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Treatment of High Fluoride Drinking Water Using Bioadsorbent

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Abstract

Recent surveys carried out to investigate the quality of groundwater in India indicated that some areas in the Dry Zone have the fluoride problem in endemics proportions. In these studies, it is clearly revealed that more than 60 percent of drinking water wells had fluoride levels exceeding 1.5 mg/L in the fluoride rich areas. Therefore, a technique for the defluoridation of fluoride-rich waters is necessary. This study describes the development of low cost effective adsorbent for the removal of dissolved fluoride in water using Phyllanthus emblica. The batch adsorption study was applied to analyze the defluoridating efficiency by varying contact time, adsorbent dose, adsorbate concentration, adsorbent particle size and presence of co-anions at neutral pH. Prepared adsorbent shows enhanced removal of fluoride by 82.1% at equilibrium contact time of 75 minutes. This study is a step in developing a general platform suitable for producing potable water that also specifically addresses the problem of fluoride removal.

Key words: Fluoride, adsorption, *Phyllanthus emblica,* bioadsorbent.

Introduction

Fluoride, the ionic form of fluorine is widely distributed in nature. It is a common constituent of most soils and rocks. The industrial effluent and sewage discharged from the domestic water supplies supplemented with fluoride contribute to the fluoride levels in aquatic systems. Combustion of coals and volcanic activity also contribute fluoride containing dusts and gases to the atmosphere. During rainfall, these are being dissolved in water and contaminate the water bodies. Fluoride has been considered as both an essential element and potent environmental pollutant at high concentrations causing a number of disorders (fluorosis) among the consumers. Fluorosis in general, has been identifies in various countries. In India, most of the water bodies are highly contaminated by fluoride with varying concentration in the range of 0.5-20 mg/L[1, 2].

According to World Health Organization norms, the upper limit of fluoride concentration in drinking water is 1.5 mg/l[3]. Excessive presence of fluoride (F) in potable water continues to be a serious public health concern in many parts of the world, including India. Adsorption has shown considerable potential in defluoridation of wastewater. The viability of such technique is greatly dependent on the development of suitable adsorptive materials. In this respect, literature is replete with studies on defluoridation, albeit using mostly alumina and oxides of a few metals as adsorbents[4-12]. In most of these studies, performance of the adsorbents has been evaluated under batch conditions, with temperature, pH, and dose of adsorbents being the primary variables[2-7]. Few column studies have also been carried out with a view to determining breakthrough curves and throughput volume during dynamic (flow) conditions in packed beds[10-12].

Traditional adsorbent like granular activated carbons (GAC) has also been tested for defluoridation, but without much success[13,14]. The application of modified GAC in removal of dissolved solutes has drawn interest[15-19]. Although the modified GAC showed considerable potential in removing organic pollutants such as phenolic compounds and to some extent, arsenic and manganese in wastewater, only partial success has been reported on defluoridation. In one such study, equilibrium and kinetic studies were carried out on fluoride adsorption from water by zirconium ion impregnated activated carbon[20-22].

In another study on defluoridation using aluminum (Al)-impregnated activated carbon, the adsorption of fluoride was shown to be strongly dependent on pH of the solution and as a consequence the method required pre- and post-treatment of the aqueous solution[23]. On the basis of literature survey, it is fair to say that despite several studies carried out on the adsorptive removal of fluoride ions, the maximum removal efficiency reported is between 60-90%. Removal in excess of 90% has also been reported, however, in acidic medium (pH = 4.0), thus requiring post treatment for preparing potable water at suitable pH. In addition to these limitations, there are several operational difficulties such as plugging, fouling, and excessive pressure-drop, encountered during defluoridation using packed beds of granular adsorbent particles, leading to periodic disruption of operation.

Within last few years, the plant based bioremediation approach to improve the quality of water has become an area of intense study[24]. Bioremediation is recognized as a cost-effective and environmental friendly option for cleanup of contaminated water. The present study has been carried out to remove fluoride using a plant, *Phyllanthus emblica* under laboratory conditions.

Material and Methods

Adsorbent preparation: The *Phyllanthus emblica* sample (powdered seed), common name, Indian gooseberry, was purchased from market. Then the material was dried at 378-383K for 24 hours. It was washed with doubly distilled water to remove the free acid and dried at the same temperature for 3 hours. Later the dried adsorbent was thermally activated in Muffle furnace at 1073K (here we avoid acid treatment for charring). The resulting product was cooled to room temperature and sieved to the desired particle sizes, namely, <53, 53 - 106, 106 - 150, 150 - 225 and 225 - 305 mesh. Finally, the product was stored in vacuum desiccators until required.

Batch Adsorption Study: The batch adsorption defluoridation study was conducted for the optimization of various experimental conditions like contact time, initial fluoride concentration, adsorbent dose, particle size and influence of co-ions with fixed dosage. The mixture was agitated in a thermostatic shaker at a speed of 250 rpm at room temperature. The reagents used in this present study are of analytical grade. A fluoride ion stock solution (100 mg/L) was prepared and other fluoride test solutions were prepared by subsequent dilution of the stock solution. All the experiments were carried out at room temperature. Fluoride ion concentration was measured with a specific ion selective electrode by use of total ionic strength adjustment buffer II (TISAB II) solution to maintain pH 5–5.5 and to eliminate the interference effect of complexing ions [9]. The pH of the samples was also measured by Orion ion selective equipment. All other water quality parameters were analysed by using standard methods[25]. Kinetic studies of sorbent were carried out in a temperature controlled mechanical shaker. The effect of different initial fluoride concentrations viz., 2, 4, 6, 8 and 10 mg/L were studied by keeping the mass of sorbent as 0.75 g and volume of solution as 100 ml in neutral pH.

The fluoride concentration retained in the adsorbent phase, q_e (mg/g), was calculated according to[26],

$$q_e = \frac{(C_o - C_e)}{W} \qquad (1)$$

Where q_e is the amount of fluoride adsorbed (mg/g); C_o and C_e are the initial and residual concentration at equilibrium (mg/L), respectively, of fluoride in solution; and W is the weight (g) of the adsorbent.

Results and Discussion

Effect of Contact Time and Initial Fluoride Concentration: Contact time plays a very important role in adsorption dynamics. The effect of contact time on adsorption of fluoride onto *Phyllanthus emblica* is shown in figure 1. Batch adsorption studies using the concentrations 2.0, 3.0, 4.0, 6.0, 8.0 and 10.0 mg/L of fluoride solution and with 0.75 g of the adsorbent were carried out at 303K as a function of time to evaluate the defluoridation and adsorption rate constants. The adsorption of fluoride increases with time and gradually attains equilibrium after 75 minutes. From Fig.1, the time to reach equilibrium conditions appears to be independent of initial fluoride concentrations. Therefore 75 minutes was fixed as minimum contact time for the maximum defluoridation of the sorbent. The adsorption of fluoride decreased from 87.95 to 47.22% by increasing fluoride concentration from 2.0 to 10.0 mg/L. Further, it was observed that the removal curves are smooth and continuously indicating the possibility of the formation of monolayer coverage of fluoride ion at the interface of adsorbent.

Effect of Particle Size: The defluoridation experiments were conducted using *Phyllanthus emblica* with five different particle sizes viz. >53, 53–106, 106–150, 150–225 and 225–303µm. As the adsorption process is a surface phenomenon, the defluoridation efficiency of the sample with 53µm registered high defluoridation efficiency due to larger surface area (figure 2). The variation in the percentages of fluoride removal by the sample with different particle sizes was studied. Hence, the material with particle size of 53µm has been chosen for further experiments. Higher percentage of adsorption by *Phyllanthus emblica* with smaller particle size is due to the availability of more specific surface area on the adsorbent surface.

Influence of Adsorbent Dose: The influence of varying concentrations of adsorbent on the adsorption of fluoride at neutral pH is shown in figure 3. While increasing the adsorbent dose proportional removal was observed for fluoride until some extent. After that, the curve lapse as flat indicating the higher fluoride adsorption occurs at 0.75 g and the followings remains constant. A distribution coefficient K_D reflects the binding ability of the surface for an element. The K_D value of a system mainly depends on pH and type of surface. The distribution coefficient K_D values for fluoride and *Cynodon dactylon* at neutral pH were calculated[27] with

$$K_D = \frac{C_s}{C_w} \qquad (15)$$

Where C_s is the concentration of fluoride in the solid particles (mg/kg) and C_w is the concentration in water (mg/L). It is seen that the distribution coefficient K_D increases with an increase in adsorbent concentration, indicating the heterogeneous surface of the adsorbent[26]. It is observed in figure 4 that K_D increases with an increase in adsorbent concentration at constant pH. If the surface is homogeneous, the K_D values at a given pH should not change with adsorbent concentration. All the forthcoming experiments were carried out using constant adsorbent dose 0.75 g.

Effect of Interfering co-ions: The effects of coexisting anions such as sulfate, nitrate, chloride, and bicarbonate on fluoride adsorption by the *Phyllanthus emblica* adsorbent were examined and the results are given in figure 5. Chloride and nitrate did not perceptibly interfere with fluoride removal even at a concentration of 500 mg/L, while sulfate began to show some adverse effects when the SO_4^{2-} concentration increases. However, bicarbonate showed great competitive adsorption with fluoride. The fluoride adsorption amount decreased quickly from 82.1 to 51.9% with the increase of bicarbonate concentration 0–500 mg/L. This may be attributed to the competition of bicarbonate ions with the fluoride ions at the active site, on the surface of the sorbents. The selective nature of the fluoride by the sorbent depends on size, charge, polarizability, electronegativity difference, etc. The order of interference for fluoride removal observed as in the following order, HCO_3^- >SO_4^{2-} >Cl^- ≥NO_3^- for the adsorbent *Phyllanthus emblica*. Similar trend was reported while studying *cynodon dactylon* as a sorbent for fluoride removal[24].

Conclusion

The activated carbon was prepared from *Phyllanthus emblica* by the thermal process. At neutral pH, the success rate of defluoridation was observed as 82.1 percent for the 3 ppm initial fluoride concentration at the optimal adsorbent value. Also the presence of bicarbonate ions interfere the defluoridating property of this adsorbent; but this interference is insignificant for other co-anions. This study also indicates that the adsorbent is heterogeneous in nature. Based on the above said descriptions, *Phyllanthus emblica* bioadsorbent can be utilized to remove fluoride selectively from water.

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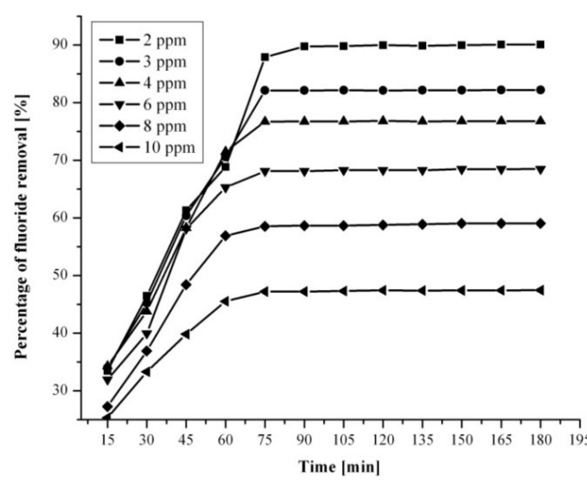

Figure-1: Effect of contact time on Defluoridation

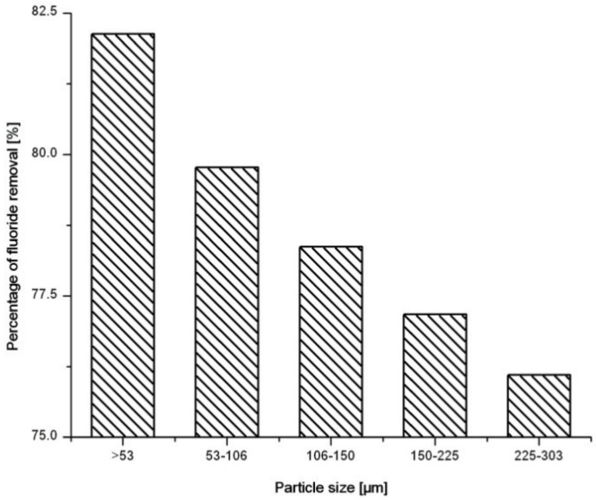

Figure-2: Particle size role of fluoride removal

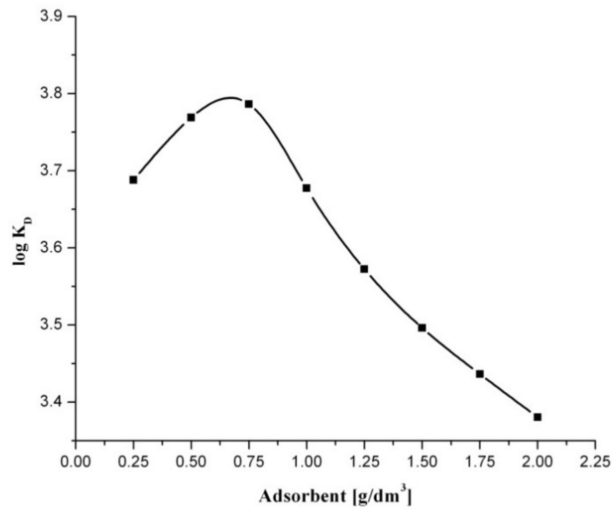

Figure-4: Plot for log K_D with Adsorbent concentration

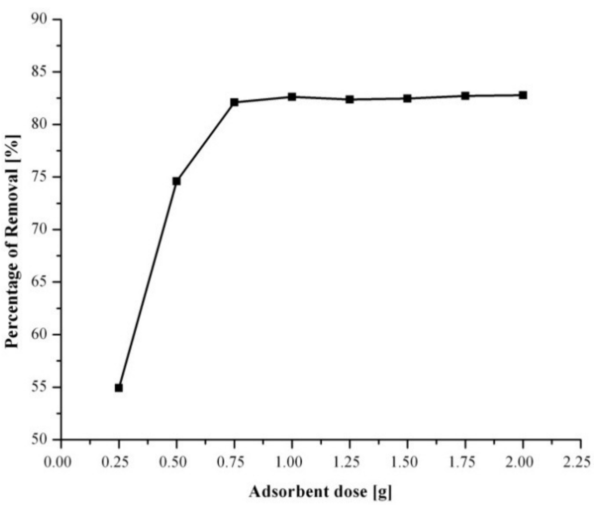

Figure-3: Percentage of fluoride removal while varying adsorbent

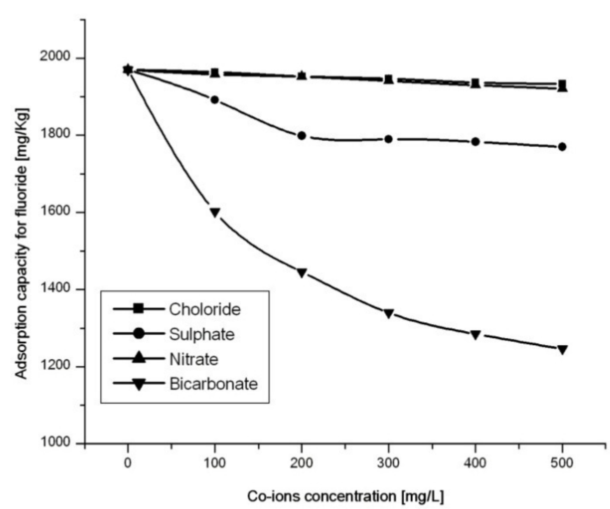

Figure-5: The change in adsorption capacity for various concentrations of co-anions