

PREPARATION OF CHITOSAN AND ITS USE IN DEFLUORINATION OF WATER

*A Dissertation
Submitted in partial fulfillment*

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NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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CERTIFICATE

*This is to certify that the dissertation entitled “**PREPARTION OF CHITOSAN AND ITS USE IN DEFLUORINATION OF WATER**” submitted by **Bhargabi Shur** to the department of chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain in the bonafide project work carried out by her under my Guidance and supervision.*

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Contents

1	Introduction	
	1.1 Introduction to chitosan	2
	1.2 History	4
	1.3 Chemistry	5
	1.4 Important properties of chitosan	7
	1.5 Advantage of Chitosan in purifying water	11
2	Review	
	2.1 Review of previous work	13
3	Objective	
	3.1 Objective of the work	16
4	Materials and Method	
	4.1 Raw materials	18
	4.2 General method	19
	4.3 Preparation	20
	4.3.1 Demineralization	20

4.3.2	Deproteinisation	21
4.3.3	Removal of water	21
4.3.4	Deacetylation of chitin	21
4.3.5	Drying	21
4.3.6	Precautions	22
4.4	Defluorination	22
4.4.1	Thermal activation of adsorbent materials	22
4.4.2	Chemicals used	22
4.4.3	Procedure	23
5	Results and discussion	
5.1	<i>Results and discussion</i>	25
5.1.1	<i>Effect of initial fluoride concentration</i>	25
5.1.2	<i>Effect of adsorbent dose</i>	26
6	Conclusion	29
	Bibliography	30

CHAPTER 1

INTRODUCTION

1.1 Introduction

A **polymer** is a substance composed of molecules with large molecular mass composed of repeating structural units, or monomers, connected by covalent chemical bonds. The term is derived from the Greek words: *polys* meaning *many*, and *meros* meaning *parts*. The individual molecules which comprise a polymer are referred to as **polymer molecules**, where the word "polymer" functions as an adjective. Well known examples of polymers include polysaccharides and celluloses.

Polymers are divided into two parts: natural polymer and synthetic polymer. Natural polymers are the natural occurring polymers generally found in living organisms and plants e.g., rubber, cellulose, polysaccharides, DNA, RNA, proteins etc. Synthetic polymers are the tailor made e.g, bakelite, MF, PF, nylon etc.

Chitin is natural polymer. It is one of the three most abundant polysaccharides in nature, in addition to cellulose and starch. It ranks second to cellulose as the most plentiful organic compound on earth. Chitin is the main component of the cell walls of fungi. It is also a major component of the exoskeletons of arthropods, such as the crustaceans (e.g. crab, lobster, and shrimp), and the insects (e.g. ants, beetles, and butterflies), and of the beaks of cephalopods (e.g. squids, and octopus). Chitin has also proven useful for several medical and industrial purposes. It is constructed from units of N-acetylglucosamine (more completely, N-acetyl-D-glucos-2-amine). These are linked together in β -1,4 fashion (in a similar manner to the glucose units which form cellulose). In effect chitin may be described as cellulose with one hydroxyl group on each monomer replaced by an

acetylamine group. This allows for increased hydrogen bonding between adjacent polymers, giving the polymer increased strength.

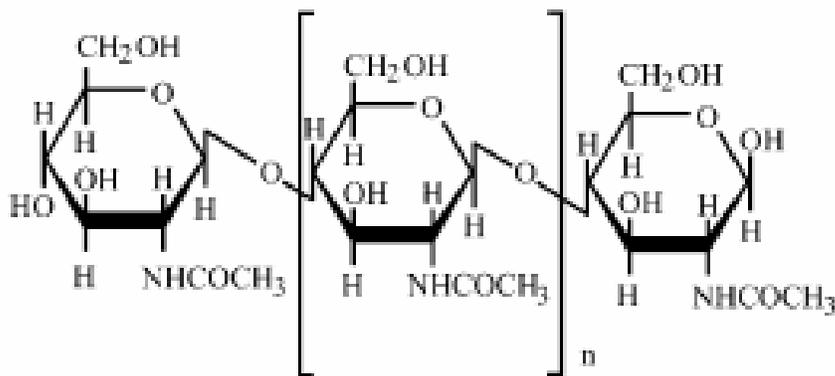


Figure 1. Structure of Chitin

In its unmodified form, chitin is translucent, pliable and resilient, and quite tough. In arthropods, however, it is frequently modified, by being embedded in a hardened proteinaceous matrix, which forms much of the exoskeleton. The difference between the unmodified and modified forms can be seen by comparing the body wall of a caterpillar (unmodified) to a beetle (modified).

Chitin is one of the many naturally occurring polymers. Its breakdown may be catalyzed by enzymes called chitinases, secreted by microorganisms such as bacteria. Some of these microorganisms have receptors to simple sugars from the decomposition of chitin. If chitin is detected, they then produce enzymes to digest the chitin by reducing it to simple sugars and ammonia.

Chemically, chitin is closely related to chitosan (a more water-soluble derivative of chitin). It is also closely related to cellulose in that it is a long

unbranched chain of glucose derivatives. Both materials contribute structure and strength, protecting the organism.

Chitin and its derivatives like Chitosan have many properties that make them attractive for a wide variety of applications, from food, nutrition and cosmetics to biomedicine, agriculture and the environment.

1.2 History

Chitosan is collective name for a group of partially and fully deacetylated chitins. Chitosan was first discovered in 1811 by Henri Braconnot, director of the botanical garden in Nancy, France. Braconnot observed that a certain substance (chitin) found in mushrooms did not dissolve in sulfuric acid. Over the last 200 years, the exploration of chitosan has taken on many different forms. Several other researchers continue to build on the original finding of Braconnot, discovering new uses for chitin as they find different forms of it in nature.

Physical characteristics: It's off white amorphous translucent flake or powder with pearly color. Insoluble in water or alkali solution, soluble in inorganic acid like diluted hydrochloric acid and nitric acid etc. and most organic acid. In diluted acid solution, backbone chain of chitosan will hydrolyze slowly. There are of α , β and γ three crystallographic forms.



Figure 2. Different grades of chitosan

1.3 Chemistry: Chitosan is formed through N-deacylation of the chitin molecule. Some chemical properties of Chitosan:

- Reactive amino groups
- Bacteriostatic and fungistatic effect
- Linear polyamine (poly-D-gulconsamine)
- Protein separations
- Chelates many transitional metal ions

Chitosan and chitin are polysaccharide polymers containing more than 5,000 glucosamine and acetylglucosamine units, respectively, and their molecular weights are over one million Daltons.

Chitin, the polysaccharide polymer from which chitosan is derived, is a cellulose-like polymer consisting mainly of unbranched chains of N-acetyl-D-glucosamine. Deacetylated chitin, or chitosan, is comprised of chains of D-glucosamine. When ingested, chitosan can be considered a dietary fiber. Chitosan has the following chemical structure:

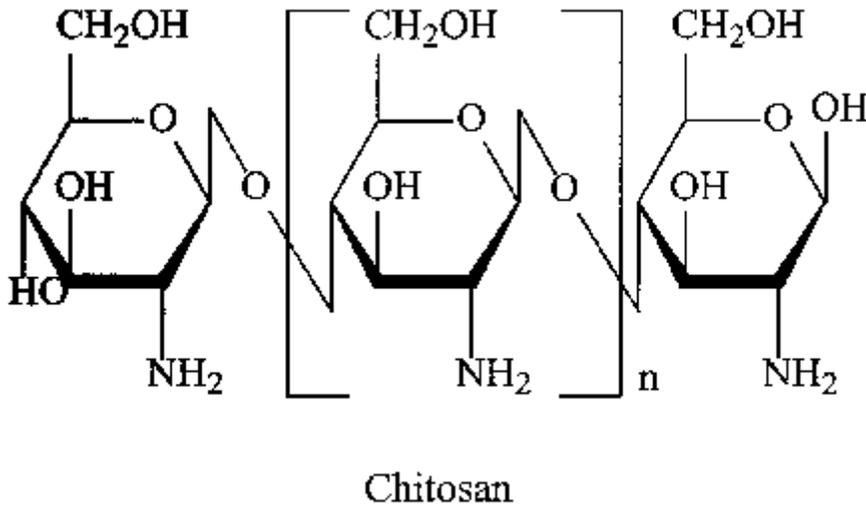


Figure 3. Structure of Chitosan

Chitosan, the partially deacetylated polymer of N-acetyl-D-glucosamine, is water-soluble. Rheology, flocculation and film formation testing have been performed with chitosan, demonstrating its usefulness in medical and analytical applications. Biodegradable and biocompatible properties of chitosan films have been studied with good outcomes. N-carboxymethylchitosan solubility and structure have been reported, along with its ability to chelate metal ions and to enhance binding of dyes.

Other chemical aspects involving chitin or chitosan include: Optical isomer separation, mass-spectrometric analysis, polyelectrolyte and sulfation studies, adherence to liposomes and absorption property of chitosan.

1.4 Important properties of chitosan

Important properties of chitosan are as follows:

- Medical grade micronised chitosan is biodegradable, non allergic, haemostatic, non toxic and wound healing accelerator.
- Chitosan films are flexible, tough, transparent, clear and oxygen permeable with good tensile strength.
- Chitosan could be used to make single and bipolymer membranes, non woven fabrics and sponges for surgical applications.
- It is resistant to alkali, digestive enzymes and urine.
- Chitosan also could be cross linked.

Chitosan is a positively charged compound, it is able to attract and bind to fatty acids (which carry a negative charge). As such, chitosan can absorb up to 4-6 times its weight in fat (including cholesterol) and prevent that fat from being absorbed into the body. This means that for every gram of chitosan that is consumed as a supplement, it will prevent the absorption of approximation 4-6 grams of fat.

Chitosan is used in fields as diverse as health care to agriculture to dyes for fabrics ie;

- a. **Water Waste Treatment:** removal of metal ions and coagulants like dye etc.
- b. **Food Industry:** As preservative, Color Stabilizer.
- c. Medical Bandages, Contact Lens and other equipments.

- d. **Biotechnology:** Enzyme Immobilization, Cell Recovery, Chromography.
- e. **Agriculture:** Seed coating, Fertilizer, Controlled Agrochemical Release.
- f. **Cosmetics:** Moisturizer, Creams, Lotion.
- g. **Pulp and Paper:** Surface treatment, Photographic paper.

In medicine and healthcare field, chitosan is widely applied for its multi-function of improving immunity, activating cells, preventing cancer, decreasing blood fat and blood pressure, adjusting blood sugar, fighting against aging and adjusting organism environment etc.

In environment protection field, chitosan can be applied in waste water disposal, protein recycle and water purification.

In functional material field, chitosan can be applied in membrane material, carrier, sorbet, fiber and medical materials etc.

In light textile field, chitosan can be applied in fabric sorting, healthcare underwear and paper making additives.

In agriculture field, chitosan can be applied in feedstuff additive, seed disposal, soil amelioration and fruit refresh-keeping etc.

In tobacco field, for its characteristics of improving taste, non-poisonous and odorless burning, chitosan can be applied as tobacco slice glue.

The international shrimp industry from harvest through various processing operations produces a vast amount of potentially recoverable proteinaceous by-products in the form of shrimp heads and shells which is one of the major raw materials for chitin/chitosan production. Shells of other crustaceans viz. crabs, prawns, fish bones also could be profitably utilised.

Utilizing these by-products (e.g. chitosan), it is possible to remove fluoride from contaminated water. It is necessary to remove excessive amount of fluoride in water due to these reasons.

In areas of India, where food and water are naturally fluoride-abundant, severe fluoride toxicity is common and manifests as debilitating and disfiguring diseases(d). Well-known is that fluoride excess irreversibly cripples bones and crumbles teeth (fluorosis).

1) aches and pain in the joints, i.e. neck, back, hip, shoulder and knee without visible signs of fluid accumulation

2) non-ulcer dyspepsia such as nausea, vomiting, pain in the stomach, bloated feeling or gas formation in the stomach, constipation followed by diarrhea

3) polyuria (frequent urination) and polydipsia (excessive thirst)

4) muscle weakness, fatigue, anemia with low hemoglobin level

5) complaints of repeated abortions/still birth

6) complaints of male infertility with abnormality in sperm morphology, oligospermia (spermatozoa deficiency in the semen), azoospermia (spermatozoa absence in the semen) and low testosterone levels.”

Widespread occurrence of fluoride above the prescribed limit in groundwater meant for human consumption has caused multidimensional health problems, most common being dental fluorosis and skeletal fluorosis. Fluoride is one of the most abundant constituents occurring in groundwater in India and creates a major problem in safe drinking water supply. Several methods of defluoridation of drinking water have been developed. However, in India, precipitation and adsorption are the most preferred. Precipitation process is based on the addition of chemicals and removal of insoluble compounds as precipitates. In adsorption method, different types of adsorbents are being used for defluoridation, e.g. activated alumina, coconut shell carbon, chemically activated carbon, bone charcoal, natural zeolites, burnt clay and other low-cost adsorbents.

The shortcomings of most of these methods are high operational and maintenance costs, low fluoride removal capacity, lack of selectivity for fluoride, undesirable after effects on water quality, generation of large amount of sludge and complicated procedure involved in the treatment. The most commonly adopted method in India, Nalgonda technique of community defluoridation, is based on precipitation process and is very efficient and cost effective. The major limitations of Nalgonda technique are daily addition of chemicals, large amount of sludge production, least effective with water having high total dissolved solids and high hardness. Besides, it converts a large portion of ionic fluoride (67–87%) into soluble

aluminium complex and practically, removes only a small portion of fluoride in the form of precipitate (18–33%). Therefore, this technique is erroneous. Residual aluminium ranging from 2.01 to 6.86 mg l⁻¹ was also reported in Nalgonda technique, which is dangerous to human health as aluminum is a neurotoxin, concentration as low as 0.08 mg l⁻¹ in drinking water has been reported to cause Alzheimer's disease and has strong carcinogenic properties.

In the present study, an attempt has been made for defluoridation of drinking water using chitosan as a new, feasible, suitable and low-cost adsorbent.

1.5 Advantage of Chitosan in purifying water:

- The efficiencies of removal of fluoride ions of chitosans vary from 47.9-68.7 % depending upon the characteristics and particle size of adsorbent(s).
- Chitosans require simple alkali or/and acid treatment for the removal of lignin before their application and to increase efficiency.
- Chitosans require less maintenance and supervision. Separation is possible and it is biodegradable. So, it reduces pollution.
- These chitosans can be disposed off easily and safely. Used adsorbents can be reused as a filler material in low-lying areas and hence their disposal does not pose any serious problem.

CHAPTER 2

REVIEW

2.1 Review of Previous work

Yadav et al. developed a method for the defluoridation of groundwater using brick powder as an adsorbent. Feasible optimum conditions were applied to two groundwater samples of high fluoride concentration to study the suitability of adsorbent in field conditions. Comparison of adsorption by brick powder was made with adsorption by commercially available activated charcoal. In the optimum condition of pH and dose of adsorbents, the percentage defluoridation from synthetic sample, increased from 29.8 to 54.4% for brick powder and from 47.6 to 80.4% for commercially available activated charcoal with increasing the contact time starting from 15 to 120 min. Fluoride removal was found to be 48.73 and 56.4% from groundwater samples having 3.14 and 1.21 mg l⁻¹ fluoride, respectively, under the optimized conditions. Presence of other ions in samples did not significantly affect the defluoridation efficiency of brick powder. The optimum pH range for brick powder was found to be 6.0–8.0 and adsorption equilibrium was found to be 60 min. These conditions make it very suitable for use in drinking water treatment. Defluoridation capacity of brick powder can be explained on the basis of the chemical interaction of fluoride with the metal oxides under suitable pH conditions. The adsorption process was found to follow first order rate mechanism as well as Freundlich isotherm.

Islam et al. evaluated the removal efficiency of fluoride from aqueous solution using quicklime. Their studies indicate that the adsorption process is chemisorption along with precipitation. Removal efficiency was found to be maximum when the initial fluoride concentration was high. Their technique of removal may be suitably employed to treat industrial effluent where the concentration of fluoride is high. But the removal of fluoride using quick lime cannot be used for domestic purpose, since it cannot bring fluoride concentration within permissible limit, and also increases the pH of the treated water.

Durmaz et al. proposed a new technique for the removal of fluoride from diluted solution with Neosepta AHA anion exchange membrane has been studied by Donnan dialysis. The effects of concentration, pH, and accompanying anion on feed phase and receiving phase composition were investigated. Neosepta AHA anion exchange membrane was used for the removal of fluoride and the flux of fluoride with respect to the concentration, pH, and the effect of the counter-ions (HCO_3^- , Cl^- , SO_4^{2-}) were obtained between $34\text{-}136 \cdot 10^{-7}$ ($\text{m.mol.cm}^{-2} \cdot \text{s}^{-1}$). The effect of the fluoride flux increased with increasing of concentration on the feed phase. The flux of fluoride was found to be higher at higher pH in the feed phase. In addition, the accompanying counter-anions also influenced the flux of fluoride and the order of flux was founded as $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$.

CHAPTER 3

OBJECTIVE

3.1 Objective

The objective of the project work is to remove fluoride from contaminated water using chitosan. To do this, we have planned to prepare good quality chitosan and to measure the rate of adsorption by putting measured amount of chitosan in standard fluoride solution in two ways:

- Changing the concentration of fluoride solution with certain amount of chitosan.
- Changing the amount of adsorbent with the standard solution.

Then, we study the efficiency of fluoride removal using chitosan.

CHAPTER 4

**MATERIALS AND
METHODS**

4.1 Raw Materials

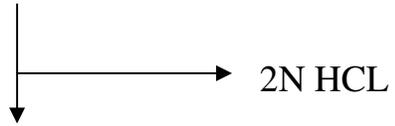
We have taken marine water prawns for this project work. Generally the species taken were *palemon malcomsoni* and *pandalus borealis*. These are collected from chilika lake and puri sea shore.



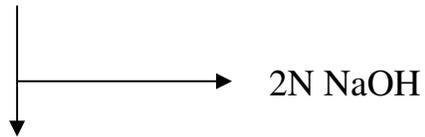
Figure 4. *Pandalus borealis*

4.2 General method

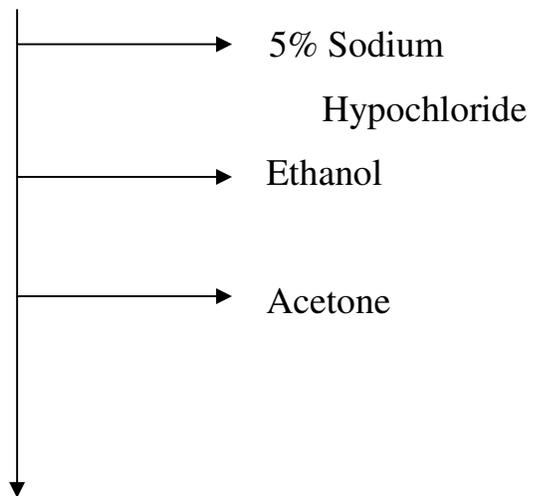
Shrimp Shells



Decarbonated Shells



Deproteinized Shells



Chitin



Chitosan

4.3 Preparation

Prawns were collected in a huge amount, washed it thoroughly. These are deshelled gently removing the shell around the body. The shrimp shells were then washed thoroughly under cold running water to remove sands, mud and other dirty things, then sun dried. These hard shells were taken and grinded to 35-80 mesh size.



Figure 5. After deshelling the prawn shell

4.3.1 Demineralisation

The shrimp shells were transferred to a mild steel vessel lined with fiber glass and was treated with 2N hydrochloric acid. This is kept for 3 hours with occasional stirring till the reaction is complete. The excess acid was decanted and the residue is washed till the p H is normal.

4.3.2. Deproteinisation

The decarbonated shells were boiled with 2N sodium hydroxide for 30 minutes in a mild steel vessel to remove protein stuck to head and shell. The boiled raw materials were allowed to cool and it was washed with water to remove all traces of alkali (could be tested with a pH paper).

Then these deproteinised shells were treated with sodium hypochloride for 30 minutes and then treated with ethanol.

4.3.3 Removal of water

Excess water was removed using a screw press till the moisture is below 60%. The product thus obtained is called chitin.

4.3.4 Deacetylation of Chitin

It is the process of conversion of chitin to chitosan.

Chitin was heated at 90-95⁰ C for about one and a half hour with 50 percent caustic soda in a mild steel vessel. Excess alkali was drained off and the mixture was washed with water several times till it is free from alkali. Eighty percent of the alkali, thus removed .

4.3.5 Drying

The above product was sun dried for 6-8 hours or in drier till the moisture content is very less Chitosan thus obtained was in the form of flakes.

4.3.6 Precautions

- Spoiled shells should be avoided .
- Drying temperature of wet chitosan flakes should neither exceed 60⁰ C nor decomposed.
- Raw material should be thoroughly free from extraneous matter like sand, clay etc.

4.4 Process of fluoride removal

After preparation of chitosan, these were stored in air tight bottles for further studies.

4.4.1 Thermal activation of adsorbent materials

The preliminary adsorption studies of various adsorbent showed that thermal treatment of adsorbent significantly enhances the adsorbing capacity by increasing the porosity and surface area. And hence the chitosan samples were thermally treated at a temperature of 50 °C for 2 h before adsorption studies were carried out. An accurately weighed quantity of chitosan lime was activated in a preheated muffle furnace. The weight of chitosan sample after heating was taken and was used to calculate loss of water and other volatiles (if any).

4.4.2 Chemicals used

All the reagents used were of AR grade. Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in 1000 ml distilled water in volumetric flask. Fluoride standard solution was prepared

by diluting 100 ml stock solution to 1000 ml distilled water in volumetric flask. This 1 ml solution has 0.1 mg of fluoride.

4.4.3 Procedure

The fluoride adsorption experiments from its aqueous solution on thermally activated quick lime samples were carried out using standard 10 and 50 mg/L fluoride solution in absence of any other competing ions. All the experiments were carried out at ambient temperature (25 ± 2 °C). After continuous stirring in magnetic stirrer at about 400 rpm for 1 hour interval, the solid was separated by filtration through Whatman 42 filter paper and the remaining fluoride was estimated by Orion ion selective electrode.

CHAPTER 5

**RESULTS AND
DISCUSSION**

5.1 Results and discussion

Putting the adsorbent e.g chitosan in the fluoride solution, the following observations were taken, which are given in the table 1.

Q0 (mg/l)	Qe (mg/l)	Q0-Qe (mg/l)	(Q0-Qe)/Q0 x 100
10	6.8	3.2	32
20	11.8	8.2	41
30	12.3	17.7	59
40	23.8	16.2	40.5
50	31.5	18.5	37

Table 1. Rate of adsorption using fluoride solution of 10-50 mg/l

5.1.1 Effect of initial fluoride concentration

The adsorption data are represented in Table 1. The thermal pretreatment of chitosan strongly influences the adsorption of fluoride. The adsorption of fluoride onto chitosan was studied by varying initial fluoride concentration using optimum adsorbent dose (0.5 g/100 mL) at ambient temperature (25 ± 2 °C) for a contact time of 1 hour. The results are represented in graphical form as percentage removal versus initial fluoride concentration. The initial fluoride concentration was increased from 10 to 100 mg/L and the corresponding removal gradually increased from 32 (initial concentration of 10 mg/L) and achieved a maximum value of 59 (initial concentration of 30 mg/L) and then it is gradually decreased to 37 (initial concentration of 50 mg/L). However, it is clear from the Figure 6

that, maximum removal takes place when the initial concentration is high (i.e. 10 mg/L) and removal is very less at lower concentrations.

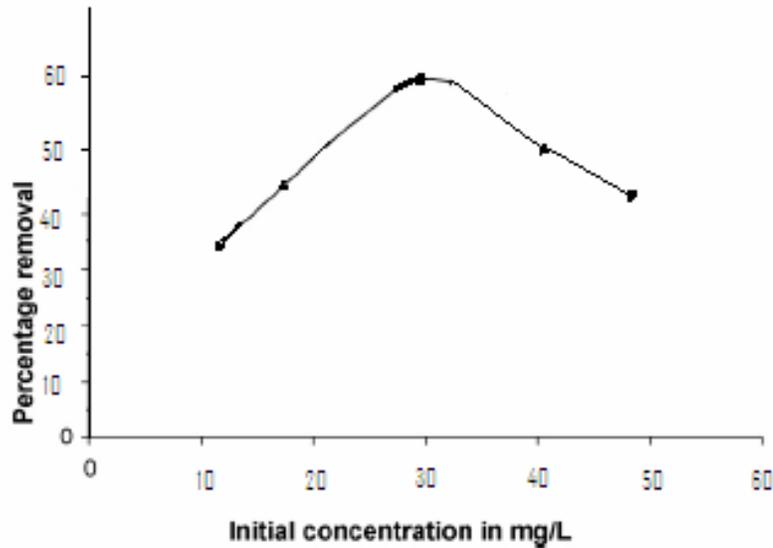


Figure 6. Initial fluoride concentration Vs. Percentage removal

5.1.2 Effect of adsorbent dose

The effect of adsorbent dose on the removal of fluoride was studied at ambient temperature (25 ± 2 °C) and contact time of 75 min for initial fluoride concentration of 50 mg/L. The results are presented in Fig.7. It is evident from the figure that the removal of fluoride increased from 19.8 to 59.7 for 0.1–1.0 g/100mL of chitosan. However, it is observed that after dosage of 0.5 g/100 mL, there was no significant change in percentage removal of fluoride. It may be due to the overlapping of active sites at higher dosage.

Weight of adsorbent (g/100 mL)	Fluoride adsorbed in percentage
0.1	19.8
0.2	29.1
0.3	44.3
0.4	52.7
0.5	59.7

Table 2. Percentage removal of fluoride using different weight of chitosan

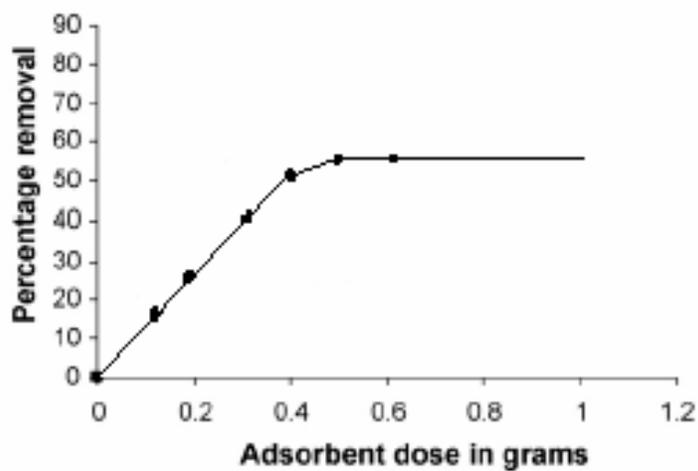


Figure 7. Adsorbent dose vs. percentage removal of fluoride with initial concentration of 50 mg/L.

CHAPTER 6

CONCLUSION

Conclusion

In this project work, we got good quality, off white crystalline, odourless chitosan. It is experimentally proved that the prepared chitosan is able to remove 59% fluoride from water. So, it can be widely used for defluorination. Though it is nontoxic biodegradable, it can be used repeatedly for fluoride removal process. By adding different binding materials and additives, the properties of chitosan can be enhanced, which may increase the fluoride adsorption property. The further study is in progress.

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