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Adsorption of Fluoride from water using Spirulina *platensis* and its Measurement using Fluoride Ion Selective Electrode

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Abstract

Fluorosis is an endemic worldwide, including India due to consumption of Fluorine containing underground water (>1.5 mg/l) routinely. Defluoridation is very essential. Adsorption of fluoride from contaminated water is economic yet efficient method. Considering bioadsorbent for defluoridation is more beneficial than conventional adsorbents such as alumina, activated carbon etc., both in terms of quality and quantity. In our experimental studies, we have used dry biomass of Spirulina platensis as a bioadsorbent to defluoridate water samples. Based upon the multivariable studies pH, adsorbent dosage, initial fluoride concentration and contact time, we have found that in lab scale, at pH 5 and adsorbent dosage of 1.0g/100ml and at the fluoride concentration of 20 mg/l, maximum adsorption (97.10%) takes place. Langmuir isothermal model suits well for the adsorption of fluoride from water using Spirulina as bioadsorbent. The FTIR spectroscopy results were also checked to know the cause of adsorption.

Keywords: Fluorosis, defluoridation, bioadsorbent, spirulina platensis and FTIR Spectroscopy.

Introduction

Water is an essential natural resource for sustaining life and environment. Excessive use of underground water for domestic and industrial purpose has been resulted in increase of fluoride content. Drinking-water is the main source to fluoride consumption[1,2].

Fluoride is found in all natural waters at some concentration. Seawater typically contains about 1mg/l, while rivers and lakes exhibit concentrations of less than 0.5 mg/l. In ground waters, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. Fluoride is an accumulative pollutant, it is more toxic than lead but less toxic than arsenic. Intake of fluoride content varies from country to country; it depends on the age of the people and the location. If the consumption of fluoride is more than 6mg per day, it leads to an endemic disease fluorisis. An acceptable fluoride concentration of 1.0mg F/l for drinking water and 1.5mg F/l for potable water are accepted according to Indian standards[3].

Defluoridation is the best way to tackle with the fluorosis as distillation and reverse osmosis are expensive process[4]. Hence, there is continuous need for development of more economic and efficient methods of defluoridation. In the present work, adsorption using *Spirulina platensis* as bio adsorbent has been preferred for the defluoridation of water.

Adsorption is an extensively studied mass transfer operation[5]. In this work, *Spirulina platensis* as bioadsorbents are preferred as they are cheap and more efficient than the chemical adsorbents. Bioadsorbents are used as bioremediation agents[6]. Number of bioadsorbents is used for the removal of toxic and unwanted compounds from drinking water, industrial effluents and sewage water.

Material and Methods

0.221mg of anhydrous sodium fluoride was dissolved in 1000ml of distilled water. This 1 ml solution has 0.1 mg of fluoride. From this solution desired concentration of the fluoride was taken for experiments. Experiment was carried out at room temperature ($30^0 \pm 1^0$C). Distilled water pH was maintained at 7(±0.1).

Dry powdered biomass of *Spirulina platensis* is taken as the bioadsorbent for the experimental analysis. *Spirulina platensis* was obtained from Spirulina Foundation, Tumkur, and Karnataka.

Experimental methodology: 1g of Spirulina adsorbent was dissolved in 100ml of water sample containing known concentration of fluoride ions. By adding 0.5N HNO_3, pH of the water sample was set. It was then subjected to mixing using wrist action shaking machine for different time. Experiment was carried out at room temperature ($30^0 \pm 1^0$C). The samples were withdrawn and the spent adsorbent was removed by centrifugation and final fluoride concentrations were measured using fluoride ion selective electrode (FISE). Batch studies were performed to check the effect of pH (1 to 10), contact time (30 to 180 minutes), adsorbent dose (0.2 g/100ml to 1.2g/100ml) and initial fluoride concentration (5 mg/l to 25 mg/l) at lab scale (100ml).

Results and Discussion

Bio adsorbents with cheap and non toxic nature are advantageous for adsorption process. Batch process at lab scale (100ml) was studied based on pH, adsorbent dosage, initial fluoride concentration and contact time from the kinetic view point.

Effect of pH: By varying the pH from 1 to 10 the adsorption capacity of *Spirulina platensis* was studied by keeping all other variables adsorbent dosage, initial fluoride concentration and contact time as constant. pH was adjusted by adding 0.5N HNO_3. The adsorption ability of *Spirulina platensis* increases at pH of 5 (figure 1). A maximum of 97.10 % adsorption was achieved.

Due to the anionic sorption, the removal of fluoride will be more at lower pH. The concentration of hydrogen ion will be more at low pH which neutralizes the negatively charged fluoride ions on the surface of bioadsorbent *Spirulina*[7]. But at higher pH, fluoride removal will be less; this may be due to the formation of complexes which in turn reduces the adsorption[8]. Hence the removal of fluoride using *Spirulina* as bioadsorbents from water is possibly an exchange adsorption process.

Effect of contact time: The effect of contact time was checked by keeping the other factors such as pH, adsorbent dosage and initial fluoride concentration at the constant value. It was observed from the experiment that adsorption increases as the contact time is varied from 30 min to 180 min. Maximum adsorption will be at 90 minutes (figure 2).

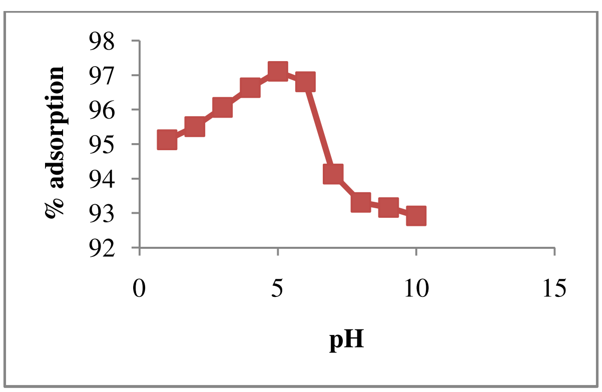

Figure 1
Effect of pH
Adsorbent dose: 1g/100ml, initial fluoride concentration: 15 mg/1, time: 180 min

Effect of adsorbent dosage: Adsorbent dose is the main parameter that influences adsorption. Theoretically, the adsorption increases as the adsorbent dosage increases[9]. Experiments were carried at pH 5 and at constant initial fluoride concentration and contact time. The adsorption increases with the addition of *Spirulina* bioadsorbent from 0.2g/100ml to 1g/100ml, further addition of bioadsorbent reduces the adsorption due to non availability of free fluoride ions. Optimum adsorbent dosage is 1 g/100ml at pH 5 (figure 3).

Effect initial fluoride concentration: Concentration of adsorbate also affects the process of adsorption. By keeping optimized pH and optimized adsorbent dosage constant, concentration of fluoride adsorbate is varied from 5mg/l to 25mg/l. From the experiment, it was seen that adsorption increases at the fluoride concentraion of 20mg/l (figure 4). Further, increase in the concentration of adsorbate indicated the decrease in % adsorption.

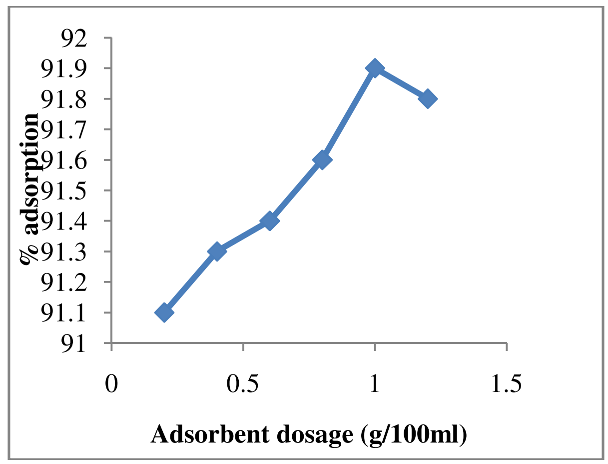

Figure 3
Effect of adsorbent dose
pH: 5, initial fluoride concentration: 15 mg/1, time: 90 min.

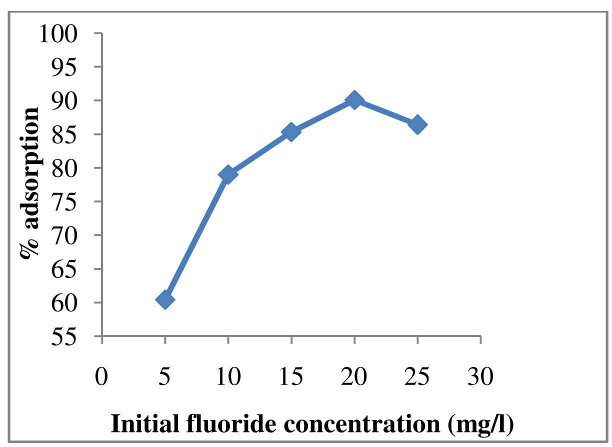

Figure 4
Effect of initial fluoride concentration
Adsorbent dose: 1 g/100m1, pH: 5, time: 90 min

Adsorption isotherm: The interaction between the adsorbate and the adsorbent can be clearly understood with the adsorption isotherms. In the present work, Freundlich and Langmuir isotherms are used to study the adsorption mechanism[10-12].

The Langmuir isotherm [9] is expressed as $q_e = \frac{q_o b C_e}{(1+bC_e)}$ (1)

Where q_e is the amount of fluoride adsorbed (mg/g), C_e is the equilibrium concentration of fluoride adsorbate (mg/l), q_o and b are the Langmuir constants related to capacity and energy of adsorption, respectively.The langumuir isotherm can be expressed in the linear form as

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{(bq_oC_e)} \quad (2)$$

From the graph of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ straight line is obtained with Langmuir constant as $\frac{1}{bq_o} = 32.22$ ($R^2 = 0.979$). The study shows that fluoride removal by *Spirulina platensis* is well correlated by Langmuir isotherm model.

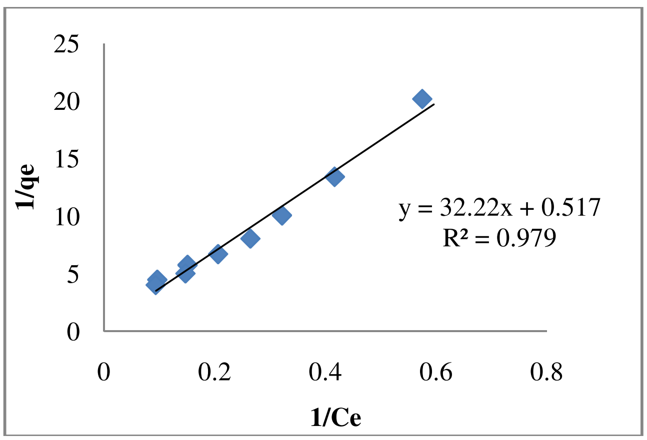

Figure 5
Langmuir isotherm model for adsorption of fluoride using Spirulina bioadsorbent

Freundlich isotherm [9] is considered for the adsorption on the heterogeneous surface and is expressed as

$$q_e = K_F Ce^{1/n} \ldots\ldots\ldots (3)$$

Where, q_e is amount of fluoride adsorbed (mg of fluoride adsorbed /g of adsorbent); C_e is equilibrium concentration of fluoride adsorbate (mg/l); K_F is adsorption capacity and $1/n$ is adsorption intensity.

If, $1/n < 1$, bond energy increases with surface density, $1/n > 1$, bond energy decreases with surface density and $1/n = 1$ all surface sites are equivalent.

By taking logarithm, linear form of equation (3) can be expressed as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \ldots\ldots\ldots (4)$$

From the graph of log q_e versus log C_e, straight line is obtained with slope (n) as 1.016 and intercept (K_F) as 14.75x10^{-3}.

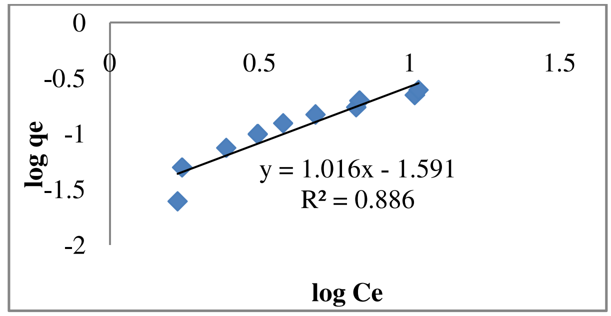

Figure 6
Freundlich isotherm model for adsorption of fluoride using Spirulina bioadsorbent

FTIR Spectroscopy method was based on the interaction between and infrared radiation and a sample. The concentration of the component can be determined based on the intensity of the absorption[13]. FTIR Spectroscopy studies shows that sulphide (SO_3^{2-}) and iodocarbonyl (CI) groups present in *Spirulina platensis* are responsible for the adsorption of fluoride.

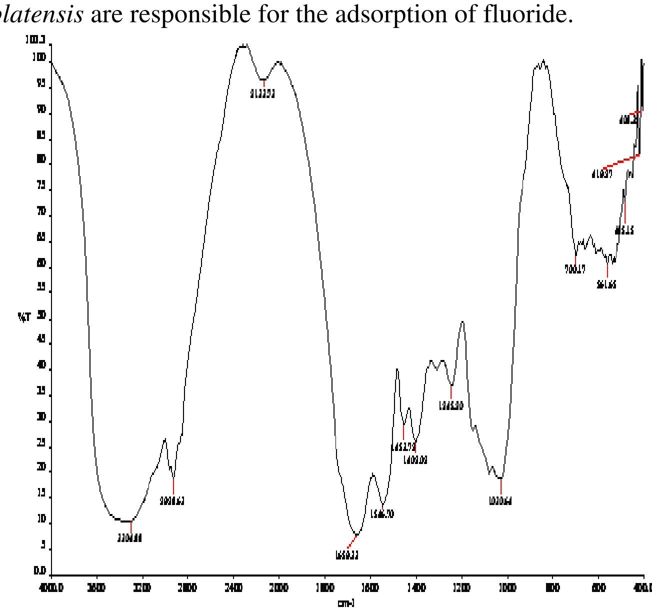

Figure 7
FTIR spectrum before Adsorption

Conclusion

Experimental study shows that fluoride can be effectively removed from water by using *Spirulina* as bioadsorbent. From the batch experimental studies, pH, contact time, adsorbent dose and fluoride concentration are optimized. Though pH and contact time are directly proportional to the % adsorption, in our experiments their optimized values are pH 5 and 90 minutes respectively. At the adsorbent dosage of 1 g/100ml and at the fluoride concentration of 20mg/l maximum adsorption takes place. It was found that adsorption by Spirulina follows

Langmuir isotherm (R^2=0.979). FTIR analysis indicated that sulphide (SO_3^{2-}) and iodocarbonyl (CI) groups are responsible for the adsorption of fluoride by *Spirulina platensis.*

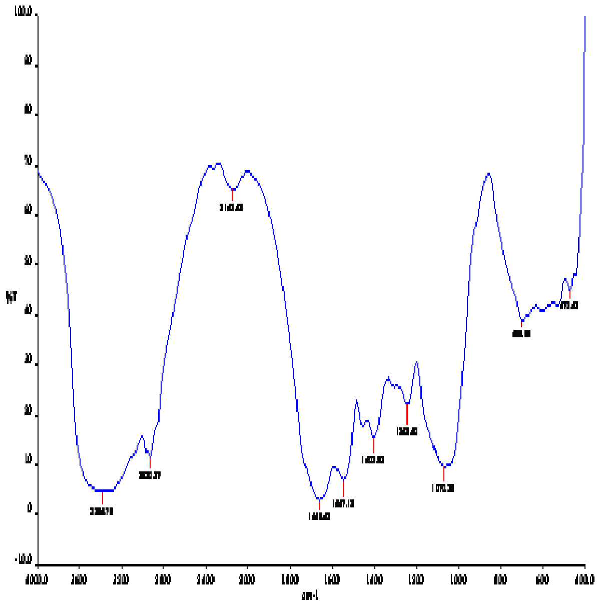

Figure 8
FTIR spectrum after Adsorption

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