process, the preserved field latex is kept for a few days for ageing. Tamarind seed powder is usually used as the creaming agent. A 3% solution of the seed powder is prepared by boiling the required quantity in water. The calculated quantity of the creaming agent solution and a 10 per cent soap solution is added to latex in order to get a latex concentration of 0.3 per cent. The latex is stirred for one hour. After stirring, the latex is allowed to remain undisturbed for a minimum period of 48 hours to obtain a desired level of creaming (1). The gravitational force brings about the separation of rubber particles in creaming. Latex with 55-58 per cent DRC is obtained by the creaming method. The skim serum left behind will contain 2-3 per cent rubber. The water requirement in a latex creaming unit is in operations like cleaning the reception tanks and floor of the factory. This water goes out as effluent.

c) Pale Latex Crepe Units

The stages in the manufacture of pale latex crepe (PLC) are shown in Fig.1.3. The field latex containing anticoagulating agents like ammonia or sodium sulphite is received at the factory. The latex is then sieved, bulked, standardised and chemically treated. The chemically treated latex is then subjected to fractional coagulation using acetic acid for removing colouring materials (6). It is then sieved through a 60 mesh sieve and the yellow pigment fraction in latex is removed. The latex after fractional coagulation and bleaching is coagulated using

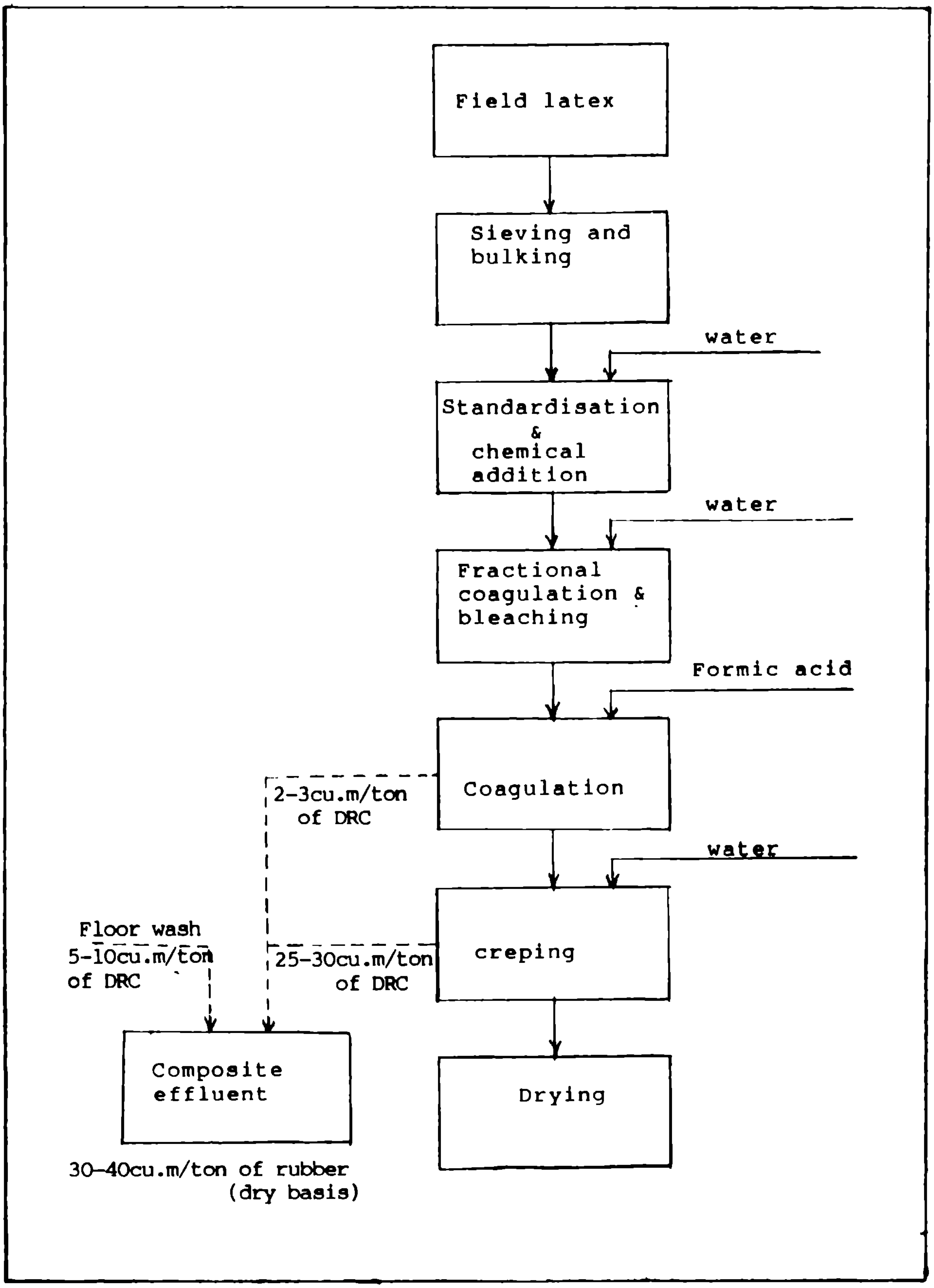


FIG.1.3 PROCESS FLOW CHART OF A PALE LATEX CREPE UNIT.

formic acid. About 4 ml of formic acid per kg. of dry rubber is used. The coagulum obtained in the form of block is milled in creping machines. Water is used during milling to wash out the serum and other non-rubber materials. The product is then dried and packed.

In a pale latex crepe unit, water is required for diluting the latex, washing the coagulum and for cooling the rollers. Waste water is released from the latex coagulation section and crepe milling section (7). Water consumption per kg drc of the product is about 20-30 litres. The quantity discharged as effluent slightly exceeds this because the serum from coagulation also goes to the effluent.

d) Estate Brown Crepe Units

Estate brown crepe (EBC) is made from field coagulum or scrap rubber. Field coagulum is the rubber collected from collection cups, trunk of the tree and from the ground beneath the collection cup. Soaking of the field coagulum, maceration, creping and finishing are the operations carried out in EBC manufacture. The soaked scrap is passed through macerator creper and finishing machines several times.

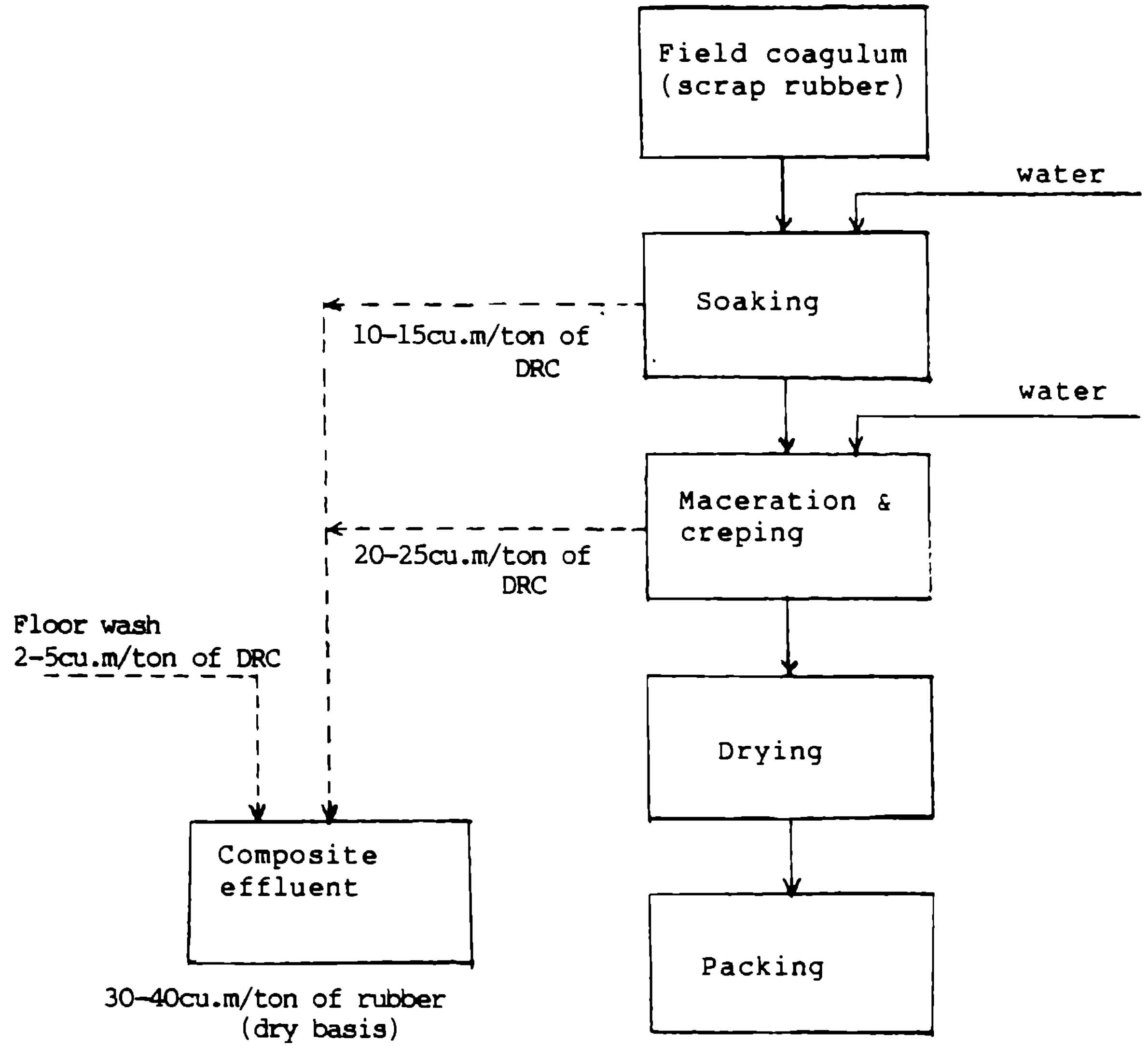


FIG.1.4 PROCESS FLOW SHEET FOR ESTATE BROWN CREPE MANUFACTURE.

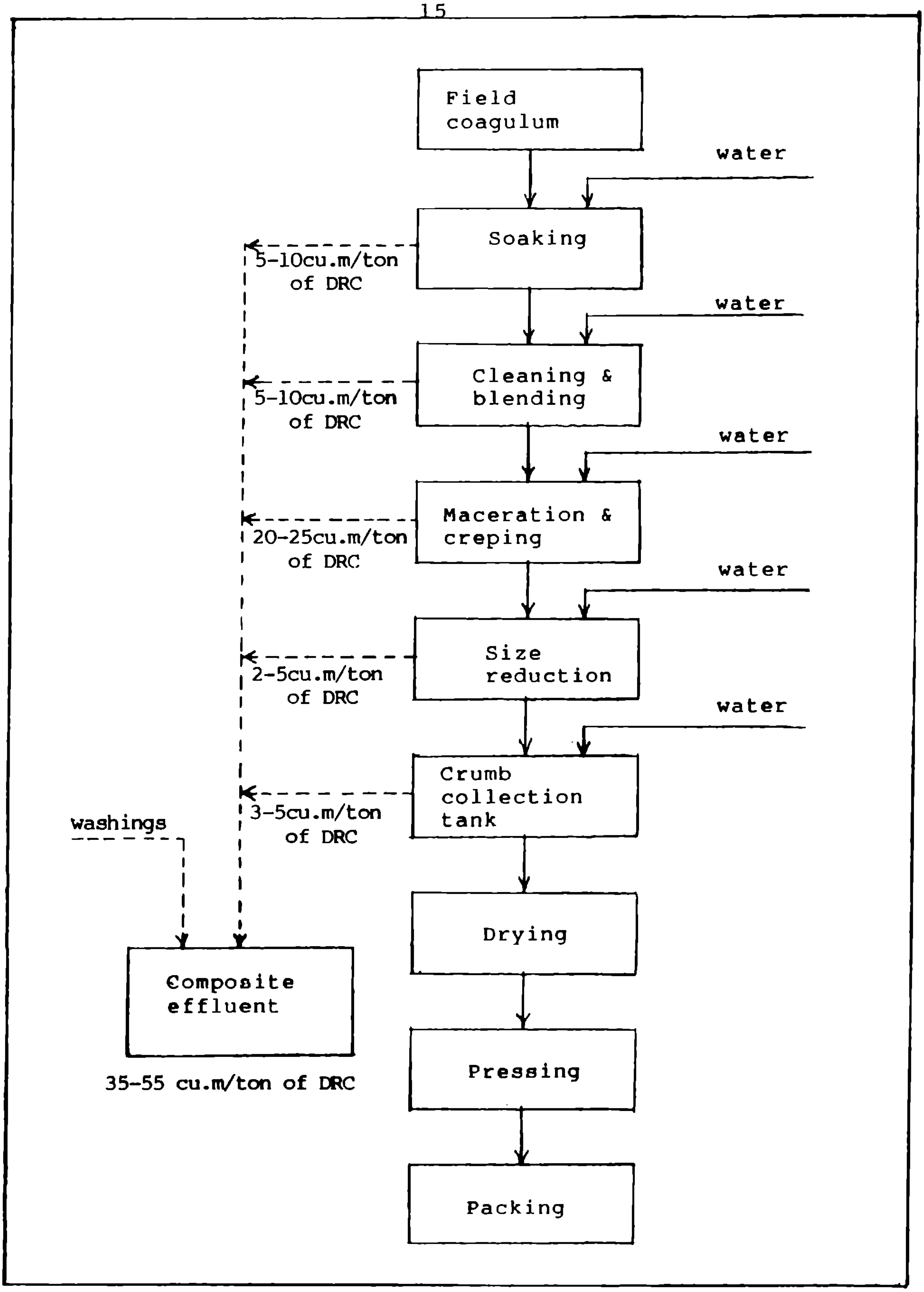


FIG.1.5 PROCESS FLOW SHEET FOR CRUMB RUBBER MANUFACTURE.

Water requirement for EBC manufacture are for the soaking of the field coagulum, maceration and milling operations and for the floor washing and other cleaning operations. The water requirement and effluent generation is between 30-40 litre/kg of DRC (7). This is higher than the water requirement for producing pale latex crepe. A flow diagram of the process with effluent generation is given in Fig.1.4.

e) Crumb Rubber Producing Units

Crumb rubber or block rubber is mostly produced from field coagulum (1). The stages in the process are collection of field coagulum, soaking and pre-cleaning, blending, milling and size reduction, drying, pressing and packing. When crumb rubber is produced from field latex, the additional stages required are that of coagulation and pre-machining. Water is required for scrap soaking, milling, size reduction and crumb collection. The water consumption and effluent generation is estimated to be 35-55 litres per kg of DRC. The flow diagram of the process is shown in Fig.1.5 with effluent quantities.

1.4 PHYSICAL, CHEMICAL AND BIOLOGICAL CHARACTERISTICS OF WASTE WATER

An understanding of the nature of wastewaters is essential in the design and operation of collection, treatment, and disposal facilities and in the engineering management of water quality (13). It is, therefore, desirable to know the physical, chemical and biological characteristics of waste water. The pollution potential of wastewaters, whether it is domestic or industrial, is expressed in terms of these characteristics.

a) Physical Characteristics

The most important physical characteristics of wastewater is its total solids content.

The other physical characteristics of importance are odour, temperature and colour (13).

Total Solids

The total solids content of wastewater is the sum total of floating matter, matter in suspension, colloidal matter, and matter in solution. Analytically, the total solids content of a wastewater is defined as all the matter that remains as residue upon evaporation at 103 to 105°C. The total solids can be classified as either suspended solids or filterable solids by passing a known volume of liquid through a filter. The filter is commonly chosen so that the minimum diameter of the suspended solids is about

1 micron (14). The filterable-solids fraction consists of colloidal and dissolved solids. The colloidal fraction consists of the particulate matter with an approximate diameter range of from 1 milli micron to 1 micron. The dissolved solids consist of both organic and inorganic molecules and ions that are present in the true solution in water.

Turbidity, a measure of the light-transmitting properties of water, is another test used to indicate the quality of waste discharges and natural waters with respect to colloidal matter. Colloidal matter will scatter or adsorb light and thus prevent its transmission (15).

Odour

Odours in wastewater usually are caused by gases produced by the decomposition of organic matter. Fresh wastewater has a distinctive, somewhat disagreeable odour, which is less objectionable than the odour of septic wastewater. The most characteristic odour of stale or septic wastewater is that of hydrogen sulphide, which is produced by anaerobic microorganisms that reduce sulphates to sulphides (16). Industrial wastewater may contain either odourous compounds or compounds that produce odours during the process of wastewater treatment.

Temperature

As the specific heat of water is much greater than that of air, the observed wastewater temperatures are higher than the local air temperatures during most of the year and are lower only during the hottest summer months. The temperature of water is a very important parameter because of its effect on aquatic life, the chemical reactions and reaction rates, and the suitability of water for beneficial uses (17).

Colour

The colour of fresh wastewater is usually grey. However, the colour changes to black as organic compounds are broken down by bacteria resulting in the depletion of dissolved oxygen in wastewater (18). In this condition, the wastewater is said to be septic (or stale). Some industrial wastewaters are coloured in nature.

b) Chemical Characteristics

In chemical characteristics, the components of importance are organic matter, inorganic matter and gases.

Organic Matter

In a wastewater of medium strength, about 75 per cent of the suspended solids and 40 per cent of the filterable solids are organic in nature (13). These solids are derived from both the animal and plant kingdoms and the activities of man as related to the synthesis of organic compounds. Organic compounds are normally composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in same cases. Other important elements such as sulphur, phosphorous and iron, may also be present. The principal groups of organic matter found in wastewater are proteins, carbohydrates and fats and oils.

The laboratory methods commonly used for the measurement of organic content in wastewater are Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

The most widely used parameter of organic pollution applied to both wastewater and surface water is the 5-day BOD (BOD_5). Its determination involves the measurement of the dissolved oxygen used by microorganisms in the bio-chemical oxidation of organic matter. Biochemical oxidation is a slow process and theoretically takes an infinite time to completion (19). The oxidation is about 95 to 99 per cent complete within a 20 day period and in the 5 day period used for the BOD test, oxidation is from 60 to 70 per cent complete. The 20°C temperature used is an average value for slow-moving streams in temperate climates and is easily duplicated in an incubator.

The COD test is used to measure the content of organic matter of both wastewater and natural waters. In this test, the oxygen equivalent of the organic matter that can be oxidised is measured by using a strong chemical oxidising agent in an acidic medium, at an elevated temperature. Potassium dichromate has been found to be an excellent oxidising agent for this purpose. Compared to the BOD test which takes 5 days, the COD can be determined in 3 hours. The total organic content (TOC) of the wastewater is also widely used as an index of organic matter.

Inorganic Matter

Some of the parameters of importance are pH, alkalinity, nitrogen and phosphorous.

pH: The hydrogen ion concentration is an important quality parameter of both natural waters and wastewaters. The concentration range suitable for the existence of most biological life is quite narrow and critical. Wastewater with an adverse concentration of hydrogen ion is difficult to treat by biological means.

Alkalinity: Alkalinity in wastewater results from the presence of the hydroxides, carbonates and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or of ammonia. Alkalinity is determined by titrating against a standard acid; the results are expressed in terms of calcium carbonate (20).

Nitrogen: Since nitrogen is an essential building block in the synthesis of protein, nitrogen data will be required to evaluate the treatability of wastewater by biological processes. Insufficient nitrogen can necessitate the addition of nitrogen to make the waste treatable. Where control of algal growths in the receiving water is necessary to protect beneficial uses, removal or reduction of nitrogen in wastewaters prior to discharge may be desirable (21).

Phosphorous: Like nitrogen, phosphorous is also essential to the growth of algae and other biological organisms. The usual forms of phosphorous that are found in aqueous solutions include the orthophosphate, polyphosphate, and organic phosphate (22). Because of the noxious algal blooms that occur in surface waters, there is presently much interest in controlling the amount of phosphorous compounds that enter surface waters in domestic and industrial waste discharges and natural runoff.

Gases

Gases commonly found in untreated wastewater include nitrogen, oxygen, carbon dioxide, hydrogen sulphide and methane. The first three are common gases of atmosphere and will be found in all waters exposed to air. The latter two are derived from the decomposition of the organic matter present in wastewater. Ammonia is also found to be present in untreated wastewater as ammonium ion.

Dissolved oxygen is required for the respiration of aerobic microorganisms as well as all other aerobic life forms. However, oxygen is only slightly soluble in water. The actual quantity of oxygen (other gases too) that can be present in solution is governed by (a) the solubility of gas; (b) the partial pressure of the gas in the atmosphere; (c) the temperature and (d) the purity (salinity, suspended solids etc.) of the water (22).

Hydrogen sulphide is formed, as mentioned previously, from the decomposition of organic matter containing sulphur or from the reduction of mineral sulphites and sulphates. It is not formed in the presence of an abundant supply of oxygen. The blackening of wastewater and sludge usually results from the formation of hydrogen sulphide that has combined with the iron present to form ferrous sulphide (23).

Methane gas is formed as the principal by-product of the anaerobic decomposition of the organic matter in wastewater. Methane is a colourless, combustible hydrocarbon of high fuel value.

c) Biological Characteristics

The biological characteristics of wastewater relate to the microorganisms present in surface and waste water as well as those responsible for biological treatment, the pathogenic organisms in wastewater and the organisms used as indicators of pollution.

The principal groups of organisms found in water and wastewater are classified as protista, plants and animals. The category protista includes bacteria, fungi, protozoa and algae. Among them, bacteria play a fundamental role in the decomposition and stabilisation of organic matter, both in nature and in treatment plants (13). Seed plants, ferns, and mosses and liverworts are classified as plants. Invertebrates and vertebrates are classified as animals. Viruses which are also found in wastewater, are classified according to the host infected.

Pathogenic organisms found in wastewater may be discharged by human beings who are infected with disease or who are carriers of a particular disease. The usual bacterial pathogenic organisms that may be excreted by man cause diseases of the gastrointestinal tract, such as dysentry, diarrhea and cholera and typhoid and paratyphoid fever (24).

Because the identification of pathogenic organisms in water and wastewater is both extremely time-consuming and difficult, the caliform group of organisms is now used as an indicator of the presence of feces in wastewater and hence pathogenic organisms (25). Coliform organisms are the countless rod-shaped bacteria present in the intestinal tract of man. Each person discharges 100 to 400 billion coliform organisms per day.

1.5 WATER POLLUTION AND ITS CONTROL IN RUBBER PROCESSING UNITS

During the processing of natural rubber, large quantity of water is used for various purposes such as dilution of latex, cleaning of various vessels and machinery used, washing, cooling etc. The quantity of water used and the volume and characteristics of wastewater generated during processing vary widely depending on the type of natural rubber processed and the product manufactured. The volume of water consumed and the volume of wastewater generated are almost the same in the case of a field coagulum processing unit; while in the case of field latex processing units the volume of wastewater is higher the volume of water consumption (6). This is due to the fact that the serum separated during latex coagulation is also discharged along with the process effluent in the case of a field latex processing unit.

a) Characteristics of Effluents from Natural Rubber Processing

A few studies have been carried out in India and Malaysia to establish the characteristics of effluents discharged from rubber processing units (26,27,28,29). The results of the studies are summaried in Table 1.1.

The acidic nature of the effluent is attributed to the use of formic, acetic, phosphoric or sulphuric acid in the process line. The high Biochemical Oxygen Demand (BOD)

TABLE 1.1

EFFLUENT CHARACTERISTICS

Sl. No.	Type of Industry	BOD mg/l	COD mg/l	Suspended solids mg/l	Total dissolved solids mg/l	Ammoniacal nitrogen mg/l	Total nitrogen mg/l	pH	Effluent generation m^3/ton of DRC
1.	Latex centrifuging units	2500 -5200	3600 -10200	500 -3600	4500 -20000	500 -900	1000 -1600	3.2 -7.4	10 -15
2.	Crumb rubber units	60 -250	200 -1300	60 -600	300 -3200	0 -230	1.0 -250	6.5 -7.5	20 -50
3.	Pale latex crepe units	1800 -2800	3000 -7000	65 -700	1800 -3000	5 -25	10 -30	5.5 -6.3	30 -50
4.	Ribbed smoked sheet units	3000 -4000	5000 -7000	100 -200	3400 -4200	10 -25	15 -30	4.5 -5.5	20 -30
5.	Estate brown crepe units	5 -400	200 -1200	65 -900	300 -1900	0 -400	10 -600	6.0 -7.6	30 -90

and Chemical Oxygen Demand (COD) of the latex concentrate and ribbed sheet factory effluent indicate that the total solids in the effluents are mainly of organic origin with high oxygen demand for their oxidation. The high ammoniacal and total nitrogen of latex concentrate effluent is due to the use of substantial quantity of ammonia in the preservation of latex. Hence the two potential pollutants in rubber effluent are organic carbon and ammoniacal nitrogen (30).

b) Effect of Effluent Discharge on Water Bodies

The effluents from natural rubber processing units has been one of the important sources of water pollution atleast in the state of Kerala (6). The effluent generally consists of process water, small amount of uncoagulated latex and serum containing small quantities of protein, carbohydrates, lipids, carotenoids, inorganic and organic salts etc. The presence of these substances leads to high BOD, COD, suspended solids, dissolved solids and nitrogen compounds in the effluent. The concentration of each component in the effluent varies considerably with the type and scale of the factory operation and in particular with the amount of water used in processing.

The unabated discharge of raw effluent into the environment if unchecked will adversely affect the quality of the receiving waterbodies. If the untreated effluents from rubber latex processing units are discharged into any stream or river, it will deplete the dissolved oxygen content of the waterbody due to high BOD and COD, thus affecting the very survival of aquatic life. The acidic nature of the effluent also may affect the growth of fish and other aquatic life. Presence of ammonia and nitrogen compounds in the effluent encourage the growth of aquatic weeds and other plants in the water body. This will lead to a phenomenon called 'entrophication' (31).

c) Present Treatment Practices

In view of the serious pollution problems created by the effluent, the rubber processing units are prevented from discharging the raw effluent into public sewers or rivers. In India the Envrionment (Protection) Rules, 1986 (32) has prescribed standards for the discharge of effluents from natural rubber industry. Separate standards are fixed for the discharge of effluents into inland surface waters and disposal on land for irrigation. These standards are given in Table 1.2. These standards serve as a guideline for the state pollution control boards.

TABLE 1.2

STANDARDS PRESCRIBED FOR EFFLUENT DISCHARGE FROM NATURAL RUBBER INDUSTRY

(all values except pH are in mg/l)

Parameter	Standards	
	Discharge into inland surface waters	Disposal on land for irrigation
Colour and odour	Absent	Absent
pH	6.0-9.0	6.0-8.0
BOD	50	100
COD	250	250
Oil and grease	10	10
Sulphides	2	--
Ammoniacal nitrogen as N	50	--
Total Kjeldhal nitrogen	100	--
Free ammonia (as NH_3)	5	--
Suspended solids	100	200
Dissolved solids (inorganic)	2100	2100

In most of the rubber processing units in India, proper treatment and discharge of effluents did not receive much attention in the past. The general practice was to discharge the effluents indiscriminately to the environment without treatment. Some of these units have provided rubber traps to detain rubber particles and one or two settling tanks before discharging the effluent to public waterways (6). Some factories discharge the effluent into their own estates where it is allowed to percolate in the soil or used for irrigation purposes. The growing environmental awareness among the people and the introduction of various environmental legislations have forced the rubber processing units in India, mostly situated in the South Indian states of Kerala, Tamil Nadu and Karnataka, to adopt some kind of effluent treatment systems. Already some of the crumb rubber factories and latex centrifuging factories have set up effluent treatment systems. The systems adopted at present are the anaerobic facultative ponding system and the oxidation ditch system. Both these systems are found suitable for the rubber processing factory effluents under Malaysian conditions (33,34).

The anaerobic-facultative ponding system involves an anaerobic decomposition of the organic materials to a level acceptable for further break down aerobically. In the breakdown process, the end products are methane and carbon dioxide. The anaerobic liquor containing part of the organic matter is further treated in facultative ponds which further converts the remaining organics into carbon dioxide, water etc. The aerobic breakdown in the facultative pond occurs in the top layer where oxygen required is available from the photosynthetic activity of the algae as well as by diffusion (35). However, in the bottom sediments anaerobic decomposition occurs.

The oxidation ditch essentially involves an aerobic process. It is elliptical in shape and is fitted with an aerator which oxygenates and circulates the effluent (36). The treated effluent from the oxidation ditch overflows into the sedimentation tank where the sludge settles at the conical bottom. A portion of the sludge is recycled back to the system. The excess sludge from the sedimentation tank is removed and dried. The clarified supernatant effluent from the sedimentation tank is discharged through a sand filter.

1.6 OBJECTIVES AND SCOPE OF THE WORK

A few treatment systems like anaerobic-facultative ponding and oxidation ditch have been found to be suitable for the rubber processing factory effluents under Malaysian conditions. However, a detailed systematic study on the efficiency of different treatment systems for the natural rubber processing factories under Indian conditions is not available (37). Having this in mind, the present study was initiated to evaluate the effectiveness of a few physico-chemical and biological methods for the treatment of effluents from natural rubber processing units. A survey (38) of the chemical characteristics of the effluents discharged from rubber processing factories showed that the effluents from latex concentration units are the most polluting. Hence the effluent samples from a centrifuge latex concentration unit were used for the treatability studies. The treatment methods evaluated in this study have been tried successfully for effluents from process industries like distilleries, textile mills, food processing etc. (18,31,36). An attempt has been made to extend these methods for the treatment of centrifuge latex concentration effluents under Indian conditions.

The following formed part of the study:

1. A complete characterisation of effluents from the various sections of a centrifuge latex concentration unit.

2. Evaluation of the effectiveness of metal coagulants in treating the centrifuge latex concentration effluents.

3. Evaluation of the effectiveness of natural and synthetic polyelectrolytes as coagulants and coagulant aids.

4. The bio-chemical oxidation kinetics of the rubber processing effluents.

5. Treatability studies in an experimental waste stabilisation pond in admixture with domestic sewage.

6. The performance evaluation of a bench scale upflow anaerobic filter for the treatment of rubber processing effluents.

This thesis is divided into seven chapters.

In chapter 1, an overview of the various methods of natural rubber processing and sources of effluent generation are presented. The physical, chemical and biological characteristics of importance in the design and operation of wastewater treatment plants have been discussed in brief. The effect of effluents on receiving waters and the present treatment practices in natural rubber processing units have been described. The scope and objectives of the present work are defined in this chapter.

Chapter 2 is divided into two parts. In part A, the characteristics of the combined effluent and the individual characteristics of effluents from the two sections of a centrifuging unit, viz., the centrifuging and skim latex coagulation are described. Correlations have been developed between the different characteristics.

In part B, the results of the experiments carried out on centrifuge latex concentration effluent using nine commonly used metal coagulants are discussed. The coagulants used in the study were alum, aluminium sulphate, ferrous sulphate, ferric chloride, ferrous chloride, aluminium chloride, lime and magnesium chloride. The effectiveness of the metal coagulants was evaluated in terms of COD reduction, turbidity removal and ammoniacal nitrogen removal.

In chapter 3, the results of the studies carried out using four natural polyelectrolytes and two synthetic polyelectrolytes are presented. The natural polyelectrolytes used were starch, sodium alginate, tamarind seed powder and chitosan. The synthetic polyelectrolytes used for the study were a cationic polyacryl amide based one and an anionic polyamine based one. The effectiveness of the polyelectrolytes as primary coagulant and coagulant aid was evaluated.

Chapter 4 deals with the bio-chemical oxidation kinetics of natural rubber processing wastewaters. The variations in the BOD values of the effluent at four temperatures 20, 25, 30 and 35°C, were studied. The bio-chemical stabilization rate constant (k) and ultimate BOD (L_o) of the wastewater was determined using the observations made at 20°C.

In chapter 5, the treatability of centrifuge latex concentration effluent in a waste stabilisation pond has been discussed. The possibility of treating the wastewater alone and in admixture with sewage in the proportions of 1:1, 1:2, 1:3, 1:4 and 1:5 was explored in an experimental pond. The pattern of algal succession in the pond was also studied.

Chapter 6 deals with the treatability of effluents from a centrifuge latex concentration unit in a laboratory scale upflow anaerobic contact filter. The effectiveness of the filter was evaluated in terms of COD removal, BOD removal and ammoniacal nitrogen removal at varying organic loadings. Based on the experimental results, kinetic parameters were estimated with respect to substrate removal, microorganism growth and gas production.

In chapter 7, the results and conclusions of the study are summarised.

REFERENCES

1. Radhakrishna Pillay, P.N., (Ed.), Handbook of Natural Rubber Production India, The Rubber Research Institute of India (1980).

2. Bateman, L. (Ed.), The Chemistry and Physics of Rubber-like Substances, Maclaren & Sons Ltd., London (1963).

3. Archer, B.L., Proc. Nat. Rubb. Prod. Res. Ass. Jubilee Conf. Cambridge, Maclaren & Sons Ltd., London (1964).

4. Archer, B.L. and Cockbain, E.G., Biochem. J., 75, 236 (1960).

5. Gorton, A.D.T. and Pillai, N.M., Plrs. Bull. Rubb. Res. Inst., Malaya, 105, 282 (1969).

6. Comprehensive Industry Document on Natural Rubber Processing Industries. Prepared by Kerala State Pollution Control Board for Central Pollution Control Board (1990).

7. Kothandaraman, R. and Balagopalan, M.K., Rubb. Board

Bull., 13, 41 (1976).

8. Roberts, A.D. (Ed.), Natural Rubber Science and Technology, Oxford University Press (1988).

9. Lowe, J.S., Trans. Instn. Rubb. Ind., 36, 225 (1960).

10. Angove, S.N., Trans. Instn. Rubb. Ind., 40, 251 (1964).

11. Angove, S.N., Trans. Instn. Rubb. Ind., 41, 136 (1965).

12. Rhodes, E.J., Rubb. Res. Inst. Malaya, 8, 324 (1956).

13. Metcalf and Eddy, Inc., Wastewater Engineering: Treatment, Disposal, Reuse, Tata McGraw Hill, New Delhi (1979).

14. Sawyer, C.N. and Mc Carty, P.L., Chemistry for Environmental Engineering, 3rd ed., McGraw Hill, New York (1978).

15. Staffman, P.G. and Turner, J.S., J. Fluid Mech., 1, 16 (1956).

16. Mc Carty, P.L., Public Works, 95 (1964).

17. Schroeder, E.D., Water and Wastewater Treatment, McGraw Hill, New York (1977).

18. Ramalho, R.S., Introduction to Waste Water Treatment Processes, Academic Press, New York (1977).

19. Moore, E.W., Thomas, H.A. and Snow, W.B., Sewage Ind. Wastes, 22 (10) (1950).

20. Standard Methods for the Examination of Water and Waste Water, 16th ed., American Public Health Association (1985).

21. Task Group Report, J. Am. Water Works Assoc., 59, 344 (1967).(not in original).

22. Fair, G.M., Geyer, T.C. and Okun, D.A., Water and Waste Water Engineering, Vol.II, John Wiley & Sons (1984).

23. Eckenfelder Jr., W.W., Industrial Water Pollution Control, McGraw Hill, New York (1966).

24. Mara, D.D., Bacteriology for Sanitary Engineers, Churchill Livingston, Edinburg (1974).

25. Kittrell, F.W. and Furfari, S.A., J. Water Poll. Control Fed., 35(11) 1361 (1963).

26. Muthurajah, R.N., John, C.K. and Henry Lee, Proc. RRIM, Planters Conf., 402 (1973).

27. Ibrahim, A., Lee, H., Ponniah, C.D., Pushparajah, E., Rao, B.S., John, C.K., Singh, M.M. and Sung, C.P., Studies on Effluents from Rubber Processing Factories in Malaysia, Rubber Research Institute of Malaysia (1974).

28. Ponniah, C.D., Chick, N.H. and Seow, C.M., Proc. Inter. Rubb. Conf., Kuala Lumpur, 367 (1975).

29. Gadkari, S.K., Aboo, K.M., Badrinath, S.D., Kothandaraman, V., Deshpande, V.P. and Kaul, S.N., IAWPC Tech. Annual, 13, 41 (1986).

30. Jacob Mathew, Kothandaraman, R., Kochuthressiamma Joseph

and Jayaratnam, K., IAWPC Tech. Annual, 13, 36 (1986).

31. Besselviere, E. and Schwartz, Treatment of Industrial Wastes, McGraw Hill Book Co. (1975).

32. The Environment (Protection) Act, 1986 and Rules.

33. Ponniah, C.D., Proc. Agro-Ind. Wastes Symp, Kuala Lumpur (1975).

34. Ponniah, C.D., John, C.K. and Lee, H., RRIM Planters Conf., Kuala Lumpur (1976).

35. Arceivala, S.J., Lakshminarayana, J.S.S., Algarsamy, S.R. and Sastry, C.A., Design, Construction and Operation of Waste Stabilization Ponds in India, CPHERI, Nagpur (1969).

36. Industrial Safety & Pollution Control Handbook, Associate (Data) Publishers Pvt. Ltd., Secunderabad (1991).

37. Kothandaraman, V., Aboo, K.M. and Sastry, C.A., Indian J. Environ. Hlth., 23(2), 123 (1981).

38. John, C.K., Ponniah, C.D., Lee, H. and Ibrahim, A., Proc. Rubb. Res. Inst., Malaysia Plrs' Conf., Kuala Lumpur (1974).

Chapter 2

EFFLUENT CHARACTERISTICS AND TREATMENT WITH METAL COAGULANTS

Part A: EFFLUENT CHARACTERISTICS

2A.1 INTRODUCTION

During the processing of natural rubber latex, water is always required in varying quantities (about 20-39 litres/kg drc) for washing, cleaning, dilution etc. The field latex itself contains about 60% water. All these constitute the effluent discharged from a rubber processing unit. The effluent thus consists of process water, uncoagulated latex and significant amount of non-rubbers which include proteins, sugars, lipids, carotenoids and organic and inorganic salts which originate from the latex (1). These constituents are excellent substrates for the proliferation of microorganisms generating high BOD and objectionable odour.

A thorough knowledge of the physico-chemical characteristics of wastewaters is necessary in the design and operation of treatment plants. In the present study, an attempt has been made to evaluate the characteristics of effluents discharged from a centrifuge latex concentration unit which has the highest pollution potential among the various methods of rubber processing. The characteristics of the combined effluent and the individual characteristics of the effluents from the different sections of the unit were determined. Correlations were developed between the various parameters representing organic matter for the combined effluent.

2A.2 MATERIALS AND METHODS

The effluent samples used for the study were collected from a centrifuge latex concentration unit in Kottayam District of Central Kerala. The sources of effluents from a centrifuging unit are shown in Fig.2A.1.

In centrifuging process, the field latex containing 30-40 per cent rubber is ammoniated and split into latex concentrate containing 50-60 per cent rubber and skim latex containing 5-10 per cent rubber. High speed centrifuges are used in this process. The concentrated latex is stored in drums and marketed. The skim latex, which contains about 0.8 per cent ammonia, is coagulated

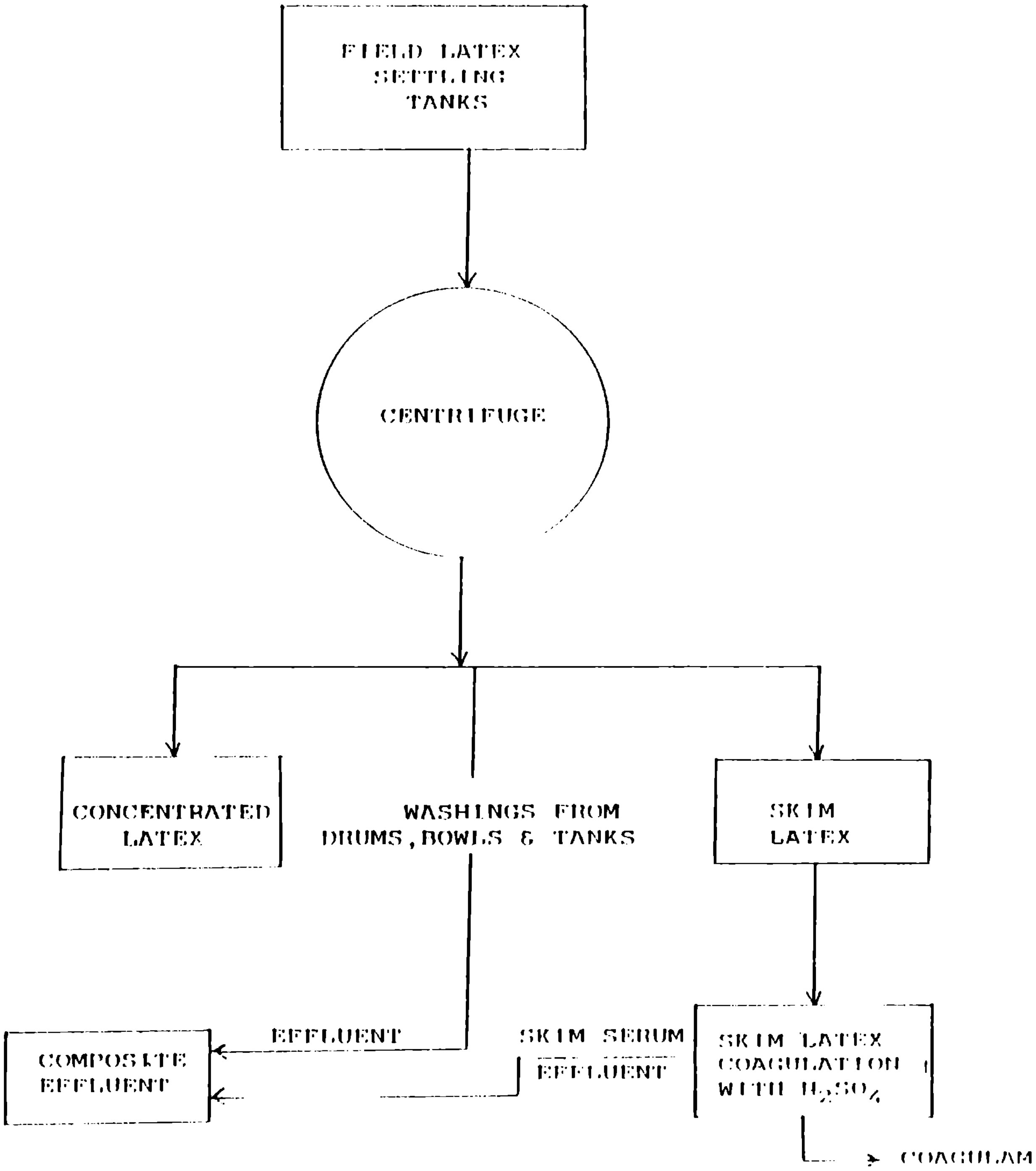


FIG.2A.1 SOURCES OF EFFLUENTS IN A CENTRIFUGE LATEX CONCENTRATION UNIT.

with sulphuric acid to recover rubber. The skim serum goes as effluent. Water is required in the process for cleaning the latex storage tanks once a week, washing the barrels, washing the bowls of the centrifuging machine twice in a shift and for coagulation of skim latex. The water requirement based on 1 kg of dry rubber is in the range of 10-15 litres. All the water used in the process comes out as effluent apart from the skim serum.

The washings from the bowls of centrifuges and drums and skim serum effluent constitute two different streams of effluent. They are collected in a tank and this forms the combined effluent. Samples of washings from centrifuges and skim serum were collected separately on different occasions for the study. Samples of the combined effluent were also collected on different occasions. The flow rate of the effluent streams was recorded at the time of sampling.

The effluent samples were analysed using the standard methods (2) for the following parameters.

1. pH
2. Turbidity
3. Total solids
4. Dissolved solids
5. Suspended solids
6. Chemical Oxygen Demand (COD)
7. Biochemical Oxygen Demand (BOD)
8. Total kjeldahl nitrogen
9. Ammoniacal nitrogen and
10. Total organic carbon

2A.3 RESULTS AND DISCUSSION

The range of variations in the physico-chemical characteristics of wastewaters are shown in Table 2A.1 and 2A.2. The values for probability of occurance of 50 and 90 per cent of time as suggested by the Handbook for Monitoring Industrial Wastewater and also shown in the tables (3). It is apparent from Table 2A.1 and 2A.2 that the range of values in most cases, varies so much that to give minimum and maximum values for the items analysed may not give sufficient data for designing a wastewater treatment plant. The best possible solution in such cases is to represent these values as 50 and 90 per cent of times

TABLE 2A.1

PHYSICO-CHEMICAL CHARACTERISTICS OF CENTRIFUGE LATEX CONCENTRATION WASTEWATER (COMBINED EFFLUENT)

Parameter	Minimum	Maximum	Average	Percentage occurance	
				50%	90%
pH	2.9	4.3	3.9	4.0	4.35
Turbidity, NTU	490	2100	1140	1040	2020
Total solids, mg/l	4565	17280	11190	11600	16800
Dissolved solids, mg/l	2640	12220	8520	8400	12000
Suspended solids, mg/l	1790	6140	2840	2600	6000
COD, mg/l	1170	10700	5630	5590	10370
BOD, mg/l	780	5680	3240	3120	5270
Total kjeldahl nitrogen, mg/l	1450	1880	1590	1450	1725
Ammoniacal nitrogen, mg/l	570	750	650	610	720
Total organic carbon, mg/l	290	2550	1375	1300	2490
Flow (m^3/day)	36	40	38	32	38

TABLE 2A.2

PHYSICO-CHEMICAL CHARACTERISTICS OF WASTEWATERS FROM THE VARIOUS SECTIONS OF LATEX CENTRIFUGING UNIT

Parameter	WASHING FROM CENTRIFUGE					SKIM SERUM				
	Minimum	Maximum	Average	Percentage occurance		Minimum	Maximum	Average	Percentage occurance	
				50%	90%				50%	90%
pH	7.0	7.02	7.1	6.9	7.0	2.5	3.4	3.1	3.0	3.3
Turbidity (NTU)	2300	4300	3375	3290	4200	300	2100	1300	1210	2000
Total solids, mg/l	8900	18400	13225	13100	17900	9400	20500	14575	14450	20100
Dissolved solids, mg/l	900	6450	3410	3340	6270	7200	14150	10810	10210	13950
Suspended solids, mg	6400	12900	9850	9760	12700	700	6350	3760	3610	6180
COD, mg/l	3600	11000	6900	6800	10900	3200	10800	6750	6640	10600
BOD, mg	1900	5700	3525	3400	5590	1870	5600	3430	3290	5450
Total kjeldahl nitrogen mg/l	420		500	420	560	1160	1430	1250	1190	
Ammoniacal nitrogen, mg/l	100	220	160	140	200	430	510	470	410	490
Flow (m^3/day)	14		15	-	-		30	27	-	-

that the values are equal to or less than 'X' where 'X' is the observed values (4). Ekenfelder and O'Cooner (5) suggested using 50 per cent of physico-chemical values for process design criteria and 90 and 99 per cent values for the estimation of hydraulic load in the design of a wastewater treatment plant.

The general trend observed for various parameters in the wastewater samples is discussed below:

a) Flow Rate

The volume of effluent discharged varied between 36 and 40 m^3/day with an average of 38 m^3/day. While the washings from centrifuges constituted a volume of 15 m^3/day on average, the skim serum effluent was in the range of 25-30 m^3/day with an average of 27 m^3/day. Hence it can be seen that the major portion of the effluents from a latex centrifuging unit originates from the skim latex coagulation section.

b) pH Values

The pH values of the combined effluent varied between 2.9 and 4.3 with an average value of 3.9. This shows the highly acidic nature of the effluent. The wastewaters from the centrifuging section and skim latex coagulation section showed average pH values of 7.1 and 3.1 respectively. It is apparent that the skim serum effluent is responsible for the highly acidic nature of the combined effluent. This can be attributed to the fact that sulphuric acid is used for the coagulation of skim latex.

c) Solids

The solids content of the wastewater samples is expressed in terms of turbidity, total solids, dissolved solids and suspended solids.

The turbidity values of the combined effluent varied between 490 and 2100 mg/l with an average value of 1140 mg/l. The average turbidity values of the effluents from centrifuging section and skim latex coagulation section were 3375 mg/l and 1300 mg/l respectively. It is evident that the turbidity of washings from the centrifuging section is higher than that of skim serum effluent. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than in straight lines through the sample (6). All suspended matter in the wastewater samples contribute to turbidity regardless of particle size. The washings from the bowls of centrifuges and drums may contain considerable amount of suspended matter and this contributes to high turbidity values.

The total solids content of the combined effluent was found to vary between 4565 mg/l and 17280 mg/l with an average value of 11190 mg/l. The suspended solids present in the wastewater varied between 1790 mg/l and 6140 mg/l whereas the concentration of dissolved solids in the combined wastewater varied between 2640 mg/l and 12220 mg/l. This shows that the effluents from a latex concentration unit contain high suspended and dissolved solids. These figures show that suspended solids range from 9.0 to 42.2 per cent of the total solids and major fraction of solids are present in the dissolved form which may vary from 57.8 to 91.0 per cent of total solids. The presence of suspended solids indicates that the wastewater has high organic matter (4).

Among the effluents from the two sections of the centrifuging unit, the effluents from the centrifuging section showed higher values of suspended solids content which varied from 6400 mg/l to 12900 mg/l. But the skim serum effluent had a higher dissolved solids content, the average value of which was 10810 mg/l.

d) Nitrogen

The total kjeldahl nitrogen (TKN) content and ammoniacal nitrogen content of the combined effluent samples and effluent samples from the two sections of the centrifuging unit did not show wide fluctuation in the values. The TKN content of the combined effluent varied between 1450 mg/l and 1880 mg/l with an average value of 1590 mg/l whereas the ammonical nitrogen content varied between 570 and 750 mg/l.

The total kjeldahl nitrogen includes ammonia and organic nitrogen but does not include nitrite and nitrate nitrogen. So the TKN content monitored in the samples include the ammonical nitrogen and organic nitrogen present in the proteinaceous matter which is a constituent of natural rubber latex. The presence of ammoniacal nitrogen in the effluent is attributed to the fact that the field latex is preserved with ammonia to prevent coagulation and microbial action. From Table 2A.2, it is evident that the ammoniacal nitrogen content of the effluents from the skim latex coagulation section is higher than that of washings from the centrifuge. While the ammoniacal nitrogen content of skim serum varied between 430 mg/l and 510 mg/l, the value varied between 100 mg/l and 220 mg/l for the washings of centrifuging section. The skim which is coagulated with sulphuric acid contains about 0.8 per cent ammonia and this should be the reason for the higher ammoniacal nitrogen content of the skim serum effluent.

a) Organic Matter

The organic matter in a wastewater is estimated in the form of COD, BOD and Total Organic Carbon (TOC).

The variations in the values of COD, BOD and TOC are given in Table 2A.1 and 2A.2. The COD, BOD and TOC values of the combined effluent were in the range of 1170-10700 mg/l, 780-5680 mg/l and 290-2550 mg/l, respectively. These figures show that the wastewaters from a latex centrifuging unit is highly organic in nature. The COD and BOD values measured for the effluents from the two different sections of the plant show that the organic content of the two effluent streams are more or less the same.

The relationship between COD and BOD is shown in Fig.2A.2. The co-efficient 'b' (intercept) and 'm' (slope) were computed by the method of least square (7). The relationship between the COD (x) and BOD (y) of the combined effluent from a centrifuge latex concentration unit can be represented by the equation $x = 1.643y + 310$.

The relationship between COD and organic carbon is shown in Fig.2A.3. The intercept and slope values are 29 and 0.24 in the case of organic carbon and COD. Fig.2A.3 shows that the intercept lies on the axis of total organic carbon indicating thereby the presence of organic substances that are not oxidised by dichromate in the COD test (ie., they do not exert COD). Ford (8) observed that a plot between COD and organic carbon would not pass necessirily through the origin and intercept would lie either on the axis of COD or organic carbon depending on the nature of wastewater.

The ratio between COD and organic carbon for the combined effluent samples is in the range of 3.95-4.20 with a mean value of 4.07. The stoichiometric COD/TOC ratio of a wastewater is the approximate molecular ratio of oxygen

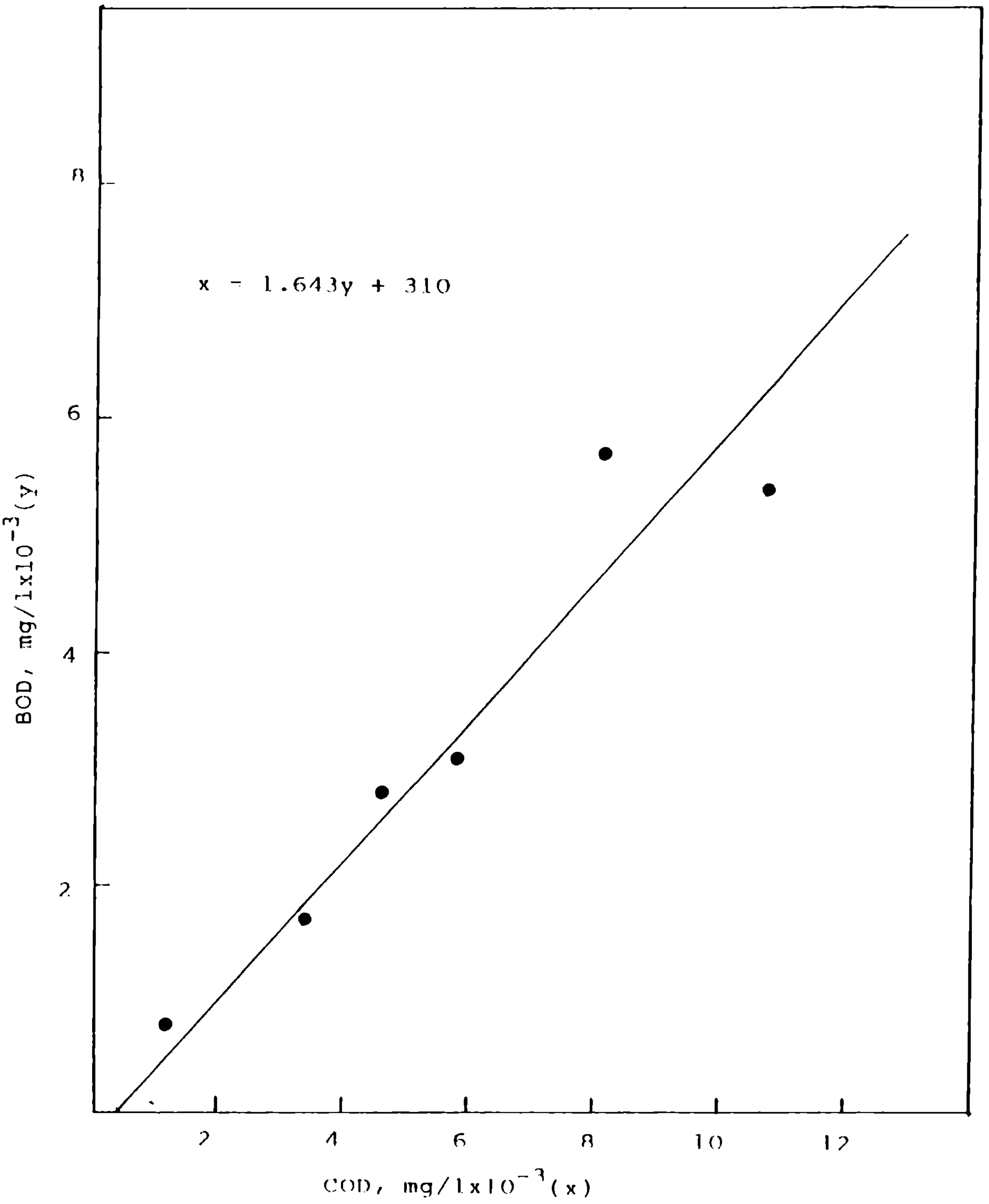


FIG.2A.2 RELATIONSHIP BETWEEN COD AND BOD.

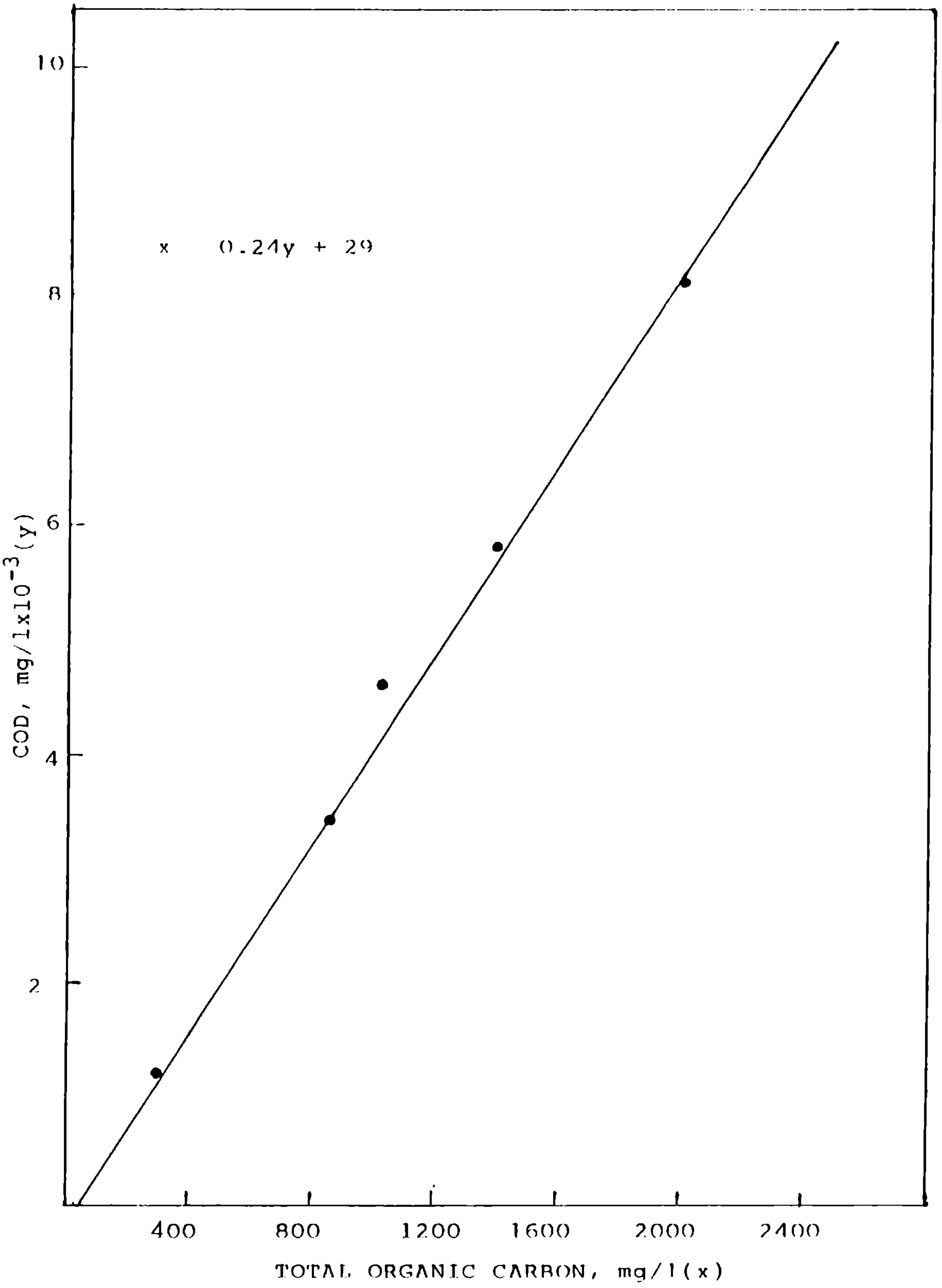


FIG.2A.3 RELATIONSHIP BETWEEN TOC AND COD.

to carbon of 32:12 = 2.66 (8). Theoretically, the ratio limits would range from zero when the organic material is resistant to dichromate oxidation to 5.33 for methane (4). It is, therefore, evident from the relationship between COD and total organic carbon that if an analyst estimates organic carbon, he can find out COD roughly using the correlation developed in Fig.2A.3.

Although good correlation has been obtained between BOD and TOC for sewage, it has been difficult to correlate BOD and TOC for industrial wastewater (4). An attempt has been made in Fig.2A.4 to develop a correlation between BOD and TOC for the combined effluent from a latex centrifuging unit. It is seen that the line fitted by least square method does not include most of the experimental data. This is reasonable, because the reported BOD yield for industrial wastewater are often erratic and highly dependant on seed acclimatization, temperature, pH and concentration of toxic substances (4). A 5-day BOD-TOC correlation for sewage has been reported by several investigators. While ratio of 1.87 has been reported by Warhmann (4), a ratio in the range of 1.35 to 2.62 has been reported by Mohlman and Edwards (9). The

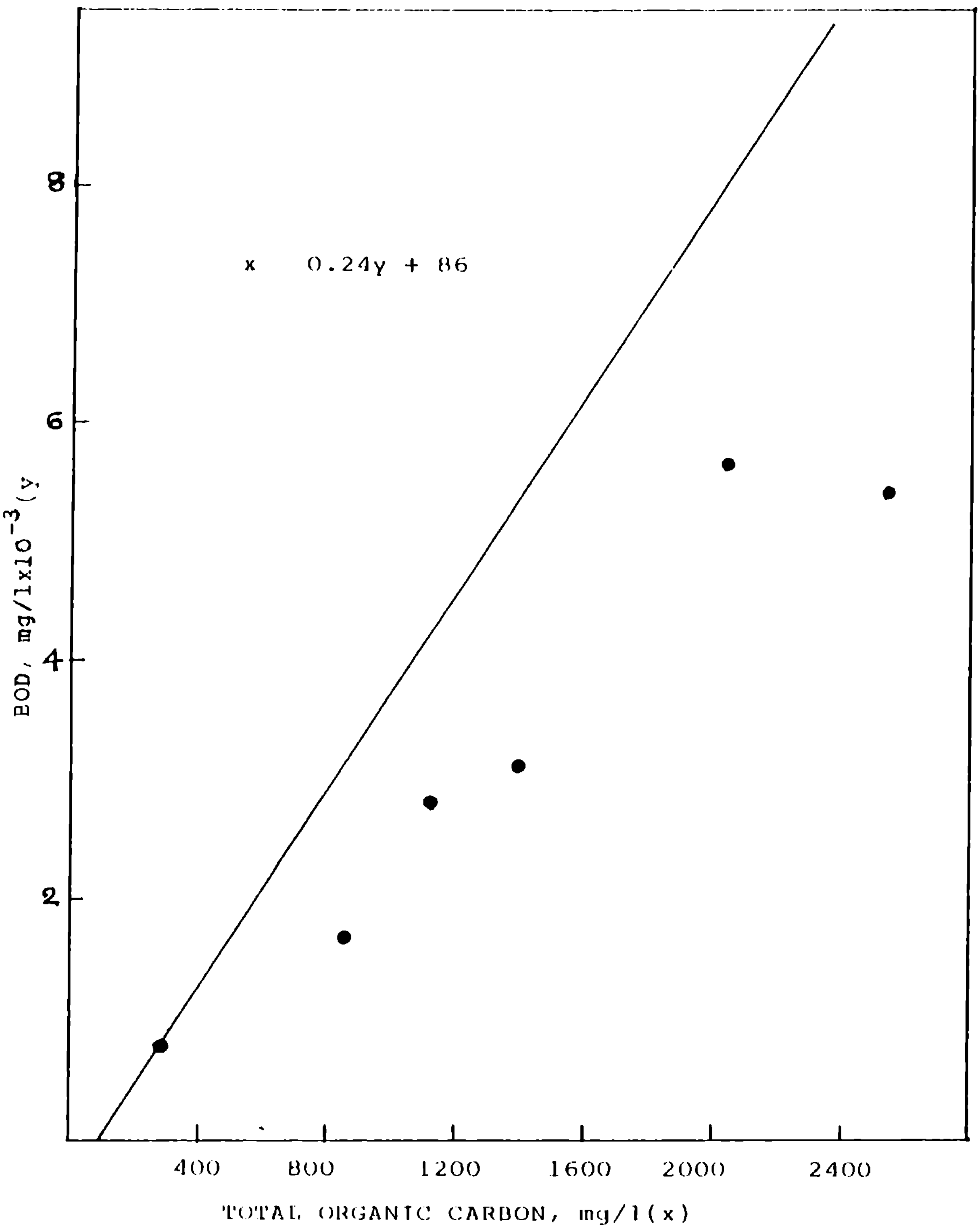


FIG.2A.4 RELATIONSHIP BETWEEN TOC AND BOD.

calculated relationship between five day BOD and TOC is,

$$\frac{BOD_5}{TOC} = \frac{O_2}{C} = \frac{32}{12}(0.90)(0.77) = 1.85$$

where,

(a) the ultimate BOD will exert approximately 90 per cent of the theoretical oxygen demand and

(b) the five-day BOD is 77 per cent of the ultimate BOD for domestic waste (4).

In view of the above mentioned facts, it is not possible to develop good correlation between BOD and TOC of latex centrifuging wastewater, but the conjunctive use of the three parameters, COD, BOD and TOC, can provide many answers when quantitatively analysing the effluents from a latex concentration unit.

f) Pollution Load

The volume of wastewater discharged from a typical latex centrifuging unit is about 40 m^3/day. This is almost the same as the volume of water used for various purposes like washing the bowls of the centrifuge and drums in the centrifuging process. The average BOD concentration of the effluent is 3200 mg/l. Thus the pollution load from a natural rubber latex centrifuging unit is about 128 kg BOD per day.

2A.4 CONCLUSIONS

1. The effluents discharged from a latex concentration unit are strongly acidic in nature. The average pH value of the effluent is 3.9. The main source of acidic effluents is the skim latex coagulation section, which discharges serum effluent having an average pH value of 3.1.

2. The 50 percent and 90 percent probability values for BOD, COD, suspended solids, total kjeldahl nitrogen and ammoniacal nitrogen of the effluent samples were determined.

3. The suspended solids content of the wastewaters range from 9.0 to 42.2 percent of the total solids and major portion of solids are present in the dissolved form which may vary from 57.8 to 91.0 percent of total solids.

4. The relationship between COD and total organic carbon indicates the presence of organic carbon which is not oxidised by dichromate during COD estimation.

5. The pollution load from a typical rubber latex centrifuging unit is about 128 kg BOD per day.

REFERENCES

1. Kumaran, M.G., Rubb. Board Bull., 24, 21 (1987).

2. Standard Methods for the Examination of Water and Waste Water, American Public Health Association, 16th edn. (1985).

3. Handbook for Monitoring Industrial Wastewater, U.S. Environmental Protection Agency, Technology Transfer, 8-9 (1973).

4. Saxena, K.L., Indian J. Environ. Hlth., 29, 2, 85 (1986).

5. Eckenfelder, Jr. W.W. and O'Conner, D.J., Biological Waste Treatment, Pergamon Press, New York (1961).

6. Staffman, P.G. and Turnur, J.S., Jour. Fluid Mech., 1, 1, 16 (1956).

7. Metcalf and Eddy Inc, Waste-water Engineering: Treatment, Disposal, Reuse, Tata McGraw Hill, New Delhi (1978).

8. Ford, D.L., Application of Total Carbon Analyser for Industrial Wastewater Evaluation, 23rd Industrial Waste Conference, p.989 (1968).

9. Mohlman, F.W. and Edwards, G.P., Ind. Eng. Chem. Anal., 3, 119 (1931).

Part B: TREATMENT WITH METAL COAGULANTS

2B.1 INTRODUCTION

The coagulation process is widely employed in the treatment of water and wastewater. Colloidal and suspended particles, organic matter imparting turbidity and colour, and bacterial and algal cells are removed efficiently by a group of chemicals known as 'coagulants'. Coagulation may be defined as the process in which chemicals are added to an aqueous system to create rapidly settling aggregates out of colloidal matter present (1). Flocculation is the second stage in the formation of these aggregates, which is achieved by gentle and prolonged mixing.

It is well known that when particles in liquid suspensions are in the low or sub-micron range they either remain in suspension or settle too slowly for subsequent filtration. Usually appreciable settling rates cannot be achieved unless individual primary particles are aggregated into larger units (2). Aggregation may result from one or more of the following mechanisms (3):

(a) Charge neutralisation by double layer

(b) The bridging action by added materials of high molecular weight.

(c) Entrapment of smaller particles within a loose fibrous structure of a floc formed.

2B.1.2 THEORY OF COAGULATION

Colloidal dispersions in water consist of discrete particles held in suspension by their extremely small size (1-200 nm), state of hydration (chemical combination with water), and surface electric charge. Surface charge develops most commonly through preferential adsorption, ionization and isomorphous replacement (4). If the particles in colloidal dispersion are to be aggregated into larger particles with enough mass to settle easily, their stability must be overcome.

There are two types of colloids - hydrophilic and hydrophobic. Hydrophilic colloids are readily dispersed in water, and their stability (lack of tendency to agglomerate) depends upon a marked affinity for water rather than upon the slight negative charge that they possess. Hydrophobic colloids have no affinity for water and owe their stability to the electric charge they possess. Metal oxide colloids, most of which are positively charged are examples of hydrophobic sols (colloidal dispersion in a liquid). A charge on the colloid is gained by absorbing positive ions from the water solution (5). Electrostatic repulsion between the charged colloidal particles produces a stable sol.

The concept of zeta potential is derived from the diffuse double-layer theory applied to hydrophobic colloids (Fig.2B.1). A fixed covering of positive ions is attracted to the negatively charged particle by electrostatic attraction. This stationary zone of positive ions, is referred to as the stern layer, which is surrounded by a movable, diffuse layer of counterions. The concentration of these positive ions in the diffuse zone decreases as it extends into the surrounding bulk of electroneutral solution. Zeta potential is the magnitude of the charge at the surface of shear. The boundary surface between the fixed ion layer and the solution serves as a shear plane when the particle undergoes movement relative to the solution. The magnitude of zeta potential can be estimated from electrophoretic measurement of particle mobility in an

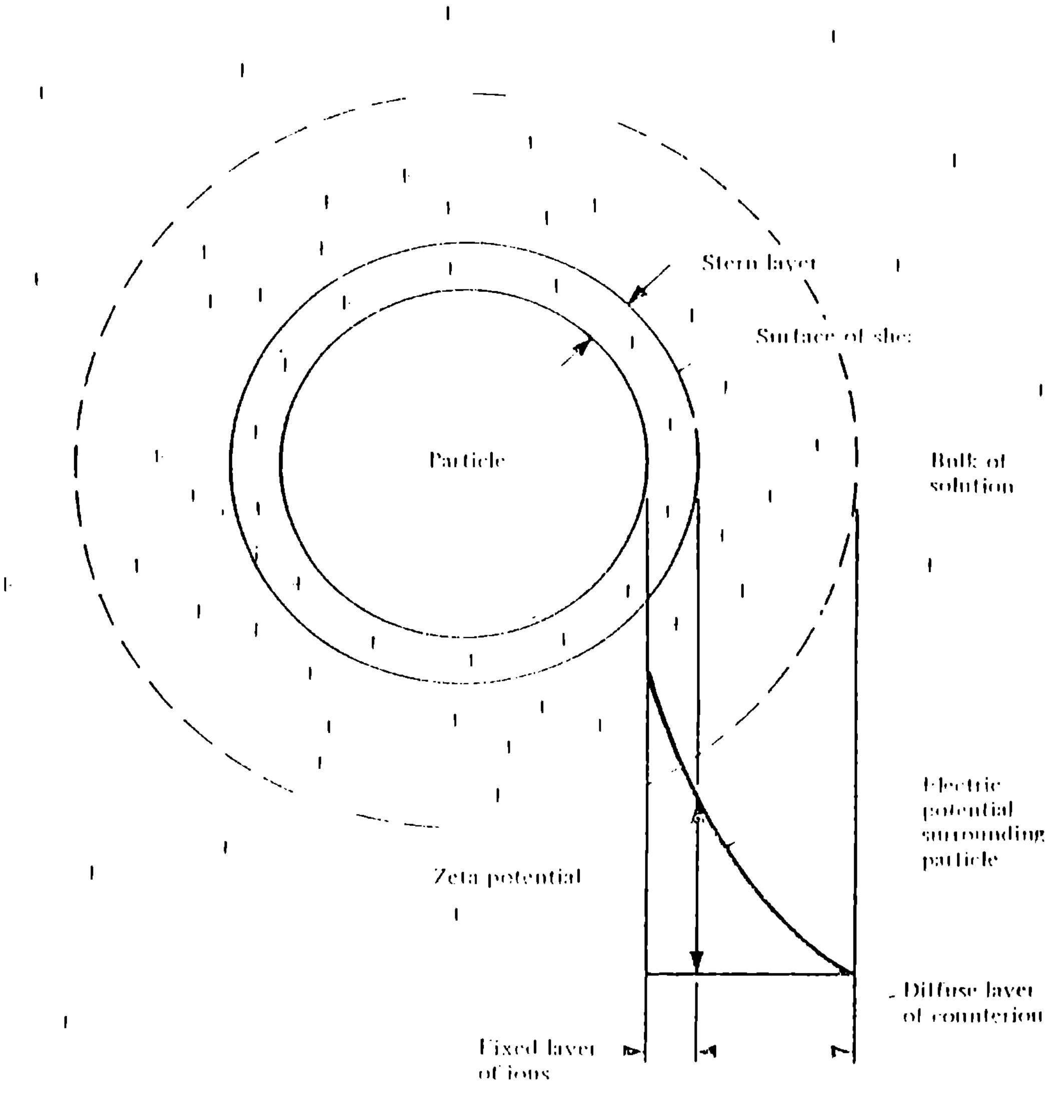


FIG.2B.1 CONCEPT OF ZETA POTENTIAL DERIVED FROM THE DIFFUSE DOUBLE-LAYER THEORY.

electric field (6).

A colloidal suspension is said to be stable when the dispersion shows little or no tendency to aggregate. The repulsive force of the charged double layer disperses particles and prevents aggregation, thus particles with a high zeta potential produce a stable sol. Factors tending to destabilize a sol are van der Waals' forces of attraction and Brownian movement (7). Van der Waals' forces are the molecular cohesive forces of attraction that increase in intensity as particles approach each other. These forces are negligible when the particles are slightly separated but become dominant when particles contact. Brownian movement is the random motion of colloids caused by their bombardment by molecules of the dispersion medium. This movement has a destabilising effect on a sol because aggregation may result.

Destabilization of hydrophobic colloids can be accomplished by adding electrolytes to the solution. Counterions of the electrolyte suppress the double layer charge of the colloids sufficiently and lower the zeta potential permitting the particles to contact closely (8).

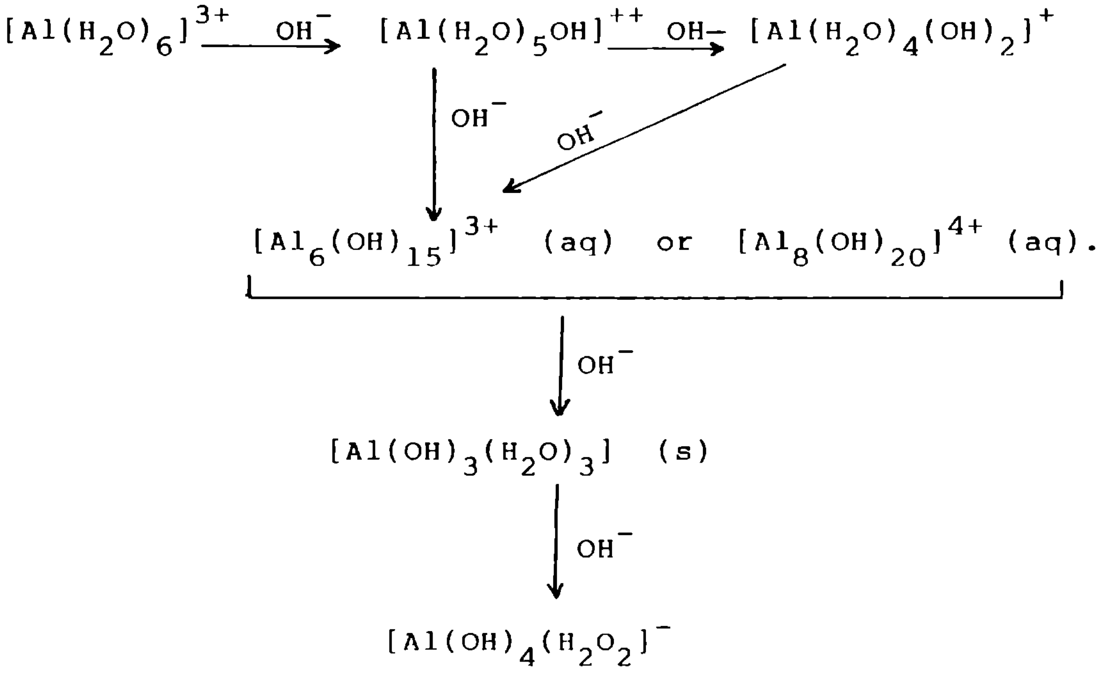
Upon meeting, van der Waals' forces of attraction become dominant and aggregation results. Electrolytes found to be most effective are multivalent ions of opposite charge to that of the colloidal particles. As counter ions in aqueous systems are mostly positively charged, destabilization is done in practice by the use of aluminium and iron salts. Highly charged hydrolysis products of these metal salts reduce the repulsive forces between the colloids by compressing the double-layer charge, bringing on coagulation. Hydrolysed metal ions are also adsorbed on the colloids, creating bridges between the particles.

Colloids in domestic wastes or inorganic wastes are hydrophillic (9). Their affinity for water arises from the presence of polar groups like -OH, -COOH, and $-NH_4$ on the particle surface. These groups are water soluble. Thus they acquire a sheath of water firmly round the particle. The primary charge on hydrophillic colloids arises from the ionisation of the chemical groups present at the surface of the particles. Extent to which these surface groups ionize, determines the charge; and therefore, charge is pH dependent (10). Most of the particles in wastewaters are stabilised by negative charges. Therefore, salts of polyvalent cations such as Al^{3+}, Fe^{3+}, Fe^{2+} and Ca^{2+} are used as coagulants in conformity with the Schulze Hardy rule (11).

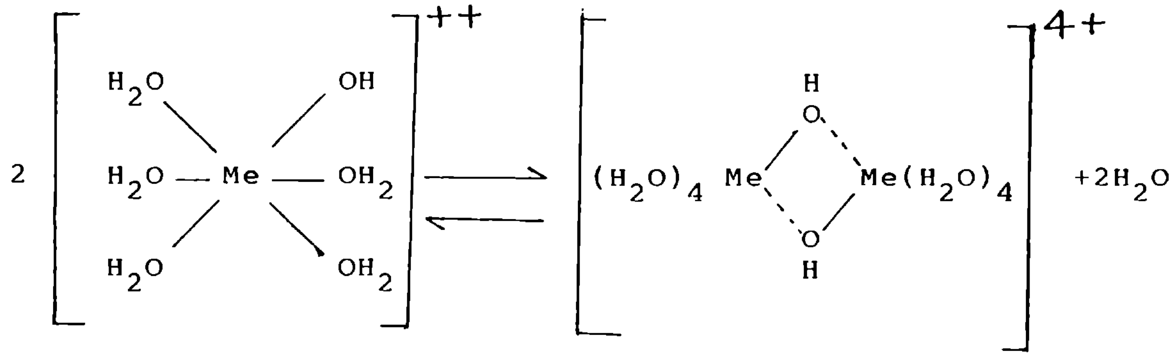
2B.1.2 HYDROLYSING METAL SALTS

When salts of metals like aluminium or iron are added to water or wastewater, they hydrolyse into polyvalent cations Al^{3+} and Fe^{3+} which reduce the zeta potential and facilitate coagulation. In the past it was thought that free Al^{3+} and Fe^{3+} were responsible for the effects observed during particle aggregation; however, it is now known that their complex hydrolysis products are responsible (12,13).

A typical hypothetical model proposed by Stumm (14) for Al^{3+} is shown below:



Before the reaction proceeds to a point where a negative ion is produced, polymerization as depicted in the following equation will usually take place (15).



One or more of the hydrolysis process may be responsible for the coagulation action of metal salts. These hydrolysis reactions are sensitive to pH and this may have to be adjusted (16).

The pH dependence of destabilisation by a hydrolysing metal is illustrated in Fig.2B.2. Laboratory analyses can be performed to find the concentration of metal salt just sufficient to cause coagulation or restabilisation in various pH solutions. These critical values can then be plotted as boundaries between stable and unstable zones,

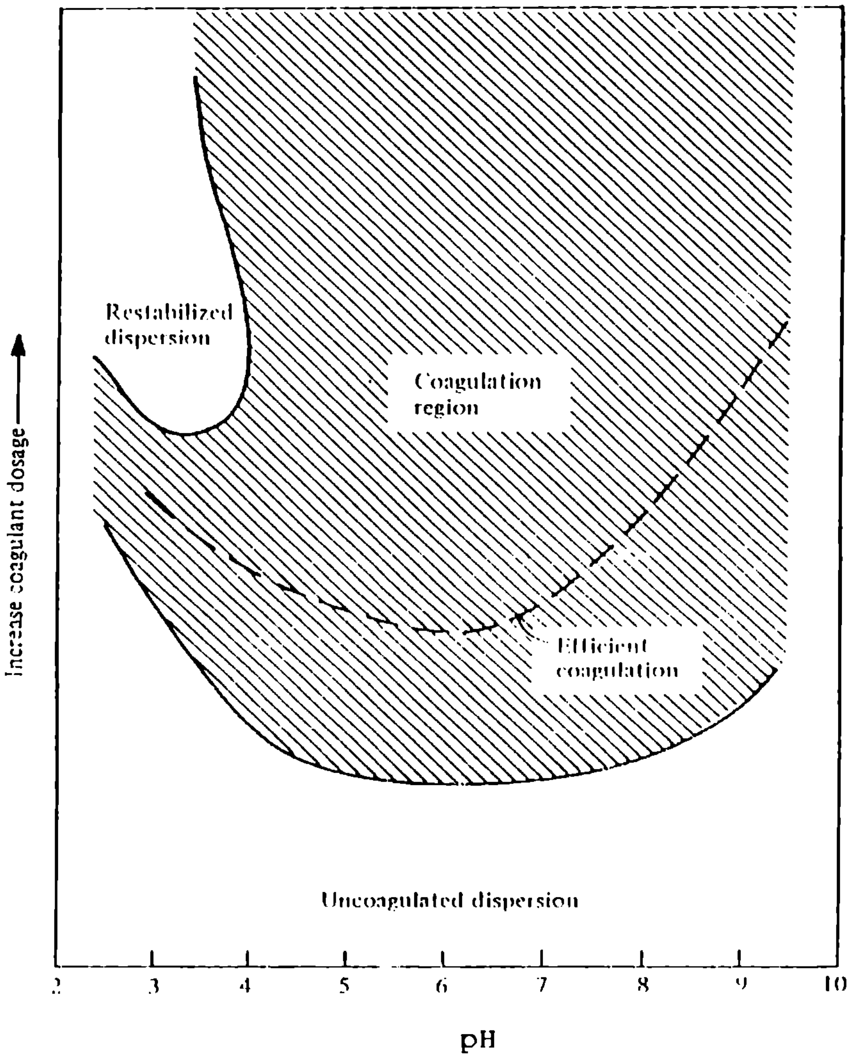


FIG.2B.2 SCHEMATIC DIAGRAM OF COAGULANT DOSAGE-pH DOMAINS FOR COAGULATION AND RESTABILIZATION thus establishing domains of stability (17). An uncoagulated dispersion zone indicates that insufficient coagulant has been applied and destabilization does not occur. A restabilization zone is generally attributed to charge reversal at higher concentrations of coagulant by adsorption of coagulant ions onto the surface of colloids. The coagulation region defines the conditions of pH and coagulant concentrations which produce rapid clarification. Turbidity removal in water treatment practice is accomplished by applying the coagulant dosage within the region where it is most efficient.

Stumm and O'Melia (13) has defined coagulation as a time-dependent process including the following reaction steps:

1. hydrolysis of multivalent metal ions and subsequent polymerisation to multinuclear hydrolysis species;

2. adsorption of hydrolysis species at the solid-solution interface to accomplish destabilisation of the colloid;

3. aggregation of destabilised particles by interparticle bridging involving particle transport and chemical interactions;

4. aggregation of destabilised particles by particle transport and van der Waals' forces;

5. "aging" of flocs, accompanied by chemical changes in the structure of metal-OH-metal linkages, concurrent change in floc sorbability and in extent of floc hydration; and

6. precipitation of metal hydroxide.

Some of these steps occur sequentially, some overlap (steps 1 and 2), and several may occur concurrently under certain conditions (steps 3 and 4, or step 6 with steps 1-5).

Several studies have been reported on the use of metal coagulants in the treatment of industrial wastewaters. Painter (18) has shown that by chemical precipitation alone, the suspended solids and BOD of farm wastewaters can be reduced by 90 per cent and 70 per cent respectively. The study revealed that the coagulant demand depends on characteristics of wastewater such as pH, solids content, phosphates etc. Loehr (19) reported that the reduction of

BOD, COD and suspended solids of agricultural wastewaters is a function of the amount and type of chemical coagulant added, pH of the effluent and type of the wastewater. Smith (20) has shown that most of the suspended solids and part of the BOD are removed by the addition of alum or ferric chloride with or without polyelectrolyte. Weber (21) states that coagulation of wastewater can be accomplished by any of the water coagulants including lime, iron and aluminium salts and synthetic polymers. The choice is to be made on the basis of suitability for a particular waste, availability, cost and sludge treatment and disposal considerations.

Several coagulants like alum, ferric chloride and ferrous sulphate have been tried for the chemical coagulation of tannery wastewaters (22). Ferrous sulphate is reported to be the best coagulant for the removal of sulphides and may be used for the effective removal of colour, BOD and suspended solids from chrome-tan wastes. Kothandaraman et al. (23) reported that calcium chloride is very effective in the treatment of wool-scouring wastes from textile mills. Bhole and Dhabadgaonkar (24) evaluated the efficiency of a number of coagulants to remove colour and

COD of textile mill waste. Aluminium chloride was found to be the best coagulant for the removal of both colour and COD.

Rao and Sastry (25) reported that several coagulants like lime and Nirmali seed extract can be effectively used for the clarification of coal washery wastes. Wastewaters from antibiotic manufacturing units can neither be clarified in settling tanks nor can be chemically coagulated to reduce BOD (26). The poor response of waste to coagulation is due to the fact that most of the substances contributing to BOD appear in solution. Thakur et al. (27) studied the chemical treatment of sewage using alum, ferric chloride, ferrous sulphate and lime.

No systematic study has been reported in literature on the use of chemical coagulants in the treatment of wastewaters from natural rubber processing units. The aim of the present study is to evaluate the effectiveness of nine metal coagulants viz., alum, aluminium sulphate, ferrous sulphate, ferric sulphate, ferric chloride, ferrous chloride, aluminium chloride, lime and magnesium chloride, in the treatment of effluents from a centrifuge latex concentration unit. The effectiveness of the coagulants was assessed in terms of COD reduction, turbidity removal and ammoniacal nitrogen removal. The influence of pH on coagulation action and sludge settling characteristics were also studied.

2B.2 MATERIALS AND METHODS

The coagulants used for the study were of commercial grade. The composition of the coagulants were as follows:

1. Potassium alum, $AlK(SO_4)_2.12H_2O$ containing 0.01 per cent iron.
2. Aluminium sulphate, $Al_2(SO_4)_3.14H_2O$ with a product strength of 17 per cent as Al_2O_3.
3. Ferrous sulphate, $FeSO_4.7H_2O$ having a strength of 55 per cent $FeSO_4$.
4. Ferric sulphate, $Fe_2(SO_4)_3.3H_2O$.
5. Ferric chloride, $FeCl_3$.
6. Ferrous chloride, $FeCl_2$.
7. Aluminium chloride, $AlCl_3$.
8. Lime, $Ca(OH)_2$.
9. Magnesium chloride, $MgCl_2$.

The composite wastewater samples used for the study were collected from a latex concentration unit situated in Kottayam district of Central Kerala. The wastewater was analysed for pH, turbidity, total solids, dissolved solids, suspended solids, COD, BOD, and ammoniacal nitrogen as per standard methods (28). Five samples collected from the composite effluent tank at five different times were selected.

The efficiency of the various coagulants was compared from their ability to reduce turbidity, COD and ammoniacal nitrogen of the effluent samples. Coagulation experiments were carried out in a Jar test apparatus provided with four stirrers having speed regulator. Required dosages of the coagulants were added to the wastewater samples, one litre each taken in beakers. The contents were stirred thoroughly at 100 rpm for 1 minute and then at a speed of 30 rpm for 15 minutes for flocculation. The contents of the beakers were then allowed to settle for 30 minutes. The supernatants were siphoned off for the estimation of pH, turbidity, COD and ammoniacal nitrogen.

The optimum pH for the effective coagulation in the case of each of the coagulants was determined using the Jar test apparatus. The pH of the samples were brought to optimum levels by adding sodium hydroxide before carrying out the coagulation studies. Four different dosages of the coagulants viz., 200, 300, 400 and 500 mg/l were tried. The dosage of lime depended on the pH required. The effectiveness of lime at pH values of 9, 10, 10.5 and 11 was studied.

The sludge settling characteristics were studied by adding optimum dosage of coagulant and adjusting the pH to the optimum value of the effluent samples taken in a 100 ml measuring cylinder. The contents in the measuring cylinder were mixed well for 3 to 4 minutes. The rate of settling of the floc formed was measured by noting the position of sludge at regular interval until further settling was negligible.

2B.3. RESULTS AND DISCUSSION

The experiments were carried out using five effluent samples. The effluent characteristics are given in Table 2B.1.

TABLE 2B.1

EFFLUENT CHARACTERISTICS

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
pH	4.3	3.9	4.0	2.9	4.2
Turbidity, NTU	490	2100	1230	680	1590
COD, mg/l	1170	8080	5790	10700	3420
Ammoniacal nitrogen, mg/l	570	750	590	630	650

(a) Effect of pH on coagulation efficiency

To determine the optimum pH of coagulation for the nine metal coagulants studied, the pH of the latex concentration wastewater samples were varied from 4 to 10. Variation in pH was controlled by 0.1N H_2SO_4 and 0.1N NaOH. The coagulation efficiency was estimated in terms of percent turbidity removal achieved at a coagulant dosage of 300 mg/l.

1. Alum

For alum, the maximum turbidity removal was obtained at a pH of 6.5 as shown in Fig.2B.3. The turbidity removal efficiency increased steadily on increasing the pH from 4 to 6.5. But on increasing the pH further, the efficiency of alum in turbidity removal was found to drop. The turbidity removal achieved for the sample having initial turbidity 680 NTU was higher than the removal efficiencies achieved for the sample with 2100 NTU for all the pH values except 7. Removal efficiencies of 43 and 44 per cent respectively were achieved for the initial turbidities of 2100 NTU and 680 NTU at the optimum pH 6.5. But at pH value of 7, the removal efficiencies were 40 per cent for 2100 NTU and 39 per cent for 680 NTU.

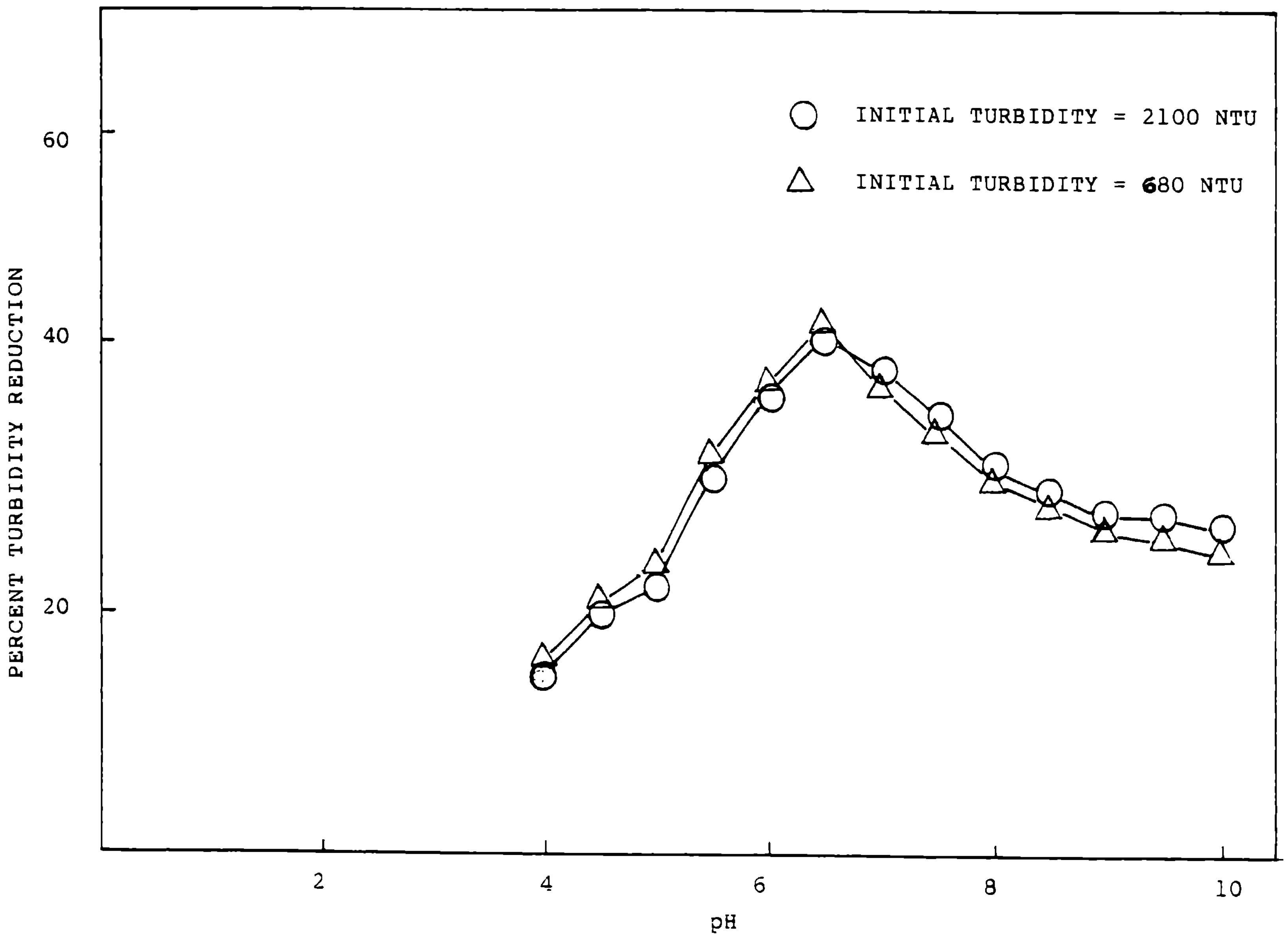


Fig.2B.3 EFFECT OF pH ON THE COAGULATION EFFICIENCY OF ALUM

2. Aluminium sulphate

The effect of pH on the coagulation efficiency of aluminium sulphate is illustrated in Fig.2B.4. The optimum pH of aluminium sulphate for the coagulation of latex concentration wastewaters was found to be 7.0. There was a steady increase in the coagulation efficiency as the pH of the wastewater was increased from 4.0 to 7.0. But from a pH value of 7.5, there was a gradual reduction in the turbidity removal efficiency. Upto a pH value of 7, the turbidity removal for the initial turbidity of 680 NTU was higher than that for 2100 NTU. But subsequently the trend reversed.

3. Ferrous sulphate

The variation of the coagulation efficiency of ferrous sulphate with pH is shown in Fig.2B.5. The optimum pH value of ferrous sulphate was found to be 8.5. In the case of initial turbidity 2100 NTU, the removal efficiency increased from 10 per cent to 30 per cent as the pH increased from 4.0 to 6.0. The rise in removal efficiency was much slower thereafter. At a pH of 6.0, the removal efficiency was 30 per cent. This went up to 35 per cent as the pH increased to 8.5. On further increasing the pH to

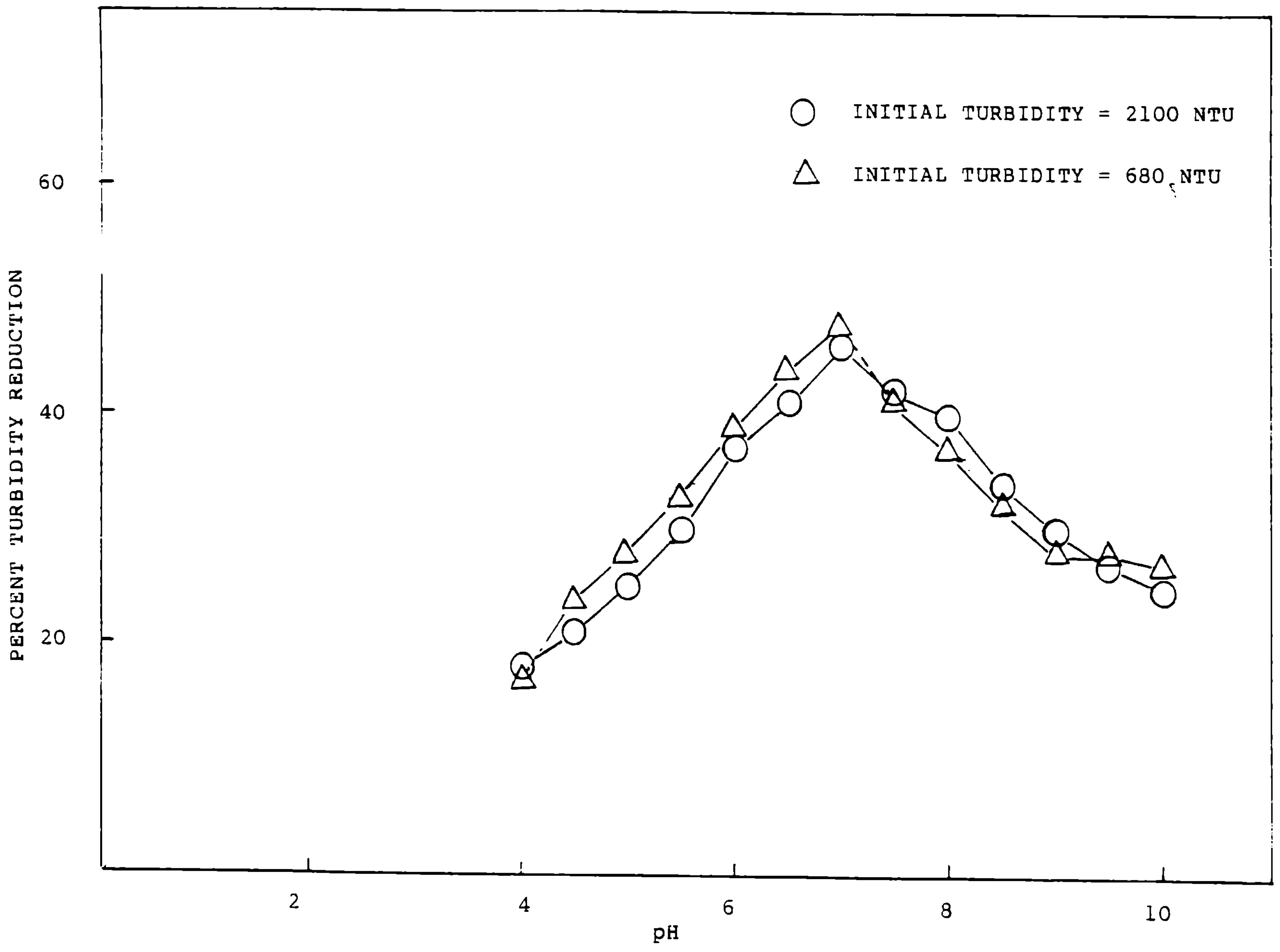


Fig.2B.4 EFFECT OF pH ON THE COAGULATION EFFICIENCY OF ALUMINIUM SULPHATE

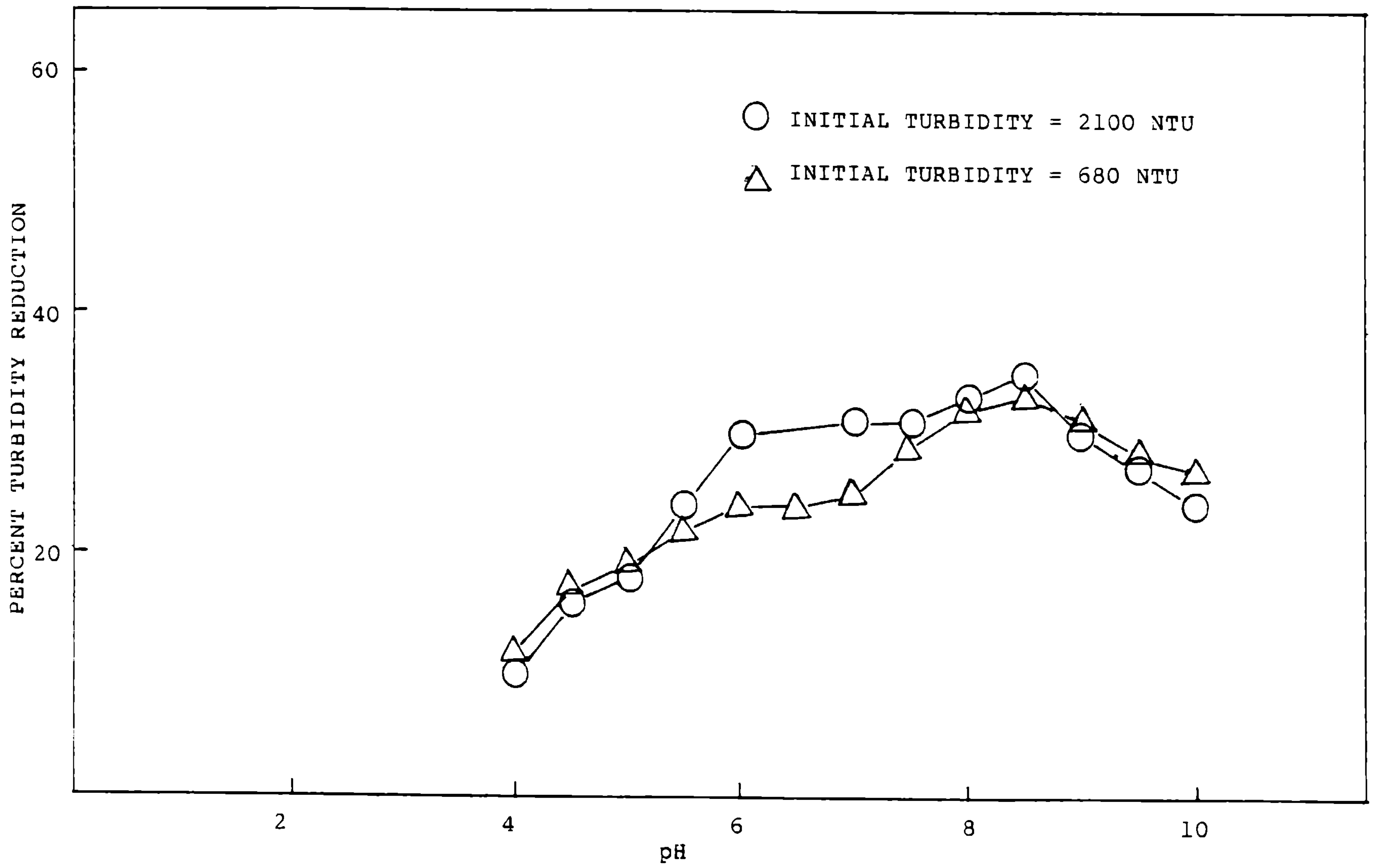


FIG.2B.5 EFFECT OF pH ON THE COAGULATION EFFICIENCY OF FERROUS SULPHATE.

9.0, the removal efficiency dropped. The same pattern was observed for the initial turbidity of 680 NTU.

4. Ferric sulphate

From Fig.2B.6, it is observed that the optimum pH of ferric sulphate for the efficient coagulation of latex concentration wastewaters is 6.5. At this pH, turbidity removal efficiencies of 30 per cent and 29 per cent respectively were obtained for the initial turbidity values of 2100 NTU and 680 NTU. In the pH range between 6.0 and 7.0, the removal efficiencies achieved were very close to each other.

5. Ferric chloride

As for ferric chloride, the effect of pH on coagulation efficiency is shown in Fig.2B.7. The optimum pH value was found to be 8.0. At this pH, the removal efficiencies achieved were 38 per cent and 41 per cent respectively for the initial turbidity values of 680 NTU and 2100 NTU. As the pH value increased from 4.0 to 8.0, there was a steady increase in the turbidity removal efficiencies.

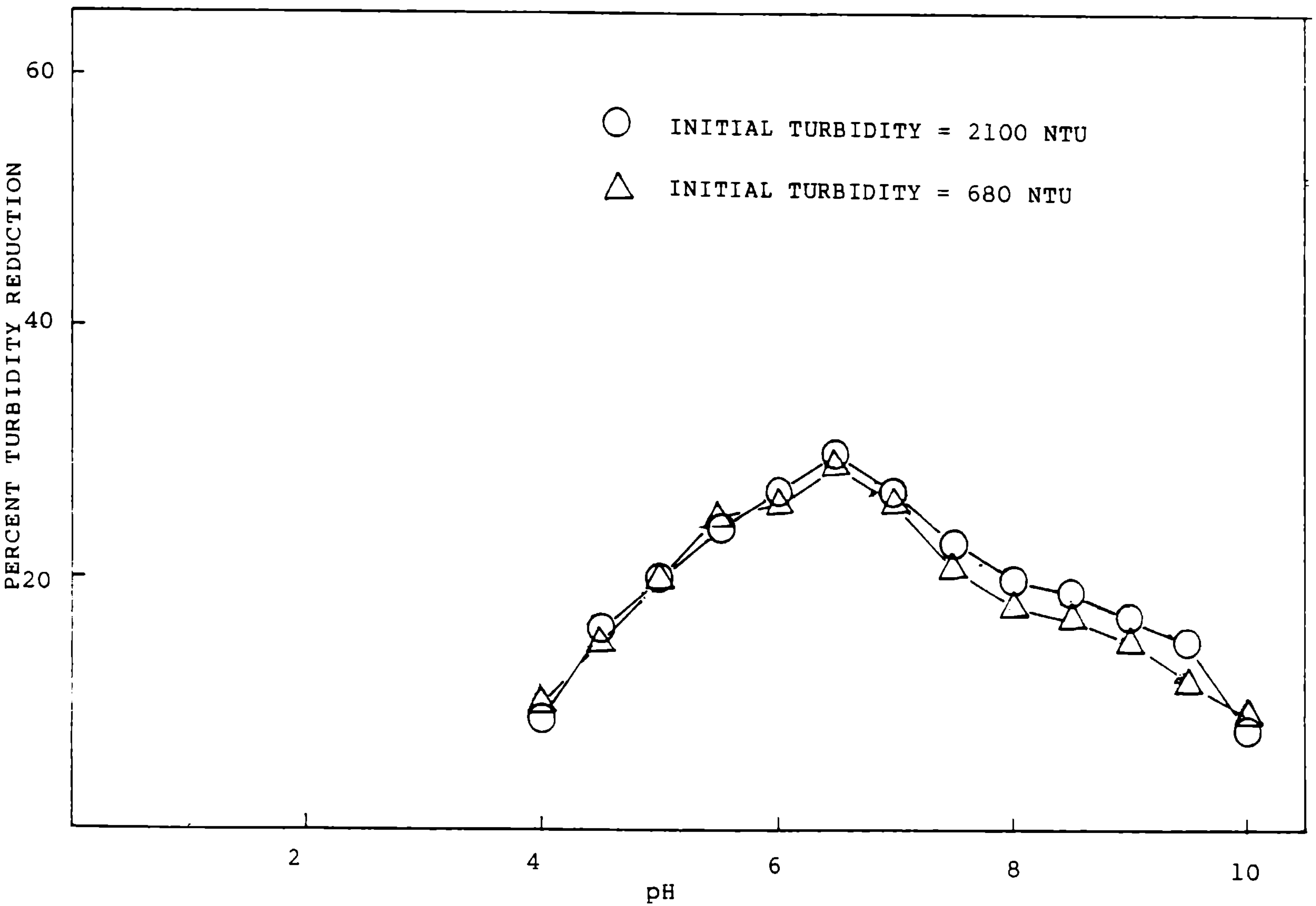


FIG.2B.6 EFFECT OF pH ON THE COAGULATION EFFICIENCY OF FERRIC SULPHATE

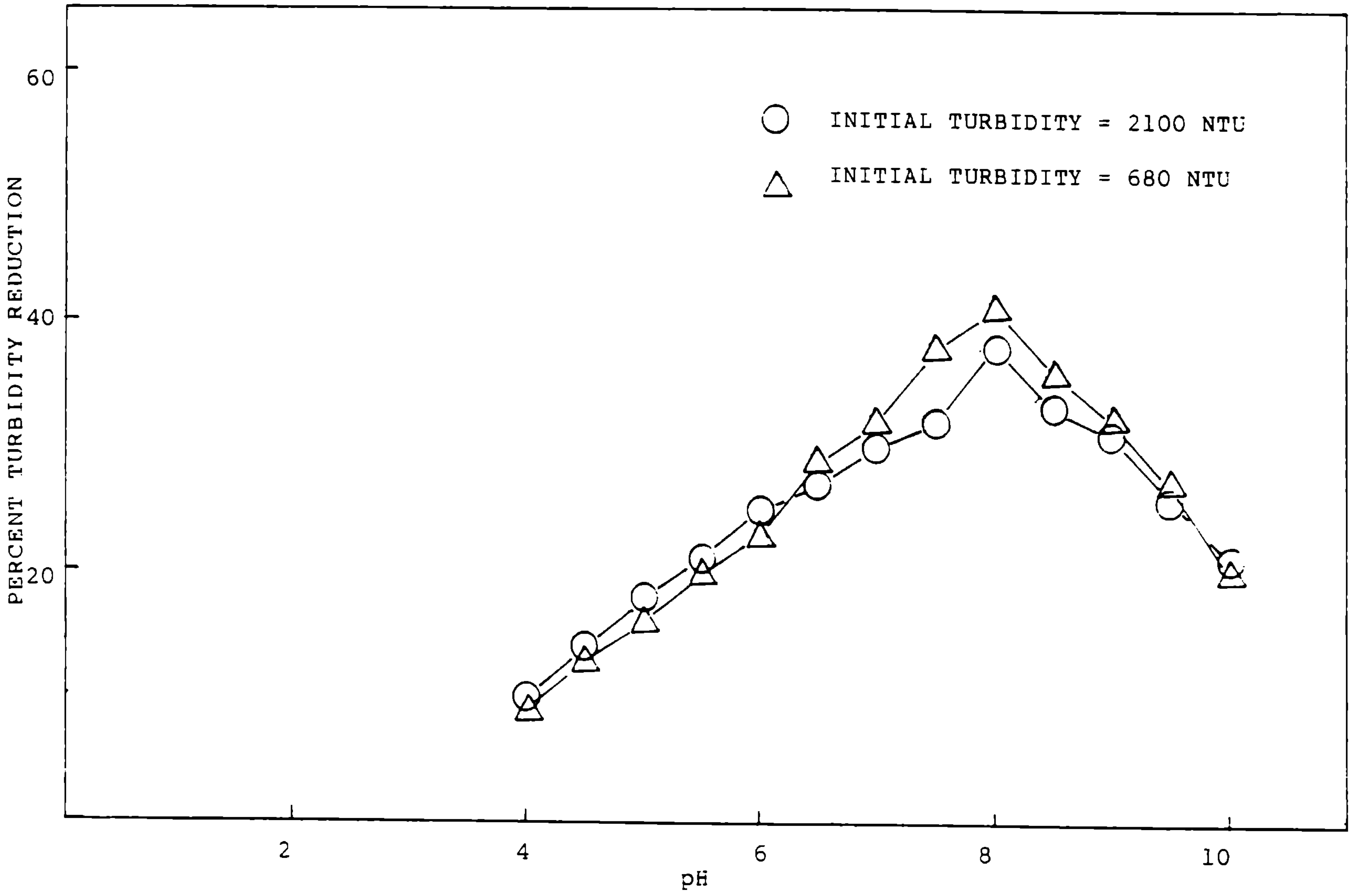


FIG.2B.7 EFFECT OF pH ON THE COAGULATION EFFICIENCY OF FERRIC CHLORIDE

6. Ferrous chloride

The variation of the coagulation efficiency of ferrous chloride with pH is shown in Fig.2B.8. The results obtained for the initial turbidity values, 2100 NTU and 680 NTU were very close to each other. The optimum pH of ferrous chloride for the effective coagulation of latex concentration waste waters was found to be 7.5. From the closeness of turbidity removal efficiencies obtained, the pH range between 7.0 and 8.0 may be considered as effective for coagulation.

7. Aluminium chloride

For aluminium chloride, the maximum turbidity removal efficiency was obtained at a pH of 7.0 as shown in Fig.2B.9. The removal efficiencies achieved for the two effluent samples tested were very close to each other. At pH 7.0, a turbidity removal efficiency of 57 per cent was obtained for the sample with initial turbidity, 2100 NTU; while the removal efficiency obtained for the sample with initial turbidity 680 NTU was 54 per cent.

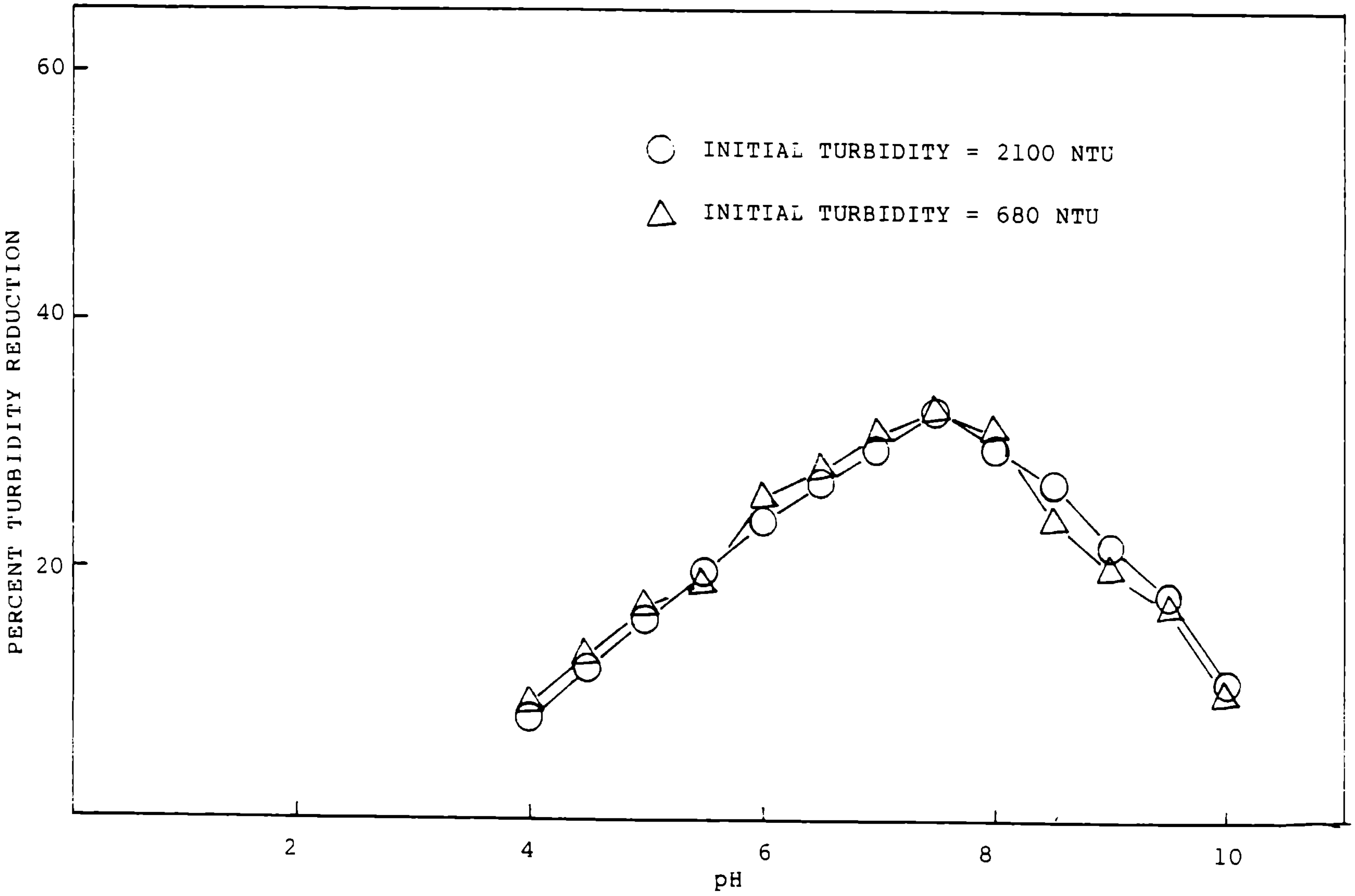


FIG.2B.8 EFFECT OF pH ON THE COAGULATION EFFICIENCY OF FERROUS CHLORIDE

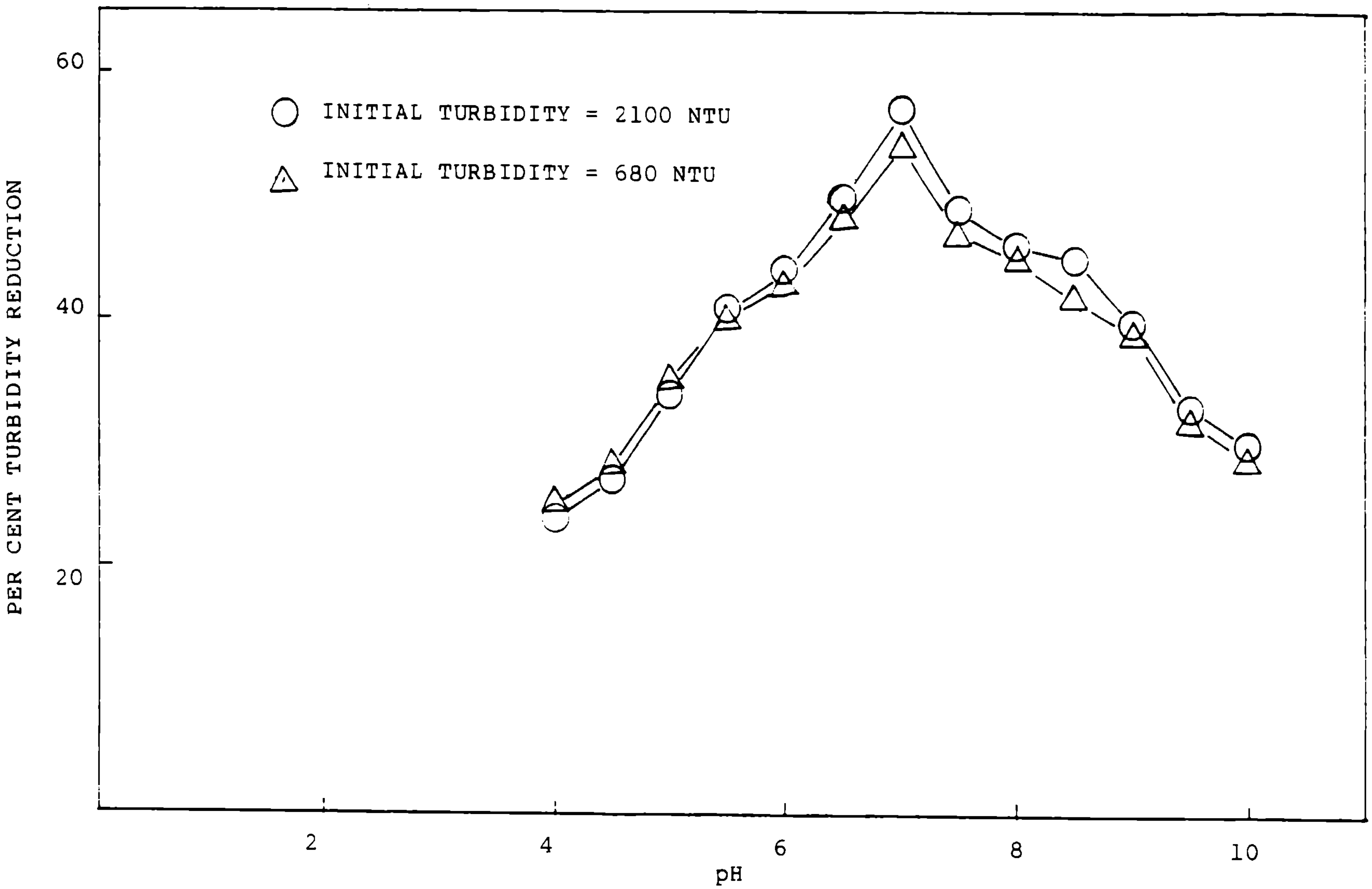


FIG.2B.9 EFFECT OF pH ON THE COAGULATION EFFICIENCY OF ALUMINIUM CHLORIDE

8. Magnesium chloride

The effect of pH on the coagulation efficiency of magnesium chloride is illustrated in Fig.2B.10. The maximum turbidity removal efficiency was achieved at a pH of 8.0. The turbidity removal efficiencies achieved for the two effluent samples tested at different pH values did not show much difference.

The optimum pH values for the effective action of each of the coagulants are listed in Table 2B.2.

(b) Effectiveness of coagulants in COD reduction, turbidity removal and ammoniacal nitrogen removal

The effectiveness of the coagulants was assessed in terms of their ability to reduce COD, turbidity and ammoniacal nitrogen from centrifuge latex concentration wastewaters. Four coagulant dosages; 200 mg/l, 300 mg/l, 400 mg/l and 500 mg/l of all the coagulants except lime were tried on each five effluent samples. For lime, the effectiveness was assessed at pH values of 9, 10, 10.5 and 11.0. The per cent COD reduction, turbidity removal and ammoniacal nitrogen removal obtained for each of the coagulants are tabulated in Tables 2 B.3 to 2B.11.

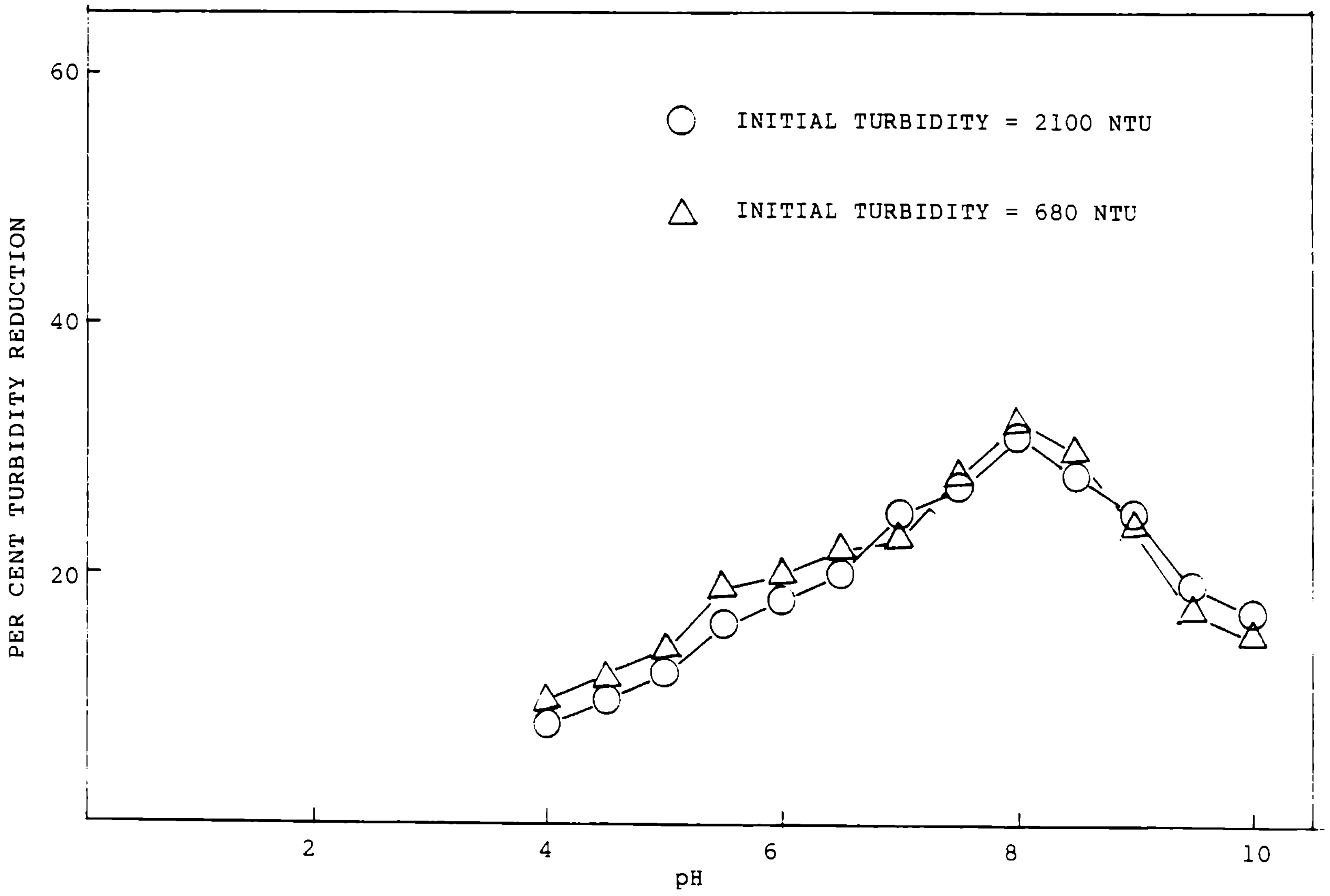


FIG.2B.10 EFFECT OF pH ON THE COAGULATION EFFICIENCY OF MAGNESIUM CHLORIDE

TABLE 2B.2

OPTIMUM pH FOR THE EFFECTIVE ACTION OF COAGULANTS

Sl.No.	Coagulant	Optimum pH
1.	Alum	6.5
2.	Aluminium sulphate	7.0
3.	Ferrous sulphate	8.5
4.	Ferric sulphate	6.5
5.	Ferric chloride	8.0
6.	Ferrous chloride	7.5
7.	Aluminium chloride	7.0
8.	Magnesium chloride	8.0

1. Alum

For alum, the maximum COD reduction ranging from 39 to 47 per cent was obtained with a dosage of 500 mg/l. The highest per cent COD reduction of 47 was obtained for the raw effluent COD concentration of 10700 mg/l. The maximum per cent turbidity removal and ammoniacal nitrogen removal were also obtained with the alum dosage of 500 mg/l. While the maximum turbidity removal of 48 per cent was obtained for the effluent sample 2 having an initial turbidity of 2100 NTU, the maximum ammoniacal nitrogen removal of 28 per cent was also obtained for sample 2 which had an initial ammoniacal nitrogen content of 750 mg/l.

2. Aluminium sulphate

In the case of aluminium sulphate, the optimum dosage for COD reduction, turbidity removal and ammoniacal nitrogen removal was found to be 400 mg/l. The per cent COD reduction obtained with this dosage was in the range of 46-56 and the maximum removal efficiency was obtained for an initial COD concentration of 8080 mg/l (Sample 2). While the per cent turbidity removal varied between 43 and 49, the ammoniacal nitrogen removal varied between 24 and 29 per

TABLE 2B.3

EFFICIENCY OF ALUM IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l
1.	29	30	38	44	43	42	44	46	23	22	24	26
2.	27	42	34	46	42	43	45	48	22	23	25	28
3.	22	41	38	42	40	41	43	46	20	21	23	26
4.	25	31	20	47	41	44	42	47	21	24	22	27
5.	20	18	29	39	43	42	41	45				

TABLE 2B.4

EFFICIENCY OF ALUMINIUM SULPHATE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l
1.	47	49	56	50	42	43	47	46	22	23	27	26
2.	51	53	59	56	45	46	49	48	25	26	29	28
3.	46	52	61	48	45	47	48	44	25	27	28	24
4.	39	47	56	46	47	48	50	49	27	28	30	29
5,	45	42	54	51	44	47	48	43				

cent. The maximum removal efficiency of turbidity removal and ammoniacal nitrogen removal was obtained for Sample 4 having an initial turbidity of 680 NTU and ammoniacal nitrogen concentration of 630 mg/l.

3. Ferrous sulphate

For ferrous sulphate, the optimum dosage was found to be 300 mg/l for COD reduction bringing about reduction efficiencies ranging from 57 to 62 per cent. The maximum removal efficiency of 62 per cent was obtained for Sample 2 with an initial COD of 8080 mg/l. The maximum turbidity removal and ammoniacal nitrogen removal were obtained at a dosage of 400 mg/l. The maximum removal efficiencies obtained for turbidity and ammoniacal nitrogen were in the ranges of 35-38 per cent and 15-18 per cent respectively.

4. Ferric sulphate

In the case of ferric sulphate, the optimum dosage for COD reduction, turbidity removal and ammoniacal nitrogen removal was found to be 200 mg/l. The per cent COD reduction obtained with this dosage was in the range of 51-53 and the maximum removal efficiency was obtained for an

TABLE 2B.5

EFFICIENCY OF FERROUS SULPHATE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l
1.	54	60	55	54	32	34	35	33	12	14	15	13
2.	57	62	54	52	30	35	37	32	10	15	17	12
3.	51	60	49	48	31	34	36	30	11	14	16	10
4.	52	59	48	53	32	33	38	34	12	13	18	14
5.	47	57	46	51	34	35	38	32				

TABLE 2B.6

EFFICIENCY OF FERRIC SULPHATE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l
1.	50	49	49	48	31	29	27	27	11	9	7	7
2.	51	49	48	47	32	30	26	25	12	10	6	5
3.	53	50	50	48	31	28	27	25	11	8	7	5
4.	52	48	47	46	33	29	27	26	13	9	7	6
5.	51	49	47	46	30	28	27	26				

effluent COD concentration of 5790 mg/l. While the per cent turbidity removal at the optimum dosage varied between 30 and 33, the per cent COD removal varied between 11 and 13.

5. Ferric chloride

The effectiveness of ferric chloride was most optimum at a dosage of 500 mg/l for COD reduction. The optimum dosage for turbidity removal and ammoniacal nitrogen removal was 400 mg/l. The COD reduction efficiencies obtained at the optimum dosage varied between 59 and 66 per cent. The turbidity removal efficiencies and ammoniacal nitrogen efficiencies achieved at the optimum dosage of 400 mg/l were in the ranges of 39-42 per cent and 19-22 per cent respectively.

6. Ferrous chloride

For ferrous chloride, the optimum dosage was found to be 400 mg/l for COD reduction bringing about reduction efficiencies varying from 52 to 54 per cent. The maximum removal efficiency of 54 per cent was obtained for Sample 4 with initial COD of 10700 mg/l. The maximum turbidity removal and ammoniacal nitrogen removal was obtained at a dosage of

TABLE 2B.7

EFFICIENCY OF FERRIC CHLORIDE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l
1.	47	51	54	59	38	36	39	37	18	16	19	17
2.	52	54	58	65	37	38	41	39	17	18	21	19
3.	53	55	59	62	39	36	40	37	19	16	20	17
4.	57	56	61	64	39	41	42	38	19	21	22	18
5.	53	59	62	66	39	40	41	38				

TABLE 2B.8

EFFICIENCY OF FERROUS CHLORIDE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l
1.	46	48	52	51	30	32	33	35	10	12	13	15
2.	47	49	53	50	31	33	34	36	11	13	14	16
3.	46	49	53	50	29	31	32	34	9	11	12	14
4.	45	48	54	51	31	33	34	35	11	13	14	15
5.	46	47	52	49	30	33	34	35				

500 mg/l. The maximum removal efficiencies obtained for COD and ammoniacal nitrogen were in the ranges of 34-36 per cent and 14-16 per cent respectively.

7. Aluminium chloride

In the case of aluminium chloride, the optimum dosage for COD reduction, turbidity removal and ammoniacal nitrogen removal was found to be 300 mg/l. The per cent COD reduction obtained with this dosage was in the range of 69-73 per cent and the maximum removal efficiency of 73 per cent was obtained for an initial COD concentration of 10700 mg/l (Sample 4). While the per cent turbidity removal for the optimum dosage of 300 mg/l varied between 52 and 57 and ammoniacal nitrogen efficiencies varied between 32 and 37 per cent.

8. Magnesium chloride

For magnesium chloride, the optimum dosage was found to be 400 mg/l for COD reduction, turbidity removal and ammoniacal nitrogen removal. At the optimum dosage of 400 mg/l, the COD removal efficiencies varied between 44 and 46 per cent and the maximum reduction of 46 per cent was

TABLE 2B.9

EFFICIENCY OF ALUMINIUM CHLORIDE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	200 mg/l	300 mg/l	400 mg/l	500 mg/l	300 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l
1.	66	70	67	65	49	53	50	51	29	33	30	31
2.	68	72	67	64	53	57	54	50	33	37	34	30
3.	66	71	68	63	48	52	51	49	28	32	31	29
4.	67	73	66	65	51	54	49	47	31	34	29	27
5.	68	69	67	64	47	54	51	50				

TABLE 2B.10

EFFICIENCY OF MAGNESIUM CHLORIDE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l	200 mg/l	300 mg/l	400 mg/l	500 mg/l
1.	40	41	45	43	28	30	32	30	8	10	12	10
2.	41	43	46	43	29	31	33	31	9	11	13	11
3.	41	42	44	42	27	31	32	31	7	11	12	11
4.	39	42	45	42	30	32	33	32	10	12	13	12
5.	40	43	46	43	27	29	32	30				

obtained for influent COD concentrations of 8080 mg/l and 10700 mg/l. As for turbidity removal, efficiencies ranging from 32 to 33 per cent were obtained for all the samples at the optimum dosage of 400 mg/l. At the optimum dosage, the ammoniacal nitrogen removal efficiencies varied between 12 and 13 per cent.

9. Lime

In the case of lime, the maximum COD removal, turbidity reduction and ammoniacal nitrogen removal was obtained at a pH of 10.5. The COD removal efficiencies achieved were in the range of 52-58 per cent and the maximum efficiency of 58 per cent was obtained for an initial COD concentration of 5790 mg/l. The turbidity removal efficiencies ranged between 40 and 43 per cent with the maximum removal obtained for an initial turbidity of 680 mg/l. As for ammoniacal nitrogen removal, the removal efficiencies were in the range of 32-33 per cent.

The optimum dosages for the most effective action of each of the coagulants and the maximum removal efficiencies obtained for COD, turbidity and ammoniacal nitrogen are summarised in Table 2B.12.

TABLE 2B.11

EFFICIENCY OF LIME IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction at pH				Percent Trubidity removal at pH				Percent Ammoniacal nitrogen removal at pH			
	9	10	10.5	11	9	10	10.5	11	9	10	10.5	11
1.	44	47	52	50	41	39	40	42	24	29	33	29
2.	43	46	54	51	40	41	42	44	23	30	32	28
3.	47	49	58	54	41	40	41	43	25	31	33	30
4.	43	47	55	49	41	42	43	44	26	30	33	28
5..	41	49	54	48	42	40	41	43				

TABLE 2B.12

COMPARISON OF VARIOUS COAGULANTS

Sl. No.	Coagulant	Optimum dosage mg/l			Maximum removal efficiency		
		COD reduction	Turbidity removal	Ammoniacal nitrogen removal	COD reduction	Turbidity removal	Ammoniacal nitrogen removal
1.	Alum	500	500	500	47	48	28
2.	Aluminium sulphate	400	400	400	56	49	29
3.	Ferrous sulphate	300	400	400	62	38	18
4.	Ferric sulphate	200	200	200	53	33	18
5.	Ferric chloride	500	400	400	66	42	22
6.	Ferrous chloride	400	500	500	54	36	16
7.	Aluminium chloride	300	300	300	73	57	37
8.	Magnesium chloride	400	400	400	46	33	13
9.	Lime	pH=10.5	pH=10.5	pH=10.5	58	43	33

From Table 2B.12, it is evident that aluminium chloride is the most effective coagulant among the nine coagulants studied in respect of COD reduction, turbidity removal and ammoniacal nitrogen removal.

In the case of COD reduction, aluminium chloride is followed by ferric chloride, ferrous sulphate, lime, aluminium sulphate, ferrous chloride, ferric sulphate, alum and magnesium chloride. In the case of turbidity removal, aluminium chloride is followed by aluminium sulphate, alum, lime, ferric chloride, ferrous sulphate, ferrous chloride, ferric sulphate and magnesium chloride, in that order. In the case of ammoniacal nitrogen removal, the order of dominance is aluminium chloride, lime, aluminium sulphate, alum, ferric chloride, ferrous sulphate, ferrous chloride, ferric sulphate and magnesium chloride.

(c) Settling characteristics of sludge

The settling characteristics of the flocs formed by each of the coagulants are plotted in Figs.2B.11 to 2B.19.

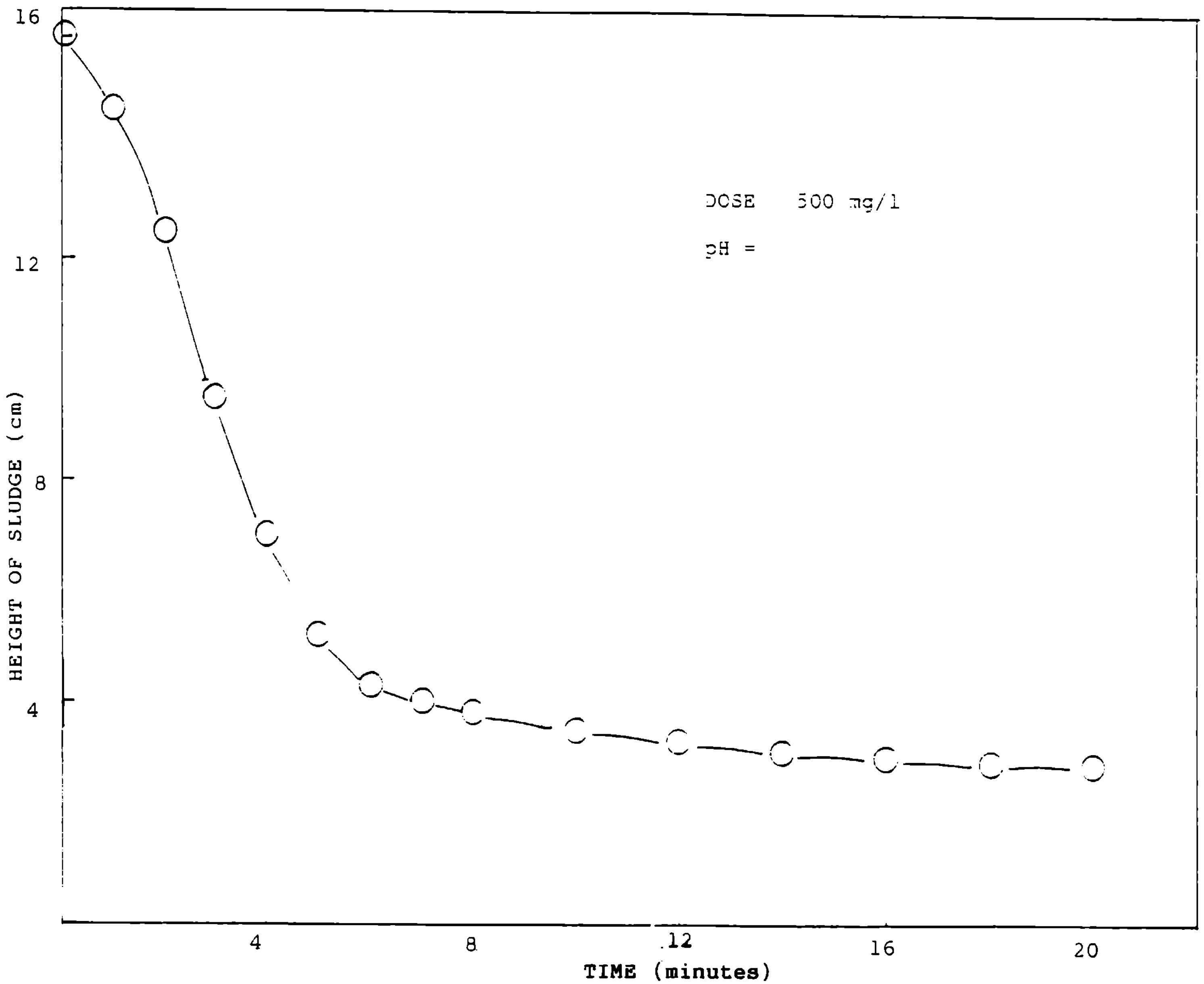


FIG.2B.11 SETTLEABILITY OF EFFLUENT COAGULATED WITH ALUM.

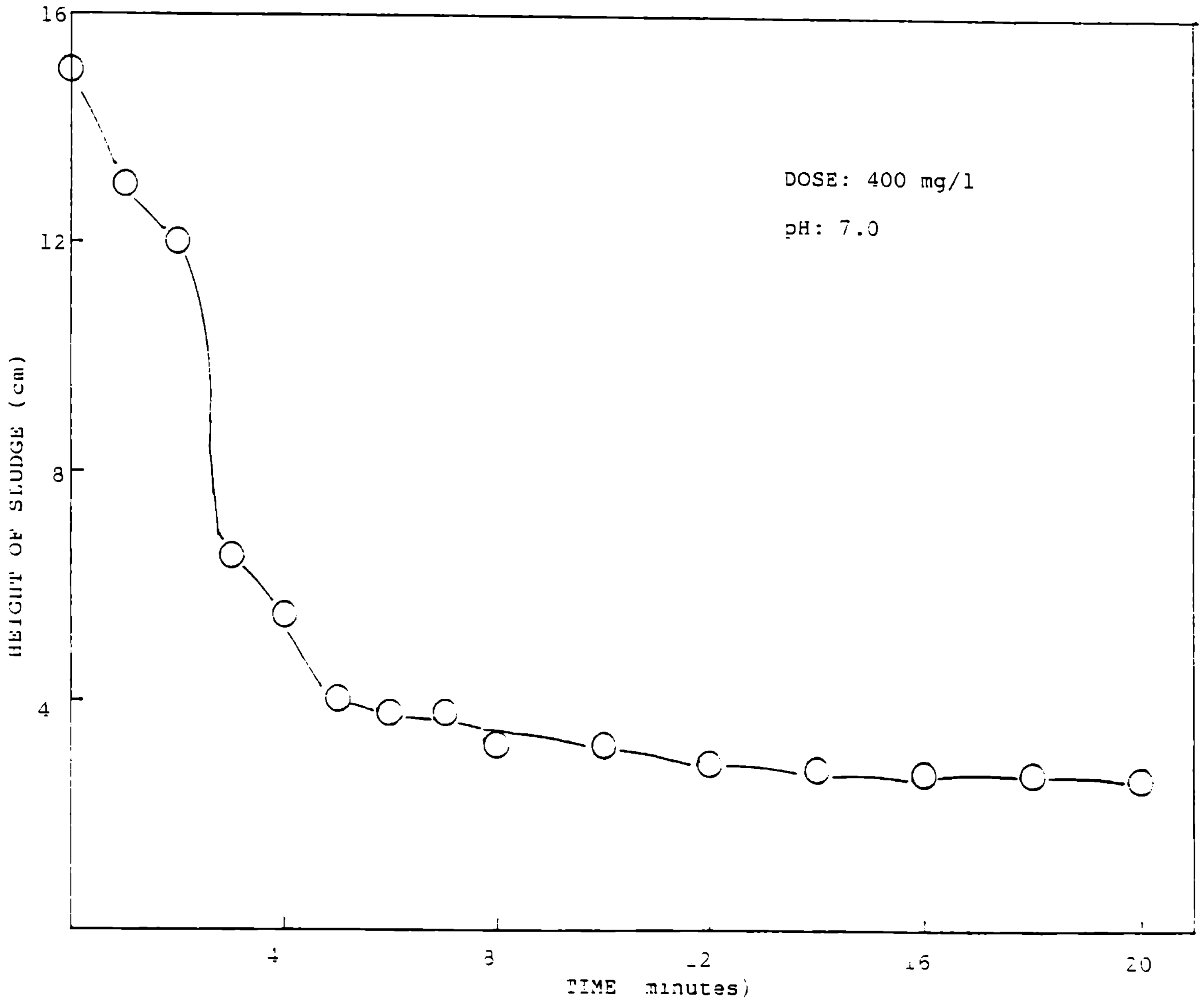


FIG.23.12 SETTLEABILITY OF EFFLUENT COAGULATED WITH ALUMINIUM SULPHATE

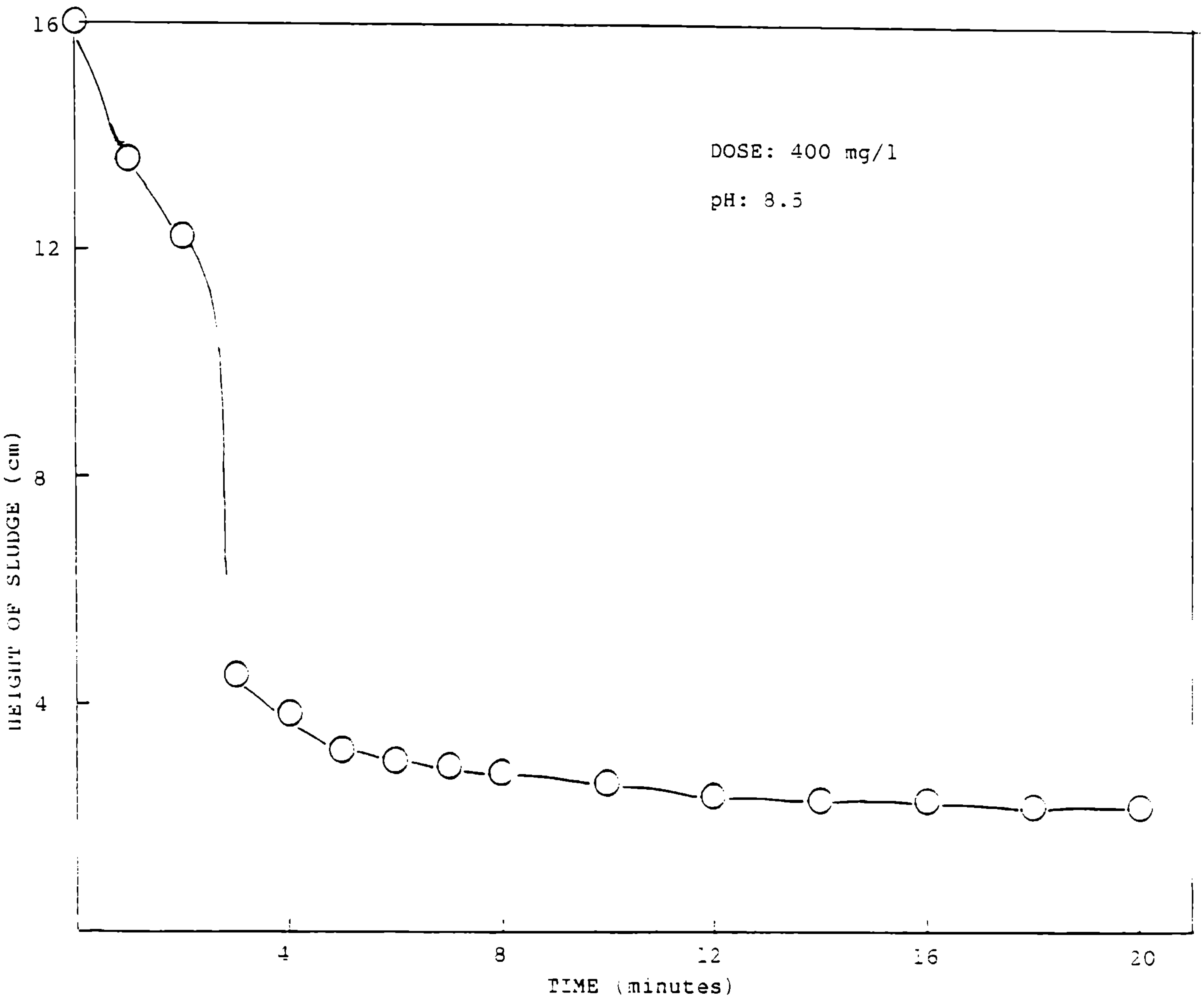


FIG.2B.13 SETTLEABILITY OF EFFLUENT COAGULATED WITH FERROUS SULPHATE

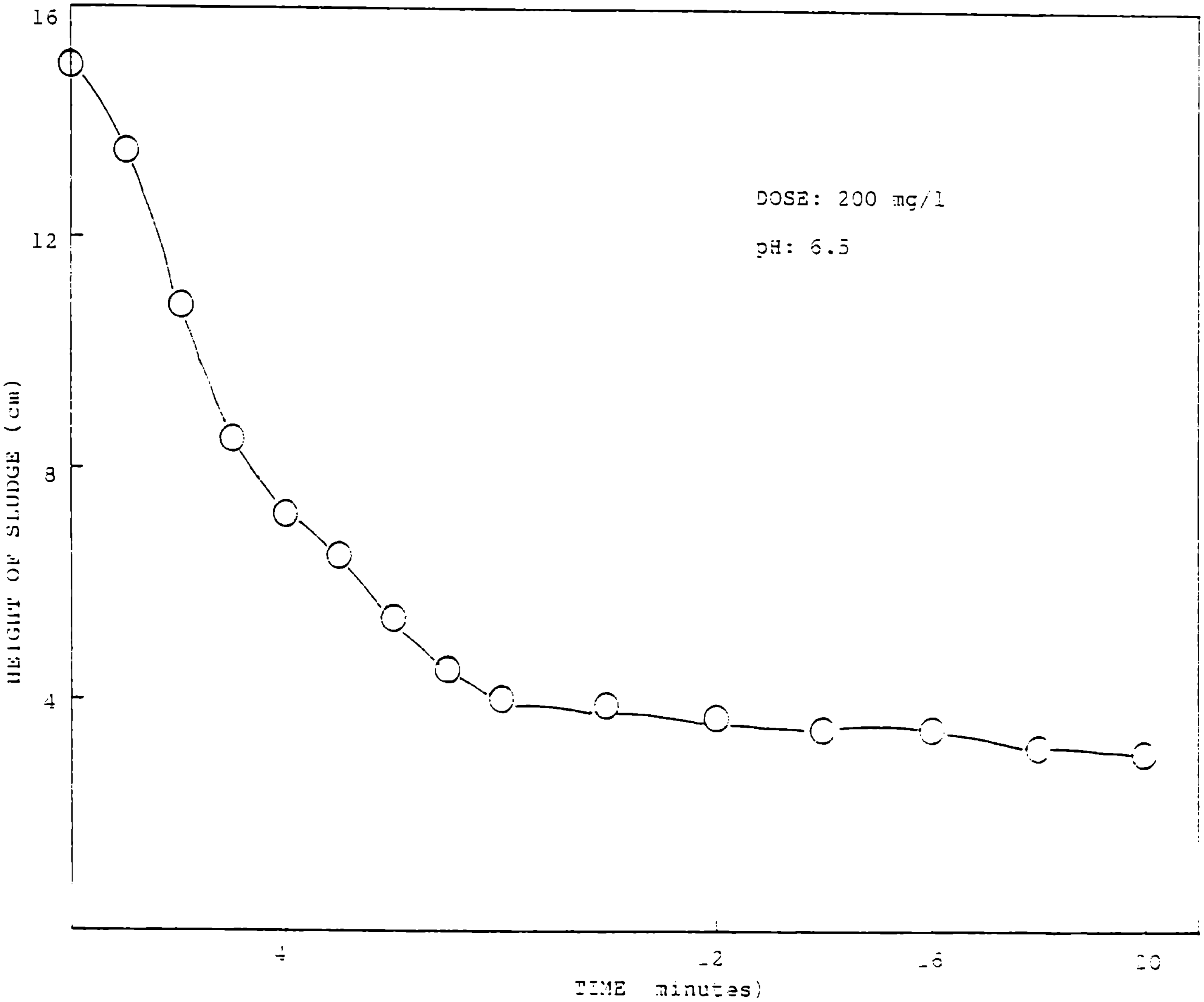


FIG.23.14 SETTLEABILITY OF EFFLUENT COAGULATED WITH FERRIC SULPHATE

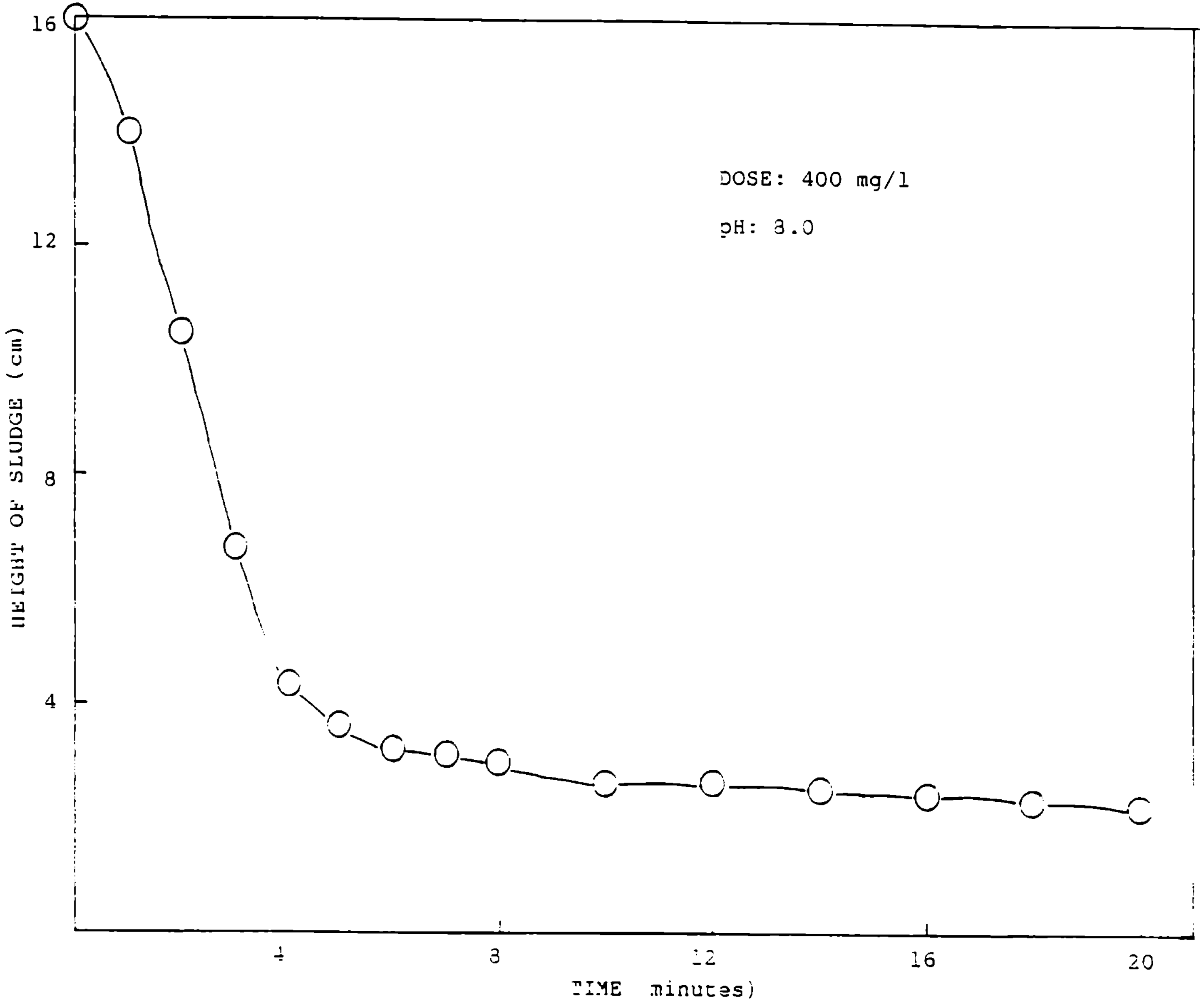


FIG.2B.15 SETTLEABILITY OF EFFLUENT COAGULATED WITH FERRIC CHLORIDE

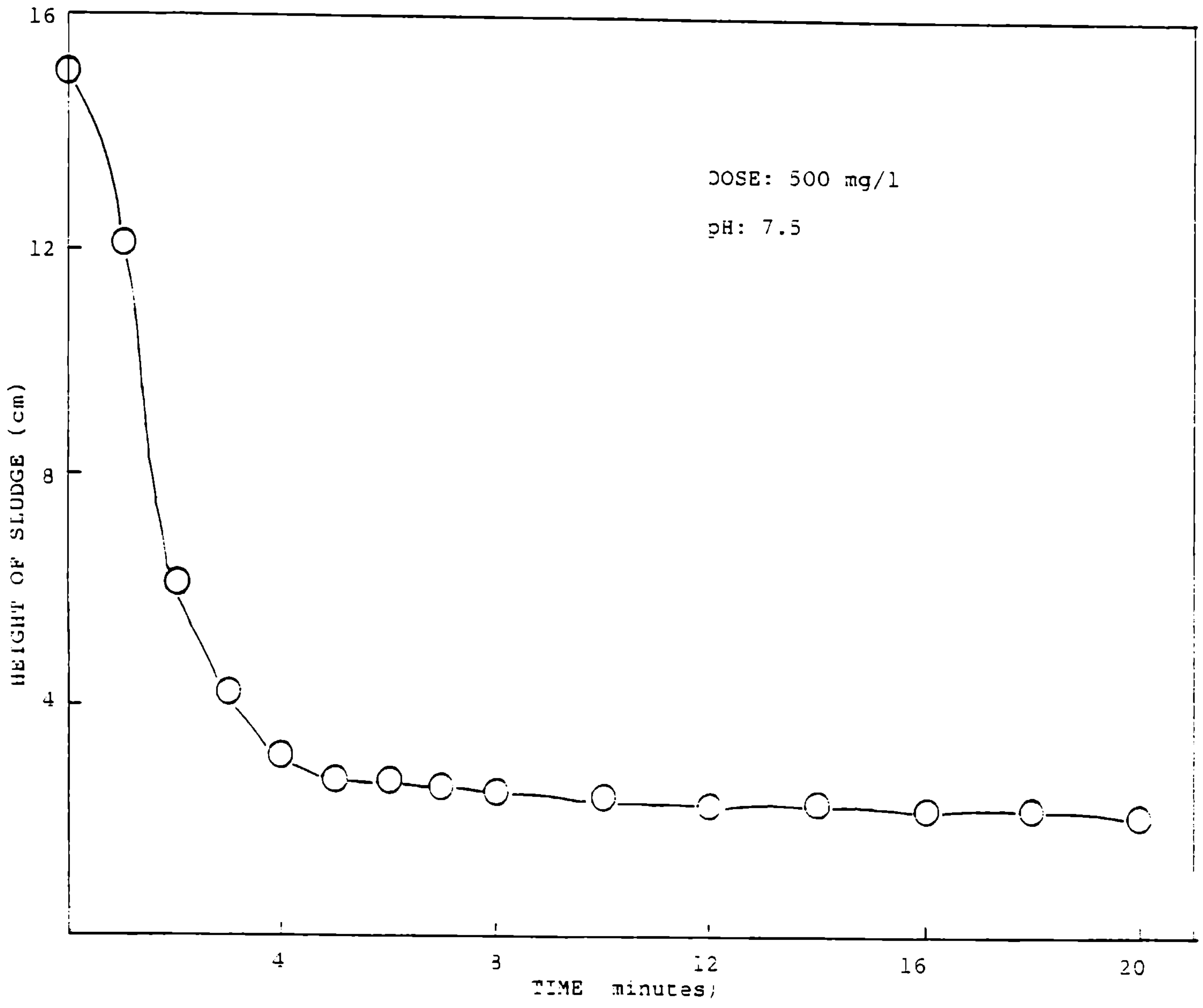


FIG.2B.16 SETTLEABILITY OF EFFLUENT COAGULATED WITH FERROUS CHLORIDE

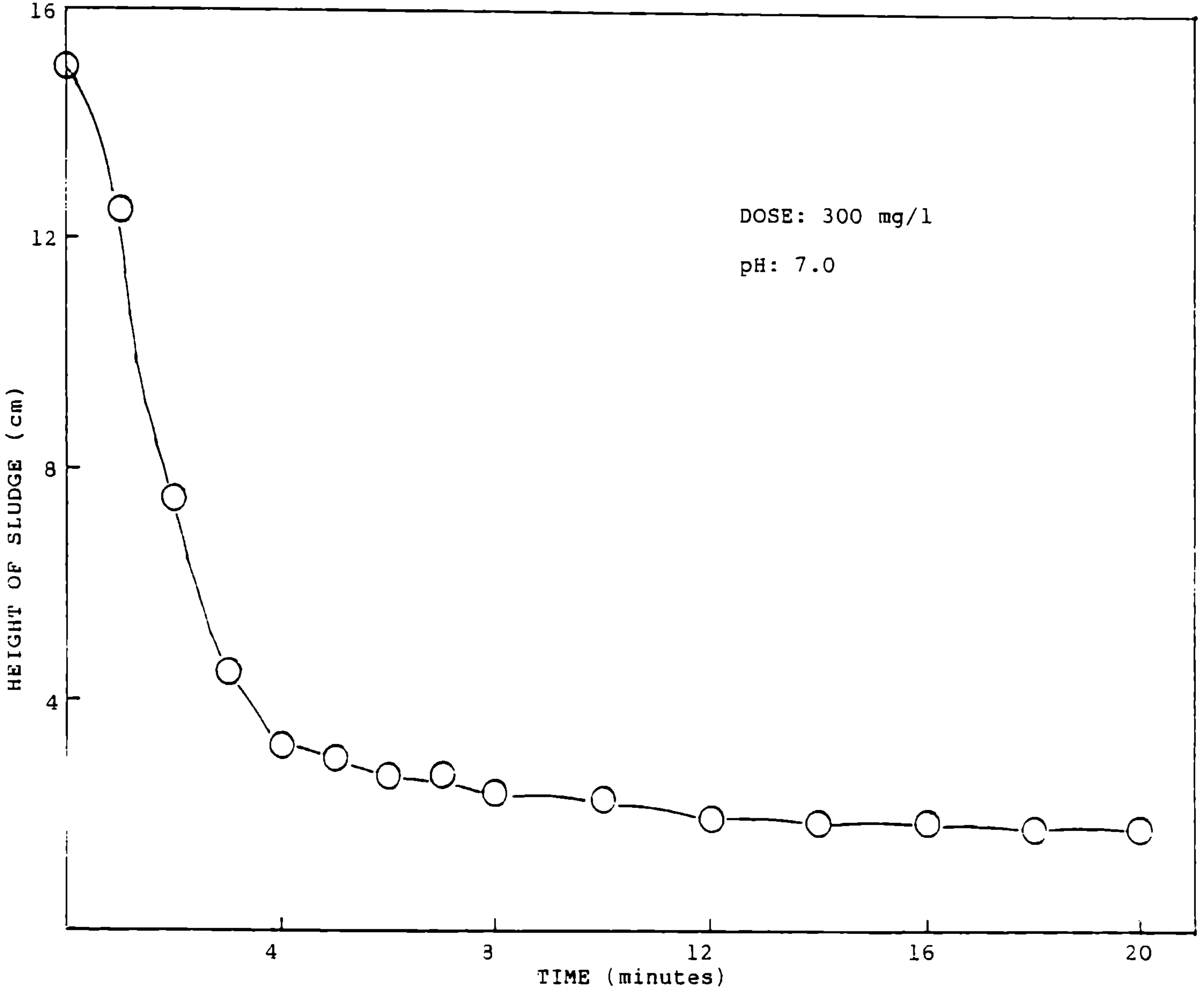


FIG.2B.17 SETTLEABILITY OF EFFLUENT COAGULATED WITH ALUMINIUM CHLORIDE

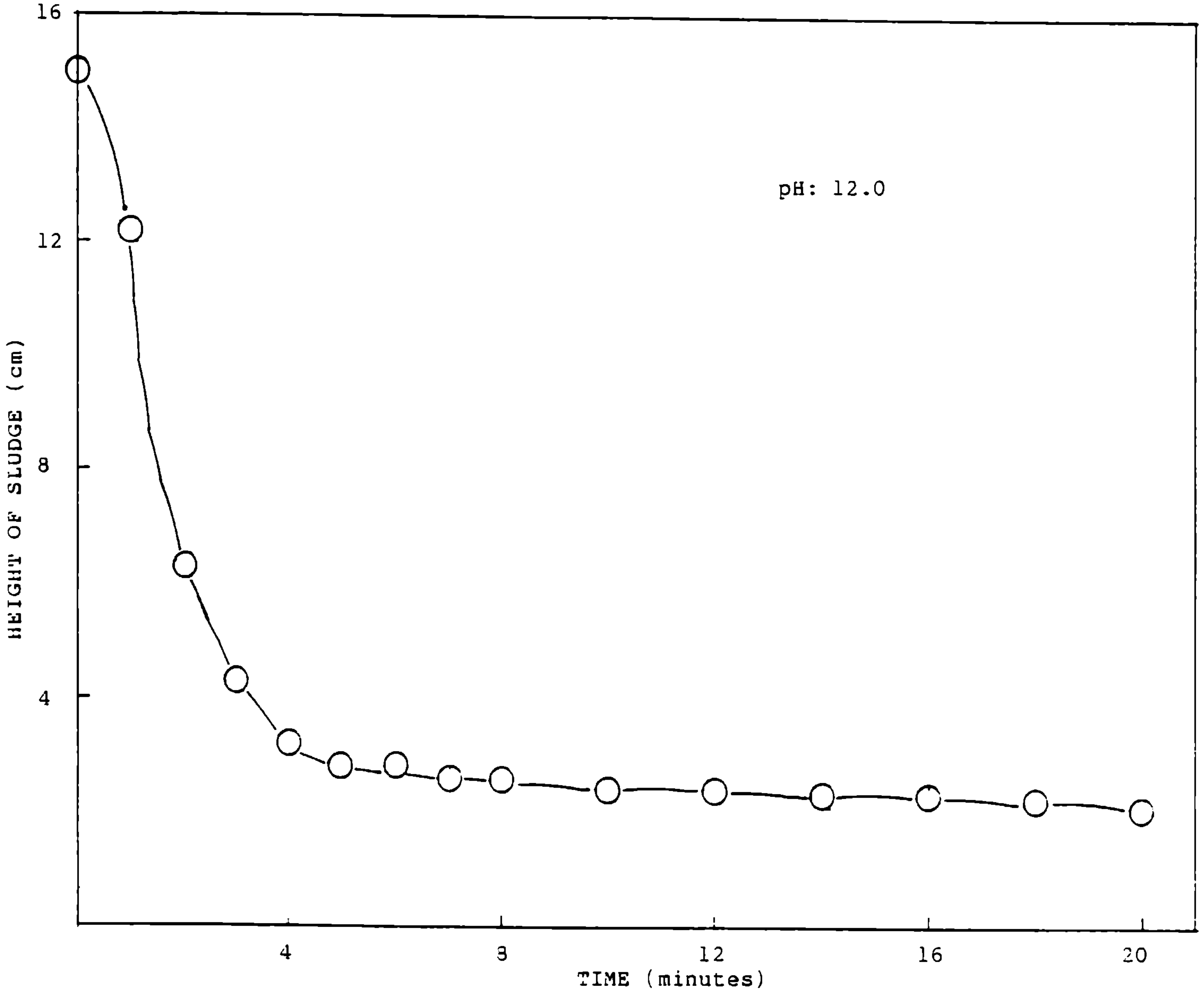


FIG.2B.18 SETTLEABILITY OF EFFLUENT COAGULATED WITH LIME.

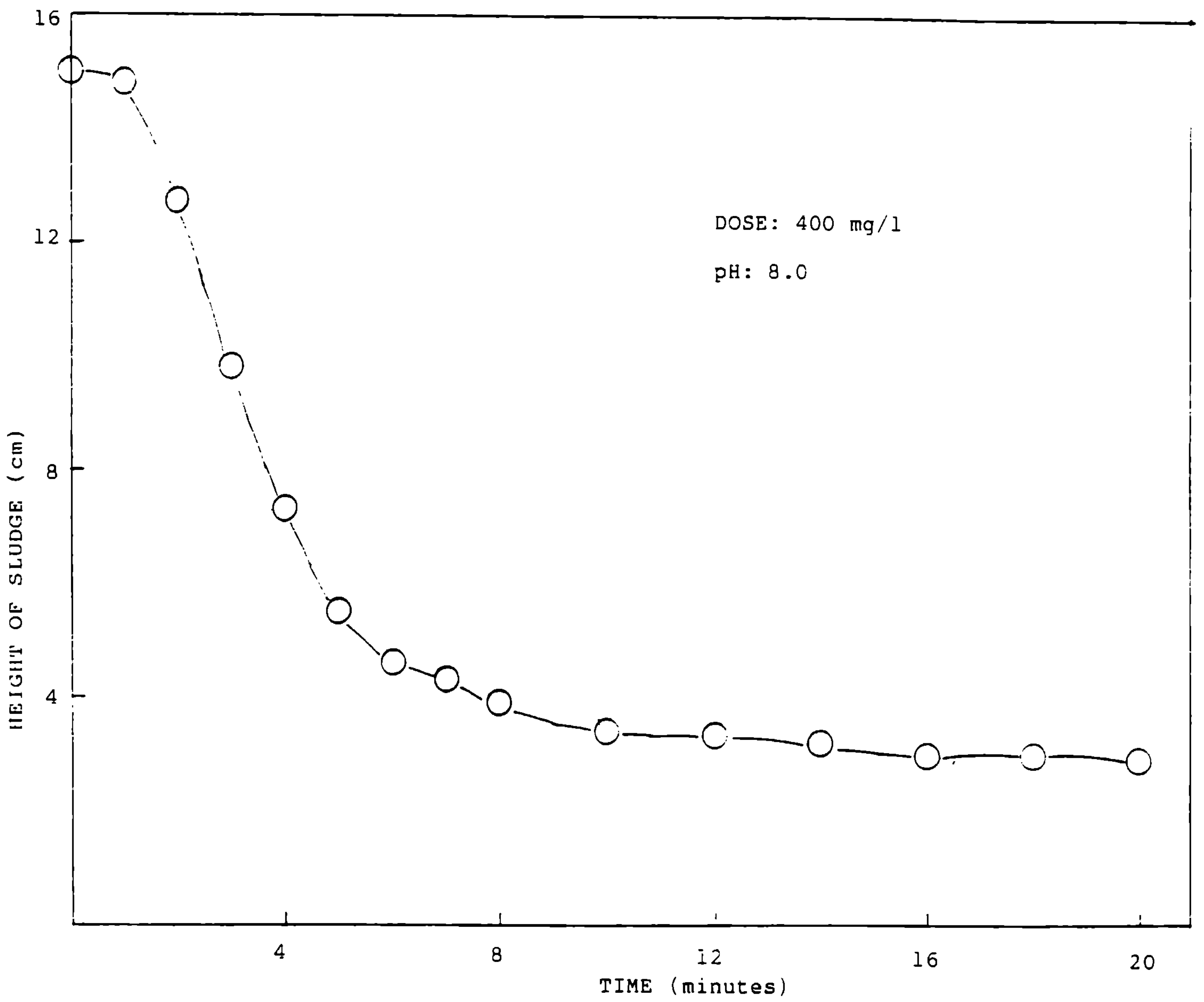


FIG.2B.19 SETTLEABILITY OF EFFLUENT COAGULATED WITH MAGNESIUM CHLORIDE

It is evident from the figures that the settling characteristics of the sludge formed by the coagulants are similar in nature. Most of the sludge settling occurred during the first 5 to 6 minutes. In the case of alum, ferric sulphate, ferric chloride and magnesium chloride, the compression of sludge was more gradual than for other coagulants.

The height of the sludge at the end of 20 minutes settling time for the effluent treated with aluminium chloride was 1.8 cm, the minimum sludge height obtained during the studies. This shows the ability of the sludge formed by aluminium chloride to get compressed better than the sludges formed by other coagulants. Aluminium chloride was followed by lime and ferrous chloride, the flocs formed by which could get compressed to 2.1 cms. Among the coagulants studied, alum and magnesium chloride showed the minimum sludge compression capacity. The less the sludge height, the less the volume of sludge generated in the coagulation process. The desludging losses in the clarification plant will be less if the volume of the sludge is kept at minimum (30).

2B.4 CONCLUSIONS

1. The optimum pH values for the most effective action of the coagulants, viz. alum, aluminium sulphate, ferrous sulphate, ferric sulphate, ferric chloride, ferrous chloride, aluminium chloride and magnesium chloride were determined. The optimum pH values were in the range 6.5-8.5. As for lime, the best results were obtained with a pH of 10.5.

2. Among the nine coagulants studied, aluminium chloride was found to be the most efficient for COD reduction, turbidity removal and ammoniacal nitrogen removal of latex concentration effluents.

3. The compressibility of the sludge produced by aluminium chloride is better than those of other coagulants tried in the treatment of latex concentration effluents.

REFERENCES

1. Ritchie, A.R., Proc. Soc. Water Treatment Exam., 5, 2, 81 (1956).

2. Camp, T.R., Trans. Am. Soc. Civil Engrs., 120 (1955).

3. Hudson, H.E. Jr., J. Am. Water Works Assoc., 49, 242 (1957).

4. Metcalf and Eddy Inc, Waste Water Engineering: Treatment, Disposal, Reuse, Tata McGraw Hill, New Delhi (1979).

5. Clark, J.W., Viessman, W., Jr. and Hammer, M.J., Water Supply and Pollution Control, Harper & Row (1977).

6. Shaw, D.J., Introduction to Colloid and Surface Chemistry, Butterworth, London (1966).

7. Stumm, W. and Morgan, J.J., Aquatic Chemistry, Wiley Interscience, New York (1970).

8. Arceivala, S.J., Wastewater Treatment and Disposal, Marcel

Dekker Inc., New York (1981).

9. Wastewater Treatment: A Course Manual, National Environmental Engineering Research Institute, Nagpur (1985).

10. Hagar, D.C. and Railly, P.B., J. Wat. Pollt. Cont. Fed., 42, 974 (1970).

11. Frisch, H.L., Jour. of Colloid Chemistry, 60, 4, 463 (1956).

12. Stumm, W. and Morgan, J.J., J. Am. Water Works Assoc. 54, 8 (1962).

13. Stumm, W. and O'Melia, C.R., J. Am. Water Works Assoc., 60, 514 (1968).

14. Fair, G.M., Geyer, J.C. and Okun, D.A., Water and Wastewater Engineering, Vol.2, Wiley, New York (1968).

15. Thomas, A.W., Colloid Chemistry, McGraw Hill, New York (1934).

16. Ramalho, R.S., Introduction to Wastewater Treatment Processes, Academic Press, New York (1977).

17. Weber, W.J. Jr., Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York (1974).

18. Painter, H.A., Wastewater Treatment Jour., p.352 (1957) (not in original).

19. Loehr, R., Agricultural Waste Management Problem, Processes and Approaches, Academic Press (1974).

20. Smith, J. Metal, Proc. Conf. on Application of New Concepts of Physical Chemical Wastewater Treatment, Vanderbilt University, Tennesse (1972) (not in original).

21. Weber, W.J., Proc. Conf. on Application of New Concepts of Physical Chemical Wastewater Treatment, Vanderbilt University, Tennesse (1972) (not in original).

22. Chattopadhyay, S.N., Arora, H.C. and Sharma, V.P., Ind. Jr. of Env. Hlth, 15, 3, 208 (1973).

23. Kothandaraman, V., Aboo, K.M. and Sastry, C.A., Ind. Jr. of Env. Hlth., 18, 2, 93 (1976).

24. Bhole, A.G. and Dhabadgaonkar, S.M., IAWPC Tech. Annual, 14, 52 (1987).

25. Rao, M.N. and Sastry, C.A., Env. Hlth., 10, 4, 265 (1968).

26. Kozirowski and Kucharski, J. Industrial Waste Disposal, Pergamon Press (1972).

27. Thakur, U.C., Dhabadgaonkar, S.M. and Deshpande, W.M., Ind. Jr. of Env. Hlth., 19, 1, 16 (1977).

28. Standard Methods for the Examination of Water and Wastewater, 16th edn., American Public Health Association (1985).

Chapter 3

POLYELECTROLYTES AS COAGULANT AND COAGULANT AID

3.1 INTRODUCTION

In recent years natural and synthetic organic polyelectrolytes have been increasingly used in the coagulation of suspended matter in water and wastewater. The polyelectrolytes are polymers with high molecular weight possessing such characteristics of simple electrolytes as electrical charges or ionisable groups. They are used in water and waste treatment either alone or together with metal coagulants to improve clarification, to reduce coagulant dosage required, or to allow an increased treatment rate without overloading existing facilities.

Coagulation basically involves two steps (a) neutralisation of the charge on the colloids and (b) agglomeration or flocculation of smaller particles into bigger particles. Black, Ruehrwein and others (1) have discussed the mechanism of coagulation of colloids caused by these long-chain compounds. According to them the polymers in water act as polyvalent ions. The polymer chain carries a very large number of ionic sites along its length. Coagulation takes place by the neutralisation of charge on the electronegative colloid particles by these ionised centres or by hydrogen bonding among the charged surfaces. Electrostatic cross-linking also binds the linear chains together. Riddick (2) has found that effective removal of colloids is obtained when the zeta potential of particles (15-25 mV) is reduced to zero plus or minus 5 mV. A polyelectrolyte aid is effective in causing large changes in the zeta potential of particles without appreciably changing either alkalinity or pH (3). Even if a polyelectrolyte is not very efficient in charge neutralisation, they may be very effective in formation of floc by what is known as "bridging". The polymer is adsorbed on the surface of the particle and bridges between them with the aid of free segments of the adsorbed polymer (1). Bridging results in the formation of large, strong, three dimensional and quickly settleable flocs.

The term polyelectrolyte was first coined by Fuoss (4) for those polymers which, by the action of an acid or alkali, can be converted into charged ions. The polyelectrolytes may be of natural or synthetic origin. Cohen (5) described the naturally occurring ones as biocolloids. The feature common to both natural and synthetic polyelectrolytes is the presence of recurring units containing ionisable groups in the molecule.

Depending on the charge of the recurring units the polyelectrolytes have been classified as cationic, anionic and non-ionic. An example of a cationic polyelectrolyte is polyvinylpyridinum butyl bromide which has a positively charged pyridine nucleas in each repeating unit. Sodium polymethacrylate is anionic, the negative charge originating from the dissociation of carboxyl groups. Gelatin belongs to the group of non-ionic polyelectrolytes. The non-ionic materials provide both positive and negative charges in solution.

The polyelectrolytes have a great role to play in the treatment of water and wastewater and in the abatement of water pollution. Yet, many a times, full benefits that can be achieved by the use of a polyelectrolyte, are not derived due to ignorance about certain practical considerations regarding their use (6). For example, some polyelectrolytes of proven value, are declared ineffective, just because some simple procedures, such as those required for making solutions of a polyelectrolyte are not followed, or the solution of the polyelectrolyte used is too concentrated to disperse in water or the mixing of the polyelectrolyte with process water is inadequate or the polyelectrolyte is subjected to vigorous agitation resulting in the shearing of its molecules or its correct dose is not applied at the correct point. The choice of a proper polyelectrolyte for a given application is of paramound importance.

The bacteria and colloidal matter present in natural waters generally carry negative charge. Hence, the cationic polyelectrolytes, which produce positively charged functional group on dissolution in water, are most suitable. If water contains only mineral suspended solids, cationic polyelectrolytes are found to be very effective as primary coagulants (7). If water contains both mineral and organic substances, a combination of inorganic coagulants such as alum or ferric chloride with cationic polyelectrolytes gives best results (8). Even for waters with mineral solids, a combination of alum with a cationic polyelectrolyte may prove to be more economical than any one coagulant (9,10) because the polyelectrolytes do not have great capacity for charge neutralisation due to their large molecules and small doses used.

If non-ionic polyelectrolytes are used, charge neutralisation has to be brought about solely by inorganic coagulants. The non-ionic polyelectrolyte serves as a bridge between neutralised particles (11). The combination generally results in excellent clarification. But the doses of non-ionic polymers required are generally ten times than those of cationic ones (12).

Anionic polymers have been found to be inefficient as primary coagulant for natural waters due to electrostatic repulsion between the colloids and the functional group obtained on dissolution of the polymer in water, having similar charges. However, for some industrial wastewaters containing positively charged colloids, the anionic polyelectrolytes would be most effective (6). They have also been used as "aid" in coagulation and filtration.

The higher the molecular weight of a polyelectrolyte, the more effective it is. Polyacrylamide which can be made cationic by special processes, gives best results at higher molecular weights (6). Non-ionic polyelectrolytes are found to be effective when molecular weight is greater than 2×10^6. This mainly applies to polyacrylamide.

The bridging mechanism basically depends on the molecular weight which determines the size and segments of the polymer formed on dissolution in water. It is on this account that even anionic polyacrylamide of high molecular weight is effective in coagulating waters containing negatively charged colloids (13). However, the dose required in such cases, may indeed be high.

The effectiveness of polyelectrolytes for various uses can be found out by suitable experimental procedures. However, jar test alone can give valuable information about the effectiveness of polyelectrolytes not only for coagulation but also for filtration and sludge conditioning. It can at least be used for indicating relative efficiency of various flocculants and possible range of effective doses (14).

Several studies have been carried out on the effectiveness of various polyelectrolytes, both natural and synthetic, for the treatment of natural water and industrial wastewater and sewage. Actually, seeds of certain plants have been used in water clarification since time immemorial. A paste made from the seed of *Strychnos potatorum* Linn commonly known as clearing nut or Nirmali seed precipitates suspended siliceous impurities in raw water (15). Subbaramiah and Sanjiv Rao (16) found from electrophoretic measurements that the paste carried a weak negative charge and attributed its coagulating properties to its strychnin and albumin content. Sen and Bulusu (17) have reported on the effect of Nirmali seed, alone and in conjunction with metal coagulants, on chemical coagulation of Jamuna River water. They concluded that the extract prepared from the seed showed promising results in the systems studied. Bulusu and Sharma (18) have confirmed these findings on a pilot plant using Jamuna River water having a turbidity between 300 and 3500 mg/l. Continued research in this field by CPHERI, Nagpur led to the development of natural polyelectrolytes namely CA3, CA4 and CA5. Bulusu et al. (19) reported that they produce excellent flocculation when added to clay suspensions in conjunction with aluminium and iron salts in dosages that are only a small fraction of those required for flocculation with metal salts. Pathak et al. (20) studied the effectiveness of CPHERI developed anionic polyelectrolytes CA11 and CA12 as coagulant aid in water treatment. Rao and Sastry (21) found that 2 mg/l of Nirmali seed extract reduce the alum dose by more than 50%. Bulusu and Pathak (22) found the seeds of Red Sorella to be very effective primary coagulant. Pandit (23) found both Maize-e and caustic starches in small doses effective as coagulant aids in conjunction with aluminium sulphate for water clarification with the additional advantage of rendering the water non-corrosive.

Tripathi et al. (24) established the anionic nature of Nirmali seed extract by I.R. spectral studies and found that eventhough it is very efficient in the coagulation--flocculation of hydrophobic colloids (such as clay turbidity), it is a poor flocculant in the case of hydrophilic colloids such as bacteria. Prasad and Jivendra (25) investigated the performance of Tamarindus indica seed extract as coagulant aid in water clarification and reported that it can reduce the alum dose by 50 per cent. Azharia and Dirar (26) reported the coagulating properties of powdered seeds of Moringa oleifera Lam, a traditional coagulant in the rural areas of Sudan. Vaidya and Bulusu (27) studied the effectiveness of chitosan as a coagulant and coagulant aid in water clarification and found it a potential candidate

Moore et al. (28) studied the effect of polyelectrolyte treatment on waste strength of snap and dry bean wastewaters and found Floculite 250 and chitosan very effective in COD and solids reduction. Karim (29) investigated the use of inorganic salts and polymers in the treatment of palm oil effluent. Prasad and Belsare (30) studied the effectiveness of polyacrylamide as a coagulant aid in water treatment and found that a relatively small concentration (0.1 ppm) of polyacrylamide could remove high turbidity (2500 ppm) to the acceptable level of 10 ppm and reduce half of the original amount of alum without any difference in the achievement of steady state. Sihorwala and Reddy (31) studied the use of synthetic polyelectrolytes and metal salts in the treatment of cotton textile waste.

No systematic study has been reported in literature on the use of natural and synthetic polyelectrolytes as coagulant and coagulant aid in the treatment of effluents from a natural rubber latex concentration unit. The purpose of the present study is to evaluate the effectiveness of four natural polyelectrolytes viz. starch, sodium alginate, tamarind seed powder and chitosan and two synthetic polyelectrolytes viz., a cationic polyacrylamide based one and the other an anionic polyamine based polyelectrolyte; as coagulant and coagulant aid in the treatment of effluents from a centrifuge latex concentration unit.

3.2 MATERIALS AND METHODS

The polyelectrolytes used for the study were:

a) Natural polyelectrolytes

1. Starch
2. Sodium alginate
3. Chitosan
4. Tamarind seed powder

b) Synthetic polyelectrolytes

1. Polyacrylamide based cationic polyelectrolyte
2. Polyamine based anionic polyelectrolyte.

Starch

Starches consist of two types of polysaccharides, linear chains of D-glucose units joined by α-D (1-4) linkages (amylose) and highly branched structures consisting of short chains of 20-25 units of the linear polysaccharide joined to each other by α-(1-6) glycosidic linkages (amylopectin). Usually amylopectin is the major component and has a much higher molecular weight, ranging upto 10^6. The amylose fraction has been reported superior to amylopectin or native starch in red-mud flocculation (32). Starches isolated from corn, wheat, sorghum, rice, potatoes and tapioca are all used to some degree as flocculants, but some work better with certain substrates than others.

Sodium alginate

This is also a polysaccharide based flocculant. Sodium alginate is produced from brown algae (sea weed) by alkaline extraction. Alginic acid is either a mixture of (1-4) - β-D mannuronic acid and of L-guluronic acid, or else is a copolymer of the two uronic acids.

Chitosan

This cationic polysaccharide is made from chitin, which is derived from crustacean shells. Chitin is a polysaccharide constituted of β-(1-4) 2 acetamido-2-deoxy-D-glucose units, some of them being deacetylated with alkali. This natural polymer that may be called poly-N-acetyl-D-glucosamine, can be considered a derivative of cellulose, where the C-2-hydroxyl groups are replaced by acetamido groups.

Tamarind seed powder

The seeds of Tamarindus indica exhibit coagulating properties. The ground seeds are sieved and a 0.1% solution is prepared by boiling.

Among the four natural polyelectrolytes studied; tapioca starch, sodium alginate and chitosan were obtained in the form of solution from commercial suppliers. Tamarind seed extract was prepared by boiling seed powder with water.

The synthetic polyelectrolytes were also obtained from commercial suppliers.

Cationic polyelectrolyte

This polyacrylamide based polyelectrolyte was obtained in the form of a viscous solution.

Anionic polyelectrolyte

This polyamine based polyelectrolyte also was available in the form of a viscous solution.

All the polyelectrolytes, both natural and synthetic were assessed for their effectiveness, both as a coagulant and coagulant aid in the treatment of latex concentration wastewaters. Their effectiveness as a coagulant was assessed in terms of turbidity removal, COD reduction, and ammoniacal nitrogen removal. The effect of pH on coagulation and sludge settling characteristics were also studied. All the polyelectrolytes were tested as coagulant aid in conjunction with three metal salts, viz., alum, ferric chloride and aluminium chloride. The efficiency of the polyelectrolytes as coagulant aid was assessed on the basis of their ability to reduce the metal coagulant dose.

The effluent samples were collected from a centrifuge rubber latex concentration unit situated in Central Kerala. The various parameters of the effluent were analysed using standard methods (33). The effluent characteristics are given in Table 3.1.

Coagulation experiments were carried out in Jar test apparatus provided with stirrers having speed regulator. Samples, one litre each were placed on a mixing pad and requisite additions were made. The contents were stirred rapidly at 100 rpm for 1 minute and then at a speed of 30 rpm for 15 minutes for flocculation. The beakers were then separated from the pad and allowed to settle for 30 minutes. The supernatants were siphoned off for the estimation of pH, COD, turbidity and ammoniacal nitrogen.

TABLE 3.1

EFFLUENT CHARACTERISTICS

Parameter	Sample 1	Sample 2	Sample 3	Sample 4
pH	4.3	3.9	4.0	2.9
Turbidity, NTU	490	2100	1230	680
COD, mg/l	1170	8080	5790	10700
Ammoniacal nitrogen, mg/l	570	750	590	630

a) Polyelectrolytes as Primary Coagulant

The optimum pH for the effective coagulation of each of the polyelectrolytes was determined using the jar test apparatus. The pH of the samples were brought to optimum levels by adding sodium hydroxide (0.1 N) before carrying out coagulation studies. Four different dosages of the polyelectrolytes, viz., 2 mg/l, 4 mg/l, 6 mg/l and 8 mg/l were tried.

b) Sludge Settling Characteristics

The sludge settling characteristics were studied by adding optimum dosage of polyelectrolyte and adjusting the pH to the optimum value of the effluent samples taken in a 100 ml measuring cylinder. The contents of the measuring cylinder were mixed well for 3 to 4 minutes. The rate of settling of the floc formed was measured by noting the position of sludge at regular interval until further settling is negligible.

c) Polyelectrolytes as Coagulant Aid

The optimum dosage of each of the three metal coagulants, alum, ferric chloride and aluminium chloride, was estimated by jar test. The corresponding pH values were also noted.

Preliminary experiments were carried out to get an idea of the range of the dosage of polyelectrolyte required and also the metal coagulant dose which can be reduced. After adding the reduced quantity of the coagulant dose (say 50% of the optimum dose determined in (a) above), the polyelectrolyte in varying doses was added to latex concentration effluent samples taken in beakers. The jar test was carried out and pH and turbidity of the supernatants were measured.

3.3 RESULTS AND DISCUSSION

a) Effect of pH on Coagulation Efficiency

To determine the optimum pH of coagulation for the four natural polyelectrolytes, the pH of the effluent samples was varied between 4 and 11. For the two synthetic polyelectrolytes, the pH was varied between 4 and 12. The coagulation efficiency of all the polyelectrolytes was estimated in terms of per cent turbidity removal achieved at a polyelectrolyte dosage of 4 mg/l.

1. Starch

Effect of pH on the coagulation efficiency of starch is shown in Fig.3.1.

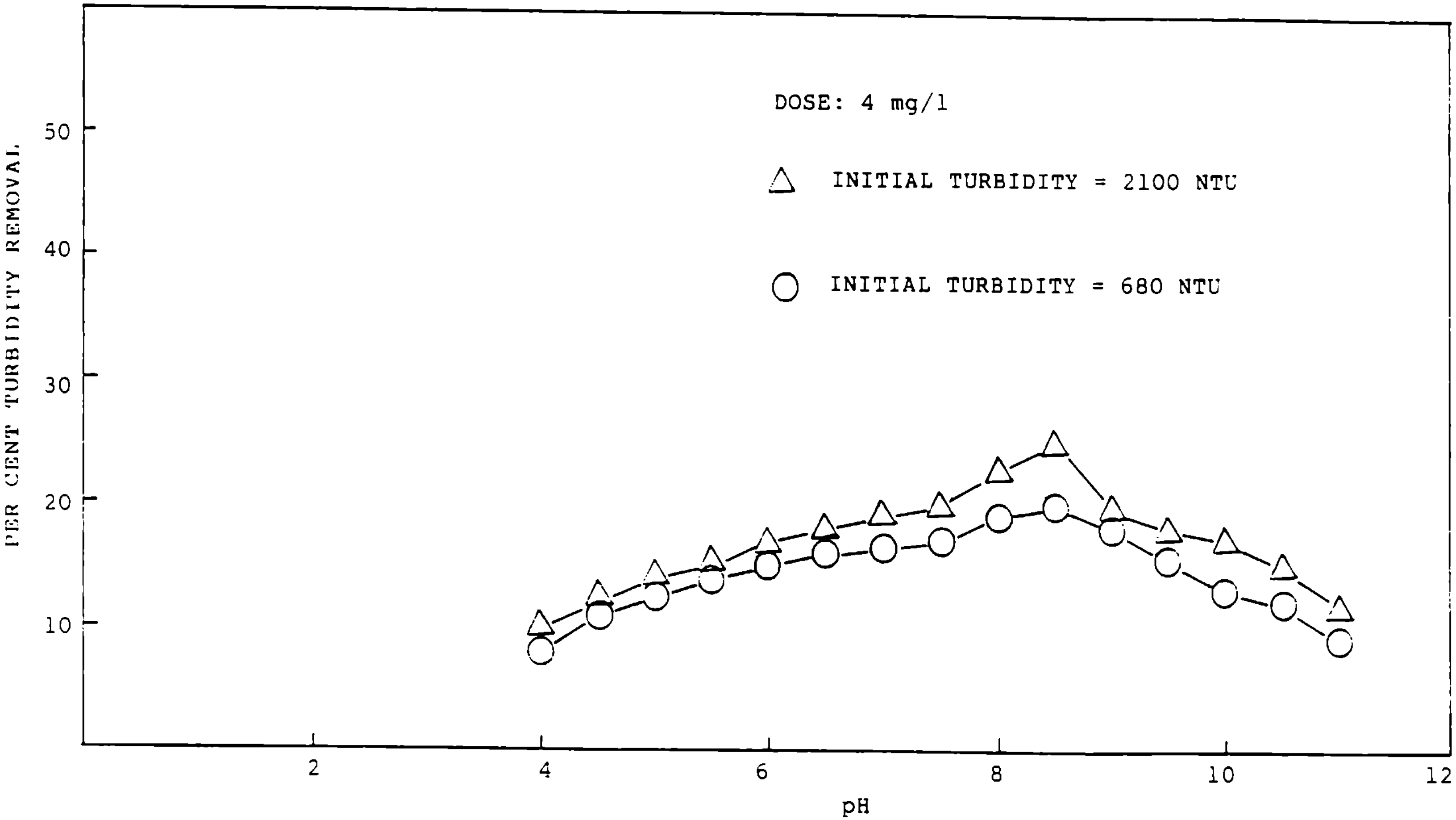


FIG. 3.1: EFFECT OF pH ON COAGULATION BY STARCH

As the pH increased from 4 to 8.5, there was a gradual increase in the per cent turbidity removal achieved by starch. The maximum turbidity removal was achieved at a pH of 8.5. Beyond this pH value, the per cent turbidity removal achieved showed a decreasing trend. Among the two samples used for the study, the one with an initial turbidity of 2100 NTU was found to be more susceptible to turbidity removal by starch compared to the sample with initial turbidity, 850 NTU.

2. Sodium alginate

The pH dependence of sodium alginate coagulant is illustrated in Fig.3.2.

The optimum pH for coagulation by sodium alginate was found to be 9.5. At this pH, the removal efficiency achieved was 29 per cent for both the initial turbidity values 2100 NTU and 680 NTU.

3. Chitosan

The variation of the coagulation efficiency of chitosan with pH is shown in Fig.3.3. The results obtained for the initial turbidity values, 2100 NTU and 680 NTU were

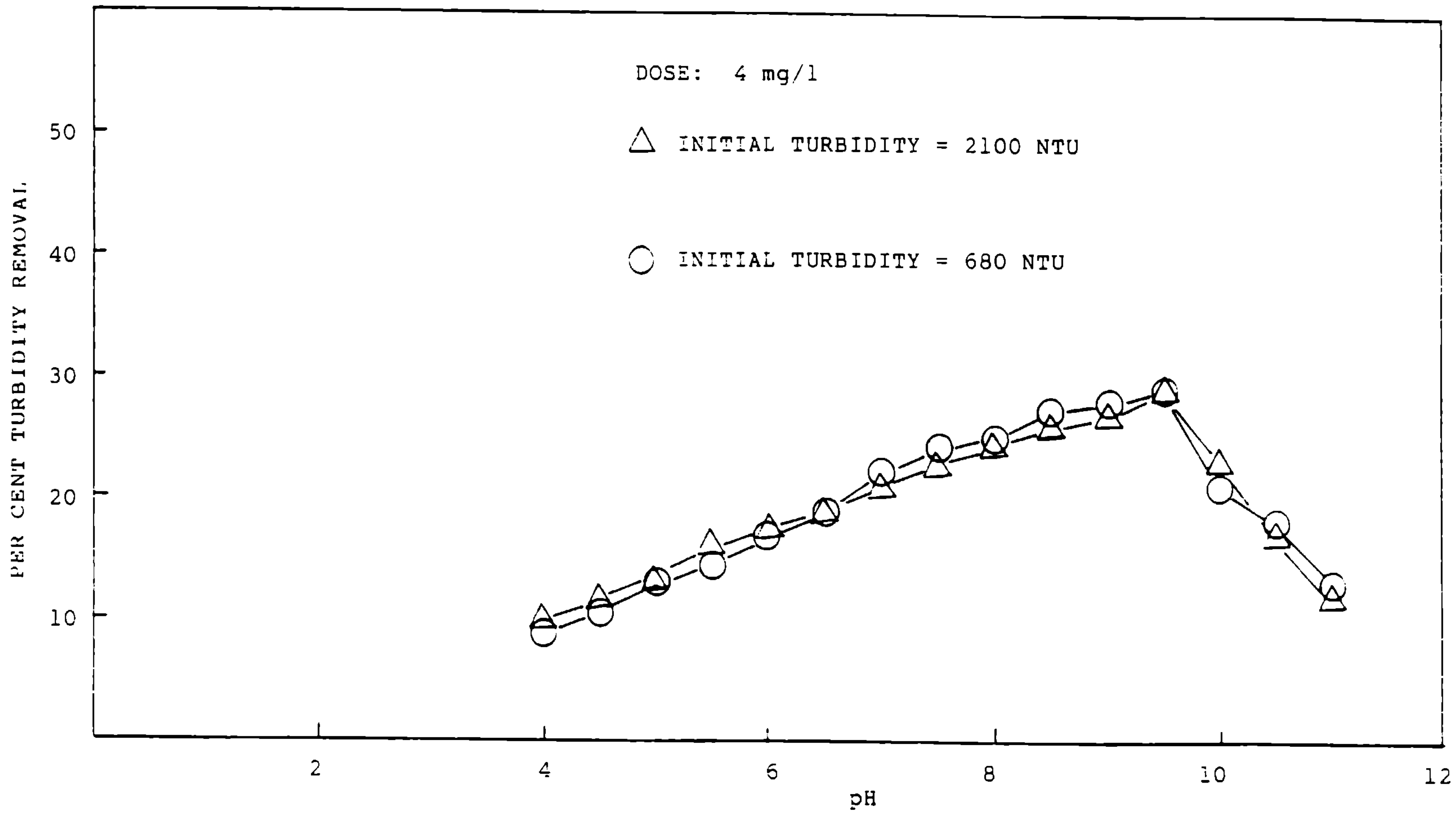


FIG.3.2: EFFECT OF pH ON COAGULATION BY SODIUM ALGINATE

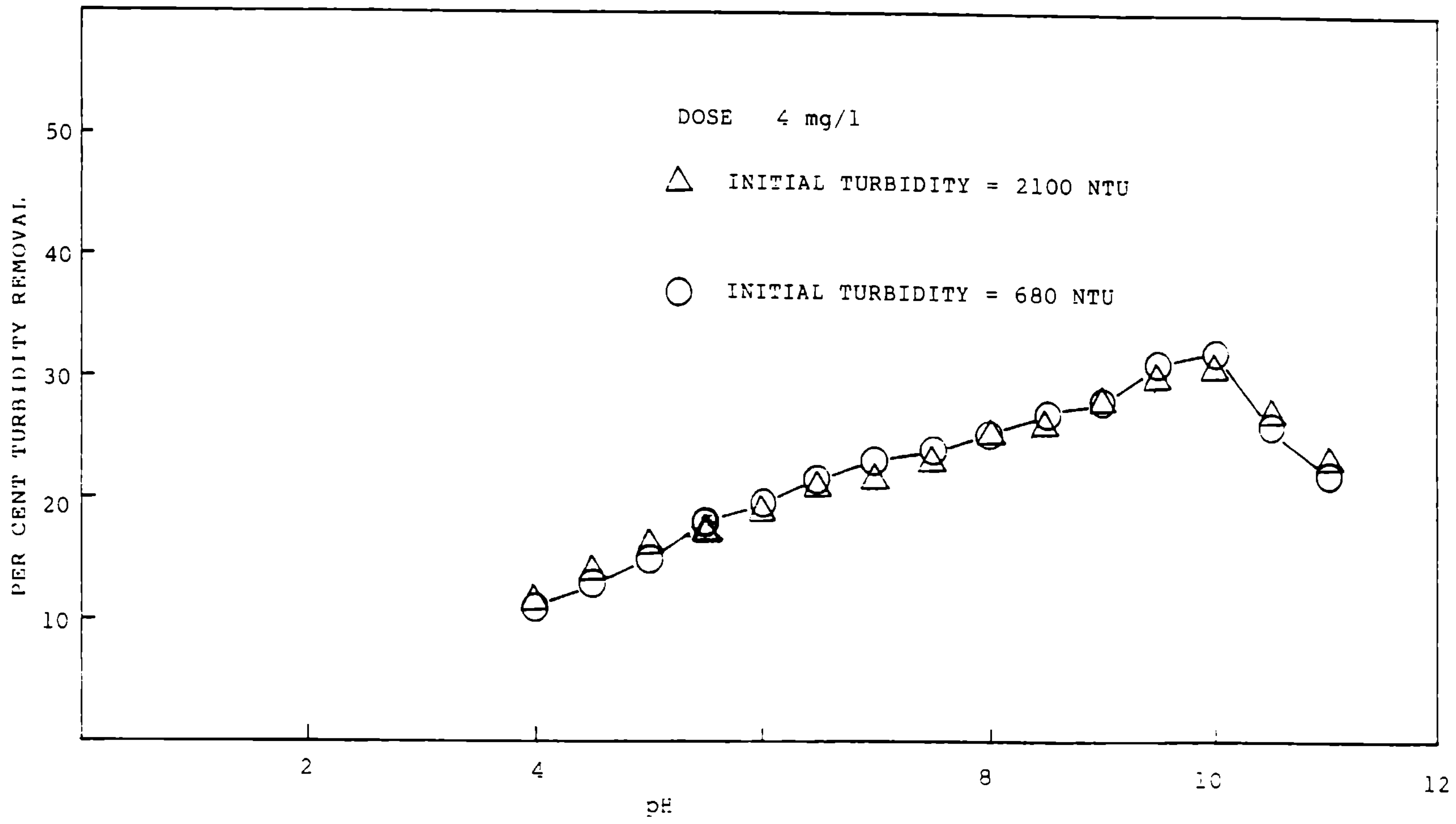


FIG.3.3: EFFECT OF pH ON COAGULATION BY CHITOSAN

very close to each other. The optimum pH of chitosan for the effective coagulation of latex concentration wastewaters was found to be 10.0.

4. Tamarind seed powder

As for *Tamarindus indica* seed powder, the effect of pH on coagulation efficiency is shown in Fig.3.4. The optimum pH value was found to be 7.5. At this pH value, the removal efficiencies achieved were 30 per cent and 31 per cent respectively for the initial turbidity values of 2100 NTU and 680 NTU. As the pH increased from 4.0 to 7.5, there was a steady increase in the turbidity removal efficiencies.

5. Polyacrylamide based synthetic polyelectrolyte

For the polyacrylamide based synthetic polyelectrolyte, the maximum turbidity removal efficiency was obtained at a pH of 10.5 as shown in Fig.3.5. At this pH value, a turbidity removal efficiency of 25 per cent was obtained for the sample with initial turbidity of 2100 NTU; while the removal efficiency obtained for the sample with initial turbidity 680 NTU was 23 per cent.

6. Polyamine based synthetic polyelectrolyte

The effect of pH on the coagulation efficiency of polyamine based anionic polyelectrolyte is illustrated in

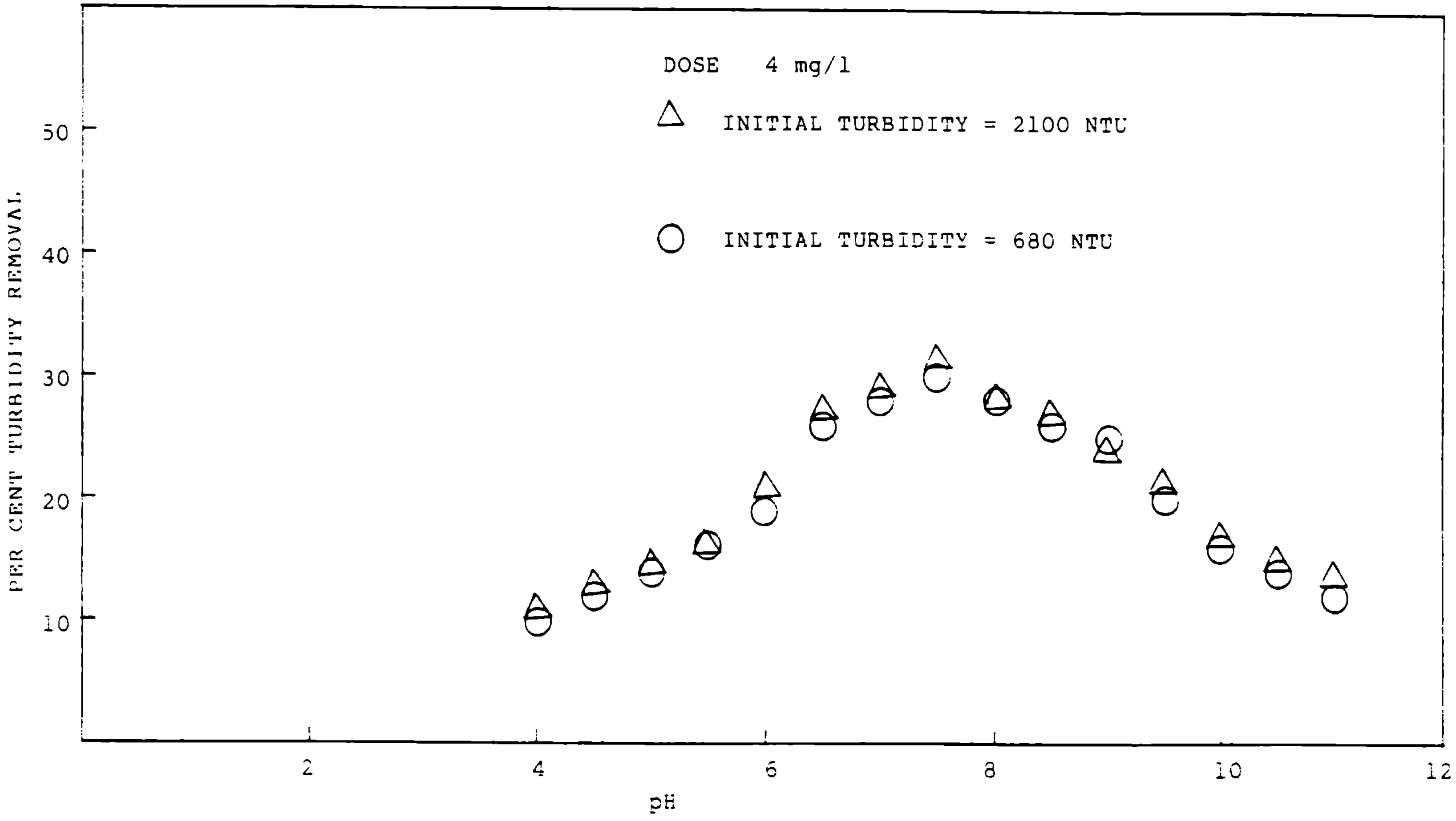


FIG.3.4: EFFECT OF pH ON COAGULATION BY TAMARIND SEED POWDER

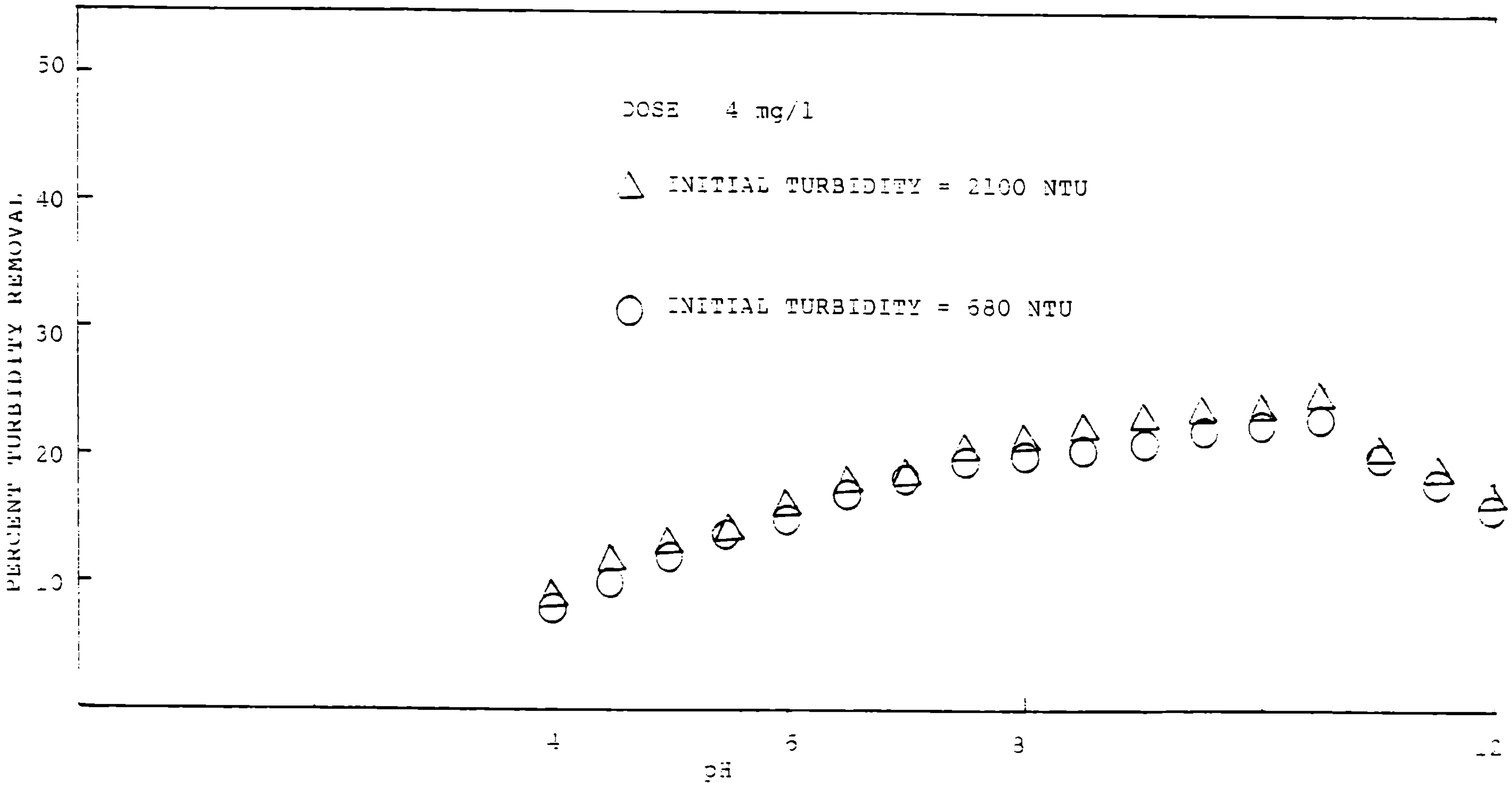


FIG.3.5: EFFECT OF pH ON COAGULATION BY CATIONIC SYNTHETIC POLYELECTROLYTE

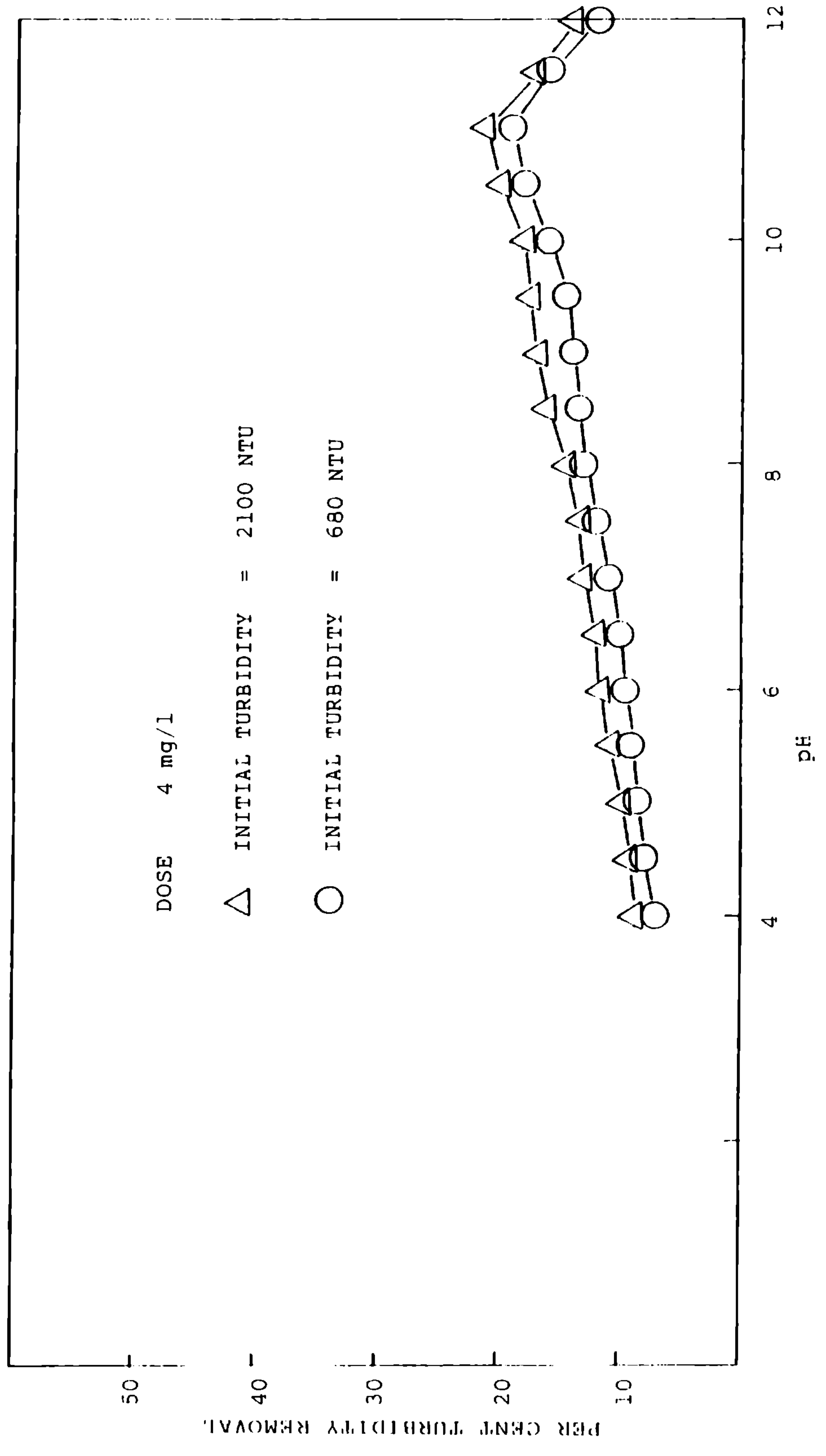


FIG.3.6: EFFECT OF pH ON COAGULATION BY ANIONIC SYNTHETIC POLYELECTROLYTE

Fig.3.6. The maximum turbidity removal efficiency was obtained at a pH of 11.0. The removal efficiencies achieved were 21 per cent and 19 per cent respectively for the initial turbidity values, 2100 NTU and 680 NTU.

The optimum pH values for the effective coagulation action of each of the polyelectrolytes are listed in Table 3.2.

b) Effectiveness of Polyelectrolytes in COD Reduction Turbidity Removal and Ammoniacal Nitrogen Removal

The effectiveness of the polyelectrolytes was assessed in terms of their ability to remove COD, turbidity and ammoniacal nitrogen from centrifuge latex concentration wastewaters. Four polyelectrolyte dosages; 2 mg/l, 4 mg/l, 6 mg/l and 8 mg/l were tried on each of the four effluent samples after adjusting the pH to optimum values. The per cent COD reduction, turbidity removal and ammoniacal nitrogen removal obtained for each of the polyelectrolytes are tabulated in Tables 3.3 to 3.8.

1. Starch

For starch, the maximum COD reduction ranging from 32 to 38 per cent was obtained with a dosage of 8 mg/l.

TABLE 3.2

OPTIMUM pH FOR THE EFFECTIVE ACTION OF POLYELECTROLYTES

Sl.No.	Polyelectrolyte	Optimum pH
1.	Starch	8.5
2.	Sodium alginate	9.5
3.	Chitosan	10.0
4.	Tamarind seed powder	7.5
5.	Cationic synthetic polyelectrolyte	10.5
6.	Anionic synthetic polyelectrolyte	11.0

TABLE 3.3

EFFICIENCY OF STARCH IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent ammonical nitrogen removal			
	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l
1.	29	28	29	37	21	23	24	26	14	16	17	18
2.	30	31	28	38	19	20	22	24	12	14	16	17
3.	29	31	27	35	17	25	24	25	14	16	16	18
4.	27	29	30	32	21	20	23	24	16	17	17	18

The highest per cent COD reduction, 38 per cent was obtained for the raw effluent COD concentration of 8080 mg/l. The maximum per cent turbidity removal and ammoniacal nitrogen removal were also obtained with the starch dosage of 8 mg/l. While the maximum turbidity removal of 26 per cent was obtained for the effluent sample-1 with an initial turbidity of 490 NTU, the maximum ammoniacal nitrogen removal of 18 per cent was obtained for the effluent samples, 1, 3 and 4 which had initial ammoniacal nitrogen content of 570 mg/l, 590 mg/l and 630 mg/l respectively.

The coagulation action of starch may be attributed to the "bridging" action brought about by the amylopectin fraction which has a very high molecular weight ranging upto 10^6 (23). In effect, starch may be considered as a non-ionic polyelectrolyte which does not ionise in solution and hence does not neutralise the charge on the colloidal particles.

2. Sodium alginate

In the case of sodium alginate, the optimum dosage for COD reduction, turbidity removal and ammoniacal nitrogen removal was found to be 4 mg/l. The per cent COD

TABLE 3.4

EFFICIENCY OF SODIUM ALGINATE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l
1.	40	43	37	38	26	28	28	22	16	20	16	14
2.	37	42	39	35	25	29	27	20	17	19	15	13
3.	39	43	35	33	23	29	25	19	18	20	17	15
4.	38	41	37	32	22	27	21	22	18	21	17	14

reduction obtained with this dosage was in the range of 41-43 and the maximum removal efficiency was obtained for the influent COD concentrations, 1170 mg/l and 5790 mg/l. While the per cent turbidity removal at the optimum dosage varied between 27 and 29, the per cent ammoniacal nitrogen removal varied between 19 and 21.

Alginic acid is either a mixture of (1-4)-β-D-mannuronic acid or of L-guluronic acid, or else is a copolymer of the two uronic acids (32) which contain the -COOH group. At pH higher than 3, -COOH will ionize as $-COO^-$ (24) which shows that sodium alginate or alginic acid is an anionic polyelectrolyte of high molecular weight. Due to its anionic nature, sodium alginate is ineffective in neutralising the charge of colloidal particles. The coagulation action can be attributed to the bridging mechanism which basically depends on the molecular weight which in turn determines the size and segments of the polymer formed on dissolution in water (6).

3. Chitosan

For chitosan, the optimum dosage was found to be 2 mg/l for COD reduction, turbidity removal and ammoniacal nitrogen removal. At the optimum dosage of 2 mg/l, the COD removal efficiencies varied between 49 and 52 per cent and

TABLE 3.5

EFFICIENCY OF CHITOSAN IN COD REDUCTION, TURBIDITY AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l
1.	51	47	46	42	34	30	29	27	22	19	17	15
2.	52	44	46	47	35	32	31	26	21	20	16	14
3.	49	45	44	42	37	21	28	25	22	20	17	15
4.	50	42	41	42	34	28	27	24	23	18	17	14

the maximum reduction of 52 per cent was obtained for the influent COD concentration of 8080 mg/l. As for turbidity removal, efficiencies ranging from 34 to 37 per cent were obtained for all the samples at the optimum dosage of 2 mg/l. At the optimum dosage, the ammoniacal nitrogen removal efficiency varied between 21 and 23 per cent.

Chitosan solution is generally prepared in acetic acid. In the chitosan solution in acetic acid, $-NH_3^+$ groups are responsible for the polyelectrolyte behaviour while CH_3COO^- counterions are free to move (27). At relatively high concentrations, the polyelectrolyte molecules overlap each other and the counterions are not allowed to leave the molecular domain. As dilution increases, and the counter ions diffuse in regions where the polymer molecules are absent, the total electric charge on each polymer chain increases and forces the molecule to extend itself to a large configuration. The large configuration results in bridging which describes the destabilization mechanism where molecules if added chemically attach on to two or more colloids causing aggregation. The polymer is useful for aggregating and binding together negatively charged aggregates into agglomerates that resist redispersion.

4. Tamarind seed powder

In the case of Tamarindus indica seed powder, the optimum dosage for COD reduction, turbidity removal and ammoniacal nitrogen removal was found to be 4 mg/l. The per cent COD reduction obtained with this dosage was in the range of 45-48 per cent and the maximum removal efficiency of 48 per cent was obtained for an initial COD concentration of 8080 mg/l. While the per cent turbidity removal for the optimum dosage of 4 mg/l varied between 31 and 34 per cent, the ammoniacal nitrogen removal efficiencies varied between 18 and 22 per cent.

The polyelectrolyte behaviour of tarmarind seed powder may be attributed to the fact that its molecules contain -COOH group which dissociates into $-COO^-$ at pH higher than 3 (24). This shows that the tamarind seed extract has anionic behaviour. Hence the coagulation action of tamarind seed powder should be due to the bridging mechanism.

5. Polyacrylamide based cationic polyelectrolyte

The effectiveness of the cationic polyelectrolyte in treating the effluent samples from a centrifuge latex

TABLE 3.6

EFFICIENCY OF TAMARIND SEED POWDER IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity reduction				Percent Ammoniacal Nitrogen removal			
	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l
1.	44	47	43	41	28	31	27	26	16	19	14	13
2.	45	48	44	42	30	32	26	24	17	18	16	15
3.	41	45	41	39	27	34	25	25	16	20	15	14
4.	42	46	42	40	26	31	24	23	18	22	15	13

TABLE 3.7

EFFICIENCY OF CATIONIC SYNTHETIC POLYELECTROLYTE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity reduction				Percent Ammoniacal nitrogen removal			
	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l
1.	32	30	29	27	23	21	23	21	15	12	10	9
2.	30	29	28	26	24	22	22	20	14	13	12	11
3.	34	31	29	28	25	24	23	21	15	12	11	10
4.	31	29	26	25	23	23	21	21	16	14	11	9

concentration unit was most optimum at a dosage of 2 mg/l. With this dosage, maximum reduction could be achieved for COD, turbidity and ammoniacal nitrogen. The COD reduction efficiency obtained at the optimum dosage varied between 30 and 34 per cent. The turbidity removal efficiencies and ammoniacal nitrogen removal efficiencies achieved at the optimum dosage were in the ranges of 24-28 per cent and 14-16 per cent respectively.

Polyacrylamide is classified as a non-ionic polyelectrolyte. It is made cationic by special processes (6) and gives best results at high molecular weights. The coagulation action of the cationic polyelectrolyte solution used in the study may be attributed to charge neutralisation and bridging action. The COD removal efficiency, turbidity removal efficiency and ammoniacal nitrogen removal efficiency achieved by the cationic polyelectrolyte was found to be less than that achieved by starch, sodium alginate and tamarind seed powder which are either non-ionic or anionic in nature. This may be due to the inadequate positive charge imparted to the polyacrylamide molecule by the special processes.

6. Polyamine based anionic polyelectrolyte

In the case of polyamine based anionic polyelectrolyte, the optimum dosage for COD reduction, turbidity removal and ammoniacal nitrogen removal was found to be 4 mg/l. The per cent COD reduction obtained with this dosage was in the range of 24-26 and the maximum removal of 26 per cent was obtained for the influent COD concentration of 5790 mg/l. While the per cent turbidity removal at the optimum dosage varied between 19 and 21 per cent, the per cent ammoniacal nitrogen removal varied between 10 and 13.

Polyelectrolytes based on polyamine are generally cationic polymers of low to medium molecular weight (34). The polyamine based used in the study should have been made anionic by special techniques (6). The coagulation action of the anionic polyelectrolyte can be attributed to bridging mechanism.

The optimum doságes for the most effective coagulation action of each of the six polyelectrolytes studied and the maximum removal efficiencies obtained for COD, turbidity and ammoniacal nitrogen are summarised in Table 3.9.

TABLE 3.8

EFFICIENCY OF ANIONIC SYNTHETIC POLYELECTROLYTE IN COD REDUCTION, TURBIDITY REMOVAL AND AMMONIACAL NITROGEN REMOVAL

Sample No.	Percent COD reduction				Percent Turbidity removal				Percent Ammoniacal nitrogen removal			
	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l
1.	22	25	23	21	17	20	18	16	10	12	10	9
2.	20	24	24	22	15	19	18	17	9	10	9	8
3.	23	26	21	20	18	21	16	15	10	12	11	9
4.	22	24	23	21	17	19	18	16	11	13	10	8

TABLE 3.9

COMPARISON OF VARIOUS POLYELECTROLYTES AS PRIMARY COAGULANTS

Sl. No.	Polyelectrolyte	Optimum dosage mg/l			Maximum removal efficiency achieved		
		COD reduction	Turbidity removal	Ammoniacal nitrogen removal	COD reduction	Turbidity removal	Ammoniacal nitrogen removal
1.	Starch	8	8	8	38	26	18
2.	Sodium alginate	4	4	4	43	29	21
3.	Chitosan	2	2	2	52	37	23
4.	Tamarind Seed Powder	4	4	4	48	34	22
5.	Polyacrilamide based cationic polyelectrolyte	2	2	2	34	25	16
6.	Polyamine based anionic polyelectrolyte	4	4	4	26	21	13

From Table 3.9, it is evident that chitosan is the most effective polyelectrolyte among the six polyelectrolytes studied as primary coagulants in respect of COD reduction, turbidity removal and ammoniacal nitrogen removal. Chitosan is followed by Tamarind seed powder, sodium alginate, starch, polyacrylamide based cationic polyelectrolyte and polyamine based anionic polyelectrolyte in that order for COD removal, turbidity reduction and ammoniacal nitrogen removal. The study clearly shows that the natural polyelectrolytes perform better than the synthetic polyelectrolytes in the treatment of effluents from a centrifuge rubber latex concentration unit.

c) Settling Characteristics of Sludge

The settling characteristics of the flocs formed by each of the polyelectrolyte are plotted in Figures 3.7 to 3.12. It is evident from the figures that the settling characteristics of the sludge formed by the polyelectrolytes are more or less similar in nature. Most of the sludge settling occured during the first 5 to 6 minutes.

The height of the sludge at the end of 20 minutes was 1.0 cm for the effluent treated with chitosan, the

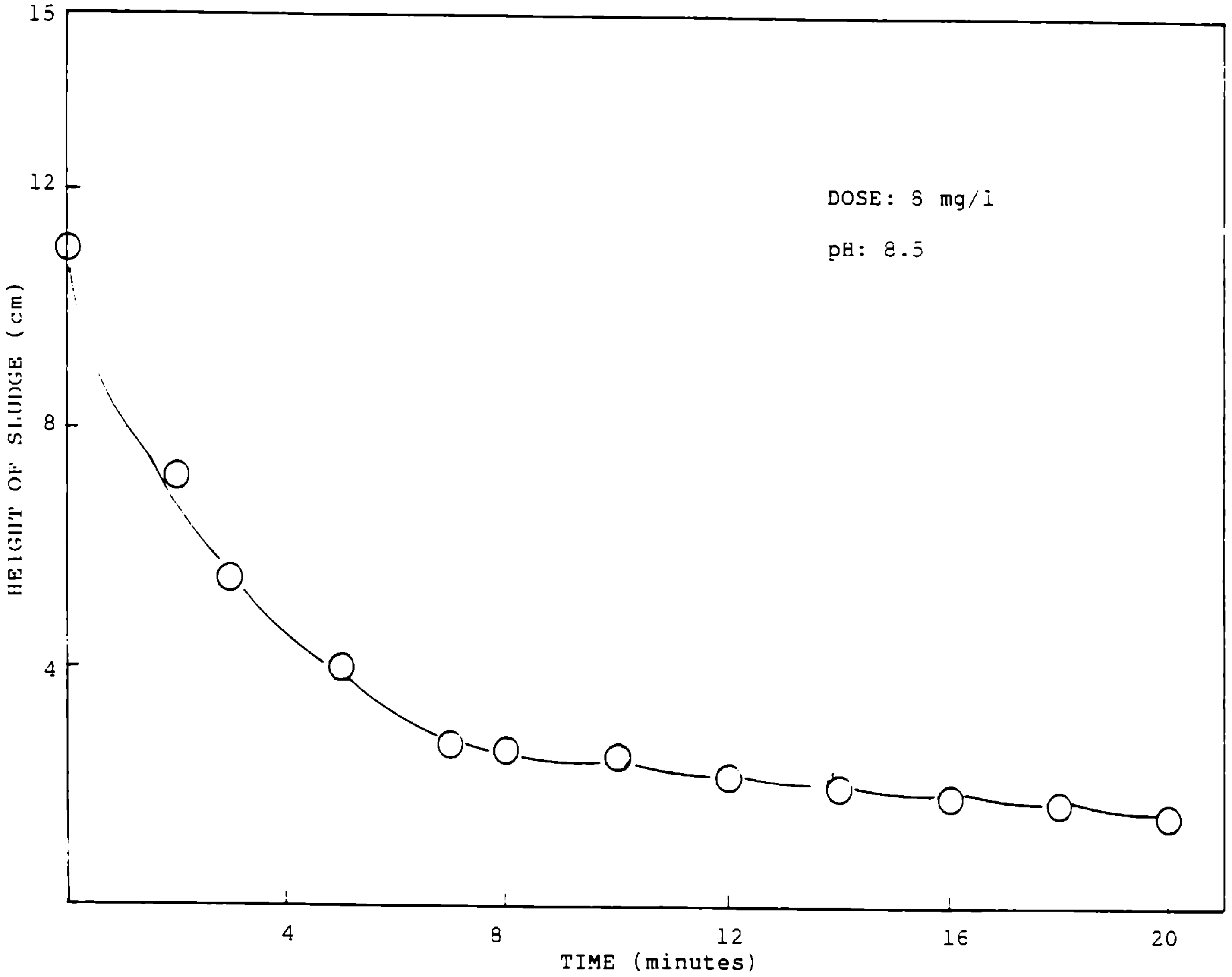


FIG.3.7 SETTLING CHARACTERISTICS OF SLUDGE FORMED BY STARCH.

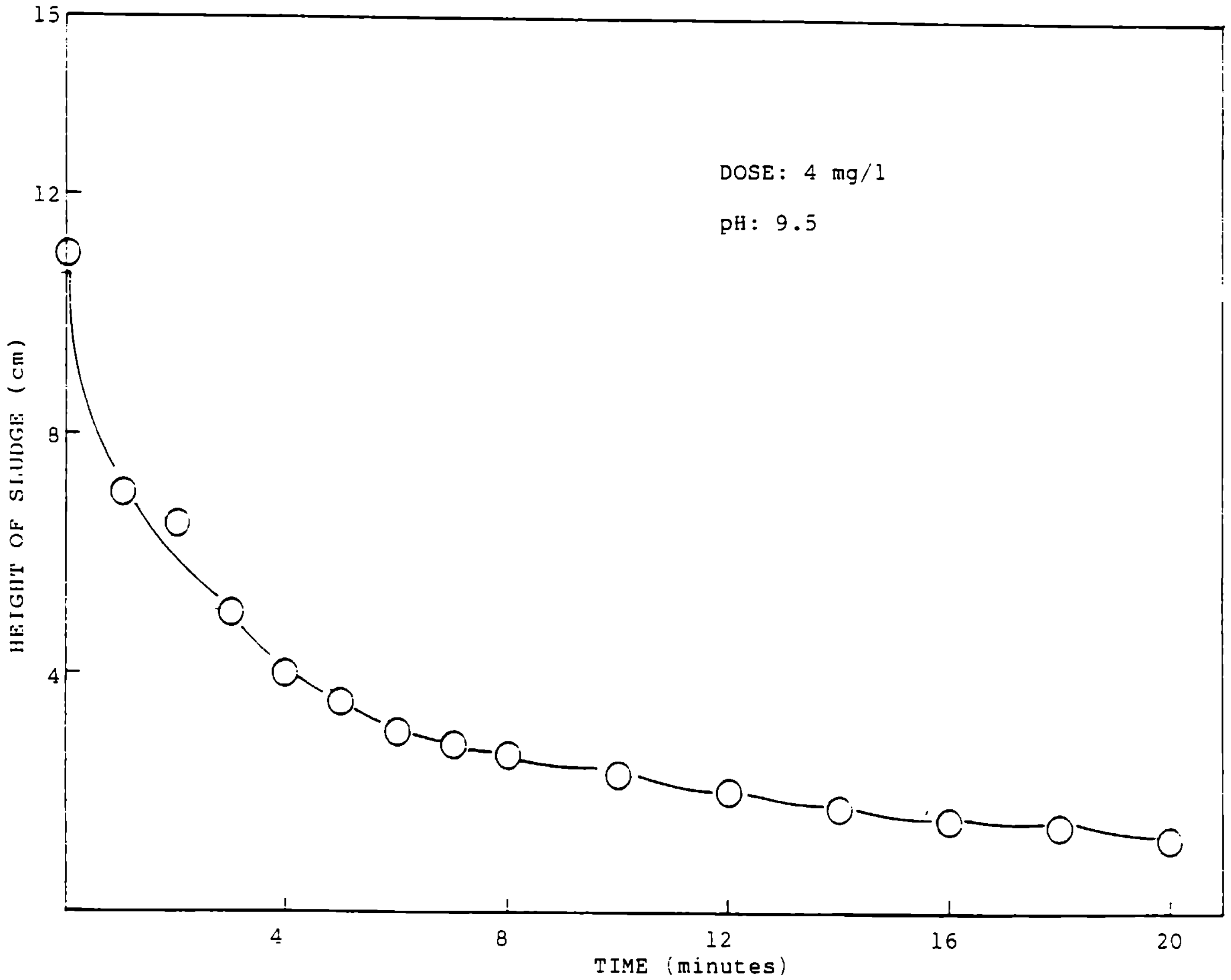


FIG.3.8 SETTLING CHARACTERISTICS OF SLUDGE FORMED BY SODIUM ALGINATE.

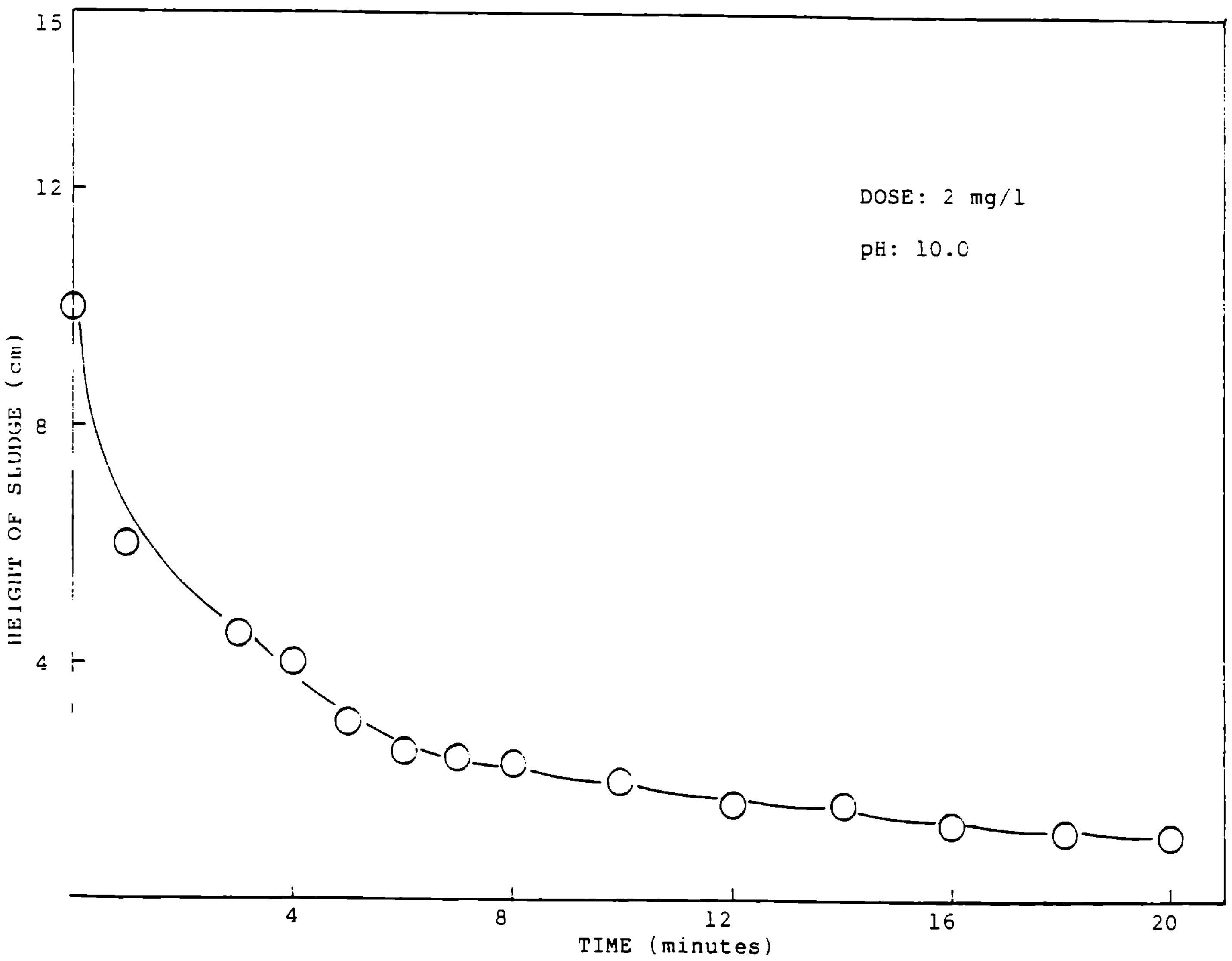


FIG.3.9 SETTLING CHARACTERISTICS OF SLUDGE FORMED BY CHITOSAN

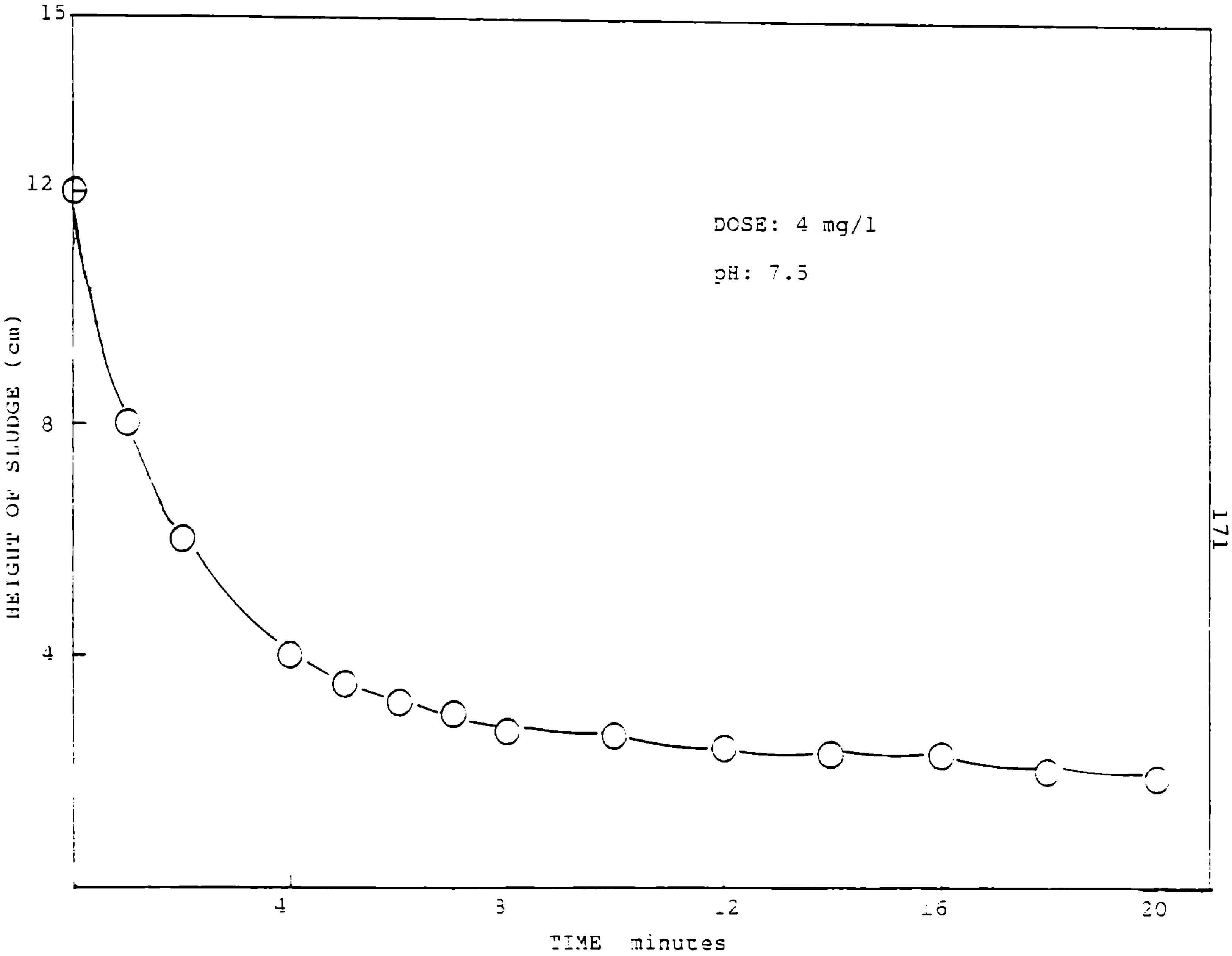


FIG.3.10 SETTLING CHARACTERISTICS OF SLUDGE FORMED BY TAMARIND SEED POWDER

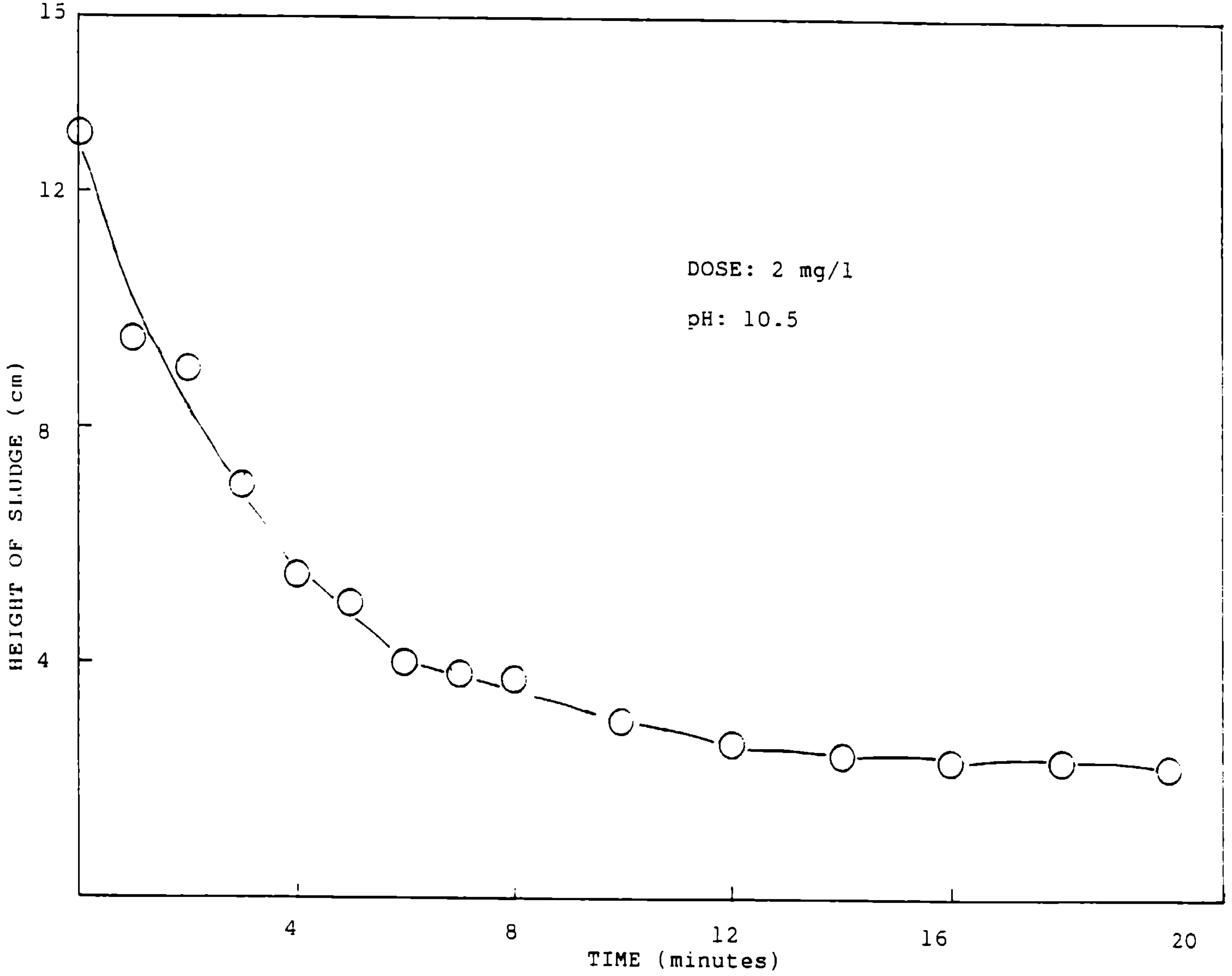


FIG.3.11 SETTLING CHARACTERISTICS OF SLUDGE FORMED BY POLYACRYLAMIDE BASED CATIONIC POLYELECTROLYTE

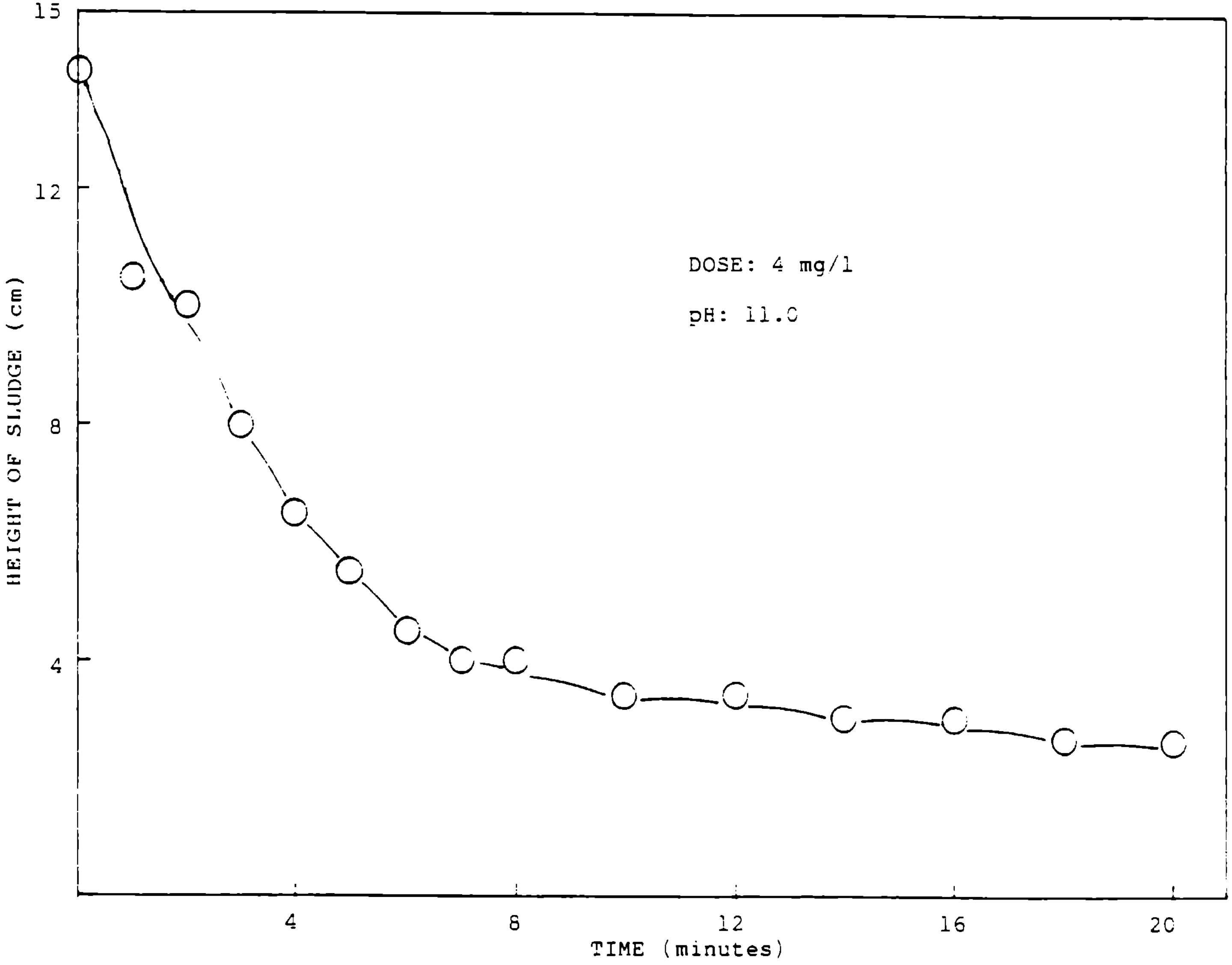


FIG.3.12 SETTLING CHARACTERISTICS OF SLUDGE FORMED BY POLYAMINE BASED ANIONIC POLYELECTROLYTE

minimum sludge height obtained during the studies. This shows that the sludge formed by chitosan gets compessed better than the sludges formed by other polyelectrolytes. Chitosan was followed by sodium alginate, starch, tamarind seed powder, cationic synthetic polyelectrolyte and anionic synthetic polyelectrolyte in that order in sludge compression ability. Compared to the metal coagulants studied in chapter 2, the polyelectrolytes have shown better sludge compression ability. Among the metal coagulants, aluminium chloride which showed the best sludge settling characteristics could compress the sludge only to 1.8 cm at the end of 20 minutes. The three natural polyelectrolytes, viz., chitosan, sodium alginate and starch performed better than aluminium chloride in sludge compression.

d) Polyelectrolytes as Coagulant Aid

The results obtained with all the six polyelectrolytes are given in Table 3.10 to 3.15. It is apparent from the tables that small quantities of polyelectrolytes effectively reduce the metal coagulant dosage.

Starch solution could bring down the dosage of alum, ferric chloride and aluminium chloride by 50 per

TABLE 3.10

EFFECTIVENESS OF STARCH AS COAGULANT AID

Metal coagulant	Dosage of metal coagulant mg/l	Dosage of starch mg/l	Turbidity NTU	Reduced metal coagulant dose mg/l	Starch dosage mg/l	Turbidity NTU	pH
ALUM	0	--	1200				
	200	--	720	250	2.0	680	8.2
	300	--	708	250	4.0	620	8.0
	400	--	684	250	6.0	610	7.5
	500*	--	648	250	8.0	590	7.8
$FeCl_3$	0	--	1200				
	200	--	732	240	2.0	750	8.1
	300	--	768	240	4.0	740	8.3
	400*	--	720	240	6.0	742	8.2
	500	--	756	240	8.0	735	8.2
$AlCl_3$	0	--	1200	138			
	200	--	624	138	2.0	630	8.1
	300*	--	576	138	4.0	592	8.0
	400	--	588	138	6.0	575	7.9
	500	--	612	138	8.0	560	8.2

* Optimum dose.

cent, 40 per cent and 54 per cent respectively. In conjunction with the reduced aluminium chloride dosage, a starch dosage of 8 mg/l could achieve better turbidity removals than that achieved by the optimum dosage of aluminium chloride when used alone.

Sodium alginate could reduce the dosage of alum, ferric chloride and aluminium chloride by 50 per cent, 42 per cent and 55 per cent respectively. Compared to the combinations with alum and ferric chloride, the combination with aluminium chloride gave better clarity of the supernatant. Sodium alginate dosage of 4 mg/l was found to be the most effective.

As for chitosan, it could bring down the dosages of alum, ferric chloride and aluminium chloride by 51 per cent, 44 per cent and 60 per cent respectively. The most effective chitosan dosage was found to be 2 mg/l.

Tamarind seed powder was found to act effectively as a coagulant aid at very low dosages. The consumption of alum, ferric chloride and aluminium chloride were reduced by 50 per cent, 42 per cent and 57 per cent respectively. Tamarind seed extract dosage of 4 mg/l was found to be the most effective.

TABLE 3.11

EFFECTIVENESS OF SODIUM ALGINATE AS COAGULANT AID

Metal coagulant	Dosage of metal coagulant mg/l	Dosage of sodium alginate mg/l	Turbidity NTU	Reduced metal coagulant	Sodium alginate dosage mg/l	Turbidity NTU	pH
ALUM	0	--	1200				
	200	--	720	250	2	710	9.0
	300	--	708	250	4	640	8.5
	400	--	684	250	6	660	8.7
	500*	--	648	250	8	684	9.2
$FeCl_3$	0	--	1200				
	200	--	732	232	2	726	9.4
	300	--	768	232	4	712	9.2
	400*	--	720	232	6	742	9.1
	500	--	756	232	8	755	9.0
$AlCl_3$	0	--	1200				
	200	--	624	135	2	580	8.9
	300*	--	576	135	4	560	9.1
	400	--	588	135	6	597	9.2
	500	--	612	135	8	621	8.8

* Optimum dose.

TABLE 3.12

EFFECTIVENESS OF CHITOSAN AS COAGULANT AID

Metal coagulant	Dosage of coagulant mg/l	Dosage of chitosan mg/l	Turbidity NTU	Reduced metal coagulant mg/l	Chitosan dosage mg/l	Turbidity NTU	pH
ALUM	0	--	1200				
	200	--	720	245	2	640	9.2
	300	--	708	245	4	725	9.1
	400	--	684	245	6	740	9.5
	500*	--	648	245	8	752	9.4
$FeCl_3$	0	--	1200				
	200	--	732	224	2	705	9.4
	300	--	768	224	4	748	9.5
	400*	--	720	224	6	767	9.3
	500	--	756	224	8	778	9.5
$AlCl_3$	0	--	1200				
	200	--	624	120	2	552	9.5
	300*	--	576	120	6	568	9.2
	400	--	588	120	6	582	9.5
	500	--	612	120	8	602	9.4

* Optimum dose.

TABLE 3.13

EFFECTIVENESS OF TAMARIND SEED POWDER AS COAGULANT AID

Metal coagulant	Dosage of coagulant mg/l	Dosage of tamarind powder mg/l	Turbidity NTU	Reduced metal coagulant mg/l	Tamarind powder dosage mg/l	Turbidity NTU	pH
ALUM	0	--	1200				
	200	--	720	250	2	710	6.8
	300	--	708	250	4	640	6.7
	400	--	684	250	6	722	6.8
	500*	--	648	250	8	682	6.7
$FeCl_3$	0	--	1200				
	200	--	732	232	2	724	7.6
	300	--	768	232	4	706	7.5
	400*	--	720	232	6	742	7.5
	500	--	756	232	8	760	7.4
$AlCl_3$	0	--	1200				
	200	--	624	129	2	580	6.9
	300*	--	576	129	4	542	7.0
	400	--	588	129	6	612	7.0
	500	--	612	129	8	630	6.8

* Optimum dose.

TABLE 3.14

EFFECTIVENESS OF CATIONIC SYNTHETIC POLYELECTROLYTE AS COAGULANT AID

Metal coagulant	Dosage of metal coagulant mg/l	Dosage of polyelectrolyte mg/l	Turbidity NTU	Reduced metal coagulant mg/l	Polyelectrolyte dosage mg/l	Turbidity NTU	pH
ALUM	0	--	1200				
	200	--	720	250	2	640	10.2
	300	--	708	250	4	680	10.3
	400	--	684	250	6	710	10.1
	500*	--	648	250	8	724	10.4
$FeCl_3$	0	--	1200				
	200	--	732	208	4	740	10.1
	300	--	768	208	4	740	10.1
	400*	--	720	208	6	765	10.3
	500	--	756	208	8	780	10.3
$AlCl_3$	0	--	1200				
	200	--	624	135	2	560	10.3
	300*	--	576	135	4	582	10.2
	400	--	588	135	6	614	10.1
	500	--	612	135	8	638	10.2

* Optimum dose.

TABLE 3.15

EFFECTIVENESS OF ANIONIC SYNTHETIC POLYELECTROLYTE AS COAGULANT AID

Metal coagulant	Dosage of metal coagulant mg/l	Dosage of polyelectrolyte mg/l	Turbidity NTU	Reduced metal coagulant dosage mg/l	Polyelectrolyte dosage mg/l	Turbidity NTU	pH
ALUM	0	--	1200				
	200	--	720	290	2	652	10.6
	300	--	708	290	4	630	10.4
	400	--	684	290	6	720	10.4
	500*	--	648	290	8	704	10.5
$FeCl_3$	0	--	1200				
	200	--	732	240	2	740	10.5
	300	--	768	240	4	700	10.6
	400*	--	720	240	6	765	10.5
	500	--	756	240	8	780	10.4
$AlCl_3$	0	--	1200				
	200	--	624	162	2	540	10.6
	300*	--	576	162	4	582	10.5
	400	--	588	162	6	578	10.5
	500	--	612	162	8	614	10.4

* Optimum dose.

In the case of polyacrylamide based cationic polyelectrolyte, a small dosage of the polyelectrolyte could bring down the consumption of alum, ferric chloride and aluminium chloride by 50 per cent, 48 per cent, and 55 per cent respectively. The most effective dosage of the cationic synthetic polyelectrolyte was found to be 2 mg/l.

The polyamine based anionic polyelectrolyte reduced the dosage of alum, ferric chloride and aluminium chloride by 42 per cent, 40 per cent and 46 per cent respectively. The most effective dosage of the anionic synthetic polyelectrolyte was found to be 4 mg/l.

Among the combinations of metal coagulants and polyelectrolytes, the combinations with aluminium chloride was found to be the most effective. This was followed by the combinations with alum and ferric chloride. Among the various combinations, a combination of chitosan and aluminium chloride could bring about better clarification of the centrifuge rubber latex concentration wastewaters compared to other combinations.

3.4 CONCLUSION

1. The optimum pH values for the effective coagulation action of the six polyelectrolytes, viz., starch, sodium

alginate, chitosan, tamarind seed powder, cationic synthetic polyelectrolyte and anionic synthetic polyelectrolyte were determined. The optimum pH values were in the range of 7.5-11.0.

2. Among the six polyelectrolytes studied, chitosan was found to be the most effective as a primary coagulant in the treatment of centrifuge latex concentration wastewaters. Chitosan could bring about the maximum COD reduction, turbidity removal and ammoniacal nitrogen removal compared to other polyelectrolytes.

3. The compressibility of the sludge produced by chitosan is better than that of other polyelectrolytes.

4. Polyelectrolyte solutions have a high potential as coagulant aid also in the treatment of effluents from a centrifuge rubber latex concentration unit. While used in conjunction with metal coagulants, a very small quantity of the polyelectrolyte could reduce the requirement of metal coagulant by 40-60 per cent with better clarity of the supernatant.

5. Among the six polyelectrolytes studied, chitosan proved to be the most efficient at a dosage of 2 mg/l bringing

about 50-60 per cent reduction in the metal coagulant dose. A combination of chitosan and aluminium chloride was the most effective.

6. Among the two synthetic polyelectrolytes studied, the polyacrylamide based cationic polyelectrolyte performed better than the anionic one. As a coagulant aid, the cationic one could bring down the metal coagulant dose by about 50 per cent at a lower dosage.

REFERENCES

1. Black, A.P. et al., J. Amer. Water Wks. Assoc., 51, 247 (1959).

2. Riddick, T.M., J. Amer. Water Wks. Assoc., 53, 1007 (1961).

3. Borchardt, J.A., Water & Sewage Wks. J., 108, 201 (1961).

4. Fuoss, R.M. and Cathers, G.I., J. Polymer Sci., 2, 12 (1947).

5. Cohen, J.M. et al., J. Amer. Water Wks. Assoc., 50, 463 (1958).

6. Singh, R.C., Indian J. Environ. Hlth., 27(1), 15 (1985).

7. Singh, R.C., Jour. Inst. of Engr. (India), 60, EN-3, 75 (1980).

8. Singh, R.C., Jour. Inst. of Engr. (India), 60, EN-3, 80 (1980).

9. Rebhun, M., D.Sc. Thesis, Haifa (1966) (not in original).

10. Singh, R.C., Proc. of the Semi Annual Paper Meeting of the Inst. of Engr. (India) held at Jabalpur (1974).

11. Dhekane, N.Y., Ambawane, G.B., Patil, B.N. and Pagar, S.D., J. Pub. Hlth. Div. Inst. of Engr. (India), 50, 10, Pt.PH3, 108 (1970).

12. Beard, J.B. and Tanska, T.S., J. Amer. Water Wks. Assoc., 66, 2, 109 (1974).

13. Rebhun, M. et al., Final Report, Technion, Hafia (1968) (not in original).

14. Adin, A., Baumann, E.R. and Cleasby, J.L., J. Amer. Water Wks. Assoc., 71, 1, 17 (1979).

15. Nadkarni, K.M., Indian Materia Medica.

16. Subbaramiah, K. and Sanjiv Rao, B., Proc. Indian Acad. Sci., 7, 59 (1937).

17. Sen, A.K. and Bulusu, K.R., Env. Hlth., 4, 233 (1962).

18. Bulusu, K.R. and Sharma, V.P., Env. Hlth., 7, 165 (1965).

19. Bulusu, K.R., Thergaonkar, V.P., Kulkarni, D.N. and Pathak, B.N., Env. Hlth., 10, 239 (1968).

20. Pathak, B.N., Thergaonkar, V.P., Kulkarni, D.N. and Bulusu, K.R., Env. Hlth., 12, 28 (1970).

21. Rao, M.N. and Sastry, C.A., J. Indian Wat. Wks. Assoc., 5, 4, 242 (1973).

22. Bulusu, K.R. and Pathak, B.N., Indian J. Env. Hlth., 16, 1, 63 (1974).

23. Pandit, R.K., Env. Hlth., 7, 1, 39 (1965).

24. Tripathi, P.N., Chaudhuri, M. and Bokil, S.D., Indian J. Environ Hlth., 18, 4, 272 (1976).

25. Prasad, D.Y. and Jivendra, J. Indian Wat. Wks. Assoc., 13, 4, 323 (1981).

26. Azharia, S.A. and Dirar, H., Water, SA, 5, 2, 90 (1979).

27. Vaidya, M.V. and Bulusu, K.R., Jour. Inst. of Engr. (India), 64, EN, 43 (1984).

28. Moore, K.J., Johnson, M.G. and Sistrunk, W.A., J. Food Sci., 52(2), 491 (1987).

29. Karim, M.I.A. et al., Biol. Wastes, 22(3), 209 (1987).

30. Prasad, D.Y. and Belsare, D.K., J. Indian Wat. Wks. Assoc., 14, 3 (1982).

31. Sihorwala, T.A. and Reddy, K.G., Indian J. Environmental Protection, 9, 7 (1989).

32. Kirk, Othmer (Ed.), Encyclopedia of Chemical Technology, Vol.10, 3rd edn., John Wiley & Sons (1980).

33. Standard Methods for the Examination of Water and Wastewater, 16th edn., American Public Health Association (1985).

34. Use of Polymeric Flocculants in Process Industries, Iron Exchange (India) Ltd.

Chapter 4

BIOCHEMICAL OXIDATION KINETICS

4.1 INTRODUCTION

Microorganisms degrade the organic matter present in any wastewater aerobically. The dissolved oxygen present in wastewater is utilised by the microorganisms for the biochemical oxidation of organic matter. The amount of oxygen required at any given time depends on the quantum of bio-degradable organic matter and also on the microbial population present in wastewater. The most widely used parameter of organic pollution is the "biochemical oxygen demand (BOD)". The determination of BOD involves the measurement of dissolved oxygen utilised by microorganisms in the biochemical oxidation of organic matter (1).

The constituents of the effluents from a centrifuge rubber latex concentration unit are mostly carbonaceous in nature (2). A procedure for BOD determination has been prescribed in standard methods (3). This test is performed at 20°C for 5 days. Many a times, BOD is estimated everyday by incubating samples for periods ranging from 1 to 15 days. BOD values on each day can be used to obtain the rate at which dissolved oxygen is being consumed during the incubation period. A constant of proportionality, 'K' exists between the rate of oxygen utilisation by microorganisms and the rate of destruction of bio-degradable organics under aerobic conditions (4). Also, after a long period of time, when the waste should have been stabilised, a constant 'k' exists which measures the biochemical stabilisation of organic matter in the system. Little work has been done on the biochemical kinetics of natural rubber processing wastewaters. Hence it has been found desirable to determine the values of k and K for the effluents from a centrifuge rubber latex concentration unit which contributes maximum to the pollution load among rubber processing units. The BOD test is affected by many variables like temperature, time, pH, essential mineral nutrients, microbiological populations, toxicity and nitrification (5). The effect of temperature is governed by the Vant Hoff Arrhenius relationship (6).

The purpose of the present study is to determine biochemical stabilization rate constant (k), oxygen utilisation rate constant (K) and ultimate BOD (L_o) on the basis of observations made at 20°C on effluents collected from a centrifuge rubber latex concentration unit. The variation in the BOD values of the effluent at four different temperatures 20, 25, 30 and 35°C was also verified.

4.2 THEORY

a) Kinetics of Organic Degradation

The organic matter present in a system is converted into various gases and cell tissue by the action of microorganisms, especially bacteria. Oxygen is utilised in the process of biodegradation. The oxygen demand by bacteria that degrade organic matter is called the first stage BOD. Noncarbonaceous matter, such as ammonia, is produced during the hydrolysis of proteins. Some of the autotrophic bacteria are capable of using oxygen to oxidise the ammonia into nitrites and nitrates (7). The nitrogenous oxygen demand caused by the autotrophic bacteria is called the second stage BOD. At 20°C, the temperature used for BOD test, the reproductive rate of nitrifying bacteria is very low (8).

The kinetics of BOD reaction can be formulated on the basis of first order reaction kinetics and may be expressed as,

$$\frac{dL}{dt} = - KL \qquad (1)$$

where L = amount of first-stage BOD remaining in the wastewater at time 't', mg/l

K = first order oxygen utilisation rate constant for organic matter by oxidation during biodegradation process.

$$\frac{dL}{L} = - K\,dt \tag{2}$$

Integrating (2) between limits L_o and L at time t = 0 and t respectively.

$$\ln\left(\frac{L}{L_o}\right) = -Kt \tag{3}$$

ie., $$\frac{L}{L_o} = e^{-Kt} = 10^{-kt} \tag{4}$$

Where L_o = BOD remaining at time, t = 0 (ie., the total or ultimate first stage BOD initially present)

k and K are related by the expression,

$$k = \frac{K}{2.303}$$

The amount of BOD remaining at any time t,

$$L = L_o \times 10^{-kt} \tag{5}$$

If 'y' is the BOD exerted at any time 't' then,

$$y = L_o - L \tag{6}$$

$$= L_o - L_o \quad 10^{-kt}$$

$$= L_o \ (1-10^{-kt}) \tag{7}$$

If the oxidation process is allowed to last for a long time, ie., as 't' tends to infinity, 10^{-kt} tends to zero and $y = L_o$. Hence 'k' measures the rate of biochemical stabilisation of organic matter present in the system and L_o measures the total amount of oxidisable organic matter present and is regarded as the ultimate BOD.

b) Determination of k, K and L_o

Some methods for the determination of k, K and L_o have been developed and discussed by many researchers like Thomas (9), Thomas et al. (10), Eckenfelder (11) and Oluwande (12). The method for the determination adopted in this study is the "log-difference" recommended by Eckenfelder (11).

c) Log-Difference Method

Differentiating Eq. (7) with respect to 't',

$$\frac{dy}{dt} = L_o(-10^{-kt})\ (2.303 \log 10)\ (-k)$$

For definite changes in the amounts of 'y' and 't', we have

$$\frac{\Delta y}{\Delta t} = 2.303\ L_o k \times 10^{-kt} \qquad (8)$$

$\frac{\Delta y}{\Delta t}$ is the rate of oxygen utilisation.

Taking decimal logarithms,

$$\log \frac{\Delta y}{\Delta t} = \log\ (2.303\ L_o k) - kt \qquad (9)$$

Thus, when log ($\Delta y / \Delta t$) is plotted against 't', a straight line graph is obtained whose slope is -k.

ie., $k = -(\text{slope})$ (10)

From equation (5), $K = 2.303 \times \text{slope}$

(N.B. The values of K and k are always rendered in positive).

The intercept of the graph on the ordinate axis

$$= \log (2.303\ L_o k) \qquad (11)$$
$$= \log (L_o K)$$

ie., $\log L_o = \text{intercept} - \log K \qquad (12)$

Hence the ultimate BOD, ie., L_o, can be calculated from Eqns. (11) and (12).

When the BOD of wastewater is determined for a long time (in days) and a graph is plotted against time, the curve obtained (not considering the effect of nitrification) is as shown in Fig.4.1.

d) Effect of Temperature on k

Rate of any chemical or biochemical reaction at two temperatures vary and they are governed by Vant Hoff Arrhenius relationship:

$$d(\ln k)/dt = E/RT^2 \qquad (13)$$

where T = temperature, °K

R = ideal gas constant, and

E = activation energy constant.

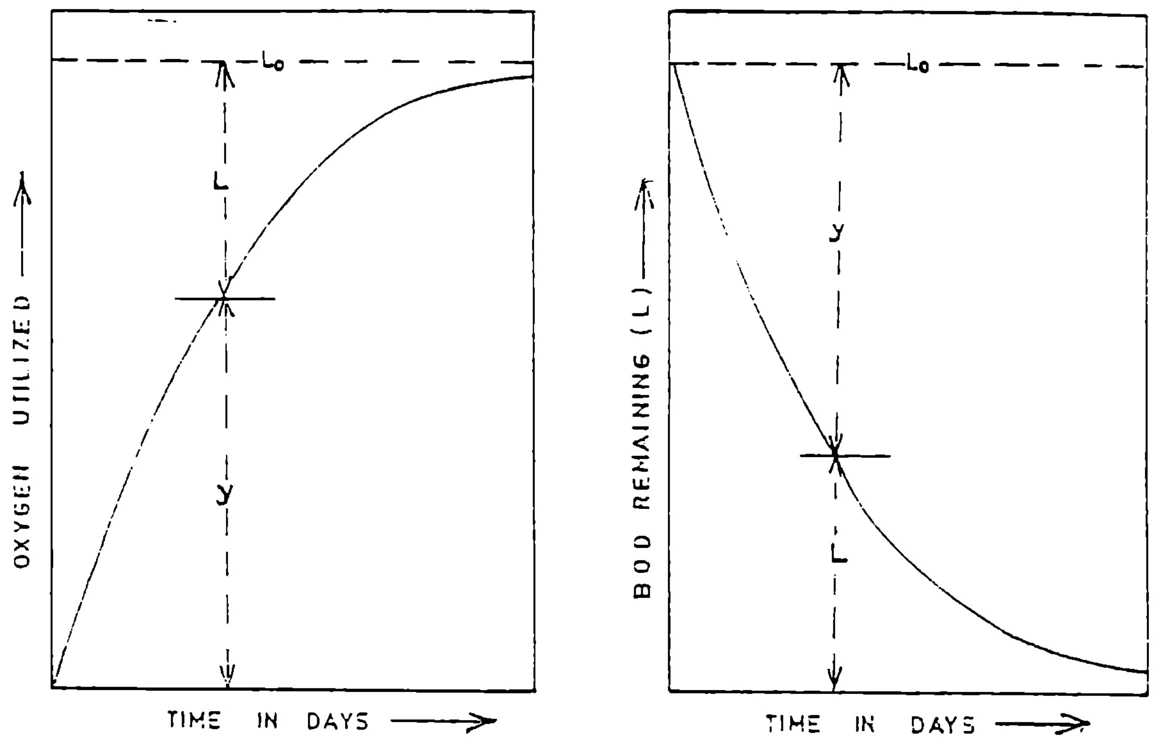


FIG.4.1: GENERALIZED BOD CURVES vs. TIME

Equation (13) on integration gives the relation

$$K_2/K_1 = \theta^{(T_2 - T_1)} \tag{14}$$

θ is called the temperature coefficient.

This equation can be used to find out the operative rate constants as a function of temperature.

If the rate constant at 20°C is found out, then the same at temperature T will be

$$K_T = K_{20} \cdot \theta^{(T-20)} \tag{15}$$

4.3 RESULTS AND DISCUSSION

Composite wastewater samples collected from a centrifuge latex concentration unit at different times were used for the study. Altogether 10 composite samples were obtained and were used for BOD determination. The determination of BOD values was made as per the standard methods (3). The dilutions found suitable for the effluents were 0.25, 0.1 and 1.0 percent. The diluted samples were incubated at 20°C, 25°C, 30°C and 35°C and the incubation period of the diluted samples varied between one day and seven days. The results of four samples for each of the four temperatures are shown in Tables 4.2 to 4.3. They are representative of the results of other samples.

4.4 RESULTS AND DISCUSSION

a) Evaluation of 'k' and 'K' values

The results of the analysis made for the various samples at four different temperatures 20°C, 25°C and 30°C and 35°C are shown in Table 4.1 and Tables 4.2-4.5.

log $(\frac{\Delta y}{\Delta t})$ values are plotted against mid-interval values of time 't' for each sample. The representative plots are shown in Figs. 4.2 to 4.5.

From Fig.4.2,

$$k = \bar{\ }(\text{slope}) \text{ using Eqn.(10)}$$

$$= \frac{-3.24 - 2.32}{6.5} \text{ day}^{-1}$$

$$= -0.142 \text{ day}^{-1}$$

$$k = 0.142 \text{ day}^{-1} \text{ (ignoring the negative sign).}$$

TABLE 4.1

CHARACTERISTICS OF THE LATEX CENTRIFUGING EFFLUENT

Characteristic	Range	Mean
pH	3.2-7.4	5.4
Biochemical Oxygen Demand (BOD), mg/l	2800-5680	4800
Chemical Oxygen Demand (COD), mg/l	3420-10700	8200
Suspended solids, mg/l	790-6140	3200
Total Dissolved Solids, mg/l	6300-15200	11140
Total Nitrogen, mg/l	1130-3940	2010

TABLE 4.2

RESULTS OF ANALYSIS OF REPRESENTATIVE COMPOSITE EFFLUENT SAMPLES OF LATEX CENTRIFUGING UNIT

(Temperature: 20°C)

Sample No.	Time (t) in days	BOD(y) values	$\Delta y/\Delta t$ (t=1)	Log $(\Delta y/\Delta t)$	Mid interval value of time 't'
(1)	(2)	(3)	(4)	(5)	(6)
Sample 1	1	1985	1985	3.30	0.5
	2	3040	1055	3.02	1.5
	3	3850	810	2.91	2.5
	4	4420	570	2.75	3.5
	5	4750	330	2.52	3.5
	6	5050	300	2.47	5.5
	7	5259	209	2.32	6.5
Sample 2	1	2095	2095	3.32	0.5
	2	3170	1075	3.03	1.5
	3	3950	800	2.90	2.5
	4	4530	580	2.76	3.5
	5	4870	340	2.53	4.5
	6	5160	290	2.46	5.5
	7	5375	215	2.33	6.5

(contd..)

TABLE 4.2 (CONTD.)

(1)	(2)	(3)	(4)	(5)	(6)
Sample 3	1	1970	1970	3.29	0.5
	2	2995	1025	3.01	1.5
	3	3725	730	2.86	2.5
	4	4305	580	2.76	3.5
	5	4680	375	2.57	4.5
	6	4950	270	2.43	5.5
	7	5140	190	2.28	6.5
Sample 4	1	2010	2010	3.30	0.5
	2	3086	1076	3.03	1.5
	3	3865	779	2.89	2.5
	4	4440	575	2.76	3.5
	5	4790	350	2.54	4.5
	6	5080	290	2.46	5.5
	7	5280	200	2.30	6.5

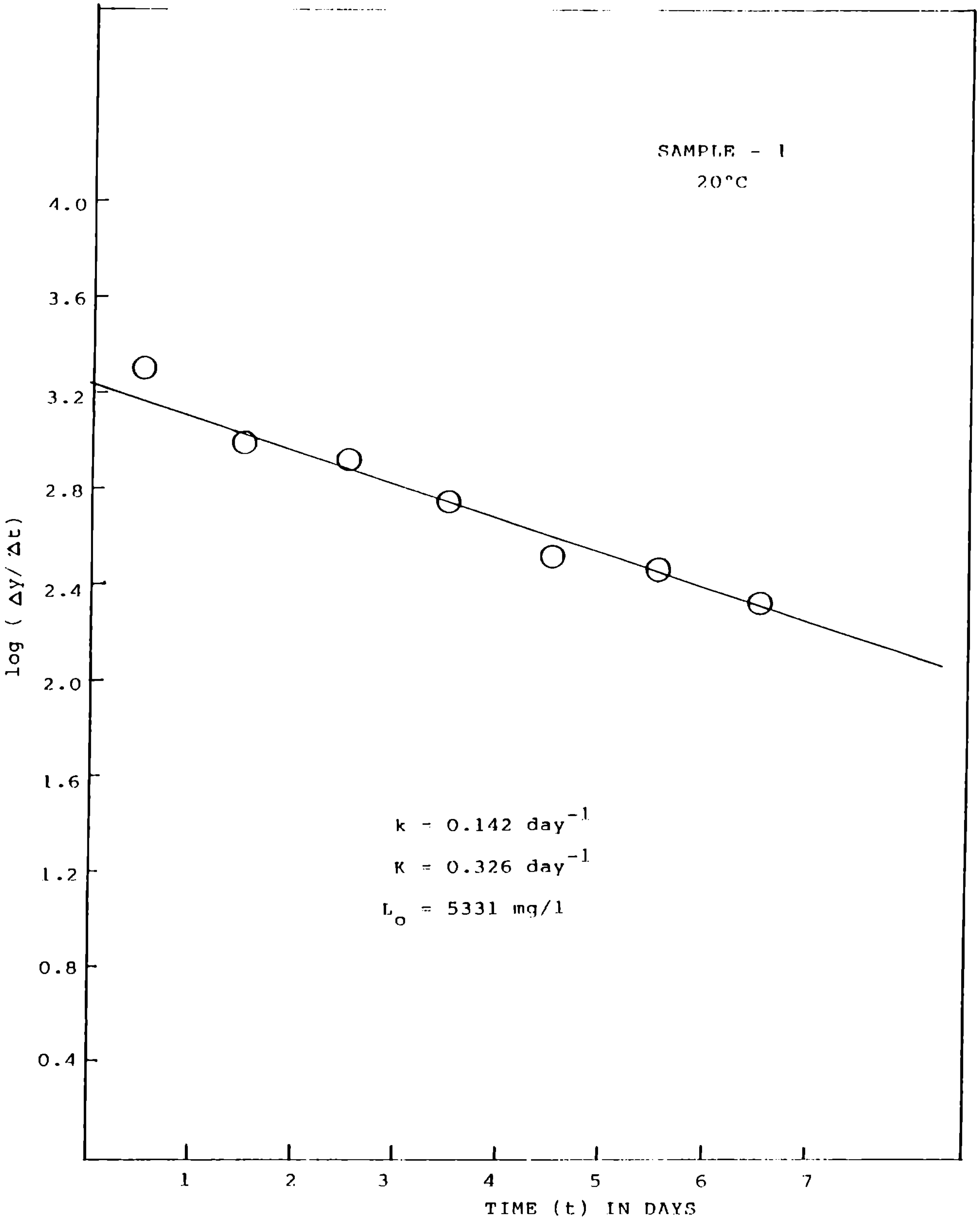


FIG.4.2: PLOT OF (Δy/ Δt) AGAINST MID-INTERVALS 't'

TABLE 4.3

RESULTS OF ANALYSIS OF REPRESENTATIVE COMPOSITE EFFLUENT SAMPLES OF LATEX CENTRIFUGING UNIT

(Temperature: 25°C)

	Time(t) in days	BOD (y) values	$\Delta y/\Delta t$ (t=1)	Log ($\Delta y/\Delta t$)	Mid interval value of time 't'
(1)	(2)	(3)	(4)	(5)	(6)
Sample 1	1	2900	2900	3.46	0.5
	2	3720	820	2.91	1.5
	3	4500	780	2.89	2.5
	4	4900	400	2.60	3.5
	5	5200	300	2.48	4.5
	6	5375	175	2.24	5.5
	7	5498	123	2.09	6.5
Sample 2	1	3100	3100	3.49	0.5
	2	3950	850	2.93	1.5
	3	4500	550	2.74	2.5
	4	5000	500	2.70	3.5
	5	5400	400	2.60	4.5
	6	5700	300	2.48	5.5
	7	5875	175	2.24	6.5

(contd..)

TABLE 4.3 (CONTD.)

(1)	(2)	(3)	(4)	(5)	(6)
Sample 3	1	2800	2800	3.45	0.5
	2	3720	920	2.96	1.5
	3	4340	620	2.79	2.5
	4	4900	560	2.75	3.5
	5	5320	420	2.62	4.5
	6	5675	355	2.55	5.5
	7	5850	175	2.24	6.5
Sample 4	1	2890	2890	3.46	0.5
	2	3800	910	2.96	1.5
	3	4590	890	2.95	2.5
	4	5000	410	2.61	3.5
	5	5350	350	2.54	4.5
	6	5650	300	2.48	5.5
	7	5850	200	2.30	6.5

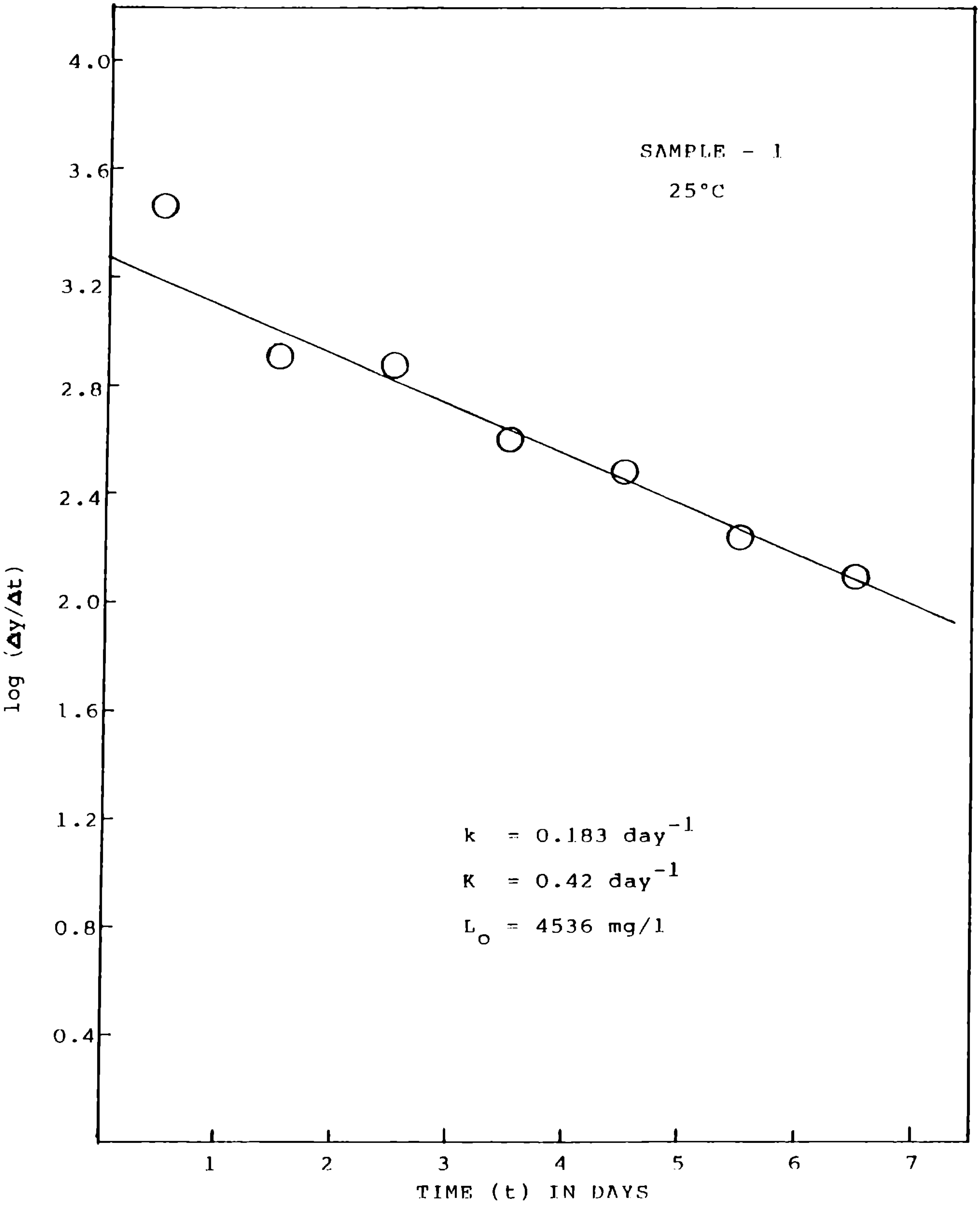


FIG.4.3: PLOT OF log (Δy/Δt) AGAINST MID-INTERNAL 't'

TABLE 4.4

RESULTS OF ANALYSIS OF REPRESENTATIVE COMPOSITE EFFLUENT SAMPLES OF LATEX CENTRIFUGING UNIT

(Temperature: 30°C)

	Time (t) in days	BOD (y) values	$\Delta y/\Delta t$ (t=1)	Log ($\Delta y/\Delta t$)	Mid interval value of time 't'
(1)	(2)	(3)	(4)	(5)	(6)
Sample 1	1	3400	3400	3.53	0.5
	2	4100	700	2.84	1.5
	3	4750	650	2.81	2.5
	4	5300	450	2.65	3.5
	5	5700	400	2.60	4.5
	6	5900	200	2.30	5.5
	7	6050	150	2.17	6.5
Sample 2	1	3575	3575	3.55	0.5
	2	4350	775	2.89	1.5
	3	4860	510	2.70	2.5
	4	5350	490	2.69	3.5
	5	5775	425	2.63	4.5
	6	5950	175	2.24	5.5
	7	6075	125	2.09	6.5

TABLE 4.4 (CONTD)

(1)	(2)	(3)	(4)	(5)	(6)
Sample 3	1	3400	3400	3.53	0.5
	2	4120	720	2.86	1.5
	3	4700	580	2.76	2.5
	4	5200	500	2.69	3.5
	5	5670	470	2.67	4.5
	6	5950	280	2.45	5.5
	7	6120	170	2.23	6.5
Sample 4	1	3350	3350	3.52	0.5
	2	4200	850	2.93	1.5
	3	4890	690	2.83	2.5
	4	5320	430	2.63	3.5
	5	5700	380	2.57	4.5
	6	5970	270	2.43	5.5
	7	6090	120	2.08	6.5

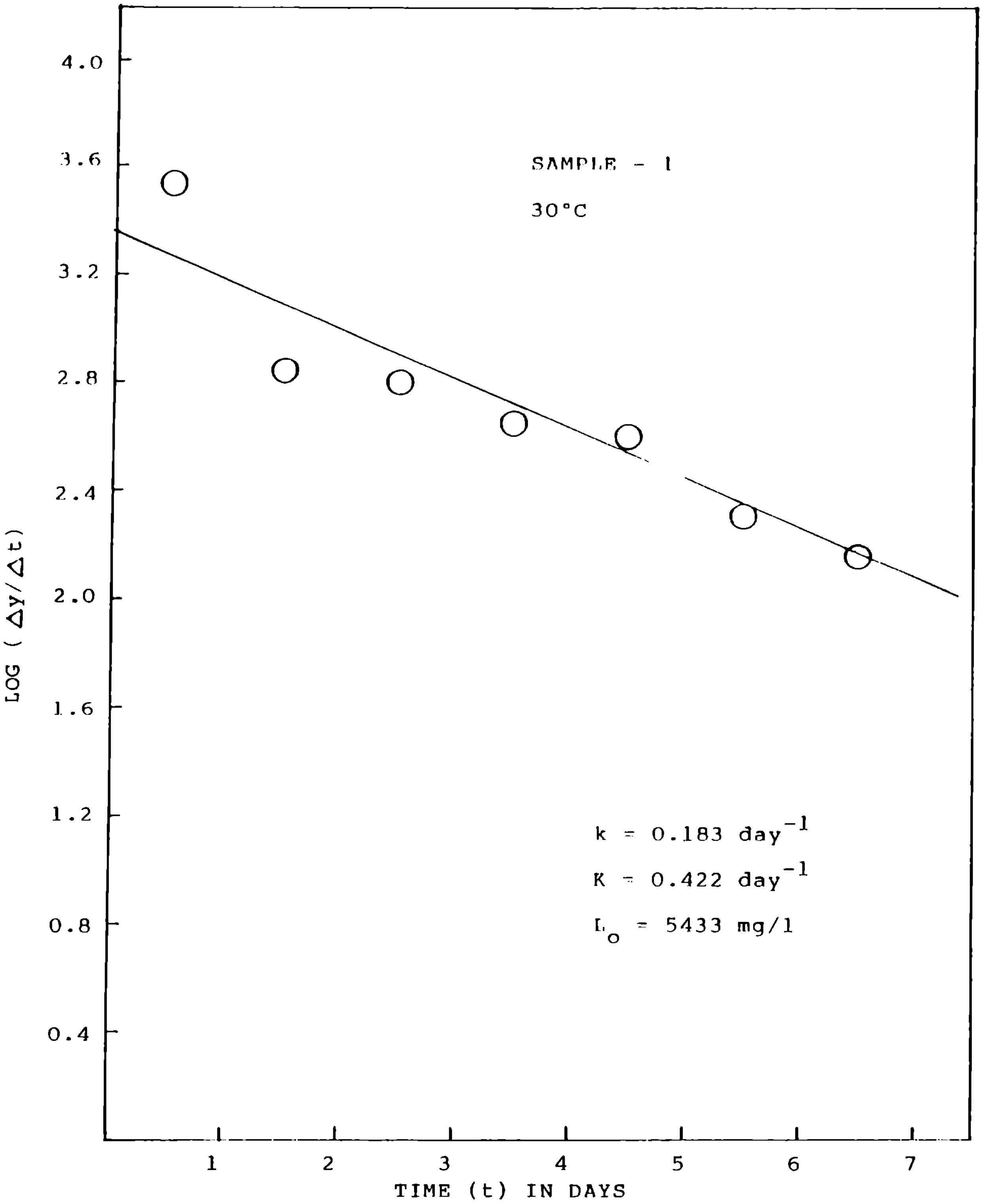


FIG.4.4 PLOT OF ($\Delta y/\Delta t$) AGAINST MID INTERVAL OF 't'

TABLE 4.5

RESULTS OF ANALYSIS OF REPRESENTATIVE COMPOSITE EFFLUENT SAMPLES OF LATEX CENTRIFUGING UNIT

(Temperature: 35°C)

	Time (t) in days	BOD (y) values	$\Delta y/\Delta t$ (t=1)	Log ($\Delta y/\Delta t$)	Mid interval value of time 't'
(1)	(2)	(3)	(4)	(5)	(6)
	1	3700	3700	3.57	0.5
	2	4500	800	2.90	1.5
	3	5070	570	2.75	2.5
	4	5500	430	2.63	3.5
	5	5890	390	2.59	4.5
	6	6000	110	2.04	5.5
	7	6075	75	1.87	6.5
	1	3900	3900	3.59	0.5
	2	4700	800	2.90	1.5
	3	5100	400	2.60	2.5
	4	5490	390	2.59	3.5
	5	5870	380	2.58	4.5
	6	6075	205	2.31	5.5
	7	6110	35	1.54	6.5

(contd..)

TABLE 4.5 (CONTD.)

(1)	(2)	(3)	(4)	(5)	(6)
Sample 3	1	3750	3750	3.57	0.5
	2	4400	650	2.81	1.5
	3	5000	600	2.77	2.5
	4	5450	450	2.65	3.5
	5	5860	410	2.61	4.5
	6	6100	240	2.38	5.5
	7	6230	130	2.11	6.5
Samsple 4	1	3600	3600	3.56	0.5
	2	4290	690	2.83	1.5
	3	4870	580	2.76	2.5
	4	5420	550	2.74	3.5
	5	5940	520	2.72	4.5
	6	6090	150	2.17	5.5
	7	6175	85	1.93	6.5

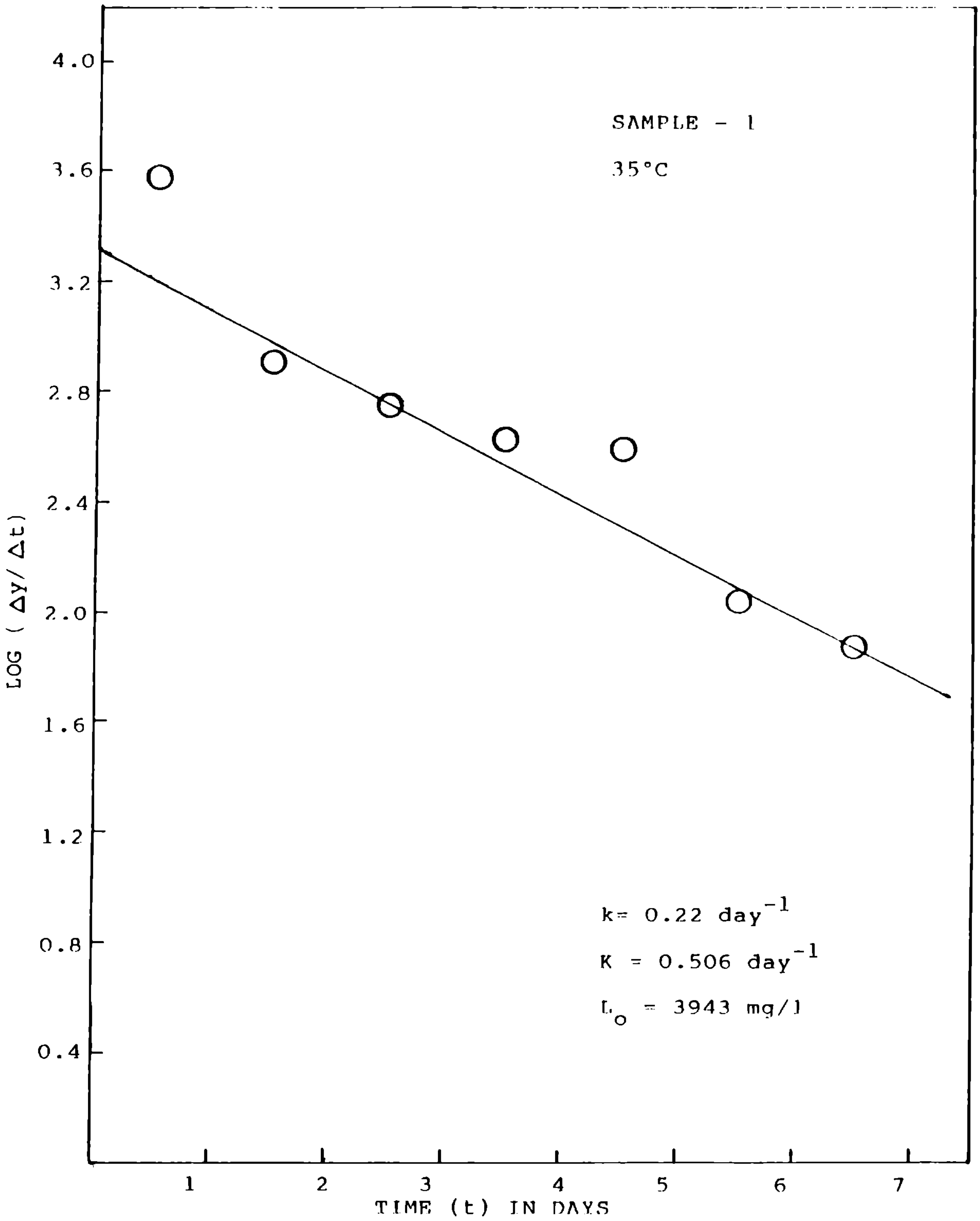


FIG.4.5 PLOT OF (Δy/ Δt) AGAINST MID INTERVAL OF 't'

This means that the biochemical stabilization rate constant for the degradation of organic matter in the centrifuge rubber latex concentration effluent after an infinitely long period of time is 0.142 day^{-1}.

Also $K = 2.303\ k$

$= 2.303 \times (^{-}0.142)$

$= 0.326\ day^{-1}$

ie., $K = 0.326\ day^{-1}$ (ignoring the negative sign).

Hence, the oxygen utilisation rate constant for the bio-degradation of organic matter present in the centrifugue latex concentration effluent is 0.326 day^{-1}.

Hence, Eqn.(11), the intercept of the graph on the ordinate axis is $\log(2.303\ L_o k)$ or $\log(L_o K)$.

From Fig.4.2,

$\log L_o = 3.24 - \log(0.326)$.

$L_o = 5331$ mg/l.

Hence, the ultimate BOD of the latex effluent is 5331 mg/l.

By adopting a similar procedure, the values of k, K and L_o were calculated for samples 2 to 4. The values obtained at 20°C for the four samples are shown in Table 4.6. From the four different values obtained for k, K and L_o, their mean values are 0.145 day^{-1}, 0.333 day^{-1} and 5475 mg/l respectively.

The mean values of k and K obtained for the four samples at different temperatures are given in Table 4.7. The values obtained for biochemical stabilization rate constant, k, for the samples varied between 0.142 and 0.147 day^{-1} at 20°C, the mean value being 0.145 day^{-1}. The values obtained for oxygen utilisation rate constant, K, at 20°C ranged between 0.326 and 0.338 day^{-1}; the mean value was 0.333 day^{-1}. The ultimate BOD values (L_o) varied from 5331 to 5671 mg/l and the mean value was 5475 mg/l.

Little work has been done on the biochemical oxidation kinetics of natural rubber processing effluents. However, the 'k' value of polluted water and wastewater has been found to be equal to 0.10 day^{-1}. (13). The corresponding K values will be approximately 0.23 day^{-1}. Also Fair et al. (4) found that K values for most sewages

TABLE 4.6

k AND 'K' VALUES AT 20°C FOR REPRESENTATIVE COMPOSITE EFFLUENT SAMPLES FROM THE LATEX CENTRIFUGING UNIT

	k, day^{-1}	K, day^{-1}	L_o, mg/l
Sample 1	0.142	0.326	5331.0
Sample 2	0.146	0.336	5671.0
Sample 3	0.144	0.330	5514.0
Sample 4	0.147	0.338	5383.0

TABLE 4.7

MEAN VALUES OF k and K AT DIFFERENT TEMPERATURES

Temperature	k, day^{-1}	K, day^{-1}
20°C	0.145	0.333
25°C	0.161	0.370
30°C	0.190	0.437
35°	0.250	0.567

were between 0.16 and 0.70 day^{-1}. The mean value was found to be 0.39 day^{-1}. This mean value is comparable to the mean value of K obtained in this study for centrifuge latex concentration wastewaters.

The experiments have shown that variations occur in the values of 'K'. Sawyer (14) has stated that variations in the composition of organic matter present in the wastewater and ability of the microorganisms present to degrade the organic matter would cause variations in 'K'. It must be noted, however, that organic matter in solution is always more readily available for biodegradation than that contained in the suspended matter which must first undergo hydralysis before use. Balmat (15) reported much higher K values for the soluble fraction than for the settleable fractions of the sewage. This implies that the BOD of raw sewage in the early stages is dominated by the dissolved organic matter. Another factor that causes variations in 'K' value is the presence or absence of toxic substances (16).

b) Progressive BOD

The progressive BOD values obtained for the centrifuge latex concentration wastewaters at four different temperatures 20°C, 25°C, 30°C and 35°C are shown in Figs.4.6-4.9.

The COD concentrations of the wastewater samples are shown in Table 4.8.

The progressive BOD curves in Fig.4.6-4.9 indicate almost identical trend in the exertion of BOD at all temperatures. Figures 4.10-4.13 show incremental increase in BOD with time at four temperatures. BOD was 24.5 percent of COD (8080 mg/l) in one day at 20°C whereas in the same period, about 45.3 percent is exerted when the temperature was raised to 35°C. This incremental exertion of BOD with time decreases after the first day at all temperatures. The decrease in the incremental exertion of BOD became sharper as the temperature was raised from 20°C to 35°C. It is possible that the microorganisms got established in the initial period itself and exerted the maximum incremental BOD on the very first day. The activity of the microorganisms should have come down thereafter for reasons like substrate inhibition and toxicity at all temperatures.

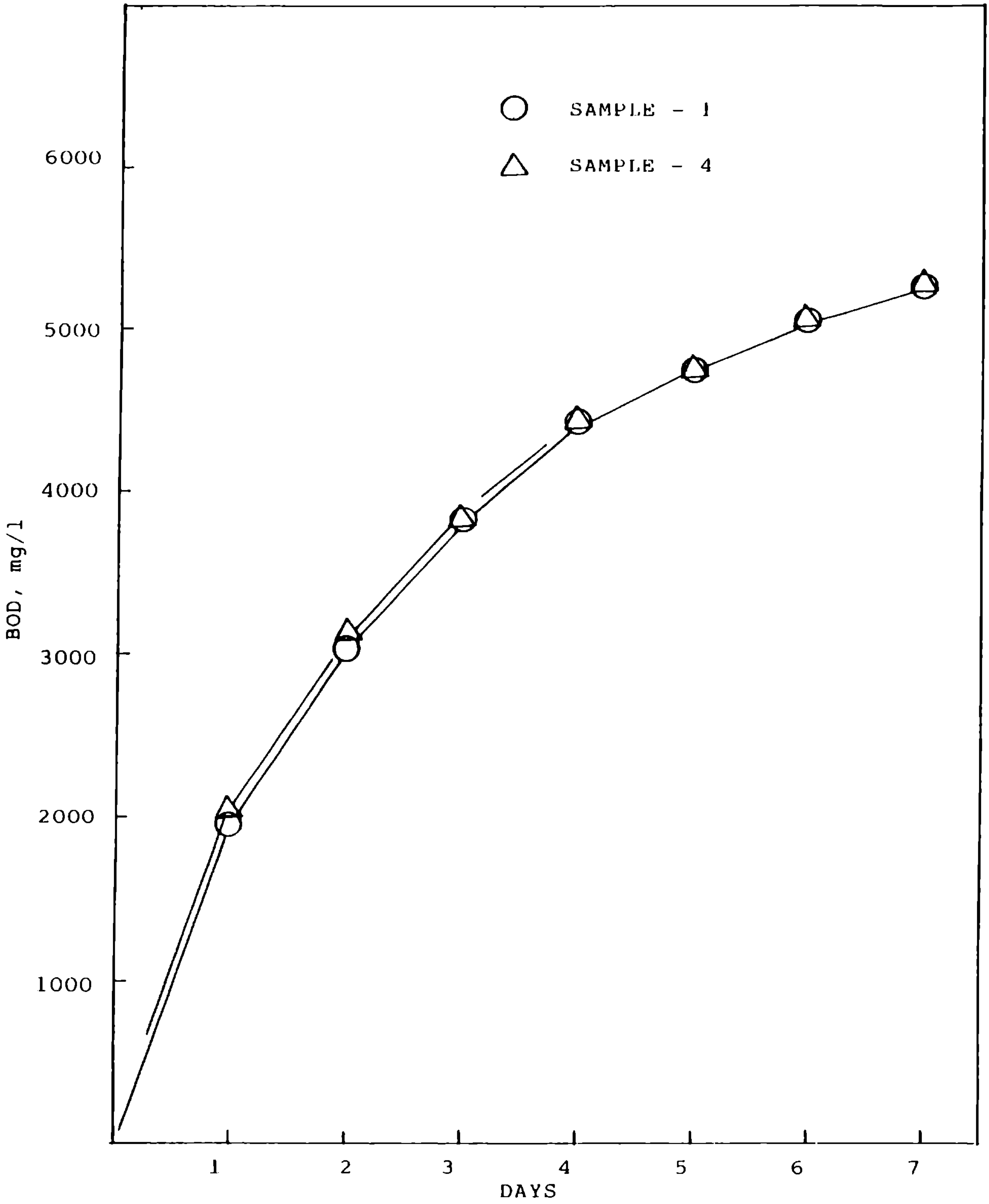


FIG.4.6 PROGRESSIVE BOD AT 20°C

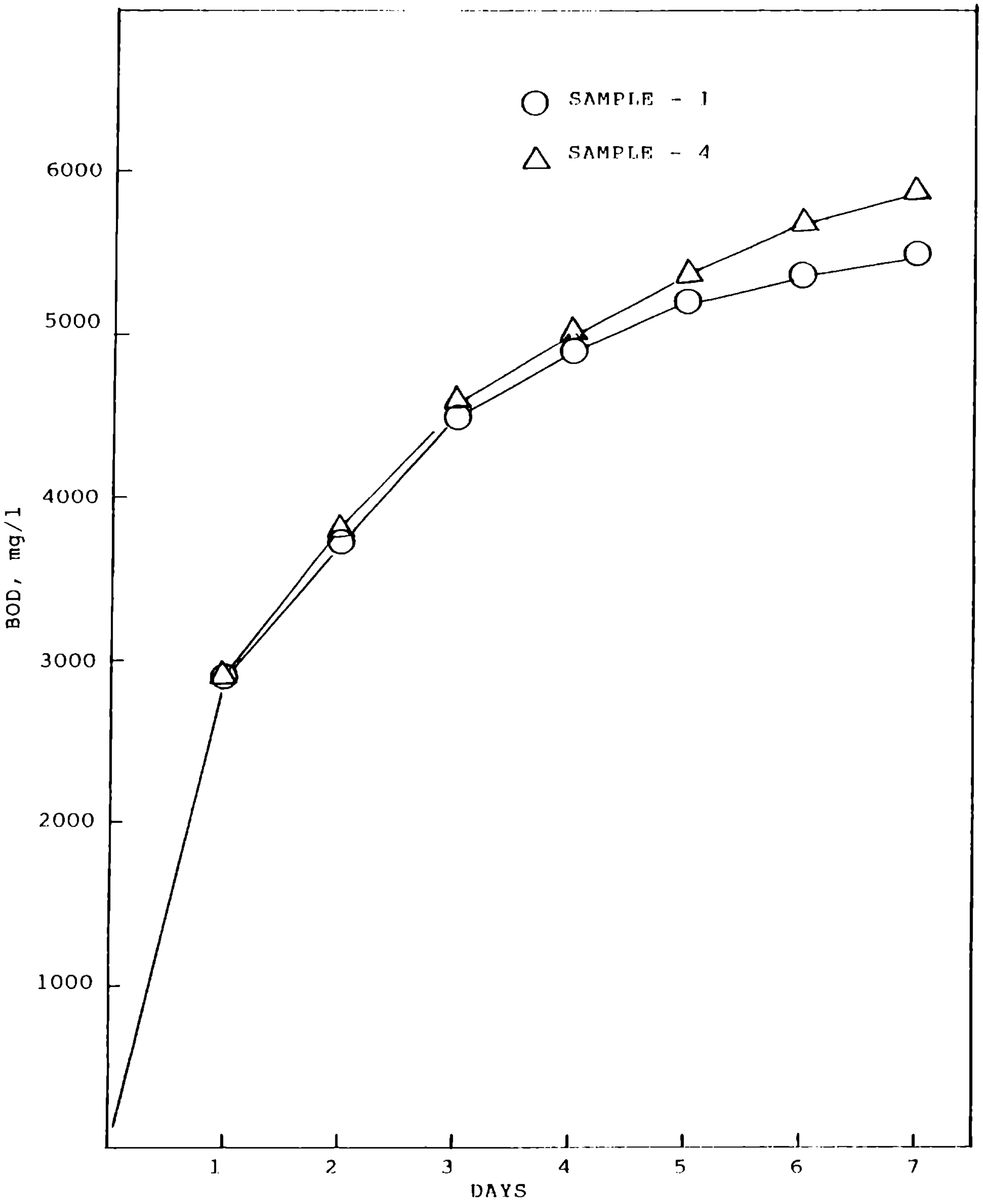


FIG.4.7 PROGRESSIVE BOD AT 25°C.

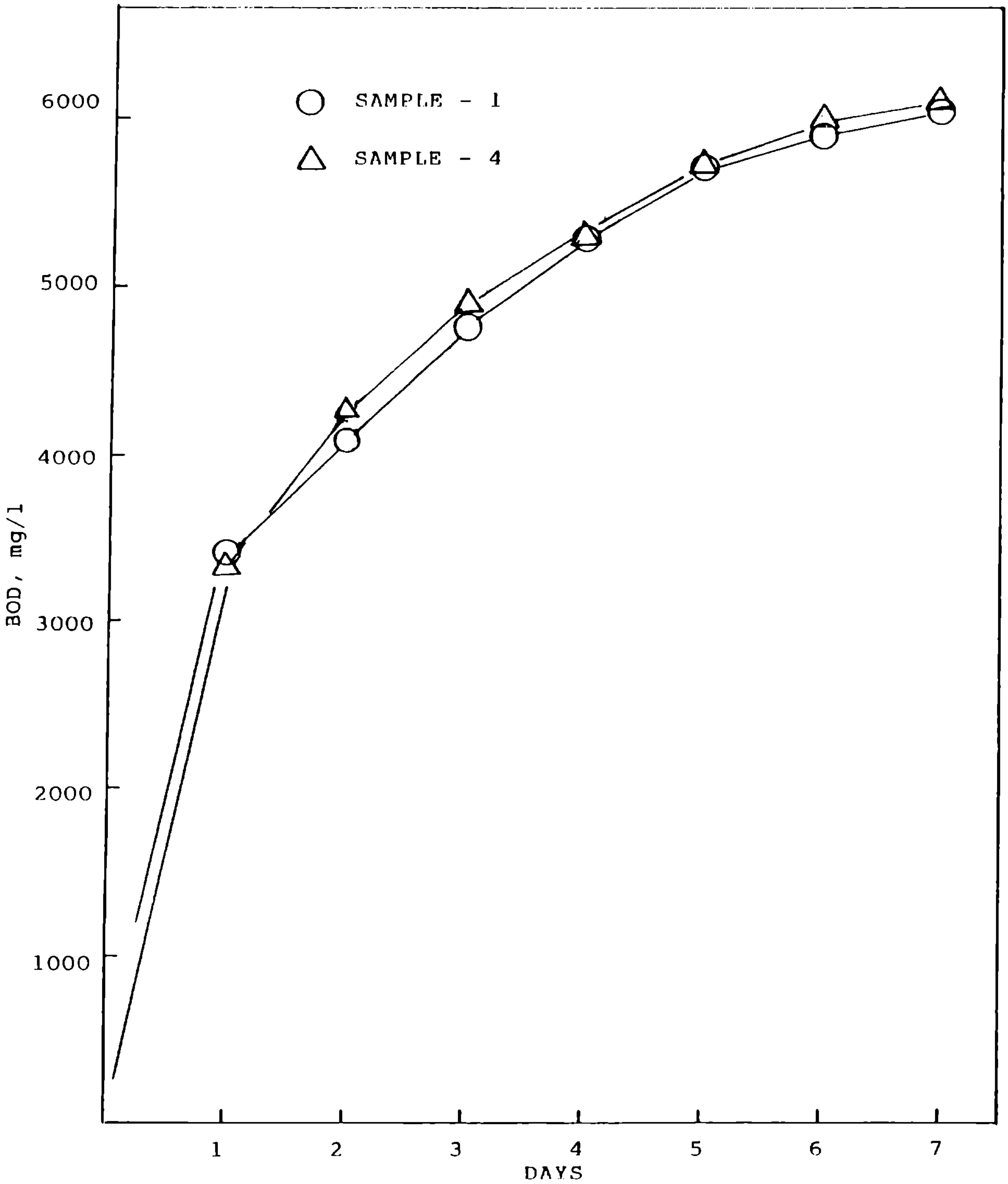


FIG.4.8 PROGRESSIVE BOD AT 30°C.

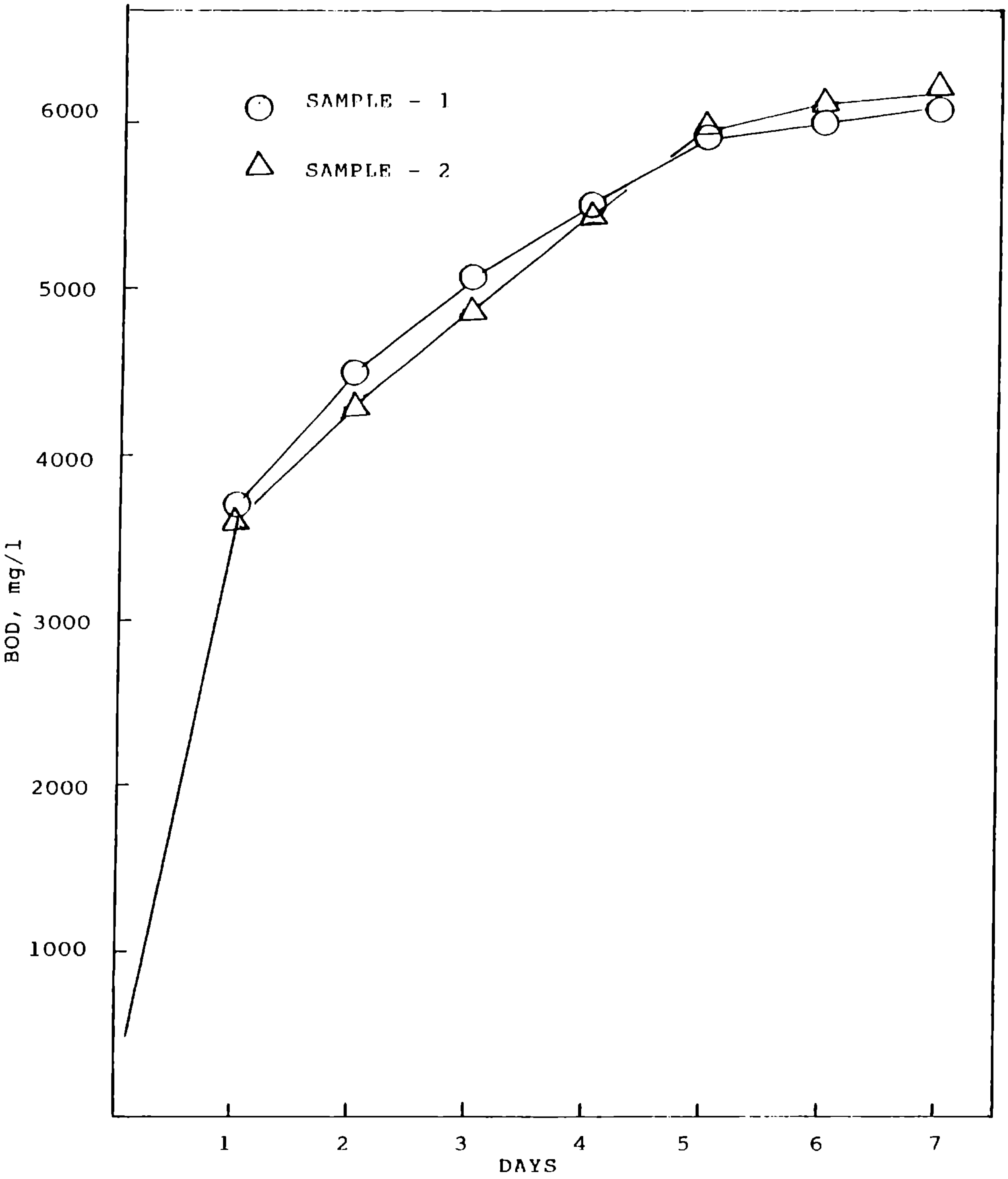


FIG.4.9 PROGRESSIVE BOD AT 35°C.

TABLE 4.8

COD CONCENTRATION OF THE WASTEWATER SAMPLES

Sample No.	COD, mg/l
1	10700
2	8080
3	4620
4	3420
5	5790
6	1170

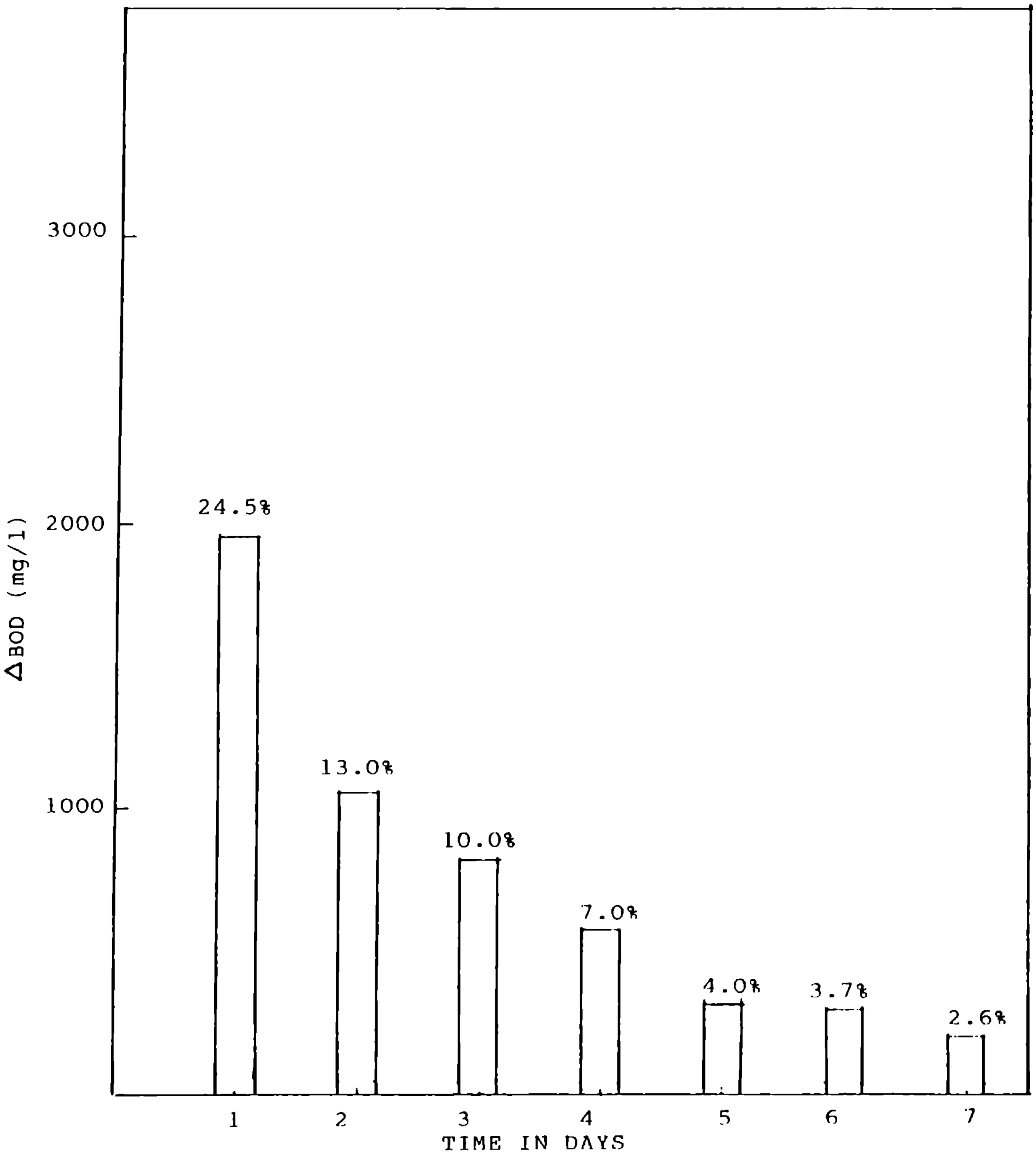


FIG.4.10 BOD PER DAY AT 20°C (PERCENTAGES ARE OF COD).

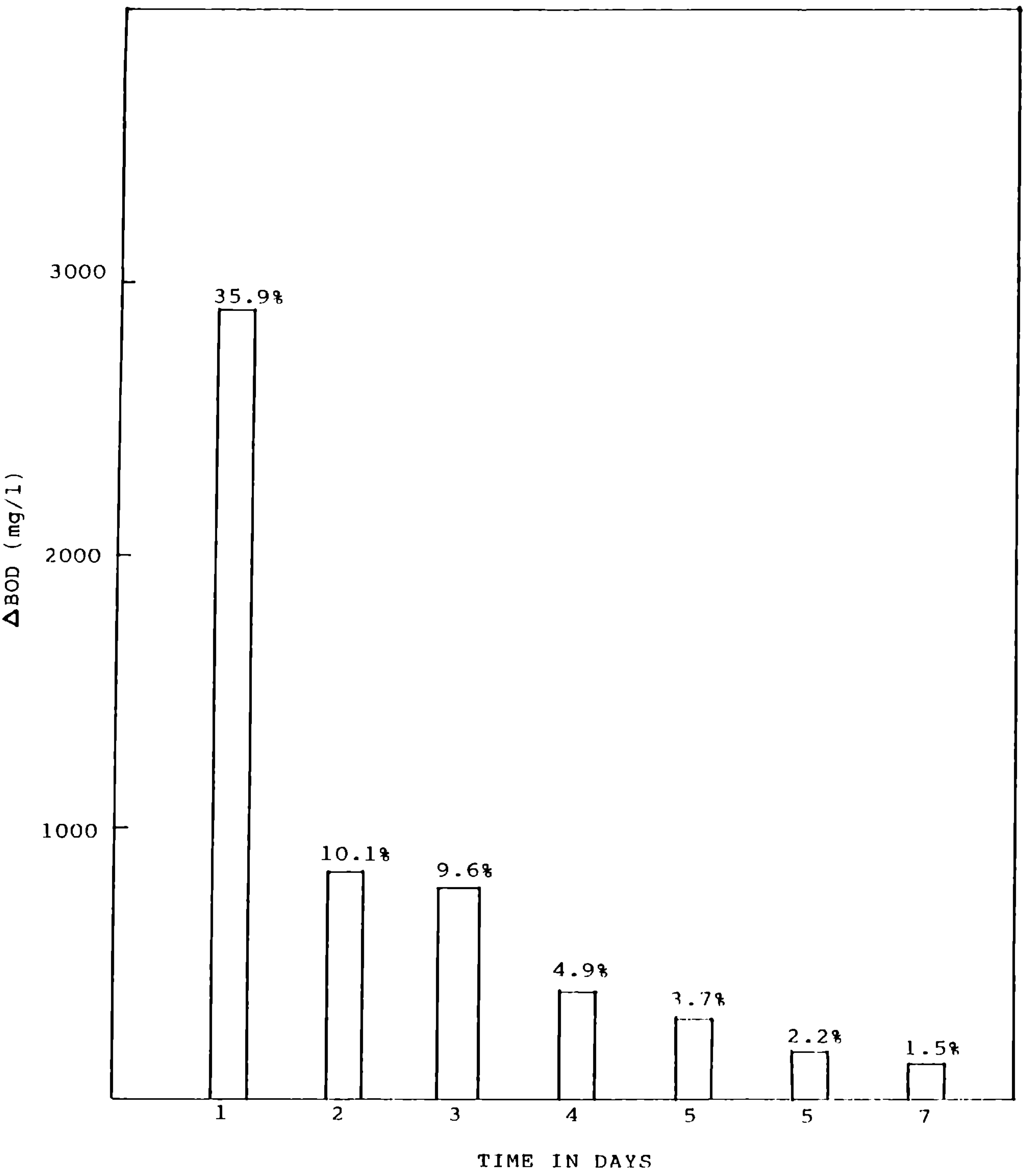


FIG.4.11 BOD PER DAY AT 25°C (PERCENTAGES ARE OF COD).

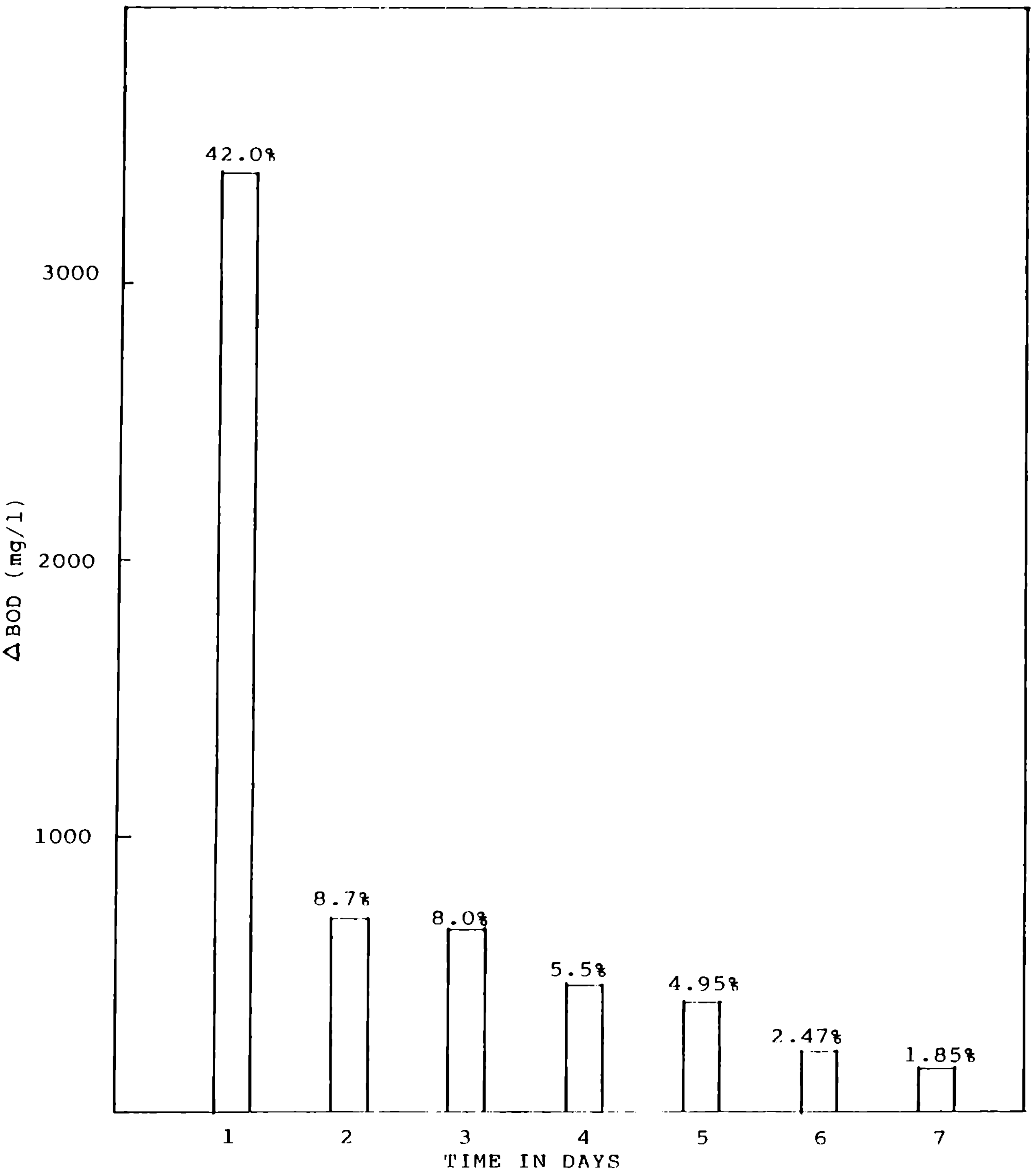


FIG.4.12 BOD PER DAY AT 30°C (PERCENTAGES ARE OF COD).

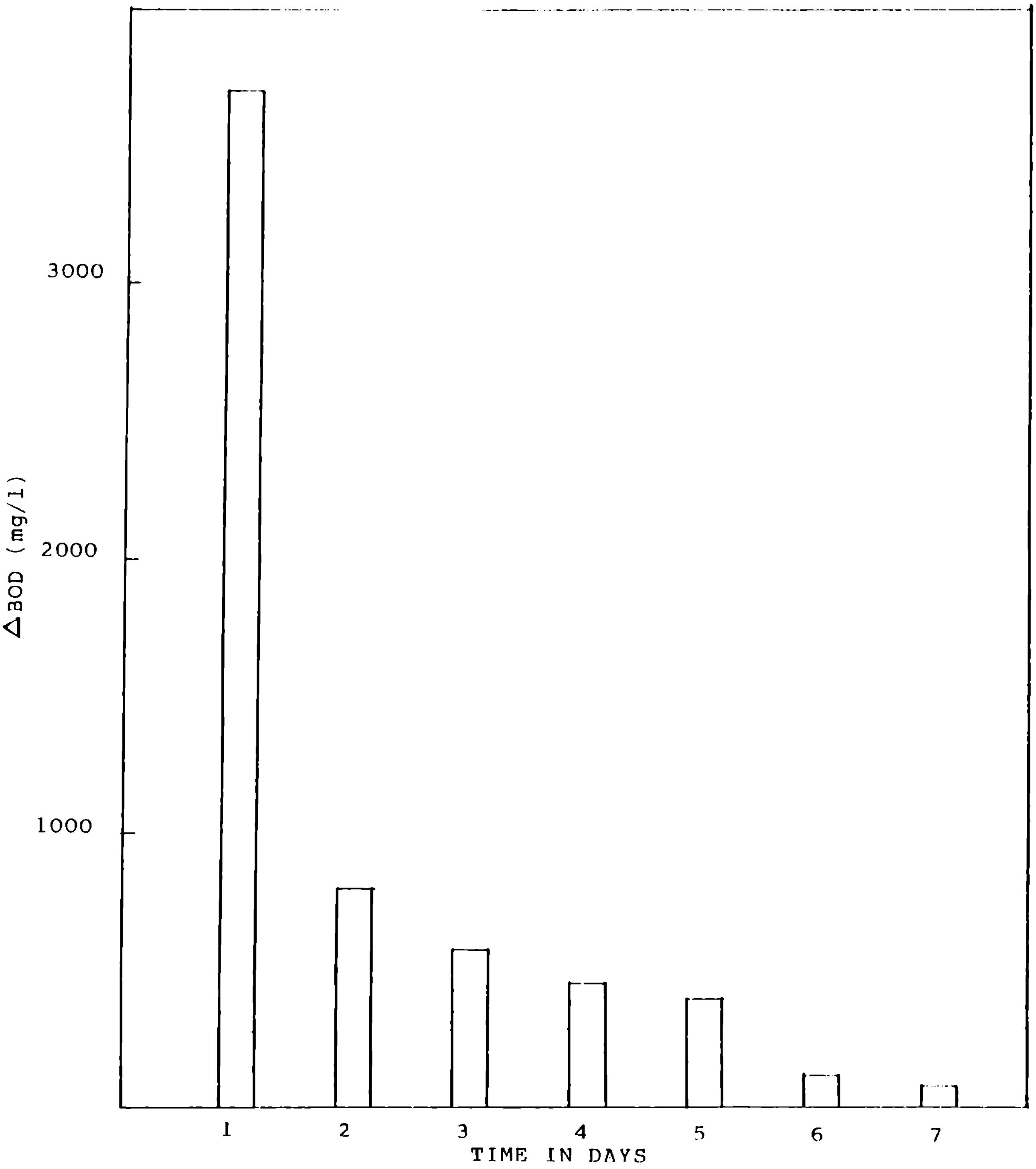


FIG.4.13 BOD PER DAY AT 35°C (PERCENTAGES ARE OF COD).

c) Effect of temperature on 'k' values

Vant Hoff-Arrhenius equation has been used to correlate reaction rate with temperature.

$$k_T = k_{20}\,\theta^{(T-20)}$$

A value of θ often quoted in literature for temperature above 20°C is 1.047 (17). This value of θ was assumed to calculate 'k' values at 25°C, 30°C and 35°C based on the k value at 20°C determined experimentally. The calculated values of 'k' are compared with the experimental values in Table 4.9.

From Table 4.9, it is evident that the calculated values of 'k' are not fully in agreement with the experimental values. The calculated values were found to be higher than the experimental values by 13-20 percent. But considering the various assumptions (1) used in the BOD test, this difference can be said to be reasonsble. Another reason for this difference may be the assumed value of θ.

It is apparent from both the calculated and experimental values that the value of 'k' increases with

TABLE 4.9

EXPERIMENTAL AND CALCULATED VALUES OF "k" (day^{-1})

Temperature	Calculated	Experimental	% difference
20°C	--	0.145	
25°C	0.182	0.161	13.0
30°C	0.229	0.190	20.5
35°C	0.288	0.250	15.2

$\theta = 1.047$ (assumed)

temperature. The increase in 'k' value in the temperature range 20-35°C may be attributed to the increased activity of the mesophilic group of bacteria which could play a major role in the degradation of natural rubber processing wastewaters. The optimum temperature range for the mesophilic group of bacteria is 25-40°C (1).

4.5 CONCLUSION

1. The biochemical stabilization rate constant (k) at 20°C for the effluents from a centrifuge rubber latex concentration unit can be taken as 0.145 day^{-1} and the corresponding oxygen utilisation rate constant (K) as 0.333 day^{-1}.

2. Bulk of the BOD is exerted within one day for the wastewater samples and the extent of this quantity depends on temperature.

3. The value of biochemical stabilization rate constant (k) and oxygen utilisation rate constant (K) increases with temperature.

REFERENCES

1. Metcalf and Eddy, Inc., Wastewater Engineering: Treatment, Disposal, Reuse, Tata McGraw Hill Publishing Co. Ltd., New Delhi (1979).

2. John, C.K., Ponniah, C.D., Lee, H. and Ibrahim, A., Proc. Rubb. Res. Inst., Malaysia Plrs' Conf. Kuala Lumpur (1974).

3. Standard Methods for the Examination of Water and Wastewater, 16th edn., American Public Health Association (1985).

4. Fair, G.M., Geyer, J.C. and Okun, D.A., Water and Wastewater Engineering, Vol.2, John Wiley, New York.

5. McKinney, R.E., Microbiology for Sanitary Engineers, McGraw Hill Book Co. (1962).

6. Schropder, E.D., Water and Wastewater Treatment, McGraw Hill, New York (1977).

7. Ramalho, R.S., Introduction to Wastewater Treatment Processes, Academic Press, New York (1977).

8. Besselviere, E. and Schwartz, Treatment of Industrial Wastes, McGraw Hill Book Co. (1975).

9. Thomas, H.A., Jr., Water and Sewage Works, 97, 123 (1940).

10. Thomas, H.A. Jr., Snow, W.B. and Moore, E.W., Sewage and Industrial Wastes, 22(1), 1343 (1950).

11. Eckenfelder, W.W. Jr., Water Quality Engineering for Practising Engineers, Barnes and Noble, New York (1970).

12. Oluwande, P.A., The Nigerian Engineer, 10(1), 17 (1975).

13. Deshkar, A.M., Srinivasan, M.V., Ratnaparkhi, D.Y., Jadhao, S.T., Deshpande, S.Y., Kshirsagar, S.R. and Thergaonkar, V.P., Indian J. Environ. Hlth., 27, 4, 330 (1985).

14. Sawyer, C.N. and McCarty, P.L., Chemistry for

Environmental Engineering, 3rd edn., McGraw Hill, New York (1978).

15. Balmat, J.L., Sewage and Industrial Wastes, J., **29**(7), 757 (1957).

16. Ademoroti, C.M.A., Inter. J. Environmental Studies, **29**, 145 (1987).

Chapter 5

WASTE STABILISATION POND METHOD

5.1 INTRODUCTION

Waste stabilisation ponds or oxidation ponds are no longer a novelty. Considerable design and operating experience has accumulated over the years and these ponds can be used as a simple and reliable means of treatment for sewage and certain industrial wastes (1). The main advantages of stabilisation ponds are their low capital requirement (except for land) and operating costs, and their ability to handle fluctuating organic and hydraulic loads.

Stabilisation is the phenomena of wastewater treatment by biological means, wherein highly unstable organic matter is converted into a stable cellular mass--the algal cell (2). This method of waste treatment in a shallow lagoon is known as "stabilisation pond method". During the process of waste stabilisation, organic matter is oxidised by the activity of bacteria into simpler algal growth substances (3). Algae while assimilating the nutrients, donate oxygen into the environment through photosynthetic activity. Thus, a waste stabilisation pond can very well be regarded as a natural aquatic ecosystem with controlled inflow and outflow; and continuous cycling of nutrients and flow of energy with constant conversion of abiotic components into biotic components.

The ecological characterisation of a waste stabilisation pond is given in Fig.5.1. The various ecological factors involved in a stabilisation pond are listed below (4):

1. Internal inputs: Solar Energy, Air and Waste
2. Photosynthesis by algae
3. Primary respiration by bacteria and zooplankton
4. Biological decomposition and excretion by aerobes and anaerobes
5. Death of algae, zooplankton and bacteria and endogenous respiration
6. Grazing by zooplankton
7. Sedimentation of waste solids and dead organisms and
8. Equilibrium of chemicals, HCO_3, CO_3 and CO_2

The ponds are often classified according to the nature of the biological activity that is taking place,

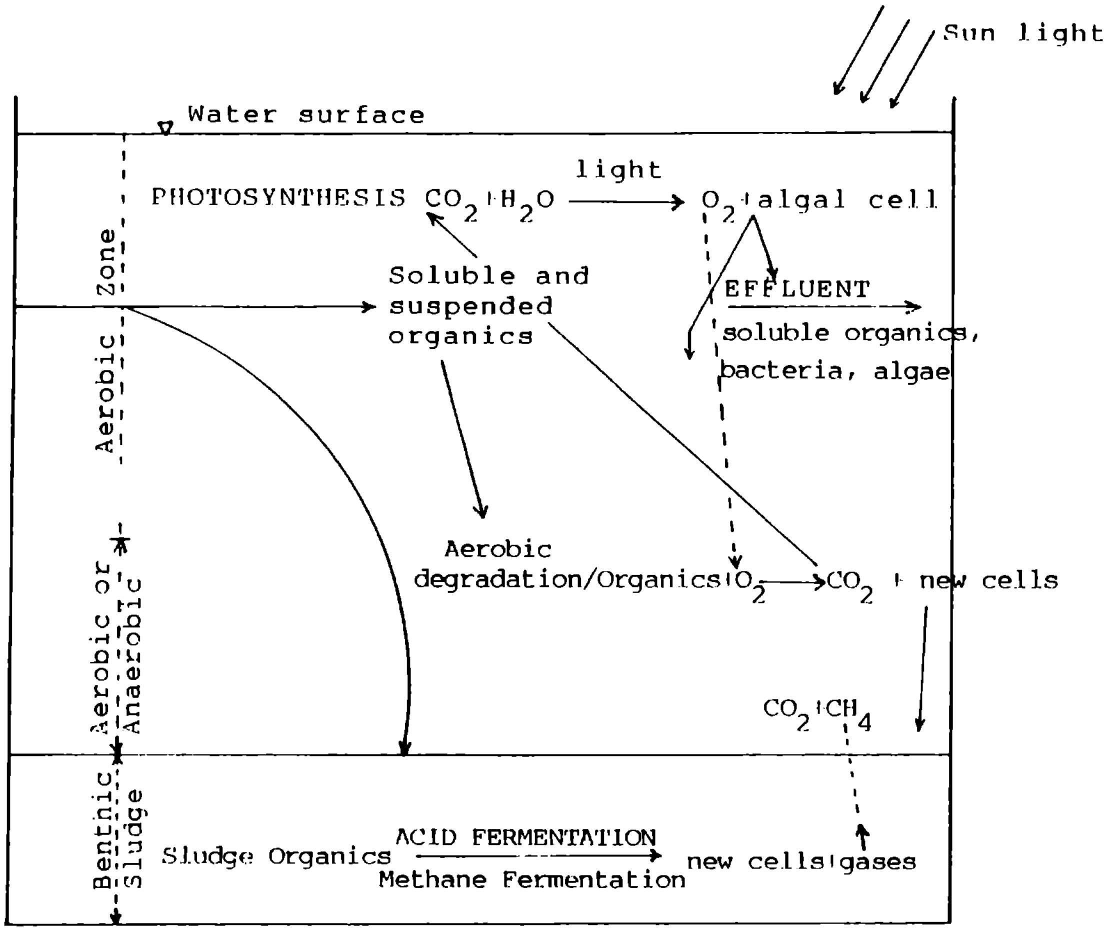


FIG. 5.1. ECOLOGICAL CHARACTERISATION OF A WASTE STABILISATION POND.

ie., aerobic, anaerobic and aerobic-anaerobic (facultative). Aerobic ponds are used primarily for the treatment of soluble organic wastes and the polishing of effluents from facultative or waste water treatment plants, while anaerobic ponds are normally employed for stabilisation of strong organic wastes. Facultative ponds are the most common type, and have been used to treat domestic and a variety of wastewaters. For better treatment efficiency, pond systems are commonly used and operated in series such as: anaerobic ponds ⟶ facultative ponds ⟶ aerobic ponds, or facultative ponds ⟶ aerobic ponds (5).

5.2 ROLE OF ALGAE AND BACTERIA

a) Algae

The successful operation of a waste stabilisation pond depends on the mutually beneficial relationship that exists between algae and bacteria. The term "symbiosis" is used to describe this mutual relationship between algae and bacteria. In the presence of sunlight and sufficient nutrients contained in the incoming waste, a healthy bloom of algae flourishes in a stabilisation pond together with a large number of aerobic bacteria and other organisms. The treatment process depends on the effective use of bacteria for breakdown or stabilisation of organic material and on the presence of algae for oxygen supply (6). As long as the algae can provide an excess of oxygen above that required by bacteria, an aerobic environment will be maintained. Under these conditions, aerobic bacteria oxidise the organic matter present in the waste resulting in the production of carbon dioxide, ammonia and water which incidentally happen to be the essential requirements along with sunlight for algal photosynthesis.

Common types of algae found in waste stabilisation ponds are the green (_Chlorophyta_) and blue-green (_Cyanophyta_) algae. Some flagellates and yellow-green algae are also usually present. Typical of the green algae in stabilisation ponds are (7):

1. _Chlorella_
2. _Scenedesmus_
3. _Chlamydomonas_
4. _Chlorococcum_
5. _Chlorogonium_
6. _Coelastrum_
7. _Gonium_
8. _Ankistrodesmus_
9. _Microtinium_
10. _Actinastrum_
11. _Eudorina_ and
12. _Pondorina_

Among the blue-green algae common to waste stabilisation ponds are:

1. Oscillatoria
2. Spirulina (Arthospira)
3. Phormidium
4. Merismopedia
5. Anabaena
6. Anacystis (Microcystis)
7. Aphanizomenon

The commonly found flagellates are:

1. Euglena
2. Phacus
3. Trachelomonas

The most common yellow-green algae are:

1. Navicula
2. Cyclotella
3. Asterionella
4. Synedra
5. Tabellaria
6. Melosira
7. Fragilaria

Blue-green algal mats frequently develop in ponds during summer months. Euglena show a high degree of adaptability to various pond conditions and are present during all seasons and under most climatological conditions (8). Probably next in adaptability are *Chlamydomonas*, *Ankistrodesmus*, *Scenedesmus* and *Chlorella*. *Chlorella* is the most desirable algae in waste stabilisation ponds as it has relatively the maximum oxygen donation capacity (9).

b) Bacteria

The bacteria necessary for the stabilisation of organic matter are present in large numbers in sewage as well as in soil washings. Depending on the conditions in the pond, aerobic, facultative or anaerobic bacteria will thrive and stabilise the organic matter in different ways.

Under aerobic conditions, part of the organic matter is used by aerobic bacteria to produce energy and is converted into stable end-products like carbon dioxide, ammonia and water and the remainder is used for synthesising new cells. A continuous supply of oxygen must be maintained during the aerobic process. The predominant bacteria present in stabilisation pond usually belong to the group of *Pseudomonas*, *Flavobacterium* and *Alcaligenes* (10).

Anaerobic decomposition of wastewater in the stabilisation pond is a mixed culture process consisting of two phases: (a) degradation of higher organic matter into volatile organic acids and (b) fermentation of these organic acids into methane and other gases. The former process is accomplished by both facultative and anaerobic bacteria which are abundant in nature. The second phase is brought about by methane bacteria which are strict anaerobes. The major reactions that take place in aerobic-anaerobic decomposition are shown in Fig.5.2.

During the last three decades, several studies have been carried out on the applicability of waste stabilisation ponds for the treatment of domestic sewage (11,12,13,14). Systematic studies on the treatment of industrial wastes combined with domestic sewage have been carried out in recent years. Govindan and Sundaralingam (15) carried out studies on the treatment of textile mill wastewaters by stabilisation pond method. It was found possible to treat textile mill wastewater in admixture with sewage (1:5) by this method with a detention time of 8-12 days using acclimatised algae culture at a BOD loading of 200 kg per hectare per day. The BOD reduction obtained was about 98 per cent. Govindan (16) studied the treatability of tannery waste waters by stabilisation pond method and obtained percentage BOD and COD reduction ranging from 64

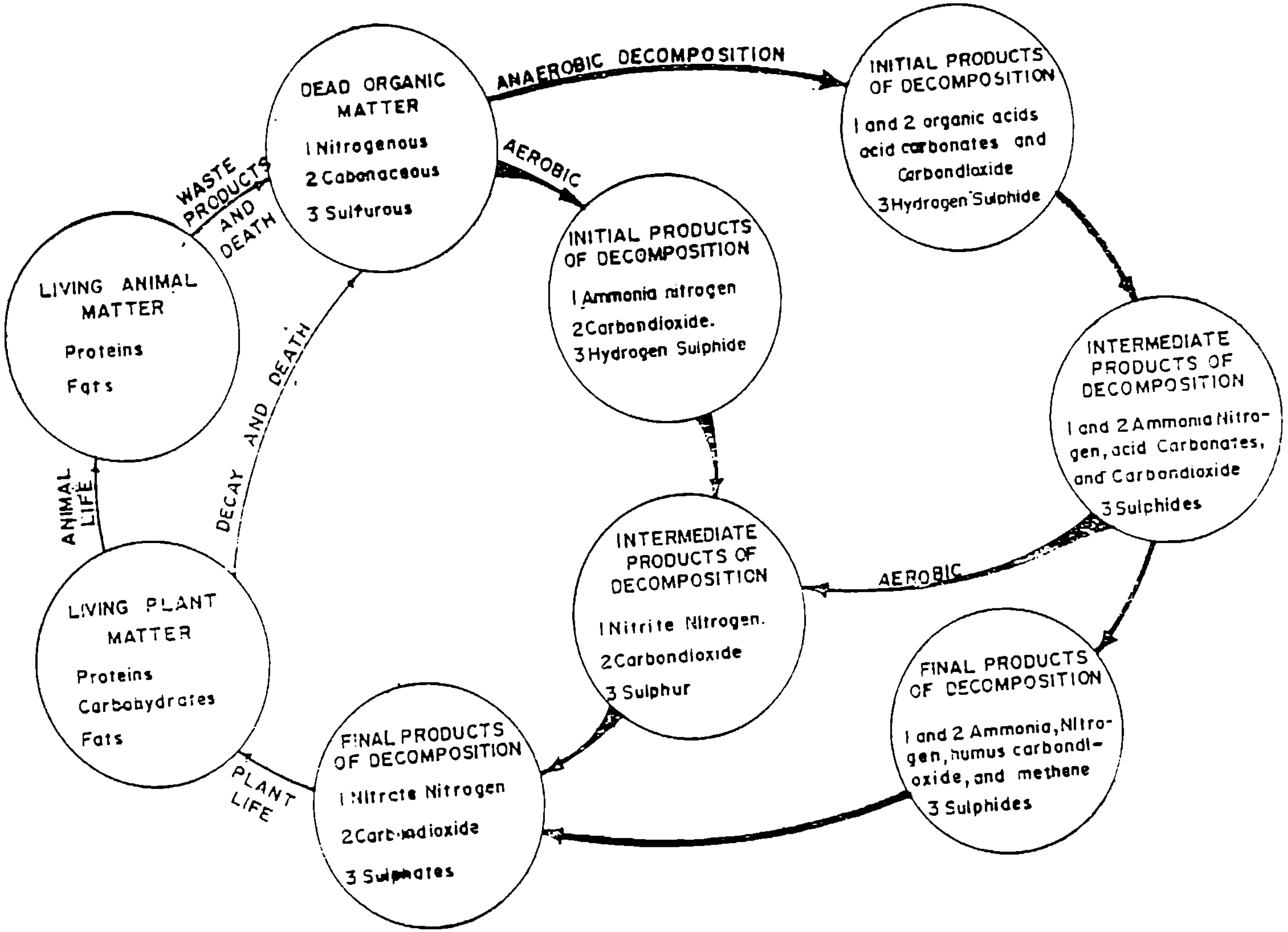


FIG.5.2 CYCLE OF AEROBIC-ANAEROBIC DECOMPOSITION.

to 93 and 60 to 89, respectively. The algal species growing well in tannery wastewater-sewage mixtures were also identified.

Very little work has been done on the treatment of natural rubber processing effluents in a waste stabilisation pond in combination with domestic sewage. The purpose of the present study is to evaluate the treatability of centrifuge latex concentration wastewater in a stabilisation pond. The possibility of treating the waste-water alone and in admixture with sewage in the proportions of 1:1, 1:2, 1:3, 1:4 and 1:5 was explored in an experimental pond (aquarium tank).

5.3 MATERIALS AND METHODS

a) Stabilisation Pond Model

The composite wastewater samples from a centrifuge latex concentration unit was used for the treatability studies. An aquarium glass tank of size 60x30x20 cm was used as the experimental stabilisation pond. Sewage was added to latex wastewater in different proportions of 1:1, 1:2, 1:3, 1:4 and 1:5 and the mixtures were placed one after another in the experimental pond. Experiments were also carried out with latex wastewater alone. pH of the samples were adjusted to the range 7.0-8.0 by adding sodium bicarbonate. Sewage and algae samples were obtained from a sewage treatment plant. Algae were acclimatized to latex centrifuging wastewaters by using dilution technique. The acclimatized algal cultures were transferred to the experimental stabilisation pond containing waste-water as such and waste-sewage mixtures. The experimental stabilisation pond was kept open in atmosphere exposed to sunlight and the wastewater-sewage mixtures were allowed to stabilise for 15 days. Samples were collected from the experimental pond unit periodically and analysed for algae and bacteria and parameters such as pH, alkalinity, COD, BOD, dissolved oxygen, ammoniacal nitrogen and suspended solids as per standard methods (17).

b) Flask Culture Experiments

Experiments to find out the influence of initial BOD strength of sewage on algal growth were carried out in flat bottomed culture flasks.

Different levels of sewage strength are made by diluting the freshly collected raw sewage with distilled water. 3 litres of the samples thus prepared were taken in culture flasks and inoculated with algal laden water collected from the experimental stabilisation pond.

Analyses of 5 day BOD were done as per the standard methods for water and wastewater analysis (17). Observations on algal growth are made by direct microscopy and counting the number of cells per ml. by drop count method (17).

5.4 RESULTS AND DISCUSSION

a) pH and Alkalinity of the Waste-Sewage Mixture

The variation of pH value of the waste-sewage mixture with detention time is given in Table 5.1. The pH of centrifuge latex concentration wastewater-sewage mixture during treatment in experimental stabilisation pond using acclimatized algal culture ranged from 6.9 to 8.0. During the first three days of detention, there was a sudden drop in pH (by 0.2-0.3). Thereafter, the pH variation remained gradual. However, the general trend was a shift in pH towards the acidic side. This should be due to the production of CO_2 in quantities in excess of the requirement of algae.

The variation of alkalinity with detention time is plotted in Fig.5.3. In all the waste-sewage combinations, the change in alkalinity with detention time was not considerable. From Fig.5.3, it is seen that the average

TABLE 5.1

pH VALUE OF WASTE-SEWAGE MIXTURES DURING TREATMENT BY WASTE STABILISATION POND METHOD

Proportion of Waste and Sewage	Period of Observations (days)					
	0	3	6	9	12	15
Waste as such	7.2	7.0	7.2	7.1	7.0	6.9
1:1	7.3	7.1	7.3	7.0	7.1	7.2
1:2	7.5	7.3	7.4	7.1	7.0	7.2
1:3	7.4	7.1	7.2	7.3	7.0	7.1
1:4	7.6	7.4	7.2	7.3	7.1	7.2
1:5	8.0	7.7	7.8	7.5	7.4	7.3

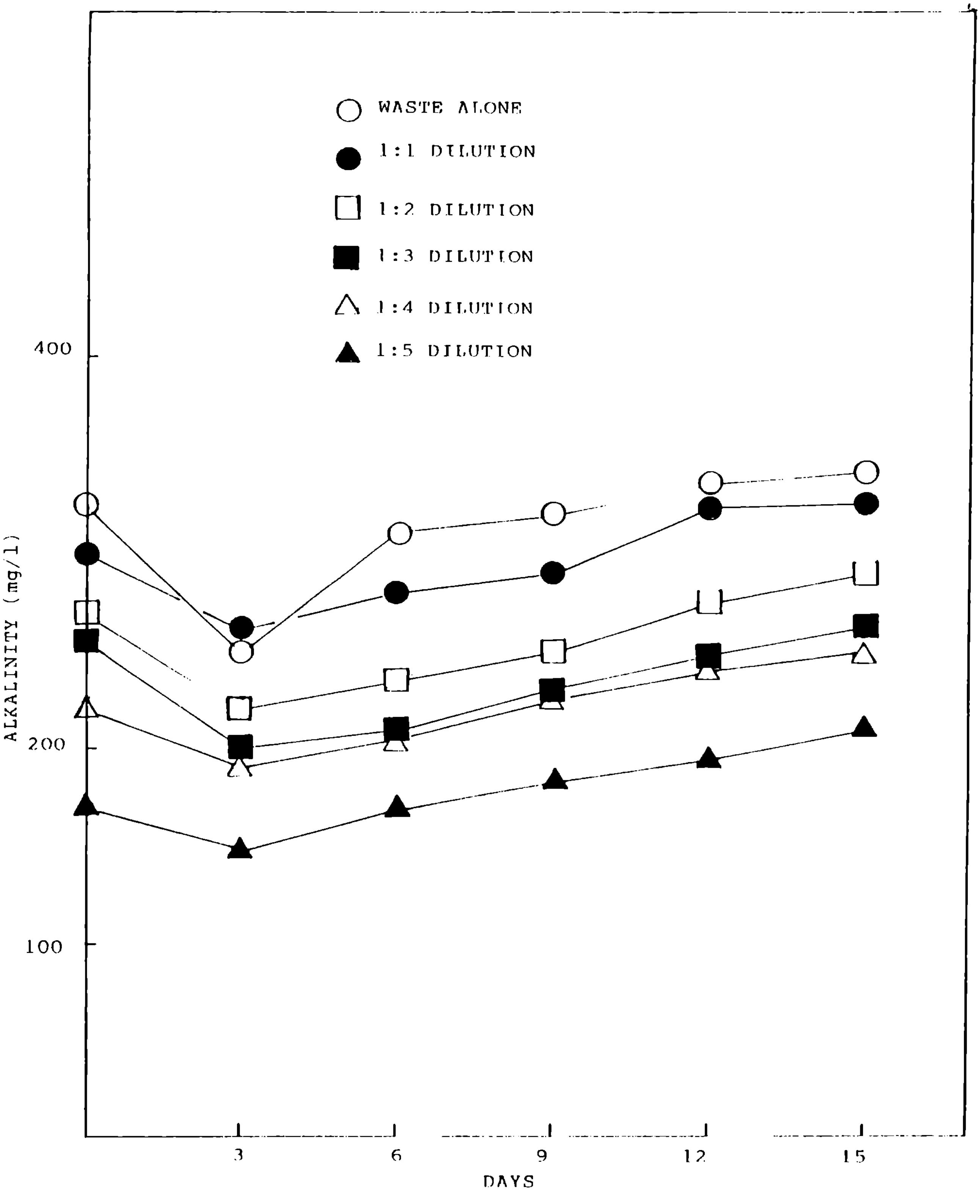


FIG.5.3 ALKALINITY 'Vs.' DETENTION TIME.

difference between the initial alkalinity and the alkalanity after 15 days of detention time is only 20-30 mg/l. This should be due to the fact that the acclimatized algal culture takes care of the alkalinity changes in the system.

b) Dissolved Oxygen in the Pond

The variation in dissolved oxygen (DO) content in the experimental stabilisation pond for various waste-sewage mixtures is shown in Fig.5.4. The dissolved oxygen content in the experimental pond was found to increase with detention time. This is an indication of the increasing photosynthetic activity in the pond which results in the release of oxygen. The difference in initial and final (after 15 days detention time) DO was found to be maximum for the 1:5 waste-sewage mixture. There was a steep increase of DO content from 0.9 to 9.4. As the proportion of sewage in the pond increases, the DO content in the pond shows a steep increase. This phenomenon may be attributed to the increasing algal growth in the waste-sewage mixture and the subsequent rise in photosynthetic activity.

In plant photosynthesis, solar energy is utilised in reducing the carbon dioxide of atmosphere to produce the

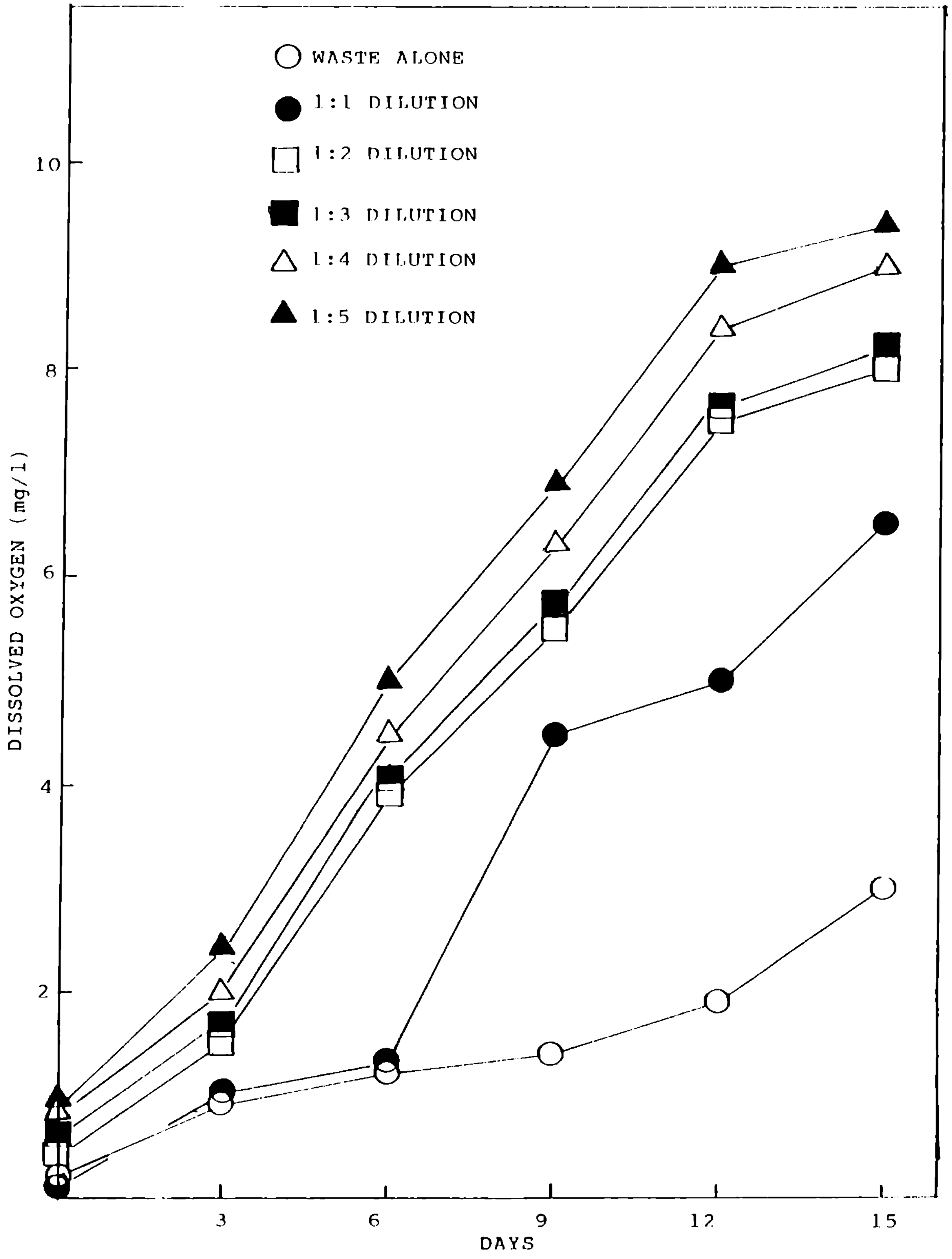


FIG.5.4 DISSOLVED OXYGEN 'Vs.' DETENTION TIME.

organic structure of the plant (18). Hydrogen for the process is obtained from water thus releasing oxygen. In otherwords, the production of new algae by photosynthesis is accompanied by the utilisation of energy and the release of oxygen. The overall equation representing the synthesis of algal cell material and release of oxygen can be stated as:

$$aCO_2 + (0.5b - 1.5d)\ H_2O + dNH_3 \longrightarrow C_aH_bO_cN_d\ \text{(Algae)}$$
$$+ (a + 0.25b - 0.75d - 0.5c)\ O_2$$

The production of oxygen during photosynthesis depends, therefore, on the coefficients a, b, c and d and can vary from one species to another (7).

c) BOD and COD Reduction

The BOD reduction in waste-sewage mixtures during treatment in experimental stabilisation pond for 15 days varied from 69 to 93 per cent and BOD was brought down to 269 mg/l. from 3845 mg/l at a dilution of 1:5. The maximum BOD reduction was achieved in the 1:5 waste-sewage mixture. When the wastewater was treated alone, the BOD reduction achieved was 68 per cent in a detention period of 15 days. The effect of detention time and dilution factor on BOD is shown in Fig.5.5.

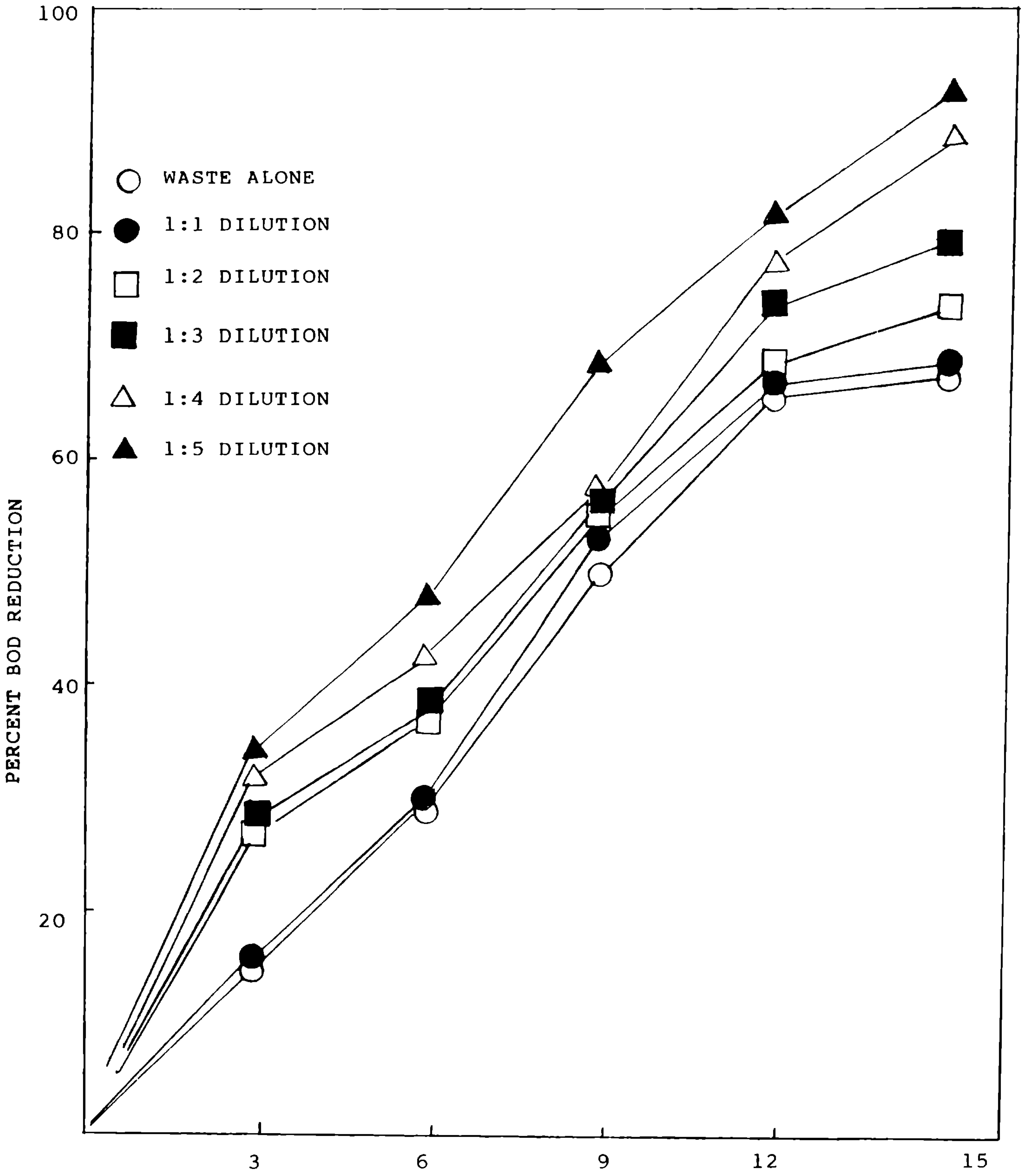


FIG.5.5 BOD REMOVAL EFFICIENCY Vs. DETENTION TIME.

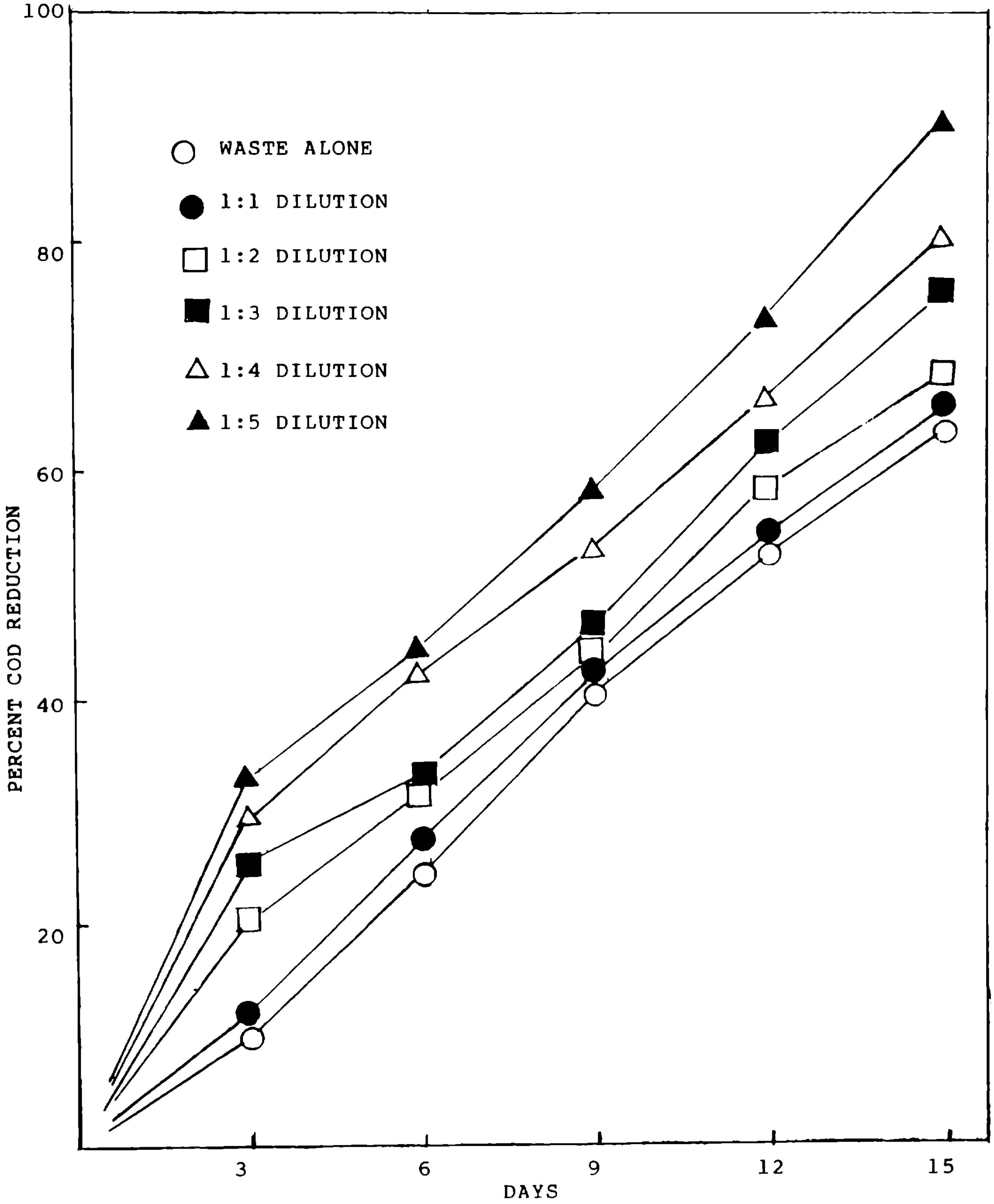


FIG.5.6 COD REMOVAL EFFICIENCY Vs. DETENTION TIME.

In a detention time of 15 days, the COD reduction in waste-sewage mixtures ranged from 65 to 90 per cent. The highest percentage reduction recorded was 90 to a dilution of 1:5 as was evident from the reduction of COD to 890 mg/l from 8905 mg/l. When the wastewater was treated alone, the COD reduction achieved was 63 per cent in a detention period of 15 days. The effect of detention time and dilution factor on COD removal efficiency is shown in Fig.5.6.

In the case of both BOD and COD reduction, the reduction efficiency was found to increase as the proportion of sewage in the waste-sewage mixture increased. This may be attributed to the increased bacterial activity at higher dilutions. The organic matter present in the waste is utilised for the synthesis of bacterial mass.

d) Algal Count and Algal Succession

The algal counts in latex wastewater-sewage mixtures are presented in Table 5.2. The algal count during stabilisation in waste-sewage mixtures varied from 30×10^4/ml to 167×10^4/ml. A maximum count of 167×10^4/ml was recorded on the 12th day in 1:5 waste-sewage mixture followed by 160×10^4/ml in the same dilution on the 9th day.

TABLE 5.2

ALGAL COUNT IN WASTEWATER-SEWAGE MIXTURES

(ALGAL COUNT IN x 10^4/ml)

Proportion of waste-water and sewage	Algal species	Period of Observations (days)					
		0	3	6	9	12	15
Waste water alone	1	8	11	18	29	39	32
	2	10	14	20	28	34	42
	3	11	12	15	16	21	22
	4	13	18	26	34	28	22
1:1	1	11	13	21	26	34	37
	2	10	12	19	31	39	38
	3	13	15	18	25	26	29
	4	10	16	25	37	29	21
1:2	1	7	10	14	28	43	34
	2	9	15	18	26	37	35
	3	8	12	17	23	31	36
	4	6	8	18	33	25	16
1:3	1	11	14	18	26	38	36
	2	13	19	30	37	44	48
	3	10	15	18	27	36	44
	4	9	16	25	37	29	18
1:4	1	10	16	25	36	35	26
	2	8	16	22	36	48	37
	3	9	14	21	34	47	40
	4	8	18	32	25	13	9
1:5	1	11	17	22	33	32	24
	2	13	20	32	45	50	44
	3	14	19	28	42	56	58
	4	9	20	37	40	29	16

Algal species: 1. *Chlorella vulgaris*, 2. *Scenedesmus quadricauda*
3. *Euglena acus*, 4. *Microcystis aeruginosa*.

Total algal count declined in all the dilutions of wastewater-sewage mixture from the 12th day onward. When the wastewater was treated alone, the algal count varied between 42×10^4/ml and 122×10^4/ml. As in the case of wastewater-sewage mixtures, the algal count declined from the 12th day onwards.

The results clearly show that the algal species Chlorella vulgaris, Scenedesmus quadricauda, Euglena acus and Microcystis aeruginosa grew well in waste and waste-sewage mixtures in the experimental stabilisation pond. Maximum number of Chlorella vulgaris was observed on the 12th day of stabilisation in 1:2 waste-sewage mixture. The BOD and COD values recorded on the days when Chlorella vulgaris dominated were 1527 mg/l and 4147 mg/l respectively. The pH on the day when maximum number of C.Vulgaris was observed was 7.0. Scenedesmus quadricauda was observed in maximum numbers on the 12th day of stabilisation in 1:5 waste-sewage mixture when the pH, BOD and COD values were 7.4, 692 mg/l and 2404 mg/l respectively. The maximum occurance of Euglena acus was observed on the 15th day of stabilisation in 1:5 waste-sewage mixture. The pH, BOD and COD values of this dilution on the 15th day of stabilisation were 7.3, 269 mg/l and 890 mg/l respectively.

On the 9th day of stabilisation in 1:5 waste-sewage mixture, maximum number of Microcystis aeruginosa were present when the pH was 7.5. The BOD and COD values were 1192 mg/l and 3740 mg/l respectively.

The influence of waste-sewage proportion on algal succession is presented in Table 5.3. Dilutions of 1:1, 1:3 and 1:5 are considered here.

For a dilution of 1:1, Euglena, a flagellete dominated the experimental pond in the initial stages. But on the 6th day, and 9th day, Microcystis, a blue green alga was found to be dominant. Then the algal succession shifted towards green algae and the species Scenedesmus dominated the pond on the 12th and 15th day of observation. For a dilution of 1:3, the green algae Scenedesmus was found to be dominant throughout the period of observation. The trend again changed for the dilution of 1:5. Euglena dominated the scene in the initial stage and final stage. The green algae, Scenedesmus were dominant on the 6th and 9th days of observation.

A definite pattern of algal succession could not be observed in the centrifuge latex concentration

TABLE 5.3

INFLUENCE OF WASTE-SEWAGE PROPORTION ON ALGAL SUCCESSION

Detention time (days)	WASTE-SEWAGE MIXTURE 1:1		1:3		1:5	
(1)	(2)		(3)		(4)	
0	*Euglena*	- D	*Scenedesmus*	- D	*Euglena*	- D
	Scenedesmus	- S	*Chlorella*	- S	*Chlorella*	- S
	Chlorella	- S	*Euglena*	- S	*Scenedesmus*	- S
	Microcystis	- S	*Microcystis*	- S	*Microcystis*	- S
6	*Microcystis*	- D	*Scenedesmus*	- D	*Scenedesmus*	- D
	Scenedesmus	- S	*Chlorella*	- S	*Microcystis*	- D
	Euglena	- S	*Euglena*	- S	*Chlorella*	- S
	Chlorella	- S	*Microcystis*	- S	*Euglena*	- S

(contd..)

TABLE 5.3 (CONTD.)

(1)	(2)	(3)	(4)
9	Microcystis - D	Scenedesmus - D	Scenedesmus - D
	Chlorella - S	Chlorella - S	Microcystis - S
	Euglena - S	Microcystis - S	Chlorella - S
	Scenadesmus - S	Euglena - S	Euglena - S
12	Scenadesmus - D	Scenedesmus - D	Euglena - D
	Euglena - S	Chlorella - S	Scenedesmus - S
	Chlorella - S	Euglena - S	Chlorella - S
	Microcystis - S	Microcystis - S	Microcystis - S
15	Scenedesmus - D	Scenedesmus - D	Euglena - D
	Euglena - S	Chlorella - S	Scenedesmus - S
	Chlorella - S	Euglena - S	Chlorella - S
	Microcystis - S	Microcystis - S	Microcystis - S

D - Dominant, S - Sub-dominant.

wastewater-sewage mixture. As a whole, green algae and flagellets were found to be predominant in the experimental stabilisation pond.

e) Removal of Ammoniacal Nitrogen

The effect of detention time and dilution factor on ammoniacal nitrogen removal is shown in Table 5.4. The per cent ammoniacal nitrogen removal that could be achieved varied between 4 and 20. The removal efficiency increased with increasing dilutions of waste-sewage mixture and with detention time. The maximum NH_4-N removal efficiency of 20 per cent was obtained at 1:5 dilution on the 15th day of observation.

The reduction in ammoniacal nitrogen in the experimental waste stabilisation pond can be attributed to the utilisation of nitrogen as a nutrient by both algae and bacteria (19).

f) Suspended Solids Removal

The effect of detention time and dilution on suspended solids removal is shown in Table 5.5. The suspended solids removal efficiency varied between 11 and 25 per cent. The removal efficiency was found to increase

TABLE 5.4

PERCENTAGE REMOVAL OF AMMONIACAL NITROGEN

Proportion of waste and sewage	Period of Observations (days)				
	3	6	9	12	15
Waste as such	4	6	7	11	11
1:1	4	6	8	12	12
1:2	5	7	9	12	13
1:3	6	8	10	13	14
1:4	7	9	11	14	15
1:5	10	12	14	17	20

TABLE 5.5

PERCENTAGE SUSPENDED SOLIDS REMOVAL

Proportion of Waste and Sewage	Period of observations (days)				
	3	6	9	12	15
Waste as such	11	13	14	15	17
1:1	12	14	16	17	19
1:2	13	15	17	18	20
1:3	14	16	18	19	19
1:4	15	17	19	20	21
1:5	17	20	22	23	25

with dilution and detention time. The maximum suspended solids removal of 25 per cent was obtained at a dilution of 1:5 on the 15th day of observation.

Removal of suspended solids is brought about by biological activity and flocculating action in a waste stabilisation pond. The suspended solids containing organic matter are decomposed by bacterial action and thus removed. A waste stabilisation pond has the characteristics of a sedimentation basin and particles of suspended solids settle by perikinetic flocculation which is brought about by Brownian motion (20).

g) Influence of Sewage Strength on Algal Growth

The influence of sewage strength on algal growth can be inferred from the results of the flask culture experiments. The results are presented in Fig.5.7.

The algal growth recorded on the 8th day of observation was maximum in the case of the sewage sample having a BOD of 200 mg/l. As the sewage strength came down, the total count of algae showed a decreasing trend and the minimum algal count was observed on the 8th day for a sewage strength of 50 mg/l (BOD). The decreasing trend

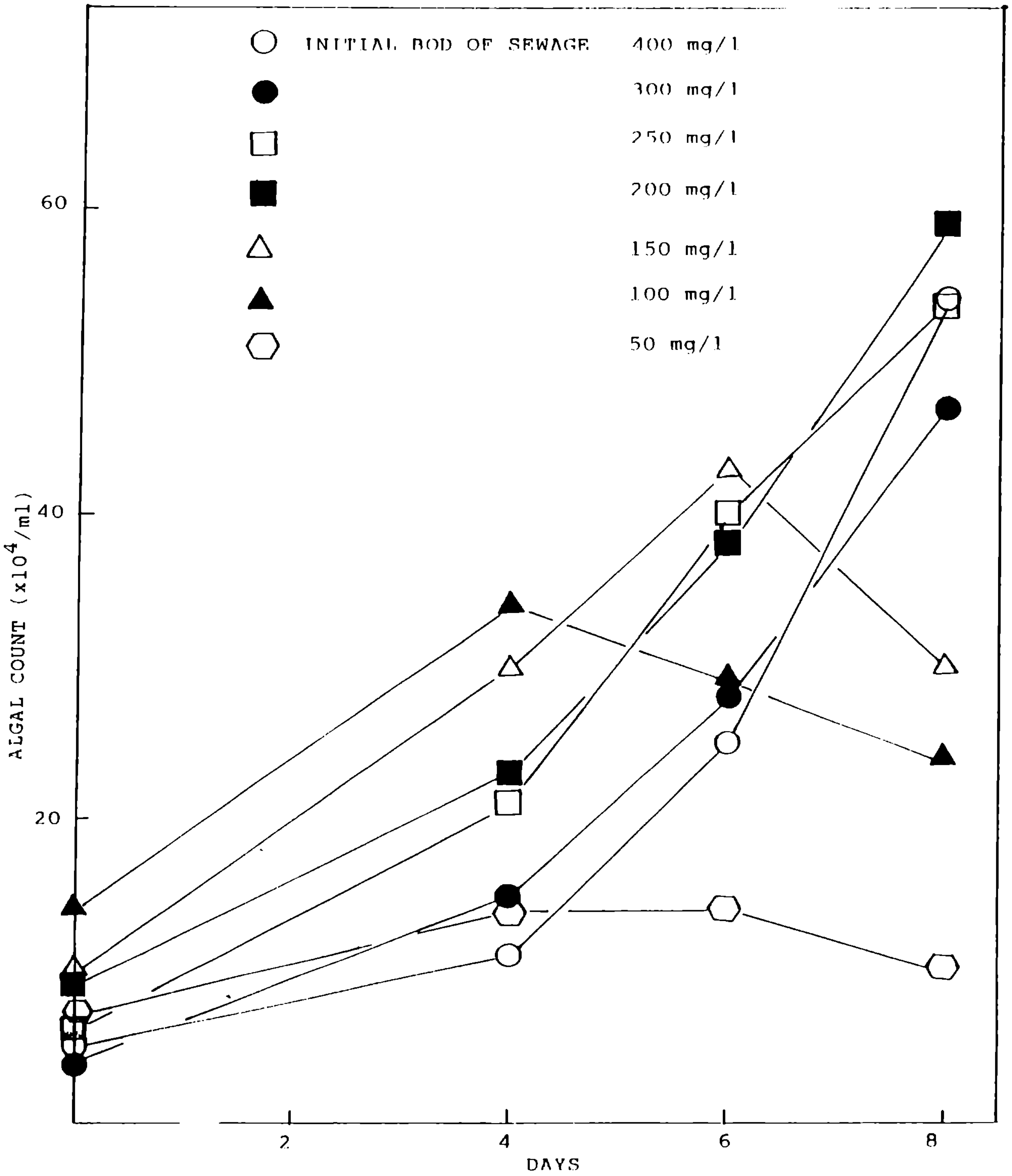


FIG.5.7 INFLUENCE OF SEWAGE STRENGTH ON ALGAL GROWTH.

in algal count was also observed when the sewage strength was increased from 200 mg/l to 400 mg/l. This shows that there is an optimum sewage strength for algal growth. This optimum strength should correspond to maximum oxygen supply and nutrient availability.

5.5 CONCLUSION

1. The wastewaters from a centrifuge rubber latex concentration unit were found to be amenable for treatment in a waste stabilisation pond in admixture with sewage using acclimatized algal culture. The greater the dilution, the more efficient was the degree of treatment. Of the five dilutions studied, 1:5 dilution gave the best performance with reference to BOD reduction, COD reduction, ammoniacal solids removal and suspended solids removal.

2. When the wastewater is mixed with sewage in the proportion of 1:5, the BOD reduction and COD reduction obtained were 93 per cent and 90 per cent respectively in a detention period of 15 days. The maximum ammoniacal nitrogen removal and suspended solids removal obtained were 20 and 25 per cent respectively.

3. The algal count during stabilisation in different latex waste-sewage mixtures varied from $3x10^4$ to $167x10^4$/ml. A maximum count of $167x10^4$/ml was recorded on the 12th day in 1:5 waste-sewage mixture.

4. *Chlorella vulgaris*, *Scenedesmus quadricauda*, *Euglena acus* and *Microcystis aeruginosa* grew well in rubber latex waste-sewage mixtures during the course of stabilisation under experimental conditions. Eventhough no definite pattern of algal succession was observed, the green algae and flagellets dominated the experimental pond.

REFERENCES

1. Arceivala, S.J., Waste Water Treatment and Disposal - Engineering and Ecology in Pollution Control, Marcel Dekker Inc., New York (1981).

2. Kuentzal, L.E., J. Wat. Pollu. Cont. Fed., **41**, 10, 137 (1969).

3. Alagarsamy, S.R., Chaudhary, K.W., Abdullappa, M.K. and Bopardikar, M.V., Env. Hlth., **9**, 241 (1976).

4. Sinha, A.K., Mathur, R.P. and Srivastava, A.K., J. IPHE, India, **4**, 75 (1980).

5. Polprasert Chongrak and Bhattarai, K.K., Journal of Environmental Engineering Division, ASCE, **111**, 1, 45 (1985).

6. Thirumurthi, D., J. Wat. Poll. Cont. Fedn., **46**, 9, 2094 (1974).

7. Arceivala, S.J., Lakshminarayana, J.S.S., Algarsamy, S.R. and Sastry, C.A., Design, Construction and Operation of Waste Stabilization Ponds in India, CPHERI, Nagpur (1969).

8. Ganapathy, S.V., Arch. Hydrobiol., 76, 3, 302 (1972).

9. Jayaangounder, I.S., Env. Hlth., 8, 190 (1966).

10. Davis, B.A., Env. Hlth., 5, 333 (1963).

11. Kumaran, P., Env. Hlth., 8, 134 (1966).

12. McGarry, M.G. and Tankasame, C., J. Water Poll. Cont. Fed., 43, 824 (1971).

13. Chatterjee, S.N., Arora, B.K. and Gupta, D.R., Env. Hlth., 9, 156 (1967).

14. Hodgson, H.T., J. Wat. Poll. Cont. Fed., 36, 51 (1964).

15. Govindan, V.S. and Sundaralingam, V.S., Indian J. Env. Hlth., 21, 4, 321 (1979).

16. Govindan, V.S., Indian J. Env. Hlth., 27, 1, 58 (1985).

17. Standard Methods for the Examination of Water and Wastewater, 16th edn., American Public Health Association (1985).

18. Hawkes, H.A., The Ecology of Waste Water Treatment, Pergamon Press (1963).

19. Govindan, V.S. and Devika, R., Instn. of Engrs. (India) Journal - Env. Engg. Div., 74, 16 (1993).

20. Camp, T.R., Trans. Am. Soc. Civil Engrs., 120 (1955).

Chapter 6

ANAEROBIC CONTACT FILTER

6.1 INTRODUCTION

Anaerobic decomposition of organic matter is a well established process for the treatment of biological sludges and wastewaters, and the process is especially useful for wastes containing a high concentration of organic matter. The process involves the breakdown of organic matter to methane and carbon dioxide in the absence of oxygen.

The biological conversion of organic matter in an anaerobic system is considered to occur in either two or three steps (1). In the three step sequence, the first step involves the enzyme-mediated transformation or liquefaction of higher weight molecular compounds into compounds for use as a source of energy and cell carbon. The second step involves the bacterial conversion of the compounds resulting from the first step into lower molecular weight intermediate compounds. The third step involves the bacterial conversion of the intermediate compounds into simpler and products, principally, methane and carbon dioxide. In the two-step sequence, the first two steps are thought to occur simultaneously and are defined as the first step (2).

In the two-step sequence, the microorganisms responsible for the decomposition of the organic matter can be divided into two groups. The first group hydrolyzes and ferments complex organic compounds to simple organic acids like acetic acid and propionic acid (1). This group of microorganisms consisting of facultative and obligate anaerobic bacteria is described as nonmethanogenic. These microorganisms are also called "acid formers". Among the nonmethanogenic bacteria that are commonly found in anaerobic sludge digesters are *Clostridium* sp, *Peptococcus anaerobus*, *Bifidobacterium* sp, *Desulphovibro* sp, *Corynebacterium*, *Lactobacillus* *Actinomyces*, *Staphylococcus* and *Escherichia coli* (3).

The second group of microorganisms converts the organic acids formed by the first group to methane gas and carbon dioxide. The bacteria responsible for this transformation are strict anaerobes and are called "methanogenic" or "methane formers". Many of the methanogenic bacteria isolated from anaerobic digesters are similar to those found in the stomachs of ruminant animals and in organic sediments taken from lakes and rivers (4). The most important among the methanogens that have been identified are Methanobacterium and Methanobacillus having rod like shape and the sphere like Methanococcus and Methanosarcina (5).

The methanogenic bacteria that degrade acetic acid and propionic acid play an important role in anaerobic decomposition. The metabolism of these bacteria is usually considered rate limiting in the anaerobic treatment of an organic waste as they have very slow growth rates (6). The actual stabilization of the waste is accomplished by the methanogenic organisms that convert organic acids into methane and carbon dioxide. Methane gas is highly insoluble, and its departure from solution represents actual waste stabilization.

6.1.1. Mechanism of methane formation

With regard to the specific mechanisms involved in the formation of methane, it appears that two pathways are possible, depending on the nature of the starting substrate (1). The methanogenic bacteria appear to be capable of using the following three categories of substrate (7):

1. The lower fatty acids containing six or fewer carbon atoms (Formic, acetic, propionic, butyric, valeric and caproic).

2. The normal and iso alcohols containing five or fewer carbon atoms (methanol, ethanol, propanol, butanol and pentanol).

3. Three inorganic gases (hydrogen, carbon monoxide and carbon dioxide).

In the first mechanism suggested for methane formation, methane is produced by the oxidation of substrates such as ethanol, butyrate, and hydrogen and by the reduction of atmospheric carbon dioxide. In the second, methane is formed by the reduction of carbon dioxide formed during the oxidation of substrates such as acetate and propionate. The two mechanisms involved can be described by considering the following equations (8):

Reduction of atmospheric CO_2:

$$2C_2H_5OH + CO_2 \longrightarrow 2CH_3COOH + CH_4$$

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O$$

Reduction of CO_2 formed from reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

$$CO + 2H_2 \longrightarrow CH_4 + H_2O$$

$$4C_2H_5COOH + 8H_2O \longrightarrow 4CH_3COOH + 4CO_2 + 24H$$

$$3CO_2 + 24H \longrightarrow 3CH_4 + 6H_2O$$

$$4C_2H_5\ COOH + 2H_2O \longrightarrow 4CH_3COOH + CO_2 + 3CH_4$$

$$CH_3\ COOH \longrightarrow CH_4 + CO_2$$

In addition, many other groups of anaerobic and facultative bacteria use the various inorganic ions present in the sludge. Desulfovibrio is responsible for the reduction of the sulphate ion SO_4^{2-} to the sulphide ion S^{--} Facultative anaerobic bacteria such as Pseudomonas reduce nitrate NO_3^- to nitrogen gas N_2 (denitrification).

To maintain an anaerobic treatment system that will stabilise an organic waste efficiently, the nonmethanogenic and methanogenic bacteria must be in a state of dynamic equilibrium (9). To establish and maintain such a state, the reactor contents should not contain dissolved oxygen and be free from inhibitory concentrations of constituents like heavy metals and sulphides. Also the pH of the aqueous environment should be in the range of 6.6-7.6 (1). Sufficient alkalinity should be present to ensure that the pH will not drop below 6.2, because the methane bacteria cannot function below this point (10). A sufficient amount of nutrients, such as nitrogen and phosphorous, must also be available to ensure the proper growth of the biological community. Temperature is another important environmental parameter. The optimum temperature ranges are the mesophilic, 30 to 38°C and the thermophilic, 49 to 57°C.

6.1.2 The concept of "Anaerobic Filter"

Anaerobic biological treatment of high strength organic wastes has a number of advantages which makes has a number of advantages which makes it preferable to either aerobic biological or physical chemical treatment methods. The major advantage is that a high degree of waste stabilization can be accomplished with a relatively low production of biological solids thus reducing the costs associated with sludge disposal. Methane gas is produced as a result of the anaerobic process and valuable energy can be recovered from the gas by subsequent combustion.

A disadvantage of the anaerobic process is the low bacterial growth rate which may result in a washout of the biomass if the solids in the effluent are not returned to the unit. Young and Mc Carty (11, 12) therefore developed an upflow anaerobic filter in which the anaerobic bacteria are present in a film attached to a rock medium to remove organics in the waste flowing upward through the column. The bacteria in the anaerobic filter are firmly attached to the medium resulting in sludge ages of more than 600 days (12) and 150 days (13). The unit can therefore be operated at temperatures substantially below 35°C which decreases the bacterial growth rate while still maintaining a sufficient biomass.

The studies carried out by Young and Mc Carty (11,12) using synthetic organic waste indicated that at the same organic loading the percentage COD removal increased when the concentration of the influent COD increased. El-shafie et al. (14) used a multiple filter system. The unit consists of a group of six filters operating in series. Their study based on a synthetic wastewater indicated that the percentage removal of organic material is constant - regardless of the concentration of the organic load applied to anaerobic filters in a continuous flow system.

Arora et al. (15) studied the suitability of an anaerobic filter for the treatment of effluents from vegetable tanning. The results of the study showed that upto a certain organic loading, the increase in COD and BOD of the effluent is accompanied by an increase in the percentage removals of COD and BOD, whereafter the decline in percentage removals with increased organic loading is exponential. A study carried out by Jennett and Dennis (16) investigated the performance of anaerobic filter for the treatment of pharmaceutical waste. During the last two decades, several studies (17, 18, 19, 20, 21) have been carried out to evaluate the performance of anaerobic filter for the treatment of wastewaters from various industries. The anaerobic filter has also been applied successfully as a reactor for the biological denitrification (22,23,24) of effluents.

The purpose of the present study is to evaluate the performance of an upflow anaerobic filter for the treatment of wastewaters from a centrifuge rubber latex concentration unit. Based on the experimental results, kinetic parameters were estimated with respect to substrate removal, microorganism growth and gas production.

6.1.3 System Analysis

The evaluation of kinetic parameters was made with respect to substrate removal, microorganism growth and gas production.

(a) Substrate Removal Kinetics

The substrate removal kinetics in fixed film biological systems can either be described in terms of substrate concentrations existing in the bulk liquid phase or simulated substrate concentrations in each layer of the biofilm, the sum of which predicts the response of the entire film. Eventhough the earlier workers (11,12) used the former approach, the recent trend is to use the second approach in which the process of substrate diffusion and bacterial uptake are simulated for each of the successive layers of the biofilm (25).

In a biological film reactor at steady state, a mass balance within the film can be made by equating:

$$\text{Input} - \text{Output} = \text{Uptake} \qquad (1)$$

Using Fick's law of molecular diffusion and biological uptake rate, equation within the biological layer can be written as

$$\frac{d^2S_z}{Dz^2} = \frac{1}{D_x} \quad \frac{US_z \ X}{K_s+S_z} \qquad (2)$$

which states that the second derivative of substrate concentration with respect to 'z' is dependent on both the substrate and biomass concentrations. S_z is the substrate concentration at depth 'z' (mass/length^3), D is the diffusion coefficient (length^2/time), U is the maximum substrate removal rate (mass of substrate/mass of biomass.time), X is the biomass concentration within the biolayer (mass/length^3) and K_s is the half-velocity concentration (mass/length^3).

Using various assumptions as given by Dewalle and Chian (25), when S_z is much larger than K_s, equation (2) can be written as

$$\frac{I}{V} \ \frac{dF}{dt} = k_1 \ \frac{A}{V} \ (S_e)^{\frac{1}{2}} \qquad (3)$$

k_1 is the coefficient based on zero order kinetics. When S_z is much smaller than K_s, equation (2) becomes,

$$\frac{I}{V} \ \frac{dF}{dt} = k_2 \ \frac{A}{V} \ S_e \qquad (4)$$

k_2 is the coefficient based on first order kinetics.

$\frac{dF}{dt}$ is the rate of mass transfer at the dinterface (mass/time)

V is the reactor volume (length^3)

A is the surface area (length^2)

and S_e is the substrate concentration in bulk liquid (mass/length^3).

The model described by the above equation has a drawback, that it cannot define a maximum rate of substrate removal (26). This value can be arrived at by assuming a Monod's hyperbolic relationship between $\frac{1}{V}\frac{dF}{dt}$ and S_e whereby the constants can be evaluated from a Line Weaver Burk Plot and is given by the equation,

$$\frac{I}{V}\frac{dF}{dt} = \frac{\frac{I}{V}\frac{dF}{dt}}{K_s+S_e} \qquad (5)$$

or

$$L = \frac{L_m \; S_e}{K_s+S_e}$$

L is the substrate loading rate (mass/length^3. time).

L_m is the maximum substrate loading rate (mass/length^3.time).

S_e is effluent substrate concentration (mass/length^3)

S_i is influent substrate concentration (mass/length^3)

K_L is substrate removal rate constant based on loading rate

K_θ is the substrate removal rate constant based on detention period, (time^{-1})

θ is the hydraulic retention period (time)

E is COD removal efficiency

E_m is the maximum substrate removal efficiency

a is the critical hydraulic retention time (HRT) (time)

(b) Microorganism Growth Kinetics

The specific growth rate of microorganism was determined by Smith et al. (26) and is given by the equation

$$E = K_\mu \cdot \theta^\mu \tag{10}$$

μ is the specific growth rate (time^{-1}).

K_μ is called the biological constant.

The determination of maximum specific growth rate (μ_{max}) and decay coefficient (k_d) was made by the use of Monod's modified model given by the equation

$$\mu = \frac{\mu_{max} \cdot S_e}{K_s + S_e} - k_d \tag{11}$$

The substrate removal kinetics in an upflow anaerobic filter can be described by considering it as a fixed film packed bed biological reactor. But the plug flow nature of the flow regime in an upflow anaerobic filter prohibits adequate mechanistic explanation of substrate removal mechanism in packed bed reactor and forces the designer to search for empirical and pseudo mechanistic models(26), viz.,

$$\frac{S_e}{S_i} = \exp(^{-}K_L/L) \tag{6}$$

$$\frac{S_e}{S_i} = \exp(^{-}K_\theta \theta) \tag{7}$$

$$E = E_m(1 - a/\theta) \tag{8}$$

A model based on total organic loading has been developed by Stover et al. (27) which defines a hyperbolic Monod form relationship between substrate removal rate and total organic loading applied and is given by the equation,

$$U = \frac{U_{max}(FS_i/A)}{(K_s+FS_i/A)} \tag{9}$$

K_s is the half velocity concentration within the biolayer (mass/length^3).

(c) Gas Production Kinetics

Methane production is generally accepted as the rate limiting step of anaerobic degradation of organic substrate. The total gas production rate and methane quantity can also be mathematically modelled and accurately predicted in a manner similar to substrate removal.

Stover at al. (27) found that the total gas and methane production are a function of total applied substrate loading rate and assumed that they should respond in a similar manner as the substrate utilisation kinetics. The models are given by the following equations:

$$G = (G_{max} FS_i/A)\Big/(G_B + FS_i/A) \qquad (12)$$

$$M = (M_{max} FS_i/A)\Big/(M_B + FS_i/A) \qquad (13)$$

G is the specific gas production rate (length^3/length^2.time)

G_{max} is the maximum specific gas production rate.

A is the surface area (length^2)

G_B is the proportionality constant (mass/length^2 time)

M is the specific methane production rate (length^3/length^2.time)

M_{max} is the maximum specific methane production rate.

M_B is the proportionality constant (mass - length^2.time).

6.2 MATERIALS AND METHODS

A bench scale anaerobic contact filter (Fig.6.1) was fabricated using PVC pipe of 9.5 cm diameter and 180 cm height having a total volume of 0.012 m^3 (12 litres). A length of 7 cm was left over for sedimentation and distribution of wastewater at the bottom of the column. Sampling ports were provided at every 30 cm height of the filter from the perforated plate upto 150 cm. Granite stones with rough surfaces of the size ranging from 1 to 3 cm were used as filter media upto a height of 130 cm from the perforated plate. A clear liquid column of 40 cm was provided above the media for the separation of the effluent, suspended solids and gas. A space of 13 cm has been provided for the accumulation of gas produced. The gas was collected by the displacement method. The filter was fed with wastewater at the point just below the perforated

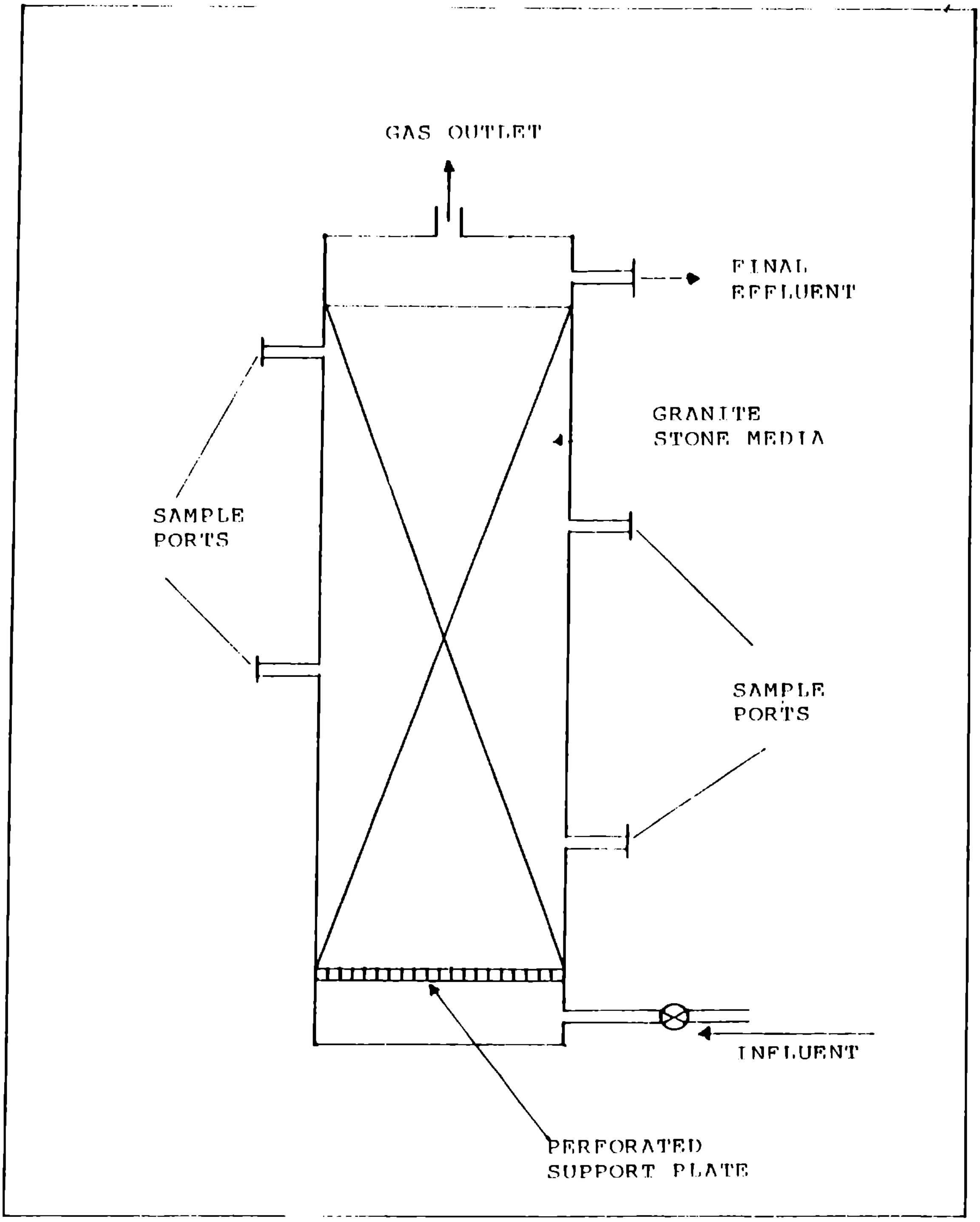


FIG.6.1 ANAEROBIC CONTACT FILTER.

support plate from an overhead reservoir by gravity flow.

Active biomass was grown on the surface of the filter media by daily feeding a mixture of sewage and cow dung slurry (1%) into the filter. Significant growth of bacteria was observed as evident from the methane gas production after 20 days of continuous operation. For proper acclimatization, the proportion of sewage was reduced to 90%, 80%, 70% etc. by adding increasing quantities of the rubber latex centrifuging effluent. After 15 days of this continuous acclimatization, steady state was achieved for a COD concentration of 9500 mg/l. The pH of the feed solution was adjusted to 6.4 by adding sodium carbonate and the solution was fed into the filter at different hydraulic loadings (7.20, 8.64, 10.08 and 11.52 litres/day).

The following observations were made during the course of the experiments which lasted for 15 days.

a) Measurement of pH and alkalinity of the influent and effluent overday.

b) Estimation of COD, BOD, volatile acids, and ammoniacal nitrogen content of the effluent daily using standard methods (28).

c) Analysis of the biogas produced for its methane content at the end of 15 days of steady state operation of the filter using a gas chromatograph.

The above procedure was repeated for other influent COD concentrations of 10400 mg/l, 5800 mg/l and 4620 mg/l. Adequate time was provided for acclimatization between change of organic as well as hydraulic loadings.

The characteristics of the centrifuge latex concentration wastewater samples used in the study are given in Table 6.1.

6.3 RESULTS AND DISCUSSION

The waste analysis indicated that the waste was nutrient-limited by phosphorous. For an unhindered anaerobic treatment of waste at full strength, at least 800 mg/l of nitrogen and 160 mg/l of phosphorous would be needed (29). In order to maintain unhindered anaerobic growth, phosphorous in the form of dibasic potassium phosphate were added to the feed wastewater in sufficient quantities to maintain a phosphorous: nitrogen: carbon ratio of 1:5.9:100

TABLE 6.1

EFFLUENT CHARACTERISTICS

parameter	Sample 1	Sample 2	Sample 3	Sample 4
pH	4.2	4.0	4.0	3.9
Total solids, mg/l	8200	17280	12875	8800
Dissolved solids, mg/l	6300	11140	10800	8010
Suspended solids, mg/l	1900	6140	2075	790
COD, mg/l	9500	10400	5800	4620
BOD, mg/l	5700	6100	3100	2800
Total kjeldahl nitrogen, mg/l	1500	1880	1580	1560
Ammoniacal nitrogen, mg/l	630	750	590	710

(29). The addition of potassium phosphate served two purposes. It not only provided the required phosphorous, but it increased the buffer capacity of the system to a limited extent. During periods of decreased alkalinity, the amount of potassium phosphate added to the feed was increased to provide additional buffer capacity.

(a) pH Value

pH range of 6.4 to 7.3 was observed for various organic loading rates of latex concentration effluent. The pH variation observed for the organic loading rates, 6 kg/day/m^3 and 7.2 kg/day/m^3 are plotted in Fig.6.2. In all the loading conditions, reduction in pH was observed in one day detention samples because of production of volatile acids but subsequently it remained neutral because of conversion of volatile acids to biogas.

(b) COD Removal

A steady state COD removal efficiency was obtained after a period of operation at a given loading. The results of a series of organic loading changes are illustrated in Fig.6.3. Initially, latex effluent with a COD of 9500 mg/l was fed to the filter at a loading rate of 6 kg COD/day/m^3

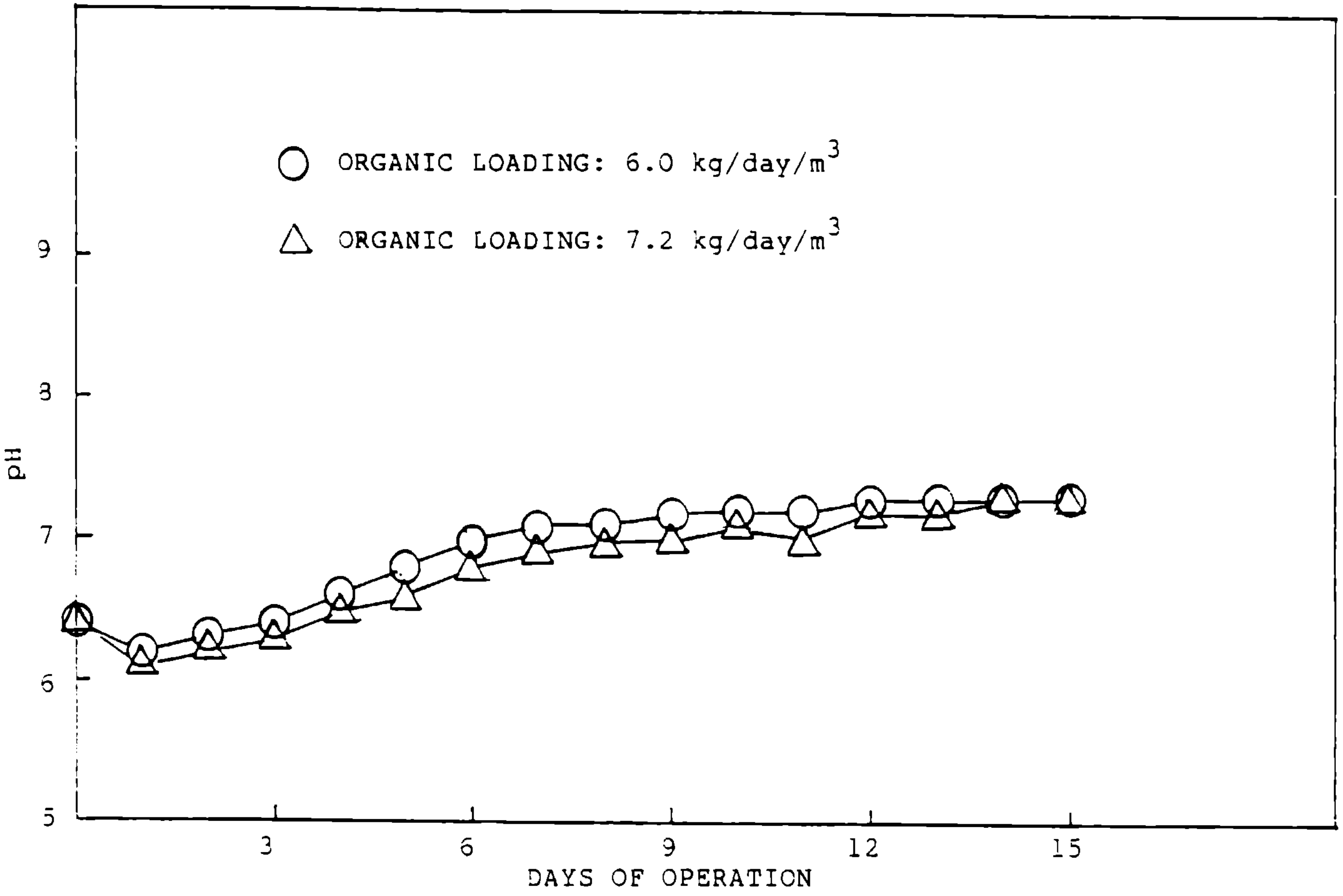


FIG.6.2 VARIATION OF pH WITH DAYS OF OPERATION.

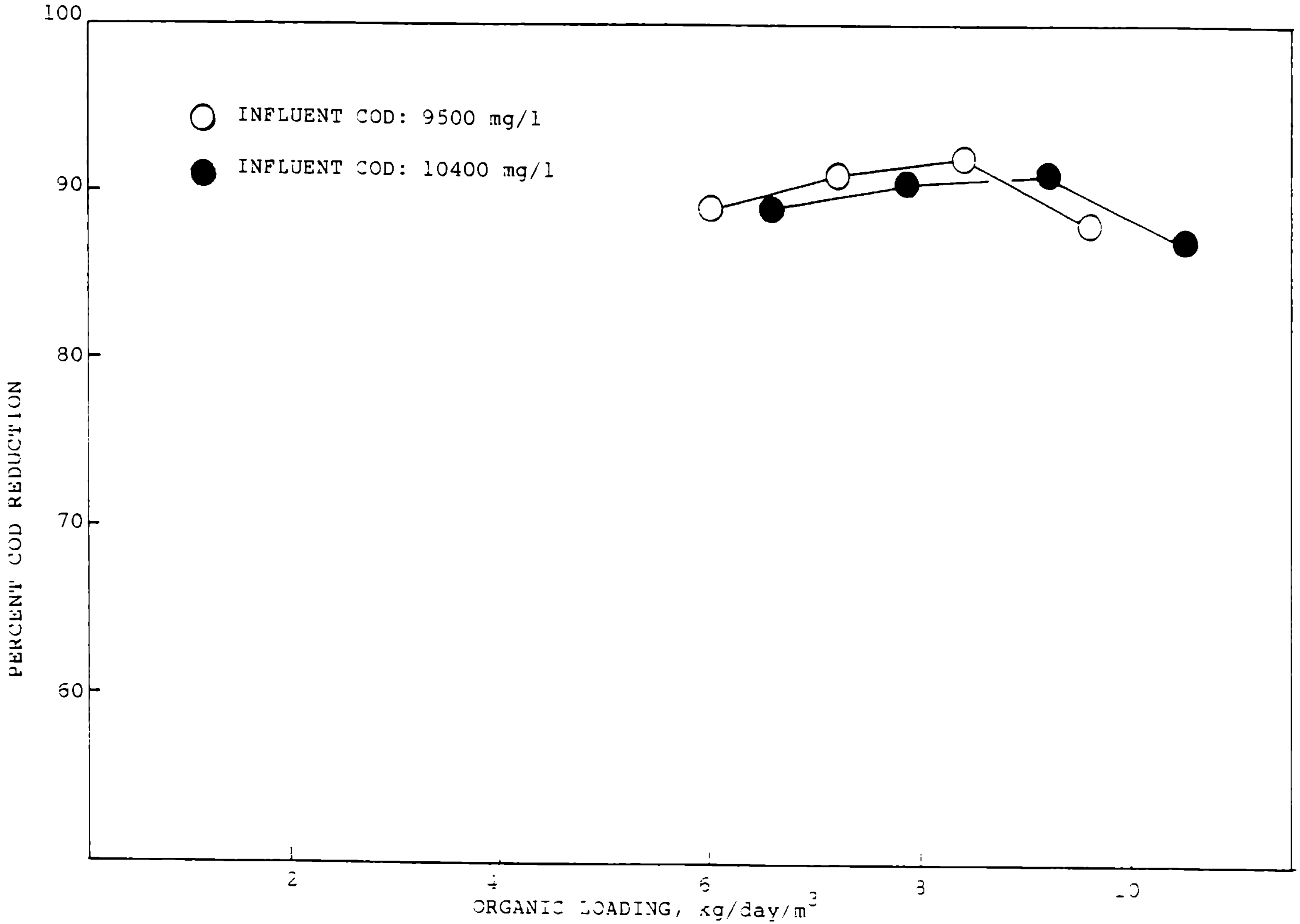


FIG.6.3 PERCENT COD REDUCTION AT VARIOUS ORGANIC LOADINGS.

This was followed by loading rates of 7.2, 8.4 and 9.6 kg/day/m^3. On increasing the loading rate from 6 to 8.4, the COD removal efficiency increased from 89 per cent to 92 per cent. But when the loading rate was further increased to 9.6 kg/day/m^3, the COD removal dropped to 88 per cent. The same trend was observed at an influent COD concentration of 10400 mg/l. Although the COD removal efficiency increased from 89 per cent to 91 per cent on increasing the organic loading rate from 6.57 kg/day/m^3 to 9.19 kg/day/m^3, it dropped to 87 per cent on further increasing the loading rate to 10.5 kg/day/m^3.

It is seen that the COD removal efficiencies decrease with increase in organic loadings beyond a particular limit This may be due to substrate inhibition, or inadequate acclimatization of bacteria or formation of propionic acids (30).

The percentage COD reduction obtained on each day of operation of the filter is shown in Fig.6.4. The curves plotted for different organic loading rates show that rapid COD removals are obtained in the first day detention samples. This should be due to the active biomass present on the filter medium which decomposes the organic matter in

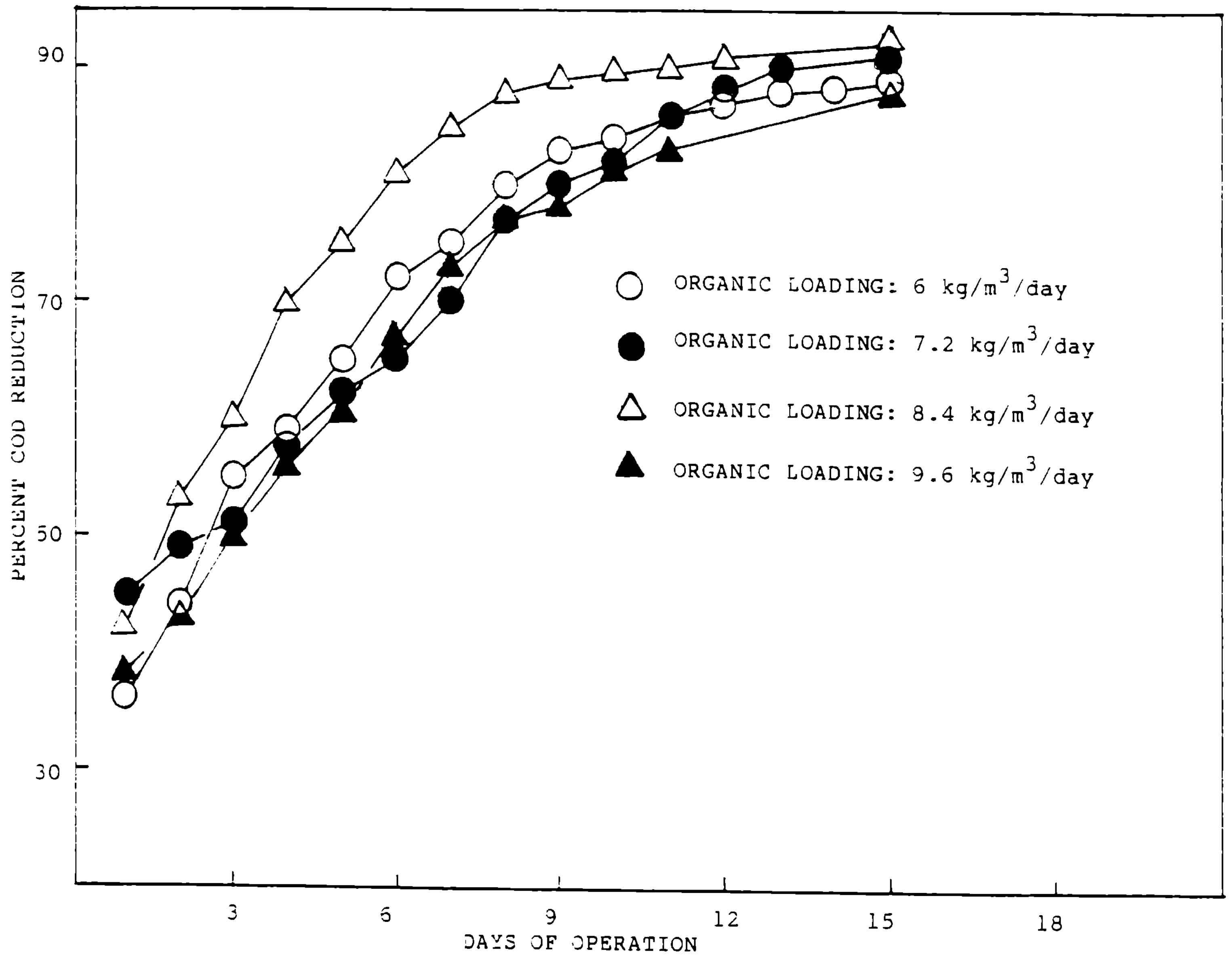


FIG.6.4 VARIATION IN PERCENT COD REDUCTION WITH DAYS OF OPERATION.

the feed wastewater very efficiently. For all the loading rates, most of the COD removal was found to take place during the first 10 days of operation. This points to the fact that most of the stabilization of the waste should be occurring during the first ten days of operation. The COD removal efficiencies achieved for different influent concentrations are summarised in Table 6.2.

(c) BOD Removal

As in the case of COD removal, the BOD removal efficiency also increased with organic loading upto a certain limit. The variation of BOD removal with organic loading is illustrated in Fig.6.5. When the organic loading rate was increased from 6 kg/day/m^3 to 8.4 kg/day/m^3 for an influent COD of 9500 mg/l, the BOD removal efficiency increased from 92.5 per cent to 95.0 per cent. But on increasing the organic loading rate to 9.6 kg/day/m^3, the BOD removal efficiency was found to drop to 91.0 per cent. The same pattern repeated for other influent COD concentrations also. The reason for this behaviour should be substrate inhibition or improper acclimatization of bacterial mass.

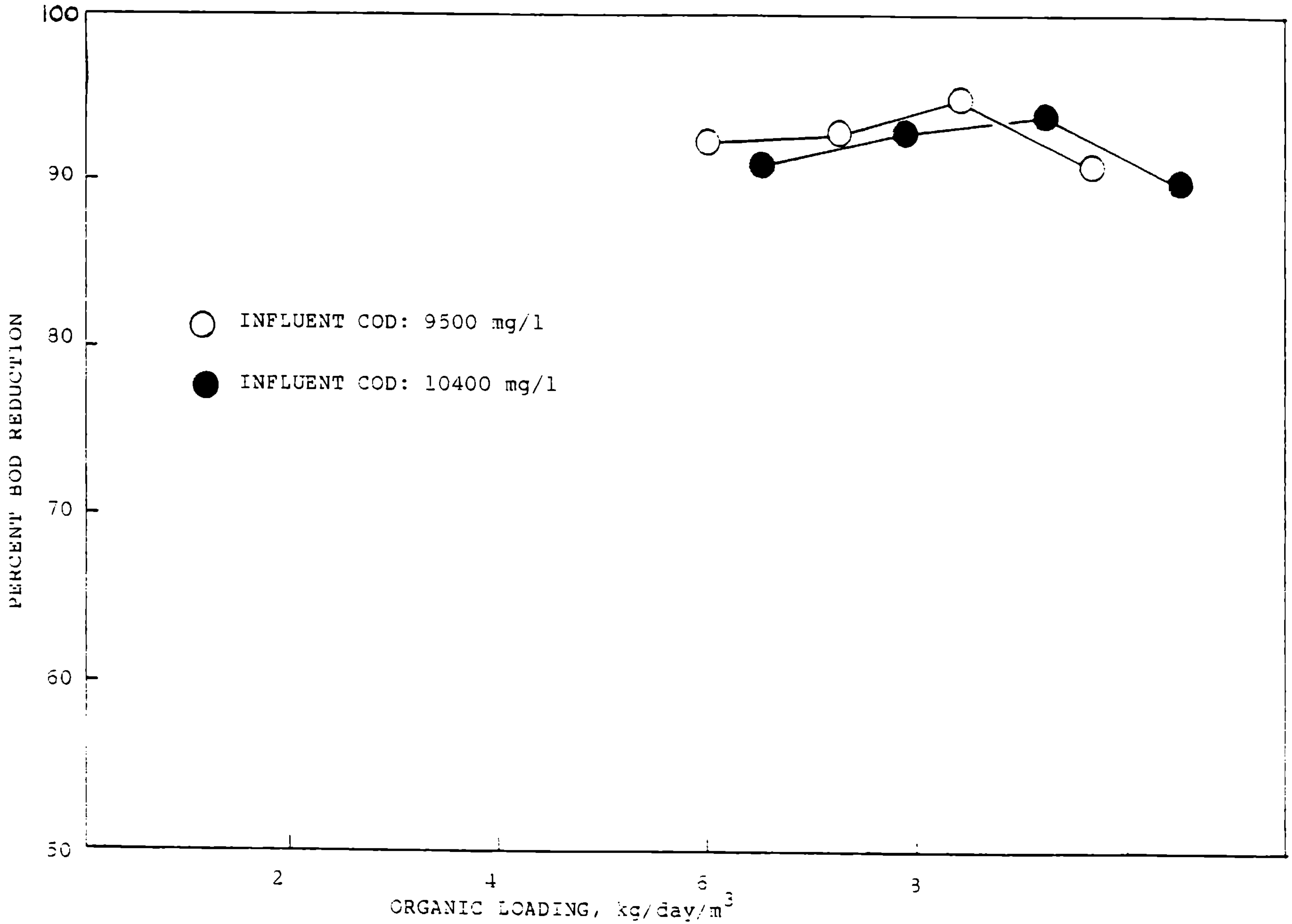


FIG.6.5 PERCENT BOD REDUCTION AT VARIOUS ORGANIC LOADINGS.

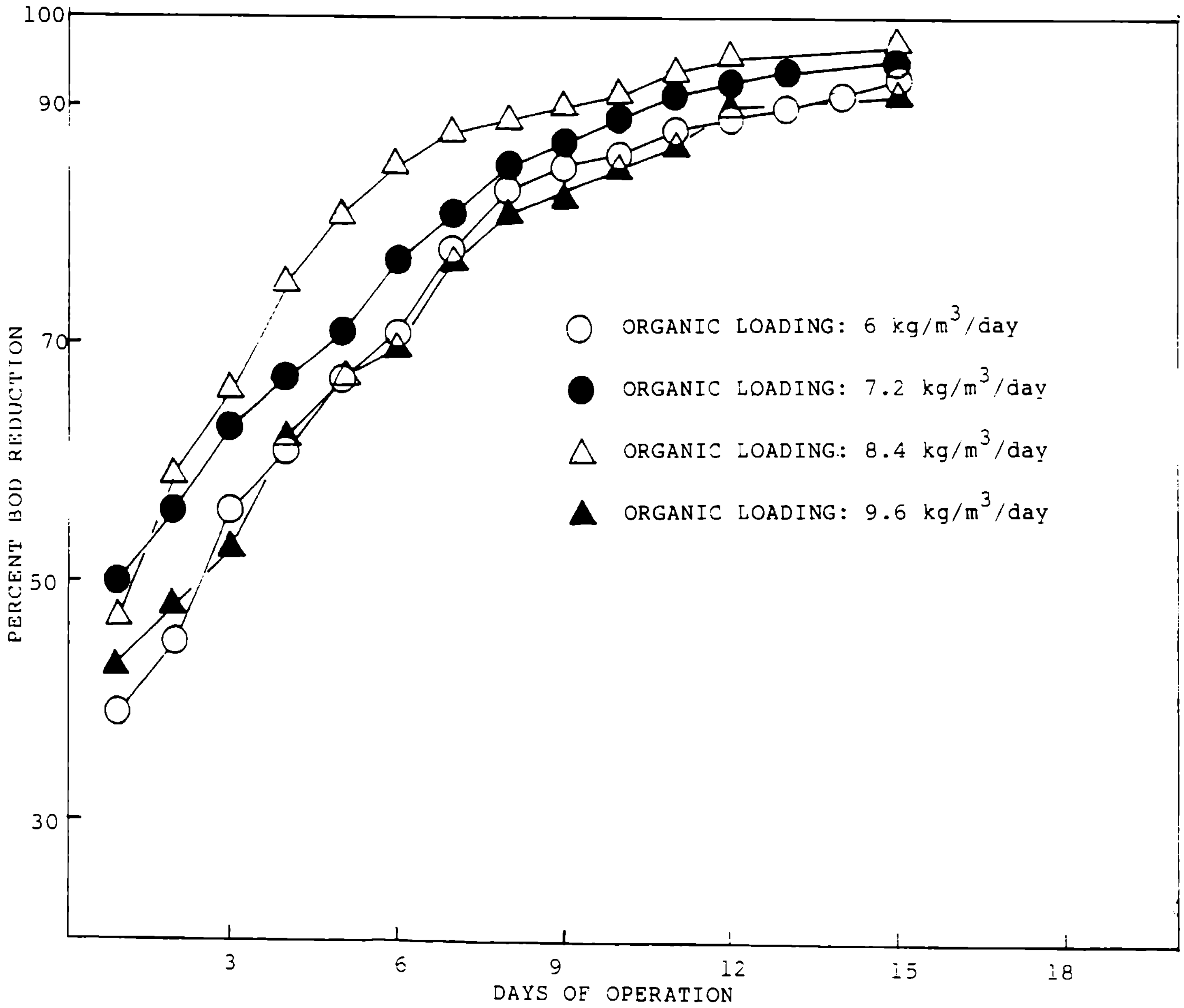


FIG.6.6 VARIATION IN PERCENT BOD REDUCTION WITH DAYS OF OPERATION.

TABLE 6.2

PERFORMANCE OF ANAEROBIC FILTER FOR VARIOUS ORGANIC LOADINGS

Influent COD concentration mg/l	Organic loading rate kg COD/day/m^3	Percent COD removal	Percent BOD removal
9500	6.0	89.0	92.5
	7.2	91.0	94.0
	8.4	92.0	95.0
	9.6	88.0	91.0
10400	6.57	89.0	91.0
	7.88	90.5	93.0
	9.19	91.0	94.0
	10.50	87.0	90.0
5800	3.66	87.0	90.5
	4.39	88.0	91.5
	5.13	89.0	93.0
	5.86	86.0	88.5
4620	2.92	87.0	90.0
	3.50	89.0	91.0
	4.08	90.5	94.0
	4.67	85.0	90.0

The variation of BOD with detention time is shown in Fig.6.6. Rapid BOD removals were observed in the first day detention samples in all the loading conditions which confirms the presence of an active biomass in the filter. The BOD removal efficiencies achieved during the course of the experiments are given in Table 6.2.

(d) Gas Production

Biogas production is the final step of anaerobic process and is due to the conversion of volatile acids to gaseous form by methanogenic bacteria. The volume of gas generated and its methane content for different organic loadings are plotted in Fig.6.7.

For an influent COD concentration of 9500 mg/l, the volume of gas collected during 15 days of operation of the filter was 5.1 litres, i.e., 0.34 litres of gas production per day on an average. The volume of gas collected rose to 5.85 litres (0.39 litre/day) on increasing the organic loading to 8.4 kg/day/m^3. But on increasing the organic loading rate further to 9.6 kg/day/m^3 the volume of methane produced was found to decrease to 5.4 litres. The same trend was observed for an influent COD concentration of

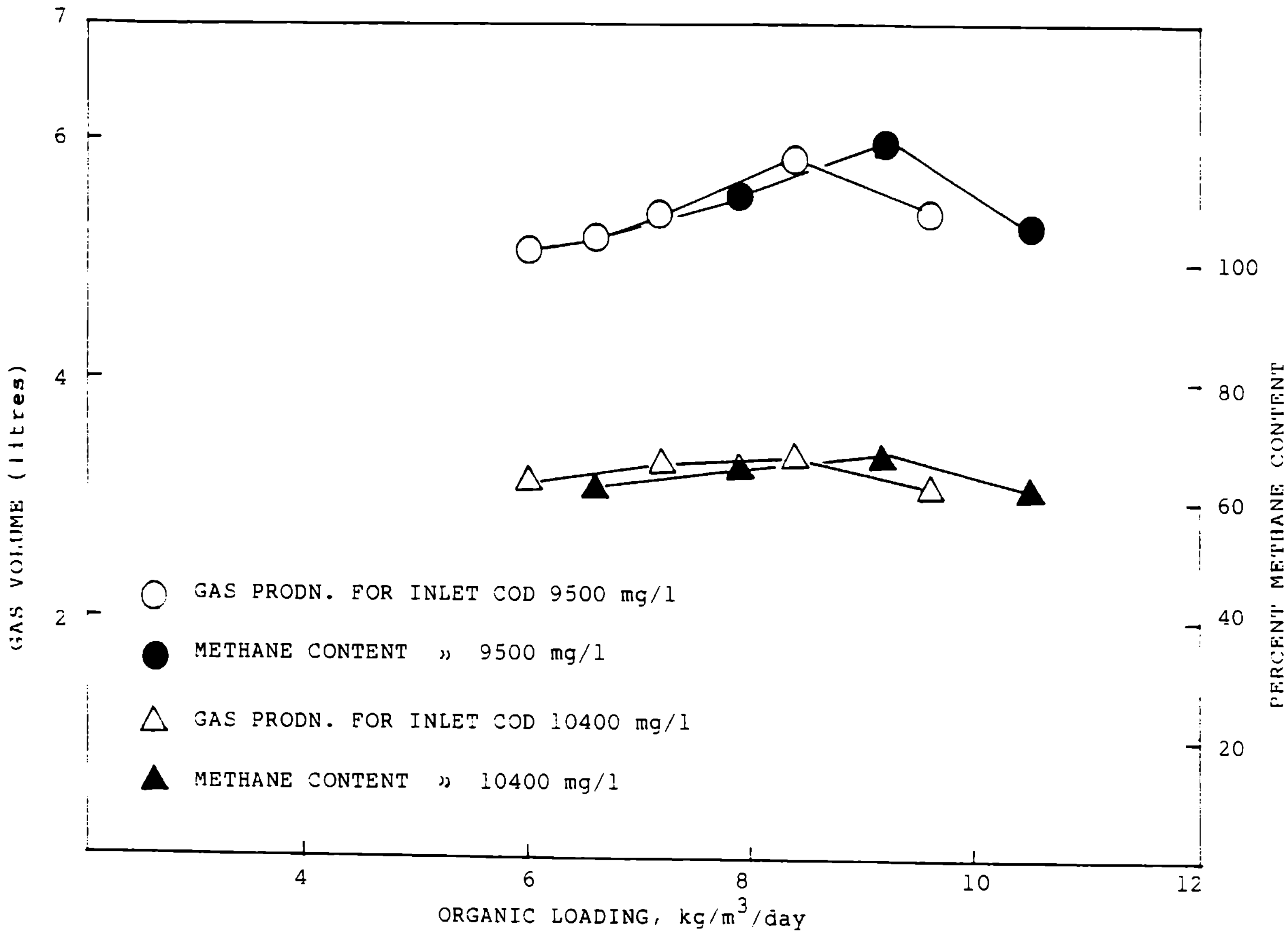


FIG.6.7 GENERATION OF BIOGAS 'Vs. ORGANIC LOADING.

10400 mg/l. On increasing the organic loading rate from 6.57 kg/day/m^3 to 9.19 kg/day/m^3, the gas production increased from 5.25 litres (0.35 litre/day) to 6 litres (0.4 litre/day). While on increasing the organic loading rate to 10.5 kg/day/m^3, the volume gas produced dropped to 5.4 litres.

The methane content of the biogas produced varied with organic loading. As in the case of gas production, the methane content of the gas increased from 63 per cent to 67 per cent on changing the organic loading rate from 6.0 kg/day/m^3 to 8.4 kg/day/m^3 for an influent COD concentration of 9500 mg/l. The methane content of the biogas was found to decrease to 62 per cent on increasing the organic loading rate to 9.6 kg/day/m^3. The same trend was observed for the influent concentration of 10400 mg/l.

The reason for the drop in gas production and methane content beyond a particular organic loading rate should be due to the lesser organic removal at higher organic loadings and lesser activation of methanogenic bacteria (30). The specific biogas yield expressed as lit CH_4/gm COD destroyed/day for the various organic loadings studied is given in Table 6.3.

TABLE 6.3

SPECIFIC METHANE PRODUCTION FOR VARIOUS ORGANIC LOADINGS

Influent COD concentration mg/l	Organic loading rate kg COD/day/m^3	Specific methane production lit CH_4/gm COD destroyed/day
9500	6.0	0.025
	7.2	0.027
	8.4	0.029
	9.6	0.026
10400	6.57	0.023
	7.88	0.025
	9.19	0.028
	10.50	0.024
5800	3.66	0.023
	4.39	0.025
	5.13	0.029
	5.86	0.024
4620	2.92	0.025
	3.50	0.026
	4.08	0.029
	4.67	0.026

(e) Variation in Alkalinity

The variation in alkalinity experienced in the filter during the experimental run of 15 days is shown in Fig.6.8. The alkalinity values measured for the two organic loadings, viz., 6 kg/m^3/day and 7.2 kg/day/m^3, show that the fluctuations occurring have been taken care of by the bacterial mass in the filter. There is practically no difference between the initial and final alkalinity values which indicates a steady state operation of the filter.

(f) Volatile Acids

The volatile acid concentration of the effluent during the period of operation of the filter is shown in Fig.6.9.

For all the organic loading rates, there was a steep increase in the production of volatile acids during the initial period. This should be due to the increased activity of non-methanogenic bacteria which produce volatile acids (31). But as the detention time increased, the volatile acid concentration came down. The conversion of volatile acids to methane by bio-methanation should have caused the drop in volatile acids concentration.

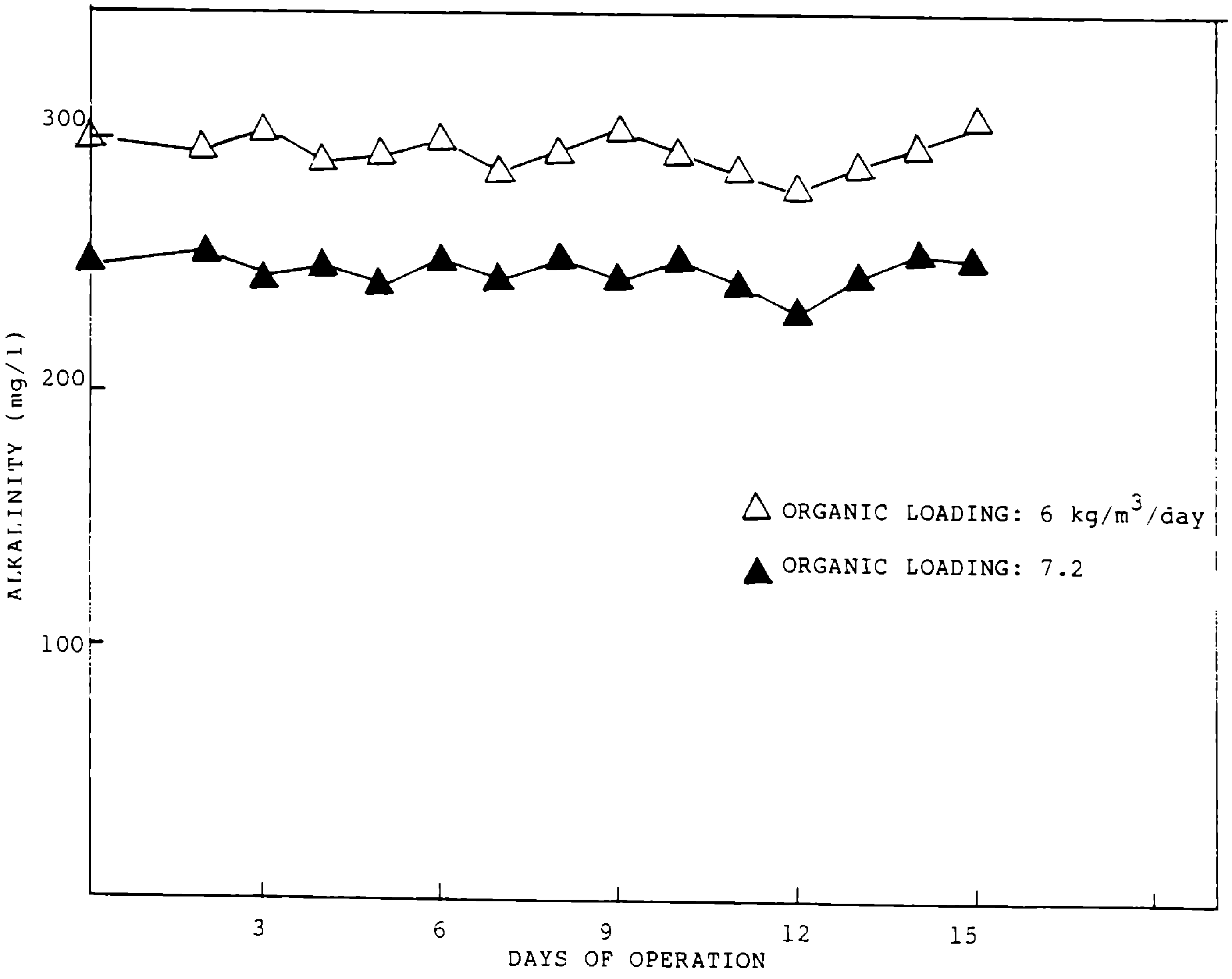


FIG.6.8 VARIATION IN ALKALINITY WITH DAYS OF OPERATION.

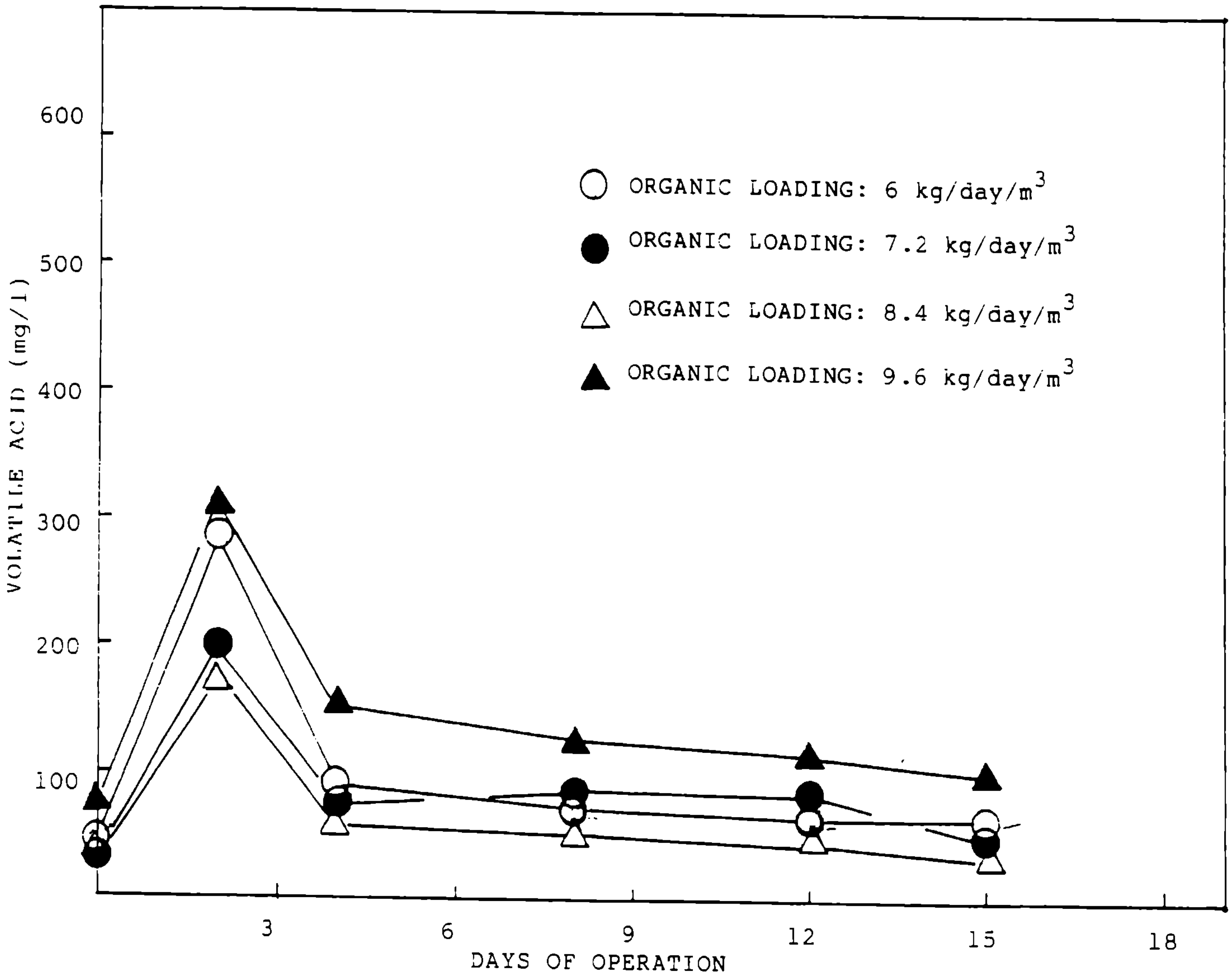


FIG.6.9. VOLATILE ACID PRODUCTION 'Vs. DAYS OF OPERATION.

(g) Effect of Filter Height

During the periods of steady-state operation of the filter, samples were collected periodically from the filter at various heights. The profiles of COD removal efficiency "Vs' filter depth at various organic loadings of the latex concentration effluent are shown in Fig.6.10.

For all the organic loadings, the maximum COD removal efficiency was observed in the samples collected at a depth of 150 cm. The samples collected from points at different depths of 120 cm, 90 cm and 30 cm showed a steep fall in the COD removal efficiency. The results indicate that the performance of the filter in terms of per cent COD removal was better at a filter height of 30 cm. This shows that the biomass is most active at the bottom portions of the anaerobic filter. Since the efficiency of treatment did not improve beyond 120 cm filter height, higher filters may not be advisable. Khan and Siddiqi (32) and Govindan (20) also reported that the efficiency of the filter was low beyond 120 cm (4 ft.).

(h) Ammoniacal Nitrogen Removal

The per cent ammoniacal nitrogen removal obtained

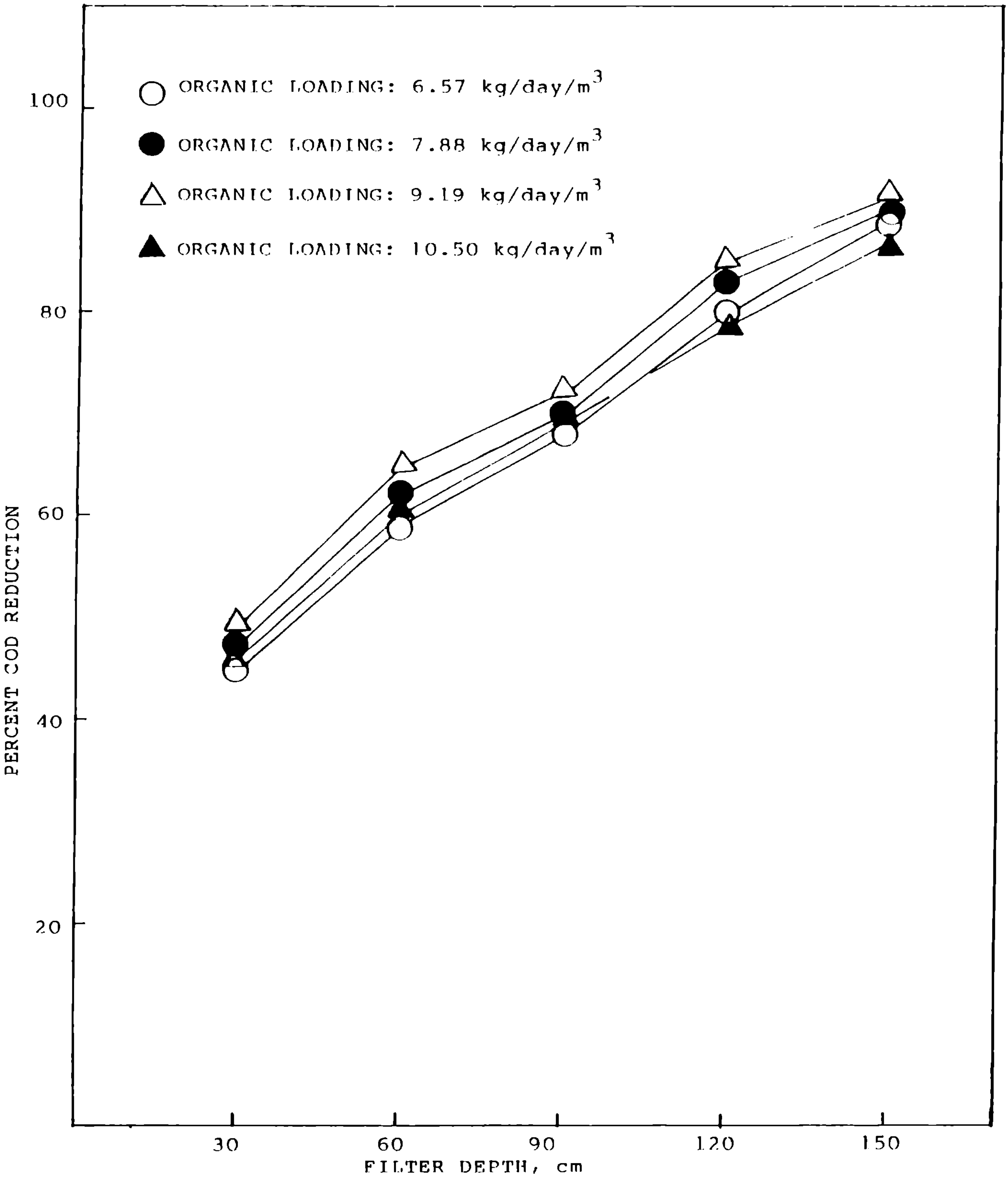


FIG.6.10 COD REMOVAL EFFICIENCY 'Vs.' FILTER DEPTH.

in the filter in a period of 15 days for different organic loading rates is shown in Table 6.4.

The results show that the upflow anaerobic filter is capable of reducing the ammoniacal nitrogen content in the filter considerably. The persistent reduction of ammoniacal nitrogen in the effluents may be due to the utilisation of nitrogen as nutrient by the microbial population. According to a study carried out by Sanders and Bloodgood (29), for an inhindered anaerobic growth of waste at full strength, at least 800 mg/l of nitrogen would be needed. All the effluent samples used for the study contained total kjeldahl nitrogen ranging from 1500 to 1880 mg/l and ammoniacal nitrogen ranging from 590 to 750 mg/l.

The trend observed in the case of COD and BOD removal is repeated for ammoniacal nitrogen removal also. For an influent COD concentration of 9500 mg/l, as the organic loading rate increased from 6.0 kg COD/day/m^3 to 8.4 kg/day/m^3, the ammoniacal removal efficiency increased from 87 to 92 per cent. But on further increasing the loading rate to 9.6 kg/day/m^3, the removal efficiency dropped to 89 per cent. This may be due to decreased bacterial activity at higher organic loads resulting from substrate inhibition.

TABLE 6.4

PERCENTAGE AMMONIACAL NITROGEN REMOVAL

Organic loading kg COD/day/m^3	Percent removal of NH_4-N
6.0	87.0
7.2	90.0
8.4	92.0
9.6	89.0
6.57	88.0
7.88	91.0
9.19	93.0
10.50	88.0
3.66	86.0
4.39	87.5
5.13	90.0
5.86	86.0
2.92	85.0
3.50	87.0
4.08	90.5
4.67	85.0

(i) Kinetics

(1) Substrate kinetics

The substrate rate constants (k_2A/V) were determined by using equation (4). From Fig.6.11, it can be observed that loading rates versus effluent concentration varied linearly as predicted by Dewalle and Chian model (25).

The maximum loading rates (L_m) and half velocity constants (K_s) were determined using equation (5). The Lineweaver Burk Plot (Fig.6.12) indicates that when reciprocal of substrate removal was plotted against reciprocal of effluent substrate concentration, a linear relationship as desired was obtained. The maximum loading rate that could be applied in the anaerobic filter was found to be 50 kg $COD_r/m^3/d$.

The substrate removal rate constants, viz., K_L, K_θ and 'a' (Figs.6.13 to 6.15) were determined using equations 6, 7 and 8. The value of K_L was found increasing with detention time, while K_θ decreased with increasing loading rates (Figs.6.16 and 6.17).

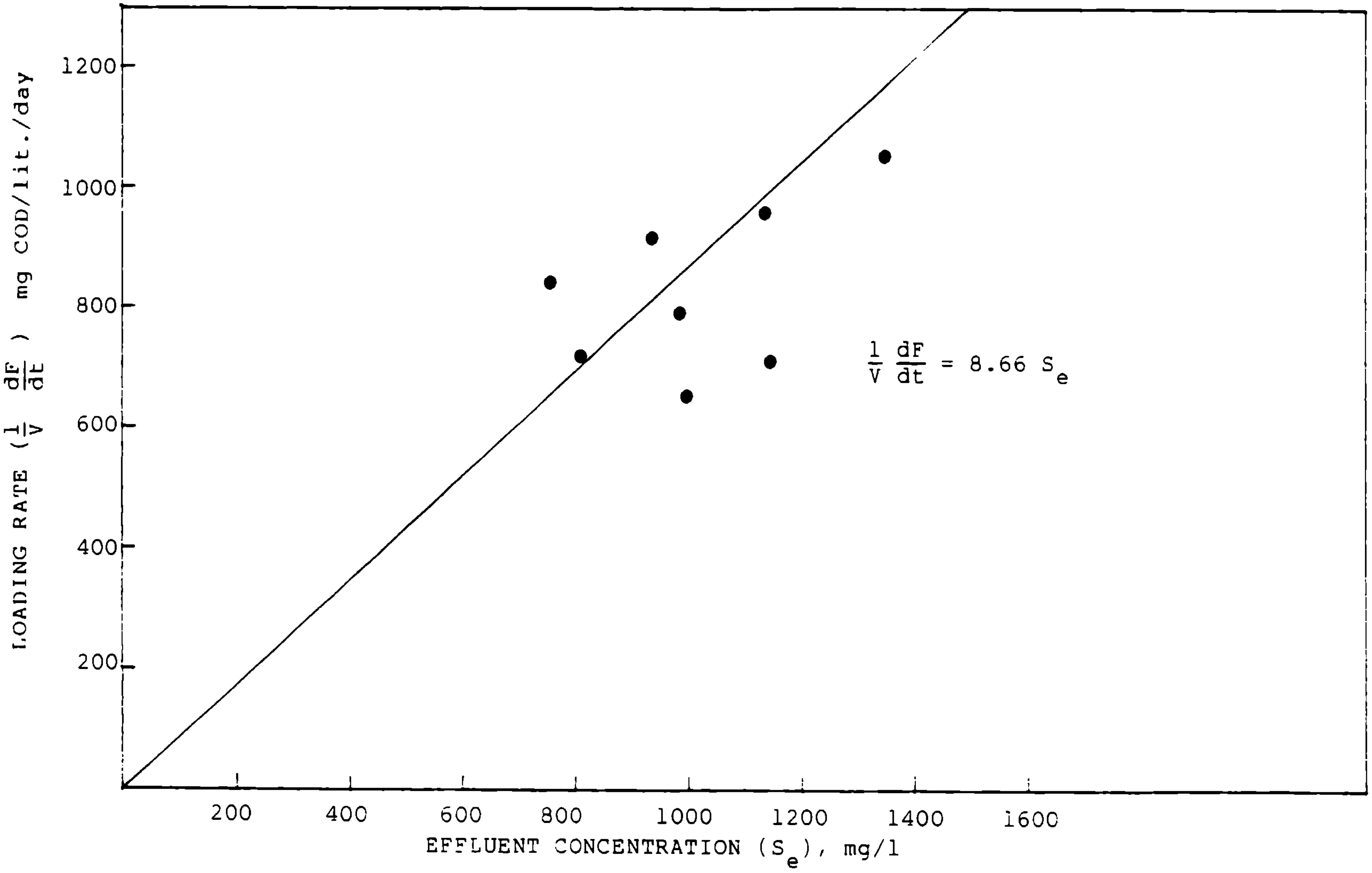


FIG.6.11 PLOT OF LOADING RATE VERSUS EFFLUENT CONCENTRATION.

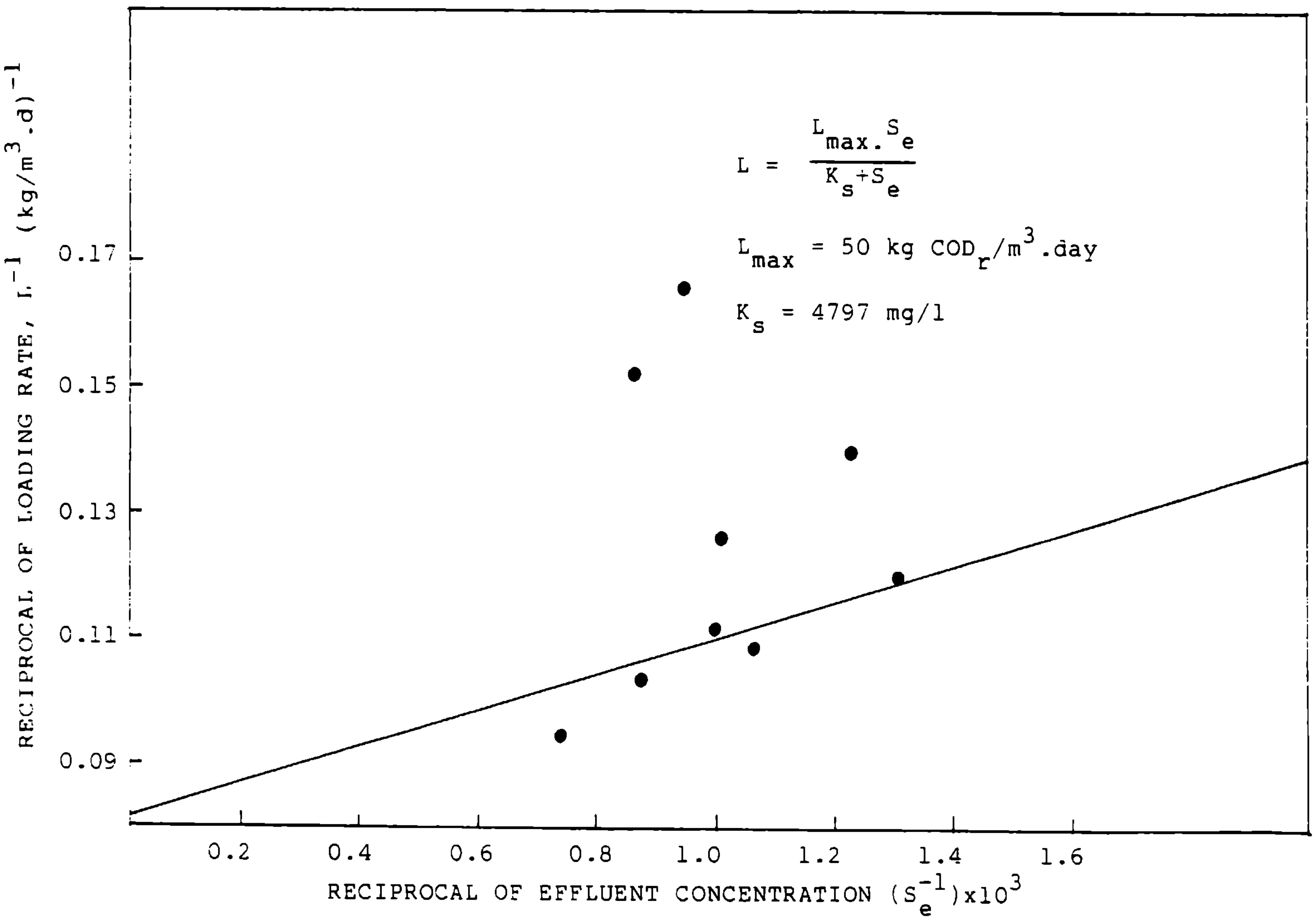


FIG.6.12 DETERMINATION OF MAXIMUM LOADING RATE.

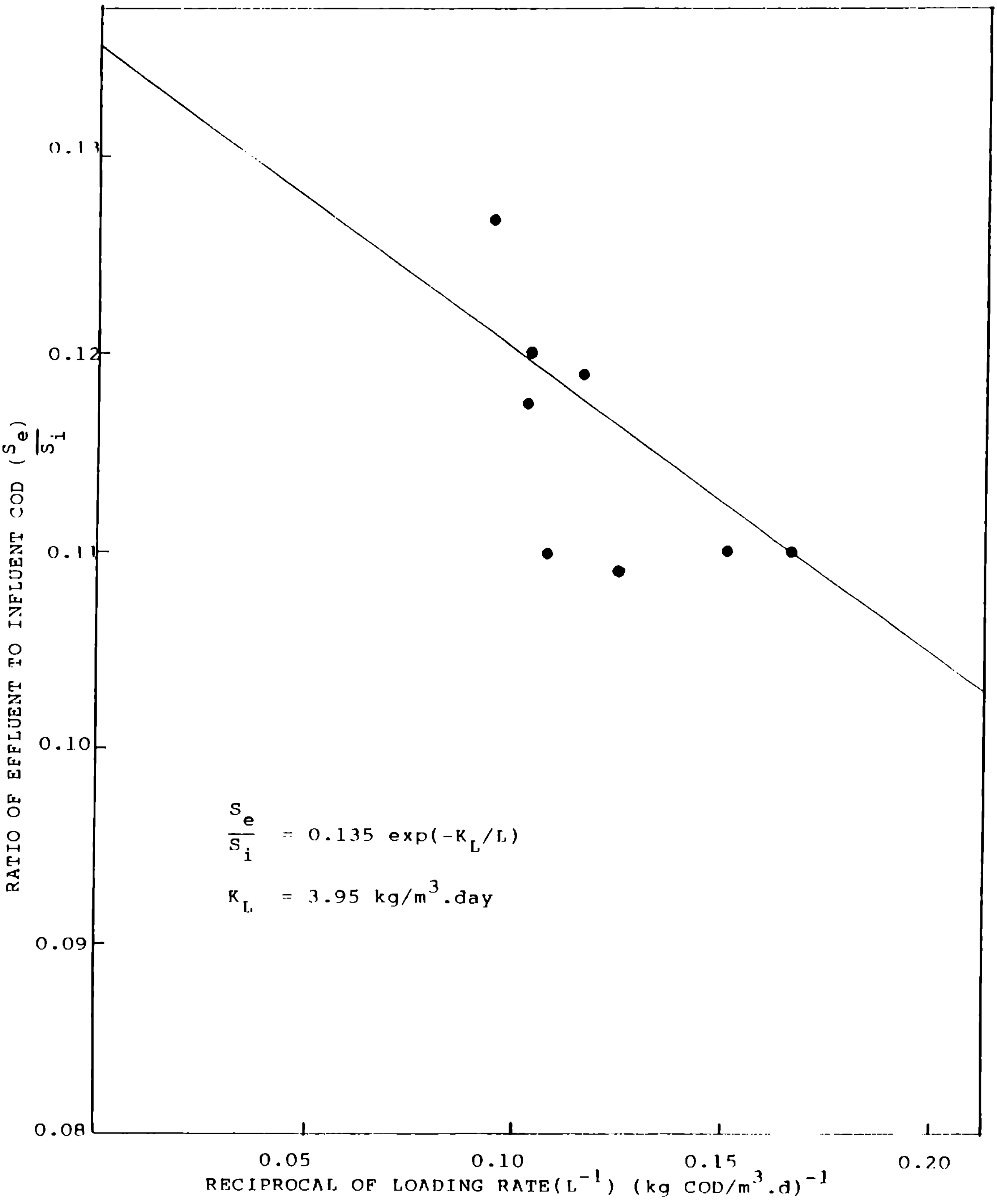


FIG.6.13 PLOT OF $(\frac{S_e}{S_i})$ VERSUS L^{-1}

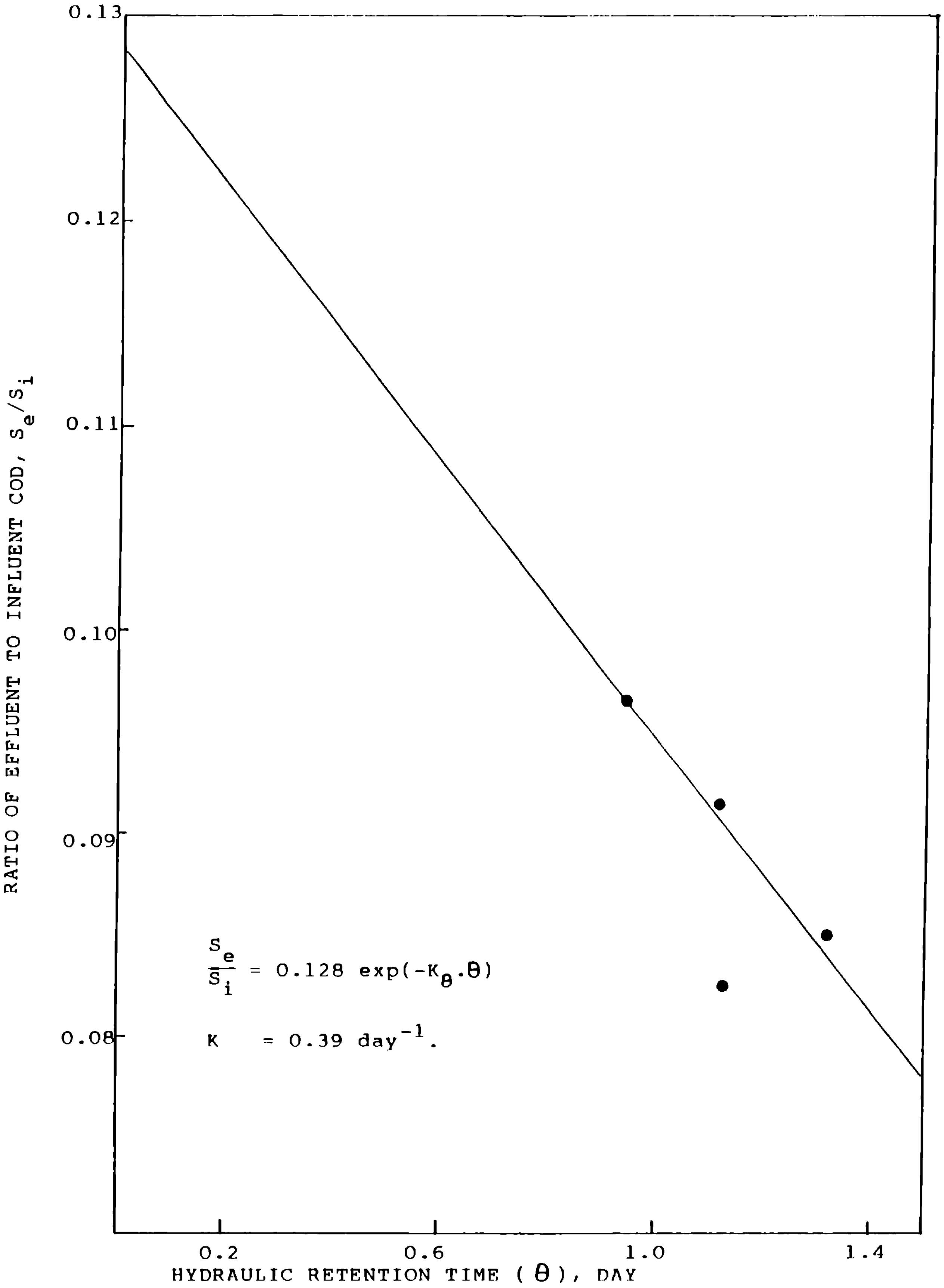


FIG.6.14 PLOT OF $\frac{S_e}{S_i}$ VERSUS HRT

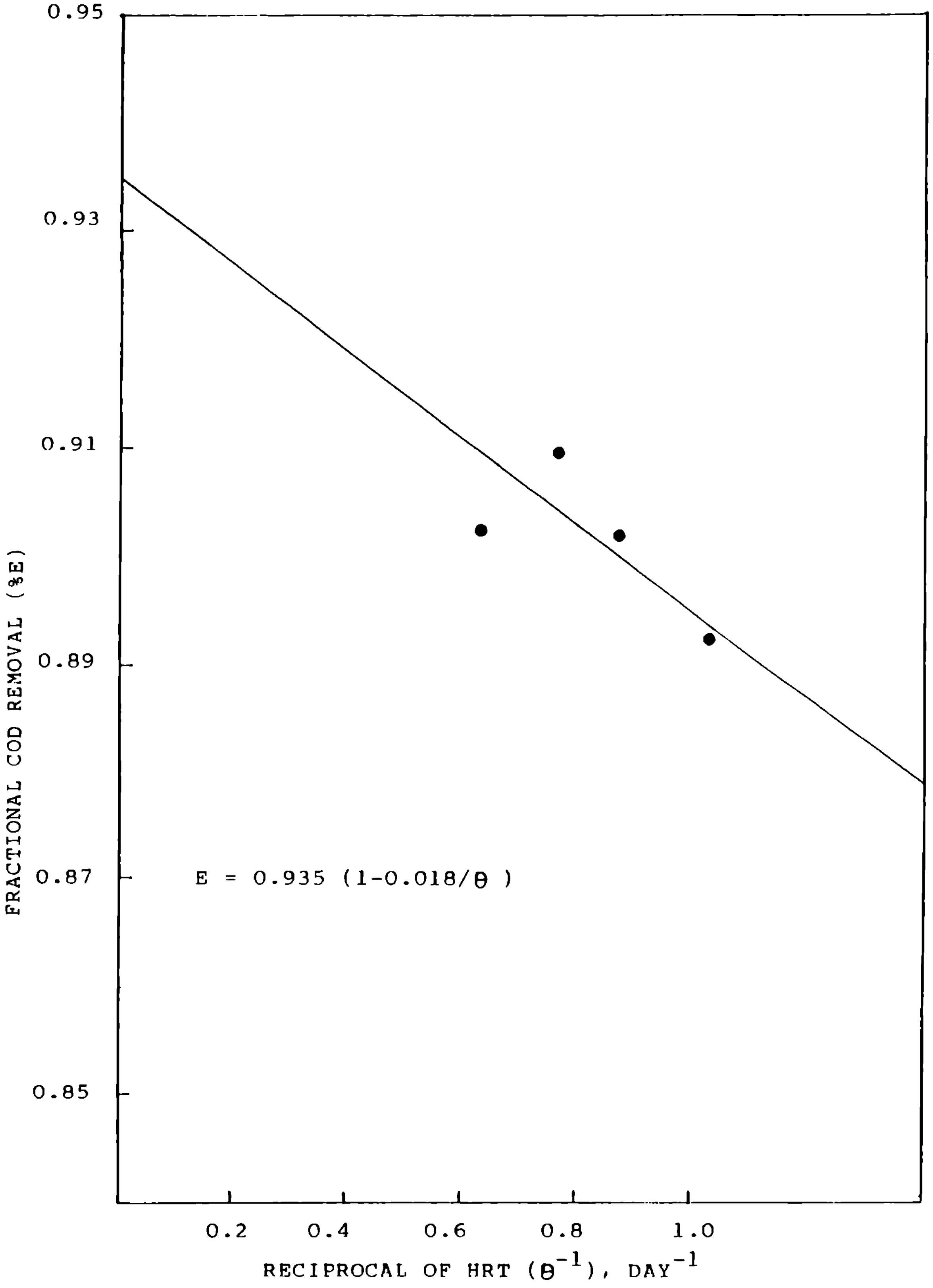


FIG.6.15 PLOT OF FRACTIONAL COD REMOVAL Vs. RECIPROCAL OF HRT.

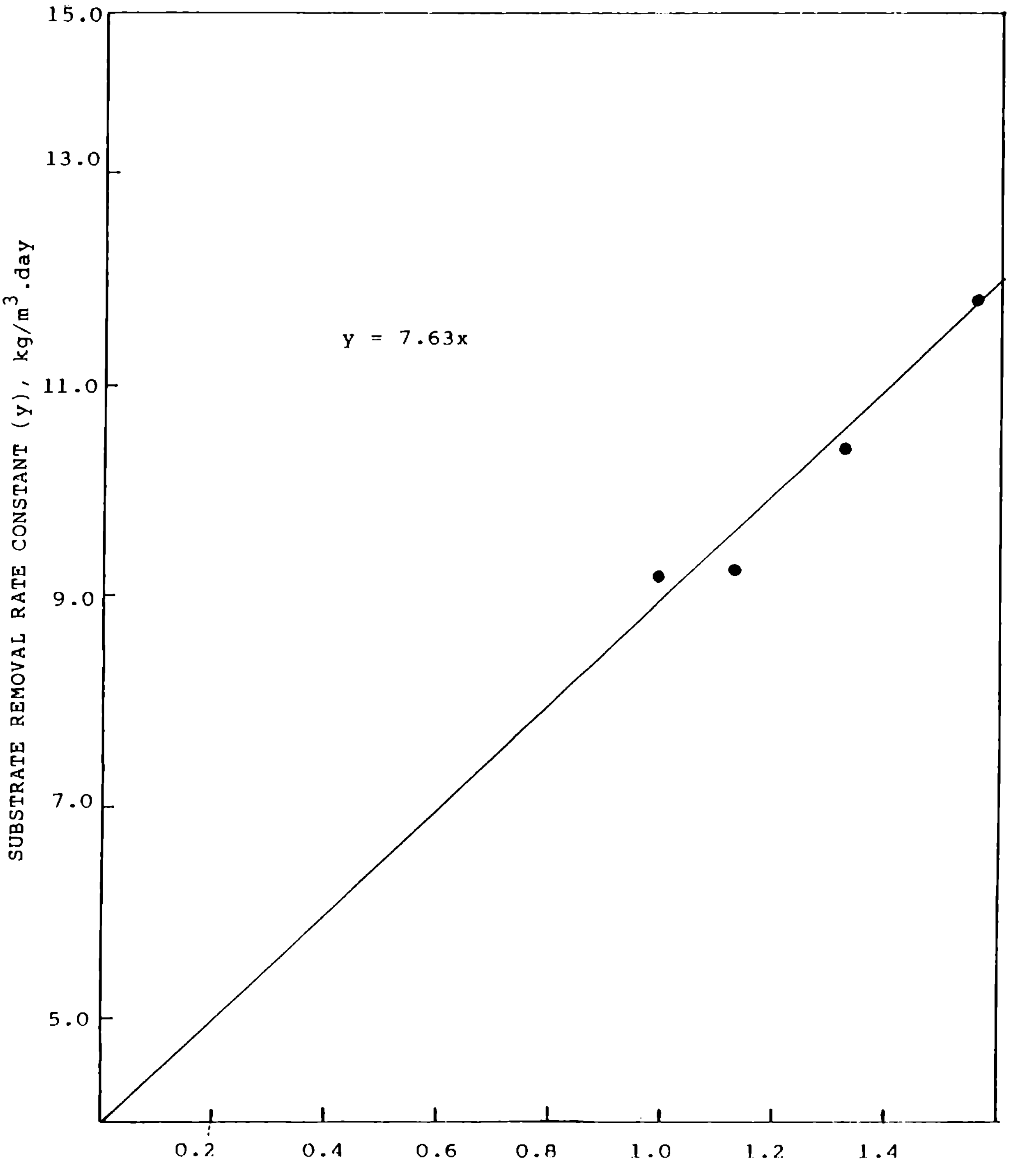


FIG.6.16 PLOT OF SUBSTRATE REMOVAL RATE VERSUS HRT.

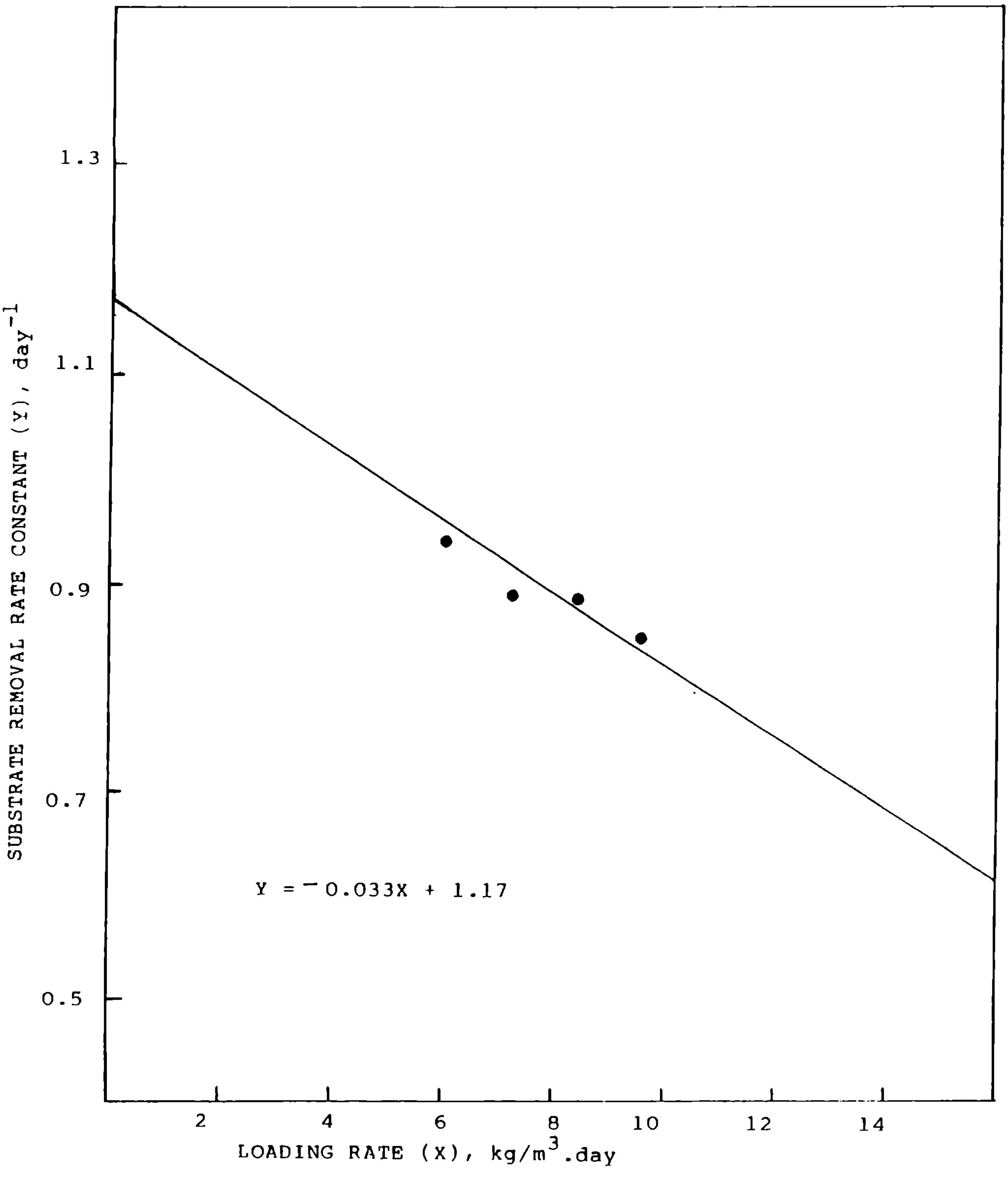


FIG.6.17 PLOT OF SUBSTRATE REMOVAL RATE CONSTANT VERSUS LOADING RATE.

The maximum removal efficiency (Esm) and theoretical detention time ('a') were determined by Young and Mc Carty Model given by equation (8). The maximum substrate removal efficiency decreased with increasing loading rate and 'a' increased with decreasing efficiency (Fig.6.18) thereby confirming the fact that 100% removal cannot be achieved even at detention times tending to infinity.

The Stover's model (equation 9) was evaluated for the anaerobic filter to determine the values of maximum specific substrate loading rate (U_{max}) and proportionality constant (K_{θ}) (Fig.6.19).

(2) Microorganism growth kinetics

The determination of specific growth rate (μ) and biological constant (K_{μ}) were estimated for the upflow anaerobic filter by making use of equation (10) (Fig.6.20). The model fitted well for the filter. The values of specific growth rate (μ) was found to increase with increasing loading rates as shown in Fig.6.21. This may be attributed to the fact that at higher loadings there is every possibility of volatile acid formation which in turn is used by methanogenic bacteria for generation of methane.

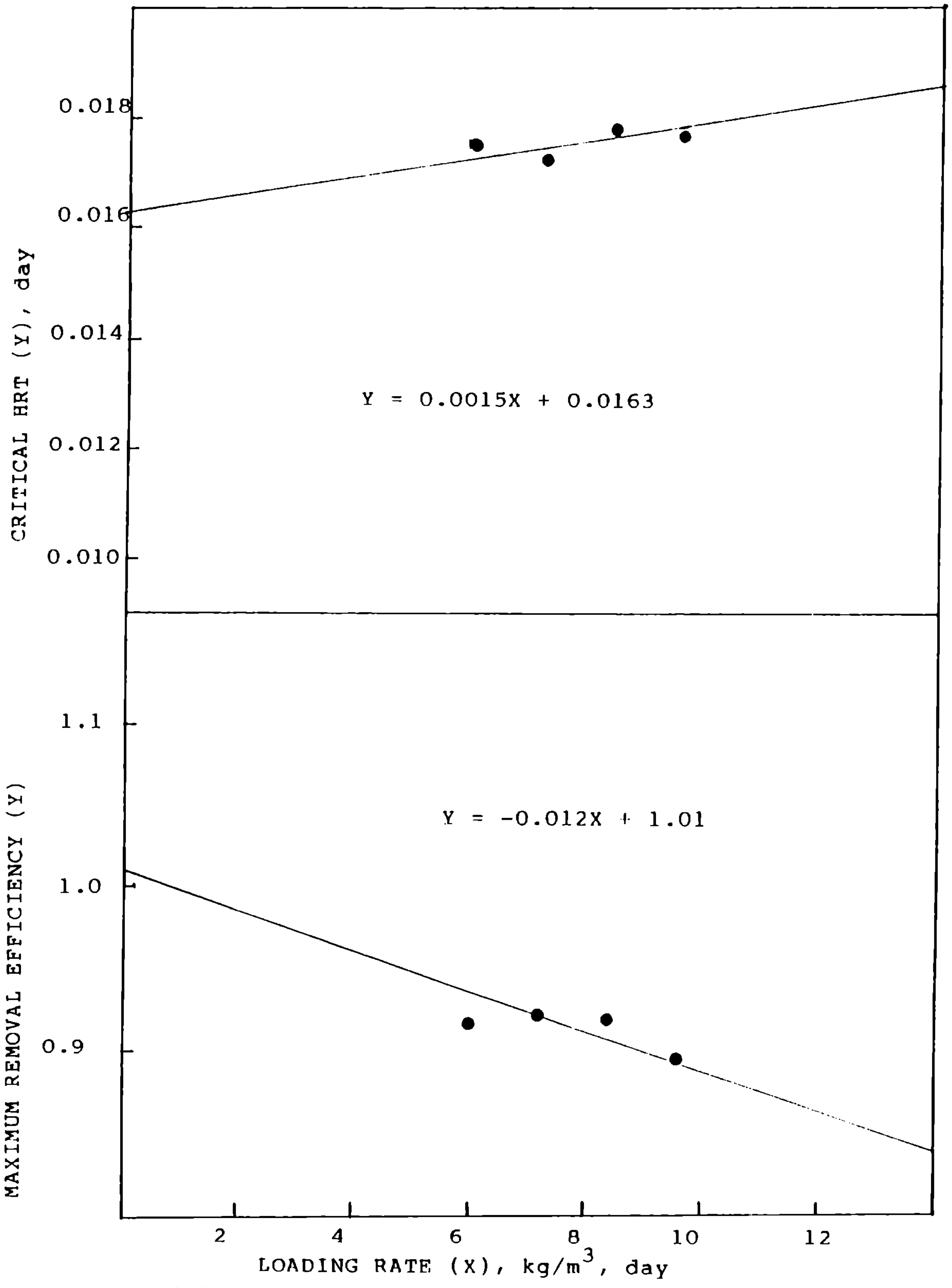


FIG.6.18 PLOT OF MAXIMUM REMOVAL EFFICIENCY AND CRITICAL HRT VERSUS LOADING RATE.

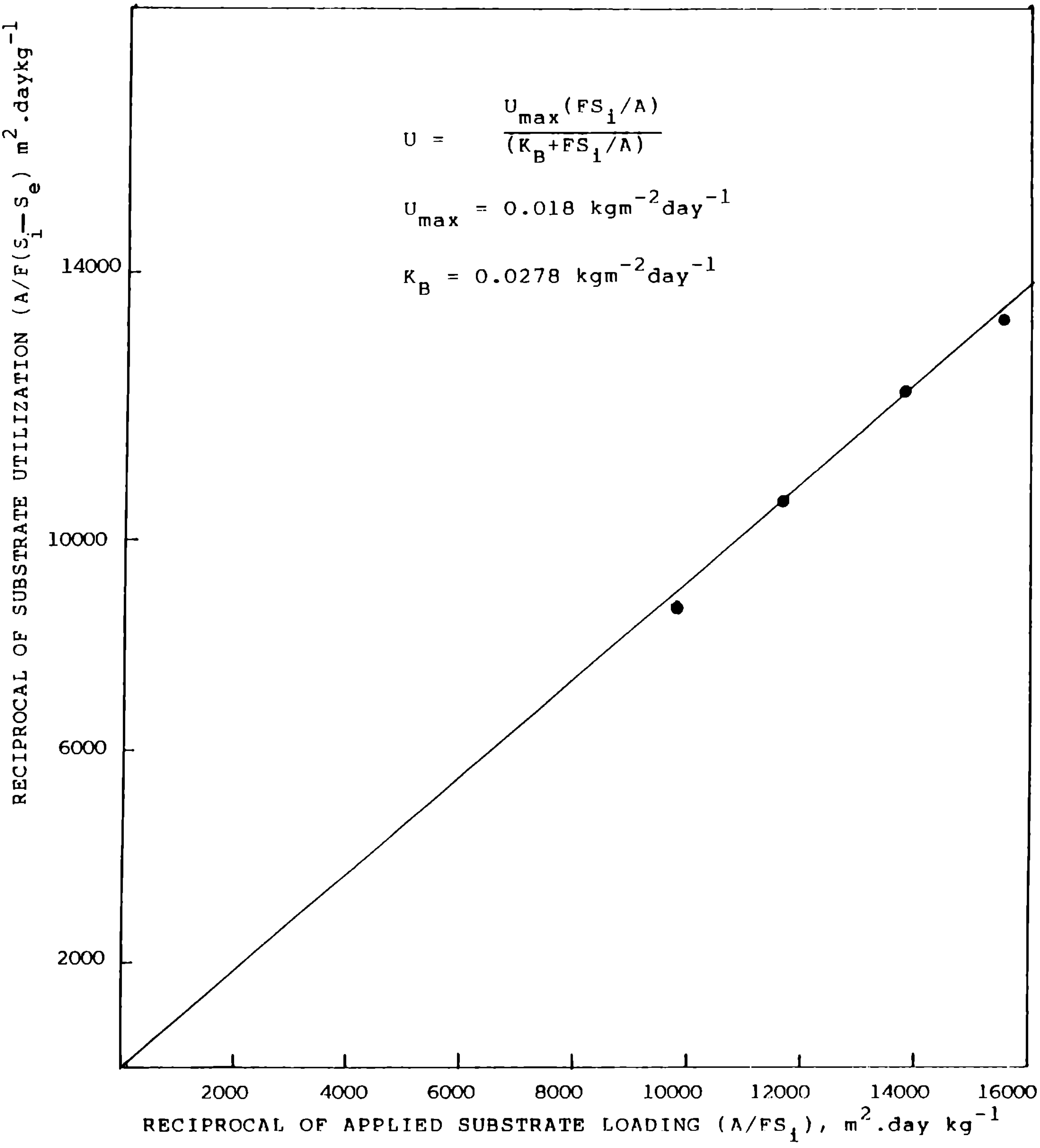


FIG.6.19 DETERMINATION OF MAXIMUM SPECIFIC SUBSTRATE REMOVAL.

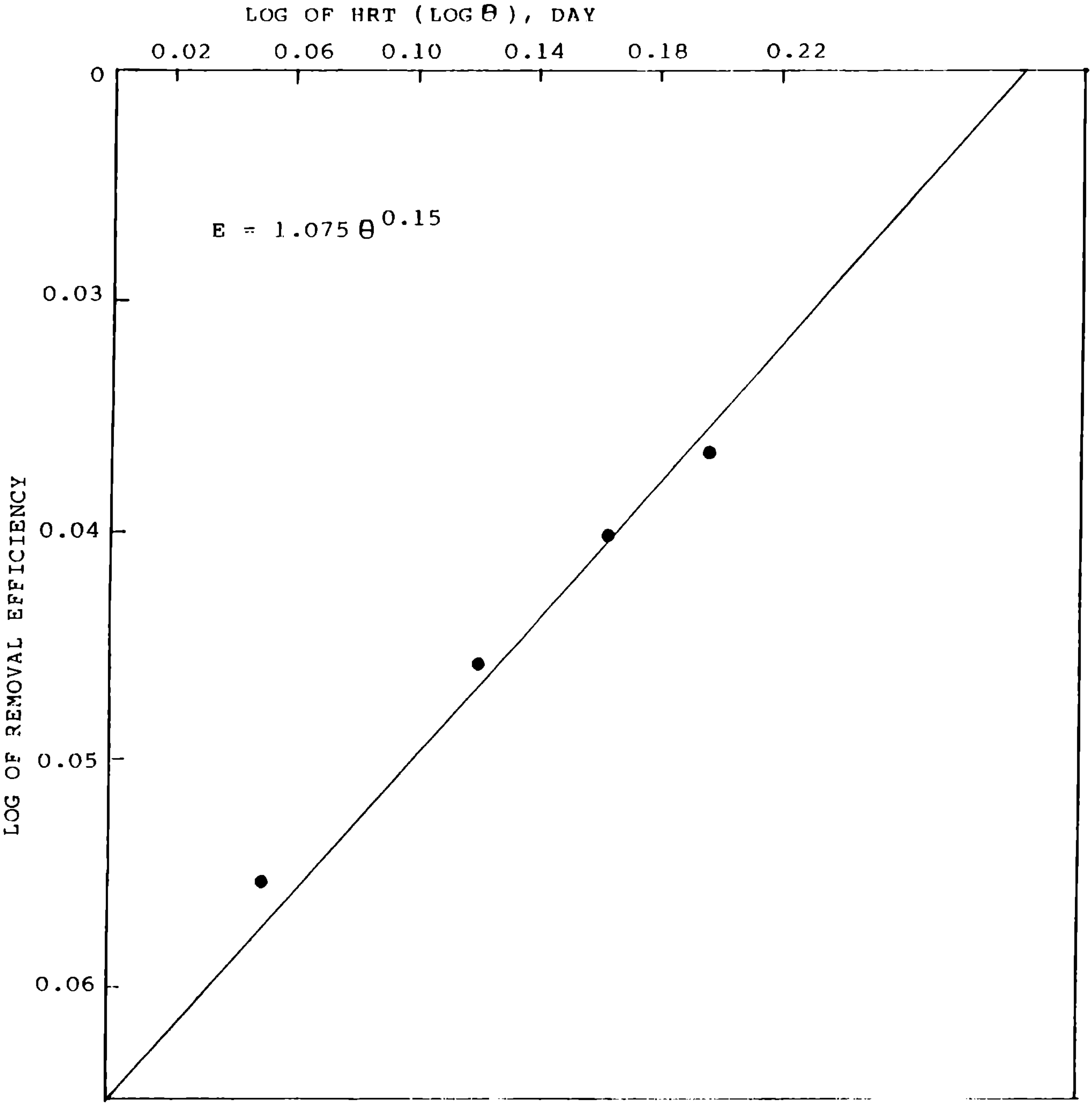


FIG.6.20 DETERMINATION OF SPECIFIC GROWTH RATE OF BIOMASS.

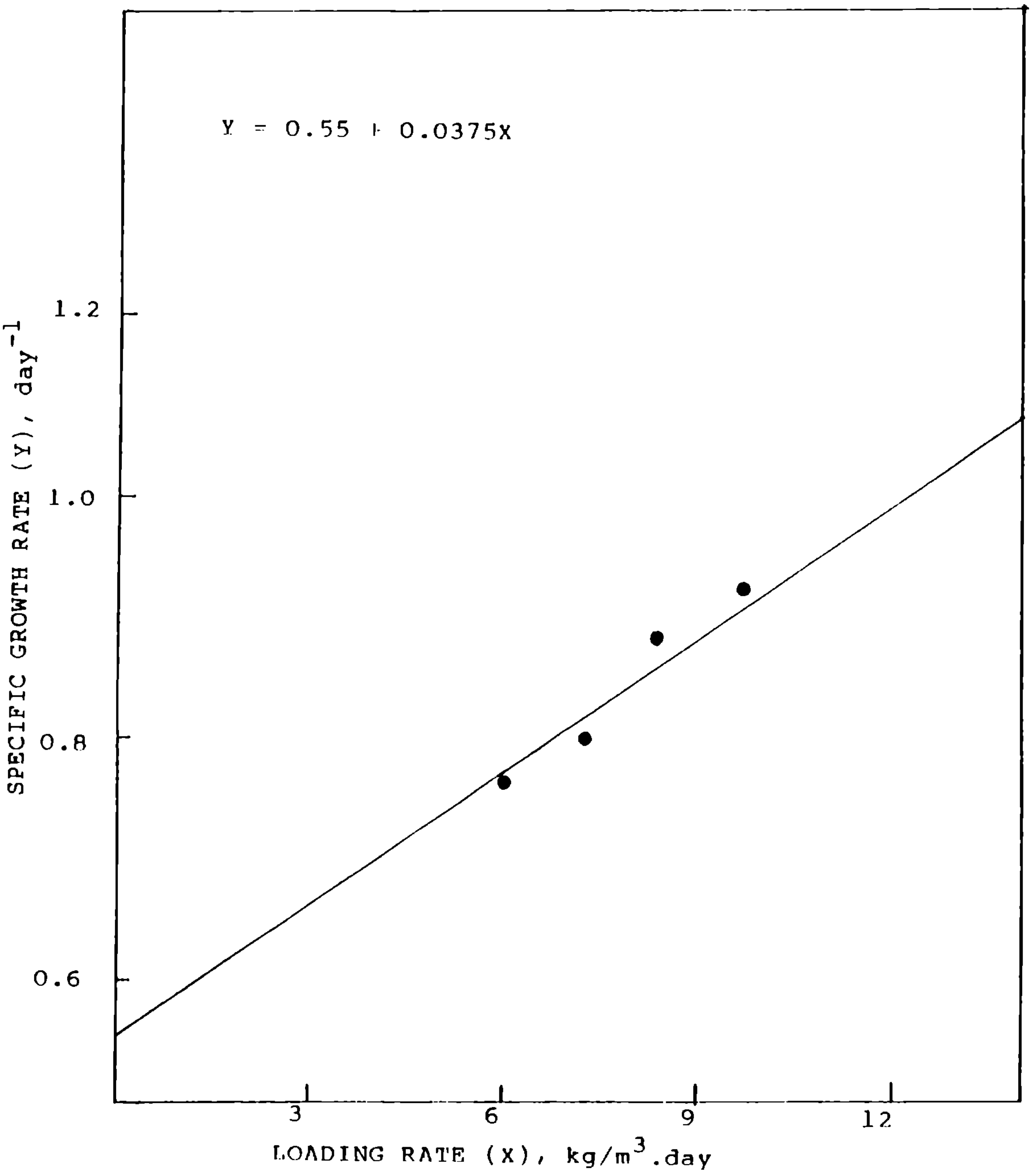


FIG.6.21 PLOT OF SPECIFIC GROWTH RATE VERSUS LOADING RATE.

The maximum specific growth rate (μ_{max}) and decay coefficient (k_d) were determined using Monod's modified model, equation (11). The values of μ_{max} and K_μ were determined by trial and error method using various assumed values of K_s until a linear relationship with a negative intercept was obtained by plotting μ against (S_e/K_s+S_e) as given in Fig.6.22.

(3) <u>Gas kinetics</u>

Total gas and methane production were defined as a function of applied substrate loading by equations (12) and (13). The reciprocal of specific gas production rate and reciprocal of applied substrate loading rate have been plotted and a linear relationship as predicted was obtained (Fig.6.23). The values of maximum specific gas production rate (G_{max}) and proportionality constant (G_B) have been determined. Similarly the maximum specific methane production rate (M_{max}) and proportionality constant (M_B) have also been found (Fig.6.24).

The values of kinetic parameters obtained are summarised in Table 6.5. Loading rates indicate maximum loading rate that can be applied to the anaerobic filter system and are not necessarily optimum values. Only typical graphs have been presented.

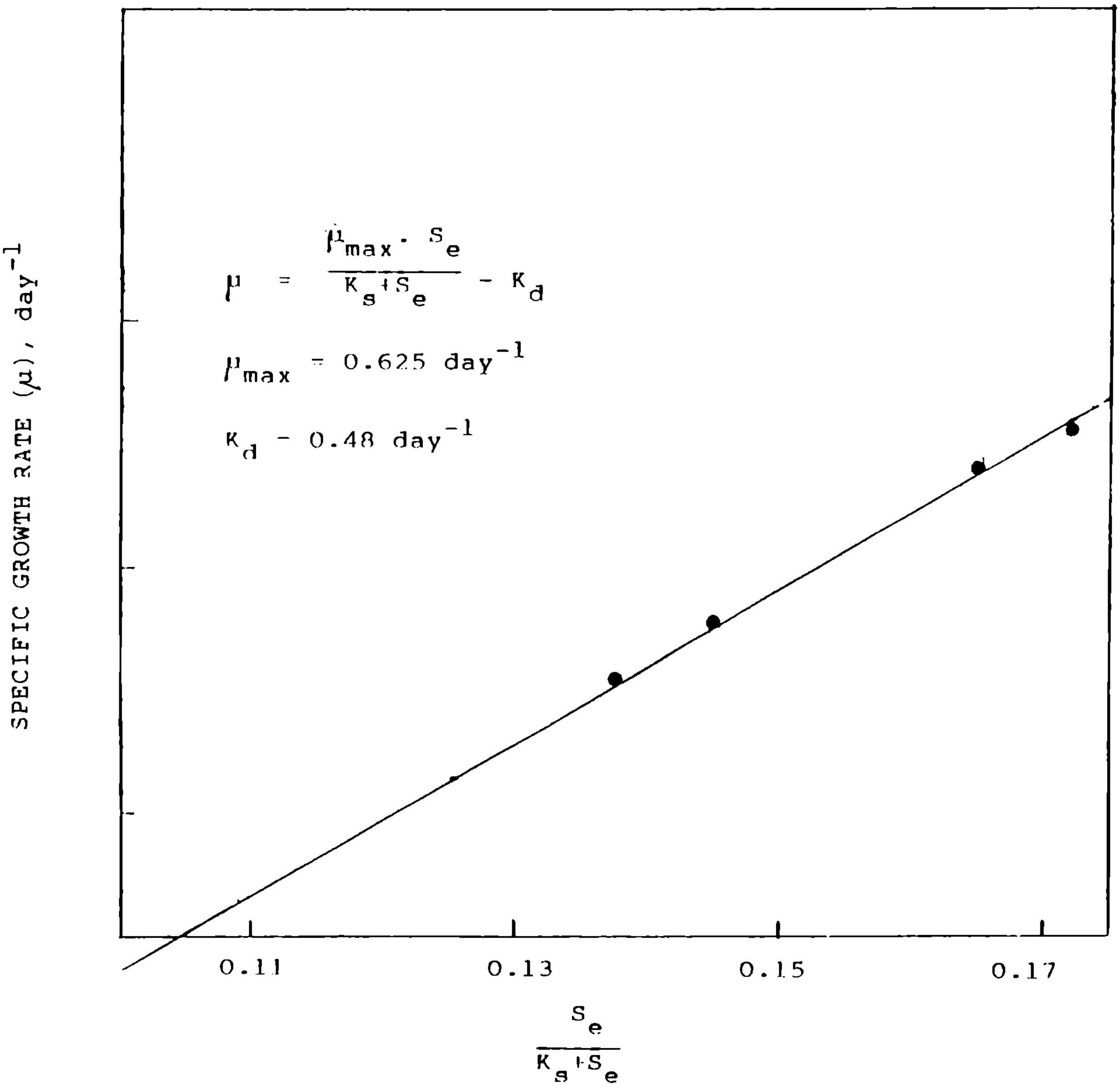


FIG.6.22 DETERMINATION OF MAXIMUM SPECIFIC GROWTH RATE.

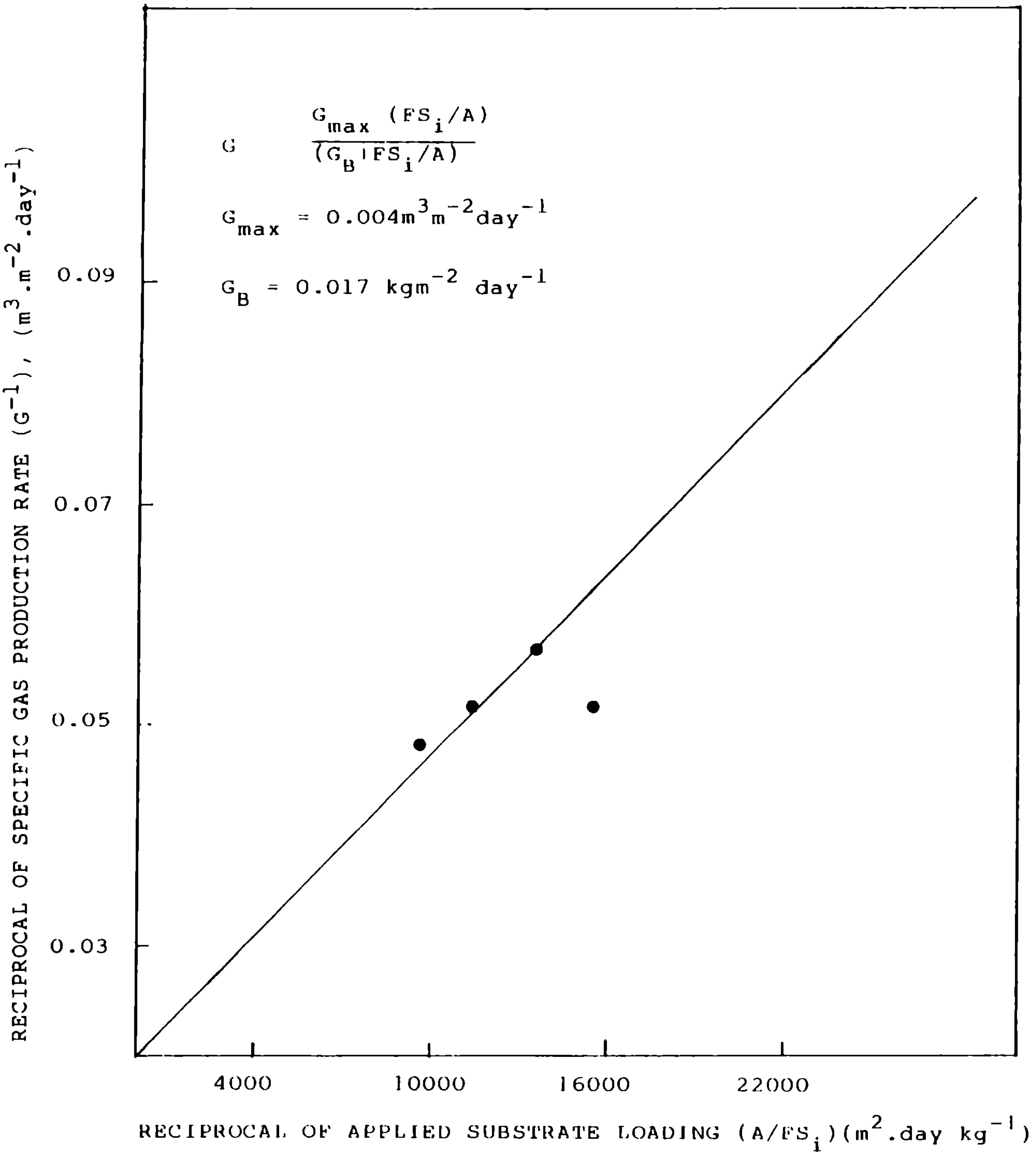


Fig.6.23 DETERMINATION OF MAXIMUM SPECIFIC GAS PRODUCTION.

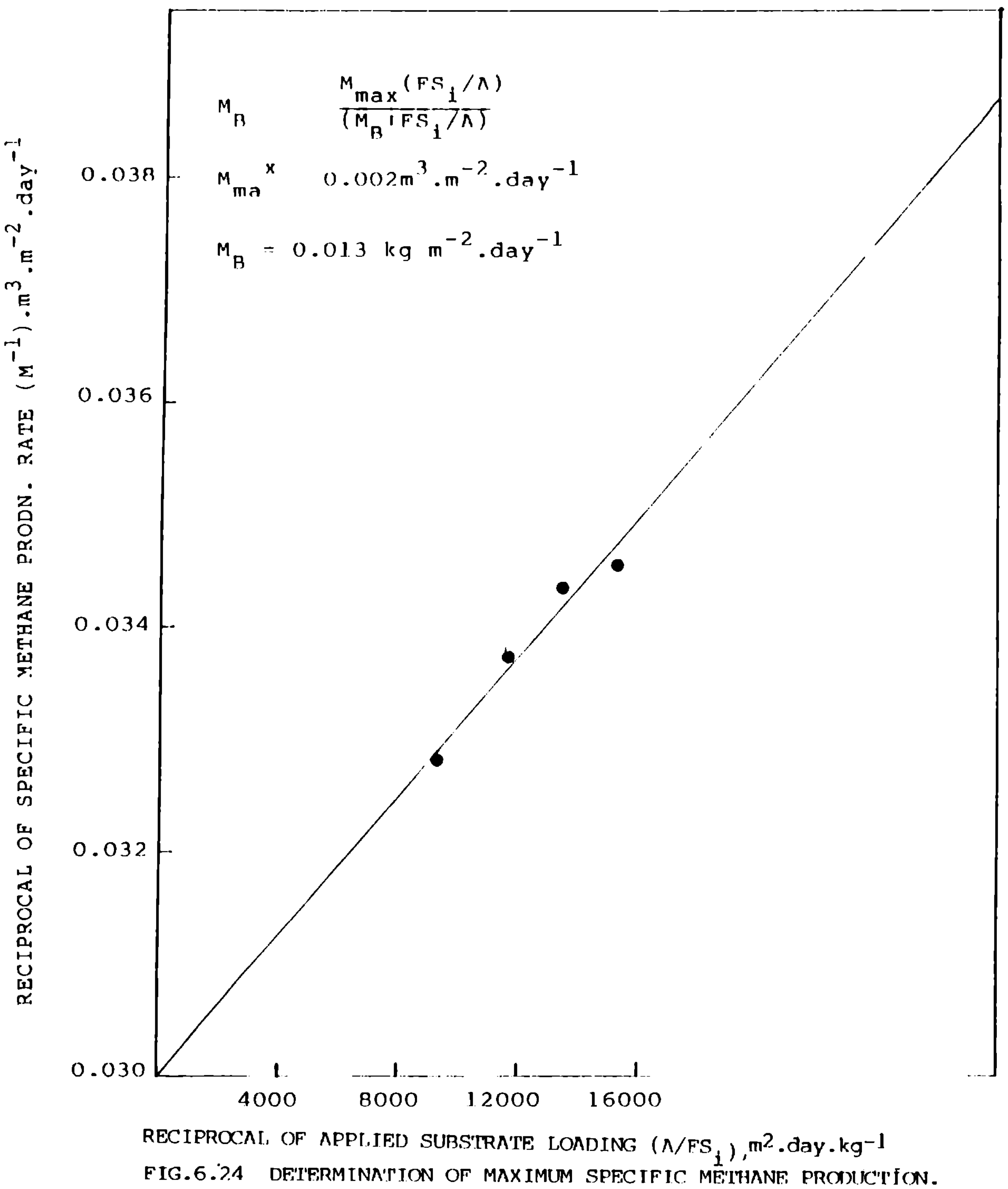


FIG.6.24 DETERMINATION OF MAXIMUM SPECIFIC METHANE PRODUCTION.

TABLE 6.5

KINETIC CONSTANTS FOR THE ANAEROBIC FILTER

I. SUBSTRATE KINETICS	
Parameter	Values
E_m	0.935
a, d	0.018
K_θ	0.39
K_L	3.95
L_{max}(kg $COD_r/m^3.d$)	50.00
K_s, mg/l	4797
U_{max},(kg $COD_r/m^3.d$)	0.018
K_B, (kg/m^2.d)	0.028
II. MICROORGANISM GROWTH KINETICS	
K_u	1.075
μ, d^{-1}	0.15
μ_{max}, d^{-1}	0.625
k_d, d^{-1}	0.48
III. GAS KINETICS	
G_{max}, $m^3/m^2.d$	0.004
G_B, kg COD/m^2.d	0.017
M_{max}, $m^3CH_4/m^2.d$	0.002
M_B, kg COD/m^2.d	0.013

6.4 CONCLUSION

1. The anaerobic filter successfully treated the effluents from a centrifuge latex concentration unit at influent COD concentrations as high as 10400 mg/l. The maximum COD removal and BOD removal recorded after 15 days of continuous steady-state operation of the filter was 91 per cent and 95 per cent respectively at an organic loading rate of 8.4 kg COD/day/m^3 and a hydraulic retention time of 1.2 days.

2. The COD and BOD removal efficiency of the filter was found to increase on increasing organic loading upto a certain limit. On increasing the organic loading further, the removal efficiency was found to drop.

3. The maximum volume of gas production recorded during the period of investigation was 0.4 litres/day. The percentage methane content of the gas ranged from 61 to 67 per cent.

4. A pH range of 6.4 to 7.3 was observed during the study. Eventhough a reduction in pH was observed initially, it remained almost neutral subsequently.

5. For all the organic loading rates, there was a steep increase in the volatile acids concentration during the initial period, but subsequently it came down.

6. The performance of the filter was found to be better at lower depths, especially at heights below 30 cm.

7. The anaerobic contact filter is capable of reducing the ammoniacal content of the latex centrifuging effluent considerably. A maximum removal efficiency of 92 per cent was observed for the organic loading rate of 8.4 kg/day/m^3.

8. The important kinetic parameters have been determined for substrate, biomass and biogas for the anaerobic filter.

REFERENCES

1. Metcalf and Eddy, Inc., Wastewater Engineering: Treatment, Disposal, Reuse, Tata McGraw Hill, New Delhi (1979).

2. Higgins, I.J. and Burns, R.G., The Chemistry and Microbiology of Pollution, Academic, London (1975).

3. Mara, D.D., Bacteriology for Sanitary Engineers, Churchill Livingstone, Edinburgh (1974).

4. Lawrence, A.W. and Mc Carty, P.L., J. Water Pollut. Control Fed., 41, 2 (1969).

5. Mc Carty, P.L., Public Works, 95, 9-12 (1964).

6. Mc Carty, P.L., Kinetics of Waste Assimilation in Anaerobic Treatment, Developments in Industrial Microbiology, Vol.7, American Institute of Biological Sciences, Washington, D.C. (1966).

7. Mc Kinney, R.E., Microbiology for Sanitary Engineers, McGraw Hill, New York (1962).

8. Schroeder, E.D., Water and Wastewater Treatment, McGraw Hill, New York (1977).

9. Brawn, R. and Huss, S., Process Biochemistry, 77, 4, 25 (1982).

10. Clark, R.H. and Spiece, R.E., Proc. 5th International Water Pollution Res. Conference, San Francisco, pp.27-38 (1970).

11. Young, J.C. and Mc Carty, P.L., Proc. 22nd Industrial Waste Conference, Purdue University, pp.559-574 (1967).

12. Young, J.C. and Mc Carty, P.L., J. Wat. Pollut. Control Fed., 41, 5 (1969).

13. Plummer, A.H., Malina, J.F. and Eckenfelder, W.W., Proc. 23rd Industrial Waste Conference, Purdue University, pp.462-478 (1968).

14. El-Shafie, Ahmed, T. and Bloodgood, D.E., J. Wat. Pollut. Control Fed., 45, 11 (1973).

15. Arora, H.C., Chottapadhya, S.N. and Routh, T., Wat. Pollut. Control, **74**, 584 (1975).

16. Jennett, J.C. and Dennis, N.D., J. Wat. Pollut. Control Fed., **47**, 104 (1975).

17. Colleran, E.M., Barry, A.W. and Newell, P.J., Process Biochemistry, **77**, 2, 12 (1982).

18. Landine, R.C., Brown, G.J. and Veeraraghavan, T., Food Science and Technology, **14**, 2, 144 (1981).

19. Lovan, C.R. and Foree, E.G., Proc. 26th Industrial Waste Conference, Purdue University, pp.1074-1086 (1971).

20. Govindan, V.S., IAWPC Tech. Annual, **15**, 199 (1988).

21. Sharma, S.R.R. and Bandopadhyay, M., Indian J. Environ. Hlth., **33**, 4, 456 (1991).

22. Seidel, D.F. and Crites, R.W., Jour. San. Eng. Div., Proc. Amer. Soc. Civil Engr., **96**, 267 (1970).

23. Polprasert, C. and Park, H.S., Wat. Res., **20**, 8, 1015 (1986).

24. Tamblyn, T.A. and Sword, B.R., Proc. 25th Ind. Waste Conf., Purdue University, p.1135 (1970).

25. Dewalle, F.B. and Chian, E.S.K., Biotechnol. Bioeng., **18**, 1275 (1976).

26. Venkataraman, J., Satyanarayan, S., Deshpande, C.V. and Kaul, S.N., Proc. Indian Chem. Engg. Cong., 479 (1989).

27. Stover, E.L., Reinaldo, G. and Gomathinayagam, G., Proc. 2nd Ind. Conf. on Fixed Film Biological Process.

28. Standard Methods for the Examination of Water and Waste Water, 16th edn., American Public Health Association (1985).

29. Sanders, F.A. and Bloodgood, D.E., Jour. Water Pollut. Control. Fed., 37, 1741 (1965).

30. Callander, I.J. and Barford, J.P., Process Biochem., **18**, 24 (1983).

31. Gadre, R.V. and Godbole, .H, Indian J. Environ. Hlth., **28**, 1, 54 (f1986).

32. Khan, A.N. and Siddiqi, R.H., Indian J. Environ. Hlth., **18**, 4, 282 (1976).

Chapter 7

SUMMARY AND CONCLUSIONS

The overall objective of the study was to evaluate the effectiveness of a few physico-chemical and biological methods for the treatment of effluents from natural rubber processing units, especially a centrifuge latex concentration unit. The effluents from a centrifuging unit was specifically selected for the study because they show the maximum pollution potential. The treatment methods evaluated in this study were earlier tried successfully for the treatment of wastewaters from process industries like distilleries, food processing, textile mills etc. An attempt was made to extend these methods to the treatment of latex concentration effluents.

This thesis is divided into seven chapters.

In Chapter 1, the composition of natural rubber latex and effluent generation are described. The importance of various physical, chemical and biological characteristics of wastewater are discussed briefly. The characteristics of effluents from natural rubber processing units, the effect of effluent discharge on water bodies and the present treatment practices have also been described. The objectives and scope of the study are defined in this chapter.

Chapter 2 is divided into two parts. In part 'A', the characteristics of the combined effluent and the individual characteristics of effluents from the two sections of a latex centrifuging unit, viz., the centrifuging section and skim latex coagulation section are described. The study showed that the effluents discharged from a latex centrifuging unit are strongly acidic in nature. The average pH of the combined effluent was found to be 3.9. The main source of acidic effluents was identified as the skim latex coagulation section where sulphuric acid is used. BOD, COD, suspended solids content, total kjeldahl nitrogen content and ammoniacal nitrogen content of the effluents were estimated and the 50 per cent and 90 per cent probability values were calculated. The suspended solids content of the wastewaters ranges from 9.0 to 42.2 per cent of the total solids and major portion of the solids are present in the dissolved form. The correlation developed between COD and total organic carbon gives the indication that organic carbon which is not oxidised by dichromate during COD estimation may be present in the latex centrifuging effluent. The pollution load from a typical rubber latex centrifuging unit is estimated to be about 128 kg BOD per day.

In part 'B' of Chapter 2, the results of the experiments carried out on latex centrifuging wastewaters using nine commonly available metal coagulants are presented. The coagulants used in the study were alum, aluminium sulphate, ferrous sulphate, ferric sulphate, ferric chloride, ferrous chloride, aluminium chloride, lime and magnesium chloride. The effectiveness of the metal coagulants was evaluated in terms of COD reduction, turbidity removal and ammoniacal nitrogen removal. The effect of pH on coagulation was also investigated. The optimum pH values for the most effective coagulation action of the metal salts except lime were in the range of 6.5-8.5. As for lime, the best results were obtained at a pH of 10.5. Among the metal salts, aluminium chloride was found to be the most efficient one for COD reduction, turbidity removal and ammoniacal nitrogen removal. The settleability characteristics of the flocs formed by all the nine coagulants were studied. The compressibility of the sludge produced by aluminium chloride was found to be better than that of the sludge generated by other coagulants.

The results of the studies carried out with four natural polyelectrolytes and two synthetic polyelectrolytes are presented in Chapter 3. The natural polyelectrolytes used were starch, sodium alginate, tamarind seed powder and chitosan. The synthetic polyelectrolytes used for the study were a cationic polyacrylamide based one and an anionic polyamine based one. The effectiveness of the polyelectrolytes as primary coagulant and coagulant aid was evaluated. The optimum pH values for the effective coagulation action of the polyelectrolytes were found to be in the range 7.5-11.0. Among the six polyelectrolytes studied, chitosan was found to be the most effective as a primary coagulant in the removal of COD, turbidity and ammoniacal nitrogen from latex centrifuging wastewaters. The compressibility of the sludge produced by chitosan was found to be superior to that of other polyelectrolytes. As a coagulant aid also, chitosan performed better than others. At a small dosage of 2 mg/l, chitosan could reduce the metal coagulant dose by about 50-60 per cent. A combination of aluminium chloride with chitosan was the most effective. Comparing the two synthetic polyelectrolytes, it was found that the cationic polyacrylamide based one performed better than the anionic one.

In Chapter 4, the biochemical oxidation kinetics of wastewaters from a latex centrifuging unit is discussed. The variations in the BOD values of the effluent at four different temperatures; 20, 25, 30 and 35°C were studied. The biochemical stabilization rate constant (k), oxygen utilisation rate constant (K) and ultimate BOD (L_o) were determined at 20°C. The study showed that bulk of the BOD is exerted within one day for the wastewater samples and the extent of this quantity was found to be dependent on temperature. The biochemical stabilization rate constant (k) and the corresponding oxygen utilisation rate constant (K) at 20°C for the effluents from a centrifuge rubber latex concentration unit were estimated as 0.145 day^{-1} and 0.33 day^{-1} respectively. The values of biochemical stabilization rate constant and oxygen utilisation constant were found to increase with temperature.

The treatability of latex centrifuging effluent in a waste stabilisation pond is the topic of discussion in Chapter 5. The possibility of treating the wastewater alone and in admixture with sewage in the proportions of 1:1, 1:2, 1:3, 1:4 and 1:5 was explored in an experimental pond. The wastewaters from a latex centrifuging unit were found to be amenable for treatment in a waste stabilisation pond in admixture with sewage using acclimatized algal culture. The greater the dilution, the more efficient was the degree of treatment. Of the five dilutions studied, 1:5 dilution gave the best performance in respect of BOD reduction, COD reduction, ammoniacal nitrogen removal and suspended solids removal. When the wastewater was mixed with sewage in the proportion of 1:5, the BOD reduction and COD reduction obtained were 93 per cent and 90 per cent respectively in a detention time of 15 days. The maximum ammoniacal nitrogen removal and suspended solids removal obtained were 20 and 25 per cent respectively. The algal succession in the pond was also studied. The algal count during stabilisation in different wastewater-sewage mixtures varied between 3×10^4 and 167×10^4 per ml. Chlorella vulgaris, Scenedesmus quadricauda, Euglena acus and Microcystis aeruginosa grew well during the course of stabilisation under experimental conditions. Eventhough no definite pattern of algal succession was observed, the green algae and flagellets dominated the experimental pond.

In Chapter 6, the treatability of effluents from a centrifuge latex concentration unit in a laboratory fabricated upflow anaerobic contact filter is discussed.

The effectiveness of the filter was evaluated in terms of COD removal, BOD removal and ammoniacal nitrogen removal at varying organic loadings. The anaerobic filter successfully treated the effluents from a centrifuge latex concentration unit at influent COD concentration as high as 10400 mg/l. The maximum COD removal and BOD removal recorded after 15 days of continuous steady state operation of the filter were 92 per cent and 95 per cent respectively at an organic loading rate of 8.4 kg COD/day/m^3 and a hydraulic retention time of 1.2 days. The COD and BOD removal efficiency of the filter was found to increase on increasing the organic loading upto a certain limit. On increasing the organic loading beyond this limit, the removal efficiencies dropped. The maximum volume of gas production recorded during the period of investigation was 0.4 litres/day. The percentage methane content of the gas ranged from 61 to 67 per cent. For all the organic loading rates, there was a steep increase in the volatile acids concentration during the initial period, but subsequently it came down. The performance of the filter was found to be better at lower depths, especially at heights below 30 cm. Based on the experimental results, kinetic parameters were estimated with respect to substrate removal, microorganism growth and gas production.

LIST OF PUBLICATIONS FROM THE PRESENT WORK

1. Characterisation and Treatment of Effluents from a Centrifuge Rubber Latex Concentration Unit
   Indian J. Nat. Rubb. Res., 4(2), 97-102 (1991).

2. Use of Synthetic Polyelectrolytes in the Treatment of Effluents from Small Scale Natural Rubber Processing Units
   Presented at Indian Chem. Engg. Congress, Manipal, December 1992.

3. Tamarind Seed Powder as Coagulant and Coagulant aid in the Treatment of Effluents from Natural Rubber Processing Units
   Proceedings of the Fifth Kerala Science Congress, 53-55 (1993).

4. Use of Natural Polyelectrolytes in the Treatment of Effluents from Centrifuge Latex Concentration Units
   Communicated to 'Asian Environment'.

5. Treatment of Natural Rubber Latex Concentration Waste Waters by Stabilisation Pond Method
   Communicated to 'Int. J. Environmental Studies'.

6. Biochemical Oxidation Kinetics of Waste Waters from a Natural Rubber Processing Industry
   Communicated to 'Water Pollution Control', U.K.

7. Anaerobic Contact Filter for the Treatment of Effluents from a Rubber Latex Concentration Unit
   Accepted for Presentation at the Sixth Kerala Science Congress, January 1994.