Removal of Fluoride from Water by using Natural Absorbent ALGAE

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Abstract— Fluoride is present in most natural waters at concentrations varying from 0.05 to 100 mg/L. In India, there are many areas where groundwater contains high concentrations of fluorides. Fluoride seems to be both beneficial and toxic to humans depending upon the concentration of the ion in drinking water. Considering the range of health effects associated with high levels of fluoride in water, algae has been used in this study for fluoride removal. The influence of various operational parameters i.e., effect of adsorbent dosage, effect of pH and effect of contact time were studied by a series of batch operation experiments at room temperature of 15±30C.80-85% removal was found with the increase of adsorbent dosage in (g/l), pH from acidic to basic and time for a given initial fluoride concentration 5 ppm.

Key words: Fluoride, Adsorbent Algae, pH, Agitation Time

I. Introduction

Fluoride ion in water exhibits unique properties as its concentration in optimum dose in drinking water is advantageous to health and excess concentration beyond the prescribed limits affects the health adversely. High fluoride concentration in groundwater's and surface waters in many parts of the world is a cause of great concern. High fluoride in drinking water was reported from different geographical regions. Though fluoride enters the body mainly through water, food, industrial exposure, drugs, cosmetics, etc., drinking water is the major source (75%) of daily intake [1].A fluoride ion is attracted by positively charged calcium in teeth and bones, due to its strong electro-negativity. Major health problems caused by fluoride are dental fluorosis (teeth mottling), skeletal fluorosis (deformation of bones) and non-skeletal fluorosis [2 & 3]. It can interfere with carbohydrates, lipids, protein, vitamins, enzymes and mineral metabolism when the dosage is high. In some parts of India, the fluoride levels are below 0.5 mg/L, while at certain places, fluoride levels are as high as 35 mg/L [4].

Defluoridation is performed by adsorption, chemical treatment, ion exchange, membrane separation, electrolytic defluoridation, and electro dialysis, etc. Among various processes, adsorption was reported to be effective. Investigators reported various types of adsorbents namely activated carbon, minerals, fish bone charcoal, coconut shell carbon and rice husk carbon, with different degrees of success [5]. Different materials like crushed limestone, alum, rice husk etc. are inexpensive sorbents for fluoride removal. Moreover, bio sorption by algae is proven to be quite effective at removing metal ions from contaminated solutions in a low-cost and environment-friendly manner [6]. Although much of the current bio sorption researches using algae are oriented towards the removal of metal cations, the binding of anions like fluoride to this biomass is a growing area of study.

C.M.Vivek Vardhan and J.Karthikeyan [7] conducted experiment on removal of fluoride from water using low-cost materials. This paper presents the results of investigations carried out for removal of fluoride from water employing physico-chemical processes of adsorption and coagulation employing abundantly available and low-cost materials like Rice Husk, seed extracts of Maringa Oleifera (Drum stick), and chemicals like Manganese Sulphate and Manganese Chloride. Rice husk of 6g/l accomplished a removal of 83% of Fluoride from a 5mg/l of Fluoride solution requiring an equilibrium time of 3 hours. Viswanathan and Meenakshi [8] studied the defluoridation efficiency of alumina particles incorporated in the chatoyant polymeric matrix. They observed defluoridation capacity of 3809 mg/kg was not influenced by the pH of the medium. Having seen the past research, this study investigates the removal of fluoride in water using algae (spirogyra) biomass as bio sorbent.

II. Materials

A. *Collection of Bio Sorbent Material*

Fresh sample of algae was used in this study as a bisorbent. This material was collected from the artificial irrigation canal in Tirupati. The unwanted matters were removed manually from the collected algae, then rinsed with tap and distilled water to remove dirt, sands, and external salts. Afterwards, the washed algae were kept in air for evaporating of water and dried in an oven at 65 °C for 48 h. The dried biomass were roughly chopped, grounded into powder, sieved, and kept in air-tight polyethylene container at room temperature. An average size of 0.55 mm was used for bisorption experiments with required amounts.

Fig. 1: Collection of Algae

Fig. 2: Dried Algae

B. Chemicals

All chemicals used in this study were of analytical grade obtained either from Merck, Germany or SD Fine Chem. Ltd., India. Stock solution of fluoride was prepared by using sodium fluoride of 221mg in double distilled water. Purified water was prepared using a Millipore Milli-Q (Bedford, MA, USA) water purification system. Fluoride solutions of different concentrations were obtained by diluting the stock solution. Standard solution of fluoride (100 mg/L) for atomic adsorption spectrophotometer was obtained from Merck, Germany. Standard acid and base solutions (0.1N HCl and 0.1N NaOH) were used for pH adjustments. Infra-red spectra of the samples were recorded on a Perkin Elmer FTIR, Spectrophotometer model-1600 (Perkin Elmer, USA).

C. Fluoride Solution

All the chemicals used in this study were of analytical grade, and de-ionized water was used for solution preparation. A stock solution (100 mg/l) of fluoride ions was prepared by dissolving appropriate amount of sodium fluoride (provided by Merck, Germany) in distilled water and stored in glass container at room temperature. The working fluoride ions solutions were prepared by appropriate dilution in accurate proportions of the stock solution immediately prior to use. The ph of the working solution was adjusted by using dilute HCL or NaOH solutions. Prior the experiments, all the glassware used for dilution, storage, and experimentation were cleaned with detergent, thoroughly rinsed with tap water, soaked overnight in a 20% HNO_3 solution, and finally rinsed with distilled water before use.

III. EXPERIMENTAL METHODS

To the standard fluoride solution, the prepared algae are added as adsorbents. The fluoride content in the sample is determined after defluoridation by using SPADNS method. All the chemicals used are of analytical reagent grade. The reagents prepared are (1) Standard fluoride solution: 221.0 mg of anhydrous sodium fluoride (98% pure, LR quality, supplied by Ranboxy Laboratories Ltd.,) has been weighed accurately and is transferred into 1000 ml volumetric flask. The substance is dissolved in double distilled (fluoride free) water and then the solution is diluted to 1 litre. The resultant solution contains 1000 ppm of fluoride. This solution is stock fluoride solution. 100 ml of this stock fluoride solution is diluted to 1000 ml with double distilled water to get 100 ppm of fluoride solution. Standard fluoride solutions of different concentrations ranging from 1 ppm to 6 ppm have been prepared from this 100 ppm of fluoride solution.

The apparatus used are

1) U V - Visible Spectrophotometer (Chemeto, model no: UV - 2600)
2) Elico - pH Meter, Elico Pvt Ltd; India.
3) Elico- Conductivity meter, Elico Pvt Ltd; India.
4) Remi shaker

A. Procedure

Preparation of standard curve: Fluoride standards are prepared in the range of 0 to 1.40 mg F/L by diluting appropriate quantities of standard fluoride solution to 50 ml with distilled water. 5.00 ml of each SPADNS solution and Zirconyl-acid reagent, or 10.00 ml of mixed acid-Zirconyl SPADNS reagent is pipetted and is added to each standard fluoride solution and is mixed well. Contamination is to be avoided. Photometer is set to zero absorbance with the reference solution and absorbance readings of standard fluoride solutions are obtained. A curve of the milligrams fluoride Vs absorbance relationship is plotted. A new standard curve is prepared whenever a fresh reagent is made or a different standard temperature is desired. As an alternative of using a reference, photometer is set at some convenient point (0.300 or 0.500 absorbance) with the prepared 0 mg F/L standard.

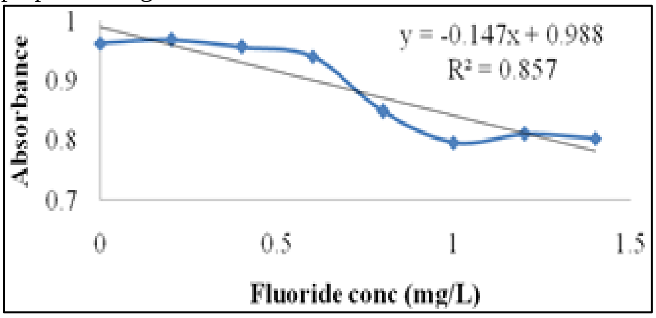

Fig. 3: Calibration curve

Procedure for the defluoridation of standard fluoride solution, using the prepared carbons as adsorbents: 50 ml of standard fluoride solution (5mg/L) is pipetted out into a conical flask. 0.5 g/L of one of the prepared carbons is added and is stirred at 240 rpm mechanically for 30 minutes. The solution is filtered through Whatmann No- 42 filter paper. 10 ml of acid Zirconyl -SPADNS reagent is added to the filtrate and absorbance is noted at 570 nm, using UV- visible spectrophotometer against the reference. The fluoride concentration in the sample after defluoridation is determined from the standard curve. The same procedure has been adopted for the experiments carried out by varying algae dosage, pH and Contact time.

B. Batch Adsorption Studies

Equilibrium studies have been made at room temperature (30 +1°C) by employing the batch adsorption technique. All the experiments were carried out at specified optimum conditions. This is the logical choice in most applications as it minimizes the pre-treatment costs in the overall purification scheme. The percentage removal of fluoride and the amount adsorbed (in mg/g) have been calculated by using the following relationships:

$$\text{Percentage removal} = 100\,(Q - Ce)/\,C$$

$$\text{Amount adsorbed } (Qe) = (Cj - Ce)\,/\,m$$

Where Q is the initial concentration and Ce is the final concentration of the fluoride respectively, and m is the weight of adsorbent in g/L. Adsorption Experiments have been carried out with a view to determine the impacts of the effects like particle size, pH, contact time, dose and initial concentration of fluoride. The data have been analyzed in the light of adsorption isotherms, adsorption kinetic equations and intra particle diffusion model.

IV. RESULTS AND DISCUSSION

A. *Influence of Adsorbent Dosage*

To determine the effect of adsorbent dose, different amounts (0.5-2.5 g/L) of adsorbent were suspended in fluoride solution in which the concentration of fluoride was 5 mg/L. The effect of adsorbent dose on the extent of removal of fluoride is shown in Fig. 4. The amount of adsorbent significantly influenced the extent fluoride adsorption. The extent of fluoride bisorption was 77.98% for 0.5 g/L of algal biomass, while it was greatly increased to 82.9% for 1.5 g/L of adsorbent. However, there was only a slow change in the extent of fluoride adsorption when the adsorbent dose was over 1.5 g/L. Furthermore, higher adsorbent dose will result in lower adsorption capacity value at a fixed fluoride concentration (5 mg/L). At low algal dose, all types of sites are entirely exposed and the adsorption on the surface is saturated faster. But at higher adsorbent dose, the availability of higher energy sites decreases with a larger fraction of lower energy sites occupied, resulting minute adsorption of fluoride.

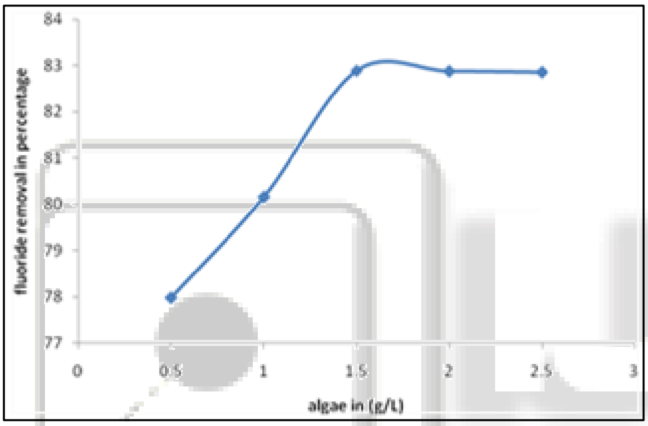

Fig. 4: Adsorbent dosage

B. *Effect of pH*

The pH of the aqueous solution is an important controlling factor in the adsorption process. pH levels of 3,5,7,9,11and 13 which is maintained by adding 0.1N solutions of HC1 and NaOH with 50 ml of standard solution of 5ppm of fluoride with a contact time of 120 minutes and a dose of 1.5g/L is maintained. The influence of the pH on the sorption rate is shown in Fig.5. It is observed from the Fig.5 that the percentage of removal fluoride is pH dependant. The results obtained shows that the maximum efficiency of percentage of fluoride removal is 82.60 at pH 7.00. It is observed that percent removal increased from, acid media to basic media but after pH level 7.0 the percent removal vary very little. The results agree well with those reported in the past research. At pH value of 7.0, the adsorption site may be fully activated and at pH after 7.0 when all the carbons acquire negative carbon, still there is a sufficient defluoridation capacity, therefore at pH greater than 7 it appears that fluoride removal by activated carbons may be purely governed by physisorption. In fact fluoride adsorption through Vander Waals type of forces may be taking place to some extent through the pH range.

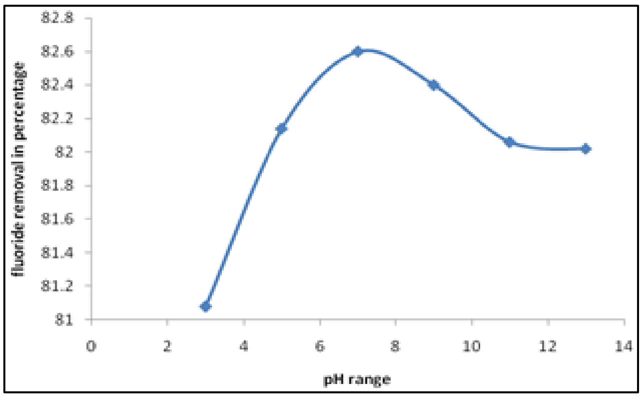

Fig. 5: pH vs. fluoride removal

C. *Effect of Agitation Time*

In the adsorption system contact time plays a vital role, irrespective of the other experimental parameters affect the adsorption kinetics. In order to study the kinetics and dynamics of adsorption of fluoride by adsorbents, the adsorption experiments are conducted and the extent of removal of fluoride is known by varying the contact time (range: 5-240 minutes) .The percentage of fluoride removal at different time was worked out using above equations and a plot was prepared between the percentage of fluoride removal and contact time (Fig.6). It can be noted that the percentage fluoride removal is increasing with time and attained almost an equilibrium condition at 120 minutes (at which the rate of adsorption of solute is equal to the rate of desorption). The removal of fluoride by these adsorbent samples is rapid at the initial period but becomes slow and almost stagnates with the increase in the contact time. The relative increase in the extent of removal of fluoride is substantially low after 120 minutes of contact time by the adsorbents, which is fixed as the optimum contact time. This indicates that the rate of removal of fluoride is higher in the initial stage due to the availability of adequate surface area of the adsorbent. With increase in contact time and due to the decrease in the availability of active sites the adsorption process decreases. Though equilibrium of the adsorption process is found to be attained in. about 120 minutes, the particle contact time for the adsorption process under the condition chosen may be taken as 120 minutes as most of the fluoride adsorption took place by then. The higher initial rate of removal may be occurring due to the vacant adsorption sites, high solute concentration gradient and the electrostatic affinity between the adsorbent and the solute adsorbate.

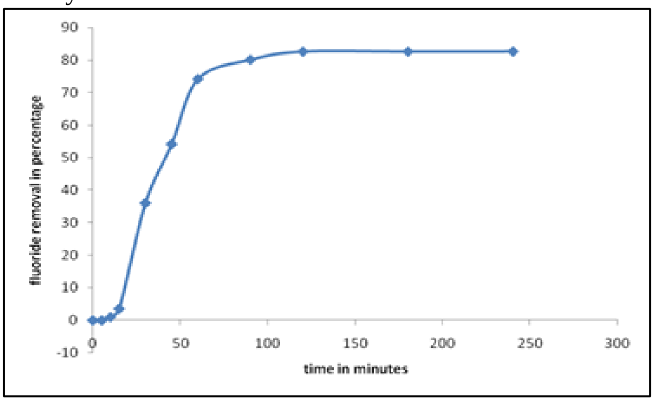

Fig. 6: Agitation time vs. fluoride removal

V. CONCLUSIONS

The results obtained from the present work demonstrate that algae generally has advantages characterizes as an economical and viable substitutes when compared to other adsorbents. One of the major advantages of using algae over other chemical treatment methods is that, along with being a disinfectant, it also acts as a defluoridation agent, this study concludes the following:

1) Optimum dose of adsorbent was found 1.5mg/l for removal of fluoride of 5ppm concentration.
2) Adsorption capacity is more when ph is about 7.
3) Optimum agitation time is found to be 120 min.

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