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Defluoridation of Water by Adsorption Phenomenon of the Powdered Ficus Religiosa in Batch and Continuous Mode

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Abstract: ***Ficus religiosa leaves are considered to be one of the most efficient and economic adsorbents used for the removal of fluorides from water because of their ready availability. In the present work, the batch experiment was optimised for the contact time, pH and dose of adsorbent. The experiments were conducted for 5- 30 mg/l initial fluoride ion concentration in water. It was thus observed that the ficus religiosa leaf gives the 70 % removal of efficiency at 2 pH, contact time for 120 min and with the dose of 2.5 g/100 m. The continuous column experimentation gives the breakthrough curve result for experiment carried out for 5 mg/l initial fluoride ion concentration at 48ml/min flow rate range. Overall, the results could be efficiently used for defluoridation of drinking water.***

Keywords: Fluoride, Ficus religiosa Leaf, Langmuir Isotherm, Freundlich Isotherm.

1. Introduction

In daily life we require water and it's readily available on the earth. It has been observed that groundwater consists of assorted hazardous and toxic impurities like arsenic, fluoride, pesticides, nitrate, sulphate and other heavy metals. [1] Due to its chemical nature, all of the water content is not safe for drinking. [2] Only 0.6% of water is convenient for drinking purpose which is observed to be underground in agrarian and metropolitan areas of the total water reserve of the earth. [3] Because of industrialization and urbanization of water reserves have widen the pollution. [1],[3]

Surface water generally contains 0.3 mg/l of fluoride more than that they are polluted from other sources. [4] Generally large amount of fluoride comes from groundwater [5]. The amount of fluoride contain in water are not fixed its varying. [6] In India more than fifteen states reported that rivers are flowing with fluoride contain (0.1-12 ppm) including Maharashtra state. [2] Fluoride in water have unique properties, exceed limit of WHO is dangerous to health.[piyush] Intake of fluoride have dental and skeletal problems.[5] According to WHO safe limit of fluoride contain is 1.5mg/l and it is estimated that all over world near about 200 million people are crossed that safe limit of drinking water. [7]

There is many techniques are available for fluoride removal such as precipitation [9], ion-exchange [10], reverse osmosis [11], membrane based methods [15], Donnan dialysis [12], electro dialysis [13], nano filtration [14], electro coagulation [16] and adsorption on to various adsorbents [17]. Defluoridation of water is very effective way to solve this problem. This technique is very economic and their materials are easily available so it's better to go with defluoridation technique. [1] Adsorption methods for fluoride removal by using several adsorbents such as zeolites, activated carbon, activated alumina, bentonite, charcoals and fly ash these adsorbents. But all these are expensive adsorbents so, world focus on natural, waste and low cost material or adsorbents like baggsse ash, thermally activated neem, brick powder for fluoride removal. [8]

In the present work, adsorbent have developed from leaves of Ficus Religiosa (Pipal) to remove fluoride from water. The leaves of the plants are easily available in India and are known for their medicinal and other purposes. Moreover, they have high fibre content making them suitable to be converted in bio sorbents. Effect of various parameters like pH, dose of adsorbent, initial concentration of fluoride ion, and contact time was studied in Batch experiment. Breakthrough curves were investigated and analyzed at different bed depth.

2. Materials and Methods

2.1 Reagents

The reagents used in the experimentation are as follows:

- Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride [NaF] in 1000 ml distilled water in flask.
- SPADNS Solution – Dissolve 0.958 g of SPADNS in distilled water and dilute to 500 ml.
- Zirconium Acid Solution- Dissolve 0.133g of Zirconium oxychloride octahydrate in about 25 ml of distilled water add 350 ml concentrated HCL and dilute to 500 ml with distilled water.
- Acid Zirconyl SPADNS reagent (Mixed Reagent) - Mix equal volumes of spadns solutions & Zirconium Acid Solution.

2.2 Adsorbent Preparation:

The fresh Ficus Religiosa leaves were taken locally, from Bharati University campus area Pune and properly wash it then sun dried for 3 to 4 days in an open atmosphere and crushed manually. This crushed materials were sieved with

standard screen to get 1 to 1.5 mm. Leaves Powder further by chemical digestion using both acid and alkali treatment.

a) Acid treatment:
Ficus religiosa leaf powder sample and 1N Nitric acid were taken in a 1000-ml conical flask. The mixture was heated for 20 min after boiling starts. Treated sample was washed with distilled water. Washing was done until maximum colour was removed.

b) Alkali treatment:
Ficus religiosa leaf powder sample and 0.5 N Sodium Hydroxide were taken in a 1000-ml conical flask. The mixture was heated for 20 min after boiling starts. Treated sample was washed with distilled water for maximum colour removal.

2.3 SEM Analysis Coupled with X-ray Energy Dispersive Spectroscopy (EDX)

SEM and EDX analysis are useful tools for evaluating the elemental characteristics of the adsorbents and it is widely used in adsorption studies. The SEM images and EDX spectra for Ficus Religiosa leaf powder before fluoride adsorption are shown in Fig 1 and Fig. 2 respectively. The SEM images show the rough surface and porosity of ficus religiosa leaf powder, conditions which might similar to the adsorption of fluoride ions.

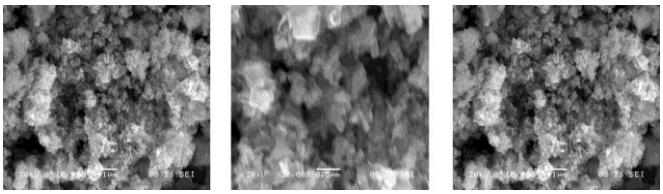

Figure 1: SEM micrographs of Ficus Religiosa Leaf Powder

The EDX spectrum for Ficus religiosa leaf powder before adsorption showed some peaks for O, Na, Cu, Zn and Ce species. This EDX analysis could be used to confirm the attachment of F ions onto leaf surface. Both SEM and EDX analysis was carried out at Department of Physics of Savitribai Phule Pune University, Pune, India.

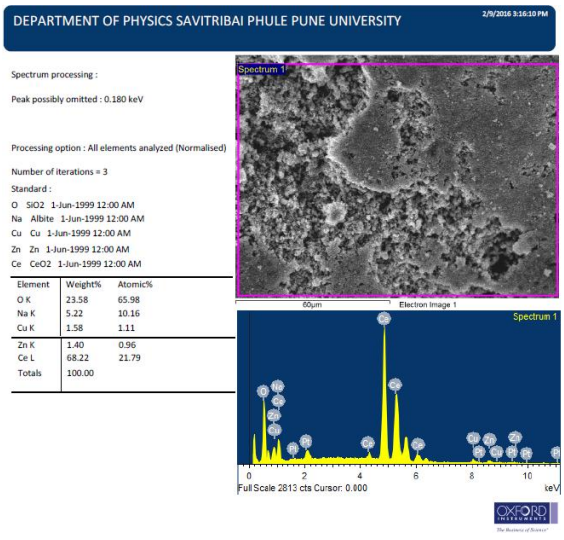

Figure 2: EDX analysis of Ficus Religiosa Leaf Powder

3. Batch Experiment

Batch Adsorption experiments were conducted by taking the known concentration of fluoride stock solution of 1000 ml and known amount of adsorbent, were shaken in a horizontal shaker at speed of 100 rpm for 2 hr, to study the various parameters at room temperature. The contents of the beakers were then allowed to settle for 2 minutes and filtered through filter paper. The filtrate from each batch was analyzed for residual fluoride concentration by SPADNS photometric method at 570 nm using the UV–Vis spectrophotometer. Batch experiment carried out the effect of adsorbent dose, pH, Time and initial fluoride ion concentration for the optimization of adsorbent condition. The removal of Fluoride is calculated by the following formula:

$$\text{Removal of fluoride (\%)} = \frac{(\text{Initial Fluoride Concentration} - \text{Final Fluoride Concentration})}{\text{Initial Fluoride Concentration}} \times 100$$

The flow diagram for the batch experimentation is given below:

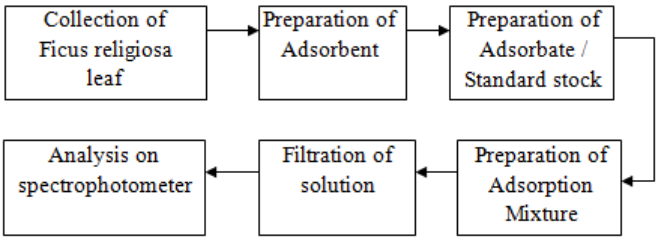

Figure 3: Flow diagram of Batch Experimentation

4. Results and Discussions

4.1 Effect of Contact time on Ficus religiosa leaf:

Time adjustment experiment is carried out for 120 min with the 30 min intervals. During the experiment other parameters like adsorbent dose 2.5 g/100ml and initial fluoride ion concentration are kept constant were pH adjusted on 6 pH. It is observed that the increasing contact time effect on removal of fluoride ion. It was gradually increases but after some time it gives equilibrium value. The fluoride removal increases from 30 to 60 % at 30 min to 120 min of contact time respectively.

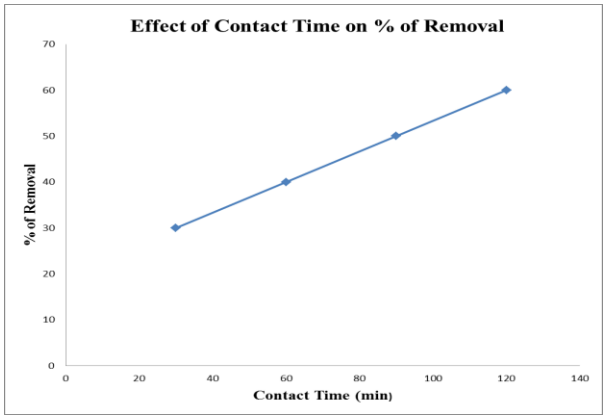

Figure 4: Effect of Contact time on % of Removal

4.2 Effect of Adsorbent Dose on Ficus religiosa leaf:

Optimization of adsorbent experiment was carried out with dosages 0.5, 1, 1.5, 2 and 2.5 gm per 100 ml. during experiment other parameters kept constant. This experiment conducted at room temperature. Every dose of adsorbent added in 5 mg/l fluoride ion concentration and pH was maintained on 6 pH. The dose of adsorbent increases with the increasing fluoride ion removal percentage but after sometime it gradually approaches equilibrium value. Initial fluoride ion concentration at 6 pH was 5 mg/l and contact time was as 120 min ficus religiosa powder gives result 30 to 60 % fluoride removal at doses of 0.5 g/100ml to 2.5 g/100ml respectively at room temp.

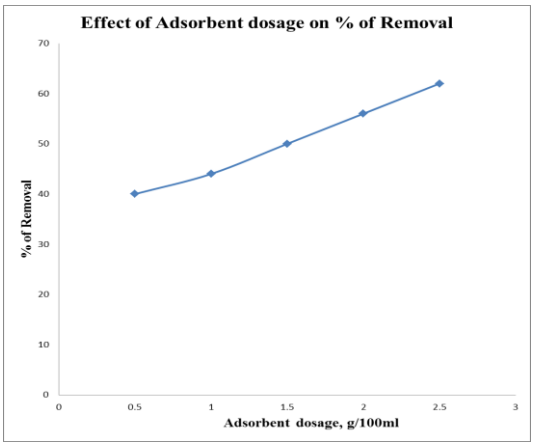

Figure 5: Effect of Adsorbent dosage on % of Removal

4.3 Effect of pH on Ficus religiosa leaf :

The effect of pH on the fluoride removal experiment was conducted for alkaline and acidic range at room temperature. Experiment were conducted with initial concentration of fluoride ion 5 mg /l for 100 ml and contact time for 120 min. Observation test made at the pH range of 2, 4, 6, 8 and 10. The pH was maintained by adding 0.5 N HNO_3 or 0.1 N NAOH. It has been noticed that the removal of fluoride ion decreases with increase in pH. It is also observed that maximum fluoride removal was 70 % at 2 pH.

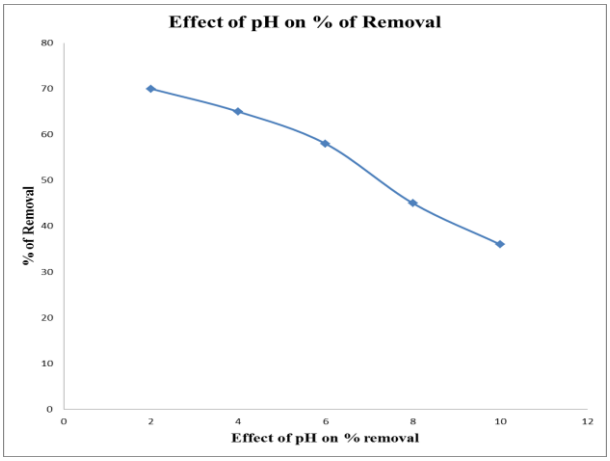

Figure 6: Effect of pH on % of Removal

4.4 Effect of Initial Fluoride Ion Concentration

The Effect of initial fluoride ion concentration experiment were conducted with concentration range 5 mg/l to 30 mg/l. during experiment other parameters are kept constant like pH is on 6 and adsorbent dose 2.5 g /100ml . Each experiment 5, 10, 15, 20 and 30 mg/l concentration was carried out for 120 min contact time. The effect of initial fluoride ion concentration was observed that the removal of fluoride ion concentration. The percentage fluoride removal falls from 60 to 16 % by using ficus religiosa leaf powder as an adsorbent.

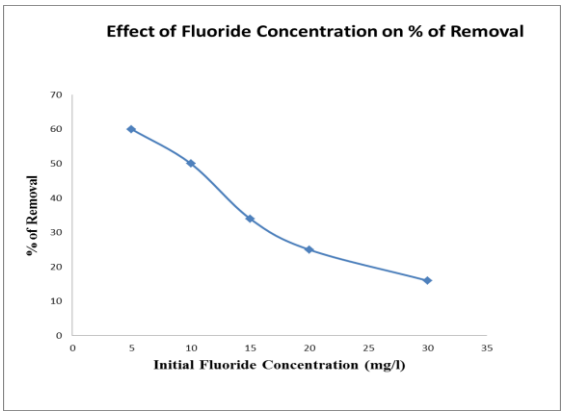

Figure 7: Effect of Fluoride Concentration on % of Removal

4.5 Effect of Time on % of Removal during continuous experimentation

Continuous Adsorption experiments were conducted by taking the known concentration of fluoride stock solution and known amount of adsorbent for removal of fluoride was studied in a fixed bed column system were used to analyze the performance of the column and the effect of the different operating variables such as bed depth, flow rate and initial concentration were tested at room temperature.The Column designed as height 60 cm and width 6 cm. The breakthrough curves for the adsorption of fluoride on the data estimated from bed depth service time model showed that the adsorption capacity of the adsorbent were found to be 10,20,30,40 and 50 gm for 2880 ml/hr flow rate . The experiment carried out for known 5mg/l initial fluoride ion concentration at 2880 ml/hr flow rate. It is observed at varied bed height 10, 20 ,30, 40 and 50 gm.

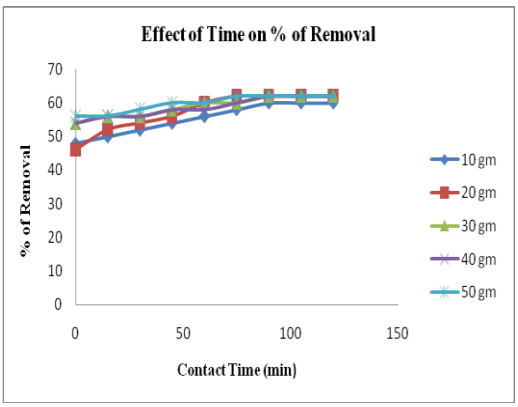

Figure 8: Effect of Time on % of Removal

4.6 Adsorption Models

a) Freundlich Isotherm: The linear Freundlich adsorption isotherm is given in Equation,

$$\log q_e = \log K_f + 1/n \log C_e$$

Where,
q_e: Amount of adsorbate adsorbed per unit weight of adsorbents, mg /g,
C_e: equilibrium adsorbate concentration in solution, mg/l,
K_f ,1/n : Freundlich constants.

The logarithmic behaviour of the equilibrium adsorbate concentration in solution with respected to the amount of solute adsorbed per gram of adsorbent by using the Freundlich model is expressed in the graph below:

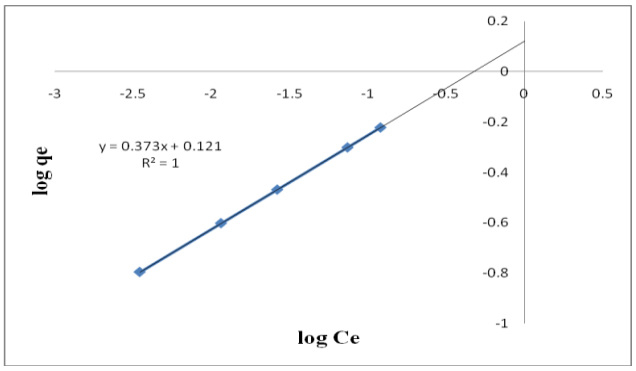

Figure 9 : Freundlich Isotherm for Ficus religiosa leaf

b) Langmuir Isotherm : The Langmuir equation is commonly written as,

$$q_e = abC_e / (1+bC_e)$$

The linear form of Langmuir isotherm can be expressed as,

$$1/q_e = (1/a) + (1/abC_e)$$

Where,
q_e: The amount of solute adsorbed per gram of adsorbent, mg/g
C_e:The equilibrium Adsorbate concentration in solution, , mg/l
a: Number of moles of solute adsorbed per unit weight of adsorbent in forming monolayer on the surface.
b: Constant related to energy
The behaviour of the equilibrium adsorbate concentration in solution with respected to the amount of solute adsorbed per gram of adsorbent using the Langmuir model is expressed in the graph below:

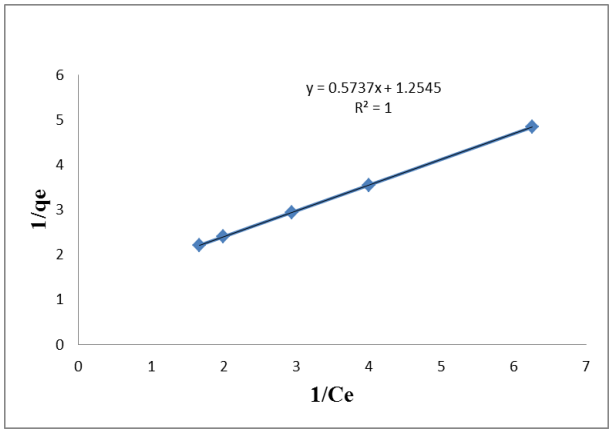

Figure 10 : Langmuir Isotherm for Ficus religiosa leaf

The kinetic constants referred for Ficus religiosa leaf are as follows:

Kinetic Constants	Ficus Religiosa
Kf	0.474
1/n	2.68
a	0.8
b	2.189
Freundlich Isotherm	$q_e = 0.474C_e^{2.680}$
Langmuir Isotherm	$q_e = (1.744C_e)/[1+(2.189\ C_e)]$

5. Conclusion

The implementation of ficus religiosa leaf material for the removal of fluoride from water by the adsorption method was thoroughly in the present study. The utmost adsorption of fluoride for ficus religiosa leaf powder was observed to be 70% (with the maintenance of pH 2) with initial fluorine concentration of 5 mg/l, contact time of 120 min, adsorbent dosage of 2.5g/100ml. From the experimental data, the Langmuir isotherm was found to be the best fit as the correlation coefficients for Langmuir isotherm was greater than that of Freundlich isotherm. Therefore, with the increase of amount of adsorbent, it was observed that the percentage removal of fluoride increases, however the adsorption capacity decreases due to the availability of spare unsaturated adsorption sites. Fluoride removal for a given adsorbent is observed to be increasing with time, accomplishing equilibrium within 120 min.

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