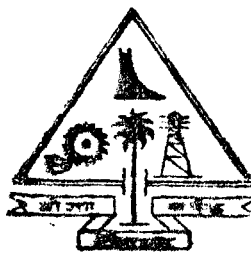


**STUDIES ON THE REMOVAL OF HEAVY METAL IONS FROM
INDUSTRIAL WASTE WATER BY ADSORPTION TECHNIQUES**

*Thesis submitted in partial fulfilment of
the requirements for the award of the degree of*

Doctor of Philosophy in Chemical Engineering

To The University of Calicut



By

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DEPARTMENT OF CHEMICAL ENGINEERING

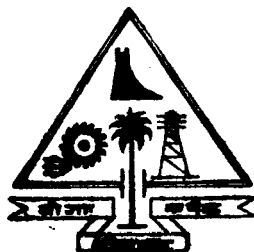
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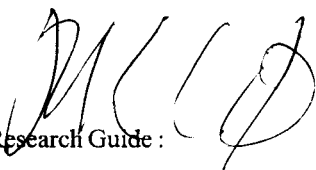
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STUDIES ON THE REMOVAL OF HEAVY METAL IONS FROM
INDUSTRIAL WASTE WATER BY ADSORPTION TECHNIQUES

which is being submitted by

R. JAYACHANDRAN

is a record of bonafied work carried out by him for the award of
Doctor of Philosophy in Chemical Engineering under my
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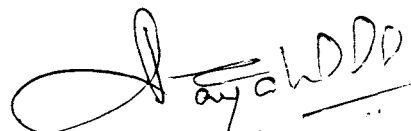
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R. Jayachandran.

ABSTRACT

The thesis concerns primarily with the removal of toxic heavy metals like mercury, cadmium, lead and chromium from aqueous solutions including industrial effluents employing chitosan, a natural polymeric material obtained from prawn shell waste and to compare its effectiveness with standard adsorbents like synthetic polymeric materials as well as activated carbon. The dual function of chitosan as flocculating agent as well as an adsorbent in the removal of heavy metals from effluents has also been investigated. With a view to explore the commercial application of this dual function of chitosan treatability studies were conducted on industrial effluents for the removal of heavy metals along with other pollutants.

The sorption kinetics of Mercury, Cadmium, Lead and Chromium on chitosan were studied at different initial concentrations. It is observed that the initial

sorption rate is high for all the metal ions and the equilibrium is reached within one hour. The rate of sorption is very rapid initially and decreased markedly, finally approaching zero. The rate of sorption on chitosan is highest for mercury followed by cadmium, lead and chromium in the decreasing order.

The sorption data fitted to the reversible first-order kinetic model rate equation. The results of the equilibrium study conducted at different initial concentrations show that the data fitted to the linear form of the Freundlich equation.

Mercury sorption capacity of chitosan is the highest among the four adsorbents studied. Owing to extremely favourable equilibrium distribution of mercury towards chitosan, adsorption system employing contact filtration technique can be conveniently employed for the removal and recovery of mercury from industrial effluents on a commercial scale. It is also possible to predict the adsorbent to solution ratio for a given change in concentration of adsorbate in solution by applying Freundlich equation.

When chitosan is employed as a flocculating agent, the percentage removal of heavy metal is found to be more than when chemical precipitation is conducted without chitosan. The reason for this additional removal of heavy metal over and above that is possible by normal chemical precipitation, may be due to the great affinity of certain heavy metal ions towards chitosan. Thus chitosan is having a dual function in such cases, as a flocculating agent as well as an adsorbent.

CHAPTER - 1

INTRODUCTION

1. INTRODUCTION

Heavy metal pollution of aquatic environment due to industrial effluents is a much debated topic and we are fully aware of the damages it causes to humanity. Some of the toxic metals that endanger human life, are mercury, cadmium, lead and chromium. Removal of such toxic metal ions from industrial waste water have received much attention in recent years. The catastrophic episodes of metal poisoning especially that of mercury poisoning in the Minmatha Bay in South Western Kyushu, Japan during 1953-1960 which caused untold suffering and death of many people who consumed fish and shell fish from that region is indelible in history. The extremely high toxicity of methyl mercury to man and its concentration in the environment are of particular concern. In aquatic ecosystems, other forms of mercury including inorganic mercury is likely to get converted into methyl mercury which may be absorbed and concentrated by aquatic species and further concentrated

along the food chain. Cadmium has become infamous through Itai Itai disease. Cadmium has unquestioned chronic toxicity leading to serious pathological consequences. Chromium compounds, particularly the hexavalent chromates produce irritation of the skin and respiratory tract, ulcers and cancer of the respiratory tract. The effect of lead poisoning are loss of appetite, metallic taste in the mouth, irritability, muscle and joint pains, etc.

In this context, the removal of such heavy metal from aquatic environment has gained considerable importance in the recent past. Many attempts have been made to develop methods and materials for the removal of heavy metal contaminants from industrial and domestic effluents that are discharged into aquatic system.

A lot of natural and synthetic ion exchange resins have been developed for heavy metal removal from waste waters. Among them chitosan - a deacetylated derivative of chitin, a long straight chain natural polymer of N- acetyl D-glucosamine which is abundantly available in the exoskeleton of crustacea such as shrimps,

crabs, lobster and squilla merits special mention because of its surprising ability to adsorb many metals from solutions. Chitosan is obtained in India mainly from the head and body peeling of prawns. Nearly one lakh tonne of this prawn waste is thrown away every year by the fish processing industries which caused environmental pollution. Many investigators have concluded that the ability of chitosan to adsorb mercury is equal - if not superior to most of the artificial chelating resins so far commercially available. The adverse impact of such toxic metals on the fauna and flora has been elaborated in Annexure -II.

Some of the major sources of these toxic metals are effluent from industries like chlor-alkali, pulp and paper, electroplating, leather tanning, food processing, lead acid batteries, anodizing, paints and pigments, PCB manufacturing and cooling tower blow down.

The objective of the present study is to investigate thoroughly the effectiveness of Chitosan, a natural polymeric material obtained from prawn shell waste when compared to a synthetic polymeric material like

Dowex -50 and a standard adsorbent like Activated Carbon for heavy metal removal. The dual function of chitosan as a flocculating agent as well as an adsorbent in the removal of heavy metals from industrial effluents has also been investigated. Finally removal of heavy metals in combination with other pollutants has also been studied as it has many industrial applications.

As regards heavy metal removal by the adsorption technique it has been found that certain synthetic and natural materials selectively adsorb most of the heavy metal ions like mercury, cadmium, lead, chromium etc. from aqueous solutions. All the metals collected on the adsorbent can be recovered easily by using suitable eluting agents. This property can be used for the recovery of such metals from waste streams.

Chemical precipitation technique is one method now employed for removing toxic heavy metals from industrial effluents and considerable research work has been done in this area, but much work has not been done on adsorption techniques for heavy metal removal.

Chemical precipitation method is suitable only when heavy metal concentrations in the effluent is considerable, (ie. many times above the tolerance limit) and not effective when the heavy metal is present only in traces. In such cases adsorption technique is quite suitable as it can bring down the heavy metals present in the effluent well below the tolerance limits stipulated by Environmental Protection Agencies. Hence in the case of heavy metal removal from industrial effluents containing considerable concentrations of the same, adsorption technique can function as complementary to chemical precipitation process. For example, in Chlor-alkaly industries, where mercury is present upto 10 mg/litre in the combined effluent while the tolerance limit is only 0.01mg/litre. It is not economical to use adsorption technique alone, when the metal concentration is so high. Hence the best option is found to be the application of chemical precipitation to remove most of the heavy metal and balance can be removed more or less completely by adsorption technique employing chitosan.

Also in the case of removal of chromium from trade effluents, it is possible to precipitate out 98% of chromium as chromium hydroxide at optimum pH employing lime (Ca(OH)_2) and balance by adsorption employing chitosan. In the case of cadmium removal from industrial effluents, a much higher percentage of the metal can be removed by chemical precipitation alone employing lime and balance is removed completely by employing chitosan as adsorbent.

Lastly when the removal of lead from trade effluents is considered, it is seen that upto 95% reduction is possible by chemical precipitation and balance can be removed upto the required level by adsorption.

In all the above cases, when a polymeric material like chitosan was employed in the chemical precipitation step as a flocculating agent, it was found possible to remove a higher percentage of heavy metal. This happened because chitosan was also functioning as an adsorbent while it was flocculating the precipitated particles. This behaviour may probably be due to the high affinity of chitosan towards such heavy metals.

Due to this dual function of chitosan, it has been possible to bring down the concentration of heavy metal in industrial effluent well below the tolerance limit by chemical precipitation alone. Especially in the case of cadmium removal from trade effluents, it is possible to bring down the heavy metal content even upto zero in chemical precipitation step when chitosan is employed as a flocculating agent. Moreover chitosan is a natural polyelectrolyte (poly glucosamine) which is edible and quite eco-friendly while synthetic polyelectrolytes like polyacrylamide are highly toxic.

More application of this dual function of chitosan (as a flocculating agent as well as an adsorbent) has been found by conducting treatability studies of trade effluents containing only traces of heavy metals. Even traces of heavy metals present is to be removed not only for bringing it down to the tolerance limit for a specific purpose but also for protecting the life/health of the bacteria in the secondary (biochemical) process.

This last part of the present study has got considerable commercial importance as most of the trade effluents from various industries like Pulp and paper, Tannery, Textile wet processing, Oil refineries, Fertilizer industries etc. contain traces of heavy metals which can be removed along with the other pollutants in the primary treatment itself, if chitosan is added as a flocculating agent along with the coagulant for chemical precipitation.

CHAPTER - 2
LITERATURE SURVEY

2.LITERATURE SURVEY

Adsorption technique for heavy metal removal from industrial waste water is a developing area, but published literature is quite meagre because of its commercial value. Voluminous literature is available on precipitation technique for heavy metal removal from aqueous solutions and some commercially viable processes are available for treating the effluent based on this techniques.

Sorption of inorganic mercury on bituminous coal was investigated by Mahesh.P.Pandey and Malay Chaudhuri¹. They reported that equilibria was attained after 24 hr and the mercury sorption was temperature dependent. The sorption was found to increase with rising temperature indicating endothermic process. The activation energy of 8.39 KCal/mole indicated that it is high enough for physical adsorption but not significantly high to conclude the reaction

as chemisorption. They reported that mercury sorption also decreased with increasing pH. Batch sorption kinetics and equilibria were described by reversible first order reaction and Freundlich equation respectively.

Yaku and Koshijima² in their paper reported the characteristics of chitosan selectively to combine particular metal ions to form metal complexes. These tendencies are most predominant in Cu, Hg, Fe, Ag, Cd, Ni, and are weakest in Mn, Co and Cr in the order of Hg > Cd > Pb > Cr. Metal ions of Ag, Hg, Cu, Cd, Fe, and Ni took up more than 0.5 m moles/gm of chitosan. The affinities for Hg, Cu, Fe and Ni ions were especially predominant in chitosan.

Muzzarelli et al³ have reported on the chelating ability and chromatographic applications of chitosan. Significant contribution on the study of chitosan as an adsorbent was due to Muzzarelli et al. It was reported that methyl mercury acetate can be

removed from industrial wastes containing small amount of acetic acid and acetaldehyde with the aid of chitosan.

Muzzarelli et al⁴ reported that Chitosan can be considered a strong base as its primary amino groups, whose pK_a is 6.3, easily form quaternary nitrogen salts at low pH values; thus, in acidic solutions chitosan has high anion capacity. At higher pH values, however, it is a weak base because the primary amino groups are not protonated and therefore do not interact with anions and do not dissociate neutral salts. Chitosan is relatively indifferent to alkali metals and alkaline earth ions and is thus superior to other polymers tested for the recovery of transition metals in saline waters. The complexing ability of chitosan is a direct consequence of the base strength of the amino groups and is most effective for those metals which form complexes with ammonia, eg. copper, zinc and mercury.

Abuthahir Ali and Dr.P.S.Pillay⁵ conducted studies on adsorption of mercury on chitosan and collected sorption kinetic data for process development.

H.Hauer et al⁶ compared the metal binding capacity of Kytex H chitosan favourably with commercially available chelating resins. Chitosan is relatively inert to alkali metals and alkaline earth ions; it is thus superior to the other polymers tested for the recovery of transition metals in alkaline or saline waters.

Porosimetry of Chelating Polymers as reported

by H. Hauer

Sample	Mesh	Pore Characteristics			
		Median (dia (u))	Total vol. (cc/gm)	Av. Dia (4 V/A)	Total Area (m ² /g)
Kytex H (Chitosan)	>20	48.6	0.41	22.9	0.072
	20-50	69.8	0.89	23.7	0.15
	50-100	73.4	2.61	42.3	0.25

John M. Randall, Earl Hautala and Gary McDonald⁷ reported that peanut skin, when treated with formaldehyde to polymerize tannins is a highly efficient substrate for removal of many heavy metal ions like Ag, Cd, Cr, Cu, Hg, Ni, Pb & Zn.

Various operational systems using activated carbon for the removal of chromium (VI) from synthetic waste waters have been examined by A.R. Bowers and C.P. Huang⁸. The removal of anionic Cr(VI) species from solution may occur through either the adsorption of Cr(VI) species on to the carbon surface or by oxidation of the carbon surface, resulting in removal of Cr(VI) by transformation into the cationic Cr(III) species. In addition, some apparent adsorption of Cr(VI) species may occur due to the adsorption or precipitation of those Cr(III) species produced by the redox reactions.

The kinetics of Cr(VI) adsorption and reduction have been discussed. In these studies the effects of various solution parameters were evaluated and the following conclusions were made.

i) pH is one of the most significant variables; increased H^+ concentration enhances the rates of both reduction and adsorption and increases the adsorptive capacity of Filtrasorb 400 for Cr(VI) species.

ii) Mixing gradients in solution do not affect the rate of Cr(VI) adsorption; however, the reduction rate increases proportionately with the velocity gradients in the carbon reactor.

iii) Both removal reactions are first order with respect to Cr(VI) concentration; the limiting reaction mechanisms are different, however;

R.Richards⁹ developed a process for removing chromium ions from industrial waste solutions by direct precipitation with barium carbonate in such solutions acidified with nitric or hydrochloric acid or their salts.

Recently Ramachandran Nair and Madhavan¹⁰ have investigated the metal binding property of chitosan derived from different sources. They have reported that

sorption of mercury on chitosan obtained from squills was faster and that the quantity adsorbed also was more than that obtained from prawn shell.

Anderson et al¹¹ reports the use of reduction and lime precipitation to treat chromium bearing waste from a general electric appliance plant. Sedimentation of the precipitate was improved by addition of an anionic polyelectrolyte.

J.M.Lalancette and B.Coupal¹² developed a process for removing chromium ion from a chromium polluted solutions. The process involves forming a chromium sulfide complex by adding a water soluble ferric salt to the chromium polluted solution and insolubilizing the complex formed by treatment with a compound which when dissolved in water forms sulfide ions and separating the insoluble precipitate by filtration through a bed of peat moss. The peat moss containing the insoluble chromium iron sulfide complex is oxidized under heat to recover the chromium as chromium oxide.

A.J Saraceno et al¹³ developed an anion exchange process for the removal and recovery of trace quantities of chromates from water. The process utilizes a bed of basic anion exchange resin and the combination of upflow exhaustion of the chromates from the water and downflow regeneration of the resin.

Landrigan and Hallowel¹⁴ investigated the effectiveness of activated carbon for chromium removal from plating wastes and concluded that chromium concentration upto 600 mg/l in rinse water could be removed by activated carbon.

A process developed by E.R.Taylor, Jr.¹⁵ involves the removal of dissolved organic lead from an aqueous effluent produced in the manufacture of alkyl lead compounds by contacting a metal more electropositive than lead but essentially non-reactive with water with the effluent until the dissolved organic lead is converted to an insoluble lead containing product, leaving a reduced dissolved organic lead content in the effluent.

Liebig et al¹⁶ have reported the treatment of lead contaminated water by ionexchange. Lead content was reduced from 0.055 to 0.0015 mg/l.

Nozaki and Hatotani¹⁷ have described the treatment of waste waters from a tetraethyl lead manufacturing process. The two major categories of waste were inorganic lead wastewaters and organic lead wastewaters. After sedimentation in a holding basin to recover solid lead and lead oxide, the inorganic lead waste fraction was treated by coagulation with ferric and ferrous sulfate. The organic lead compounds were removed effectively on strongly acid cation exchange resin.

A process developed by C.L.Lores and R.N.Moore¹⁸ is a process for treating an aqueous medium containing dissolved organic and inorganic lead compounds with an alkali metal borohydride to substantially reduce the level of dissolved lead in the aqueous medium.

Hanson and Zabban ¹⁹ have reported on lime precipitation of cadmium from a waste at the Rochester, Minnesota IBM machine manufacturing plant. An effluent pH of 9 and cadmium concentration of 0.54 mg/l was reported for the lime precipitation process.

Linstedt et al ²⁰ have reported extremely high cadmium removal for a pilot plant lime-coagulation, settling process. Treating combined sewage effluent from a secondary treatment plant, these workers achieved 94.5% cadmium removal for the trace quantities present.

A process developed by W.E. Dean et al ²¹ (199) involves removing mercury from solution and particularly from mercury electrolytic cell effluent. The process comprises intermixing with the solution a sulfur compound in an amount sufficient to provide sulfide ion to react with the mercury and other ions present therein which react with sulfide ion and treating the resultant solution with an adsorbent, preferably activated carbon, to remove the soluble mercury.

A.E.Hatch²² developed a process in which mercury dissolved in aqueous streams are removed by contacting the aqueous stream with a pleyelectrolyte in the presence of particulate matter, allowing the mercury to be bound to the particulate matter and separating the particulate matter containing the mercury from the aqueous stream, thereby purifying it.

Fales²³ reported the use of lime in precipitating a plating bath water containing 2.0 to 140 mg/l of lead, plus other metal. The auther states that after lime treatment and settling for 1 hr the supernatent was clear and contained only a trace of heavy metals. Lead in a municipal drinking water supply has also been reported reduced by lime treatment and settling from an initial value of 0.31 mg/l down to 0.1 or less mg/l of lead.

A process developed by L.B.Fournier and R.A Meyer²⁴ is one in which the hexavalent chromium present in acqeous solution is chemically reduced to trivalent chromium

with hydrogen peroxide. This process is improved if the pH of the aqueous solution is maintained below 1.5 and the hydrogen peroxide is gradually added to the solution to keep the chromate in excess as long as possible.

Yuronis²⁵ has reported that ion exchange recovery is economically and technically feasible for wastes containing chromate ion concentrations up to 200 mg/l. This study indicated that chromate wastes of 100 to 500 mg/l were suitable for reduction and precipitation. Wastes with chromate concentration exceeding 500 mg/l were suitable for evaporative recovery.

Anderson et al²⁶ reported the use of reduction and lime precipitation to treat chromium bearing waste from a General Electric appliance plant. Sedimentation of the precipitate was improved by addition of an anionic polyelectrolyte. Plant effluent was reported to contain no hexavalent chromium and an average of 0.75 mg/l total chromium.

A process developed by J.M.Lalancette and B. Coupal²⁷ is one in which chromium-polluted solutions are treated by a process which avoids the necessity of reducing chromium (VI) to chromium (III). The process involves forming a chromium sulfide complex by adding a water-soluble ferric salt to the chromium polluted solution and insolubilizing the complex formed by treatment with a compound which when dissolved in water forms sulfide ions and separating the insoluble precipitate by filtration through a bed of peat moss.

M.S.Masri et al²⁸ demonstrated the effectiveness of chitosan for the treatment of actual waste streams to remove, or reduce to acceptable levels, the toxic metallic ions. Wastes treated were : (a) from electroplating and metal-finishing operations (with disposal problems mainly of cyanide and salts of chromium, cadmium, zinc, lead, copper, iron and nickel); (b) from a nickel-salt manufacturing plant (disposal of nickel and alkali); (c) from a lead-battery manufacturing plant (disposal of sulphuric acid and lead salts); and (d) from exhausted dyebath for wool fabrics

in which dichromate is included in the bath (disposal of chromium). The chitosan was effective for reducing the content of copper, cadmium, iron, zinc, lead and nickel salts.

3. EXPERIMENTAL

With a view to develop suitable techniques for the removal of heavy metal ions like Mercury, Cadmium, Lead and Chromium by the principle of adsorption process, batch experiments were carried out in the laboratory adopting contact filtration method. Sorption kinetics study of the metal ions on chitosan and the effect of parameters such as particle size of adsorbent, temperature, initial concentration and pH were studied. Also compared the effectiveness of chitosan as an adsorbent by studying the sorption kinetics of Activated carbon, (a standard adsorbent), Dowex-50 (a synthetic polymer) and Rice husk carbon (a waste material).

In the second part of the study experiments were done for the removal of metal ions by chemical precipitation, flocculation and subsequent adsorption using chitosan as a polyelectrolyte.

In the final part of the investigation treatability studies were conducted on industrial effluents using chitosan for the removal of heavy metals in combination with the removal of other pollutants like colour, dissolved organics (ie, BOD, COD etc) and suspended solids.

3.1. Materials and Methods

3.1.1 Adsorbents

i) Chitosan required for the experimental purpose was prepared from prawn shell waste in the laboratory of Chemical Engineering Department. The production process is given in Annexure-1. The chitosan prepared was crushed and sieved to get particles of desired sizes, 0.1mm, 0.3mm and 1mm.

ii) Chitosan solution:- 1% solution of chitosan was prepared by dissolving 1 gm chitosan powder in 100 ml of 1% Acetic Acid. This was diluted with distilled water to get 0.1 % solution.

iii) **Activated carbon :-** The activated carbon used in the experiment has a minimum total surface area of 1050 sq.m/gm and pore volume 0.90 cc/gm according to the manufacturer's specification.

iv) **Rice Husk Carbon:-** Burnt rice husk obtained from rice mill was used in the experiment.

v) **Dowex-50 :-** Dowex-50 is an acidic cation exchange resin of sphericity greater than 85%. It has a total exchange capacity of 50 meq/ml on dry basis.

3.1.2 Stock Solutions

All the chemicals used in the experiment were of analytical grade.

1000 mg/l solutions of Mercury was prepared by dissolving 1.353 gm mercuric chloride (HgCl_2) in 1000 ml distilled water. This stock solution containing 1 mg mercury/ml was diluted to get solutions of different concentrations of mercury. Similarly stock solutions of

Cadmium, Lead and Chromium were prepared by dissolving 2.28, 1.598 and 2.829 gm of Cadmium Sulphate ($3 \text{ CdSO}_4 \cdot 8\text{H}_2\text{O}$), Lead Nitrate [$\text{Pb}(\text{NO}_3)_2$] and Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) respectively in 1000 ml distilled water.

3.1.3. Analysis Techniques

Atomic Absorption Spectrophotometer (GBC 902 model) and Mercury Analyser were used for performing the analysis.

3.1.4. Experimental Setup

Contact filtration method was employed for the adsorption study. The experimental setup consisted of a reactor of 3 litre capacity fitted with a glass stirrer. The rpm was adjusted using an autotransformer.

Precipitation and settleability studies were conducted using jar tests. Settleability studies were done in 100 ml measuring cylinder.

3.2. Adsorption Techniques

3.2.1 Sorption Kinetics on Chitosan

Sorption Kinetics of mercury, cadmium, lead and chromium on chitosan were studied at different initial concentrations of metal ions. 1 litre sample solution of mercuric chloride in distilled water containing 0.5 mg/l mercury was stirred with 200 mg of 0.3 mm size chitosan at 1800 rpm for 60 minutes at room temperature. The samples were withdrawn at regular intervals of 2,5, 10, 15, 20, 25, 30, 40, 50 and 60 minutes and analysed for mercury content. The experiments were repeated with different mercury concentrations of 5, 10 and 50 mg/l.

Similar experiments were conducted with aqueous solutions of cadmium, lead and chromium at four different initial concentrations of 0.5, 5, 10 and 50mg/l to obtain sorption kinetic data of these metals on chitosan and the observations are tabulated in Table Nos. 1 to 4.

3.2.2. Effect of Particle size of Chitosan

The effect of particle size of Chitosan on adsorption was studied by using particles of 0.1, 0.3 and 1 mm size. For this 1000 ml sample solution containing 5 mg/l Hg and 200 mg of 0.1 mm size chitosan were stirred at constant rpm of 1800 for 60 minutes. Samples were drawn at regular intervals and analysed for mercury. Repeated the experiment using chitosan of 0.3mm and 1 mm size. The same procedure was followed to obtain data relating to varying particle sizes of chitosan for cadmium, lead and chromium and results are tabulated in Table 5 to 8.

3.2.3. Effect of Temperature

To study the influence of temperature, sorption tests were carried out at different temperatures of 20°C, 29°C and 36°C. 1000 ml of 5mg/l (as Hg) sample solution and 200 mg of 0.3mm size chitosan were stirred at constant speed of 1800 rpm for 60 minutes at room temperature

29°C. The final concentration of mercury in the sample at different time intervals were determined. Repeated the experiments for 5 mg/l solutions of cadmium, lead and chromium. Results of the experiments conducted with mercury, cadmium, lead and chromium are listed in Table 9,10,11 and 12 respectively.

3.2.4. Effect of pH on Adsorption

The effect of pH on adsorption was studied over a range of pH values 3.0 to 9.0. The initial pH of the sample solution of 5 mg/l mercury was adjusted to 3.0 and sorption study was conducted using 200 mg of 0.3mm chitosan at constant stirring speed of 1800 rpm for 60 minutes. The final concentration of mercury at regular intervals were determined. Repeated the experiment for all the metal ions by varying the initial pH of the solution as 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0. The results are given in Table 13 to 16.

3.2.5. Equilibrium Characteristics

Sorption equilibria study was conducted using the time required to attain equilibrium from the kinetic studies. Sample solutions of mercury, cadmium, lead and chromium containing 0.20, 0.5, 1.0, 2.0, 5.0, 8.0, 12.0, 20.0, 30.0, 40.0 and 50 mg/l metal were prepared. Each sample was treated with 200 mg of 0.3mm size chitosan at constant rpm of 1800 for one hour and analysed for metal content. The equilibrium concentration data obtained for the four metals are charted in Table No: 17 to 20.

3.2.6. Sorption Kinetics and Sorption Equilibria of Mercury on Activated Carbon

Adsorption study was conducted with Mercuric Chloride solution of 5.0 mg/l mercury and 500 mg Activated Carbon at 29°C. The rpm was fixed at 1800. The final concentration of mercury was determined during regular intervals of time. *Similar* study was conducted with initial mercury concentrations of 10 mg/l and 50mg/l.

The results are entered in Table No:21. To obtain the equilibrium data, initial concentration of mercury was varied over the range 1 mg/l to 50 mg/l and the amount of mercury remaining in solution after the contact time of 60 minutes was found out in each case. Observations are tabulated in Table 22.

3.2.7. Sorption Kinetics and Sorption Equilibria of Mercury on Dowex-50

Adsorption experiments were also done with Dowex-50, a synthetic polymer. 200 mg Dowex-50 was treated with Mercuric Chloride solution containing 5 mg/l mercury for one hour with constant stirring speed of 1800 rpm. Samples were withdrawn at regular intervals and analysed. Repeated the experiment by varying the initial mercury concentration to 10 mg/l and 50 mg/l. The observations are given in Table. 23. Equilibrium data was obtained by varying the initial mercury content from 1.0 mg/l to 50 mg/l. The final concentration of mercury in each case after adsorption was found out analytically and tabulated in Table. 24.

3.2.8. Sorption Kinetics and Sorption Equilibria of Mercury on Rice Husk Carbon

Adsorption studies were made with 500 mg Rice Husk Carbon and initial mercury concentrations of 5, 10 & 50 mg/l. The final concentration of metal ions at the end of 2, 5, 10, 15, 20, 25, 30, 40, 50 and 60 minutes were determined. The time required to attain equilibrium was found out. By varying the initial mercury concentration from 1 to 50 mg/l and with 500 mg rice husk carbon the runs were repeated to get the equilibrium concentrations. Data obtained are entered in Table. 25 and 26.

3.3. Chemical Precipitation Technique

3.3.1. Chemical Precipitation of Mercury

Experiments were carried out to find the effectiveness of chemical precipitation techniques for removing the metals of mercury, cadmium, lead and chromium. Also studied the effect of chitosan on flocculation and subsequent adsorption of metal ions from aqueous solutions.

3.3.1.1. Effect of pH

To find the optimum pH required for precipitation, experiments were done over the pH range 7.5 to 10. Mercuric chloride solution of concentration 50 mg/l mercury was prepared. To 500ml of this solution sodium sulphide was added at the rate of 40 mg/l (100% in excess of the stoichiometric requirement). Adjusted the pH to 7.5, stirred for 15 minutes and allowed to settle in a measuring jar. The supernatant solution was analysed for mercury content. Repeated the experiment at various pH values of 8.0, 8.5, 9.0, 9.5 & 10.0. The optimum pH was found out.

The optimum dosage of coagulant (FeCl_3) and polyelectrolyte(chitosan) were then found out experimentally by varying the dosages of FeCl_3 and chitosan at the optimum pH value 9.0 and entered in Table.29. The optimum dosage of FeCl_3 and chitosan were found as 100 mg/l and 2 mg/l respectively.

To find the effect of coagulant and polyelectrolyte on precipitation of mercury, experiments were done with 50 mg/l mercury for the same pH range 7.5 to 10.0 with the addition of optimum dosage of coagulant (100 mg/l FeCl₃) with the addition of optimum dosage of polyelectrolyte (2 mg/l chitosan) and finally with both FeCl₃ and chitosan. The solution was filtered and concentration of mercury in the supernatant liquid was determined in all the cases and listed in Table.30. Repeated the experiment with 10 mg/l initial concentration and data obtained are given in Table.31.

3.3.1.2. Effect of Initial Concentration

Effect of initial concentration on precipitation of mercury was studied at the optimum pH 9.0 by varying the initial mercury concentration as 5, 10, 20, 50 and 100 mg/l. The effect of adding coagulant and polyelectrolyte was also studied and tabulated in Table.32.

3.3.1.3. Settleability.

Settleability study was conducted in 100 ml measuring jar for mercuric chloride solution of 50 mg/l Hg at optimum pH 9.0. The rate of settling of the precipitated sludge was studied without adding any coagulant or polyelectrolyte, with the addition of 100 mg/l FeCl₃, with 2 mg/l chitosan and with both FeCl₃ and chitosan. The settling time and height of sludge line are noted in Table.33.

3.3.2. Chemical Precipitation of Cadmium

3.3.2.1 Effect of pH

The optimum pH for precipitation of cadmium was found out by conducting experiments over the range of pH values from 8.5 to 12.0 with initial cadmium concentrations of 50 mg/l and 10 mg/l. The optimum dosage of coagulant (FeCl₃) and polyelectrolyte (chitosan) were found out from Table.34. The effect of coagulant (FeCl₃) and polyelectrolyte (chitosan) on

precipitation was determined by studying the concentration of cadmium in the supernatant liquid with and without the addition of optimum dosage of coagulant and polyelectrolyte. Combined effect of ferric chloride and chitosan was also studied. Results obtained with 50 mg/l and 100 mg/l cadmium solution are tabulated in Table 35 and 36.

3.3.2.2 Effect of Initial Concentration

Initial Concentration of cadmium in the solution was varied from 5 mg/l to 100 mg/l and experiments were done at optimum pH 11.0 with and without the addition of FeCl₃, chitosan and combination of both. The observations are given in Table 37.

3.3.2.3 Settleability

The effect of coagulant and polyelectrolyte on the rate of settling of cadmium was found out by studying the rate of settling of the precipitated sludge in the presence and absence of coagulant, polyelectrolyte and combination of both. The results are given in Table 38.

3.3.3. Chemical Precipitation of Lead.

3.3.3.1 Effect of pH

By varying the initial pH, optimum pH for precipitation of lead was determined. After fixing the optimum pH the dosage of coagulant and polyelectrolyte were varied to find out the optimum dosage of coagulant (FeCl_3) and polyelectrolyte (Chitosan) for the removal of lead. The experimental results are given in Table No.39. Experiments were also done at the optimum pH by adding optimum dosage of coagulant, polyelectrolyte and both. The final concentration of lead was determined and listed in Table No. 40 and 41.

3.3.3.2. Effect of concentration of Lead.

The concentration effect was studied by varying the initial concentration of lead as 5, 10, 20, 50 and 100 mg/l at pH 9. The experiments were repeated with and without the addition of coagulant and polyelectrolyte. A combination of FeCl_3 and Chitosan was also studied and results are given in Table 42.

3.3.3.3. Settleability

The effect of coagulant and polyelectrolyte on settleability was studied and the observations are listed in Table 43.

3.3.4 Chemical precipitation of Chromium

3.3.4.1 Effect of Reaction Time on Reduction Reaction

Removal of chromium from aqueous solutions by reduction precipitation method was experimentally studied using potassium dichromate solution. Ferrous sulphate heptahydrate was used as reducing agent.

Effect of time on the reduction reaction was studied for the initial chromium concentrations of 50 mg/l and 10 mg/l at pH 2.5 using ferrous sulphate solution of 1000 mg/l and 200 mg/l respectively. The observations are shown in Table.44.

3.3.4.2. Effect of pH on Reduction of Hexavalent Chromium

Effect of pH on reduction reaction was studied by fixing the parameters of ferrous sulphate dosage, reaction time, and precipitation pH. Experiments were done with initial chromium concentrations of 50mg/l and 10 mg/l and listed in Table .45.

3.3.4.3. Effect of Dosage of Ferrous Sulphahte Heptahydrate

The initial pH of the dichromate solution was adjusted to 2.6 using sulphuric acid. The mixture was stirred for 20 minutes after the addition of ferrous sulphate heptahydrate solution.

The pH of the mixture was raised to 9.0 using lime. The final concentration of chromium in the supernatant was determined. Repeated the experiment at various ferrous sulphate concentrations for the initial chromium concentrations of 50 mg/l and 10 mg/l. The results are tabulated in Table.46.

3.3.4.4. Effect of pH on Precipitation of Chromium

Optimum pH for the precipitation of trivalent chromium was found out by conducting experiments at pH range of 7.5 to 11.0 with chromium concentrations of 50 and 10 mg/l. After settling the concentration of chromium in the supernatant was found out. Also the effect of polyelectrolyte over the same pH range was studied. Details are presented in Table.47 and 48.

3.3.4.5. Effect of Initial Concentration on Precipitation of Chromium

Experiments were done at initial chromium concentrations of 5, 10, 20, 50 and 100 mg/l after fixing the dosage of ferrous sulphate, reduction pH, reaction time and precipitation pH. Experiments were repeated with the addition of polyelectrolyte to find its effect on chemical precipitation. The final concentrations of chromium was found out in each case and the observations are tabulated in Table.49.

3.3.4.6. Settleability

Rate of settling of the precipitated sludge was determined at the initial chromium concentration of 50 mg/l and listed in Table.50.

3.4. Treatability studies on Industrial Effluents

Experiments were carried out on industrial effluents to study the effect of chitosan on flocculation, subsequent adsorption of traces of metals and settling of the precipitated sludge.

3.4.1. Pulp and Paper Mill Effluent

1000 ml of combined effluent from the factory of M/s. Hindustan Newsprint Ltd., Vellore having a colour intensity of 4000 PtCo units and a BOD of 480 mg/l was taken and 600 mg/l of Ferric Alum was added with thorough mixing to precipitate the colour bearing lignin and dissolved organics. The resultant pH was adjusted

to 7.0. After settling the supernatant was analysed for colour, BOD, COD, Suspended Solids and Mercury. The experiment was repeated with the addition of 2 mg/l chitosan to the precipitated sludge and the supernatant liquid was analysed for colour, BOD, COD, Suspended Solids and Mercury. The settleability of the precipitated sludge with and without the addition of chitosan was studied in 100 ml measuring cylinder. The data obtained in the study are presented in Table Nos. 51 and 52.

3.4.2. Treatability Study on Tannery Effluent

Treatability study of Tannery effluent was conducted on the combined effluent sample collected from a local tannery employing Chrome-Tanning process. The sample was found to contain 56.8 mg/l Cr^{+3} along with other organic pollutants.

One litre of this combined effluent was treated with 500 mg/l Ferric Alum and after settling the supernatant was analysed for BOD, COD, Suspended Solids and Chromium.

To study the effect of chitosan on flocculation and adsorption of pollutants the above experiment was repeated with the addition of 2 mg/l chitosan solution along with Ferric Alum. After flocculation and settling the clear solution was analysed for BOD, COD, Suspended Solids and Chromium. The values are tabulated in Table. 53.

Also conducted the settleability study on the precipitated sludge with and without chitosan and the data are entered in Table.54.

CHAPTER - 4

RESULTS AND DISCUSSIONS

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4. RESULTS AND DISCUSSIONS

Removal of heavy metal ions from aqueous solutions of mercury, lead, cadmium and chromium were studied by adsorption technique using Chitosan as an adsorbent. The effectiveness of chitosan was compared by sorption study on Mercury using a synthetic polymer (Dowex -50), Activated Carbon and Rice Husk Carbon (burnt rice husk) as adsorbents. Also investigated the effect of chitosan as a flocculant and adsorbent for the removal of heavy metal ions along with chemical precipitation. Treatability studies on trade effluents were also carried out using chitosan.

4.1. Adsorption Technique :- At the outset, the sorption kinetics of heavy metal ions like mercury, cadmium, lead and chromium on adsorbents like natural and synthetic polymeric materials as well as activated carbon were studied by varying the system and operating variables such as initial concentration of adsorbate in solution, solution temperature, pH and particle size of adsorbent.

The final concentration (equilibrium concentration) for a wide range of initial concentration employing different types of adsorbents were studied.

4.1.1 Sorption Kinetics

Sorption kinetics of Mercury, Cadmium, Lead and Chromium on chitosan were studied at different initial concentrations of 0.5, 5, 10 and 50 mg/l as metal ions keeping the pH and temperature of solution constant and the results are tabulated in Table Nos: 1 to 4 and plotted in figures 1 to 4. It is observed that the initial sorption rate is high for all the metal ions and the equilibrium is reached within one hour. The rate of sorption is very rapid initially and decreased markedly, finally approaching zero. The rate of adsorption is the highest for mercury followed by cadmium, lead and chromium in the decreasing order. This is due to the high affinity of chitosan to mercury ions and the decrease in affinity from mercury to chromium. Muzzarelli et al³ and F.Yaku and T.Koshijima² also reported the same sequence of affinity. The fraction of metal ions adsorbed at

different initial concentrations are tabulated in Table Nos : 1 to 4 and figures 5 to 8. The kinetic data and Fig.5 to 8 showed that a greater fraction of metal ion was adsorbed at constant adsorbent to solution ratio in a specified time when the initial concentration is lower.

The said sorption data when fitted according to the reversible first-order kinetic model rate equation

$$-dCR/dt = -dCA/dt = k_1[C_{Ao} - C_{Ao}X_A] - k_2[C_{Ro} + C_{Ao}X_A]$$

On integration and rearrangement becomes

$$-\ln \left[\frac{(C_A - C_{Ae})}{(C_{Ao} - C_{Ae})} \right] = k^1 t$$

where $k^1 = k_1 + k_2$

C_{Ae} = Equilibrium concentration of metal in solution

C_{Ao} = Initial Concentration of metal in solution

C_{Ro} = Initial Concentration of metal on adsorbent

C_{A-} = Concentration of metal remaining in solution at time 't'

X_A = Fractional conversion of metal

k_1, k_2 = Rate constant.

Figure 9,10,11 and 12 are plots of the LHS of the equation versus time showing sorption kinetics of all the metallic ions included in the present study.

These plots reveal that the adsorption of heavy metals on chitosan follows first order reversible kinetics. Also these plots confirm the inferences drawn earlier.

4.1.2. Effect of Particle Size

Table Nos : 5 to 8 and figures 13 -16 show the effect of particle size of Chitosan on adsorption of Hg, Cd, Pb and Cr. The figure shows that milligrams of metal ions adsorbed per gram of chitosan is highest with 0.1mm size and is lowest with 1mm size for all the metals. Thus the adsorption rate is found to increase with decrease in particle size. This is due to the increase in specific surface area of chitosan particle.

4.1.3. Effect of Temperature

The results obtained for the temperature study are tabulated in Table Nos : 9 to 12. The final concentration of the metal ions in solution is plotted

against time in fig. Nos: 17 to 20. It is observed that at a particular time, the quantity of metal ions adsorbed per unit weight of adsorbent increases with decrease in temperature. The rate of adsorption is found to be high at lower temperatures in the case of all the four metals.

Rate equation for first order kinetics of mercury sorption on chitosan at different temperatures of 20°C , 29°C , and 36°C , plotted in Fig.21 show that the sorption rate decreases with increase in temperature. From the Arrhenius Plot of $\ln k$ Vs $1/T$ (Fig.22) for the sorption of mercury on chitosan, activation energy for the system is found to be 5320 cal/mole. Comparatively low value of activation energy indicates that the initial rate of reaction is very fast. Also indicates that the sorption on chitosan is less temperature sensitive.

4.1.4 Effect of pH

The effect of pH on sorption of all the metal ions using Chitosan as an adsorbent is presented in Table Nos : 13 to 16 and the final concentrations of metal ions in solution are plotted against pH in Fig. 23. Fig 24 indicates the amount of metal ion adsorbed per unit weight of chitosan at different pH. The figure illustrates that sorption is high in the acidic range and a reduction in sorption is noticed with rising pH. In the case of mercury, adsorption remains more or less steady in the pH range of 3 to 6.5 and the optimum pH is found to be 5 to 6. A sudden decrease is noticed from pH 7.0 to 9.0. For cadmium adsorption is more or less same in the pH range of 3 to 6.5 and decreases between 6.5 and 9.0. In the case of lead, adsorption remains constant in the pH range of 4.0 to 6.0 and a decrease is noticed in the alkaline range. Adsorption is more or less steady in the pH range 3 to 4 for chromium and gradually decreases thereafter. Thus for chromium it is found that better adsorption occurs in the range of 3 to 4 and thereafter decreases gradually as pH increase.

The observed pH effect may be accounted for in the following manner. In the acidic range the prevalent metal species in the experimental system are metal ions. With rising pH the neutral species like metal hydroxide becomes more prevalent. At higher pH value, chitosan do not dissociate neutral salts. Thus adsorption decreases with increase of pH.

Riccardo A.A Muzzarelli⁴ in his paper " Modified Chitosans and their Chromatographic Performances" reported that Chitosan is a weak base at higher pH value and do not dissociate neutral salts. Thus the observed reduction on sorption with rising pH appears reasonable.

Mahesh P.Pandey and Malay Chaudhuri¹ also reported the inhibition of mercury sorption on powdered activated carbon in the alkaline pH range.

4.1.5 Equilibrium Study

The results of the equilibrium study conducted at different initial concentrations ranging from 0.2 mg/l to 50 mg/l mercury, cadmium, lead and chromium are

tabulated in Table Nos: 17 to 20 and Fig.Nos: 25 to 32. The equilibrium curve is plotted with X, milligrams of metal ions adsorbed per gram of adsorbent, on abscissa and Y* final concentration of metal ions on ordinate. Equilibrium concentrations of Y* Vs X for mercury, cadmium, lead and chromium are shown in Fig : 25 to 28.

A logarithmic plot of equilibrium relationship for adsorption of metal ions by chitosan ($\ln Y^*$ Vs $\ln X$) are given in Fig: 29 to 32, it is seen that the equilibrium data fitted to the linear form of the Freundlich Equation,

$$Y^* = m X^n$$

where Y^* = Equilibrium concentration of metal in solution

X = Weight of metal adsorbed per unit weight of Chitosan (mg/g)

m and n are constants.

n = Slope of the straight line

m = Intercept on ordinate.

Thus the sorption isotherm for the four metals on chitosan can be described by Freundlich equation as follows:

- | | | |
|-----------------------------|---|--|
| 1) Mercury Chitosan System | } | $Y^* = (2.75 \times 10^{-5}) X^{2.53}$ |
| 2) Cadmium Chitosan System | } | $Y^* = (0.01) X^{1.438}$ |
| 3) Lead Chitosan System | } | $Y^* = (0.0135) X^{1.4}$ |
| 4) Chromium Chitosan System | } | $Y^* = (0.0273) X^{1.26}$ |

It is observed that the value of 'n' is high (2.53) for the mercury - chitosan system and between 1 and 2 for other systems. It is generally stated that the value of 'n' in the range of 2 to 10 represent good, 1 to 2 moderate and less than one poor adsorption characteristics. Thus chitosan is found to be a good adsorbent for removing mercury and for cadmium, lead and chromium it is moderate.

Owing to extremely favourable equilibrium distribution of mercury towards chitosan, a single stage adsorption system employing contact filtration technique can be

conveniently employed for removal and recovery of mercury from industrial effluents on a commercial scale.

For fresh adsorbent, $X_0 = 0$, and applying Freundlich Equation, adsorbent to solution ratio for a given change in concentration of the solution from Y_0 to Y_1 is given by,

$$S/L = \frac{(Y_0 - Y_1)}{(Y_1/m)^{1/n}}$$

$$= \frac{(Y_0 - Y_1)}{(Y_1 / 2.75 \times 10^{-3})^{1/2.53}}$$

where L = mass of adsorbate free solution in mg

Y_0 = initial adsorbate concentration, mg/l solvent

Y_1 = final adsorbate concentration, mg/l solvent

S = mass of adsorbate free adsorbent added, mg

X_0 = initial solute adsorbate concentration,
^{solute}
 mg/gm of adsorbent

X_1 = final solute adsorbate concentration,
 mg solute /gm adsorbent

The savings in adsorbent by counter current operation over single stage is greater in this case as the value of n is fairly high. The intermediate concentration Y_1 for specified terminal concentration Y_0 and Y_2 can be determined from the equation

$$(Y_0/Y_2) - 1 = (Y_1/Y_2)^{1/2.53} (Y_1/Y_2) - 1$$

S/L ratio for a two stage counter current cascade when fresh adsorbent is employed in the second stage can be predicted by

$$S/L = \frac{(Y_0 - Y_2)}{(Y_1 / (2.75 \times 10^{-5}))^{1/2.53}}$$

4.1.6. Sorption studies of Mercury on Activated Carbon,

Dowex-50 and Rice Husk Carbon

Sorption of mercury on Activated Carbon, Dowex-50 and Rice Husk Carbon were investigated with a view to compare the sorption capacity of chitosan.

4.1.6.1. Sorption kinetics study of mercury on Activated Carbon

The sorption kinetics and equilibrium characteristics of mercury on Activated Carbon are given in Table Nos. 21 & 22 and Fig.33 to 36, 38 & 39. It shows that the rate of adsorption of mercury decreases with increase in initial concentration of mercury. Equilibrium is attained after 50 minutes and mg of mercury adsorbed per gm of adsorbent is 6.60. At equilibrium 66 % reduction in mercury content is achieved. It is also found that the sorption isotherm for mercury - activated carbon system and the sorption equilibria fitted to the linear form of Freundlich equation. The value of 'n' and 'm' are 1.125 and 0.212 respectively. The intensity of adsorption is less when compared with the experimental value for Mercury - Chitosan system.

4.1.6.2. Sorption Kinetic Study of Mercury on Dowex-50

The Table No.23 & 24 and Fig. 40 to 43 illustrate that the linear form of the Freundlich's equation is fitted and the sorption capacity is greater than that of

activated carbon ($n = 1.157$, and $m = 0.1405$) but less than that for mercury chitosan system. 48 % reduction in mercury concentration is arrived at (mg of mercury adsorbed/gm of adsorbent is 12.2) with an initial mercury concentration of 5 mg/l.

4.1.6.3. Sorption Kinetics of Mercury on Rice Husk Carbon.

The sorption studies as evident from Table. 25 & 26 and Fig.33 to 35, 44 to 45 illustrate that the adsorption capacity of rice husk carbon at a specified time is the least. The values of 'n' and 'm' obtained from the Freundlich's isotherm for mercury-rice husk carbon system are 1.0 and 0.6376 respectively.

4.1.7. Capacity of chitosan on adsorption of metal ions

A comparative statement shown in Table 27 and Fig.46 illustrate the sorption capacity of chitosan to adsorb the metal ions of Mercury, Cadmium, Lead and Chromium.

It is found that the sorption of mercury on chitosan is very high when compared to other metals. The high sorption of mercury on chitosan is due to its affinity towards mercury.

It is stated that the sorption on metal ions increases with decrease in electronegativity of the metal ion. The electronegativity is the least for mercury when compared with other metals which justifies the high sorption for mercury.

Sorption capacity of different adsorbents on mercury are compared in Table 28 and Fig.47. It is found that among the natural, synthetic and standard adsorbents studied, chitosan has got high capacity to adsorb mercury. At equilibrium, mg of mercury adsorbed per gm of adsorbent is 24.6 for chitosan, 12.2 for Dowex-50, 6.6 for activated carbon and 4.0 for rice husk carbon.

The sorption kinetics of Hg, Cd, Pb and Cr on chitosan agrees with the findings of F.Yaku and T.Koshijima. They have reported that chitosan has the characteristics to

combine selectively particular metal ions and that the tendencies are most predominant in Copper, mercury, silver, cadmium, nickel and are weakest in manganese, cobalt and chromium. The affinity of chitosan towards the metal ions is decreasing from mercury to chromium in the order $Hg > Cd > Pb > Cr$.

4.2. Chemical Precipitation

Chemical precipitation technique is employed when substantial quantity of heavy metal is to be removed from solution. Traces of metal remaining after chemical precipitation can then be removed by adsorption. In order to increase the settleability of the precipitated sludge the capability of chitosan as a flocculating agent has been exploited. Synthetic polyelectrolyte of Polyacrylamide type generally employed for this purpose is quite toxic in nature and hence a natural polyelectrolyte like chitosan which is edible and quite eco-friendly was employed for this purpose. When chitosan is thus employed as a flocculating agent, the

percentage removal of heavy metal is found to be more than when chemical precipitation is conducted without chitosan. The reason for this additional removal of heavy metal over and above that is possible by normal chemical precipitation may be due to the great affinity of certain heavy metal ions towards chitosan. Thus chitosan is having a dual function in such cases, as a flocculating agent as well as an adsorbent.

4.2.1. Chemical Precipitation of Mercury.

4.2.1.1. Effect of Dosage of coagulant and polyelectrolyte

The effect of dosage of coagulant and polyelectrolyte are given in Table No: 29. The optimum dosage of coagulant (ferric chloride) and polyelectrolyte (chitosan) are found to be 100 mg/l and 2 mg/l respectively.

4.2.1.2. The effect of pH on precipitation of mercury

The pH effect is shown in Table Nos: 30 & 31 and fig: 48 & 49. It is found that the final concentration of mercury in solution decreases with increase of pH upto

a pH of 9.0. No further reduction in mercury content is noticed beyond this pH. Hence the optimum pH for precipitation of mercury is found to be 9.0.

The tables also illustrate the effect of chitosan. At the optimum pH by sodium sulphide precipitation the mercury concentration reduced from 50 mg/l to 0.96 mg/l (98.08%) without adding any coagulant or polyelectrolyte. With the addition of 100 mg/l ferric chloride as coagulant the mercury content is further reduced to 0.4 mg/l. When 2 mg/l chitosan alone is added to the precipitated mercury solution a higher reduction in mercury content is noticed, ie. from 0.96 to 0.22 mg/l (77%). When both ferric chloride and chitosan are added to the precipitated solution the final concentration reaches 0.185 from 0.96 mg/l (80.7%). The overall reduction in mercury content for 50 mg/l mercury solution with the addition of ferric chloride and chitosan is 99.63%.

In the case of 10 mg/l initial concentration of mercury the optimum pH for precipitation is 9.0. The same trend is observed as above and the overall efficiency is found

to be 99.17%. By the addition of chitosan in to the precipitated mercury solution, a reduction of 0.38 to 0.12 mg/l is noticed (68.4%). With the addition of both ferric chloride and chitosan the final concentration becomes 0.083 mg/l.

4.2.1.3. Effect of Concentration on Precipitation of Mercury.

Effect of initial concentration of mercury on precipitation is given in Table No: 32 and fig: 50. It is observed that the percentage removal of mercury increases with increase in initial concentration. Without adding any coagulant or polyelectrolyte the mercury concentration after precipitation is reduced to the range of 0.29 to 1.28 mg/l from initial concentration of 5 to 100 mg/l. With the addition of ferric chloride further reduction in the range of 26% to 58% is noticed. But when chitosan is added as a flocculant a further reduction of 0.082 to 0.33 mg/l (60

to 74%) is observed for the concentration range of 5 to 100 mg/l. This shows that chitosan has considerable capacity to remove metallic ions when used as a flocculant.

4.2.1.4. Effect of Chitosan on Settleability.

Table No: 33 and Fig.No. 51 show the effect of chitosan on settleability. It has been observed that in all the four cases, the rate of settling is rapid in the beginning and slow tending to zero towards the end.

The top most curve shows the rate of settling in the absence of coagulant and polyelectrolyte. The second and third curves show the individual effect of coagulant (100 mg/l FeCl₃) and polyelectrolyte (2 mg/l chitosan) respectively and the bottom most curve showing the combined effect of FeCl₃ and Chitosan indicates much higher settling rate than the individual cases. The third and fourth curves show the effect of chitosan on the settleability of the precipitated sludge.

When chitosan is added as a flocculating agent in the chemical precipitation study, it reduces the mercury content in the solution and increases the rate of settling considerably. This shows the dual capacity of chitosan as an adsorbent to heavy metal ions and a flocculating agent.

4.2.2. Cadmium

4.2.2.1. Effect of Dosage of Coagulant/Polyelectrolyte

As shown in Table No: 34, the optimum dosage of coagulant (FeCl_3) is 100 mg/l and polyelectrolyte (chitosan) is 2 mg/l.

4.2.2.2. The effect of pH

The effect of pH on precipitation of cadmium is shown in Table. 35 & 36 and Fig. 52 & 53. It is seen that the concentration of cadmium decreases with increase in pH upto pH 11.0. On increasing the pH further, no reduction is noticed in the cadmium content. Thus the

optimum pH is found to be 11.0. The percentage removal of cadmium at optimum pH without the addition of any coagulant and polyelectrolyte is 99.994 for initial concentration of 50 mg/l (ie, the concentration of cadmium is reduced to 0.003 mg/l). By the addition of chitosan further reduction from 0.003 to 0.001 mg/l is obtained. When both FeCl₃ and chitosan are added, the cadmium content is completely removed with an initial concentration of 50 mg/l. 100% removal of cadmium is noticed with 10 mg/l initial concentration also.

4.2.2.3. Effect of initial concentration

The effect of concentration is shown in Table 37 and Fig 54. At optimum pH 11.0, the percentage removal of cadmium is above 99.9%. So the initial concentration has no considerable effect on cadmium precipitation. By changing the initial concentration of cadmium from 5 to 100 mg/l, it is found that the combined addition of chitosan and ferric chloride can completely remove the cadmium content.

4.2.2.4. Effect of Chitosan on Settleability

Effect of chitosan on settleability of precipitated cadmium sludge is shown by Table No:38 and Fig: 55. The rate of settling increases with the addition of 100 mg/l ferric chloride and 2 mg/l chitosan as shown by the two middle curves. The settling rate is much higher when both ferric chloride and chitosan are added. Thus chitosan increases the settling rate of precipitated sludge as well as reduces the cadmium concentration by the dual action of flocculation and adsorption for the precipitation of cadmium.

4.2.3. Chemical Precipitation of Lead

4.2.3.1. Effect of dosage of Coagulant/Polyelectrolyte

From Table No: 39, the optimum dosage of coagulant (Ferric Chloride) and Polyelectrolyte (Chitosan) are found to be 150 mg/l and 2.0 mg/l respectively.

4.2.3.1. Effect of pH on Precipitation of Lead

The effect of pH on precipitation of lead from solutions of initial concentrations 50 and 10 mg/l are shown in Table No: 40 & 41. and fig. 56 & 57. It is found that the concentration of lead in the solution decreases rapidly by increasing the pH from 7.5 to 9.5. The lead content is minimum at pH 9.5. The same trend is observed with solutions of concentrations 50 and 10 mg/l. Thus the optimum pH for precipitation of lead is 9.5.

At the optimum pH 9.5, the lead content decreases from 50 to 2.15 mg/l (95.7% reduction) due to precipitation alone. With the addition of 150 mg/l ferric chloride the percentage reduction increases to 96.40 and with 2 mg/l chitosan it reaches 97.80%. The concentration of lead further reduces to 0.85 mg/l (98.30%) with the addition of both the ferric chloride and chitosan..

For an initial concentration of 10 mg/l lead, the maximum reduction achieved without the addition of

any coagulant or polyelectrolyte is 92.50%. When chitosan is added along with chemical precipitation the lead content further reduces from 0.58 to 0.40 mg/l (31%). The addition of both ferric chloride and chitosan brings down the lead concentration to 0.33 mg/l. Thus an overall reduction of 96.70% is obtained.

4.2.3.3. Effect of Concentration of Lead

From Table No: 42 and fig. 58, it is found that with increase in concentration of lead from 5 to 100 mg/l the percentage removal increases from 91.40 to 97.20. With ferric chloride a reduction of 93.0 to 97.80% is obtained. When chitosan is added the concentration of lead further reduces in the range of 95.40 to 98.20%. The combination of ferric chloride and chitosan reduces the metal content still further from 96.4 to 98.58%.

4.2.3.4. Effect of Chitosan on Settleability

The effect of chitosan on settleability of precipitated sludge is shown in Table No: 43 and fig. 59. It shows

that with the addition of chitosan the rate of settling of the sludge is increased. It can be seen that with the addition of chitosan in chemical precipitation the final concentration of lead in the solution is reduced considerably. Thus chitosan acts as an adsorbent and flocculating agent.

4.2.4. Precipitation of Chromium

4.2.4.1. Effect of Time on Reduction of Hexavalent Chromium

Table No: 44 shows that the percentage removal of chromium is increased as the time of reduction reaction is increased from 5 to 20 minutes. As the reduction reaction time is increased beyond 20 minutes, the percentage removal remains more or less constant irrespective of the initial concentration of the solution. So a period of 20 minutes is given for the reduction reaction.

4.2.4.2. Effect of pH on Reduction of Hexavalent Chromium

This effect is shown in Table No: 45. The initial pH of the dichromate solution affects the reduction reaction and hence the percentage removal of chromium. It is found from the table and figure that the reduction is most effective around a pH 2.5.

4.2.4.3. The Effect of Dosage of Ferrous Sulphate on Reduction of Hexavalent Chromium

The effect of varying ferrous sulphate dosage is given in Table Nos: 46. Stoichiometrically around 16 parts by weight of ferrous sulphate hepta hydrate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$) is required to reduce one part by weight of hexavalent chromium (Cr^{+6}) to trivalent Chromium (Cr^{+3}). Thus for a 50 mg/l chromium solution around 800 mg/l ferrous sulphate hepta hydrate is stoichiometrically required. But this dosage when used for reduction gives only 96.4% conversion of hexavalent to trivalent chromium. When 1000 mg/l solution is added, 98.2% reduction/removal is obtained. Further increase in dosage has no noticeable

effect. Hence for 50 mg/l solution the optimum dosage is fixed as 1000 mg/l. In the case of 10 mg/l solution, the optimum dosage is found to be 200 mg/l.

4.2.4.4. Effect of pH on precipitation of Chromium.

The effect of pH on precipitation of trivalent Chromium as its hydroxide is given in Table Nos. 47 & 48 and Fig No. 60 & 61. It is seen that precipitation is maximum in the pH range 8.5 to 9. Both above and below this pH, precipitation and hence percentage removal is less. Thus the optimum precipitation pH for maximum chromium removal is found to be in the range of 8.5 to 9. The concentration of chromium decreases from 50 to 1.15 mg/l on precipitation (97.7%). Addition of chitosan reduces the chromium content in solution from 1.15 to 0.50, i.e. a further reduction of 56.52% is obtained. The overall percentage removal is 99.0.

4.2.4.5. Effect of Initial Concentration on Precipitation of Trivalent Chromium

Table No. 49 and Fig.No. 62 show the effect of initial concentration of chromium on removal of chromium by reduction precipitation. As the concentration increases, the percentage removal of chromium also increases. It is also seen that chitosan enhances the percentage removal by 97 to 99.2 % by varying the initial concentration from 5 mg/l to 100 mg/l.

4.2.4.6. Settleability Study.

The rate of settling of the precipitated sludge and the effect of polyelectrolyte (Chitosan) are shown in Table No.50 and Fig 63. It is seen that rate of settling increases considerably with the addition of chitosan as is evident from the graphs.

4.3. Treatability Study - On Removal of Heavy Metals in Combination With Other Pollutants by Chemical Precipitation

Treatability studies were conducted on the combined effluent collected from M/s. Hindustan Newsprints Ltd, Velloor and M/s. Kainady Tanneries Ltd, Edayar using chitosan as a flocculating agent as well as an adsorbent for removing traces of heavy metals. The action of chitosan as an adsorbent and flocculant for removing traces of heavy metals present along with other pollutants like BOD, COD, Colour and suspended Solids were investigated.

4.3.1 Treatability Studies on Pulp and Paper Mill Effluent

The data obtained from the studies conducted on pulp and paper mill effluent is given in Table No. 51 & 52. When chemical precipitation is conducted without adding chitosan there is no considerable change in the

concentration of mercury in the effluent. When chitosan is employed as a flocculant along with chemical precipitation traces of mercury (0.002 mg/l) present in the raw effluent is completely removed. Along with complete removal of mercury other parameters like color, BOD, COD, SS are further reduced when chitosan is used as a flocculant. This shows the ability of chitosan as a flocculant and as an adsorbent for removing metals like mercury. The settling rate of precipitated sludge with and without the addition of chitosan is shown in Fig 64. This figure and the photograph in Annexure -I clearly indicate the high rate of settling when chitosan is added as a flocculant.

4.3.2 Treatability study on Tannary Effluent

The Experimental data shown in Table No. 53 & 54 and Fig. 65 indicate the effect of chitosan as adsorbent for removing trace quantities of chromium present in the effluent and also act as a flocculating agent to increase the settleability. Without adding chitosan ^{by} chemical precipitation alone the chromium content is

reduced from 56.8 mg/l to 1.56 mg/l. But chitosan is added along with chemical precipitation as a flocculant, the chromium content in the final effluent could be brought down to 0.63 mg/l ie. a further reduction of about 60% is obtained, which is below the tolerance limit.

Thus it is possible to bring down trace amount of chromium present in the treated effluent after chemical precipitation by adding 2 mg/l chitosan as a flocculant. Fig. 65 and the photograph in Annexure - I show the high rate of settling of the precipitated sludge with the addition of chitosan.

Considerable reduction is also noted in other pollutants like BOD, COD, SS, etc. with chitosan. This is because of the high affinity of chitosan towards heavy metal ions like mercury, cadmium and lead.

In an existing treatment plant having primary treatment facilities it is possible to remove traces of metal ions like mercury, chromium, lead and cadmium in combination with other pollutants by chemical precipitation when chitosan, a natural polymer is added as a flocculant.

5. SUMMARY AND CONCLUSIONS

The heavy metal pollution is a problematic issue facing the vegetable and animal life in the aquatic as well as terrestrial environment. People are becoming more and more aware of the harmful effects of heavy metal pollution. Many attempts have been made to develop methods and materials for the removal of the heavy metals present in industrial and domestic effluent. These include the traditional methods such as ion exchange, adsorption, chemical precipitation, reverse osmosis etc.

With a view to develop suitable techniques for the removal of heavy metal ions like Mercury, Cadmium, Lead and Chromium by the principle of adsorption process, batch experiments were carried out in the laboratory adopting contact filtration method. Sorption kinetics study of the metal ions on chitosan and the effect of parameters such as particle size of adsorbent, temperature, initial concentration and pH were studied.

Also compared the effectiveness of chitosan as an adsorbent by studying the sorption kinetics of Activated carbon (a standard adsorbent), Dowex-50 (a synthetic polymer) and Rice husk carbon (a waste material).

In the second part of the study experiments were done for the removal of metal ions by chemical precipitation, flocculation and subsequent adsorption using chitosan as a flocculating agent.

In the final part of the investigation treatability studies were conducted on industrial effluents using chitosan for the removal of heavy metals in combination with the removal of other pollutants like colour, dissolved organics (ie, BOD, COD etc) and suspended solids.

Removal of Heavy metal in combination with other pollutants has much practical application in the treatment of industrial effluents and that may have commercial importance. Hence in the last phase of the study stress has been given on that aspect.

CHAPTER - 5

SUMMARY AND CONCLUSIONS

Sorption kinetics of Mercury, Cadmium, Lead and Chromium on chitosan were studied at different initial concentrations of 0.5, 5, 10 and 50 mg/l as metal ions keeping the pH and temperature of solution constant. Following are the important observation made from the sorption kinetic study.

i) It is observed that the initial sorption rate is high for all the metal ions and the equilibrium is reached within one hour. The rate of sorption is very rapid initially and decreased markedly, finally approaching zero.

ii) The rate of adsorption is the highest for mercury followed by cadmium, lead and chromium in the decreasing order.

iii) Greater fraction of metal ions is adsorbed at constant adsorbent to solution ratio in a specified time when the initial concentration is lower.

iv) The sorption data fitted to the reversible first-order kinetic model rate equation

$$-\ln \left[\frac{[C_A - C_{Ae}]}{[C_{Ao} - C_{Ae}]} \right] = k^1 t$$

Where $k^1 = k_1 + k_2$.

v) The adsorption rate is found to increase with decrease in particle size. This is due to the increase in specific surface area of chitosan particle.

vi) It is observed that at a particular time, the quantity of metal ions adsorbed per unit weight of adsorbent increases with decrease in temperature. The rate of adsorption is found to be high at lower temperatures in the case of all the four metals.

Rate equation for reversible first order kinetics of mercury sorption on chitosan at different temperatures of 20°C, 29°C, and 36°C, when plotted, show that the sorption rate decreases with increase in temperature.

vii) From the Plot of $\ln k$ Vs $1/T$ for the sorption of mercury on chitosan, activation energy for the system is found to be 5320 cal/mole. Comparatively low value of

activation energy indicates that the reaction is very fast. Also indicates that the sorption on chitosan is less temperature sensitive.

viii) Sorption is high and more or less steady in the acidic range and a reduction in sorption is noticed with rising pH.

ix) The results of the equilibrium study conducted at different initial concentrations ranging from 0.2 mg/l to 50 mg/l mercury, cadmium, lead and chromium show that the equilibrium data fitted to the linear form of the Freundlich Equation as follows.

- | | | |
|-----------------------------|---|--|
| 1) Mercury Chitosan System | } | $Y^* = (2.75 \times 10^{-5}) X^{2.53}$ |
| 2) Cadmium Chitosan System | } | $Y^* = (0.01) X^{1.438}$ |
| 3) Lead Chitosan System | } | $Y^* = (0.0135) X^{1.4}$ |
| 4) Chromium Chitosan System | } | $Y^* = (0.0273) X^{1.26}$ |

x) Mercury sorption capacity of chitosan is the highest among the four adsorbents studied. Isotherm equation for other adsorbents employed in the present study is given below:

Comparative Study of Mercury Sorption on Different Adsorbents

Initial concentration : 5 mg/l as Hg.
of solution
Temperature : 29°C
pH : 6

Adsorbent	Freundlich isotherm $Y^* = m X^n$.	mg of Hg adsorbed per gm of adsorbent at equilibrium	Remarks
Chitosan, (Natural Polymer)	$Y^* = (2.75 \times 10^{-5}) X^{2.53}$	24.6	n > 2 Good Adsorbent.
Dowex 50 (Synthetic Polymer)	$Y^* = (0.15) X^{1.157}$	12.6)))
Activated Carbon (A Standard Adsorbent)	$Y^* = (0.212) X^{1.125}$	6.6) n between 1 to 2) Moderate))
Rice husk Carbon	$Y^* = (0.6376) X^1$	4.0)

Owing to extremely favourable equilibrium distribution of mercury towards chitosan, adsorption system employing contact filtration technique can be conveniently employed for the removal and recovery of mercury from industrial effluents on a commercial scale. It is also possible to predict the adsorbent to solution ratio for a given change in concentration of adsorbate in solution by applying Freundlich equation.

Chemical precipitation technique is employed when substantial quantity of heavy metal is to be removed from solution. Traces of metal remaining after chemical precipitation can then be removed by adsorption. In order to increase the settleability of the precipitated sludge the capability of chitosan as a flocculating agent has been exploited. Synthetic polyelectrolyte of Polyacrylamide type generally employed for this purpose is quite toxic in nature and hence a natural polyelectrolyte like chitosan which is edible and quite eco-friendly was employed for this purpose. When chitosan is thus employed as a flocculating agent, the percentage removal of heavy metal is found to be more

than when chemical precipitation is conducted without chitosan. The reason for this additional removal of heavy metal over and above that is possible by normal chemical precipitation may be due to the great affinity of certain heavy metal ions towards chitosan. Thus chitosan is having a dual function in such cases, as a flocculating agent as well as an adsorbent.

When the treatability of pulp mill effluent from Hindustan Newsprints Ltd., employing a standard coagulant was studied for the precipitation of colour bearing lignin, it was found that more than 60 to 70% removal of COD and BOD could be obtained along with more or less complete removal of colour, but noticeable reduction of mercury was not obtained. When one mg per litre of chitosan was added as a flocculating agent along with the coagulant more or less complete removal of mercury was obtained.

When the treatability of tannary effluent was conducted for the precipitation of dissolved organics and trivalent chromium, it was found that the final concentration of chromium reduced from 56.8 mg/l to 1.56

mg/l. But when chitosan is added along with chemical precipitation as a flocculant chromium content in the final effluent could be brought down to 0.63 mg/l ie. a further reduction of about 60% is obtained.

The results of chemical precipitation studies inferred that the addition of chitosan can remove/considerably reduce the concentration of heavy metal from effluent. Also found that the rate of settling of the precipitated sludge is considerably increased with the addition of chitosan as a flocculating agent. The dual action of chitosan as an adsorbent and flocculant in chemical precipitation find extensive industrial application when the quantity of effluent is so large and heavy metal concentration after chemical treatment is too small, necessitating huge investment for bringing down the concentration of heavy metal ions.

NOMENCLATURE

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NOMENCLATURE

CA ₀	-	Initial concentration of metal in solution, mg/l.
CR ₀	-	Initial concentration of metal on adsorbent, mg/l.
CA	-	Concentration of metal remaining in solution at time t, mg/l.
t	-	Time, minutes.
CA _e	-	Equilibrium Concentration of metal in solution, mg/l.
X _A	-	Fractional conversion of metal.
k ₁ , k ₂	-	rate constant, (min) ⁻¹ .
T	-	Temperature °K.
Y*	-	Equilibrium concentration of adsorbate, mg/l.
X	-	Weight of adsorbate adsorbed per unit weight of chitosan, mg/g.
m, n	-	Constant.
n	-	Slope of Freundlich isotherm.
m	-	Intercept on ordinate.
S	-	Mass of adsorbate free adsorbent added, mg.
L	-	Mass of adsorbate for solution, mg.
Y ₀	-	Initial adsorbate concentration, mg/l Solvent.

Y_1	-	Final adsorbate concentration, mg/l Solvent.
X_0	-	Initial solute adsorbate concentration, mg/gm of adsorbate.
X_1	-	Final solute adsorbate concentration, mg solute/adsorbent.
BOD	-	Bio Chemical Oxygen Demand, mg/l
COD	-	Chemical Oxygen Demand, mg/l.
SS	-	Suspended Solids, mg/l.

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TABLE NO: 1

SORPTION KINETICS OF MERCURY ON CHITOSAN

Adsorbent : 200 mg of 0.3mm size chitosan
 Solution : 1000 ml Mercuric Chloride
 Initial Concentration : 0.5 mg/l / 5 mg/l / 10 mg/l / 50 mg/l as Hg
 Temperature : 29°C
 pH : 6.0

Time in minutes	Final concentration of Mercury in solution Hg, mg/l				Percentage Removal of Mercury			
	Initial conc. 0.5 mg/l	Initial conc. 5.0 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l	Initial conc. 0.5 mg/l	Initial conc. 5.0 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l
0	0.5	5.0	10.0	50.00	0	0.00	0.00	0.00
2	0.3	3.10	6.42	33.00	40	38.00	35.80	34.00
5	0.18	1.90	4.46	24.80	64	62.00	55.40	50.40
10	0.10	1.10	3.20	18.30	80	78.00	68.00	63.34
15	0.05	0.55	2.08	14.80	90	89.00	79.20	70.40
20	0.02	0.27	1.20	13.00	96	94.6	88.00	74.00
25	0.00	0.12	0.92	12.75	100	97.60	90.80	74.50
30	0.00	0.08	0.66	12.00	100	98.40	93.40	76.00
40	0.00	0.08	0.45	11.70	100	98.40	95.50	76.60
50	0.00	0.08	0.45	11.50	100	98.40	95.50	77.10
60	0.00	0.08	0.45	11.50	100	98.40	95.50	77.10

TABLE NO: 2

SORPTION KINETICS OF CADMIUM ON CHITOSAN

Adsorbent : 200 mg of 0.3mm size chitosan
 Solution : 1000 ml Cadmium Sulphate
 Initial Concentration : 0.5 mg/l / 5 mg/l / 10 mg/l / 50 mg/l as Cd
 Temperature : 29°C
 pH : 6.0

Time in minutes	Final concentration of Cadmium in solution Cd mg/l				Percentage Removal of Cadmium			
	Initial conc 0.5 mg/l	Initial conc. 5.0 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l	Initial conc. 0.5 mg/l	Initial conc. 5.0 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l
0	0.50	5.00	10.00	50.00	0.00	0.00	0.00	0.00
2	0.35	3.60	7.80	40.00	30.00	28.00	22.00	20.00
5	0.23	2.80	6.00	34.30	54.00	44.00	40.00	31.40
10	0.18	1.86	4.43	26.40	64.00	62.80	55.70	47.20
15	0.125	1.42	3.20	22.80	75.00	71.60	68.00	54.40
20	0.09	1.08	2.60	20.20	82.00	78.40	74.00	59.60
25	0.062	1.00	2.15	17.50	87.60	80.00	78.50	65.00
30	0.040	0.82	1.86	16.30	92.00	83.60	81.40	67.40
40	0.036	0.70	1.63	15.20	92.80	86.00	83.70	69.60
50	0.033	0.65	1.58	14.80	93.40	87.00	84.20	70.40
60	0.033	0.65	1.58	14.80	93.40	87.00	84.20	70.40

TABLE NO: 3

SORPTION KINETICS OF LEAD ON CHITOSAN

Adsorbent : 200 mg of 0.3mm size chitosan
 Solution : 1000 ml Lead Nitrate
 Initial Concentration : 0.5 mg/l / 5 mg/l / 10 mg/l / 50 mg/l as Pb
 Temperature : 29°C
 pH : 6.0

Time in minutes	Final concentration of Lead in solution Pb, mg/l				Percentage Removal of Lead			
	Initial conc. 0.5 mg/l	Initial conc. 5.0 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l	Initial conc. 0.5 mg/l	Initial conc. 5.0 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l
0	0.50	5.00	10.00	50.00	0.00	0.00	0.00	0.00
2	0.37	3.80	7.80	41.00	28.00	24.00	22.00	18.00
5	0.33	3.34	6.72	36.00	34.00	33.20	32.80	28.00
10	0.225	2.26	5.20	29.60	55.00	54.80	48.00	40.80
15	0.15	1.76	4.10	25.30	70.00	64.80	59.00	49.40
20	0.11	1.43	3.32	21.50	78.00	71.40	66.80	57.00
25	0.085	1.36	3.20	19.30	83.00	72.80	68.00	61.40
30	0.063	1.20	2.90	18.75	87.40	76.00	71.00	62.50
40	0.06	1.00	2.40	16.80	88.00	80.00	76.00	66.40
50	0.05	0.88	2.20	16.00	90.00	82.40	78.00	68.00
60	0.05	0.88	2.20	16.00	90.00	82.40	78.00	68.00

TABLE NO: 4

SORPTION KINETICS OF CHROMIUM ON CHITOSAN

Adsorbent : 200 mg of 0.3mm size chitosan
 Solution : 1000 ml Potassium Dichromate
 Initial Concentration : 0.5 mg/l / 5 mg/l / 10 mg/l / 50 mg/l as Cr
 Temperature : 29°C
 pH : 4.0

Time in minutes	Final concentration of Chromium in solution, mg/l				Percentage Removal of Chromium			
	Initial conc. 0.5 mg/l	Initial conc. 5.0 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l	Initial conc. 0.5 mg/l	Initial conc. 5.0 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l
0	0.50	5.00	10.00	50.00	0.00	0.00	0.00	0.00
2	0.40	4.20	8.65	45.00	20.00	16.00	13.50	10.00
5	0.33	3.46	7.60	40.90	34.00	30.80	24.00	18.20
10	0.28	2.90	6.33	35.80	44.00	42.00	36.70	28.40
15	0.235	2.43	5.36	31.68	53.00	51.40	46.40	36.64
20	0.192	2.10	4.46	28.75	61.60	58.00	55.40	42.50
25	0.148	1.80	3.75	25.30	70.40	64.00	62.50	49.40
30	0.112	1.64	3.30	23.60	77.60	67.20	67.00	52.80
40	0.080	1.33	2.80	19.30	84.00	73.40	72.00	61.40
50	0.065	1.20	2.62	17.20	87.00	76.00	73.80	65.60
60	0.065	1.20	2.62	17.20	87.00	76.00	73.80	65.60

TABLE NO : 5

EFFECT OF PARTICLE SIZE OF CHITOSAN ON
ADSORPTION OF MERCURY

Adsorbent : 200 mg of 0.10 / 0.30 / 1.0mm size Chitosan
 Initial Concentration of solution : 5 mg/l as Hg
 Temperature : 29°C
 pH : 6.0

Time in minutes	Final concentration of Solution as Hg, mg/l			mg. of Hg adsorbed/gm. of Chitosan		
	0.1mm size	0.3mm size	1.0mm size	0.1mm size	0.3mm size	1mm size
0	5.00	5.00	5.00	0	0	0
2	1.80	3.10	3.70	16.00	9.50	6.50
5	0.96	1.90	2.76	20.20	15.50	11.20
10	0.43	1.10	1.80	22.85	19.50	16.00
15	0.20	0.55	1.20	24.00	22.25	19.00
20	0.10	0.27	0.84	24.50	23.65	20.80
25	0.08	0.12	0.46	24.60	24.40	22.70
30	0.08	0.08	0.25	24.82	24.60	23.75
40	0.036	0.08	0.22	24.82	24.60	23.90
50	0.036	0.08	0.22	24.82	24.60	23.90
60	0.036	0.08	0.22	24.82	24.60	23.90

TABLE NO : 6

EFFECT OF PARTICLE SIZE OF CHITOSAN ON
ADSORPTION OF CADMIUM

Adsorbent : 200 mg of 0.10 / 0.30 / 1.0mm size Chitosan
 Initial Concentration of solution : 5 mg/l as Cd
 Temperature : 29°C
 pH : 6.0

Time in minutes	Final concentration of Solution as Cd, mg/l			mg.of Cd.adsorbed/gm of chitosan		
	0.1mm size	0.3mm size	1.0mm size	0.1mm size	0.3mm size	1.0 mm size
0	5.00	5.00	5.00	0	0	0
2	3.25	3.60	4.25	8.75	7.00	3.75
5	2.10	2.80	3.72	14.50	11.00	6.40
10	1.20	1.86	2.90	19.0	15.70	10.50
15	0.76	1.42	2.38	21.20	17.90	13.10
20	0.52	1.08	1.86	22.50	19.60	15.70
25	0.36	1.00	1.46	23.20	20.00	17.70
30	0.30	0.82	1.30	23.50	20.90	18.50
40	0.25	0.70	1.18	23.75	21.50	19.10
50	0.25	0.65	1.15	23.75	21.75	19.25
60	0.25	0.65	1.12	23.75	21.75	19.40

TABLE NO : 7

EFFECT OF PARTICLE SIZE OF CHITOSAN ON
ADSORPTION OF LEAD

Adsorbent : 200 mg of 0.10 / 0.30 / 1.0mm size Chitosan
 Initial Concentration of solution : 5 mg/l as Pb
 Temperature : 29°C
 pH : 6.0

Time in minutes	Final concentration of Solution as Pb, mg/l			mg.of Lead adsorbed/gm.of chitosan		
	0.1mm size	0.3mm size	1.0mm size	0.1mm size	0.3mm size	1.0mm size
0	5.00	5.00	5.00	0	0	0
2	3.40	3.80	4.40	8.00	6.00	3.00
5	2.30	3.34	3.96	13.50	8.30	5.20
10	1.25	2.26	2.98	18.75	13.70	10.10
15	0.93	1.76	2.45	20.35	16.20	12.75
20	0.76	1.43	2.08	21.20	17.85	14.60
25	0.63	1.36	1.76	21.85	18.20	16.25
30	0.55	1.20	1.52	22.25	19.00	17.40
40	0.40	1.00	1.36	23.00	20.00	18.20
50	0.40	0.88	1.28	23.00	20.60	18.60
60	0.40	0.88	1.24	23.00	20.60	18.80

TABLE NO : 8

EFFECT OF PARTICLE SIZE OF CHITOSAN ON
ADSORPTION OF CHROMIUM

Adsorbent : 200 mg of 0.10 / 0.30 / 1.0mm size Chitosan
 Initial Concentration of solution : 5 mg/l as Cr
 Temperature : 29^oC
 pH : 4.0

Time in minutes	Final concentration of Solution as Cr, mg/l			mg.of Cr. adsorbed/gm of chitosan		
	0.1mm size	0.3mm size	1.0mm size	0.1mm size	0.3mm size	1.0mm size
0	5.00	5.00	5.00	0	0	0
2	3.75	4.20	4.60	6.25	4	2
5	2.94	3.46	4.20	10.3	7.7	5
10	2.22	2.90	3.73	13.9	10.5	6.35
15	1.60	2.43	3.25	17.0	12.85	8.75
20	1.42	2.10	2.86	17.9	14.50	10.70
25	1.16	1.80	2.50	19.2	16.00	12.50
30	0.96	1.64	2.16	20.2	16.80	14.20
40	0.68	1.33	1.75	21.6	18.35	16.25
50	0.68	1.20	1.60	21.6	19.00	17.00
60	0.68	1.20	1.50	21.6	19.00	17.50

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TABLE NO : 9

EFFECT OF TEMPERATURE ON ADSORPTION OF MERCURY

Adsorbent : 200 mg, 0.3mm size Chitosan
Solution : 1000 ml Mercuric Chloride solution
Initial Concentration : 5 mg/l as Hg
pH : 6.0

Time in minutes	Final concentration of Mercury mg/l		
	20°C	29°C	36°C
0	5.00	5.00	5.00
2	2.50	3.10	3.50
5	1.30	1.90	2.50
10	0.46	1.10	1.45
15	0.25	0.55	0.88
20	0.15	0.27	0.46
25	0.06	0.12	0.35
30	0.06	0.08	0.25
40	0.06	0.08	0.25
50	0.06	0.08	0.20
60	0.06	0.08	0.20

TABLE NO : 10

EFFECT OF TEMPERATURE ON ADSORPTION OF CADMIUM

Adsorbent : 200 mg, 0.3mm size Chitosan
Solution : 1000 ml Cadmium Sulphate Solution
Initial Concentration : 5 mg/L
pH : 6.0

Time in minutes	Final concentration of Cadmium mg/l		
	20 ^o C	29 ^o C	36 ^o C
0	5.00	5.00	5.00
2	3.20	3.60	3.75
5	2.25	2.80	2.93
10	1.40	1.86	2.20
15	0.95	1.42	1.73
20	0.70	1.08	1.55
25	0.50	1.00	1.22
30	0.46	0.82	1.15
40	0.45	0.70	1.10
50	0.45	0.65	1.00
60	0.45	0.65	1.00

TABLE NO : 11

EFFECT OF TEMPERATURE ON ADSORPTION OF LEAD

Adsorbent : 200 mg, 0.3mm size Chitosan
 Solution : 1000 ml Lead Nitrate Solution
 Initial Concentration : 5 mg/l
 pH : 6.0

Time in minutes	Final concentration of Lead mg/l		
	20 ^o C	29 ^o C	36 ^o C
0	5.00	5.00	5.00
2	3.40	3.80	4.20
5	2.62	3.34	3.16
10	1.83	2.26	2.60
15	1.25	1.76	2.12
20	1.00	1.43	1.75
25	0.80	1.36	1.60
30	0.65	1.20	1.40
40	0.54	1.00	1.20
50	0.54	0.88	1.15
60	0.54	0.88	1.15

TABLE NO : 12

EFFECT OF TEMPERATURE ON ADSORPTION OF CHROMIUM

Adsorbent : 200 mg, 0.3mm size Chitosan
 Solution : 1000 ml Potassium Dichromate Solution
 Initial Concentration : 5 mg/l
 pH : 4.0

Time in minutes	Final concentration of Chromium mg/l		
	20 ^o C	29 ^o C	36 ^o C
0	5.00	5.00	5.00
2	3.80	4.20	4.40
5	3.10	3.46	3.83
10	2.23	2.90	3.25
15	1.96	2.43	2.90
20	1.52	2.10	2.56
25	1.40	1.80	2.25
30	1.16	1.64	2.12
40	0.95	1.33	1.73
50	0.95	1.20	1.52
60	0.95	1.20	1.52

TABLE NO : 13

EFFECT OF pH ON ADSORPTION OF MERCURY

Adsorbent : 200 mg, 0.3mm size chitosan
Initial concentration of solution : 5 mg/l as Hg.
Temperature : 29⁰C

Initial pH	Final conc. of solution as Hg, mg/l	Milligram of Mercury adsorbed/gm. of chitosan
3.0	0.13	24.35
4.0	0.10	24.50
5.0	0.08	24.60
6.0	0.08	24.60
7.0	0.20	24.00
8.0	0.58	22.10
9.0	0.85	20.75

TABLE NO : 14

EFFECT OF pH ON ADSORPTION OF CADMIUM

Adsorbent : 200 mg, 0.3mm size chitosan
Initial concentration of solution : 5 mg/l as Cd.
Temperature : 29°C

Initial pH	Final conc. of solution as Cd mg/l	Milligram of Cd. adsorbed per gm. of chitosan
3.0	0.60	22.00
4.0	0.65	21.75
5.0	0.65	21.75
6.0	0.68	21.60
7.0	0.72	21.40
8.0	0.93	20.35
9.0	1.10	19.50

TABLE NO : 15

EFFECT OF pH ON ADSORPTION OF LEAD

Adsorbent : 200 mg, 0.3mm size chitosan
Initial concentration of solution : 5 mg/l as Pb.
Temperature : 29°C

Initial pH	Final conc. of solution as Pb, mg/l	Milligram of Lead adsorbed per gm. of chitosan
3.0	0.95	20.25
4.0	0.88	20.60
5.0	0.88	20.60
6.0	0.92	20.40
7.0	1.10	19.50
8.0	1.20	19.00
9.0	1.28	18.60

TABLE NO : 16

EFFECT OF pH ON ADSORPTION OF CHROMIUM

Adsorbent : 200 mg, 0.3mm size chitosan
 Initial concentration of solution : 5 mg/l as Cr.
 Temperature : 29°C

Initial pH	Final conc. of solution as Cr mg/l	Milligram of Cr. adsorbed per gm. of chitosan
3.0	1.20	19.00
4.0	1.20	19.00
5.0	1.35	18.25
6.0	1.56	17.20
7.0	1.80	16.00
8.0	2.20	14.00
9.0	2.50	12.50

TABLE NO : 17

EQUILIBRIUM CHARACTERISTICS OF MERCURY ON CHITOSAN

Adsorbent : 200 mg, 0.3mm size Chitosan
 Solution : 1000 ml Mercuric Chloride Solution
 Contact Time : 1 hr
 Temperature : 29°C
 pH : 6.0

Initial con. of solution as Hg. mg/l	Equilibrium conc. of solution mg/l as Hg. Y*	Milligram of Hg adsorbed/gm of chitosan X	ln Y *	ln X	Percentage removal of Hg
0.20	0	1.00	-	0	100
0.50	0	2.50	-	0.92	100
1.00	0	5.00	-	1.67	100
2.00	0.01	9.95	- 4.61	2.30	99.50
5.00	0.08	24.60	-2.53	3.20	98.40
8.00	0.23	38.85	-1.47	3.66	97.10
12.00	0.68	56.60	-0.39	4.04	94.30
20.00	1.75	91.25	+0.56	4.51	91.25
30.00	3.80	131.00	1.34	4.88	87.33
40.00	7.20	164.00	1.97	5.10	82.00
50.00	11.5	191.50	2.44	5.25	77.00

TABLE NO : 18

EQUILIBRIUM CHARACTERISTICS OF CADMIUM ON CHITOSAN

Adsorbent : 200 mg, 0.3mm size Chitosan
 Solution : 1000 ml Cadmium Sulphate Solution
 Contact Time : 1 hr
 Temperature : 29°C
 pH : 6.0

Initial conc. of solution as Cd. mg/l	Equilibrium conc. of solution mg/l as Cd Y*	Milligram of Cd adsorbed/gm of chitosan, X	ln Y*	ln X	Percentage removal of Cd
0.20	0.01	0.95	- 4.61	0.05	95.00
0.50	0.033	2.34	- 3.81	0.85	93.40
1.00	0.096	4.52	- 2.34	1.51	90.40
2.00	0.24	8.80	- 1.43	2.17	88.00
5.00	0.65	21.75	- 0.431	3.08	87.00
10.00	1.58	42.10	0.46	3.75	84.20
20.00	4.26	78.70	1.45	4.37	78.70
30.00	7.43	112.85	2.00	4.73	75.23
40.00	10.62	146.90	2.36	4.99	73.45
50.00	14.80	176.00	2.69	5.17	70.40

TABLE NO : 19

EQUILIBRIUM CHARACTERISTICS OF LEAD ON CHITOSAN

Adsorbent : 200 mg, 0.3mm size Chitosan
 Solution : 1000 ml Lead Nitrate Solution
 Contact Time : 1 hr
 Temperature : 29°C
 pH : 6.0

Initial conc. of solution as Pb mg/l	Equilibrium conc. of solution mg/l as Pb Y*	Milligram of Lead adsorbed/gm of chitosan, X	ln Y *	ln X	Percentage removal of Pb
0.2	0.01	0.95	- 4.61	- 0.05	95.00
0.5	0.050	2.25	- 3.00	0.81	90.00
1.00	0.11	4.45	- 2.21	1.49	89.00
2.00	0.28	8.60	- 1.27	2.15	86.00
5.00	0.88	20.6	- 0.13	3.04	82.40
10.00	2.20	40.7	0.621	3.71	81.40
20.00	4.66	76.7	1.54	4.34	76.70
30.00	7.85	110.75	2.06	4.71	73.80
40.00	11.34	143.3	2.43	4.96	71.65
50.00	16.00	170.00	2.77	5.14	68.70

TABLE NO : 20

EQUILIBRIUM CHARACTERISTICS OF CHROMIUM ON CHITOSAN

Adsorbent : 200 mg, 0.3mm size Chitosan
 Solution : 1000 ml Dichromate Solution
 Contact Time : 1 hr
 Temperature : 29°C
 pH : 4.0

Initial conc. of solution as Cr, mg/l	Equilibrium conc. of solution mg/l as Cr Y*	Milligram of Chromium adsorbed/gm of chitosan X	ln Y *	ln X	Percentage removal of Chromium
0.2	0.016	0.92	- 4.135	-0.0833	92.00
0.5	0.065	2.175	-2.733	0.7770	87.00
1.00	0.180	4.10	-1.714	1.4109	82.00
2.00	0.41	7.95	-0.891	2.073	79.50
5.00	1.20	19.00	-0.182	2.944	76.00
10.00	2.62	36.90	0.963	3.608	73.80
20.00	5.76	71.20	1.7509	4.2654	71.20
30.00	9.28	103.60	2.227	4.6405	69.07
40.00	12.80	136.00	2.549	4.9126	68.00
50.00	17.20	164.00	2.8449	5.0998	65.60

TABLE NO : 21

SORPTION KINETICS OF MERCURY ON ACTIVATED CARBON

Adsorbent : 500 mg. Activated Carbon
 Solution : 1000 ml Mercuric Chloride
 Initial Concentration : 5 mg/l / 10 mg/l / 50 mg/l as Hg.
 pH : 6.0
 Temperature : 29°C

Time in minutes	Final concentration of Mercury			Percentage removal of Mercury		
	Initial conc. 5 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l	Initial conc. 5 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l
0	5.00	10.00	50.00	0.00	0.00	0.00
2	4.50	9.20	46.50	10.00	8.00	7.00
5	4.10	8.30	43.00	18.00	17.00	14.00
10	3.40	6.96	36.40	32.00	30.40	27.20
15	2.95	6.10	32.50	41.00	39.00	35.00
20	2.72	5.80	30.00	45.60	42.00	40.00
25	2.40	5.10	27.60	52.00	49.00	44.80
30	2.10	4.60	26.50	58.00	54.00	47.00
40	1.80	4.00	25.00	64.00	60.00	50.00
50	1.70	3.75	24.00	66.00	62.50	52.00
60	1.70	3.75	24.00	66.00	62.50	52.00

TABLE NO : 22

EQUILIBRIUM CHARACTERISTICS OF MERCURY ON ACTIVATED CARBON

Adsorbent : 500 mg of activated carbon
 Solution : 1000 ml of Mercuric Chloride
 Temperature : 29°C
 pH : 6.0

Initial conc. of Hg. mg/l	Final conc. of Hg. mg/l Y*	Milligram of mercury adsorbed/gm of activated carbon. X	ln Y*	ln X	Percentage Removal
1	0.31	1.38	- 1.17	0.32	69.00
2	0.64	2.72	- 0.45	1.00	68.00
5	1.70	6.60	0.53	1.89	66.00
10	3.75	12.50	1.32	2.53	62.50
20	8.00	24.00	2.08	3.18	60.00
30	12.36	35.28	2.51	3.56	58.80
40	17.85	44.30	2.88	3.79	55.38
50	24.00	52.00	3.18	3.95	52.00

TABLE NO : 23

SORPTION KINETICS OF MERCURY ON DOWEX - 50

Adsorbent : 200 mg. Dowex -50
 Solution : 1000 ml of Mercuric Chloride
 Initial Concentration : 5 mg/l / 10 mg/l / 50 mg/l as Hg.
 pH : 6.0
 Temperature : 29⁰C

Time in minutes	Final concentration of Mercury mg/l			Percentage removal of Mercury		
	Initial conc. 5 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l	Initial conc. 5 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l
0	5.00	10.00	50.00	0.00	0.00	0.00
2	4.56	9.60	48.20	8.80	4.00	3.60
5	4.30	8.96	45.85	14.00	10.40	8.30
10	3.76	8.25	42.40	24.80	17.50	15.20
15	3.40	7.36	39.36	32.00	26.40	21.28
20	3.15	6.82	36.80	37.00	31.80	26.40
25	2.83	6.45	34.30	43.40	35.50	31.40
30	2.68	6.18	32.45	46.40	38.20	35.10
40	2.62	5.53	30.56	47.60	44.70	38.88
50	2.56	5.40	30.00	48.80	46.00	40.00
60	2.56	5.40	30.00	48.80	46.00	40.00

TABLE NO : 24

EQUILIBRIUM CHARACTERISTICS OF MERCURY ON DOWEX - 50

Adsorbent : 200 mg of Dowex - 50
 Solution : 1000 ml of Mercuric Chloride
 Temperature : 29°C
 pH : 6.0
 Contact Time : 1 hr

Initial conc. of Hg. mg/l	Final conc. of Hg. mg/l Y*	Milligram of mercury adsorbed/gm of Dowex-50, X	ln Y*	ln X	Percentage Removal
1	0.45	1.818	- 0.7985	0.5978	55.00
2	0.96	5.20	-0.0408	1.6486	52.00
5	2.56	12.20	0.9400	2.5014	48.80
10	5.40	23.00	1.6863	3.13549	46.00
20	11.05	44.75	2.4024	3.80109	44.75
30	17.20	64.00	2.8449	4.1588	42.66
40	23.42	82.90	3.1535	4.4176	41.45
50	30.00	100.00	3.4011	4.6051	40.00

TABLE NO : 25

SORPTION KINETICS OF MERCURY ON RICE HUSK CARBON

Adsorbent : 500 mg. Rice Husk Carbon
 Solution : 1000 ml Mercuric Chloride
 Initial Concentration : 5 mg/l / 10 mg/l / 50 mg/l as Hg.
 pH : 6.0
 Temperature : 29⁰C

Time in minutes	Final concentration of Mercury, mg/l			Percentage removal of Mercury		
	Initial conc. 5 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l	Initial conc. 5 mg/l	Initial conc. 10 mg/l	Initial conc. 50 mg/l
0	5.00	10.00	50.00	0.00	0.00	0.00
2	4.72	9.73	48.70	5.60	2.70	2.60
5	4.53	9.50	48.00	9.40	5.00	4.00
10	4.16	9.00	45.56	16.80	10.00	8.90
15	3.93	8.55	43.60	21.40	14.50	12.80
20	3.70	8.00	42.90	26.00	20.00	15.20
25	3.56	7.63	41.16	28.80	23.70	17.68
30	3.40	7.25	39.52	32.00	27.50	20.96
40	3.22	6.70	37.00	35.60	33.00	26.00
50	3.06	6.40	35.30	38.80	36.00	29.40
60	3.00	6.28	34.60	40.00	37.20	30.80

TABLE NO : 26

EQUILIBRIUM CHARACTERISTICS OF MERCURY ON RICE HUSK CARBON

Adsorbent : 500 mg of Rice Husk Carbon
 Solution : 1000 ml of Mercuric Chloride
 Temperature : 29⁰C
 pH : 6.0
 Contact Time : 1 hr

Initial conc. of Hg. mg/l	Final conc. of Hg. mg/l Y*	Milligram of mercury adsorbed/gm of Rice husk carbon, X	ln Y*	ln X	Percentage Removal
1	0.53	0.94	-0.6348	-0.0618	47.00
2	1.14	1.72	0.1310	0.5423	43.00
5	3.00	4.00	1.0986	1.3862	40.00
10	6.28	7.44	1.8373	2.0068	37.20
20	12.80	14.40	2.5494	2.6672	36.00
30	19.46	21.08	2.9683	3.0483	35.13
40	26.65	26.70	3.2827	3.2846	33.37
50	34.60	30.80	3.5438	3.4275	30.80

TABLE NO : 27

CAPACITY OF CHITOSAN ON ADSORPTION OF METAL IONS

Adsorbent : 200 mg 0.3mm size Chitosan
 Initial Concentration of solution : 5 mg/l as Hg/Cd/Pb/ Cr

Time in minutes	Final concentration of metal ions, mg/l				Milligram of metal ions adsorbed/gm of adsorbent			
	Mercury	Cadmium	Lead	Chromium	Mercury	Cadmium	Lead	Chromium
0	5.00	5.00	5.00	5.00	0.00	0.00	0.00	0.00
5	1.90	2.80	3.34	8.46	15.50	11.00	8.30	7.70
10	1.10	1.86	2.26	2.90	19.50	15.70	13.70	10.50
15	0.55	1.42	1.76	2.43	22.25	17.90	16.30	12.85
20	0.27	1.08	1.43	2.10	23.65	19.60	17.85	14.50
25	0.12	1.00	1.36	1.80	24.40	20.00	18.20	16.00
30	0.08	0.82	1.20	1.64	24.60	20.90	19.00	16.80
40	0.08	0.70	1.00	1.33	24.60	21.50	20.00	18.35
50	0.08	0.65	0.88	1.20	24.60	21.75	20.60	19.00
60	0.08	0.65	0.88	1.20	24.60	21.75	20.60	19.00

TABLE NO : 28

MERCURY SORPTION ON DIFFERENT ADSORBENTS

Adsorbent : Chitosan/Activated Carbon/Dowex-50/Rice Husk Carbon
 Solution : 1000 ml Mercuric Chloride
 Initial Concentration of Mercury : 5 mg/l as Hg
 pH : 6.0

Time in minutes	Final concentration of Mercury Hg, mg/l				Milligram of Mercury adsorbed/gm of adsorbent			
	Chitosan 200 mg	Activated carbon 500 mg	Dowex-50 200 mg	Rice Husk Carbon 500 mg	Chitosan	Activated Carbon	Dowex-50	Rice Husk Carbon
0	5.00	5.00	5.00	5.00	0.00	0.00	0.00	0.00
5	1.90	4.10	4.30	4.53	15.50	1.80	3.50	0.94
10	1.10	3.40	3.76	4.16	19.50	3.20	6.20	1.68
15	0.55	2.95	3.40	3.93	22.25	4.10	8.00	2.14
20	0.27	2.72	3.15	3.70	23.65	4.56	9.25	2.60
25	0.12	2.40	2.83	3.56	24.40	5.20	10.75	2.88
30	0.08	2.10	2.68	3.40	24.60	5.80	11.60	3.20
40	0.08	1.80	2.62	3.22	24.60	6.40	11.90	3.56
50	0.08	1.70	2.56	3.06	24.60	6.60	12.20	3.88
60	0.08	1.70	2.56	3.00	24.60	6.60	12.20	4.00

TABLE NO : 29

EFFECT OF COAGULANT/FLOCCULANT DOSAGE
ON PRECIPITATION OF MERCURY

Initial Concentration of solution : 50 mg/l as Mercury
 pH : 9.0
 Stirring Time : 15 min.
 Sodium Sulphide : 40 mg/l
 Temperature : 29°C

Coagulant (FeCl ₃)			Polyelectrolyte (Chitosan)		
Dosage mg/l	Final conc. mg/l	% Removal	Dosage mg/l	Final conc. mg/l	% Removal
0	0.96	98.00	0.00	0.96	98.00
25	0.68	98.64	0.50	0.66	98.68
50	0.55	98.90	1.00	0.30	99.40
75	0.45	99.10	1.50	0.23	99.50
100	0.40	99.20	2.00	0.22	99.56
150	0.40	99.20	2.50	0.22	99.56

TABLE NO : 30

EFFECT OF pH ON PRECIPITATION OF MERCURY

Initial concentration : 50 mg/l as Mercury
 Stirring Time : 15 min.
 Temperature : 29^oC
 Sodium Sulphide : 40 mg/l
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (FeCl₃) : 100 mg/l

Initial pH	Final concentration, mg/l				Percentage Removal			
	Without coagulant & Polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan	Without coagulant & Polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
7.5	2.62	1.25	1.10	0.86	94.76	97.50	97.80	98.28
8.0	1.23	0.66	0.46	0.23	97.54	98.68	99.08	99.54
8.5	1.06	0.45	0.23	0.20	97.88	99.10	99.54	99.60
9.0	0.96	0.40	0.22	0.185	98.08	99.20	99.56	99.63
9.5	0.96	0.40	0.22	0.185	98.08	99.20	99.56	99.63
10.0	0.96	0.40	0.22	0.185	98.08	99.20	99.56	99.63

TABLE NO : 31

EFFECT OF pH ON PRECIPITATION OF MERCURY

Initial concentration : 10 mg/l as Mercury
 Stirring Time : 15 mts.
 Temperature : 29°C
 Sodium Sulphide : 8 mg/l
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (FeCl₃) : 100 mg/l

Initial pH	Final concentration, mg/l				Percentage Removal			
	Without coagulant & Polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan	Without coagulant & Polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
7.5	1.26	0.96	0.75	0.63	87.40	90.40	92.50	93.70
8.0	0.66	0.43	0.22	0.12	93.40	95.70	97.80	98.80
8.5	0.45	0.30	0.14	0.086	95.50	97.00	98.60	99.14
9.0	0.38	0.28	0.12	0.083	96.20	97.20	98.80	99.17
9.5	0.38	0.28	0.12	0.083	96.20	97.20	98.80	99.17
10.0	0.38	0.28	0.12	0.083	96.20	97.20	98.80	99.17

TABLE NO : 32

EFFECT OF CONCENTRATION ON PRECIPITATION OF MERCURY

pH : 9.0
 Stirring Time : 15 min
 Temperature : 29°C
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (FeCl₃) : 100 mg/l
 Sodium Sulphide : 100% Excess of Stoichiometric Requirement

Initial Conc. mg/l as Hg	Final concentration , mg/l as Hg				Percentage Removal			
	Without coagulant & Polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan	Without coagulant & Polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
5.0	0.29	0.20	0.080	0.05	94.80	95.60	98.28	99.00
10.0	0.38	0.28	0.12	0.083	96.20	97.20	98.80	99.17
20.0	0.56	0.38	0.16	0.12	97.20	98.10	99.10	99.40
50.0	0.96	0.40	0.22	0.185	98.08	99.20	99.56	99.63
100.0	1.28	0.53	0.33	0.22	98.72	99.47	99.64	99.78

TABLE NO : 33

SETTLABILITY OF PRECIPITATED SLUDGE

PRECIPITATION OF MERCURY

Initial concentration of Mercuric Chloride Solution : 50 mg/l
 pH : 9.0
 Sodium Sulphide : 40 mg/l
 Coagulant (Ferric Chloride) : 100 mg/l
 Polyelectrolyte (chitosan) : 2 mg/l

Time in minutes	Height of Sludge Line , cm			
	Without coagulant & polyelectrolyte	with FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
0	16.00	16.00	16.00	16.00
0.50	14.80	14.50	14.10	13.00
1.00	13.70	12.80	11.10	9.20
1.50	12.70	11.20	8.60	6.00
2.00	11.80	10.20	6.30	3.70
2.50	10.90	8.40	4.70	3.00
3.00	10.00	6.40	3.50	2.60
3.50	9.30	5.50	3.10	2.50
4.00	8.60	4.60	2.90	2.30
5.00	6.70	3.40	2.60	2.10
6.00	5.80	2.70	2.30	1.90
8.00	3.80	2.30	1.90	1.60
10.00	3.00	1.90	1.60	1.30
12.00	2.60	1.60	1.30	1.00
14.00	2.30	1.40	1.10	0.80
16.00	2.20	1.30	1.00	0.60
20.00	2.10	1.20	0.90	0.50

TABLE NO : 34

EFFECT OF COAGULANT /FLOCCULANT DOSAGE ON
PRECIPITATION OF CADMIUM

Initial concentration : 50 mg/l as Cadmium
 pH : 11
 Stirring Time : 15 min.
 Temperature : 29⁰C

Coagulant (Ferric Chloride)			Polyelectrolyte (Chitosan)		
Dosage mg/l	Final conc. mg/l	% Removal	Dosage mg/l	Final conc. mg/l	% Removal
0	0.003	99.994	0	0.003	99.994
50	0.0025	99.995	0.50	0.002	99.996
100	0.002	99.996	1.00	0.0015	99.997
150	0.002	99.996	2.00	0.001	99.998
200	0.002	99.996	2.50	0.001	99.998

TABLE NO : 35

EFFECT OF pH ON PRECIPITATION OF CADMIUM

Initial concentration : 50 mg/l as Cadmium
 Stirring Time : 15 min
 Temperature : 29°C
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (Ferric Chloride) : 100 mg/l

Initial pH	Final concentration as Cd, mg/l				Percentage Removal			
	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
8.5	33.00	26.80	23.20	22.40	34.00	46.40	53.40	55.20
9.0	16.00	9.76	8.160	7.12	68.00	80.40	83.68	85.76
9.5	4.80	2.50	2.00	1.60	90.40	95.00	96.00	96.80
10.0	0.025	0.02	0.01	0.005	99.95	99.96	99.98	99.99
10.5	0.01	0.006	0.003	0.001	99.98	99.988	99.994	99.998
11.0	0.003	0.002	0.001	0.00	99.994	99.996	99.998	100.00
12.0	0.003	0.002	0.001	0.00	99.994	99.996	99.998	100.00

TABLE NO : 36

EFFECT OF pH ON PRECIPITATION OF CADMIUM

Initial concentration : 10 mg/l as Cadmium
 Stirring Time : 15 min.
 Temperature : 29°C
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (Ferric Chloride) : 100 mg/l

Initial pH	Final concentration mg/l				Percentage Removal			
	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
8.5	6.75	5.46	4.80	4.62	32.50	45.40	52.00	53.80
9.0	3.60	2.05	1.66	1.44	64.00	79.50	83.40	85.60
9.5	1.58	0.63	0.46	0.33	84.20	93.70	95.40	96.70
10.0	0.015	0.01	0.006	0.003	99.83	99.90	99.94	99.97
10.5	0.008	0.004	0.002	0.001	99.92	99.96	99.98	99.999
11.0	0.0025	0.002	0.001	0.00	99.975	99.98	99.999	100.00
12.0	0.0025	0.002	0.001	0.00	99.975	99.98	99.999	100.00

TABLE NO : 37

EFFECT OF CONCENTRATION ON PRECIPITATION OF CADMIUM

pH : 11.00
 Stirring Time : 15 min.
 Temperature : 29°C
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (Ferric Chloride) : 100 mg/l

Initial conc . mg/l	Final concentration mg/l				Percentage Removal			
	Without coagulant & polyelectrolyte	With FeCl3	With Chitosan	With FeCl3 & Chitosan	Without coagulant & polyelectrolyte	With FeCl3	With Chitosan	With FeCl3 & Chitosan
5	0.0025	0.002	0.001	0.00	99.95	99.96	99.98	100
10	0.0025	0.002	0.001	0.00	99.975	99.98	99.99	100
20	0.0025	0.002	0.001	0.00	99.988	99.99	99.995	100
50	0.003	0.002	0.001	0.00	99.994	99.996	99.998	100
100	0.003	0.0025	0.001	0.00	99.997	99.998	99.999	100

TABLE NO : 38

SETTLABILITY OF PRECIPITATED SLUDGE

PRECIPITATION OF CADMIUM

Initial concentration of Cadmium Sulphate Solution : 50 mg/l
 pH : 11.0
 Coagulant (Ferric Chloride) : 100 mg/l
 Polyelectrolyte (Chitosan) : 2 mg/l

Effect of Chitosan	Height of Sludge Line , cm				
	Time in minutes	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
	0	16.00	16.00	16.00	16.00
	0.50	15.50	15.40	13.60	13.40
	1.00	14.00	12.70	9.60	6.50
	1.50	12.00	10.00	6.00	4.80
	2.00	10.10	5.90	3.30	2.50
	2.50	8.00	4.20	3.00	2.30
	3.00	6.90	3.70	2.80	2.10
	3.50	4.90	3.50	2.60	2.00
	4.00	4.30	3.30	2.50	1.90
	5.00	3.50	2.90	2.30	1.80
	6.00	2.90	2.60	2.10	1.70
	8.00	2.30	2.00	1.70	1.30
	10.00	2.00	1.60	1.30	0.90
	12.00	1.90	1.40	1.10	0.70
	16.00	1.80	1.10	0.80	0.50
	20.00	1.70	1.00	0.70	0.40

TABLE NO : 39

EFFECT OF COAGULANT / FLOCCULANT DOSAGE ON
PRECIPITATION OF LEAD

Initial Concentration : 50 mg/l as Lead
 pH : 9.5
 Stirring Time : 15 min.
 Temperature : 29°C

Coagulant (Ferric Chloride)			Polyelectrolyte (Chitosan)		
Dosage mg/l	Final conc. mg/l	% Removal	Dosage mg/l	Final conc. mg/l	% Removal
0	2.15	95.70	0	2.15	95.70
25	2.90	96.00	0.50	1.90	96.20
50	1.90	96.20	1.00	1.75	96.50
100	1.83	96.34	1.50	1.50	97.00
150	1.80	96.40	2.00	1.10	97.80
200	1.80	96.40	2.50	1.10	97.90

TABLE NO : 40

EFFECT OF pH ON PRECIPITATION OF LEAD

Initial concentration : 50 mg/l as Lead
 Stirring Time : 15 min.
 Temperature : 29°C
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (Ferric Chloride) : 150 mg/l

Initial pH	Final concentration, Pb mg/l				Percentage Removal			
	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
7.50	30.00	28.50	27.56	27.20	40.00	43.00	44.88	45.60
8.00	18.00	16.80	15.30	15.00	64.00	66.40	69.40	70.00
8.50	8.40	6.90	5.80	5.46	83.20	86.20	88.40	89.00
9.00	3.90	2.80	2.00	1.72	92.20	94.40	96.00	96.56
9.50	2.15	1.80	1.10	0.85	95.70	96.40	97.80	98.30
10.00	2.15	1.80	1.10	0.85	95.70	96.40	97.80	98.30
10.50	2.15	1.80	1.10	0.85	95.70	96.40	97.80	98.30
11.00	2.15	1.80	1.10	0.85	95.70	96.40	97.80	98.30

TABLE NO : 41

EFFECT OF pH ON PRECIPITATION OF LEAD

Initial concentration : 10 mg/l as Lead
 Stirring Time : 15 min.
 Temperature : 29⁰C
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (Ferric Chloride) : 150 mg/l

Initial pH	Final concentration, Pb mg/l				Percentage Removal			
	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
7.5	6.65	6.20	5.50	4.86	33.50	38.00	45.00	51.40
8.0	3.86	3.30	2.70	2.56	61.40	67.00	73.00	74.40
8.5	1.88	1.64	1.40	1.10	81.20	83.60	86.00	89.00
9.0	0.93	0.76	0.50	0.40	90.70	92.40	95.00	96.00
9.5	0.75	0.58	0.40	0.33	92.50	94.20	96.00	96.70
10.0	0.75	0.58	0.40	0.33	97.50	94.20	96.00	96.70
10.5	0.75	0.58	0.40	0.33	97.50	94.20	96.00	96.70
11.0	0.75	0.58	0.40	0.33	97.50	94.20	96.00	96.70

TABLE NO : 42

EFFECT OF CONCENTRATION OF LEAD

pH : 9.5
 Stirring Time : 15 min.
 Temperature : 29^oC
 Polyelectrolyte (Chitosan) : 2 mg/l
 Coagulant (FeCl₃) : 150 mg/l

Initial conc. of Pb mg/l	Final concentration, Pb mg/l				Percentage Removal			
	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan	Without coagulant & polyelectrolyte	With FeCl ₃	With Chitosan	With FeCl ₃ & Chitosan
5.00	0.43	0.35	0.23	0.18	91.40	93.00	95.40	96.40
10.00	0.75	0.58	0.40	0.33	92.50	94.20	96.00	96.70
20.00	1.20	0.90	0.70	0.56	94.00	95.50	96.50	97.20
50.00	2.15	1.80	1.10	0.85	95.70	96.40	97.80	98.30
100.00	2.80	2.20	1.80	1.42	97.20	97.80	98.20	98.58

TABLE NO : 43

SETTLABILITY OF PRECIPITATED SLUDGE
PRECIPITATION OF LEAD

Initial concentration of Lead Nitrate Solution : 50 mg/l as Pb
 pH : 9.5
 Coagulant (Ferric Chloride) : 150 mg/l
 Polyelectrolyte (Chitosan) : 2 mg/l

Time in minutes	Height of Sludge Line , cm			
	Without coagulant & polyelectrolyte	With coagulant	With polyelectrolyte	with coagulant and polyelectrolyte
0	16.00	16.00	16.00	16.00
0.50	15.10	14.80	14.00	13.00
1.00	13.70	13.00	11.00	9.00
1.50	12.10	9.90	6.50	4.10
2.00	10.00	6.40	4.20	3.10
2.50	8.50	5.00	3.40	2.50
3.00	7.00	4.20	3.10	2.30
4.00	5.60	3.40	2.50	2.10
5.00	4.90	2.90	2.30	1.90
6.00	4.30	2.70	2.20	1.80
8.00	3.60	2.40	1.90	1.50
10.00	3.10	2.10	1.60	1.20
12.00	2.70	1.90	1.40	1.00
16.00	2.40	1.60	1.10	0.70
20.00	2.20	1.40	0.90	0.50

TABLE NO : 44

EFFECT OF REACTION TIME ON REDUCTION
OF HEXAVALENT CHROMIUM

Reduction pH : 2.5
Precipitation pH : 8.5

Time in minutes	Initial conc. : 50 mg/l Ferrous Sulphate : 1000 mg/l		Initial conc. : 10mg/l Ferrous Sulphate : 200mg/l	
	Final conc. mg/l as Cr.	Percentage Removal	Final conc. mg/l as Cr	Percentage Removal
0	50.00	0	10.00	0
5	2.65	94.70	1.26	87.40
10	1.56	96.88	0.80	92.00
15	1.25	97.50	0.48	95.20
20	1.15	97.70	0.33	96.70
25	1.15	97.70	0.33	96.70
30	1.15	97.70	0.33	96.70

TABLE NO : 45

EFFECT OF pH ON REDUCTION OF HEXAVALENT CHROMIUM

Reaction time : 20 minutes
 Precipitation pH : 8.5

Initial pH	Initial conc. : 50 mg/l Ferrous Sulphate : 1000 mg/l	Initial conc. : 10 mg/l Ferrous Sulphate : 200 mg/l	Final conc. of Cr, mg/l	Percentage Conversion	Final conc. of Cr, mg/l	Percentage Conversion
4.0			3.10	93.80	1.40	86.00
3.5			2.29	95.60	0.96	90.40
3.0			1.30	97.40	0.62	93.80
2.5			1.15	97.70	0.33	96.70
2.0			1.15	97.70	0.33	96.70
1.5			1.15	97.70	0.33	96.70

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TABLE NO : 46

EFFECT OF DOSAGE OF FERROUS SULPHATE ON
REDUCTION OF HEXAVALENT CHROMIUM

pH of Reduction reaction : 2.50
Reduction Reaction time : 20 minutes
Precipitation pH : 8.5

Initial conc. : 50 mg/l			Initial conc : 10 mg/l		
Dosage of FeSO ₄ .7 H ₂ O mg/l	Final conc.of Cr. mg/l	% Removal	Dosage of FeSO ₄ .7 H ₂ O mg/l	Final conc.of Cr. mg/l	% Removal
500	13.40	73.20	100	2.46	75.40
600	10.65	78.70	125	1.90	81.00
800	4.20	96.40	150	1.10	89.00
900	1.80	96.40	175	0.50	95.00
1000	1.15	97.70	200	0.33	96.70
1100	1.15	97.70	225	0.33	96.70
1200	1.15	97.70	250	0.33	96.70

TABLE NO : 47

EFFECT OF pH ON PRECIPITATION OF CHROMIUM

Initial Concentration : 50 mg/l
 Reduction Reaction pH : 2.5
 Reduction Reaction Time : 20 min.
 Ferrous Sulphate : 1000 mg/l
 Polyelectrolyte (Chitosan) : 2 mg/l
 Temperature : 29°C

Initial pH	Final concentration, mg/l		Percentage Removal	
	Without Chitosan	With Chitosan	Without Chitosan	With Chitosan
7.5	2.10	1.80	95.80	96.40
8.0	1.26	0.75	97.48	98.50
8.5	1.15	0.50	97.70	99.00
9.0	1.15	0.50	97.70	99.00
9.5	1.30	0.63	97.40	98.74
10.0	1.40	1.10	97.20	97.80
10.5	2.90	2.40	94.20	95.20
11.0	6.20	5.60	87.60	88.80

TABLE NO : 48

EFFECT OF pH ON PRECIPITATION OF CHROMIUM

Initial Concentration : 10 mg/l
 Reduction Reaction pH : 2.5
 Reduction Reaction Time : 20 min.
 Ferrous Sulphate : 200 mg/l
 Polyelectrolyte (Chitosan) : 2 mg/l
 Temperature : 29°C

Initial pH	Final concentration, mg/l		Percentage Removal	
	Without Chitosan	With Chitosan	Without Chitosan	With Chitosan
7.5	0.56	0.38	94.40	96.20
8.0	0.40	0.24	96.00	97.60
8.5	0.33	0.20	96.70	98.00
9.0	0.33	0.20	96.70	98.00
9.5	0.40	0.26	96.00	97.40
10.0	0.55	0.35	94.50	96.50
10.5	0.86	0.72	91.40	92.80
11.0	1.40	1.25	86.00	87.50

TABLE NO : 49

EFFECT OF CONCENTRATION ON PRECIPITATION
OF CHROMIUM

Reduction pH : 2.5
Reduction Reaction Time : 20 min.
Precipitation pH : 8.5

Initial conc. mg/l	Final concentration, mg/l		Percentage	
	Without Chitosan	With Chitosan	Without Chitosan	With Chitosan
5	0.20	0.15	96.00	97.00
10	0.33	0.20	96.70	98.00
20	0.58	0.33	97.10	98.35
50	1.15	0.50	97.70	99.00
100	1.30	0.80	98.70	99.20

TABLE NO : 50

SETTLABILITY OF PRECIPITATED SLUDGE

PRECIPITATION OF CHROMIUM

Initial concentration of Potassium Chromate Solution : 50 mg/l
 pH : 8.5
 Polyelectrolyte (chitosan) : 2 mg/l

Time in minutes	Height of Sludge Line. cm	
	without polyelectrolyte	With polyelectrolyte
0.00	16.00	16.00
0.50	14.30	14.00
1.00	13.00	11.00
1.50	10.70	8.00
2.00	9.10	5.40
2.50	7.90	4.00
3.00	6.80	3.60
3.50	5.90	3.20
4.00	5.10	2.90
5.00	4.20	2.50
6.00	3.90	2.30
8.00	2.90	2.00
10.00	2.40	1.80
12.00	2.10	1.60
14.00	1.90	1.40
16.00	1.70	1.20
20.00	1.50	1.00

TABLE NO : 51

TREATABILITY STUDY OF PAPER MILL EFFLUENT

Sample : Combined effluent from Pulp & Paper Mill
(Hindustan News Print Ltd., Velloor, Kottayam)
Reagent : 600 mg/l Ferric Alum.

Parameters	Characteristics of Combined Effluent		
	Raw Effluent	Treated Effluent without Chitosan.	Treated Effluent with Chitosan, 2 mg/l
pH	8.2	7.0	7.0
Colour Pt.Co Units	3500	120	80
BOD , mg/l	486	210	196
COD , mg/l	1450	475	450
Suspended Solids, mg/l	1200	85	40
Mercury, mg/l	0.002	0.0016	Nil

TABLE NO : 52

EFFECT OF CHITOSAN ON SETTLEABILITY OF PRECIPITATED
SLUDGE FROM PAPER MILL EFFLUENT

Time in minutes	Height of Sludge line, cm	
	Without Chitosan	With 2 mg/l Chitosan
0	16.00	16.00
1	14.60	13.20
2	12.70	5.40
3	9.00	3.40
4	5.80	2.80
5	4.50	2.50
6	3.90	2.40
8	3.30	2.10
10	3.00	2.00
15	2.70	1.90
20	2.50	1.80

TABLE NO : 53

TREATABILITY STUDY OF TANNERY EFFLUENT

Sample : Combined Effluent from Tannery
(Kinadi Tanneries Ltd, Development Area, Edayar, Aluva)

Parameters	Characteristics of Combined Effluent		
	Raw Effluent	Treated Effluent without Chitosan	Treated Effluent with Chitosan
pH	9.0	8.5	8.5
Suspended Solids mg/l	1680	94.0	33
BOD, mg/l	2850	1380	1340
COD, mg/l	4680	1610	1550
Cr ⁺³	56.80	1.56	0.63
Rate of Settling	----	Good	Very fast

TABLE NO : 54

EFFECT OF CHITOSAN ON SETTLEABILITY OF PRECIPITATED
SLUDGE FROM TANNERY EFFLUENT

Time in minutes	Height of Sludge line, cm	
	Without Chitosan	With 2 mg/l Chitosan
0	16.00	16.00
1	14.80	14.00
2	13.20	11.50
3	11.20	8.50
4	9.00	6.00
5	7.80	4.60
6	6.70	3.90
8	5.20	3.50
10	4.20	3.00
12	3.80	2.80
16	3.20	2.50
20	2.80	2.30

FIGURES

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FIG
1

SORPTION KINETICS OF Hg/Cd/Pb/Cr. ON CHITOSAN

Initial conc 0.5 mg/l

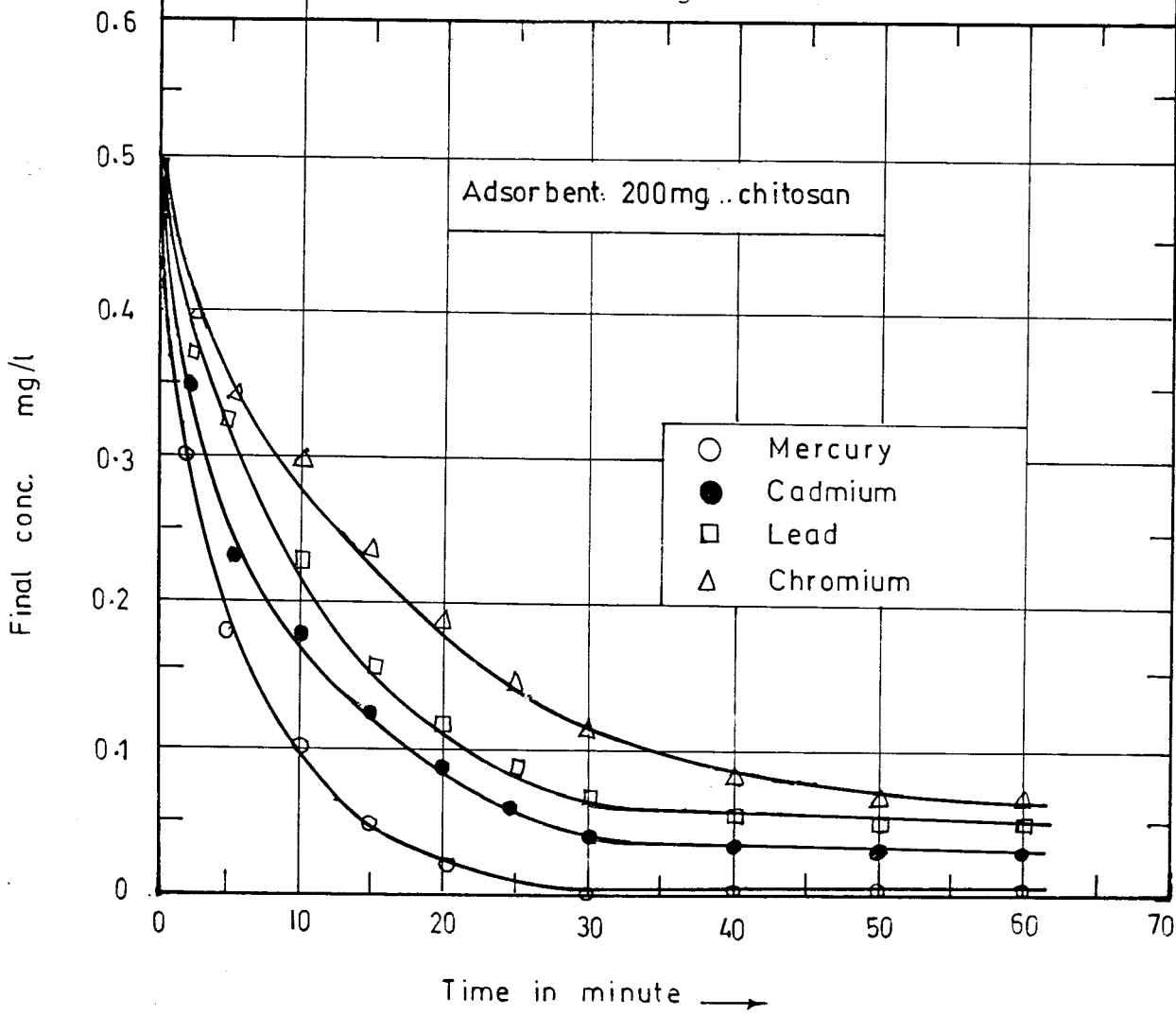


FIG 2

SORPTION KINETICS OF Hg/Cd/Pb/Cr. ON CHITOSAN
Initial conc. 5 mg/l

Adsorbent: 200mg chitosan

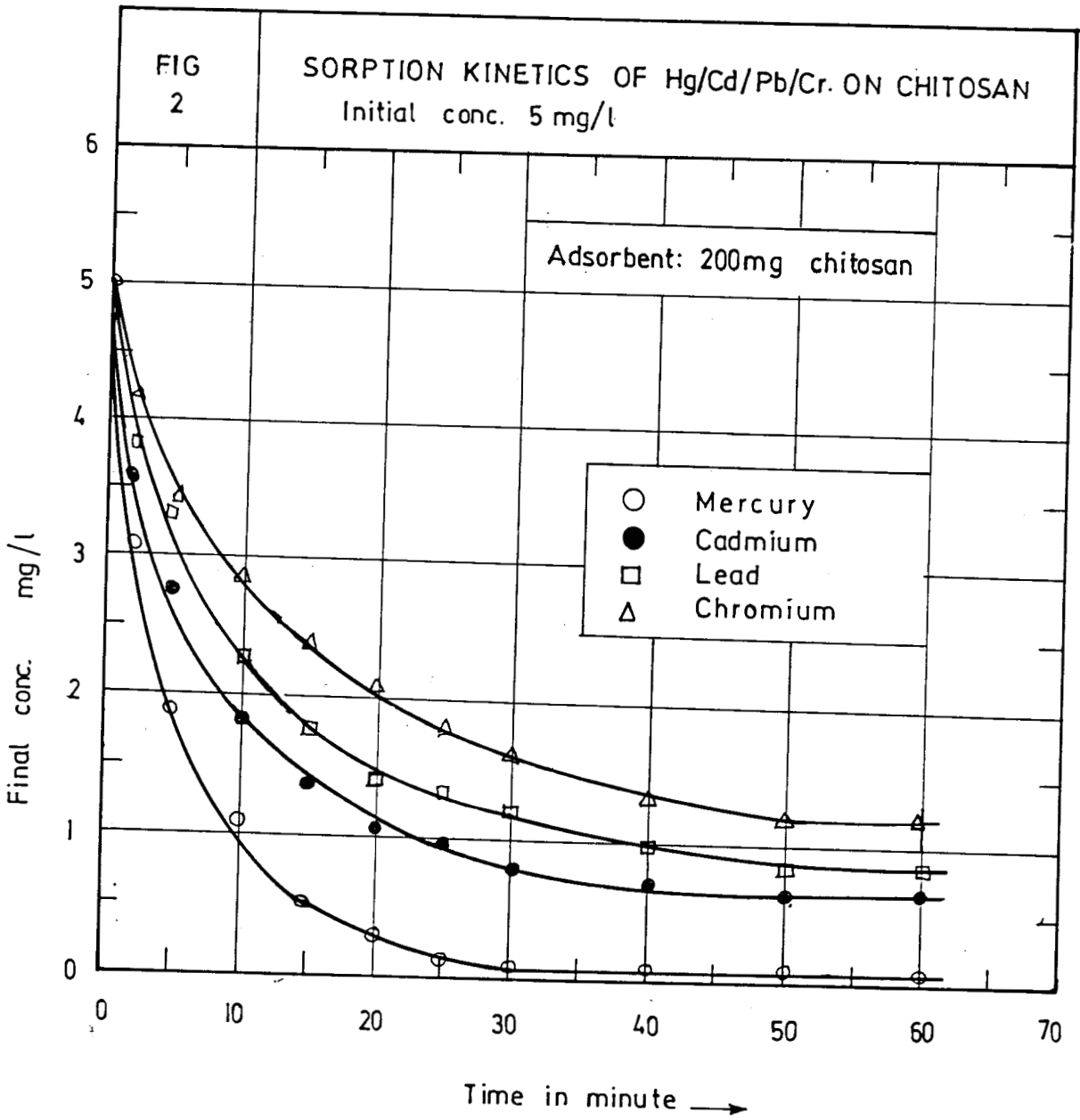


FIG 3

SORPTION KINETICS OF Hg/Cd/Pb/Cr. ON CHITOSAN
Initial conc. 10 mg/l

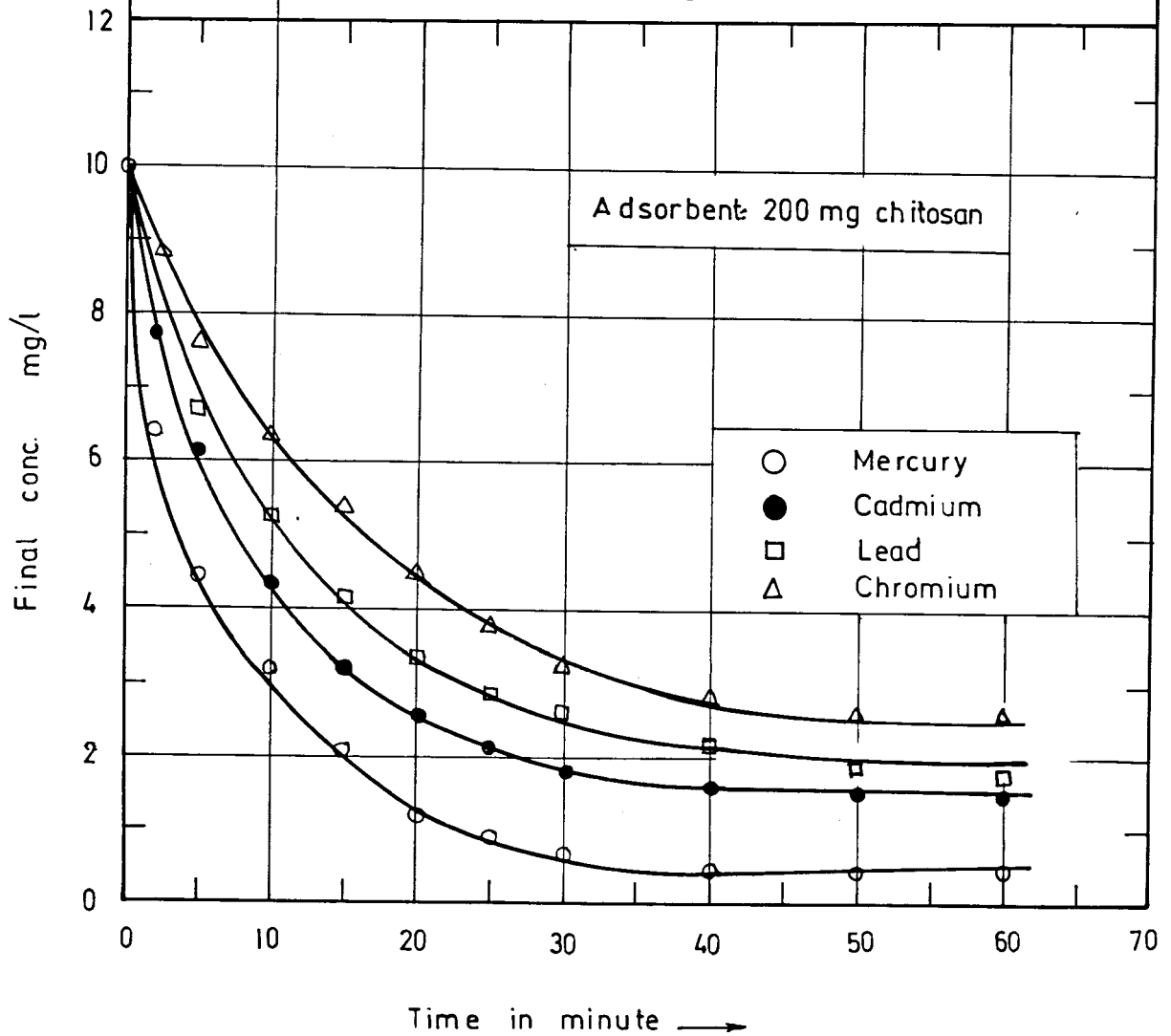


FIG
4

SORPTION KINETICS OF Hg/Cd/Pb/Cr. ON CHITOSAN

(Initial conc. 50mg/l)

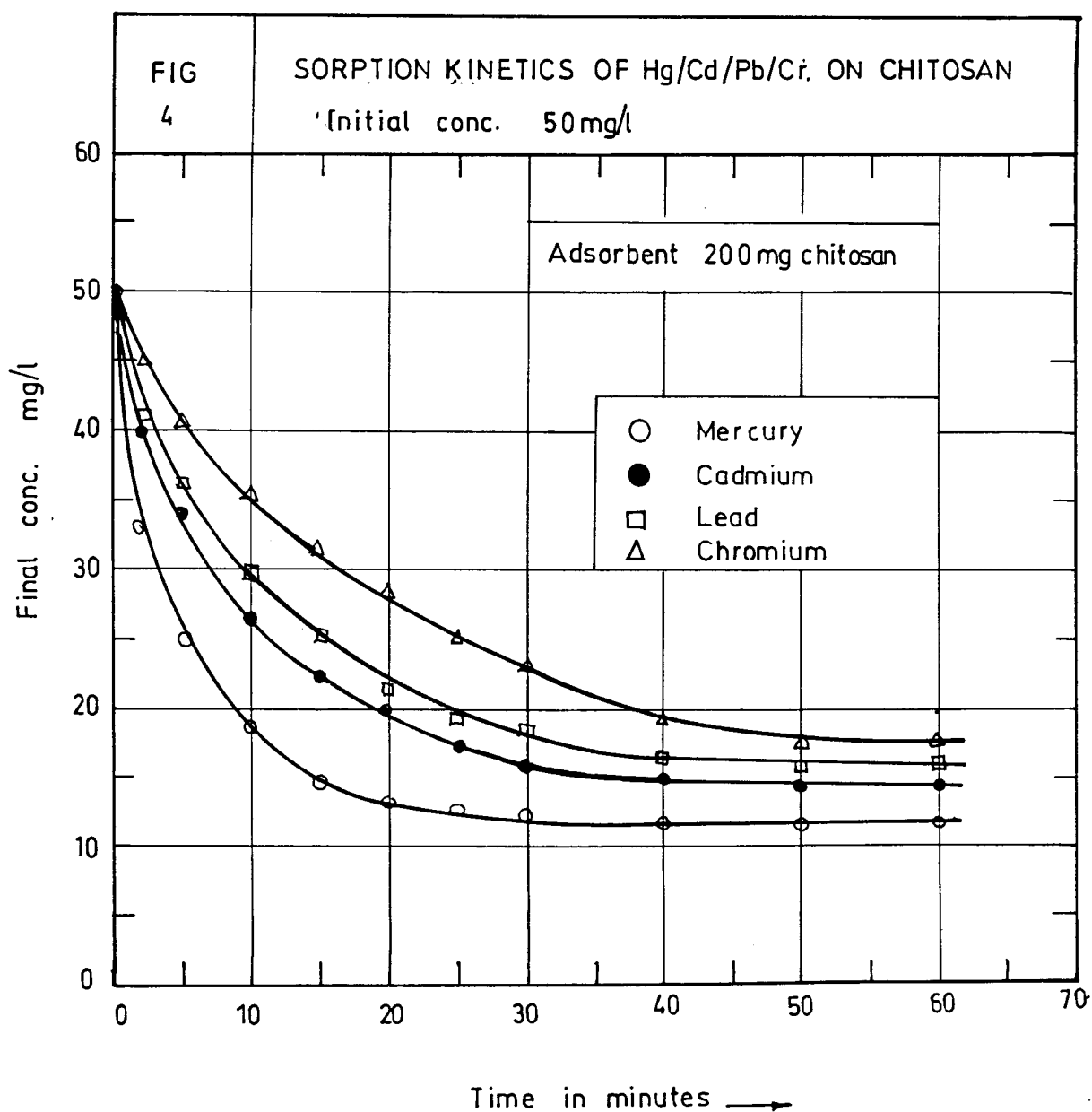


FIG
5

SORPTION KINETICS OF MERCURY ON CHITOSAN
EFFECT OF INITIAL CONC.

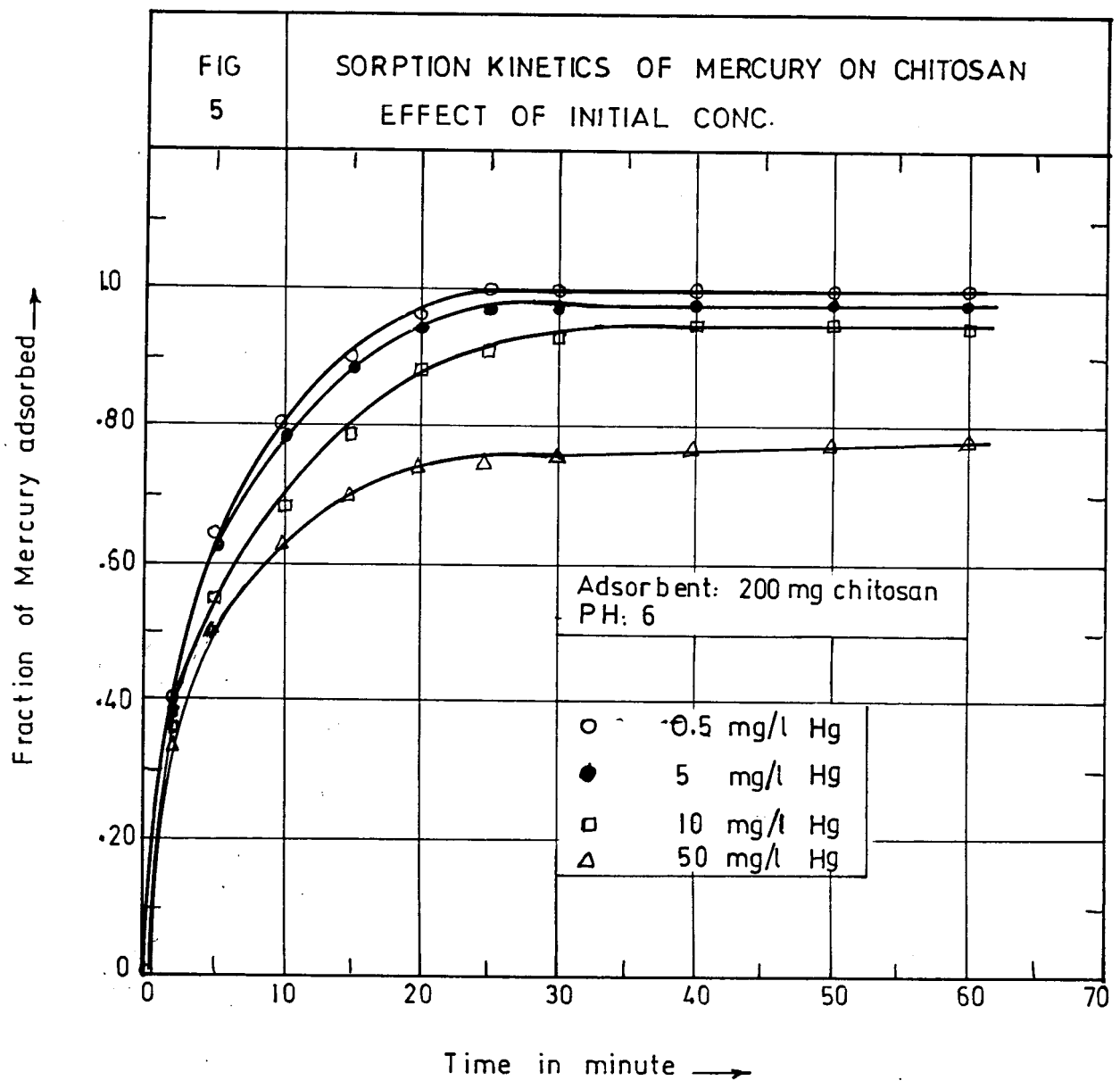


FIG
6

SORPTION KINETICS OF CADMIUM ON CHITOSAN
EFFECT OF INITIAL CONC.

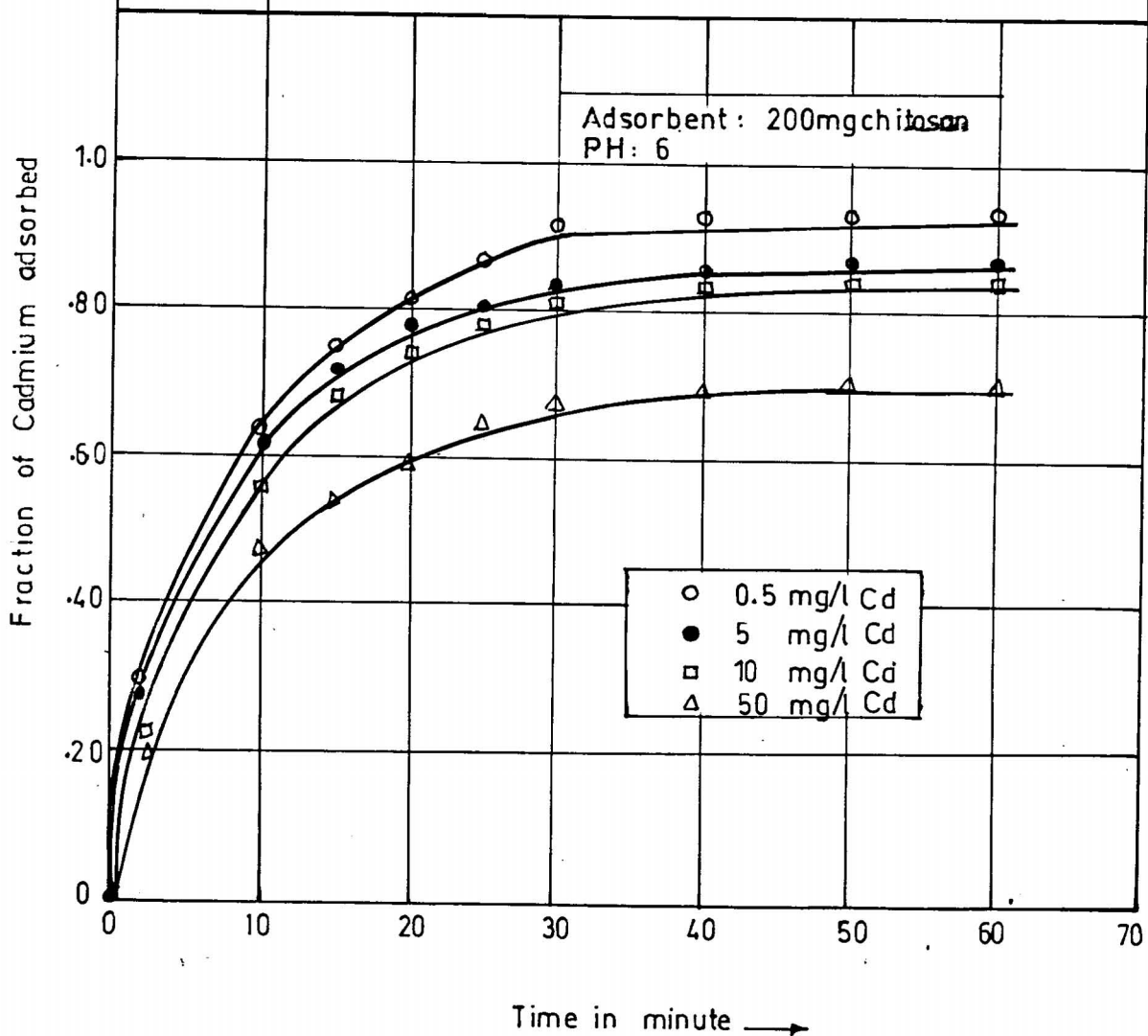


FIG
7

SORPTION KINETICS OF LEAD ON CHITOSAN
EFFECT OF INITIAL CONC.

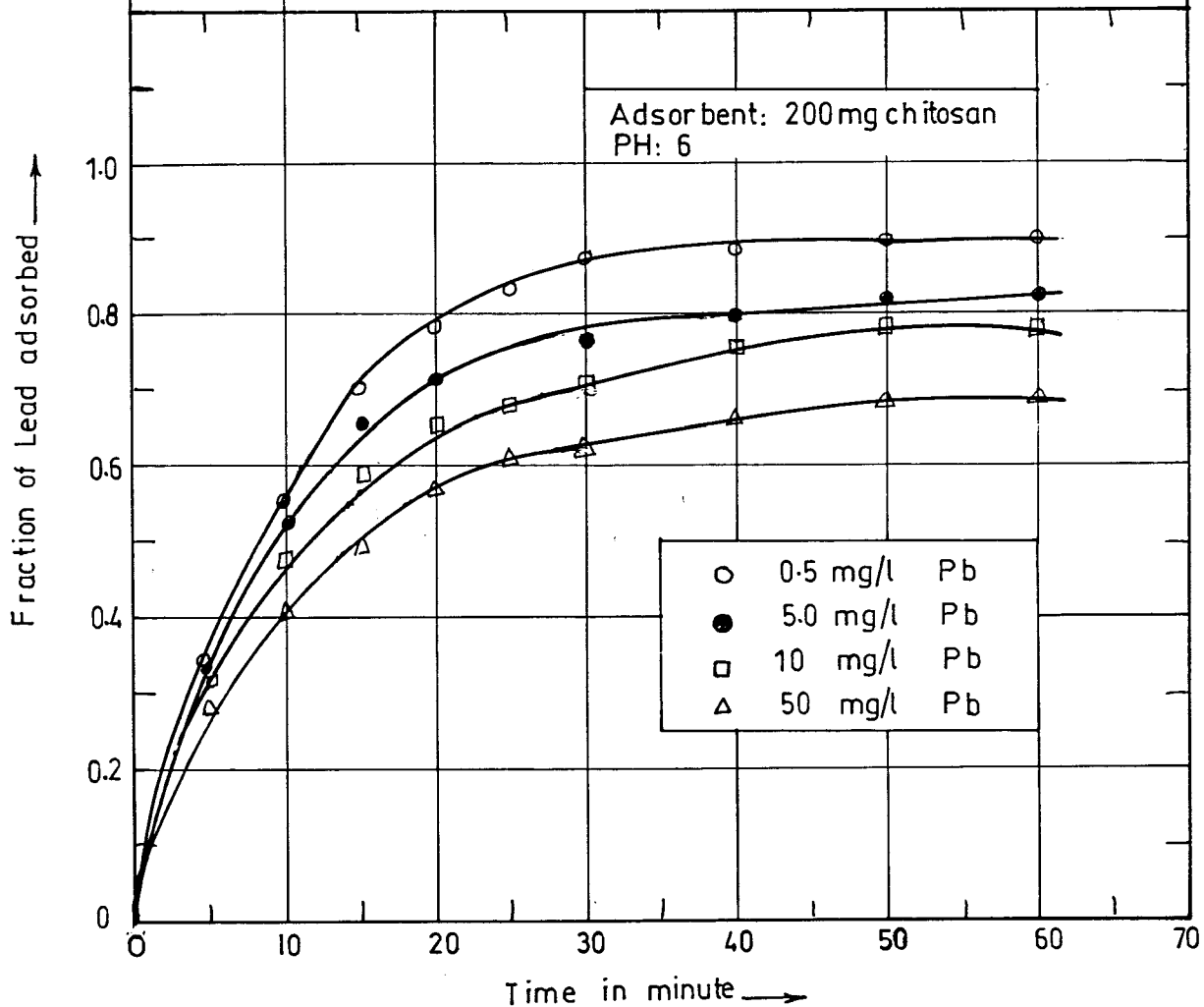


FIG
8

SORPTION KINETICS OF CHROMIUM ON CHITOSAN
EFFECT OF INITIAL CONC.

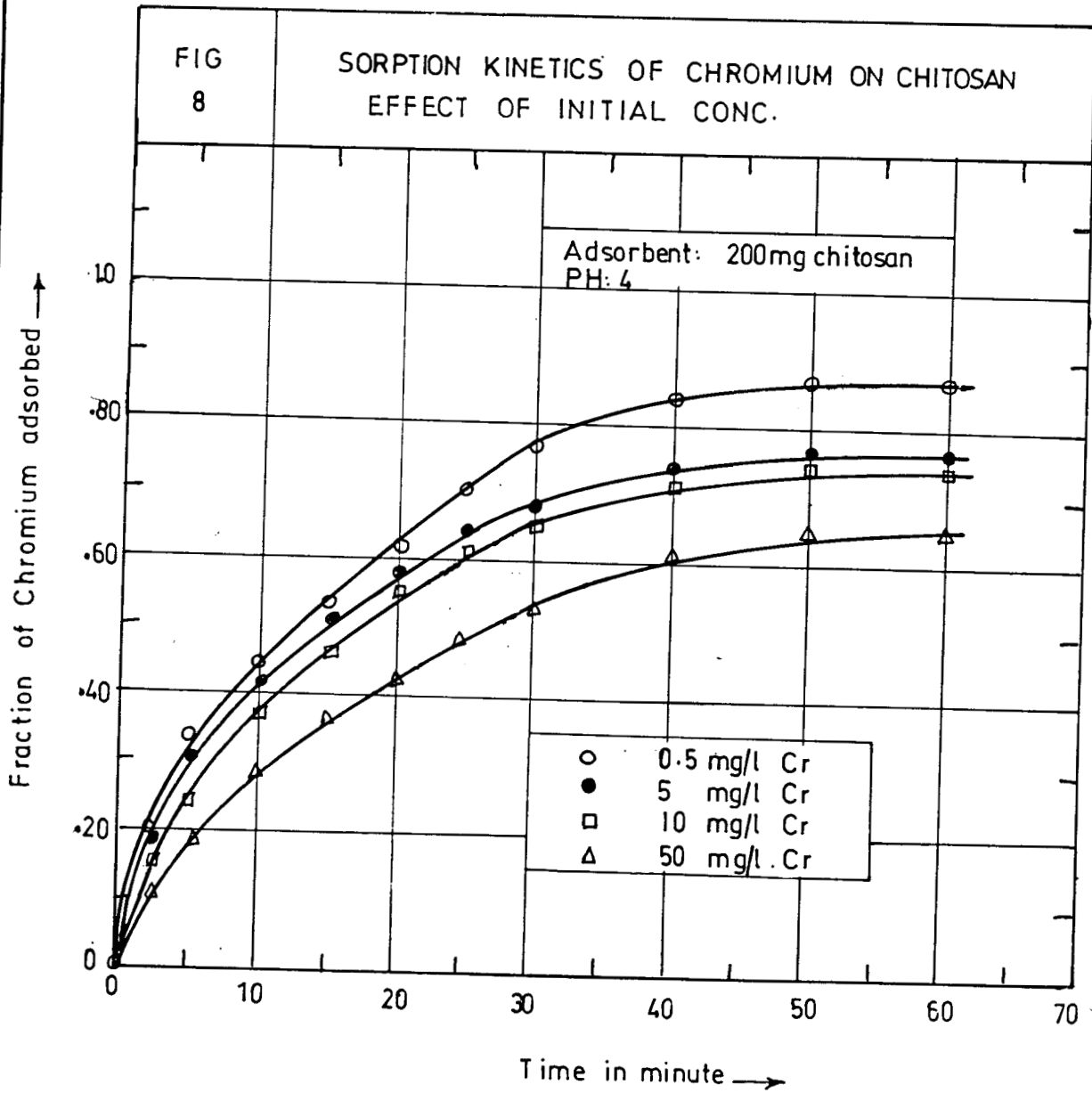
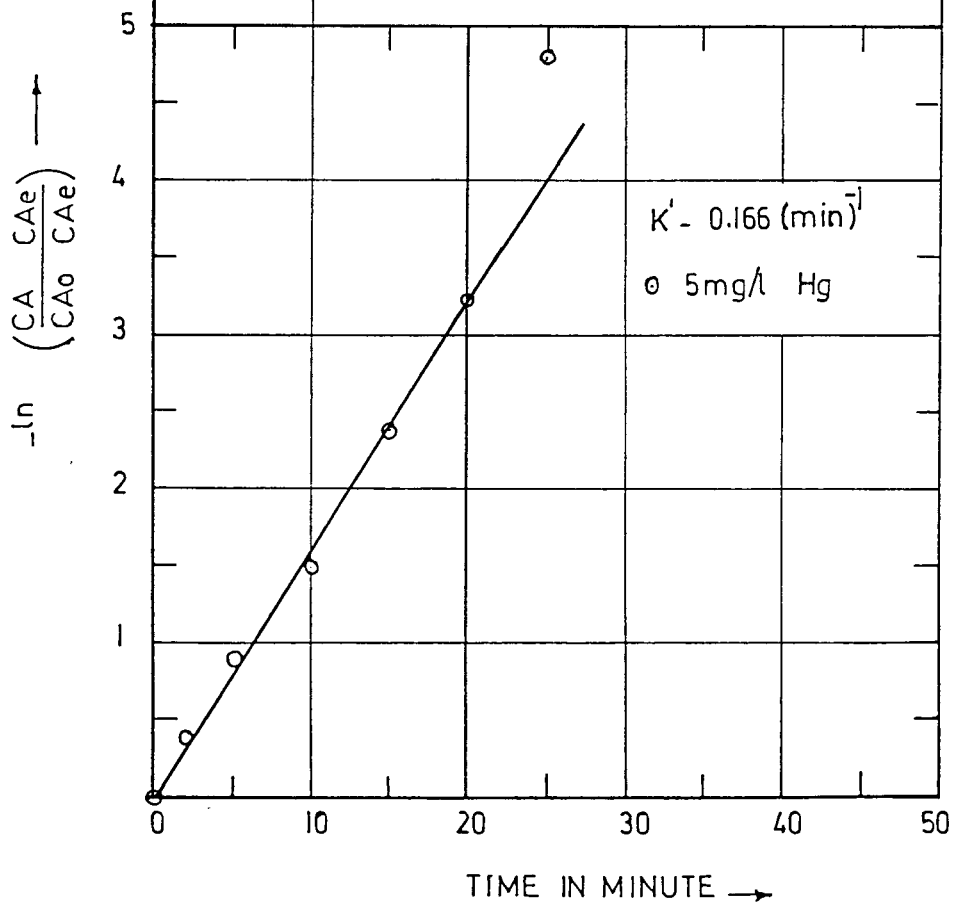


FIG
9

FIRST ORDER REVERSIBLE KINETIC
FIT OF MERCURY SORPTION ON CHITOSAN



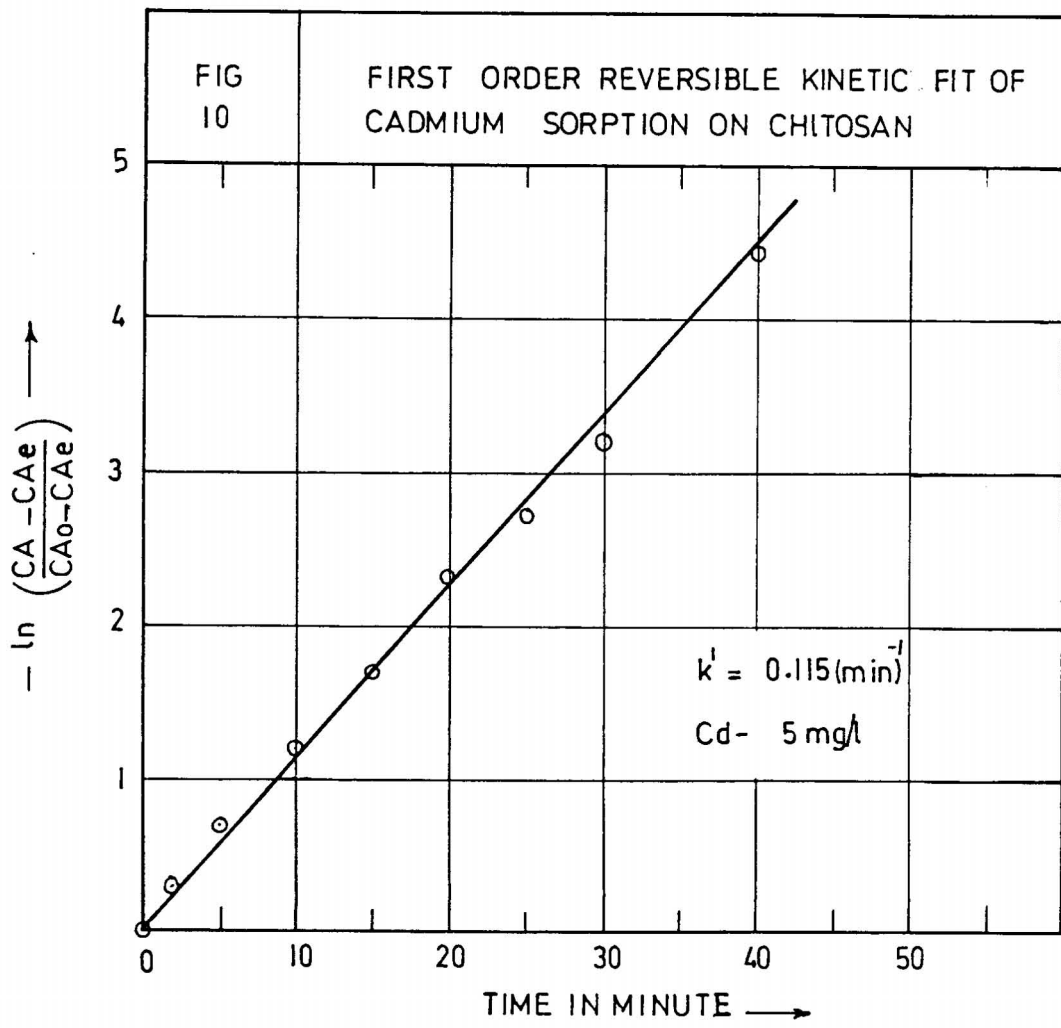


FIG
11

FIRST ORDER KINETIC FIT OF LEAD
SORPTION ON CHITOSAN. Pb-5 mg/l

$$-\ln \left(\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} \right)$$

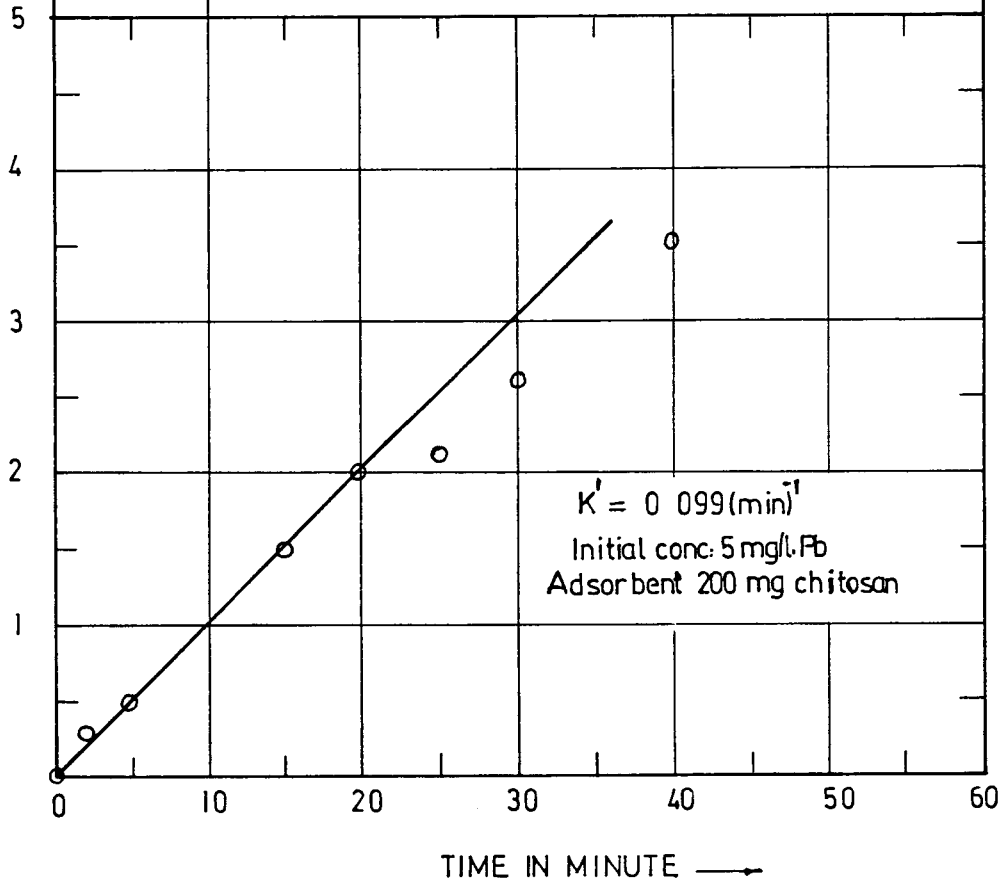


FIG
12

FIRST ORDER KINETIC FIT OF
CHROMIUM SORPTION ON CHITOSAN

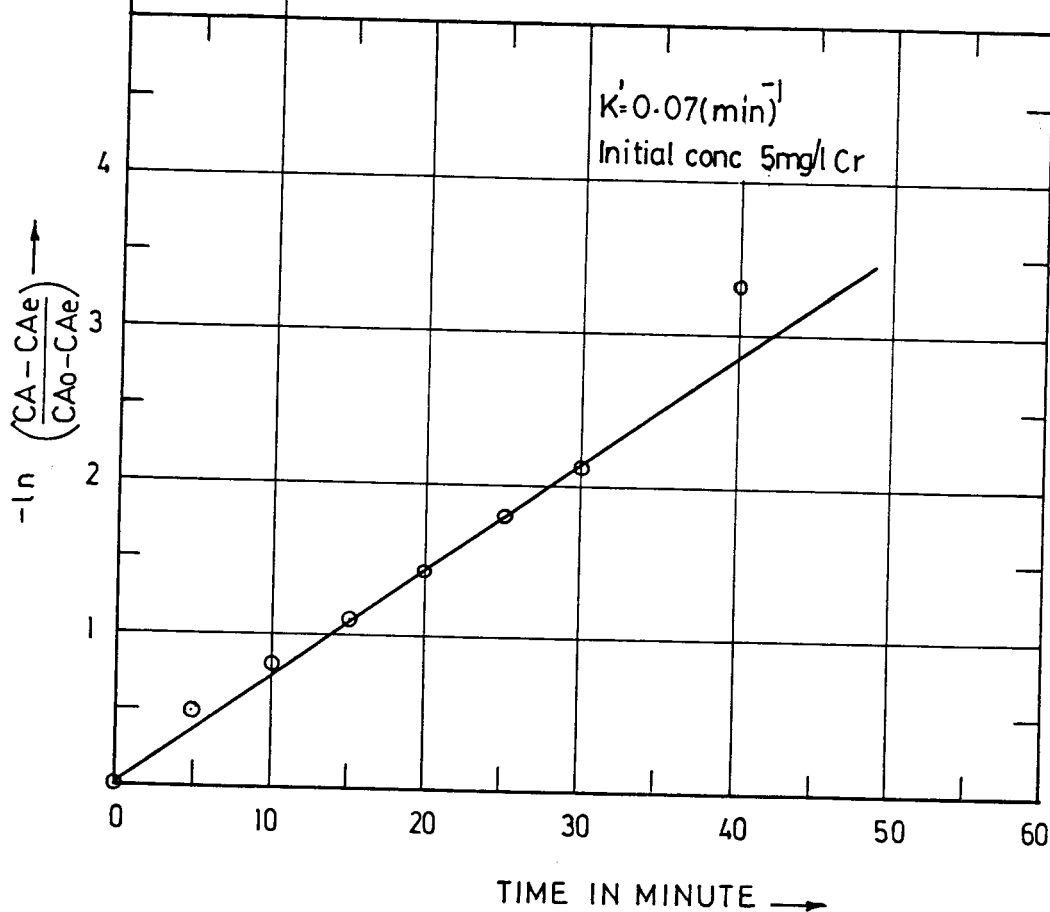


Fig. 13

EFFECT OF PARTICLE SIZE OF CHITOSAN ON ADSORPTION OF MERCURY

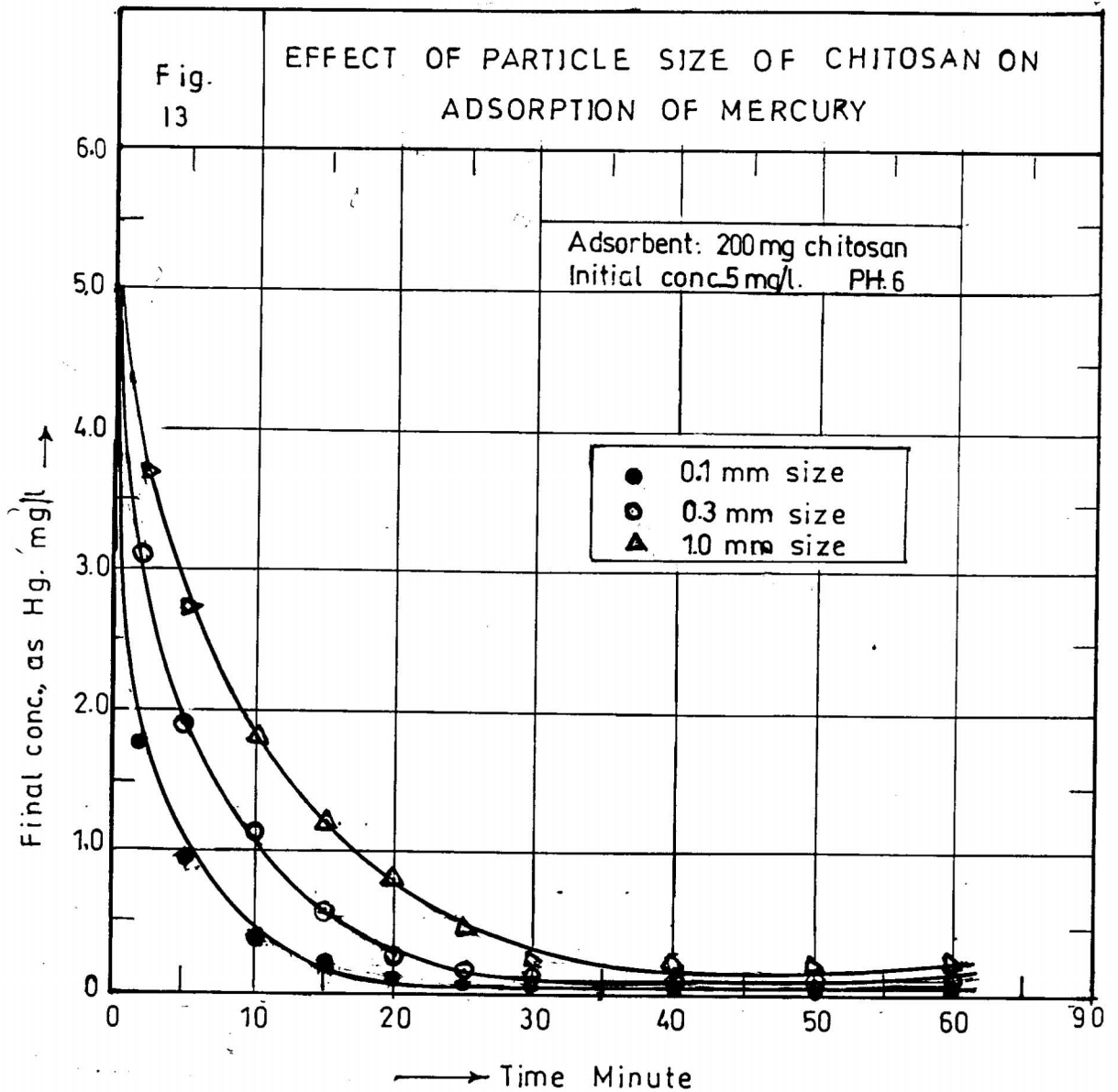


FIG
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EFFECT OF PARTICLE SIZE OF CHITOSAN ON
ADSORPTION OF CADMIUM

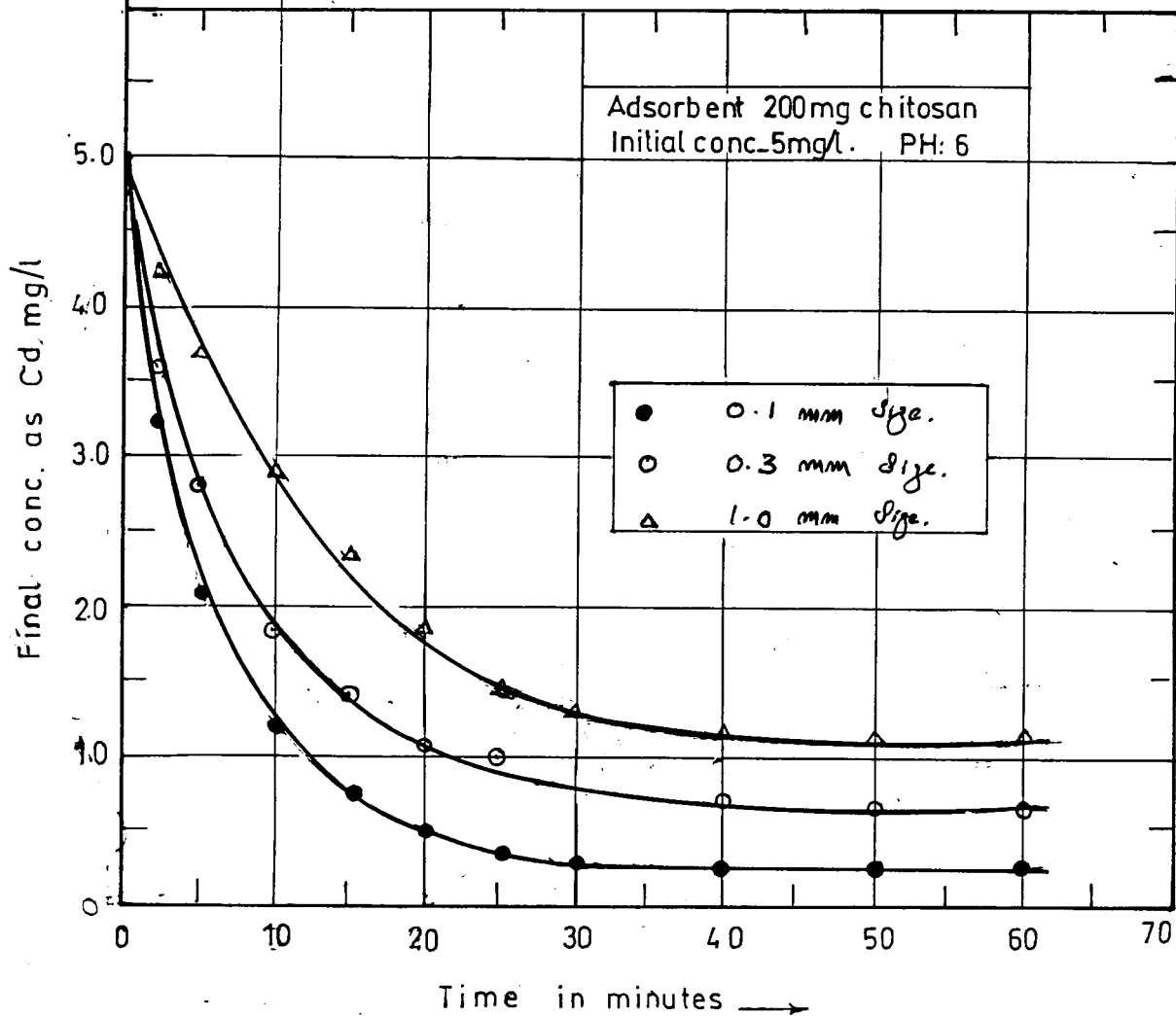


FIG
15

EFFECT OF PARTICLE SIZE OF CHITOSAN ON
ADSORPTION OF LEAD

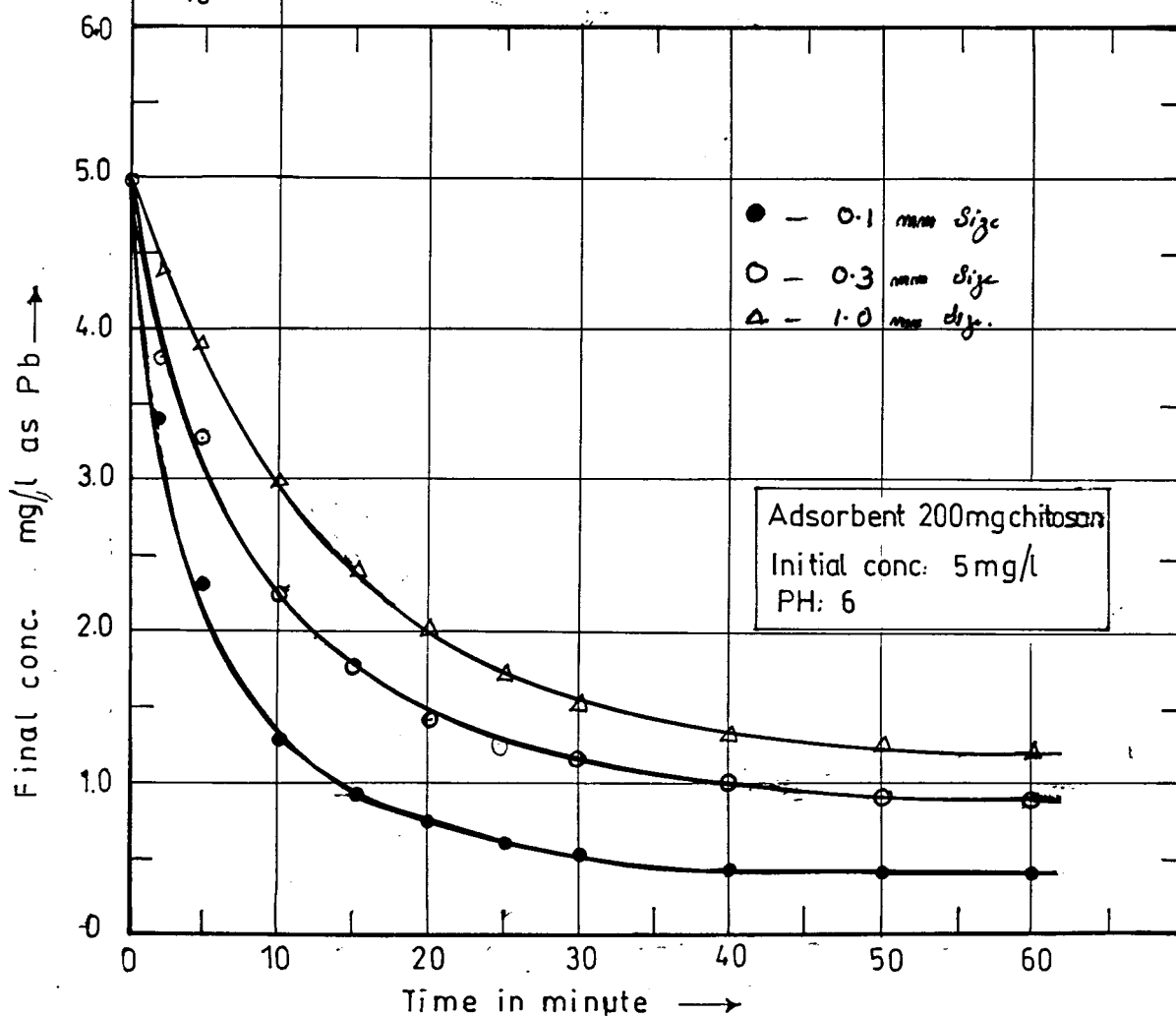


FIG
16

EFFECT OF PARTICLE SIZE OF CHITOSAN ON
ADSORPTION OF CHROMIUM

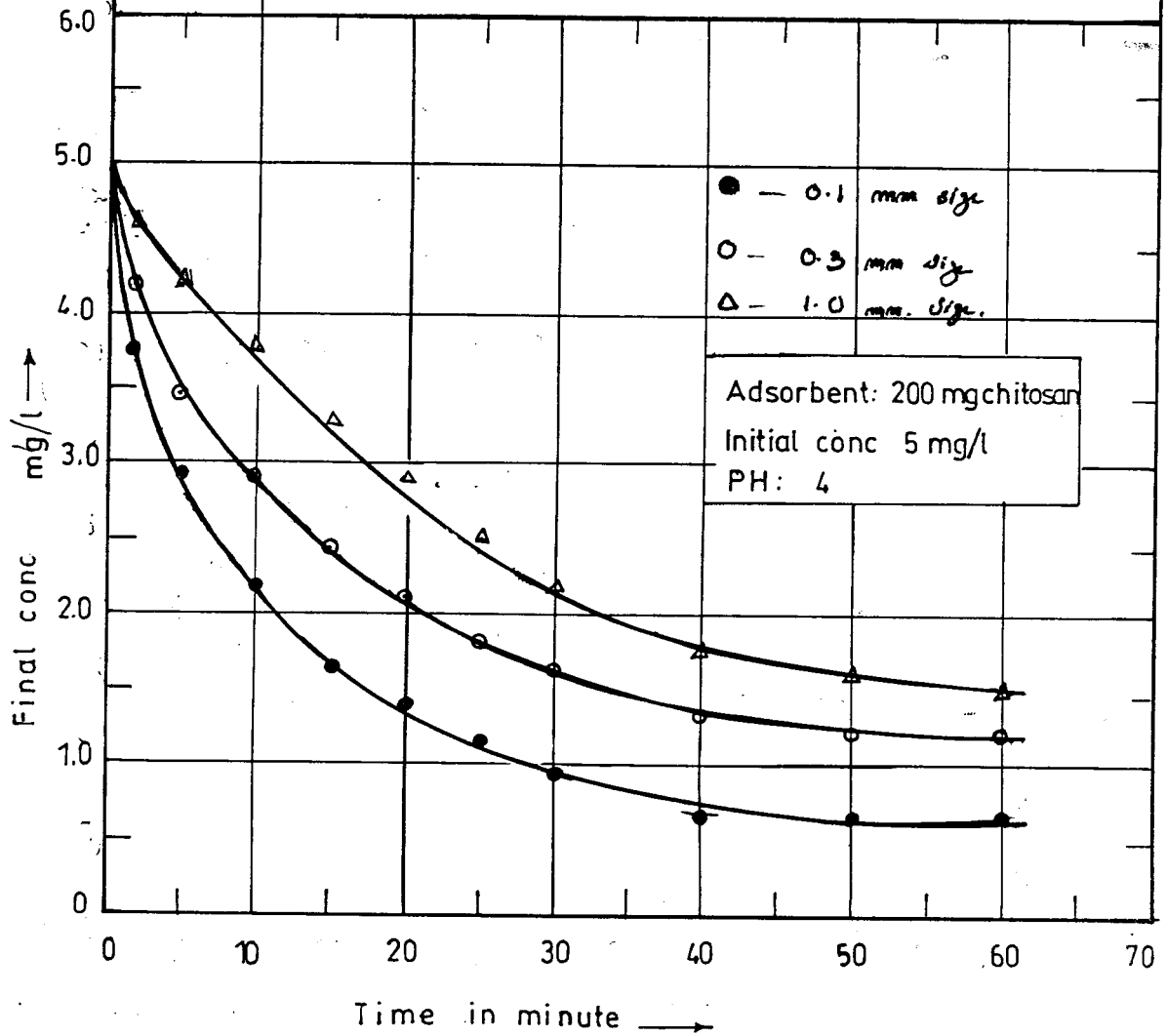


FIG
17

EFFECT OF TEMPERATURE ON ADSORPTION
OF MERCURY

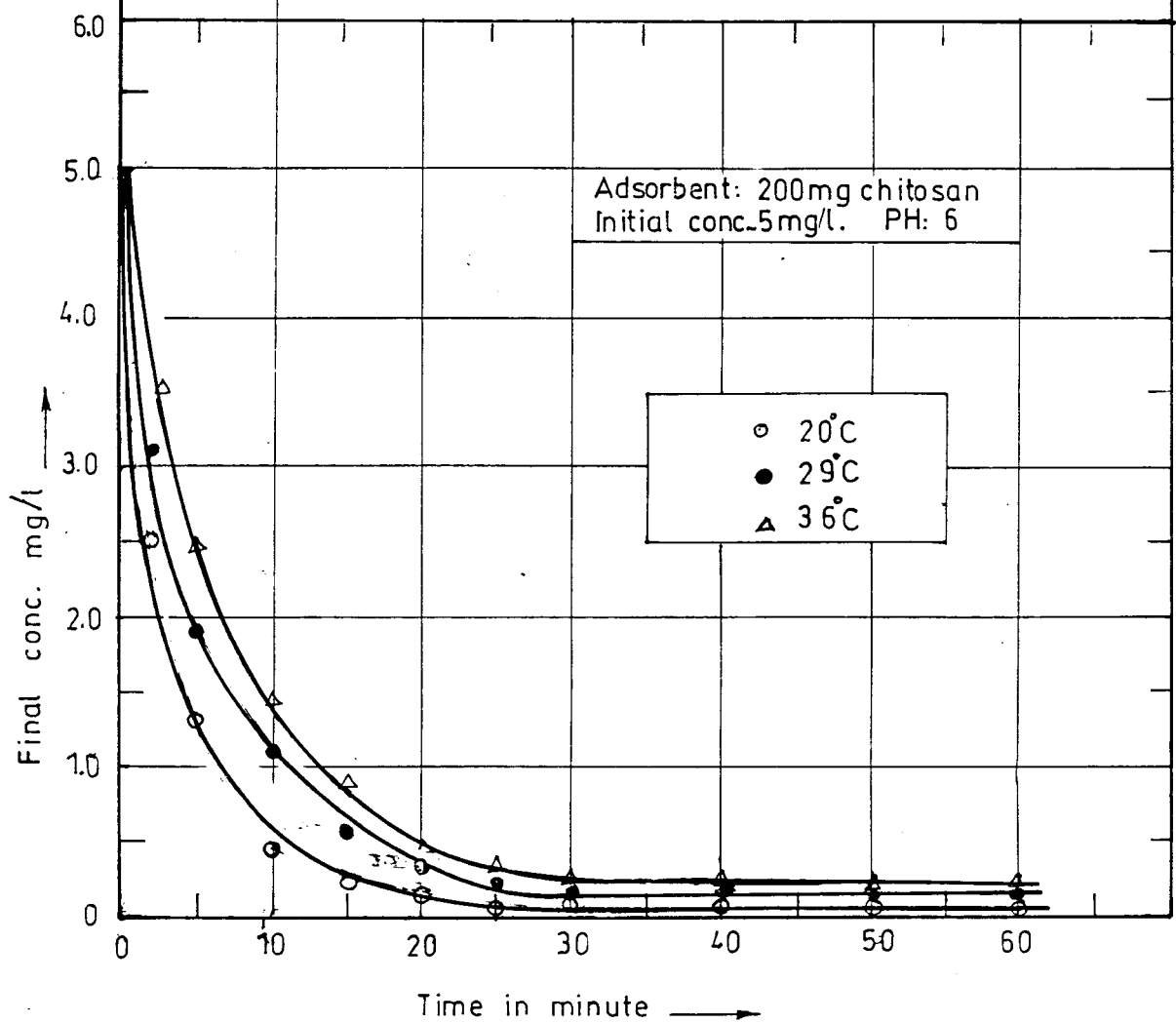


FIG
18

EFFECT OF TEMPERATURE ON ADSORPTION
OF CADMIUM

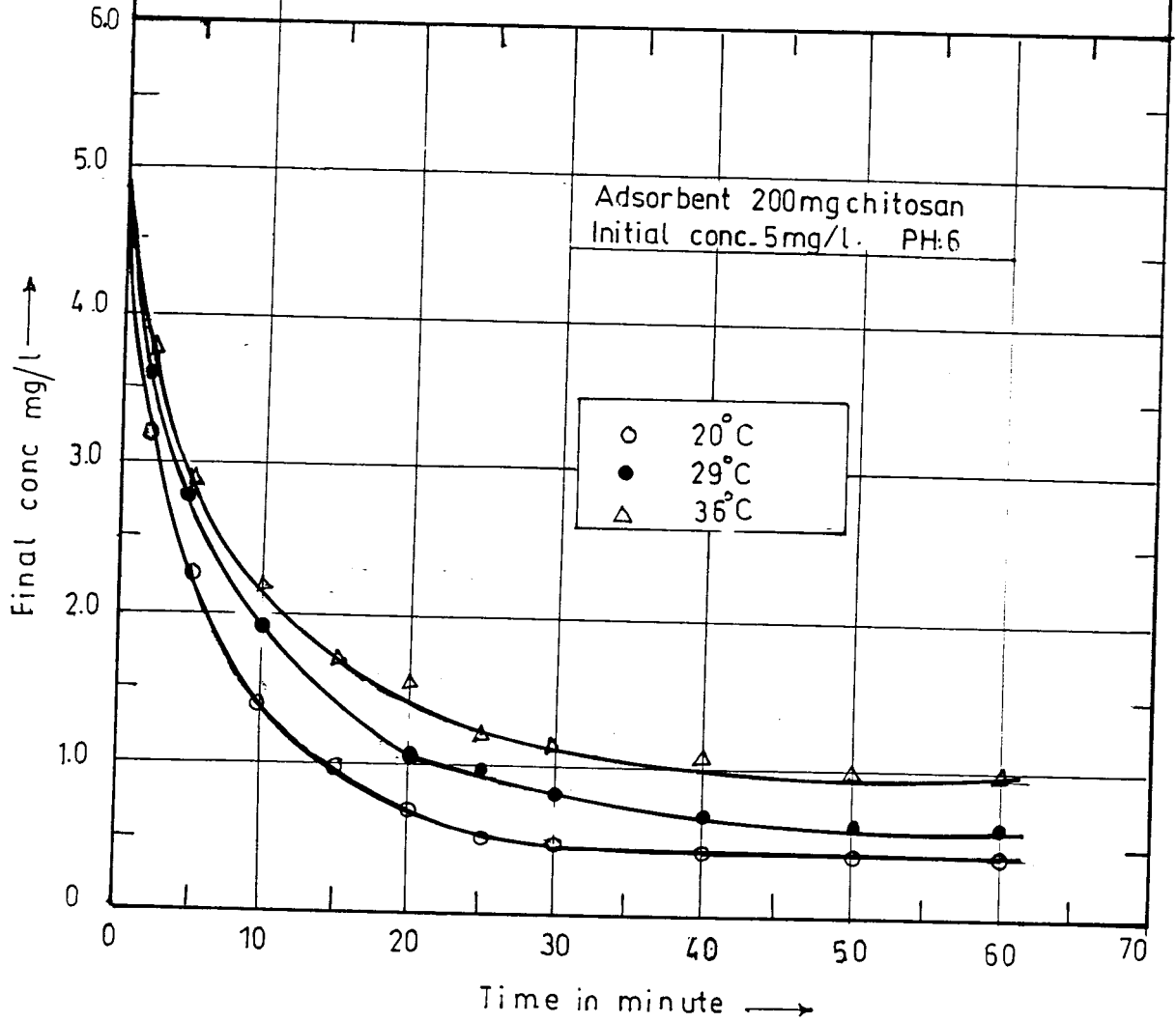


FIG
19

EFFECT OF TEMPERATURE ON ADSORPTION
OF LEAD.

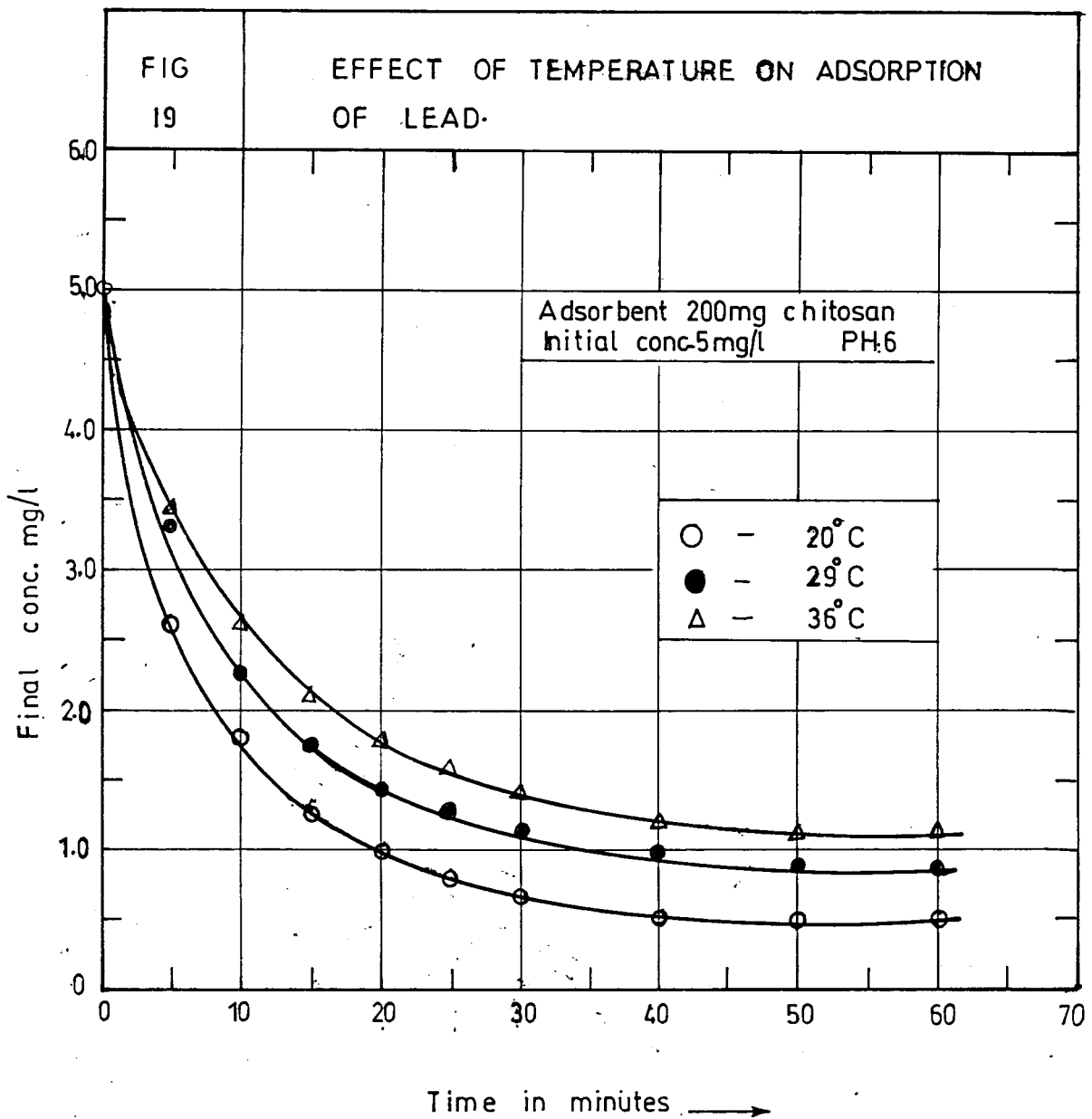


FIG
20

EFFECT OF TEMPERATURE ON ADSORPTION
OF CHROMIUM

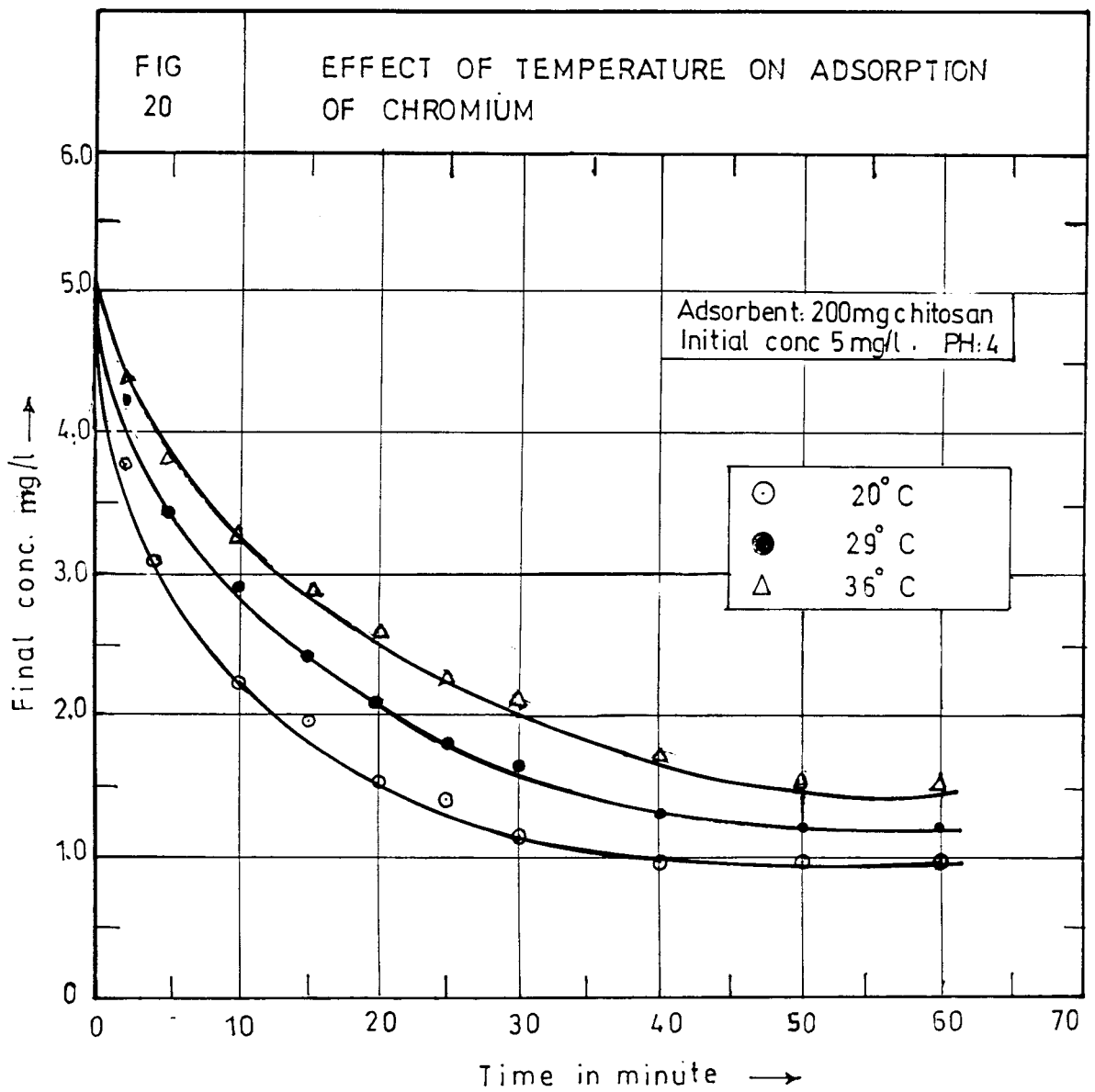


FIG
21

FIRST ORDER REVERSIBLE KINETIC FIT
OF MERCURY SORPTION AT DIFFERENT TEMP

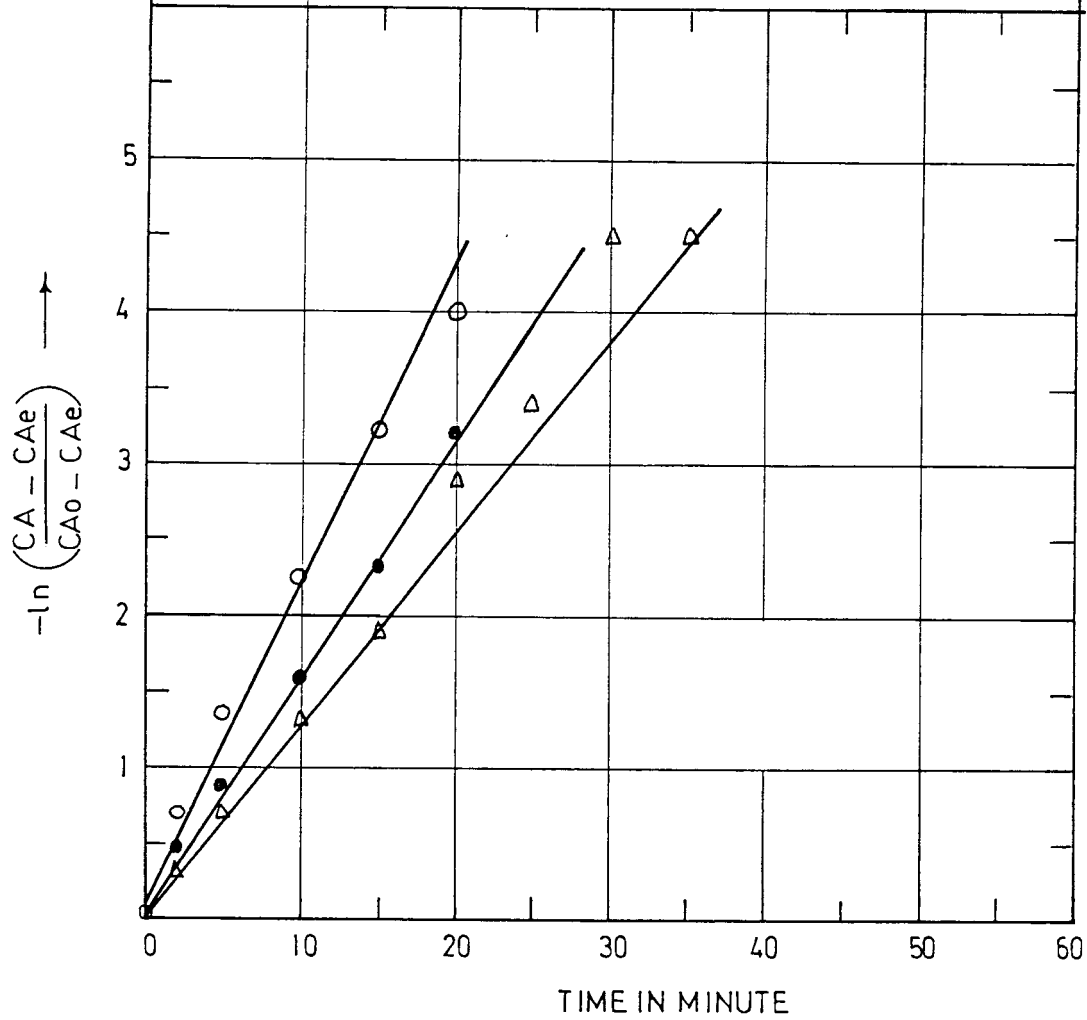


FIG
22

TEMPERATURE DEPENDENCY OF
MERCURY SORPTION ON CHITOSAN

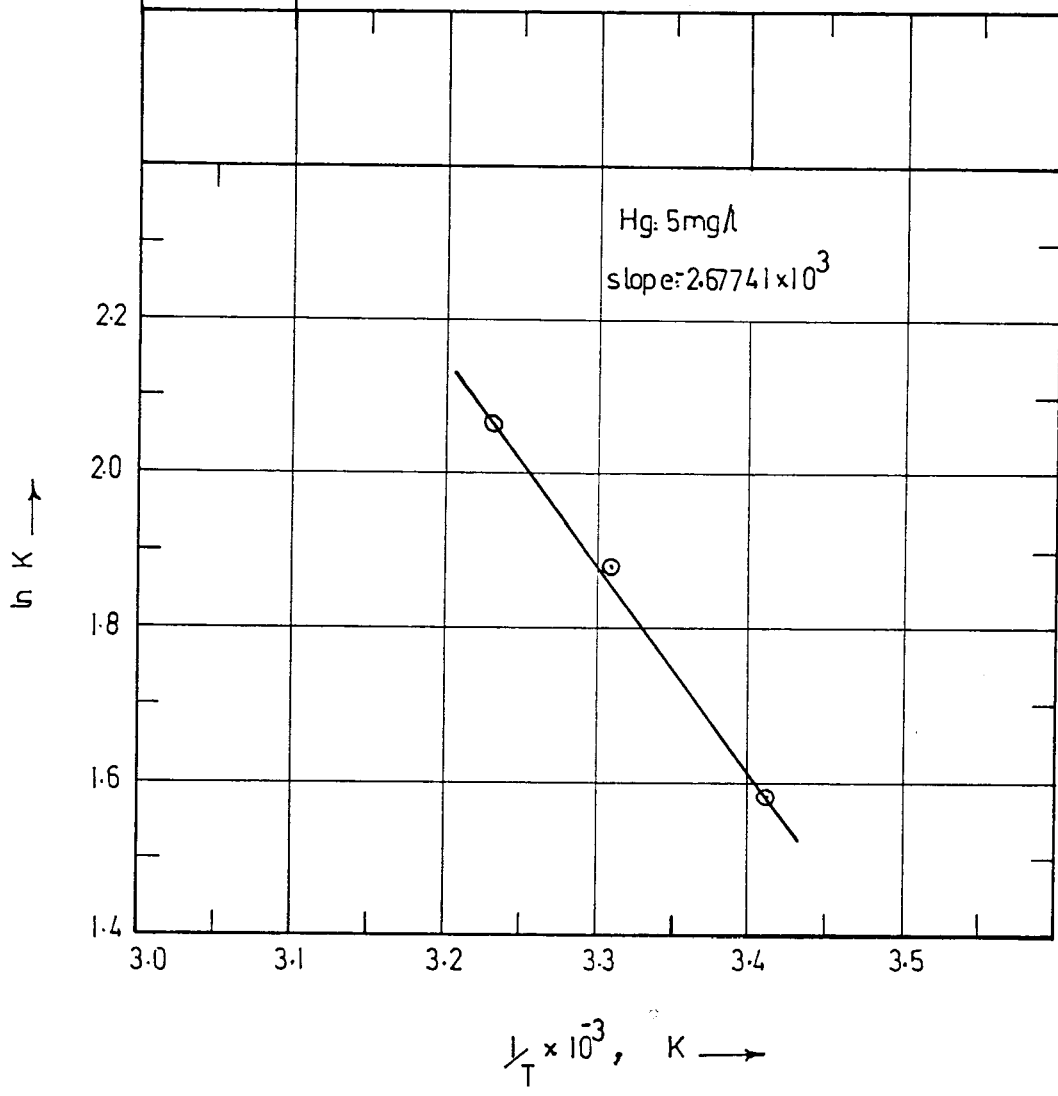


FIG
23

EFFECT OF PH ON ADSORPTION

Adsorbent: 200mg chitosan
Initial conc. 5mg/l

- MERCURY
- CADMIUM
- LEAD
- △ CHROMIUM

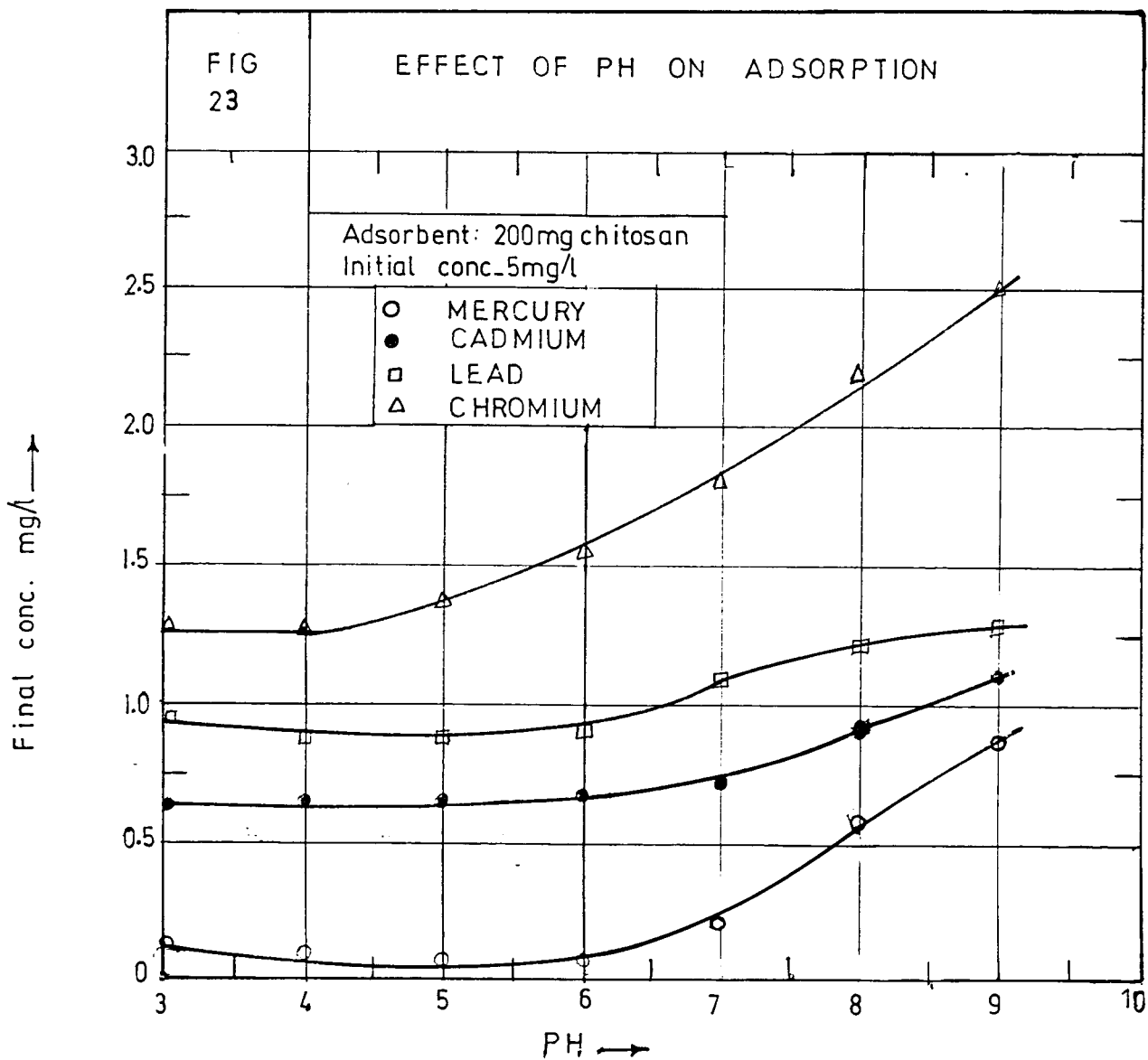


FIG 24

EFFECT OF PH ON ADSORPTION-mg OF IONS ADSORBED / gm OF ADSORBENT

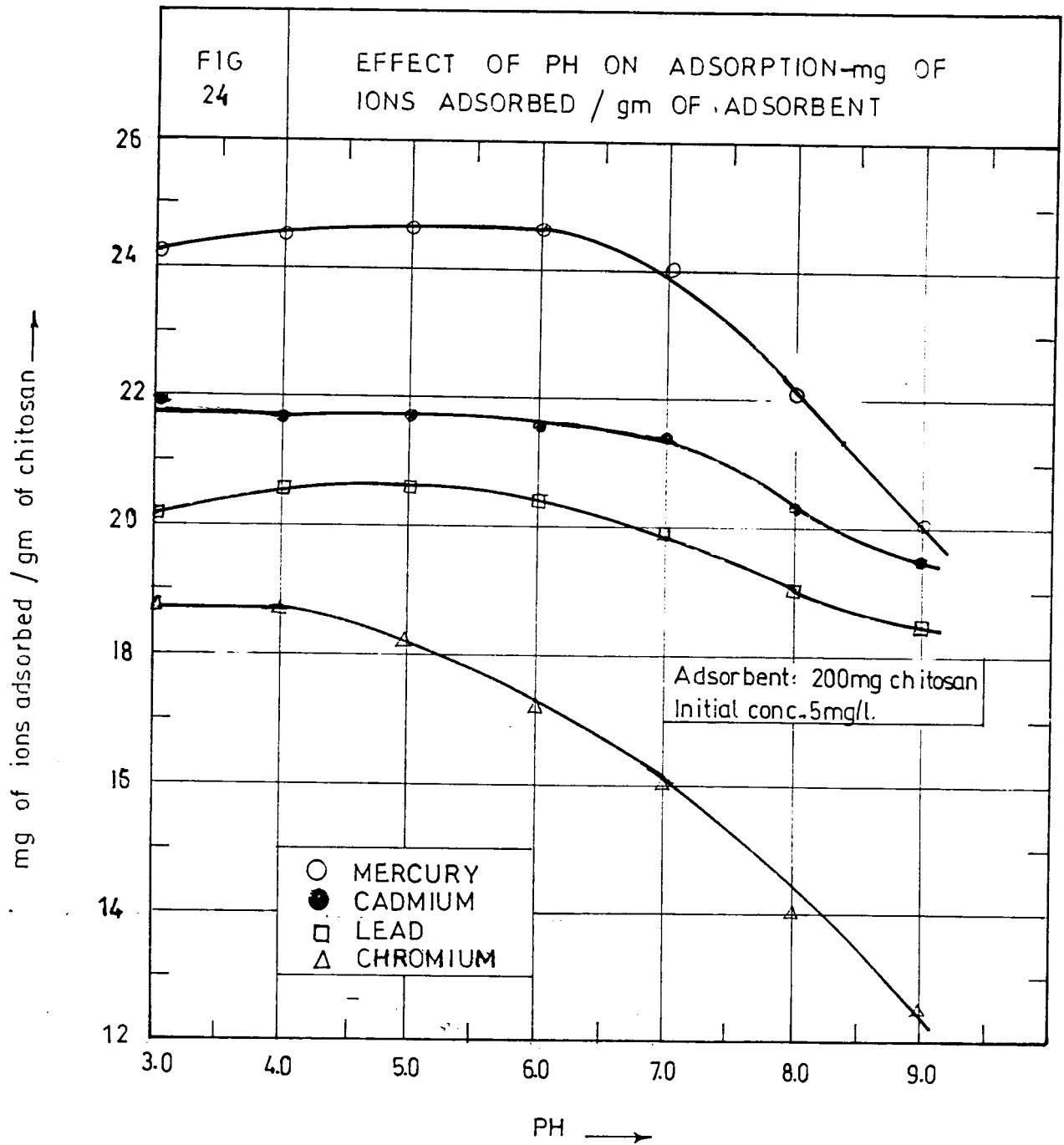


FIG
25

EQUILIBRIUM CHARACTERISTICS OF
CHITOSAN AGAINST MERCURY

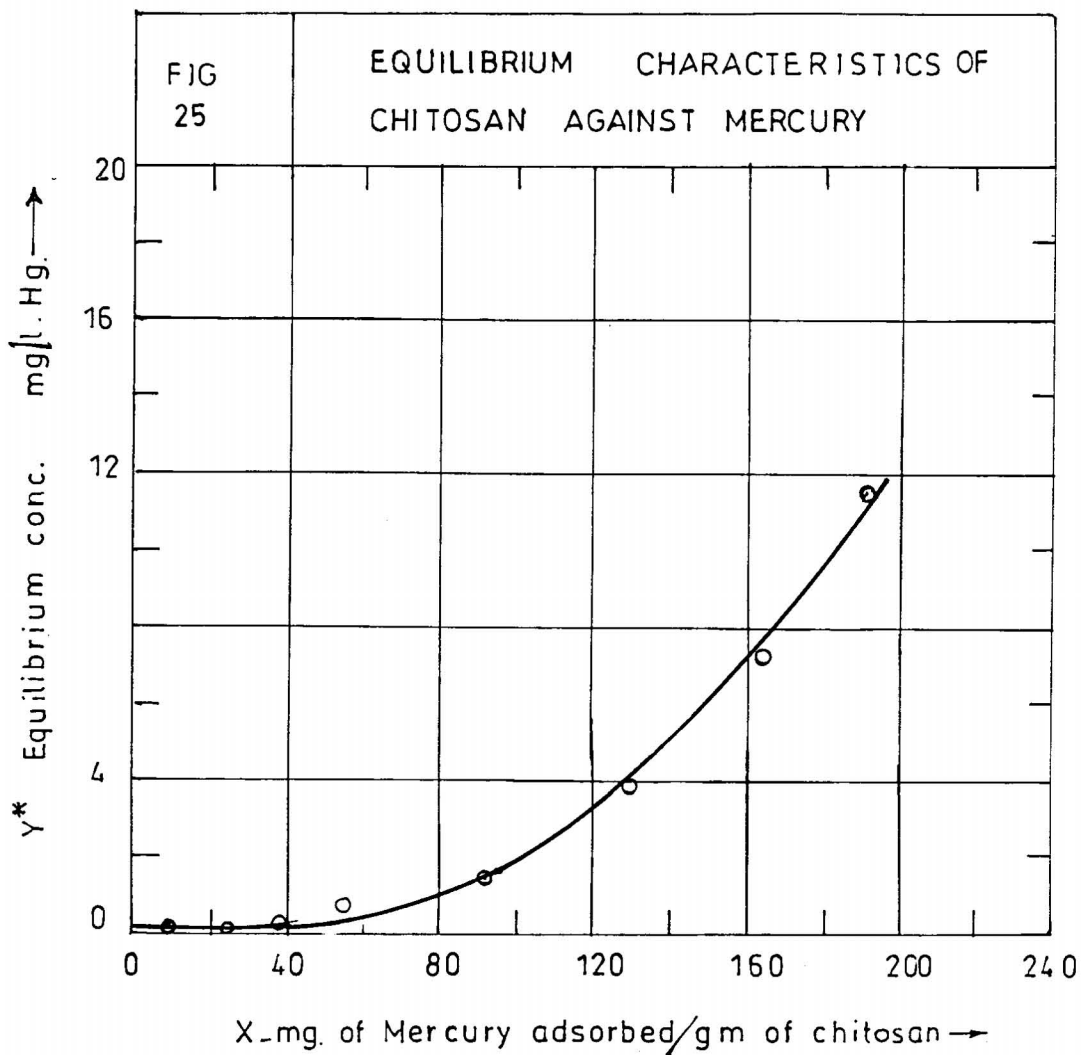


FIG
26

EQUILIBRIUM CHARACTERISTICS OF
CHITOSAN AGAINST CADMIUM

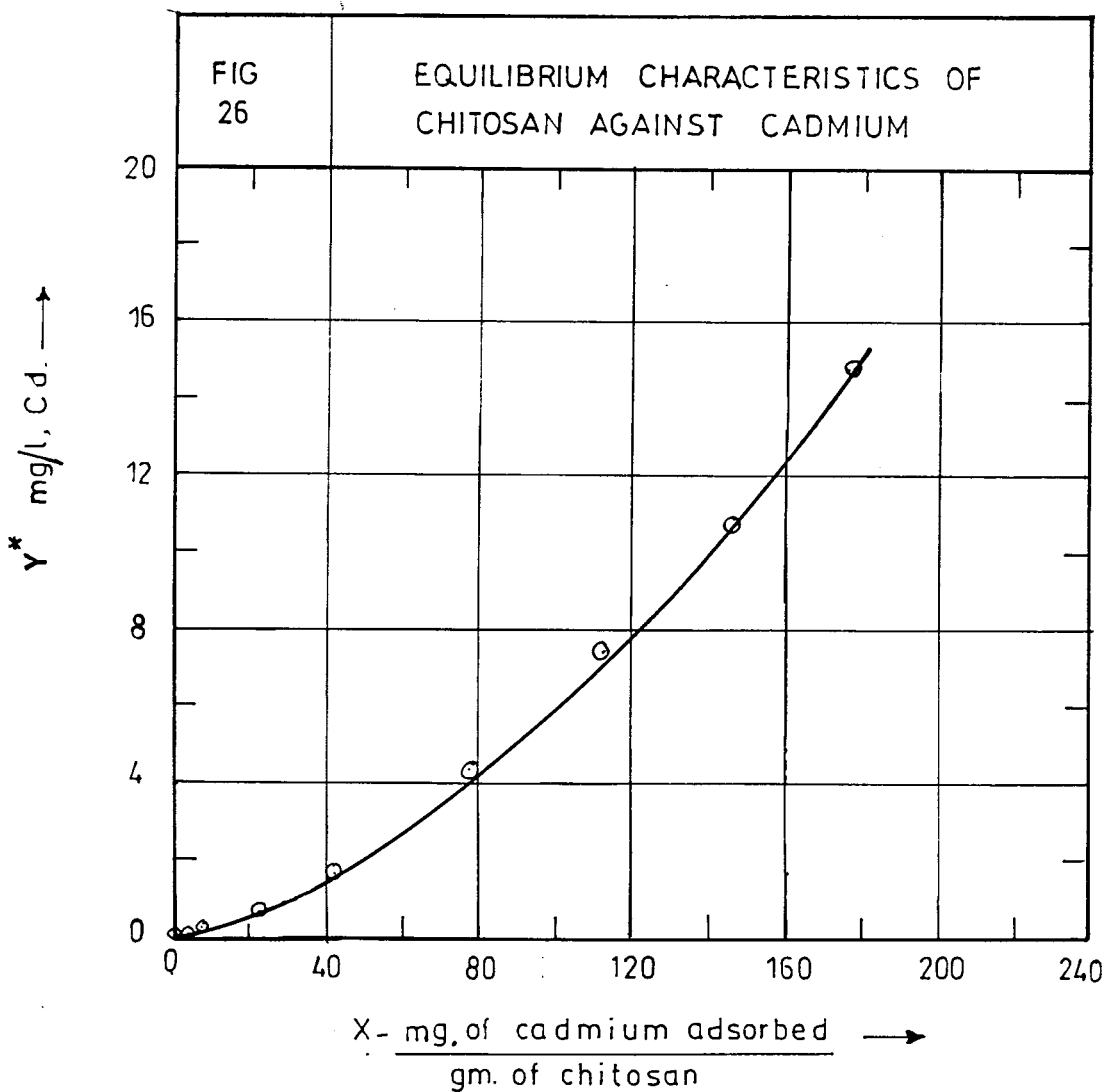


FIG
27

EQUILIBRIUM CHARACTERISTICS OF
CHITOSAN AGAINST LEAD

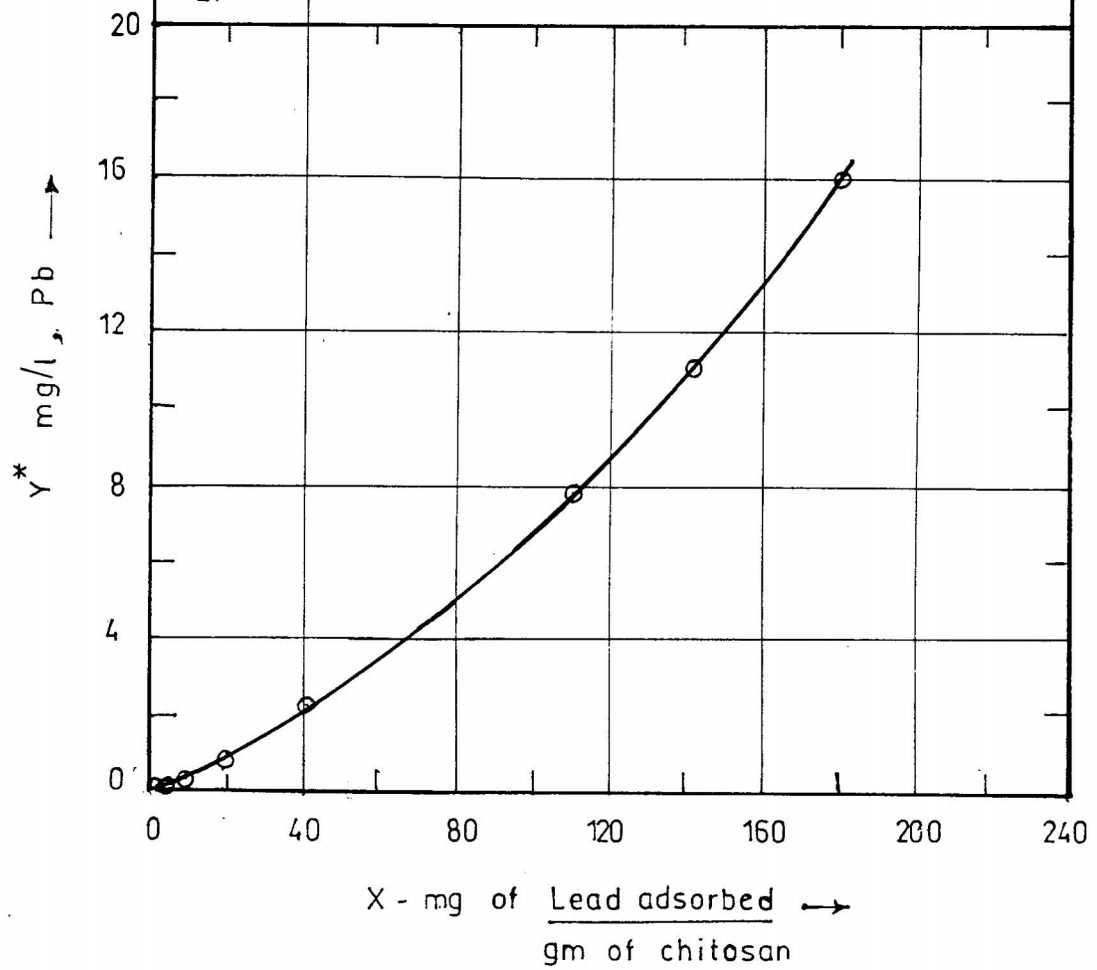


FIG
28

EQUILIBRIUM CHARACTERISTICS OF
CHITOSAN AGAINST CHROMIUM

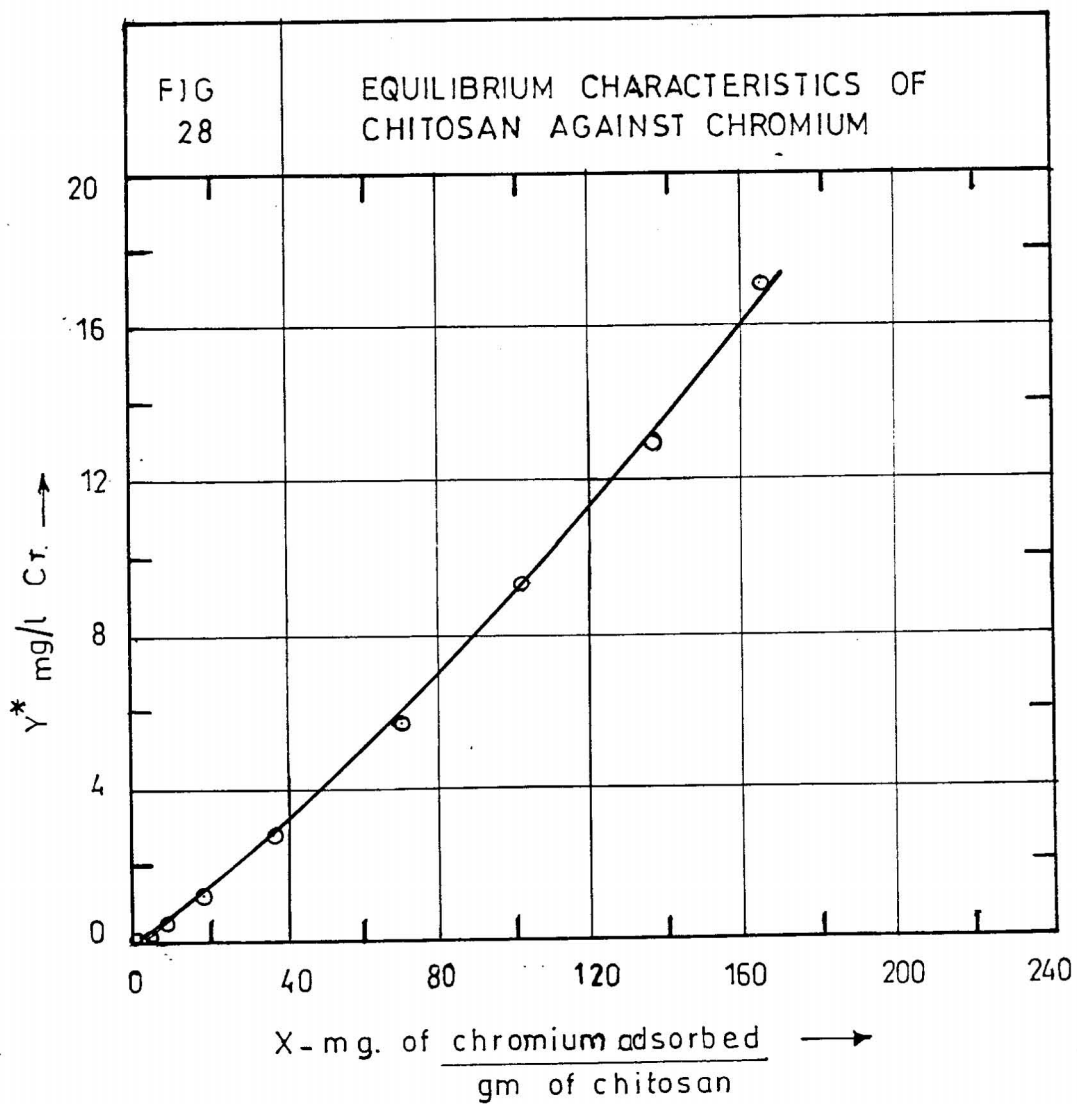


FIG
29

FREUNDLICH ISOTHERM FOR
MERCURY SORPTION ON CHITOSAN

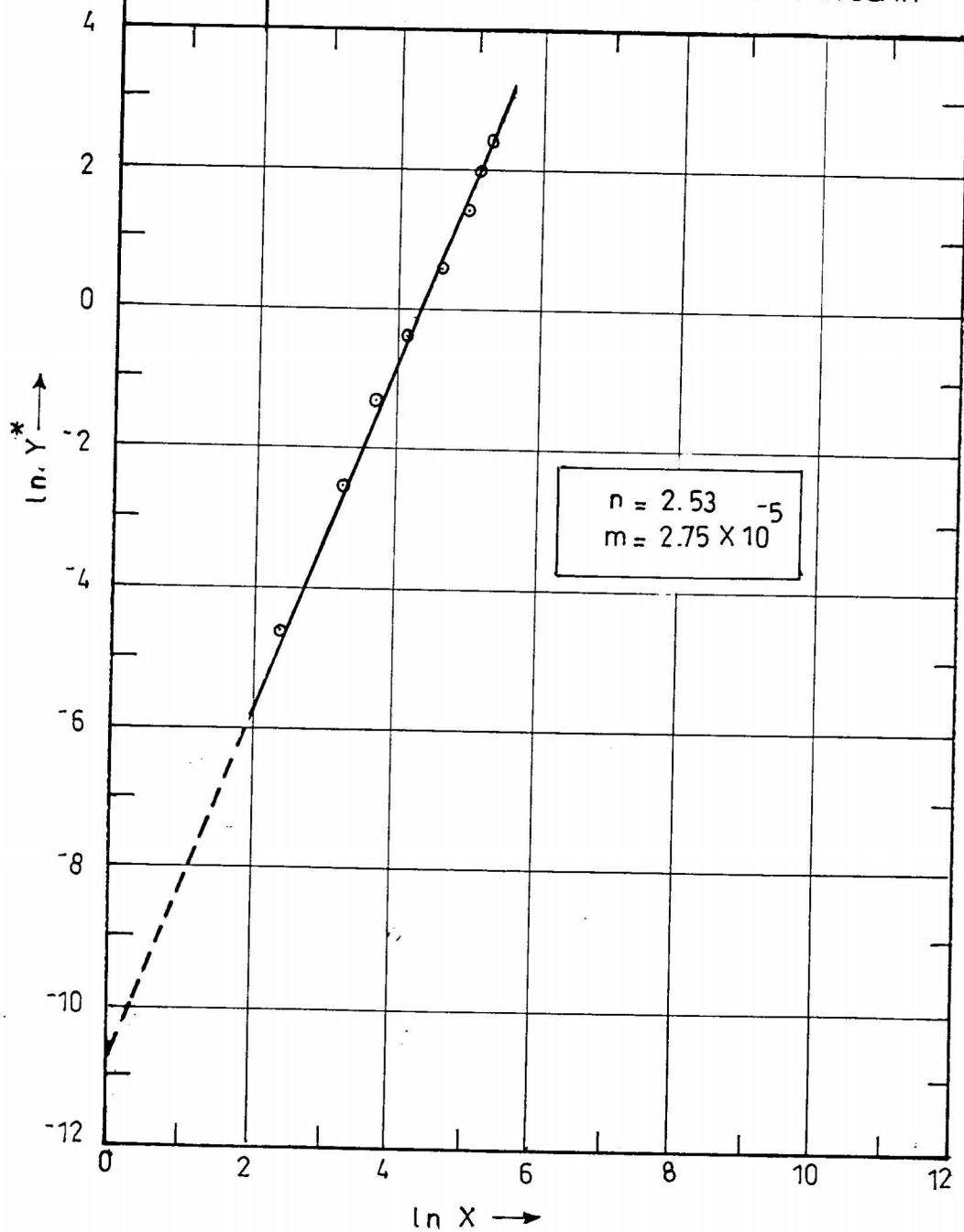


FIG.
30

FREUNDLICH ISOTHERM FOR
CADMIUM SORPTION ON CHITOSAN

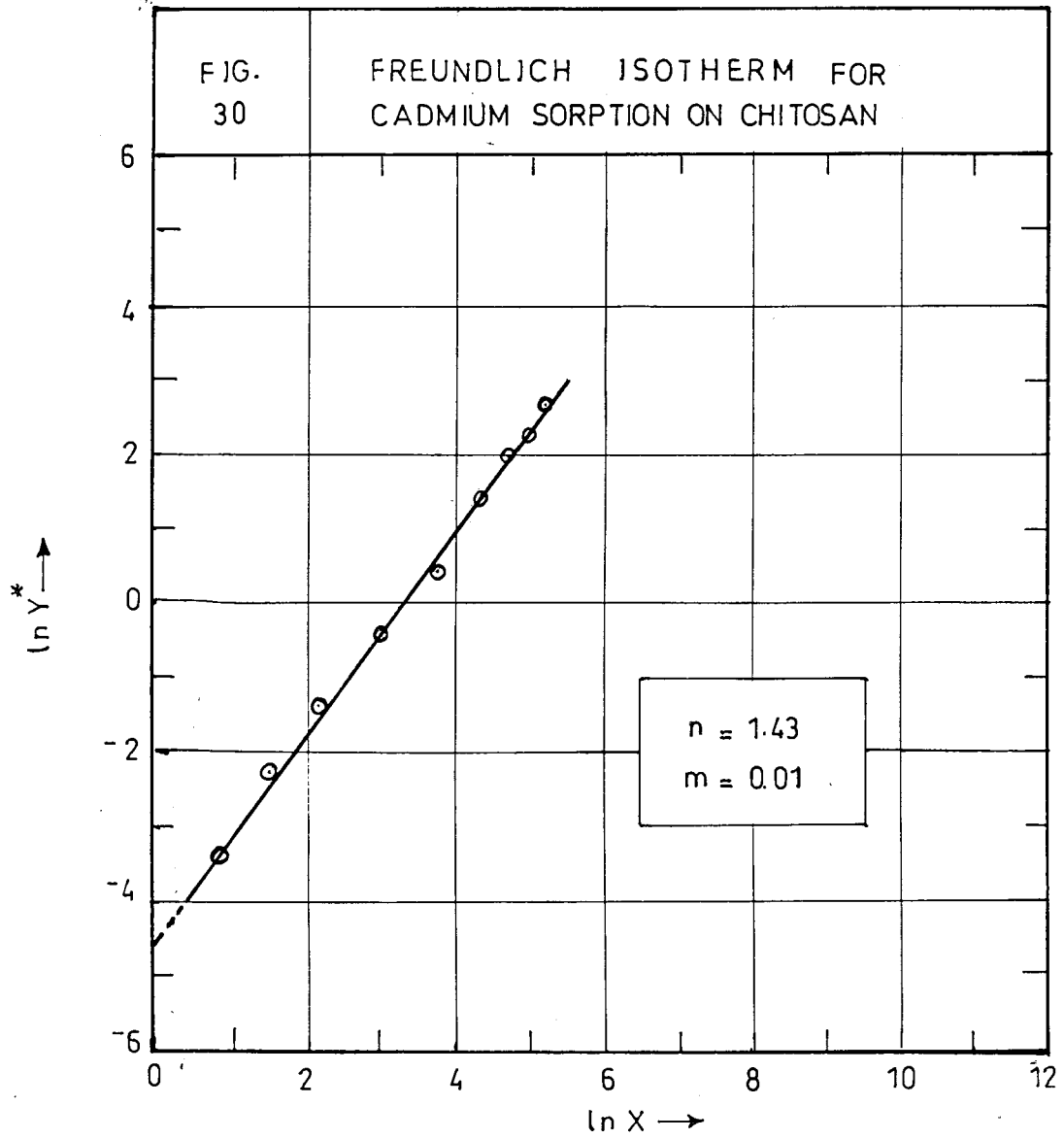


FIG
31

FREUNDLICH ISOTHERM FOR
LEAD SORPTION ON CHITOSAN

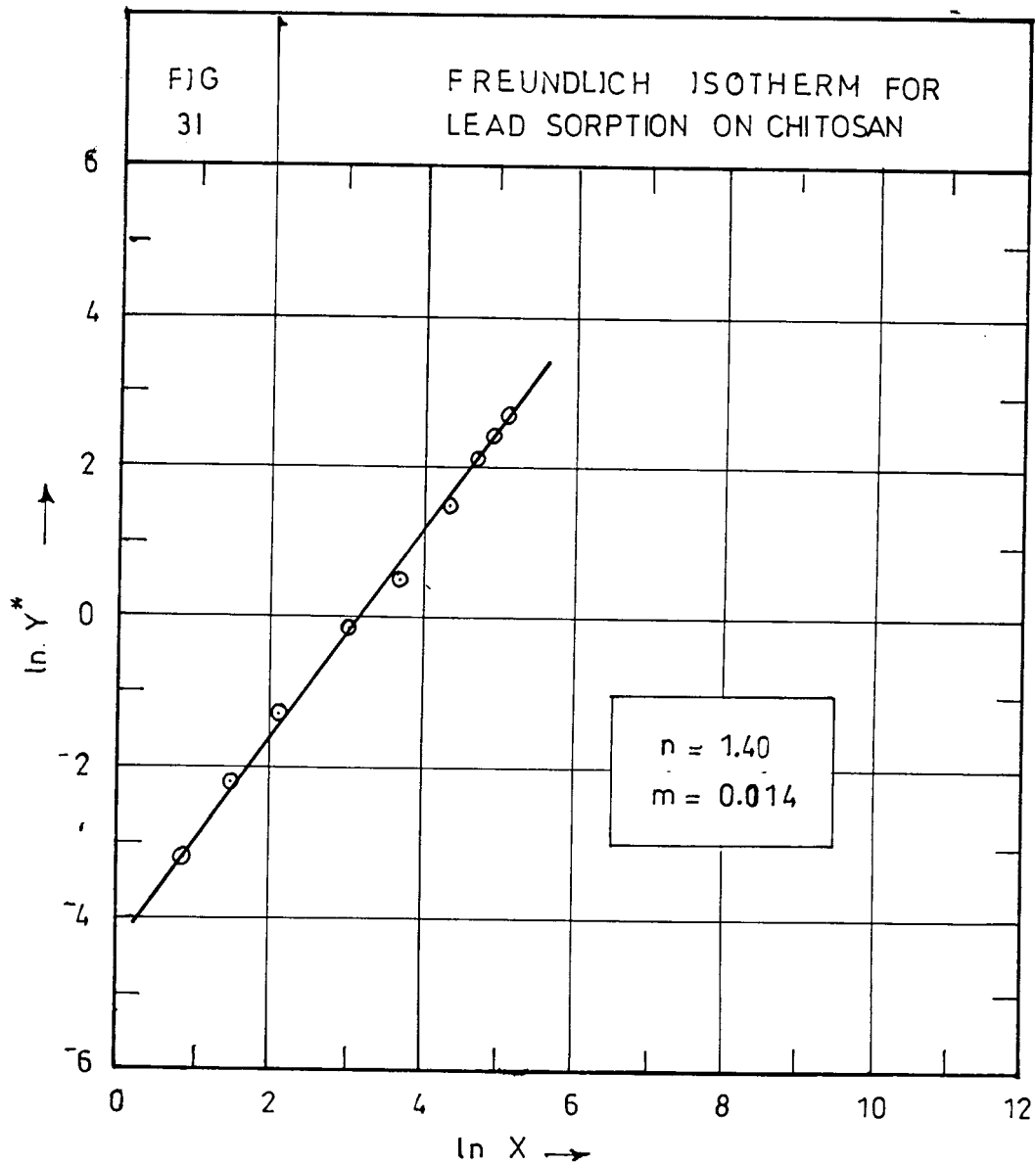


FIG.
32

FREUNDLICH ISOTHERM FOR
CHROMIUM SORPTION ON CHITOSAN

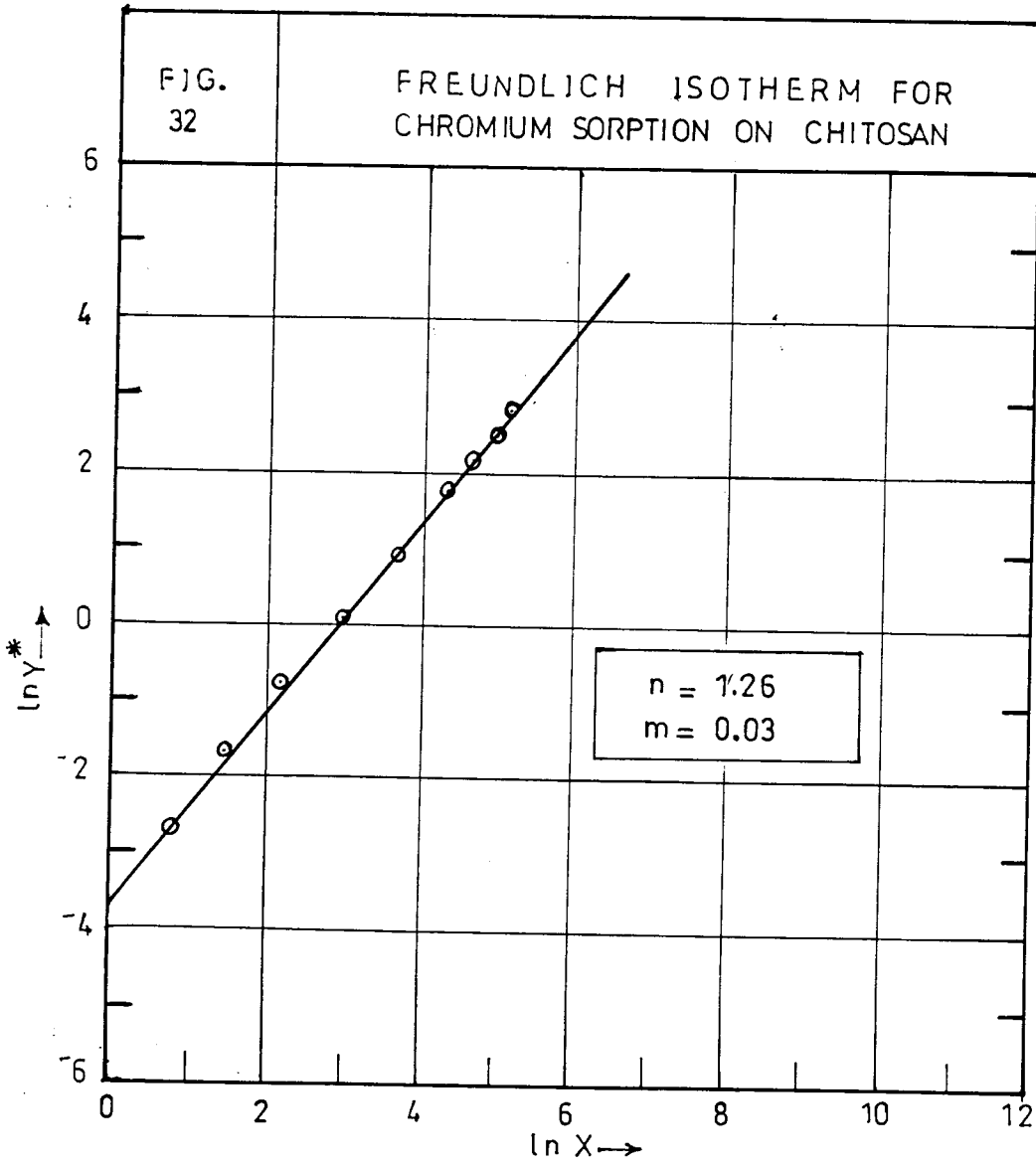


FIG
33

SORPTION KINETICS OF MERCURY
ON ACTIVATED CARBON & RICE HUSK CARBON

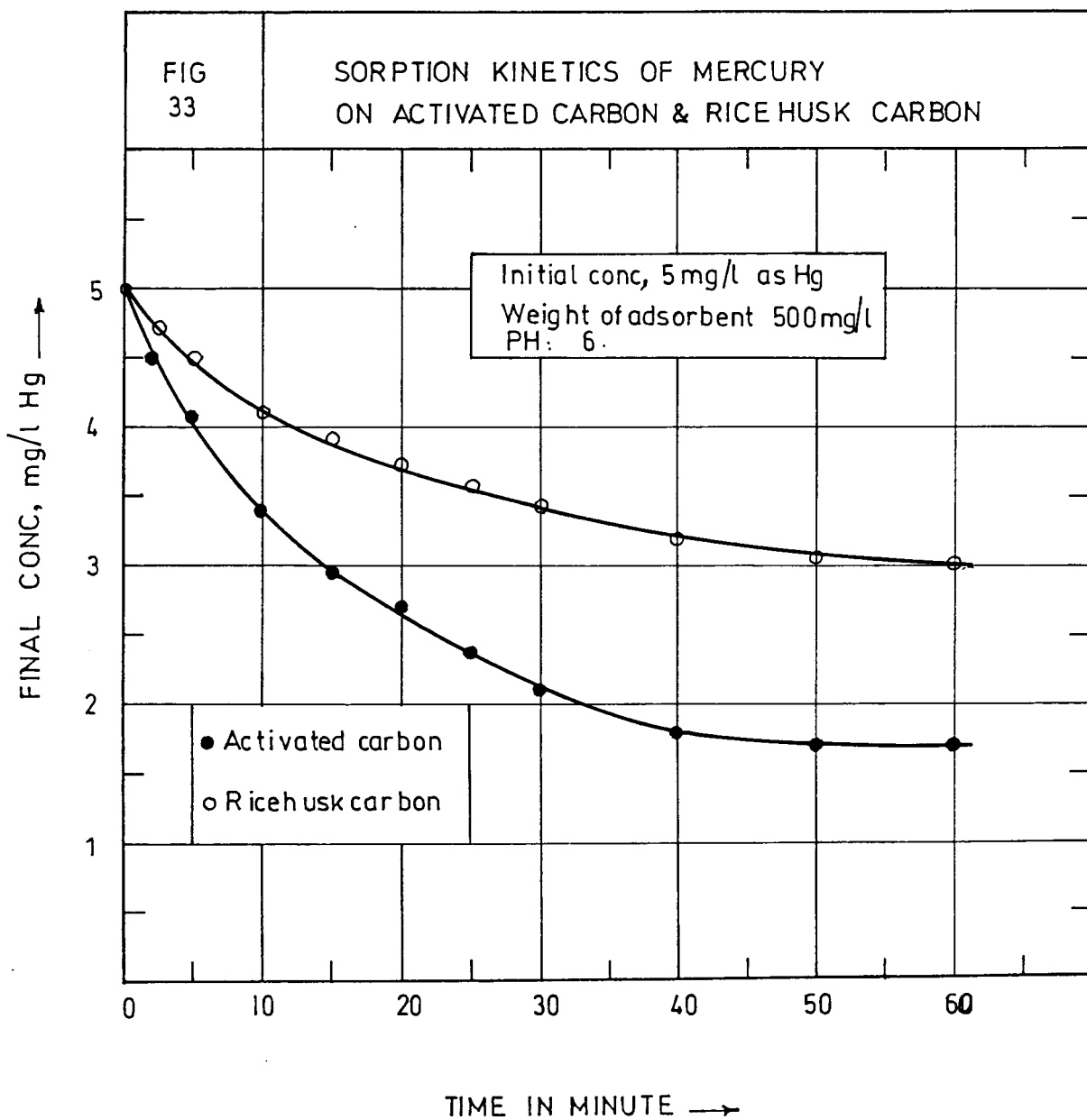


FIG 34

SORPTION KINETICS OF MERCURY ON ACTIVATED CARBON & RICEHUSK CARBON

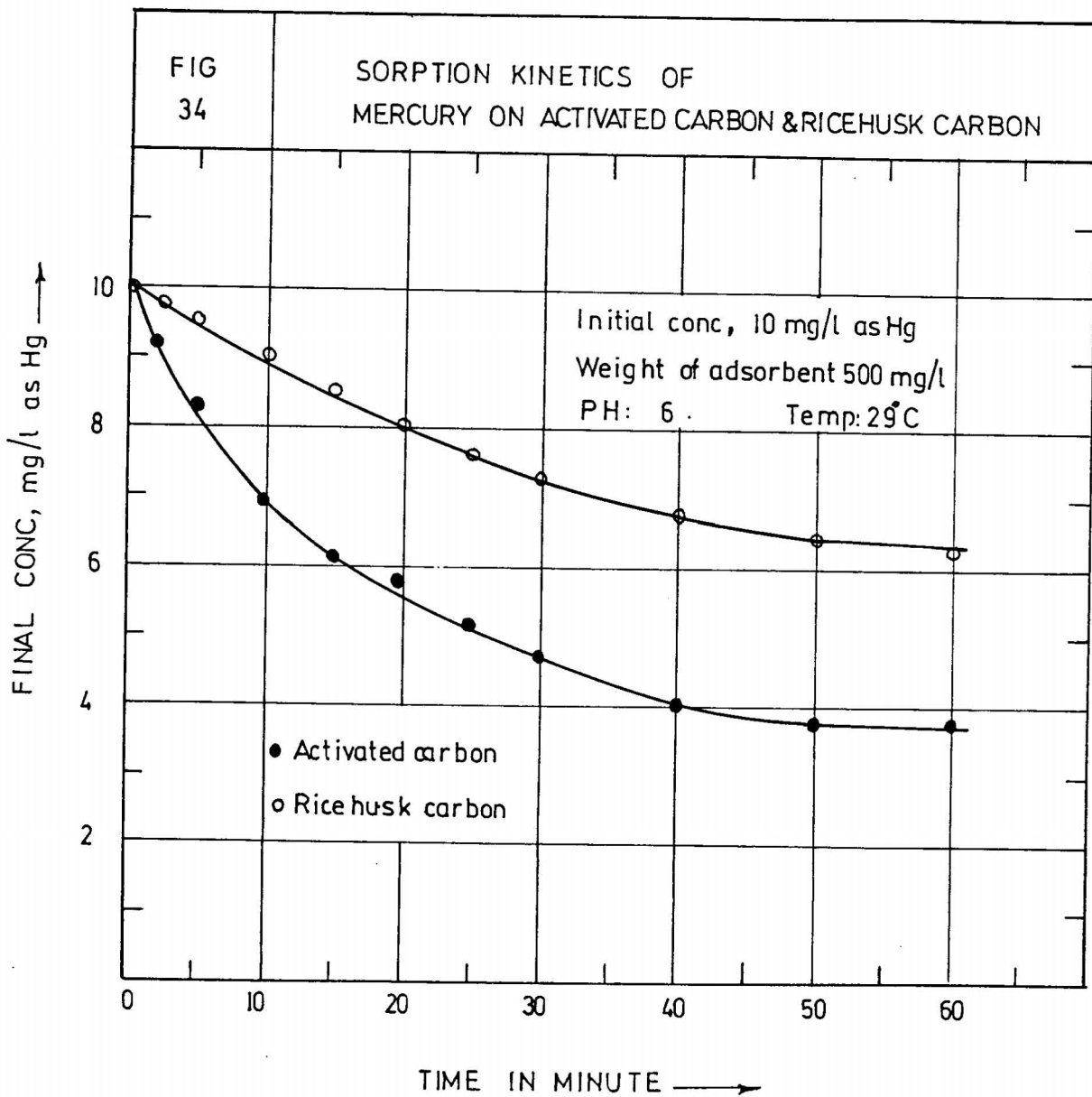


FIG 35

SORPTION KINETICS OF MERCURY ON ACTIVATED CARBON & RICEHUSK CARBON

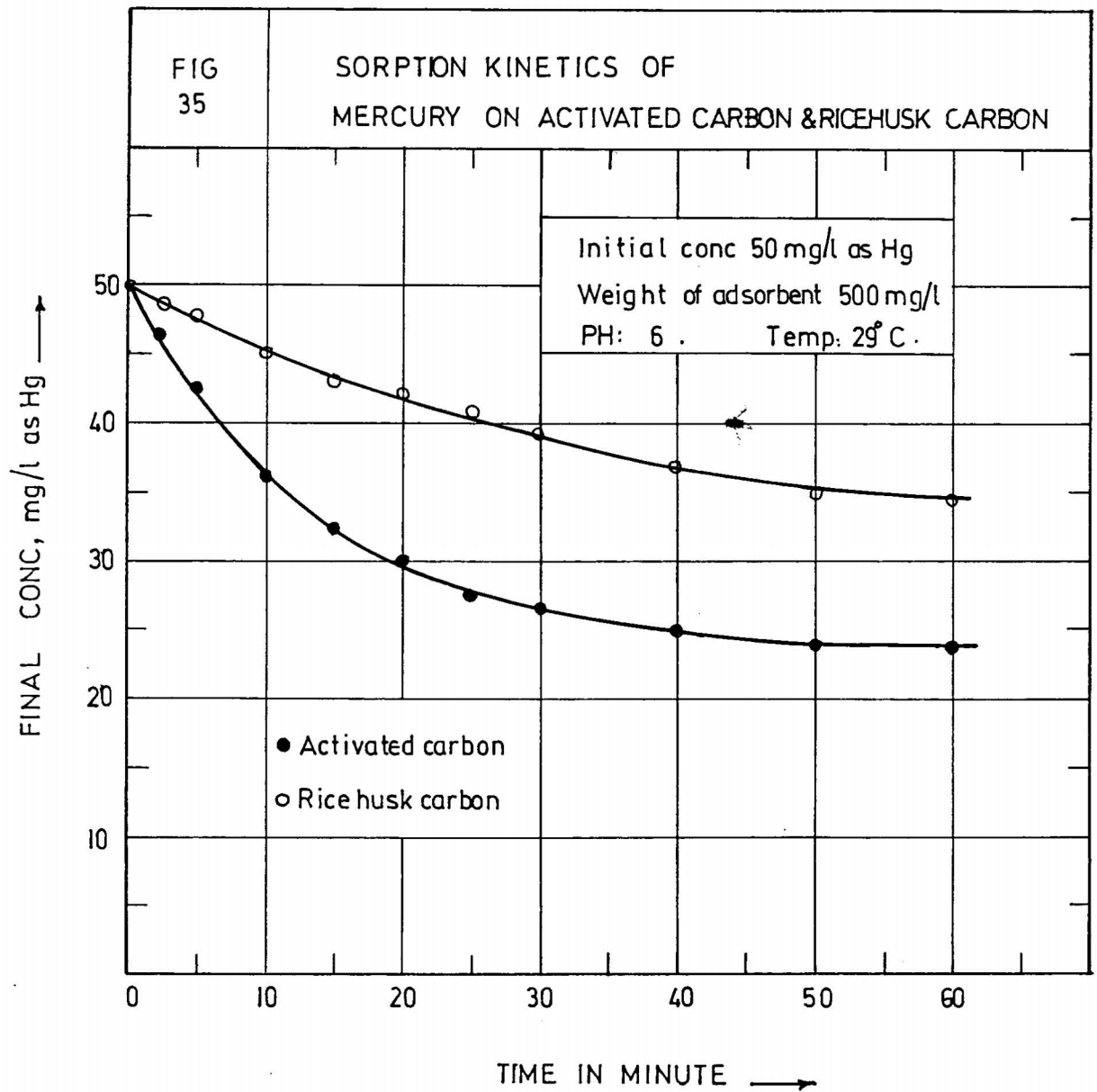
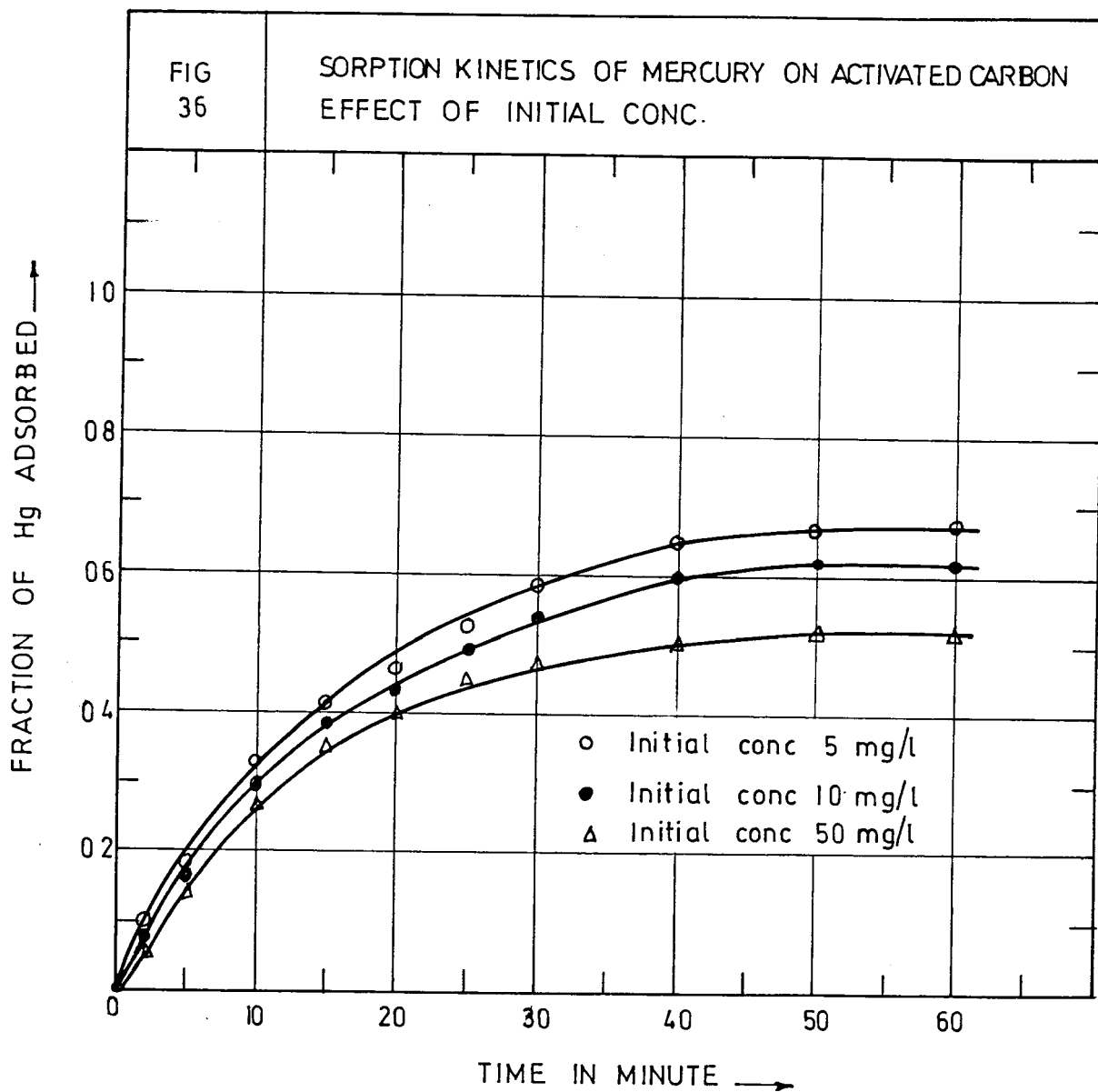


FIG
36

SORPTION KINETICS OF MERCURY ON ACTIVATED CARBON
EFFECT OF INITIAL CONC.



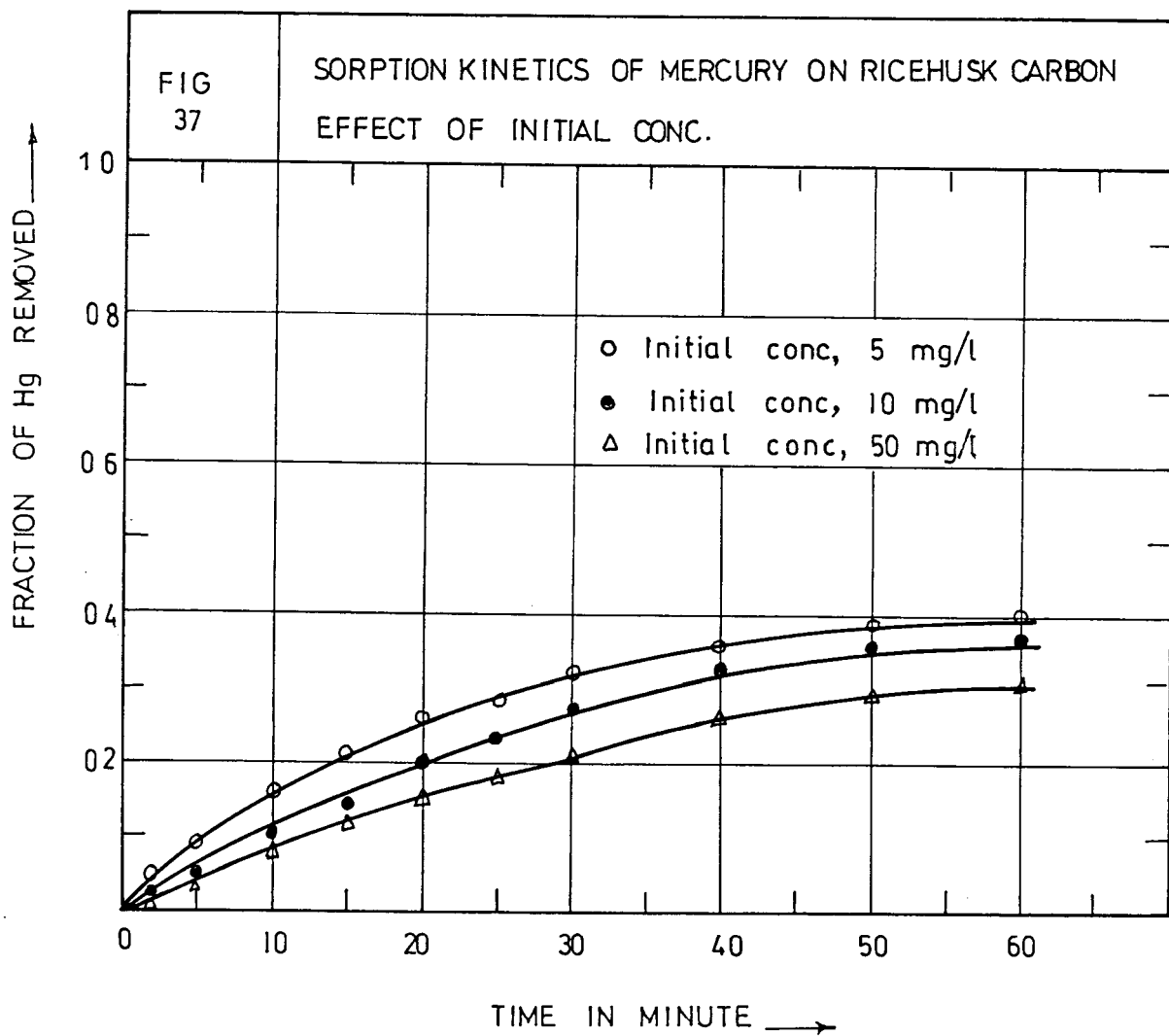


FIG
38

EQUILIBRIUM CHARACTERISTIC OF ACTIVATED
CARBON AGAINST MERCURY

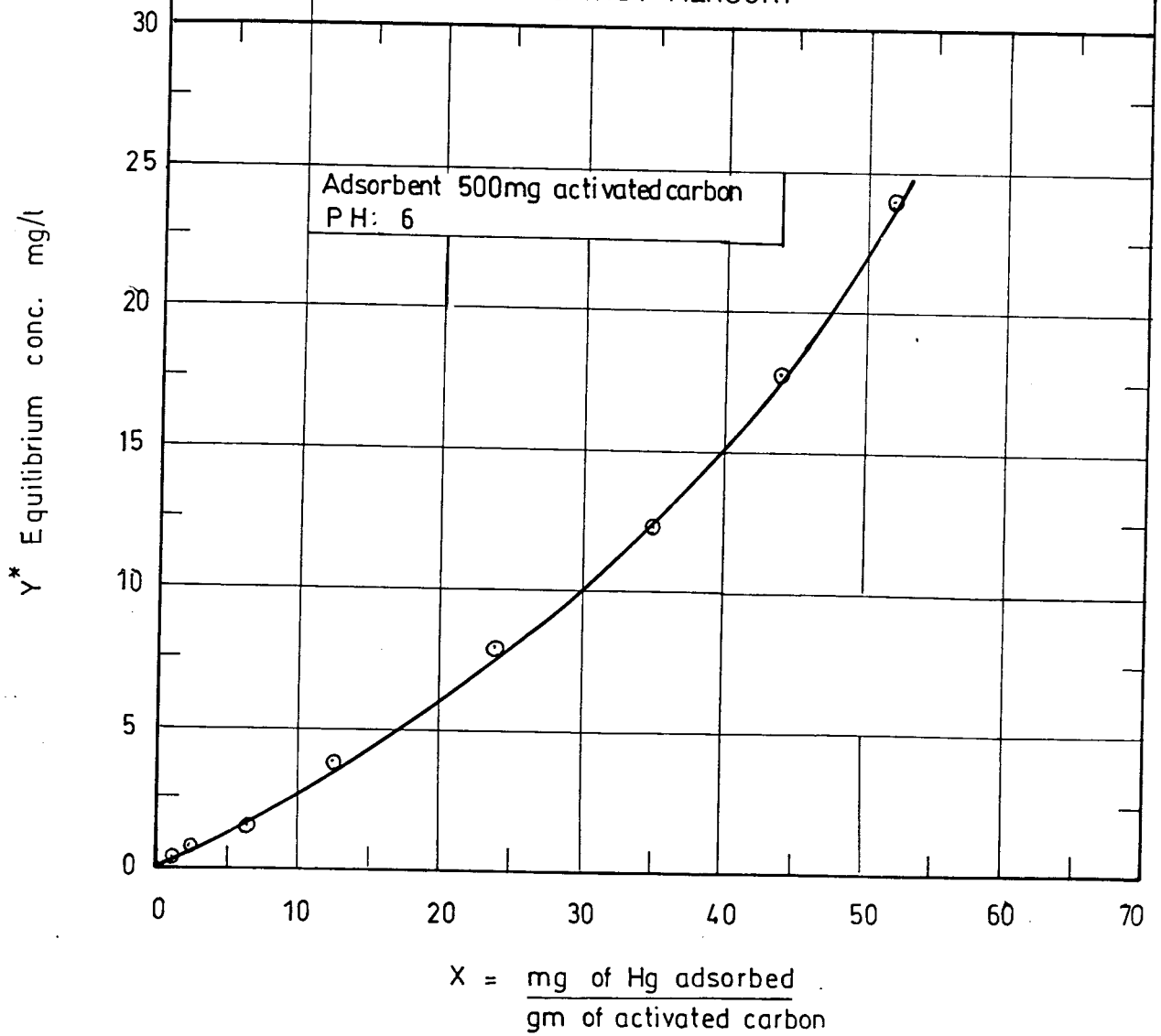


FIG
39

FREUNDLICH ISOTHERM FOR
MERCURY SORPTION ON ACTIVATED CARBON

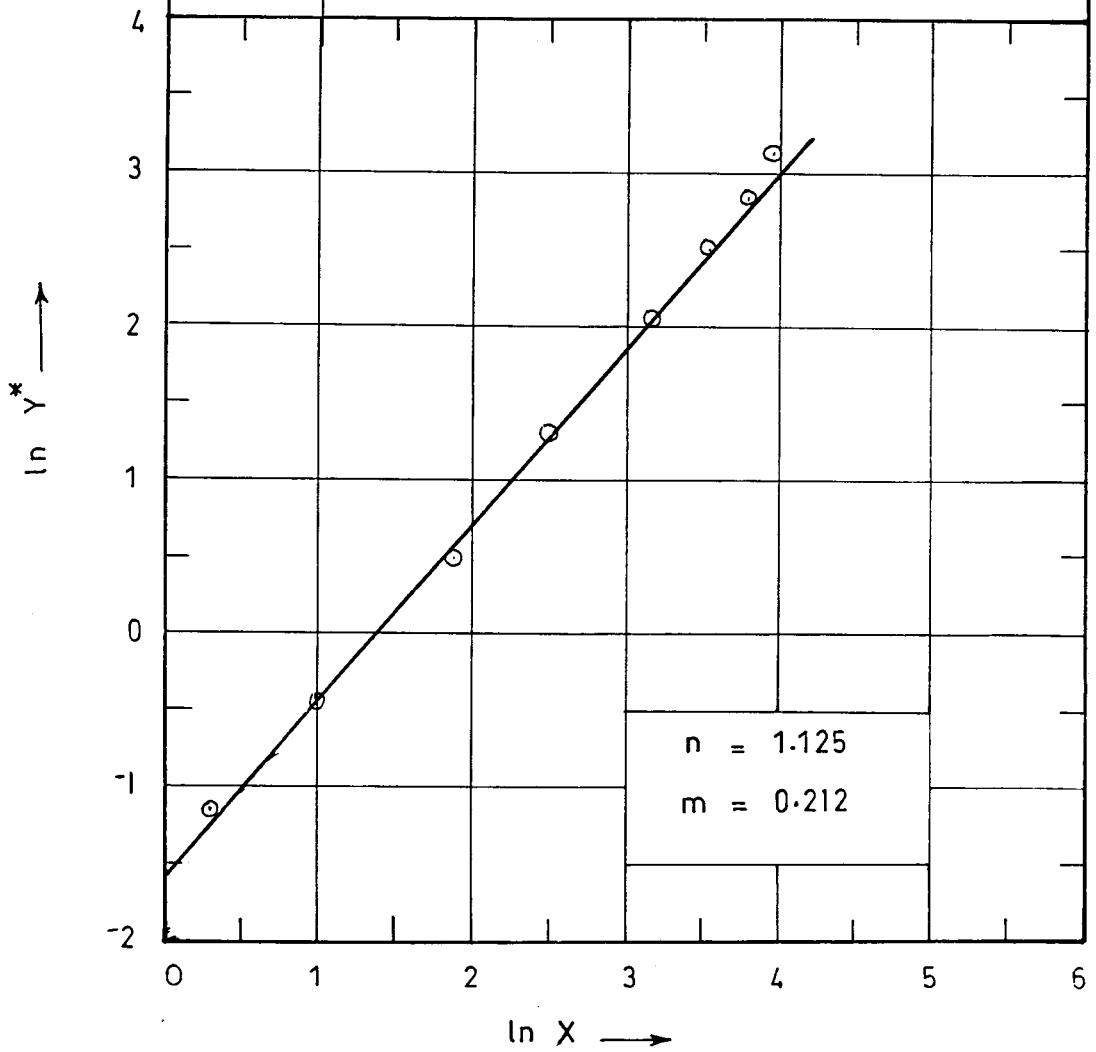


FIG
40

SORPTION KINETICS OF MERCURY ON DOWEX-50

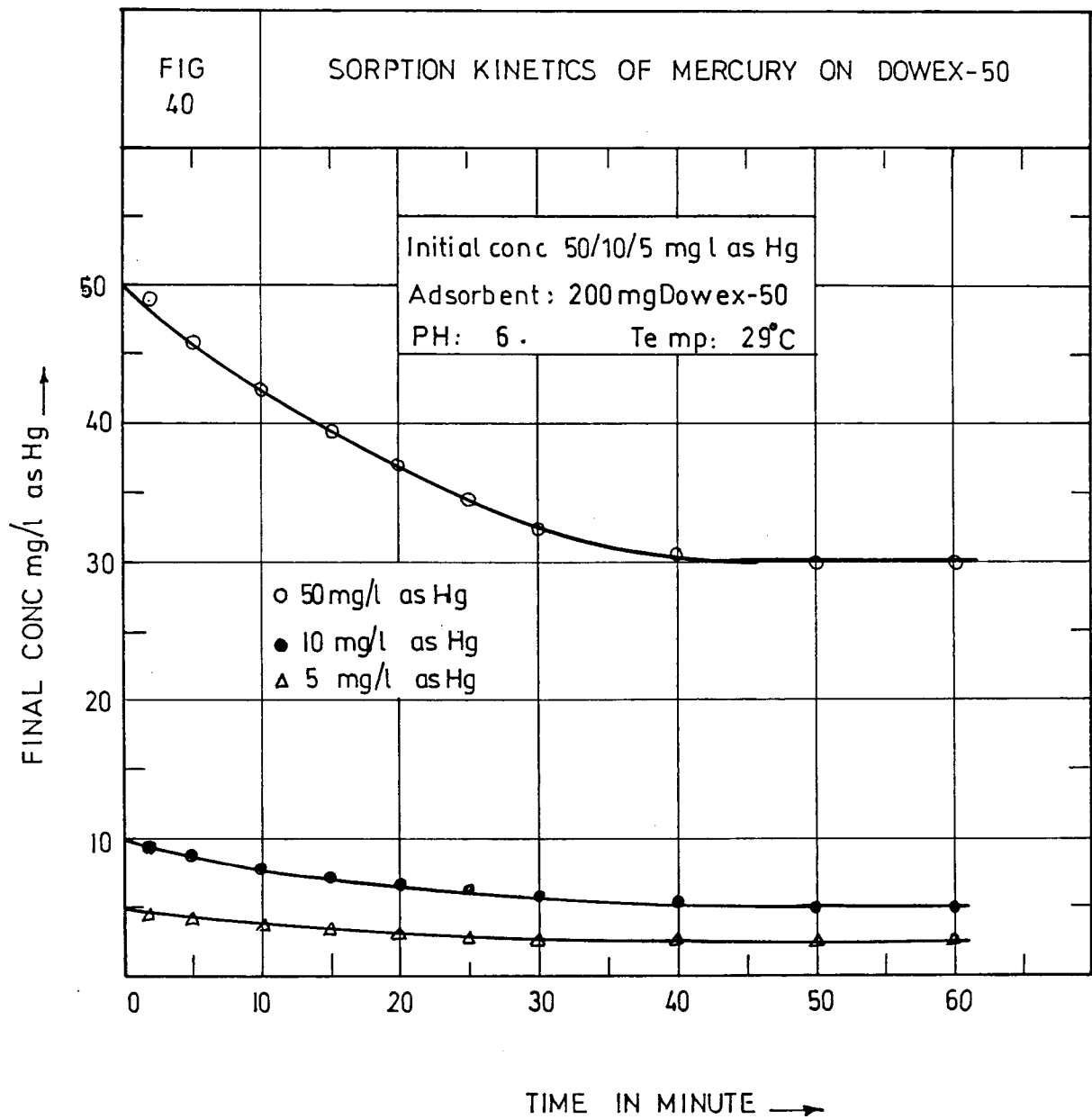


FIG
41

SORPTION KINETICS OF MERCURY ON DOWEX-50
EFFECT OF INITIAL CONC.

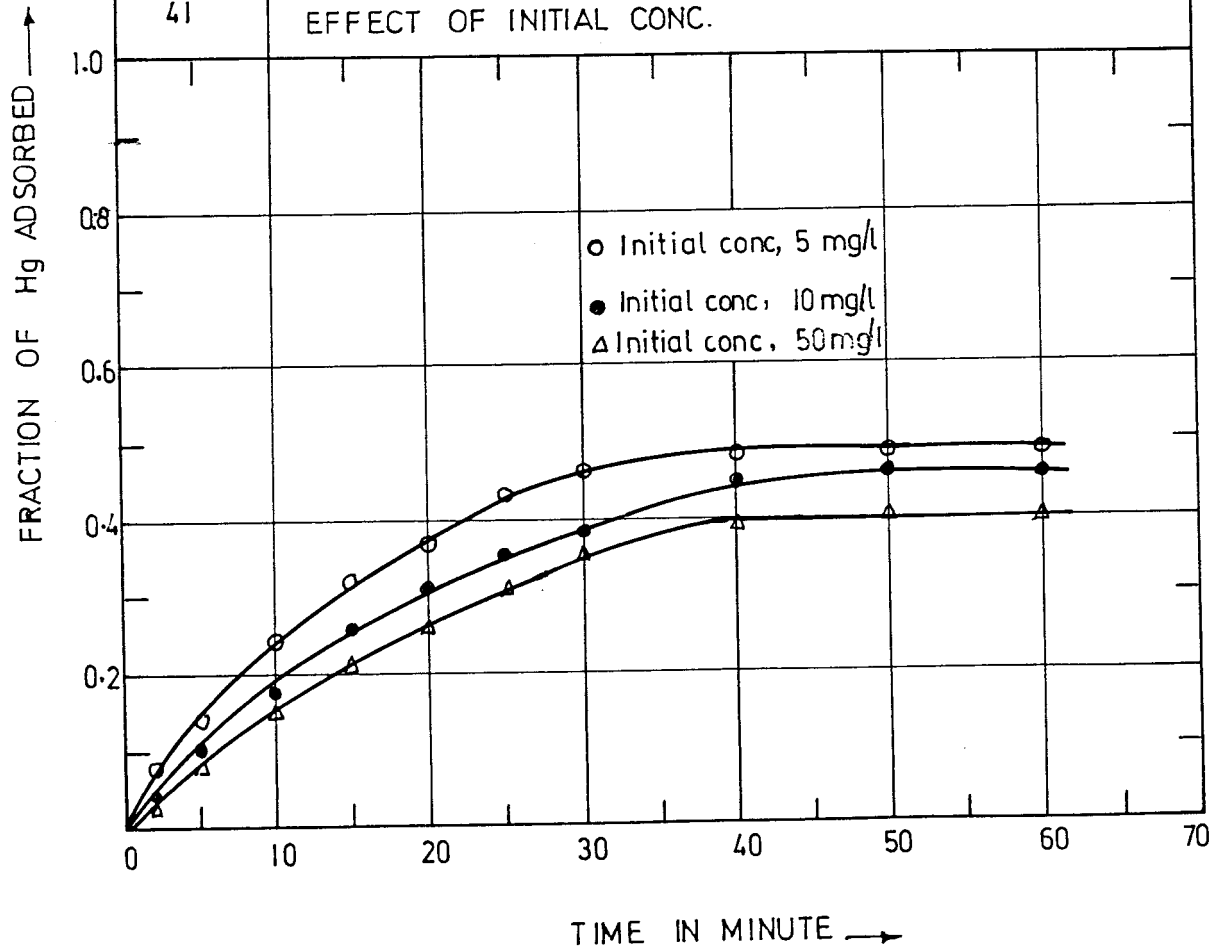


FIG
42

EQUILIBRIUM CHARACTERISTICS OF MERCURY
SORPTION ON DOWEX - 50

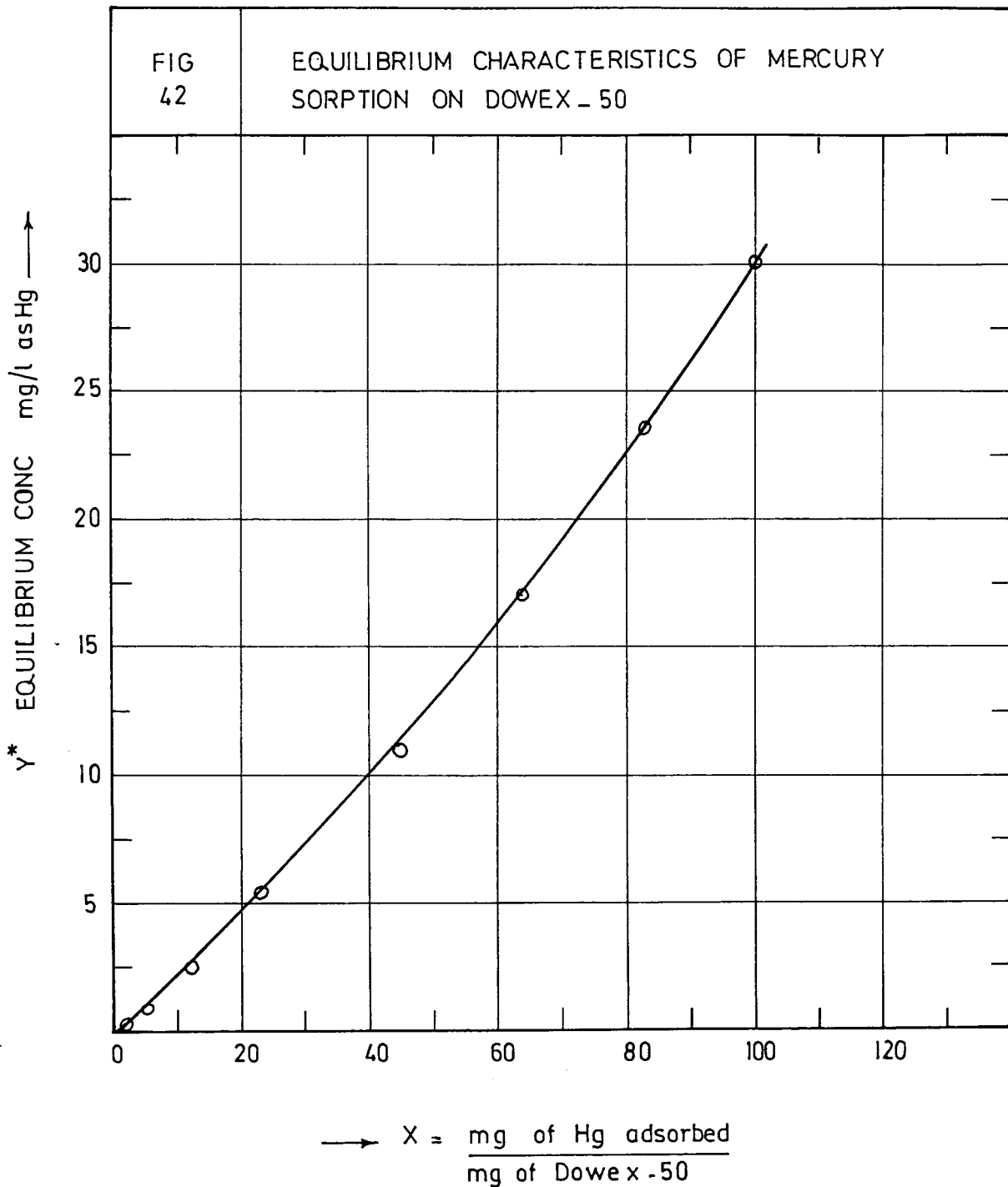


FIG
43

FREUNDLICH ISOTHERM FOR MERCURY
SORPTION ON DOWEX-50

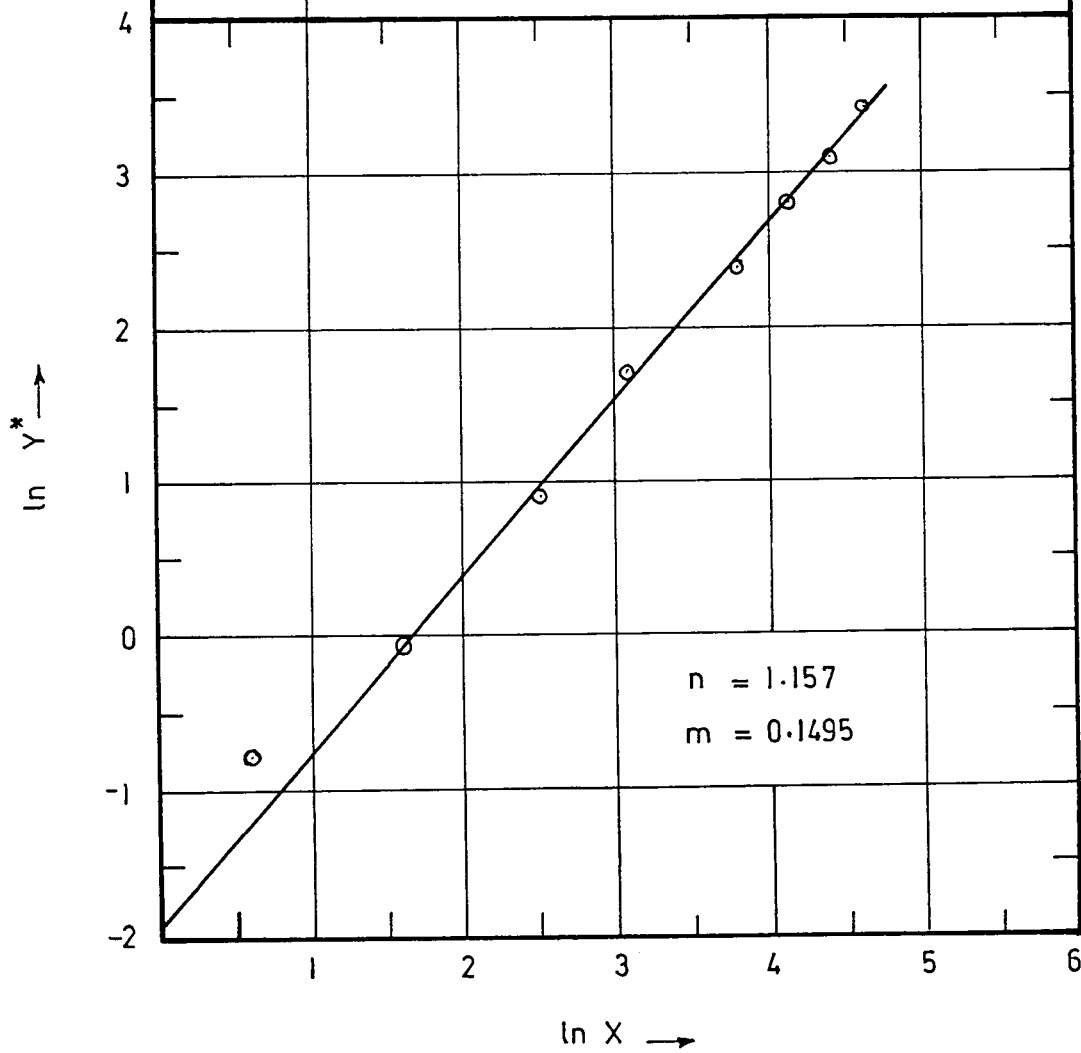
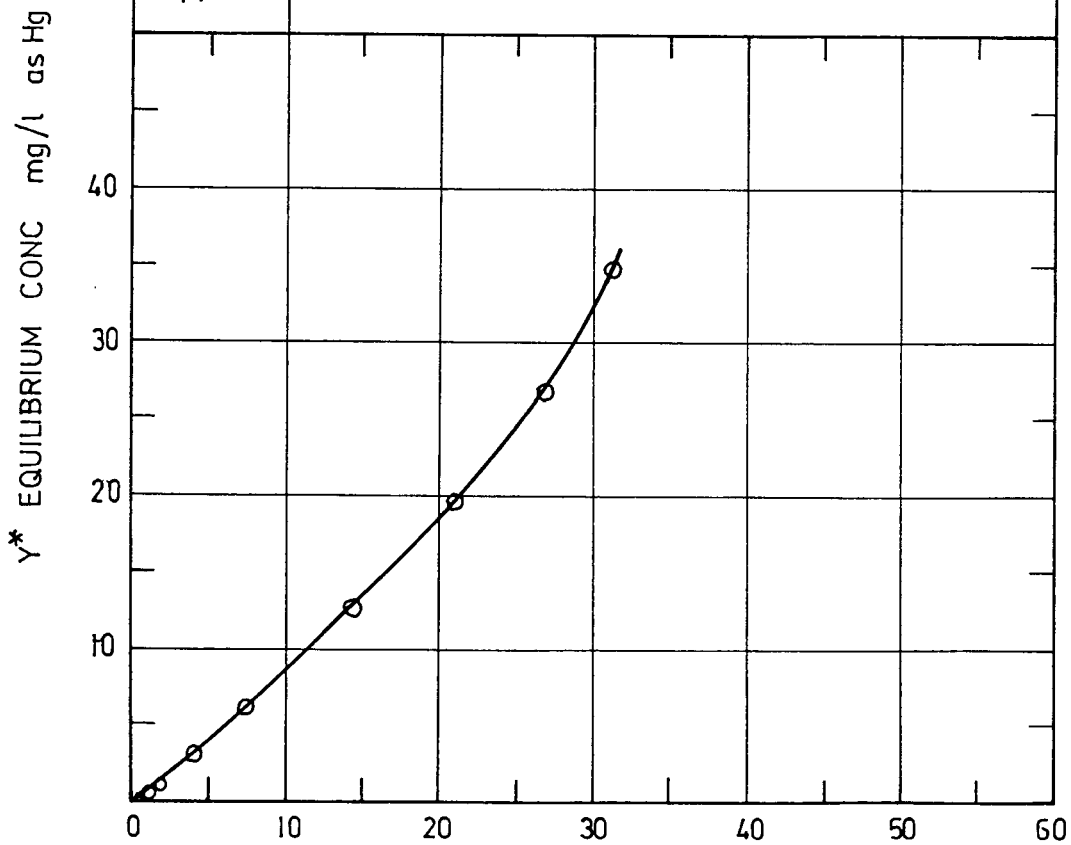


FIG
44

EQUILIBRIUM CHARACTERISTICS OF MERCURY
SORPTION ON RICE HUSK CARBON



→ X = $\frac{\text{mg of Hg adsorbed}}{\text{gm rice husk carbon}}$

FIG
45

FREUNDLICH ISOTHERM FOR
MERCURY SORPTION ON RICEHUSK CARBON

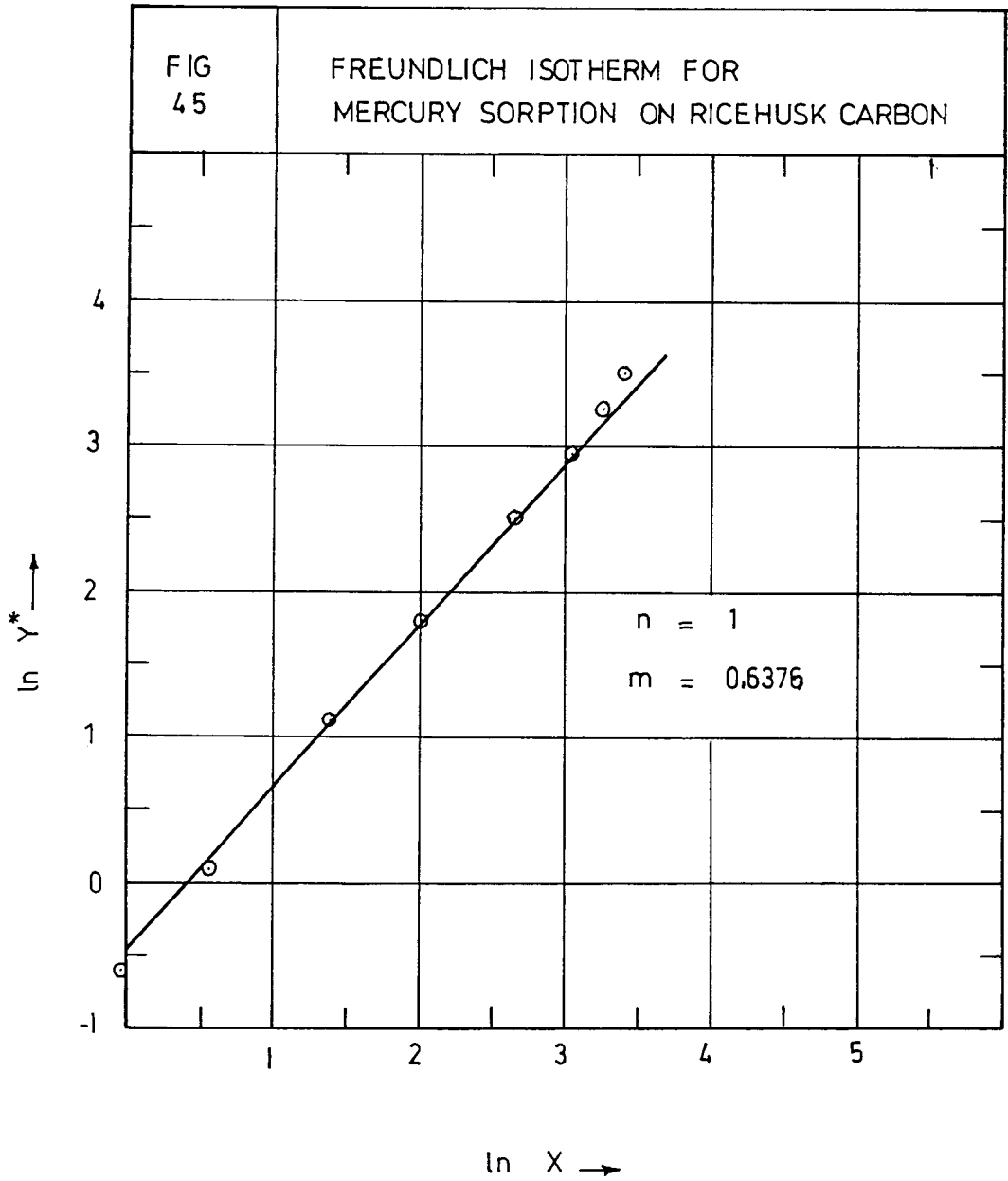


FIG
46

CAPACITY OF CHITOSAN ON
ADSORPTION OF METAL IONS

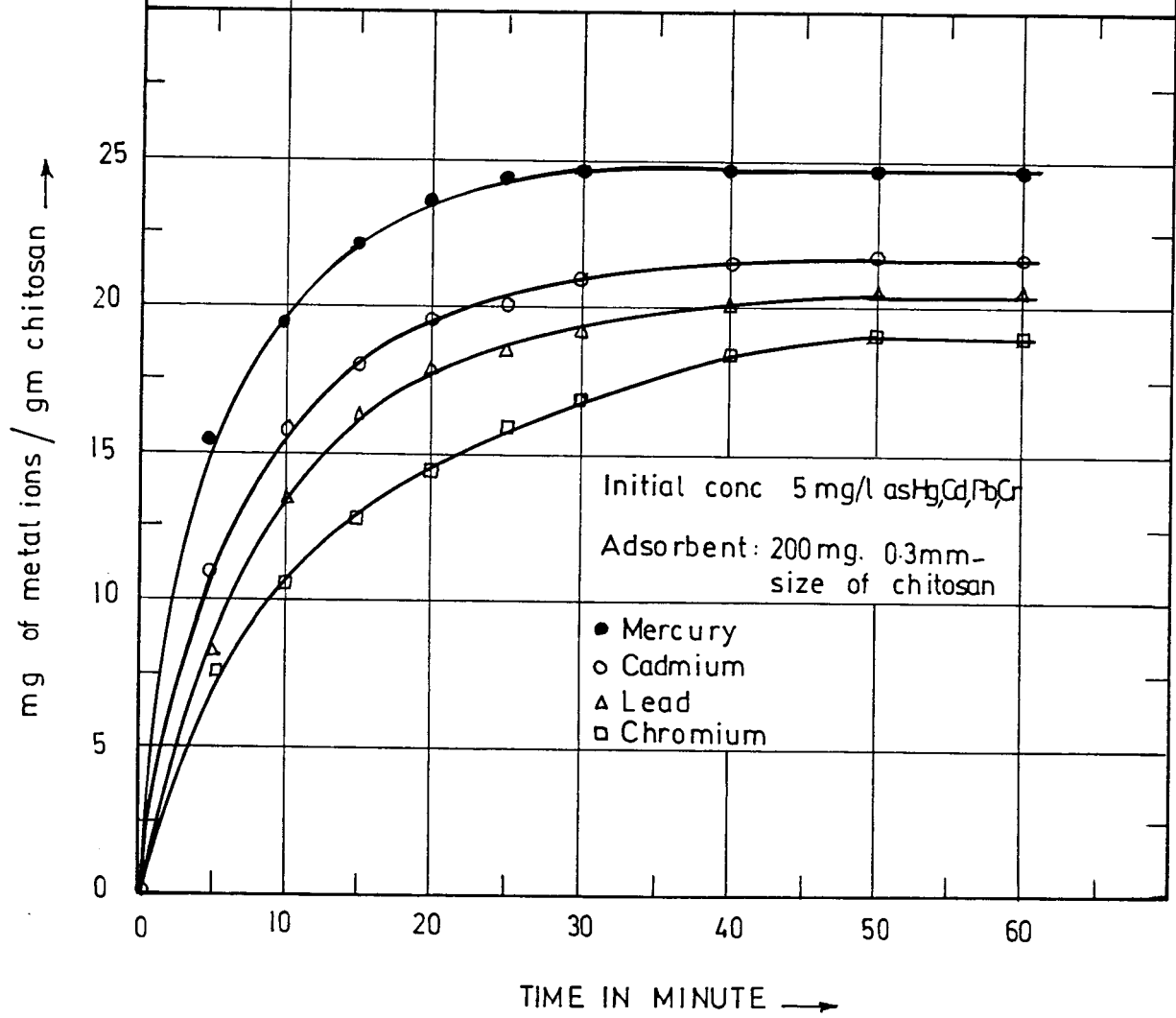
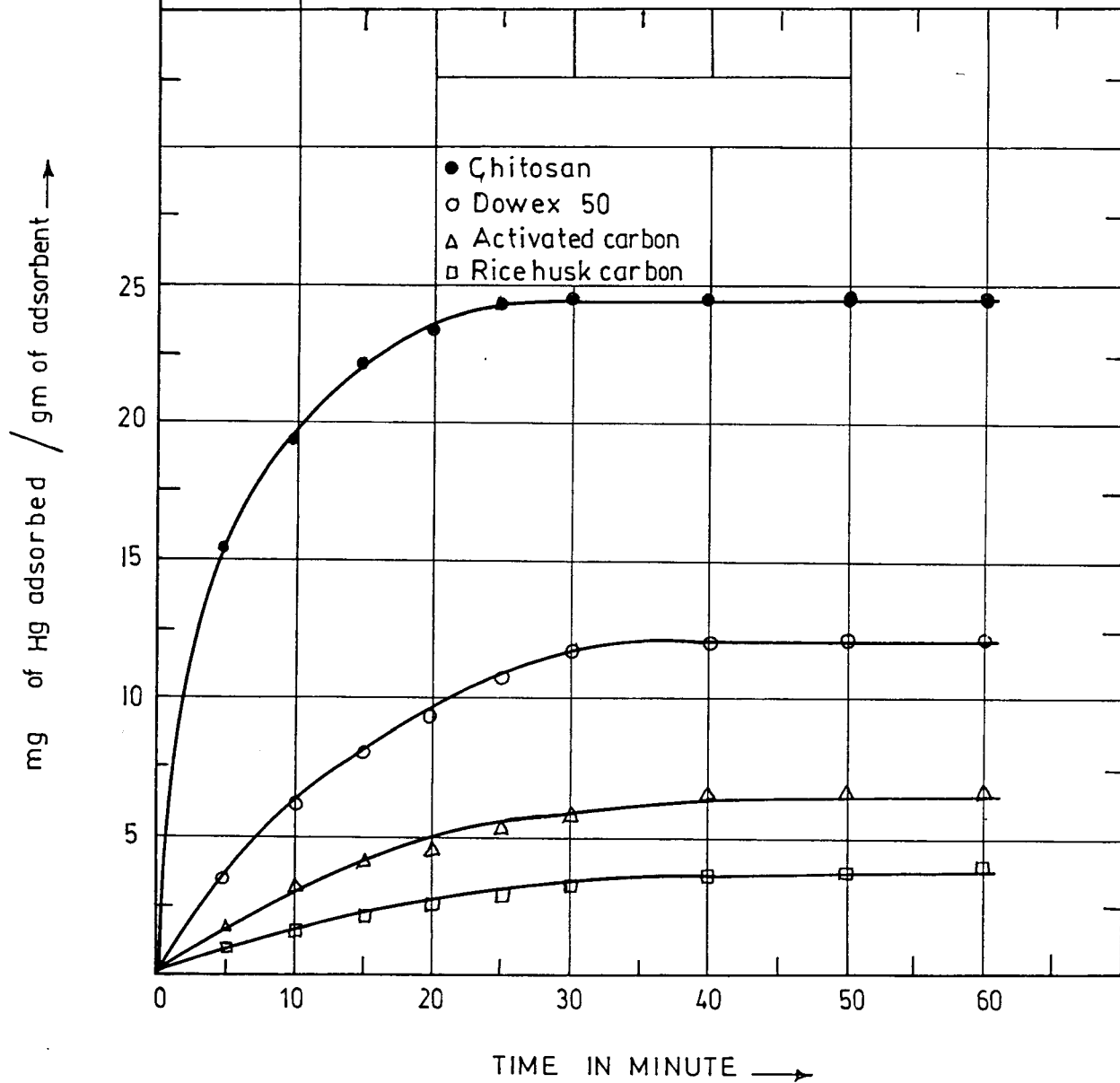


FIG
47

MERCURY SORPTION ON DIFFERENT ADSORBENTS.
INITIAL CONC OF Hg 5mg/l. PH: 6



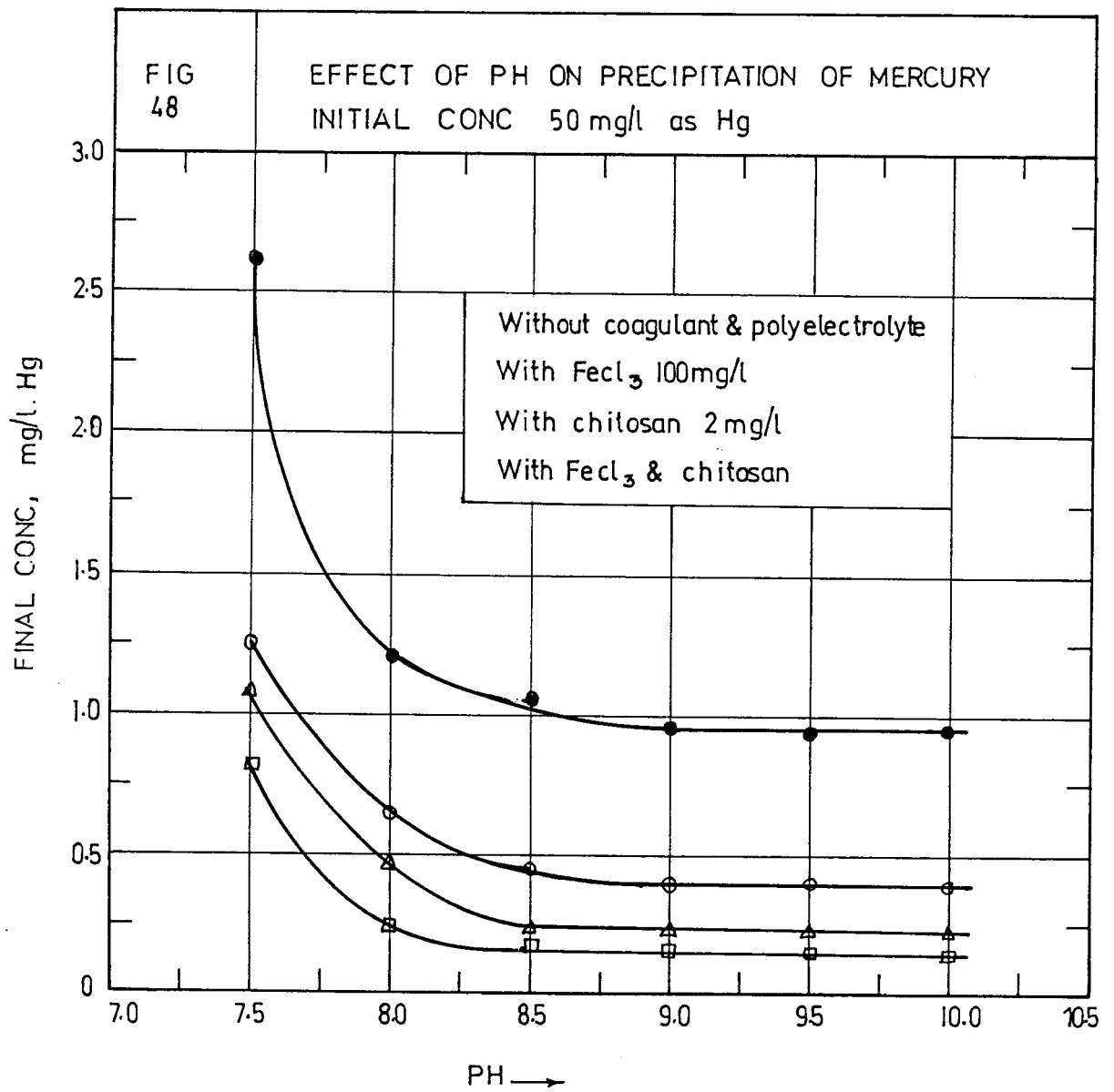
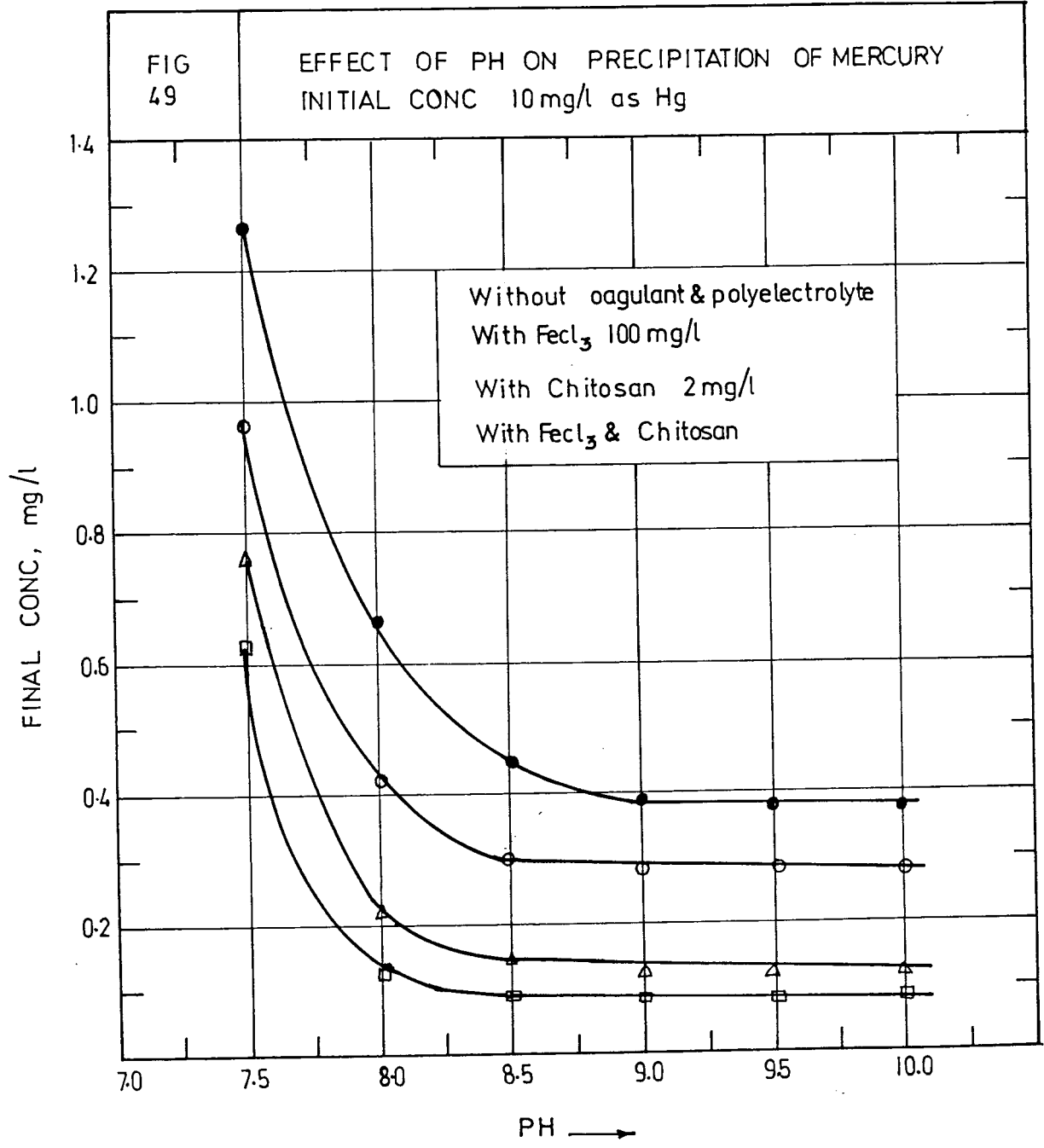


FIG 49

EFFECT OF PH ON PRECIPITATION OF MERCURY
INITIAL CONC 10mg/l as Hg



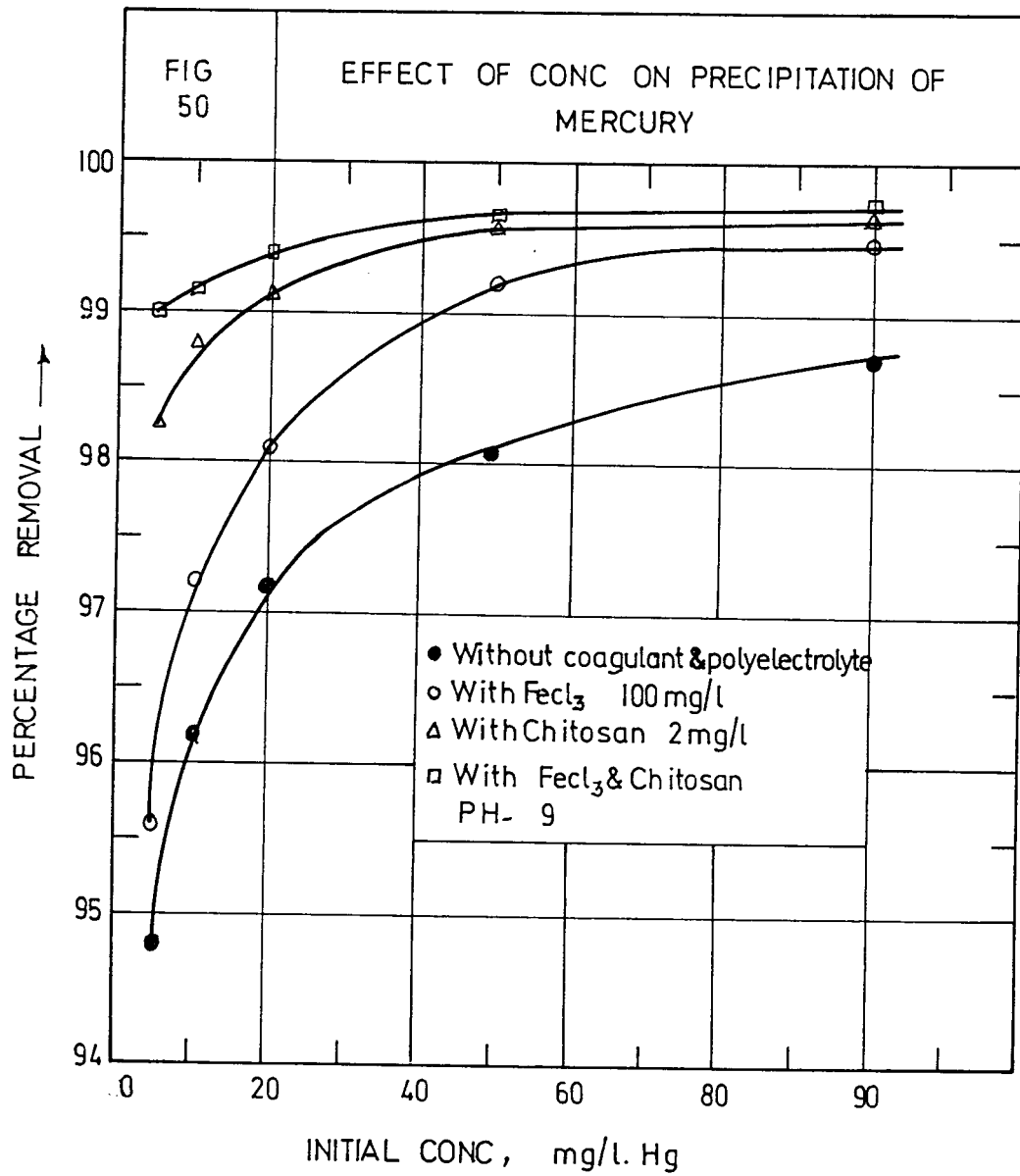


FIG 51

SETTLABILITY OF PRECIPITATED SLUDGE MERCURY

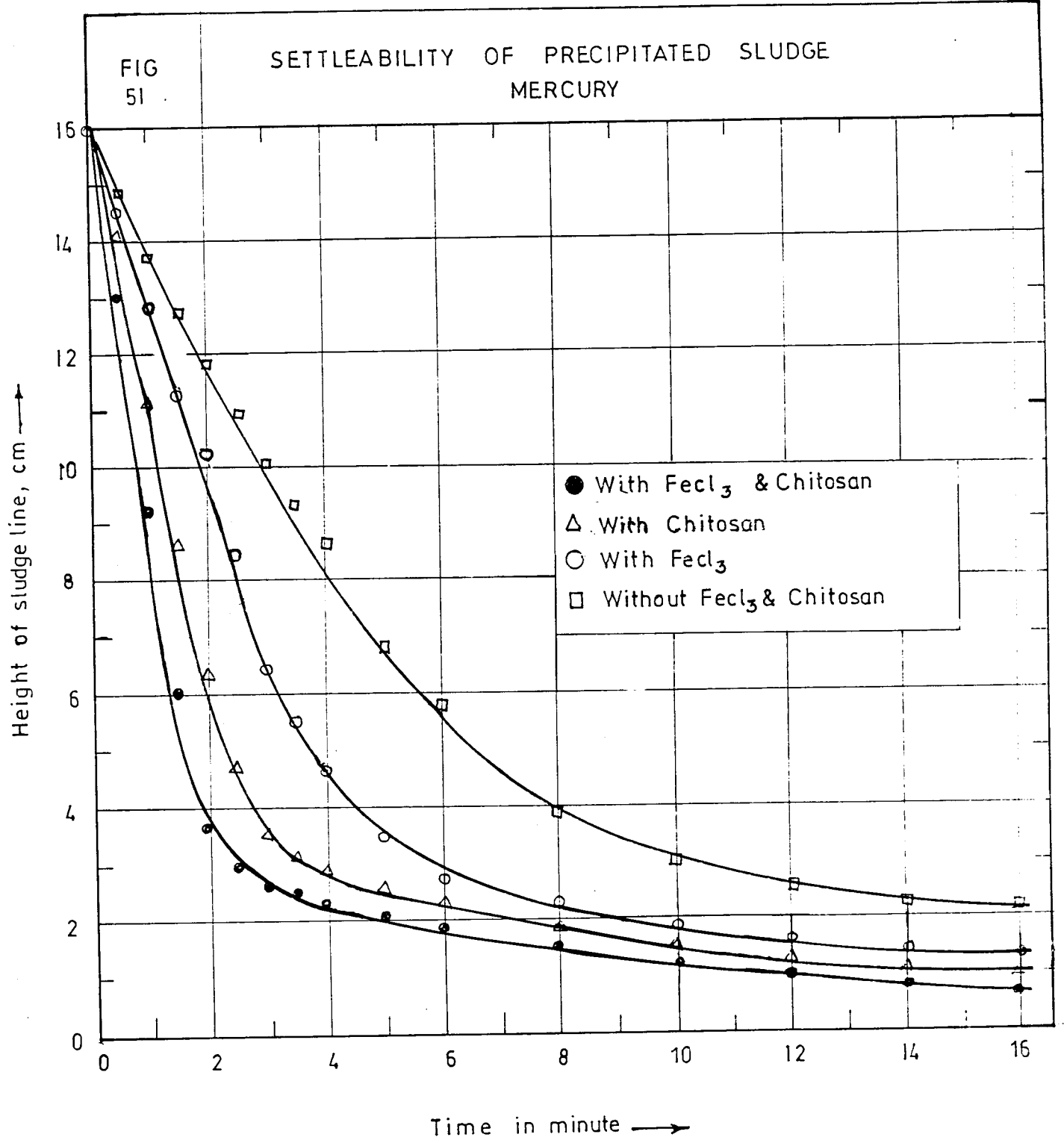


FIG
52

EFFECT OF PH ON PRECIPITATION OF CADMIUM
INITIAL CONC 50 mg/l

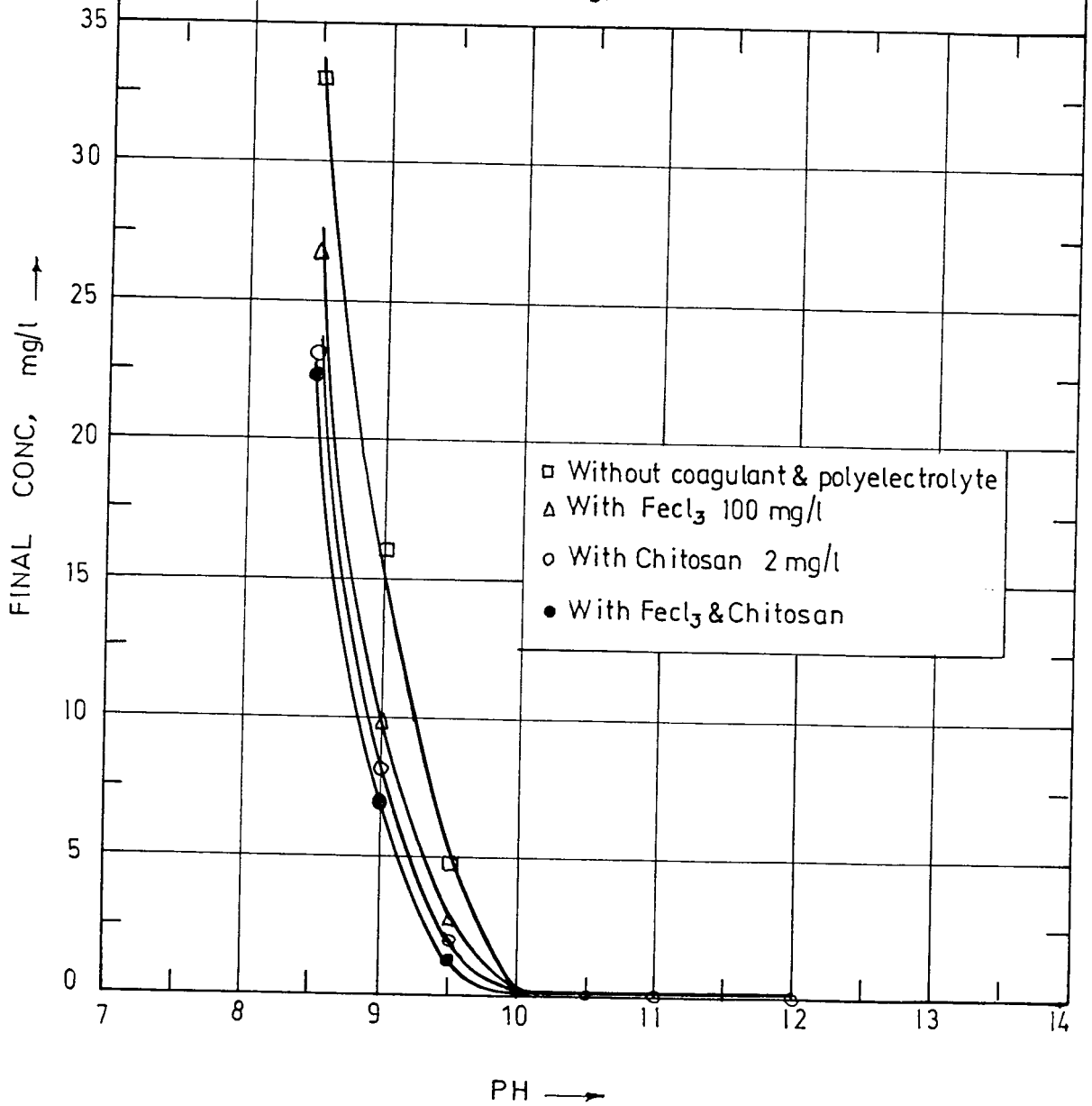


FIG
53

EFFECT OF PH ON PRECIPITATION OF CADMIUM
INITIAL CONC, 10 mg/l

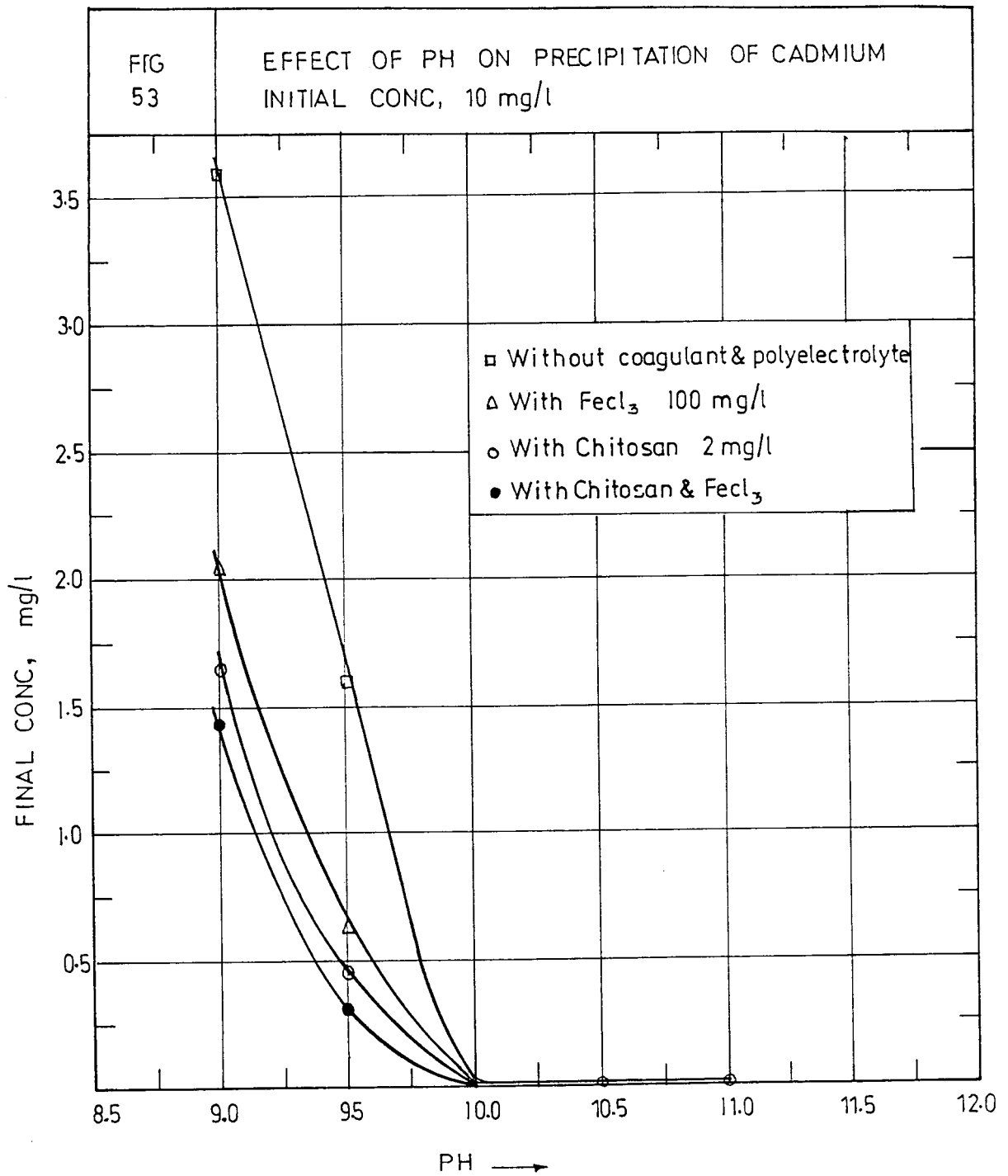


FIG
54

EFFECT OF CONC. ON PRECIPITATION
OF CADMIUM

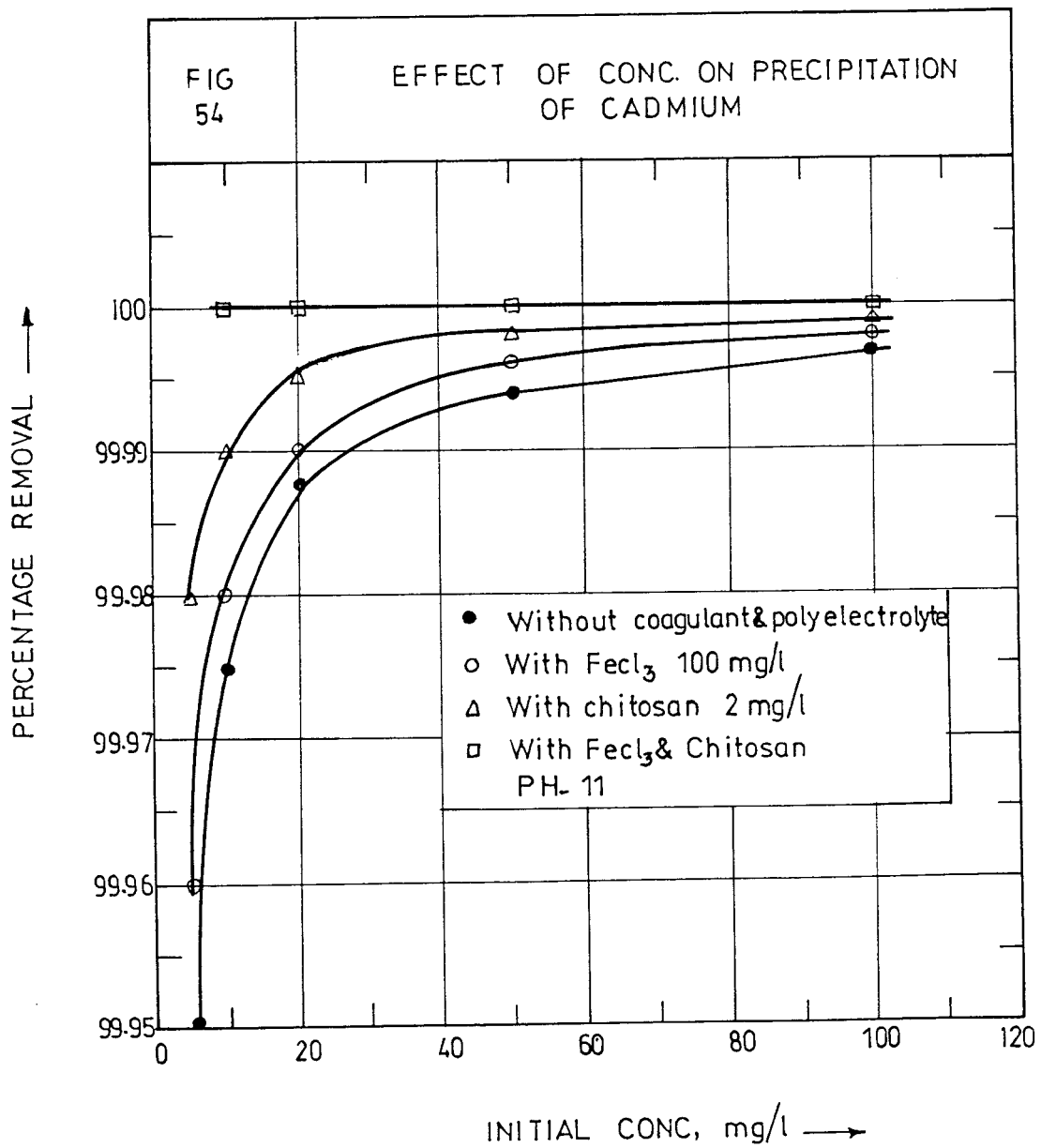


FIG
55

SETTLEABILITY OF PRECIPITATED SLUDGE
CADMIUM

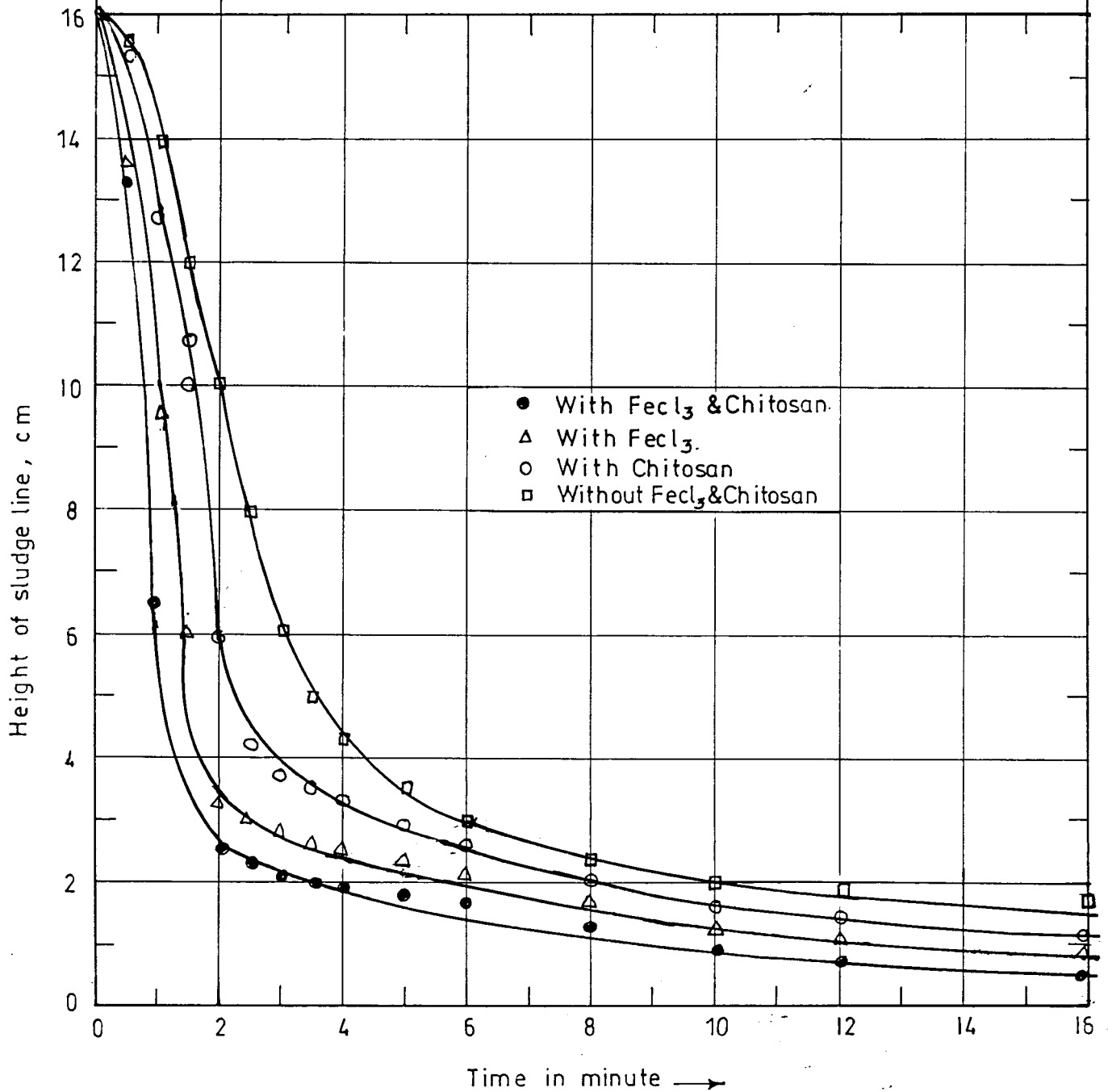
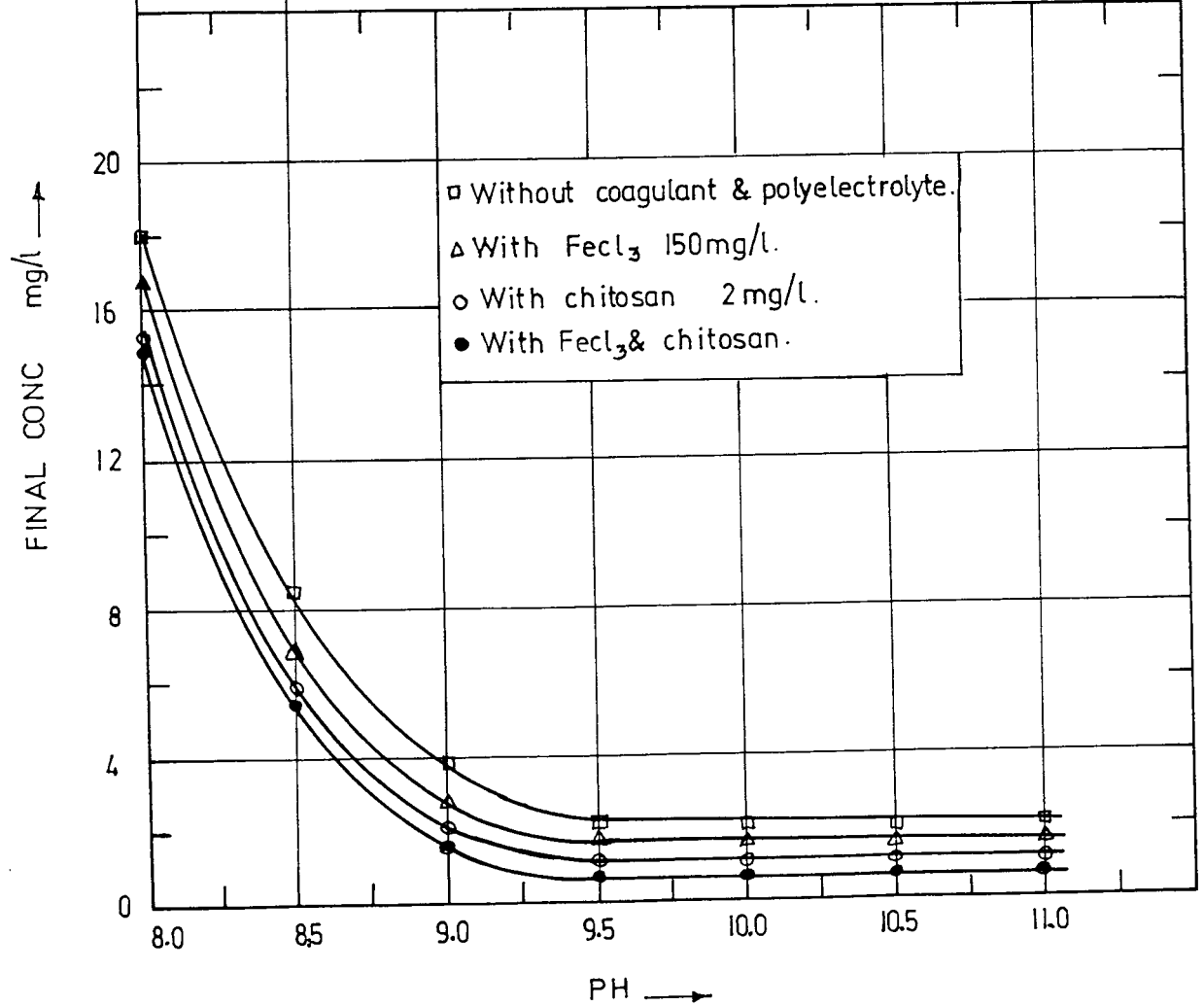


FIG 56

EFFECT OF PH ON PRECIPITATION OF LEAD
INITIAL CONC, 50 mg/l



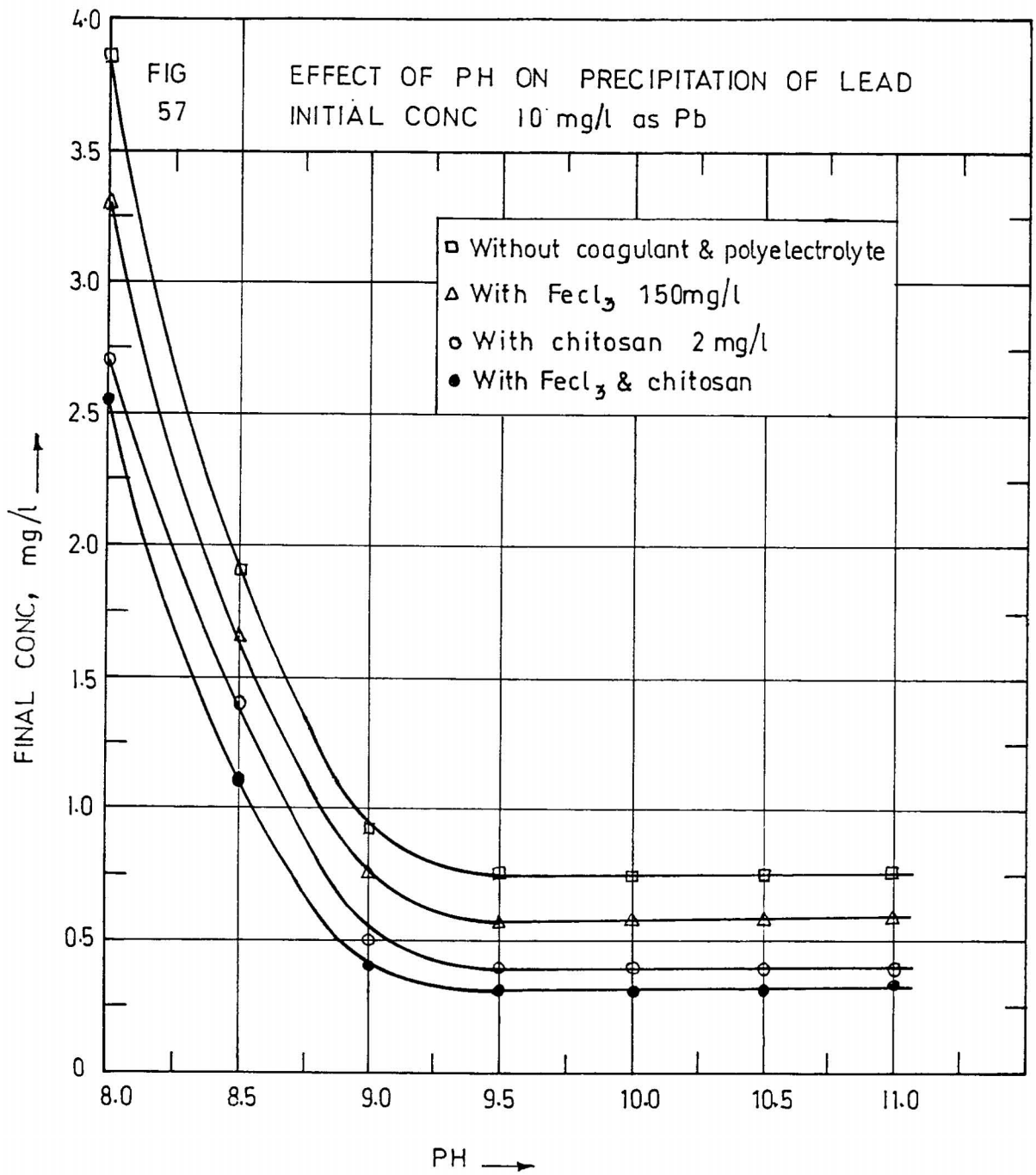


FIG 58

EFFECT OF CONC ON PRECIPITATION OF LEAD

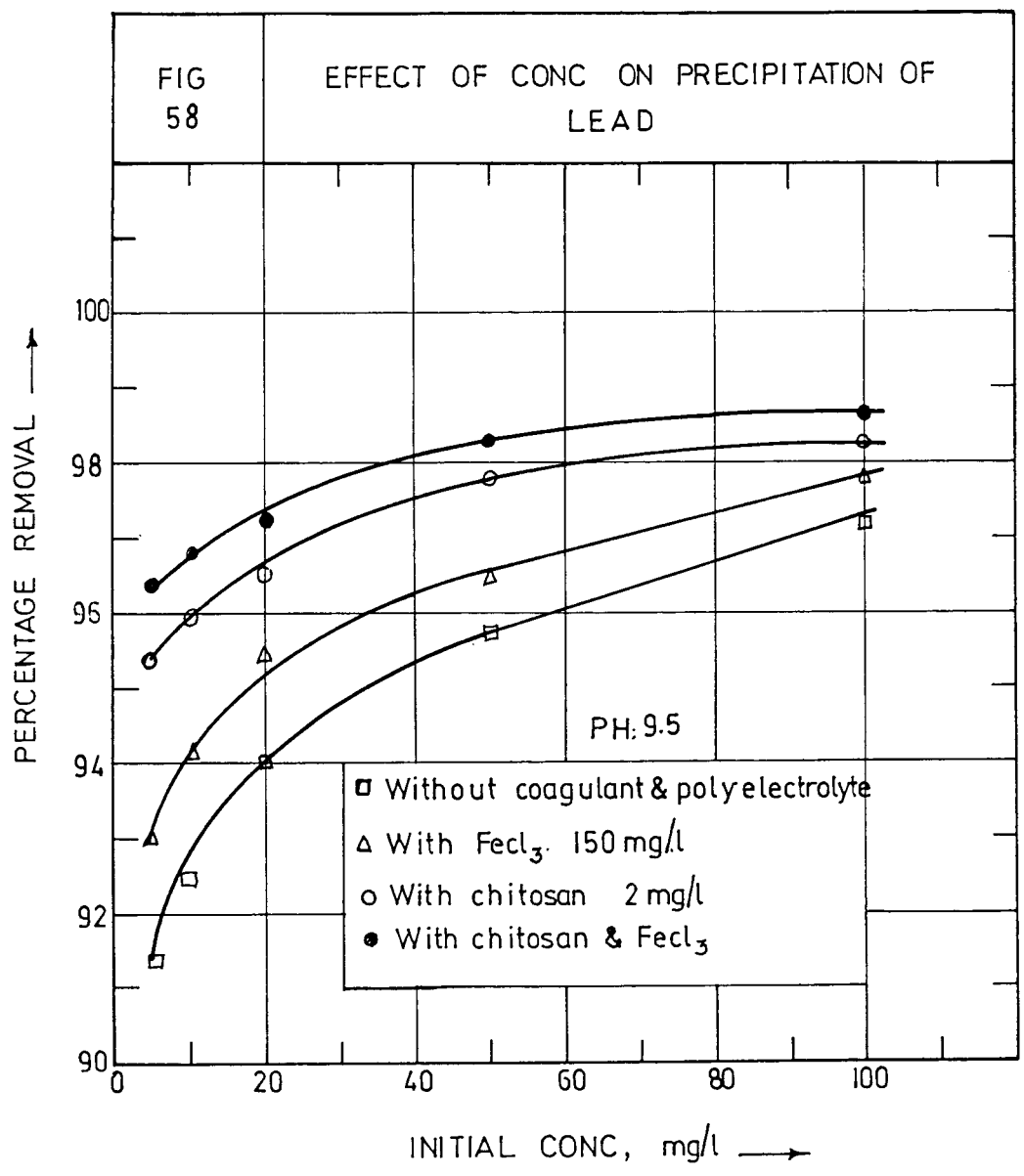
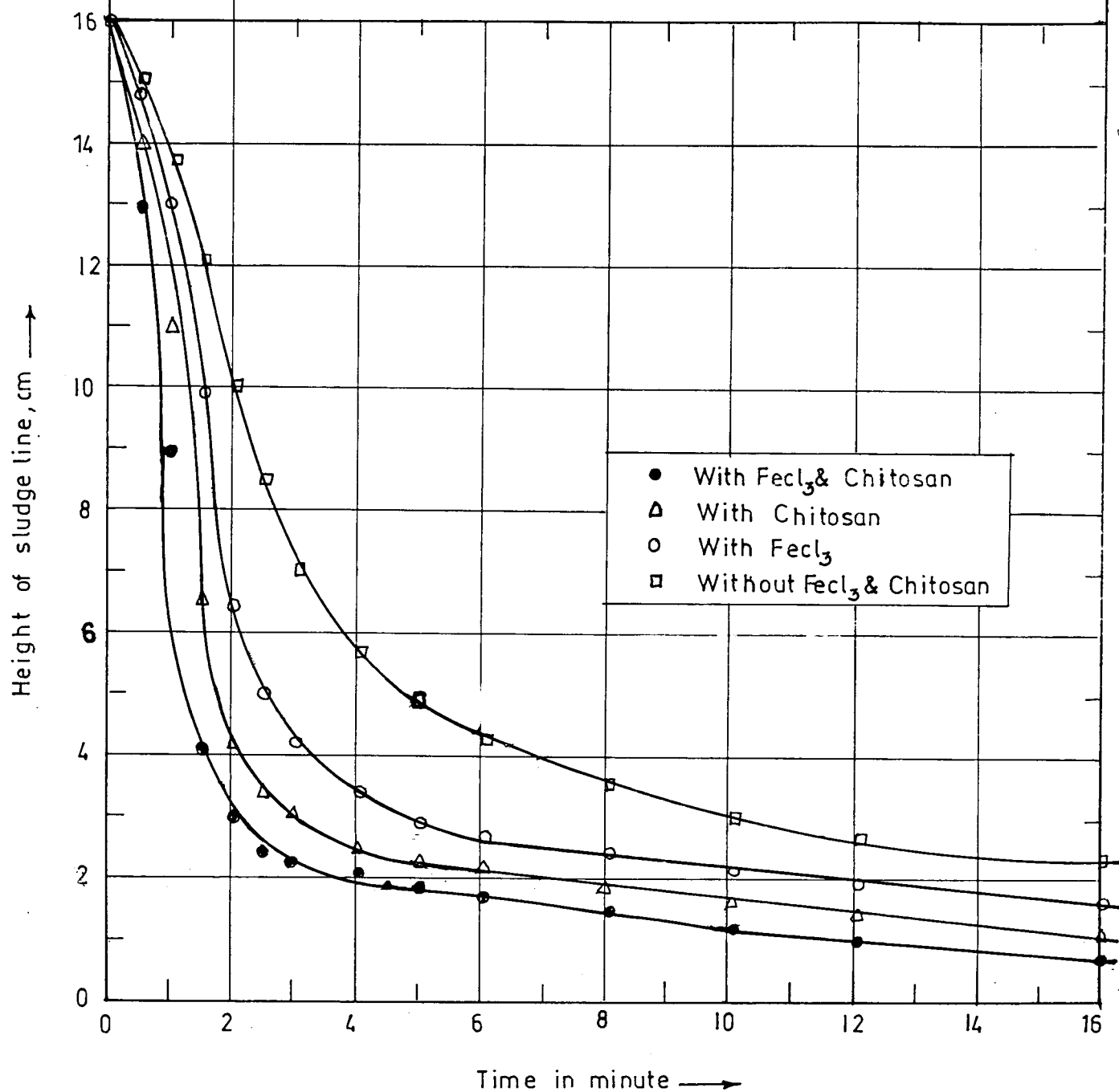
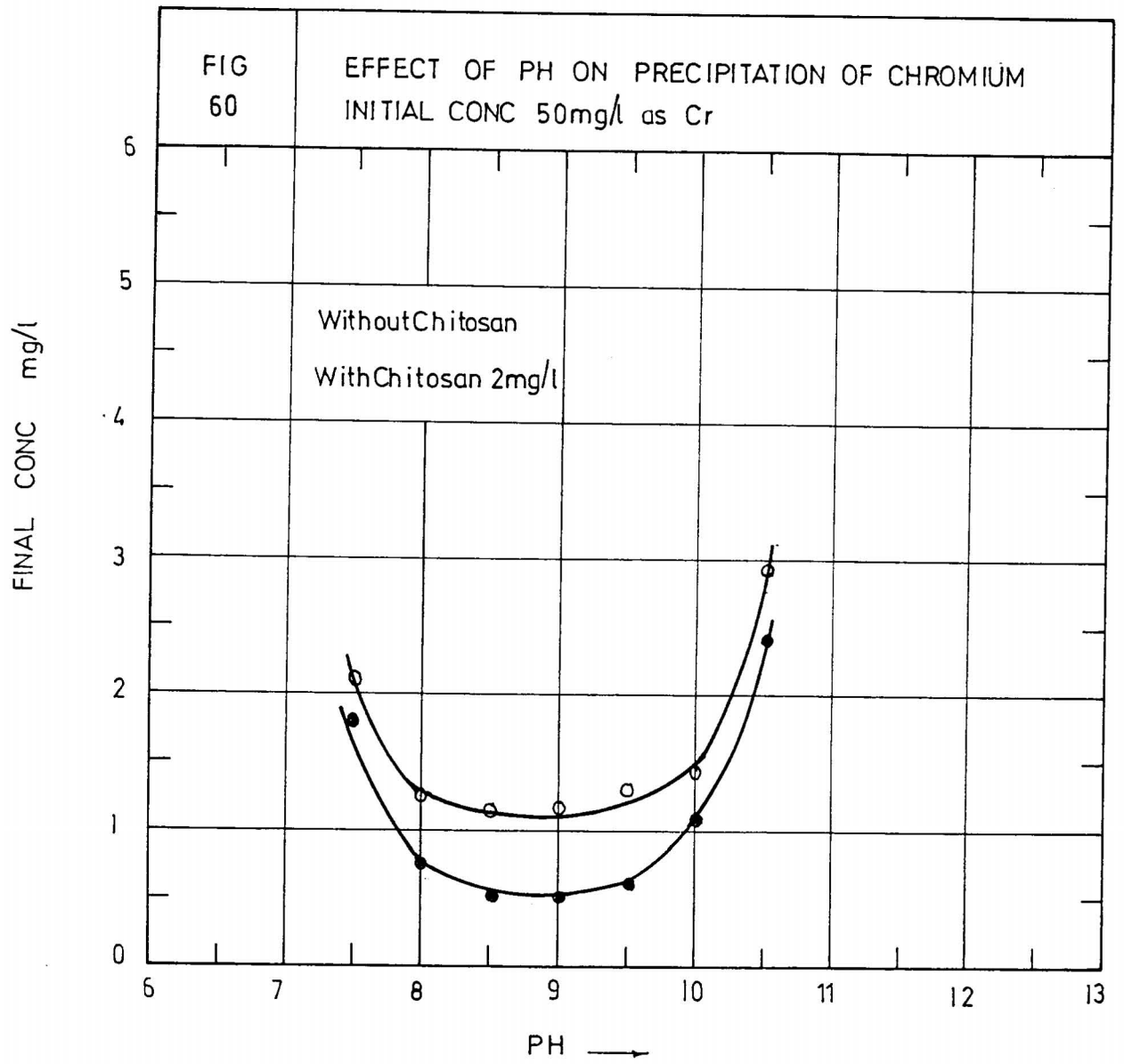


FIG 59

SETTLABILITY OF PRECIPITATED SLUDGE LEAD





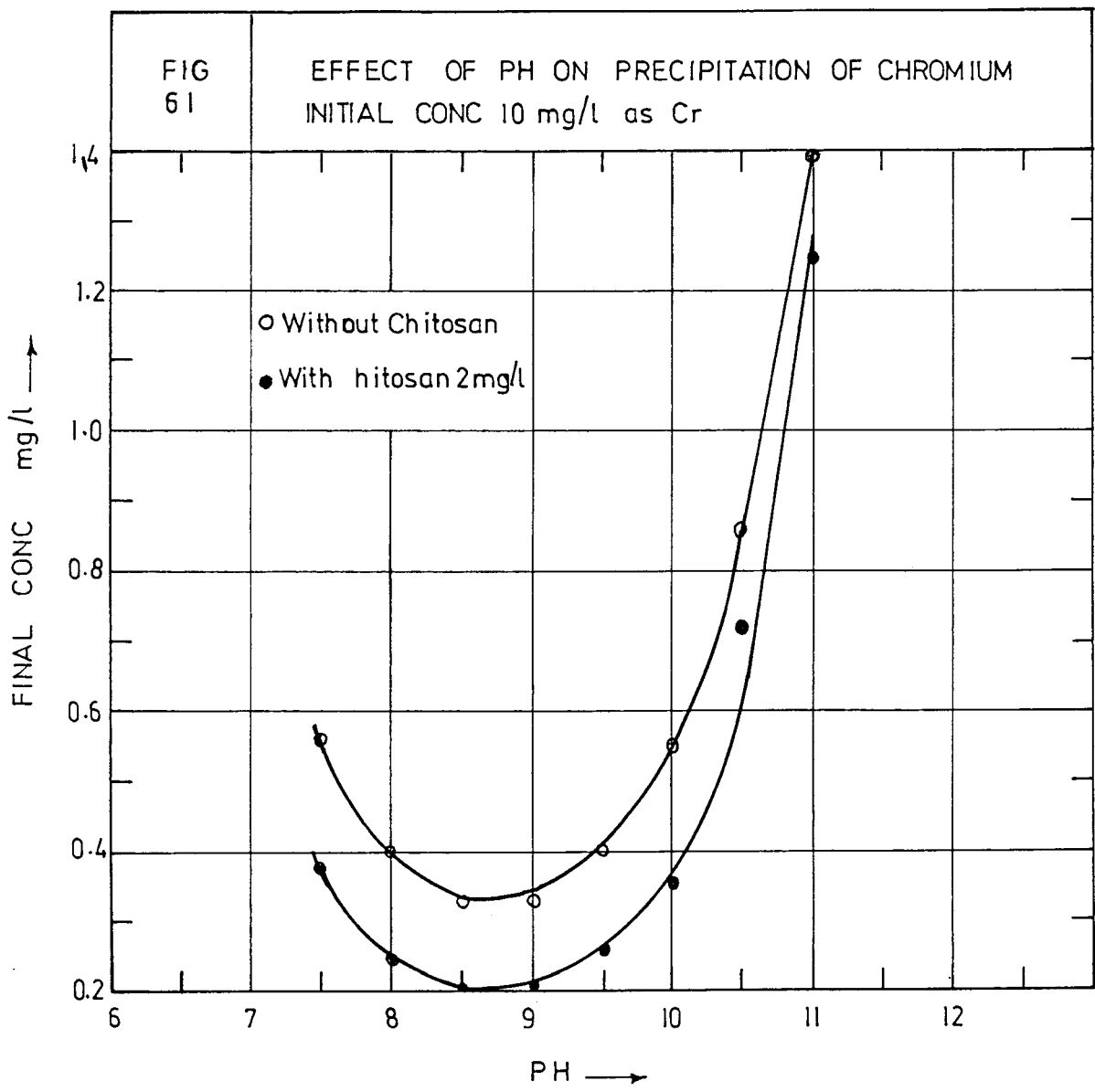


FIG
62

EFFECT OF CONC ON PRECIPITATION OF
CHROMIUM

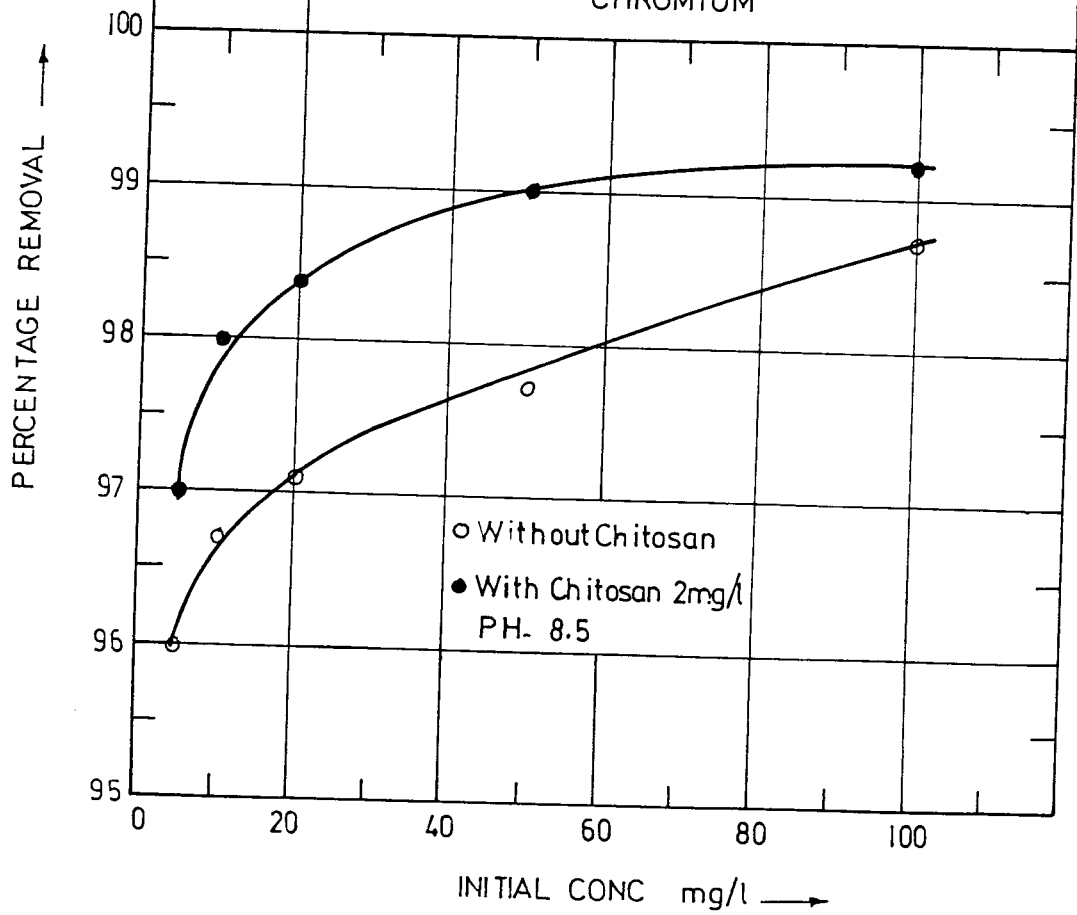


FIG
63

SETTLEABILITY OF PRECIPITATED SLUDGE
CHROMIUM

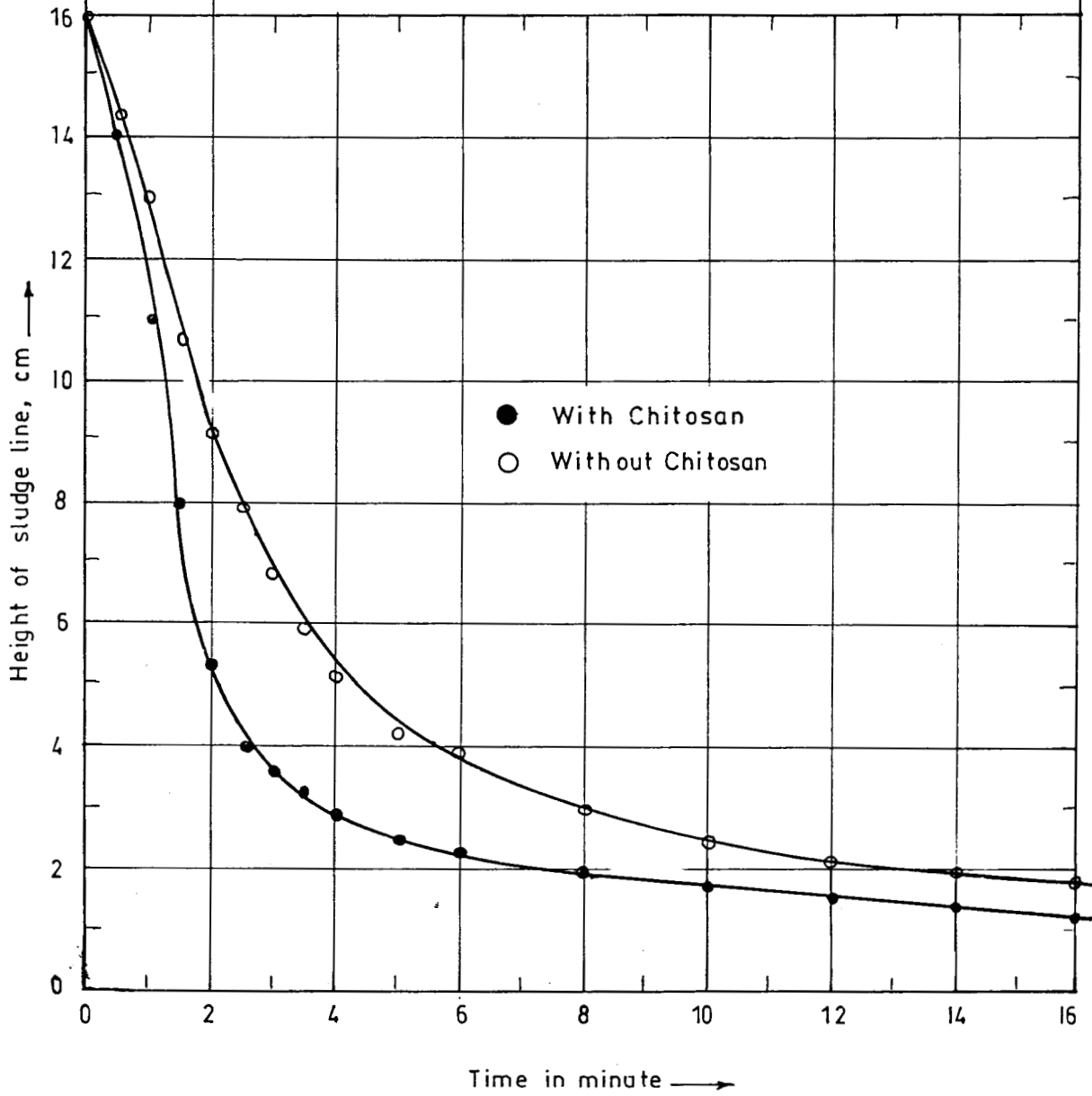
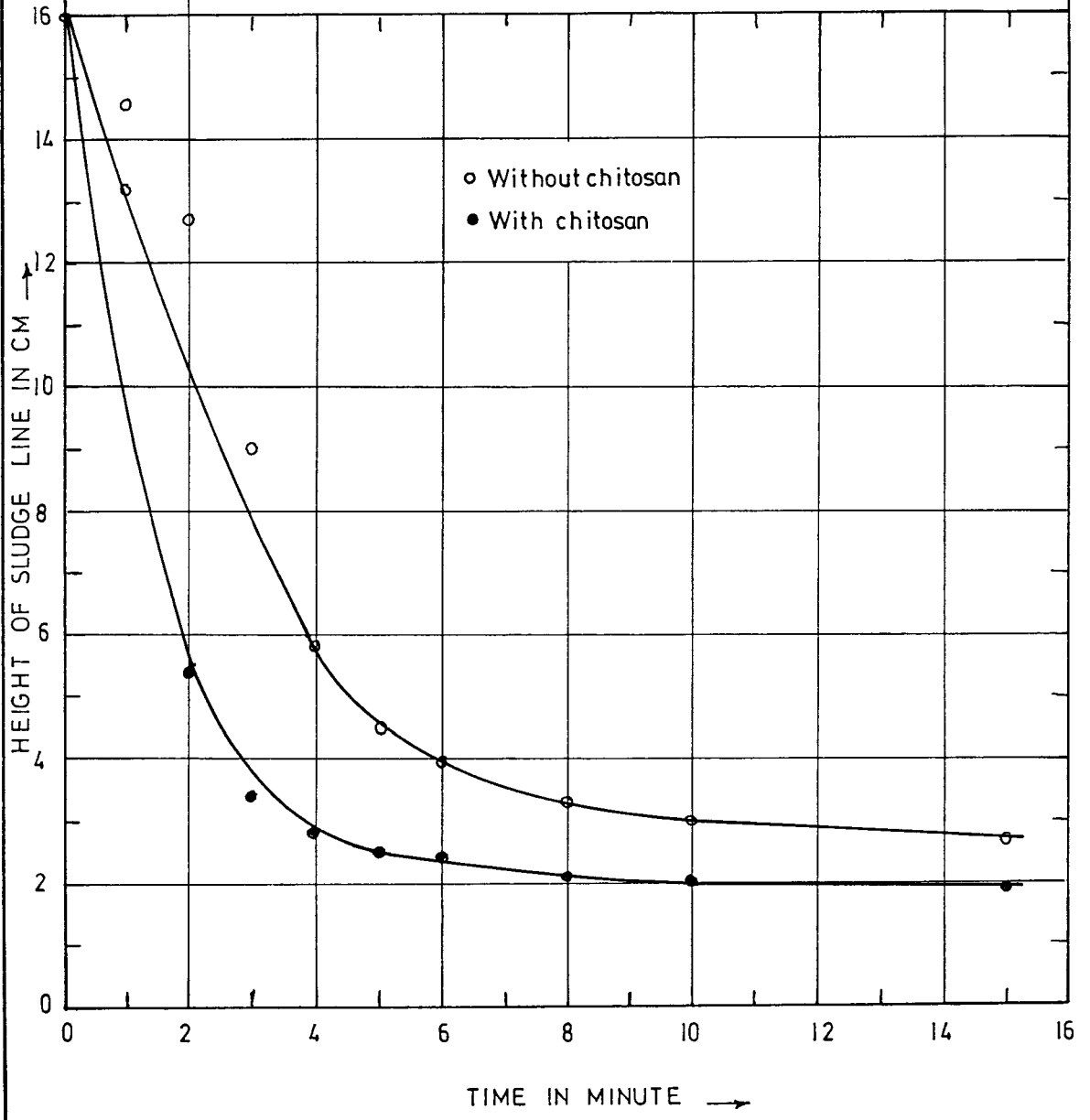
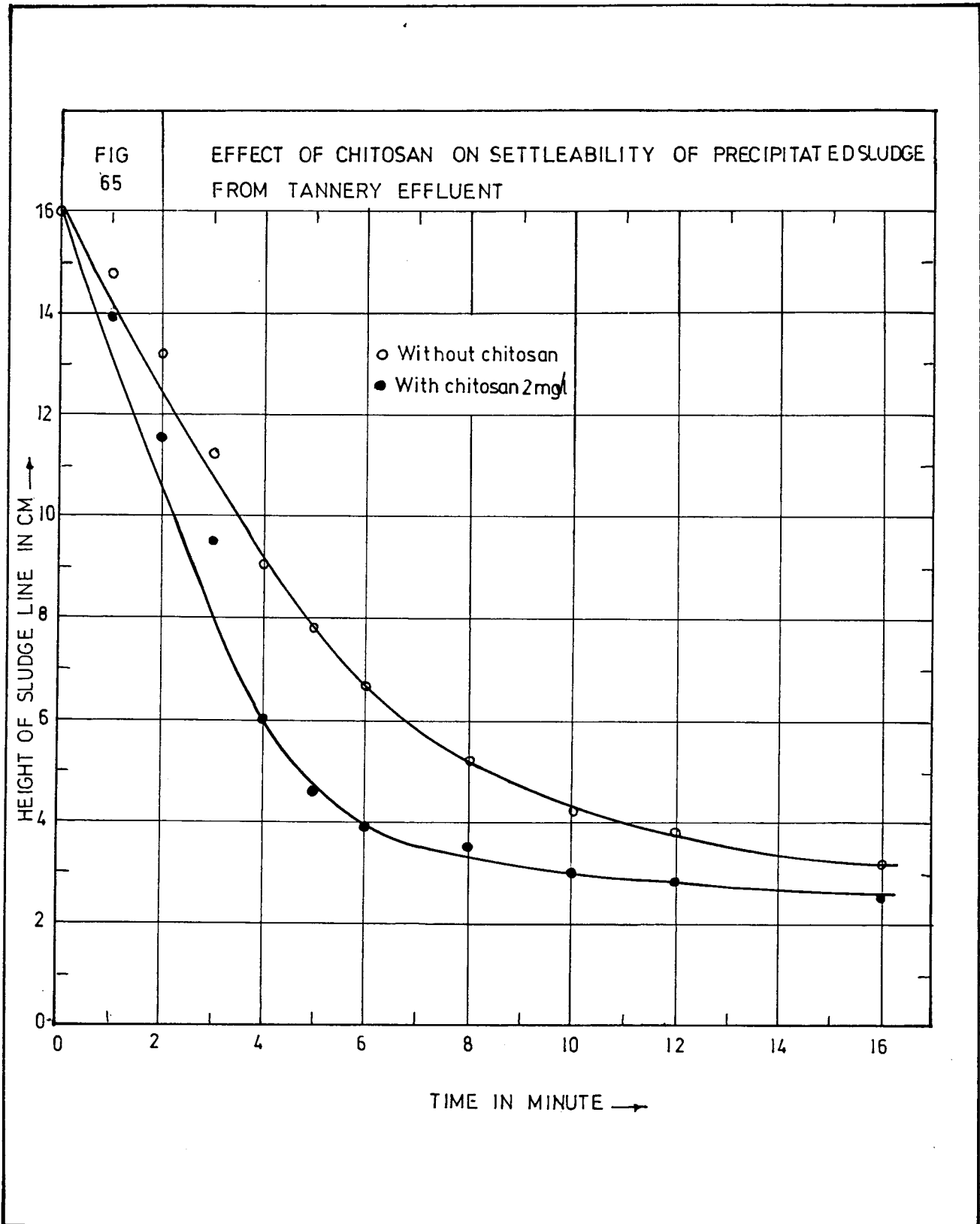


FIG 64

EFFECT OF CHITOSAN ON SETTLEABILITY OF SLUDGE FROM PAPER MILL EFFLUENT





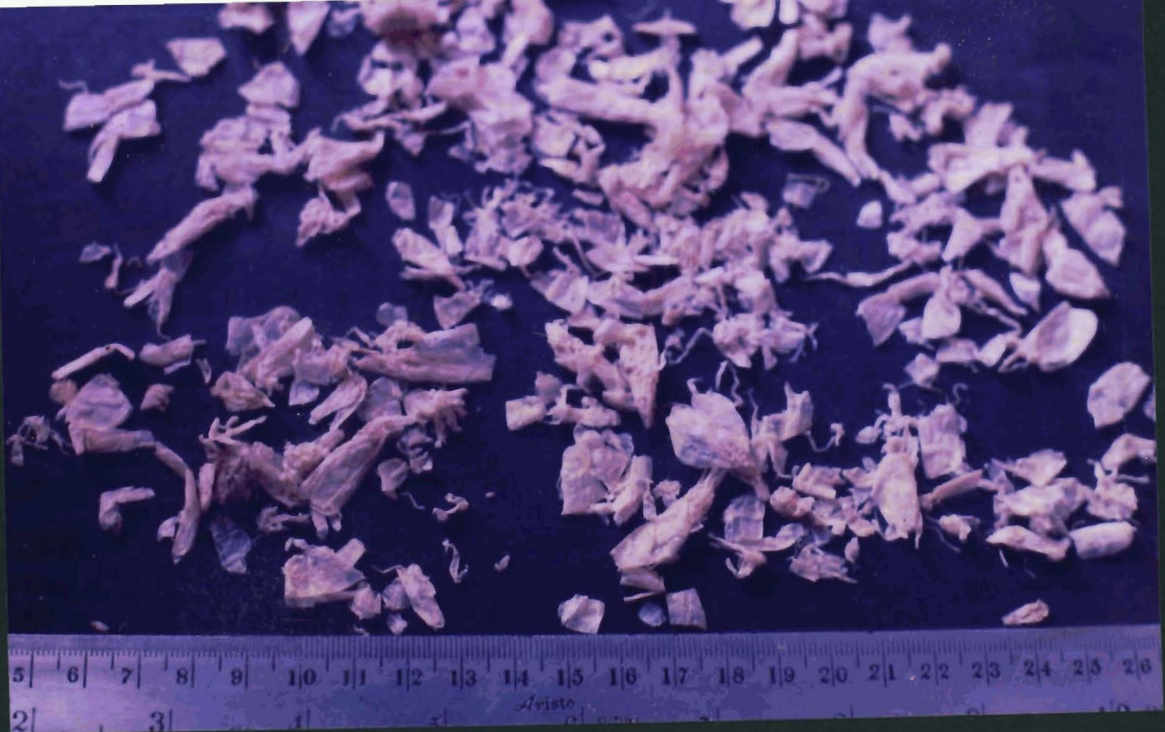
ANNEXURES



PRAWN AND PRAWN SHELL



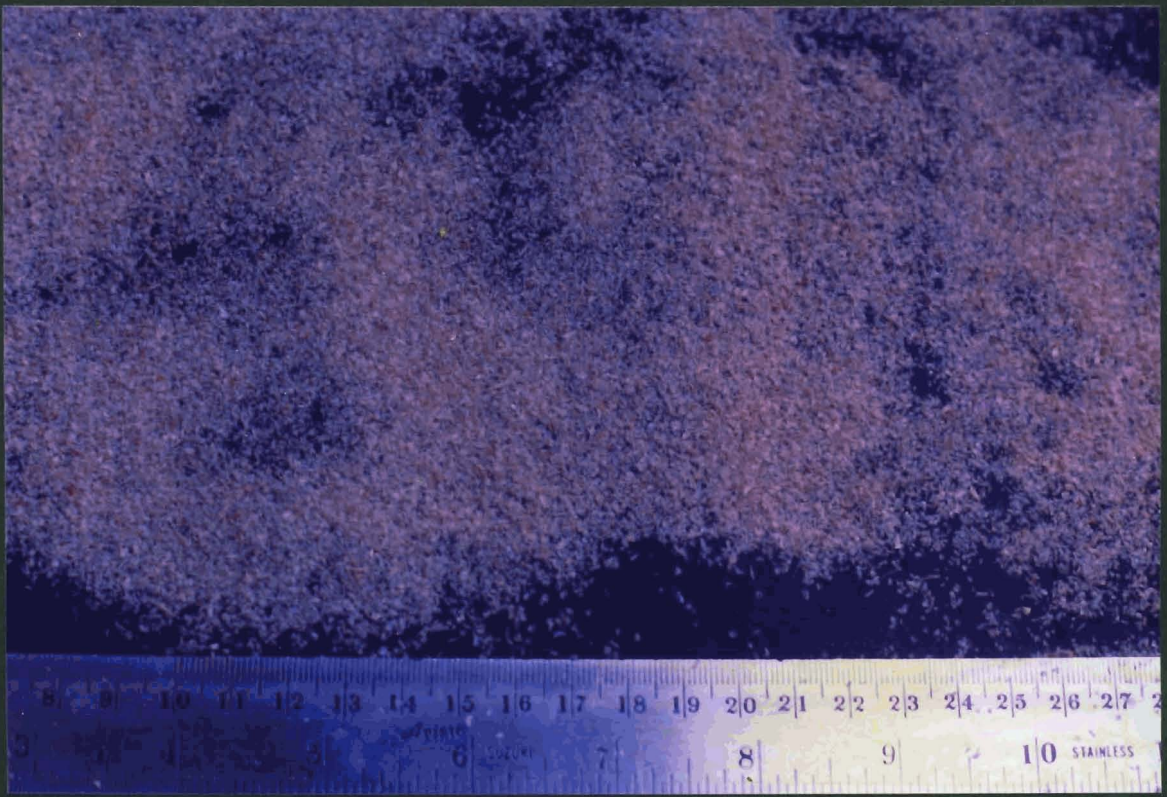
215B



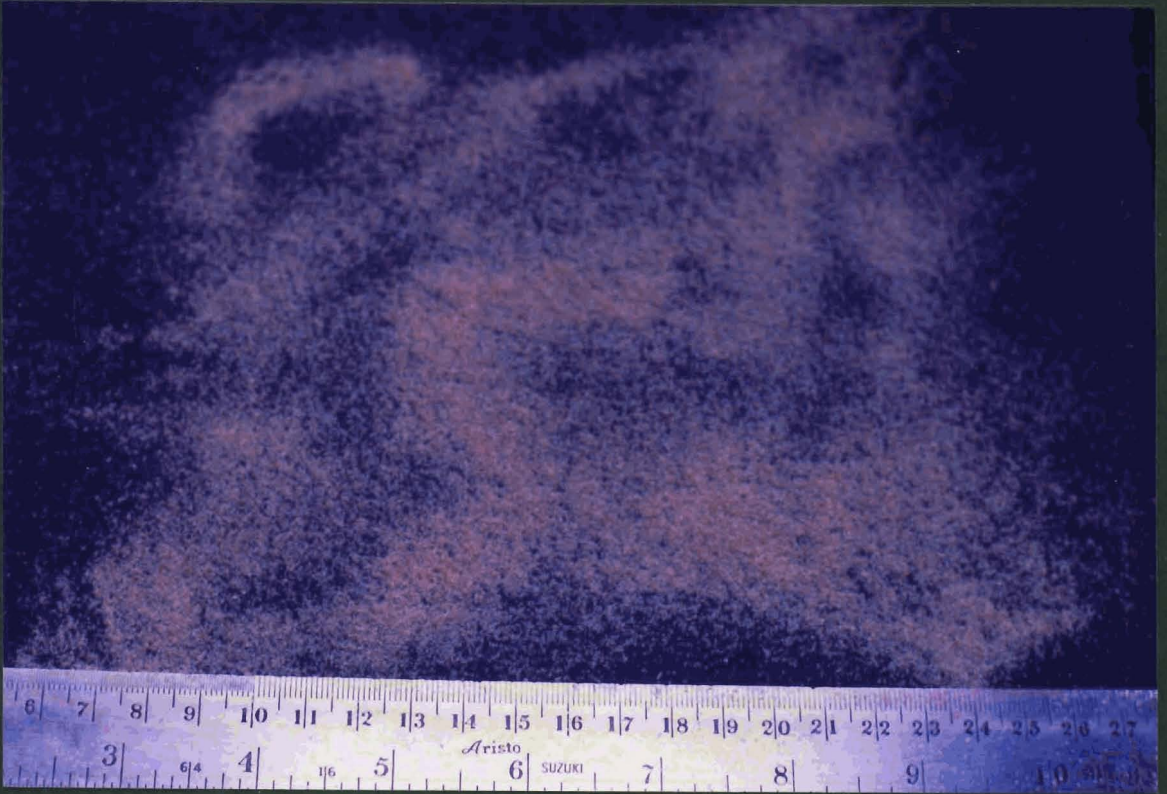
CHITOSAN FLAKES



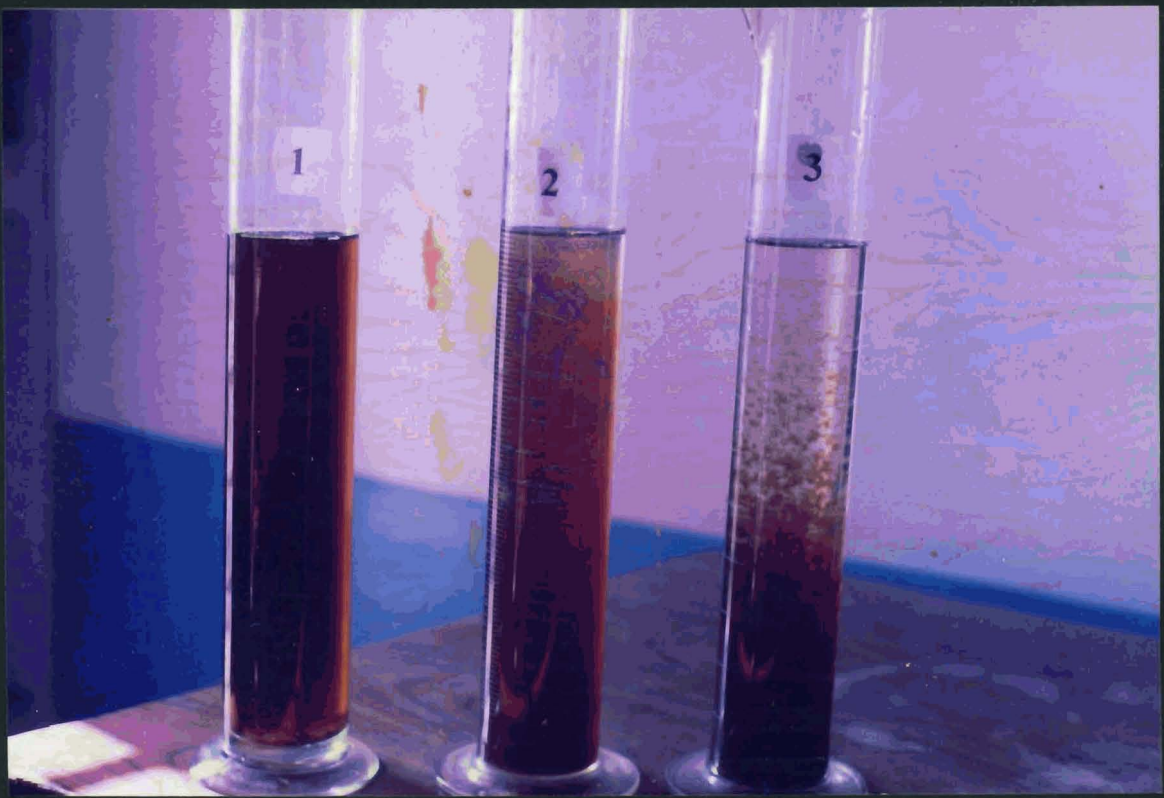
217



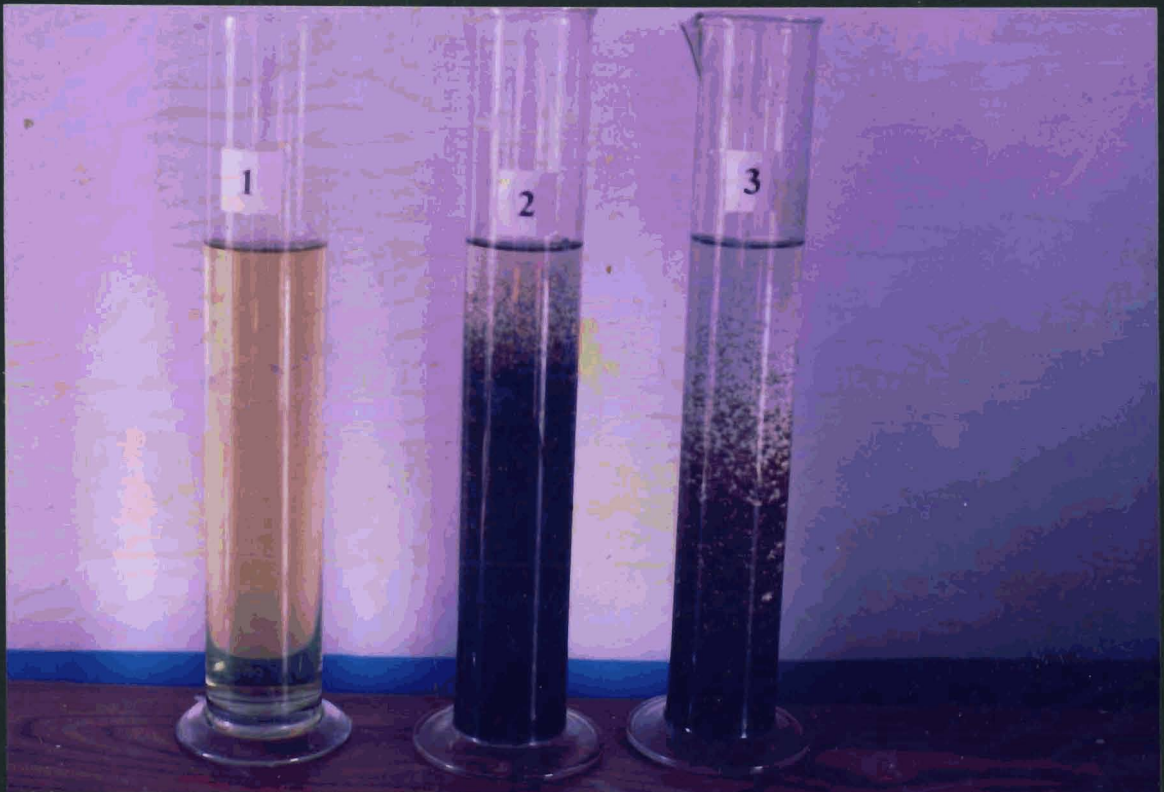
~~CHITOSAN~~ CHITOSAN- DIFFERENT GRAIN SIZES



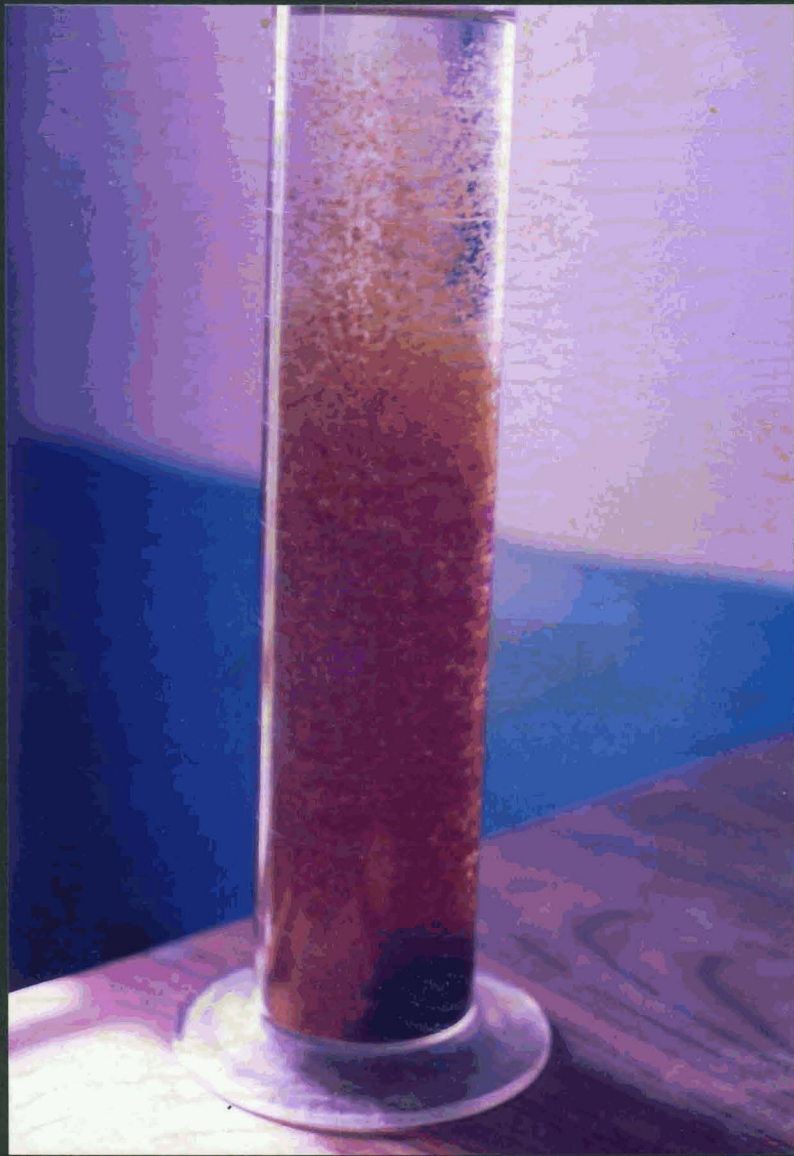
2350
218



FLOCCULATION AND SETTLING WITH CHITOSAN ✓



EFFECT OF CHITOSAN AS A FLOCCULANT AND ADSORBANT



TREATABILITY STUDIES _ PUEP AND PAPER MILL

220



TREATABILITY STUDIES TANNERY EFFLUENT

221

HEALTH EFFECTS OF MERCURY, CHROMIUM LEAD AND CADMIUM

1981.

i) **Mercury:** The toxicity of mercury varies greatly with its chemical form. Thus monovalent mercury is quite nontoxic due to the low solubility of its salts. However, tissues and erythrocytes can oxidize monovalent mercury to highly toxic divalent mercury. Organic mercurials are also highly toxic.

Acute mercury poisoning can result from inhalation of inorganic mercury at concentration from 1,200 to 8,500 micro gram per cu. meter. The kidneys and intestinal tract are primarily involved. Symptoms are metallic taste, nausea, abdominal pain, vomiting, diarrhea, headache, salivation and anuria. The stomach, gums and salivary glands may become inflamed. Acute exposure to elemental mercury can also cause pulmonary irritation and neural damage. Chronic symptoms such as muscular tremor persist in some cases. Extreme cases may lead to hemolysis, insomnia, delirium and ultimate death from exhaustion. Ingestion of 1.0 to 2 gms mercuric chloride

is frequently fatal to human beings. Inhalation of alkyl mercury can produce dryness and irritation in the nasopharynx and mouth. Alkyl mercury poisoning have caused permanent neurological damage resulting in impaired vision and hearing, sensory loss in limbs, ataxia and tremor. Fatal nerve tissue may be especially sensitive to methyl mercury.

ii. **Cadmium:-** Health problems from cadmium were suddenly brought into focus when high cadmium intake was indentified as the probable cause of the terrible itai itai* disease. This disease, really poisoning, resulted in gross deformities, pain as bones snapped under weight of the body.

Cadmium can enter the body by two routes, by inhalation into the respiratry sytem and by ingestion into the gastro-intestinal tract. About 20-30% of inhaled cadmium is deposited on the lung tissue, and about two-thirds of that is absorbed.

Absorbed cadmium is transported by the blood stream to the liver, where most is bound to a protein complex called metallothioneine. This acts as a transport

agent, carrying the cadmium to other parts of the body, notably the nerves and especially the renal cortex, where it is deposited. Cadmium is cumulative in the liver. Kidney syndrome in Japan has been associated with the ingestion of as little as 600 µg/day of cadmium.

Being excreted only very slowly from the body, cadmium is a cumulative poison. Its biological life ranges from about 40 days in the blood to 20 years or more in liver and kidneys.

Cadmium is an extremely dangerous cumulative toxicant, causing insidious progressive chronic poisoning in mammals, fish and probably other animals because the metal is not excreted. Cadmium could form organic compounds which might lead to mutagenic or teratogenic effects. Cadmium is known to have marked acute and chronic effects on aquatic organisms also.

Cadmium acts synergistically with other metals. Copper and zinc substantially increase its toxicity. Cadmium is concentrated by marine organisms, particularly molluscs, which accumulate cadmium in calcareous tissues

and in the viscera. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

iii) **Lead:-** Lead enters the body through inhalation and ingestion and absorbed into circulatory system from the lungs and digestive tract, and excreted via the urine and faeces. Normally intake of lead approximately equals the output. However, excessive exposure and intake can upset this balance and cause tissue concentrations to increase to the point where illness can result. Symptoms of lead poisoning includes anemia, fatigue, headache, weight loss and constipation. More severe manifestations include damage to the nervous system and kidneys.

The particle size and chemical composition of lead and lead compounds affect the readiness with which lead is absorbed from the lungs and digestive tract. Larger particles and compounds with lower solubility are less hazardous than finely divided particles and compounds of higher solubility.

Lead is a toxic material that is foreign to humans and animals. The most common form of lead poisoning is called plumbism. Lead can be introduced into the body from the atmosphere containing lead or from food and water. Lead cannot be easily excreted and is cumulative in the body over long periods of time, eventually causing lead poisoning with the ingestion of an excess of 0.6 mg/day over a period of years. It has been recommended that 0.05 mg/l lead not be exceeded in public water supply sources.

Chronic lead poisoning has occurred among animals at levels of 0.18 mg/l of lead in soft water and by concentrations under 2.4 mg/l in hard water. Farm animals are poisoned by lead more frequently than any other poison. Sources of this occurrence include paint and water with the lead in solution as well as in suspension. The bacterial decomposition of organic matter is inhibited by lead at levels of 0.1 to 0.5 mg/l.

Fish and other marine life have had adverse effects from lead and salts in their environment. Experiments have

shown that small concentrations of heavy metals, especially of lead, have caused a film of coagulated mucus to form first over the gills and then over the entire body probably causing suffocation of the fish due to this obstructive layer. Toxicity of lead is increased with reduction of dissolved oxygen concentration in the water.

iv) **Chromium:-** Chromium in its various valence states, is hazardous to man. The exposure of industrial workers to airborne chromium compounds and chromic acid mists, particularly the hexavalent chromates, has been observed to produce irritation of the skin and respiratory tract, dermatitis, perforation of the nasal septum, ulcers and cancer of the respiratory tract. Hexavalent compounds appears to be much more harmful than trivalent compounds, with the toxic effects depending on solubility. Hexavalent chromium is corrosive to the flesh.

It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause

inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date. The recommendation for public water supplies is that such supplies contain no more than 0.05 mg/l total chromium.

The toxicity of chromium salts to fish and other aquatic life varies widely with the species, temperature, pH, valence of the chromium and synergistic or antagonistic effects, especially those of hard water. Studies have shown that trivalent chromium is more toxic to fish of some types than hexavalent chromium. Other studies have shown opposite effects. Fish food organisms and other lower forms of aquatic life are extremely sensitive to chromium and it also inhibits the growth of algae. Therefore, both hexavalent and trivalent chromium must be considered harmful to particular fish or organisms.

PREPARATION, PROPERTIES AND USES OF CHITOSAN

(i). Preparation

There are different methods for the production of chitosan from prawn peelings viz. Cold deacetylation, Alcoholic deacetylation and Aqueous caustic soda deacetylation. Among these aqueous caustic soda process was found to be the most economical and viable one for industrial production.

The aqueous caustic soda process was used in the laboratory for producing chitosan required for experimental purpose. The raw material dry prawn shell contains about 22% chitin, 38% protein, 30% minerals (CaCO_3) and 10% sand. The unwanted materials present in the prawn shell are removed and chitin is recovered. The chitin obtained is then deacetylated to get chitosan.

The production process consist of the following steps:

1). **De-proteinisation** :- 1 Kg dry prawn shell is heated with 12 litre 0.5% caustic soda solution at 80°C for 30 minutes for removing the protein. Then the shell waste is heated with 3% caustic soda solution at 80°C for 30 minutes.

2). **De-mineralisation** :- After de-proteinisation, the shells are treated with 4 litres of 6% Hydrochloric Acid for one hour. After the reaction is over, the excess acid with mineral content is drained off and the residue is repeatedly washed with water. The material obtained after de-mineralisation is called chitin.

3). **De-acetylation** :- Chitin containing 60% moisture content is heated with 40% (w/v) caustic soda solution at 90 - 95 °C for 1 1/2 - 2 hours. After de-acetylation the material is thoroughly washed with water repeatedly and dried in a tray drier. The dried chitosan is then powdered in a pulverizer.

(ii). Properties :- Chitosan is poly 2-amino - 2 deoxy- β -D glucose in which the monomer units are linked by (1-4) - β bonds. This is an important derivative of chitin - a natural polymer of N- acetyl-D- glucosamine. The average molecular weight of chitosan is of the order of 1.2×10^5 .

Chitosan is almost colourless flakes of ridged or layered structure. Porosimetry studies suggest that the particles are gel like rather than microporous with very large (70 A median diameter). Chitosan exhibits only an 8% increase in volume upon exposure to base from acid. Columns packed with chitosan exhibit low back pressure, an effect probably due to the irregular shape of the flake.

Chitin is insoluble in water, dilute acids, cold alkalies or organic solvents. Chitosan also possess the same properties as that of chitin except that chitosan is soluble in many dilute, aqueous, organic acids such as acetic acid, formic acid etc. at a pH below 6.

Because of this property chitosan can be distinguished experimentally from chitin. Chitosan solutions are highly viscous.

Viscosity of chitosan solution in acetic acid increases with acid concentration, and decreases with temperature. Viscosity of 1% solution of chitosan in acetic acid oven aged for 5 days at 60°C is given below. Chitosan possess high thermal stability and decomposes at 230°C.

pH	Sample	Viscosity, C _p		% retained
		original	final	
4	Shrimp chitosan	2780	170	6.1
4	King-crab chitosan	1460	460	31.5
3	Shrimp chitosan	2640	385	14.6
3	King-crab chitosan	1460	570	39.0

From chemical point of view, chitosan is a primary aliphatic polyamine and can undergo all those reactions typical of amines. Chitosan possess a high density of

amino groups per unit weight. Under acidic conditions chitosan carries a strong positive charge and is water soluble. Under neutral or basic conditions the many uncharged amino groups give chitosan a high capacity for binding transitions metal ions by chelation.

The amino groups of chitin and chitosan are exceptionally soluble in 50% NaOH, even at 160°C, at which most amines liberate ammonia or yield degradation products. Amino groups of chitosan reacts with carbonyl compounds (eg. salicyl aldehyde) leading to the formation of Schiff's base. Chitosan hydroxyl groups react with sulfonium salts in alkaline media and liberate the sulfonium cation.

Chitosan is a cationic polyelectrolyte with one amino group and two free hydroxyl group for each glucose ring. Because of this cations nature chitosan spontaneously form insoluble complexes with natural tannin and other anionic polyelctrolyte.

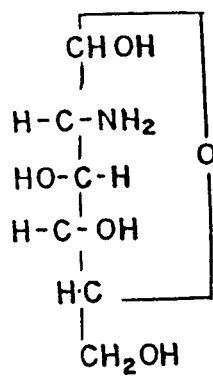
(iii). **Uses** :- Among the various uses of chitin and chitosan, the most promising one is in the treatment of industrial pollutants carrying harmful metals to the environment like mercury, lead, cadmium, copper, nickel, chromium and zinc discharged from metal finishing operations, chemical factories etc. Moreover nuclear fission products containing zirconium, hafnium, titanium, niobium, ruthenium are also collected by chitin and chitosan. Special mention may be made here of the unique ability of both chitin and chitosan in the collection of ruthenium from the nitrosyl complex of the metal, which resists attack by other chelating agents. Chitosan finds wide application in the paper and textile industry as a sizing agent and thickener. It can also be used as an aid in the dyeing of glass fabrics and plastic fabrics. It offers a superior shrink resistance to woollen fabrics.

Chitin and its many derivatives have been successfully employed as adhesive for bonding cellulose. This adhesive possesses a good tensile strength and superior water resistance when compared to other conventional adhesives such as glue.

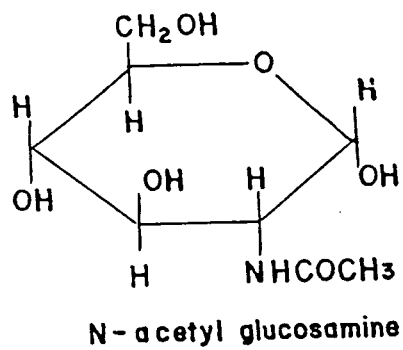
Chitosan can be used in tobacco and leather manufacture as a filler to improve the quality of these products. Chitosan can also be used in treating aqueous solutions containing suspended matter. It has been successfully tried as a coagulant for inorganic suspended solids, vegetable canning wastes and to aid in the recovery of protein from solution. It is also useful for dewatering municipal sludges.

In the field of medicine and pharmaceuticals, chitin and its derivatives find wide applications such as artificial kidney membranes, pharmaceutical carriers, blood anti-coagulants and as wound healing accelerators.

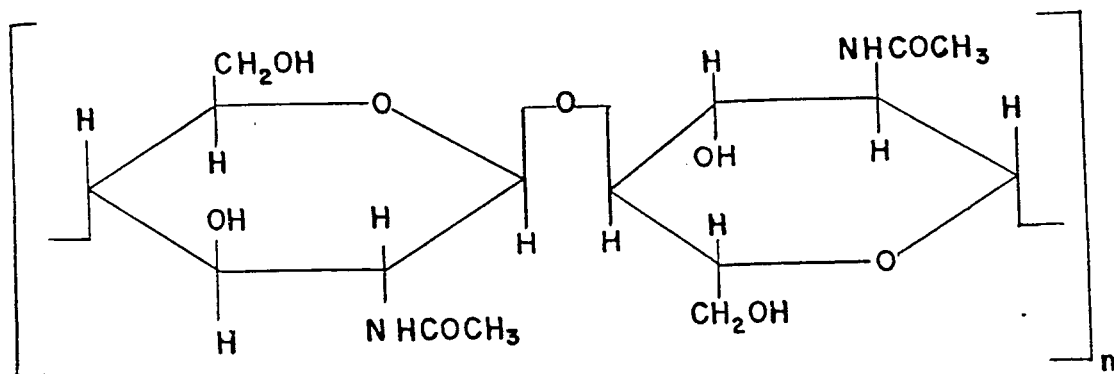
STRUCTURE OF GLUCOSAMINE , CHITIN AND CHITOSAN



D-Glucosamine

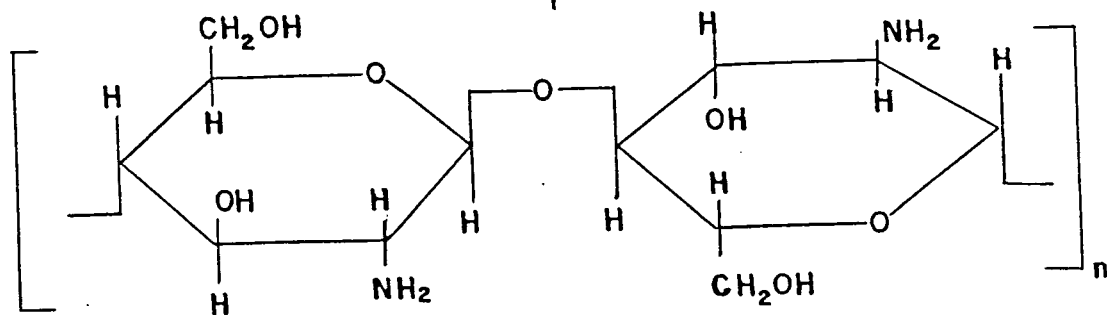


N-acetyl glucosamine



CHITIN

Deacetylation



CHITOSAN

EFFLUENT STANDARD

Tolerance limits for inland surface waters subject to pollution

(a) Drinking water source without conventional treatment but after disinfection

IS 2296-1982			
Sl. No.	Characteristic	Unit	Tolerance Limit
1.	pH		6.5 to 8.5
2.	Dissolved oxygen	mg/l, min.	6
3.	B.O.D. (3 days at 27 ^o C)	mg/l, max.	2
4.	Total coliform organisms	MPN/100 ml, max.	50
5.	Colour	Hazen unit, max.	10
6.	Odour		Unobjectionable
7.	Taste		Tasteless
8.	Total dissolved solids(T.D.S.)	mg/l, max.	500
9.	Total hardness (as CaCO ₃)	"	300
10.	Calcium hardness (as CaCO ₃)	"	200
11.	Magnesium hardness (as CaCO ₃)	"	100
12.	Copper (as Cu)	"	1.5
13.	Iron (as Fe)	"	0.3
14.	Manganese (as Mn)	"	0.5
15.	Chlorides (as Cl)	"	250
16.	Sulphates (as SO ₄)	"	400
17.	Nitrates (as NO ₃)	"	20
18.	Fluorides (as F)	"	1.5
19.	Phenolic compounds (as C ₆ H ₅ OH)	"	0.002
20.	Mercury (as Hg)	"	0.001
21.	Cadmium (as Cd)	"	0.01
22.	Selenium (as Se)	"	0.01
23.	Arsenic (as As)	"	0.05
24.	Cyanides (as CN)	"	0.05
25.	Lead (as Pb)	"	0.1
26.	Zinc (as Zn)	"	15
27.	Hexavalent chromium (as Cr ⁺⁶)	"	0.05
28.	Anionic detergents (as MBAS)	"	0.2
29.	Polynuclear Aromatic Hydrocarbons (PAH)	µg/l, max.	0.2
30.	Mineral oil	mg/l, max.	0.01
31.	Barium (as Ba)	mg/l, max.	1
32.	Silver (as Ag)	"	0.05
33.	Pesticides		Absent
34.	Alpha emitters	µCi/ml, max.	10 ⁻⁹
35.	Beta emitters	"	10 ⁻⁸

Characteristics of drinking water

IS 10500-1983

Sl. No.	Parameter	Unit	Limit	Relaxation allowed if alternate sources are not available
1.	Colour	Hazen, max.	10	
2.	Odour		Unobjectionable	
3.	Taste		Agreeable	
4.	Turbidity	NTU, max.	10	25
5.	Dissolved solids	mg/l, max.	500	3000
6.	pH		6.5 to 8.5	9.2
7.	Total hardness (as CaCO ₃)	mg/l, max.	300	600
8.	Calcium (as Ca)	..	75	200
9.	Magnesium (as Mg)	..	30	100
10.	Copper (as Cu)	..	0.05	1.5
11.	Iron (as Fe)	..	0.3	1
12.	Manganese (as Mn)	..	0.1	0.5
13.	Chlorides (as Cl)	..	250	1000
14.	Sulphates (as SO ₄) { provided magnesium [as Mg] does not exceed 30 }	..	150	400
15.	Nitrates (as NO ₃)	..	45	--
16.	Fluorides (as F)	..	0.6 to 1.20	1.5
17.	Phenolic compounds (as C ₆ H ₅ OH)	..	0.001	0.002
18.	Mercury (as Hg)	..	0.001	--
19.	Cadmium (as Cd)	..	0.01	--
20.	Selenium (as Se)	..	0.01	--
21.	Arsenic (as As)	..	0.05	--
22.	Cyanides (as CN)	..	0.05	--
23.	Lead (as Pb)	..	0.1	--
24.	Zinc (as Zn)	..	5	15
25.	Anionic detergents (as MBAS)	..	0.2	1.0
26.	Hexavalent chromium (as Cr ⁺⁶)	..	0.05	--
27.	Mineral oil	..	0.01	0.03
28.	Residual free chlorine	mg/l, min.	0.02	--
29.	Pesticides		Absent	
30.	Radioactive materials			
	Alpha emitters	μCi/ml, max.	10 ⁻⁸	
	Beta emitters	..	10 ⁻⁷	

GENERAL EFFLUENT STANDARDS

E(P)Rules, Schl. - VI, Part A, GSR 801(E) dt. 3.1.12.93.

Sl. No.	Parameter	Unit	Inland surface water	Public sewer	Land for irrigation	Marine coastal areas.
1.	Colour and odour		See 6 of Guidelines	--	See 6 of Guidelines	See 6 of Guidelines
2.	Suspended solids	mg/l, max.	100	600	200	a) For process effluent--100 b) For cooling water-- 10 percent above total suspended matter of influent.
3.	Particle size of Suspended solids		Shall pass 850 micron IS sieve	--	--	a) Floatable solids -- max.3 mm b) Settleable solids-- max.850µm.
4.	pH		5.5 to 9	5.5 to 9	5.5 to 9	5.5 to 9
5.	Temperature	°C, max.	Shall not exceed 5 °C above the receiving water temperature	--	--	Shall not exceed 5 °C above the receiving water temperature
6.	Oil and grease	mg/l, max.	10	20	10	20
7.	Total residual chlorine	"	1	--	--	1
8.	Ammoniacal nitrogen (as N)	"	50	50	--	50
9.	Total kjeldahl nitrogen (as N)	"	100	--	--	100
10.	Free ammonia (as NH ₃)	"	5	--	--	5
11.	B.O.D.(3 days at 27° C)	"	30	350	100	100
12.	Chemical oxygen demand	"	250	--	--	250
13.	Arsenic (as As)	"	0.2	0.2	0.2	0.2
14.	Mercury (as Hg)	"	0.01	0.01	--	0.01
15.	Lead (as Pb)	"	0.1	1	--	2
16.	Cadmium (as Cd)	"	2	1	--	2

NB4336

17	Hexavalent chromium (as Cr ⁺⁶)	..	0.1	2	--	1
18	Total chromium (as Cr)	..	.2	2	--	2
19	Copper (as Cu)	..	3	3	--	3
20.	Zinc (as Zn)	..	5	15	--	15
21.	Selenium (as Se)	..	0.05	0.05	--	0.05
22.	Nickel (as Ni)	..	3	3	--	5
23.	Cyanides (as CN)	..	0.2	2	0.2	0.2
24.	Fluorides (as F)	..	2	15	--	15
25.	Dissolved Phosphates (as P)	..	5	--	--	--
26.	Sulphides (as S)	..	2	--	--	5
27.	Phenolic compounds (as C ₆ H ₅ OH)	..	1	5	--	5
28.	Radioactive materials:					
	a) Alpha emitters	μCi/ml, max.	10 ⁻⁷	10 ⁻⁷	10 ⁻⁸	10 ⁻⁷
	b) Beta emitters	μCi/ml, max.	10 ⁻⁶	10 ⁻⁶	10 ⁻⁷	10 ⁻⁶
29.	Bio-assay test		90 % survival of fish after 96 h in 100 % effluent	90 % survival of fish after 96 h in 100 % effluent	90 % survival of fish after 96 h in 100 % effluent	90 % survival of fish after 96 h in 100 % effluent
30.	Manganese (as Mn)	mg/l, max.	2	2	--	2
31.	Iron (as Fe)	..	3	3	--	3
32.	Vanadium (as V)	..	0.2	0.2	--	0.2
33.	Nitrate nitrogen (as N)	..	10	--	--	20

Conversion factor : 1 Bq = 2.7 x 10⁻¹¹ Ci