

Equilibrium and Kinetics of Adsorption in the Removal of Fluoride from Water using Pinus Kesiya Bark

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ABSTRACT

Fluoride removal from water is being investigated using a natural adsorbent derived from bark of pinus kesiya. Batch studies were performed to study the effect of adsorbent dose, contact time, initial fluoride concentration and pH on the removal efficiency. The fluoride adsorption varies over wide range of pH and best in between 3 – 8. The rate of adsorption was rapid and maximum removal took place during the first 120 min and reaches pseudo-equilibrium slowly after 180 min. Kinetic study shows that adsorption follows pseudo-second-order, and that the nature of adsorption mechanism is a chemisorption process. The surface adsorption as well as intra-particle diffusion contributes to the rate-limiting step.

Keywords: Adsorption Isotherm; Fluoride Removal; Kinetics; Tree Bark Powder.

I. INTRODUCTION

Fluoride in drinking water may be beneficial or detrimental depending on its concentration and total amount ingested. Fluoride ingested in small amounts may be beneficial¹⁻⁴. Studies have shown that trace quantities of fluoride are needed for the development of cavity-resistant teeth and may also be necessary in preventing excessive demineralization of bone (osteoporosis) in aged individuals. According to 1984 guidelines of WHO, the desirable and permissible concentrations of fluoride in drinking water are 1.0 mg/L and 1.5 mg/L⁵. Fluoride concentration higher than the permissible limit in drinking water results in dental, skeletal and soft tissue fluorosis. Excess Fluoride in drinking water is a cause for concern in several countries including India. Many States in India have been identified endemic to fluorosis. In the north-east region, Assam State is most affected and in Karbi-Anglong and Nagaon districts of Assam more than 20 mg/L level of fluoride has been reported^{6,7}, while in some parts of Guwahati city about 7 mg/L fluoride level has been recorded⁸. As per the reports available⁹, in Arunachal Pradesh also more than the permissible level of fluoride (about 2 mg/L) has been recorded, but in the remaining north-eastern states the situation is not yet reported to be so alarming.

Fluoride can be removed by a number of processes, which includes adsorption and biosorption¹⁰⁻¹³, ion-exchange¹⁴, chemical precipitation including electro-coagulation/ flotation¹⁵⁻¹⁸, and membrane processes, such as reverse osmosis¹⁹, Donnan dialysis²⁰, nano-filtration²¹, and electrodialysis^{22,23}. Surface adsorption finds a major place in defluoridation research and practice because of its greater accessibility, lower cost and locally adaptable. Thus even in the past decade, when interest in alternative defluoridation approaches has been increasing rapidly, many researchers have continued to explore the development of low-cost and effective adsorbents and to improve the efficiency of adsorbents.

There are reports about the use of clays²⁴, soils^{25,26}, zeolites²⁷, rare earth oxides²⁸, ores^{29,30}, alum sludge³¹, limestone³², stone dust³³ carbon prepared from locally available materials like wood, coconut shell, bone³⁴⁻³⁷, etc. Thus, there is always scope for finding new adsorbents.

In these perspectives, adsorbent made out of natural materials are being investigated. In the present study, bark of pine belonging to the species pinus kesiya which is prevalent in the Khasi Hills of the State of Meghalaya India has been explored as an alternative adsorbent.

Pine bark has also been reported in literature as an alternative to activated carbon for organochlorine pesticides removal³⁸. However, their use for removal of fluoride from water has been attempted for the first time owing to the cost effective and easily available of these materials which is very closed to the heavily fluoride affected areas of Nagaon and Karbi Anglong districts of Assam(India).

II. Materials used and method

The dried bark of pine was collected from a nearby forest located in and around Shillong city. The materials collected was cleaned and soaked in dilute HCl overnight. After that the materials were washed repeatedly with water and then dried in oven below 100 °C. The dried material were powdered by grinding in an electric grinder and sieved to get particle size of about 200 to 250 microns. This powder was finally used as an adsorbent without further treatment.

A stock solution of fluoride (100 mg/L) was prepared by dissolving appropriate quantity of sodium fluoride (Merck, > 97%) in 1L of double distilled water. The stock solution was further diluted to desired concentrations for obtaining test solutions. Fluoride ion concentration was measured using ion analyzer (Orion Star A214) and the fluoride-selective combined electrode (Orion 9609BNWP). Total ionic strength adjustment buffer (TISAB-III) solution was used as a buffer to eliminate the interference effect of complexing ions. Double distilled water was used throughout the experiment. The pH of the solution was measured by pH meter (Systronics). Scanning Electron Microscope (JSM-6360; JEOL) and infrared spectra performed by Fourier Transform Infrared Spectroscopy (Perkin-Elmer sp-400) were used for characterisation of the adsorbent before and after treatment with fluoride.

Batch method was followed to study the effect of dose, contact time, pH, and initial fluoride concentration. Adsorption Isotherm studies were conducted by varying the initial fluoride concentration and keeping the adsorbent dose constant and kept in a shaker for 2 hours to attain the equilibrium. The filtrate solution was then analyzed for residual fluoride concentration. pH was maintained at 6.5±0.1. All experiments were performed at room temperature (25±1°C). Adsorption kinetic study was carried out keeping the adsorbent and initial fluoride concentration fixed and by varying the contact time from 15 to 300 minutes.

III. Results and discussion

3.1. Dose Effect

In general, by increasing the adsorbent dose the percentage removal of adsorbate also increases which is mainly due to the increase in the surface area and hence increase in the number of active sites. Figure 1 shows the percentage reduction and the equilibrium concentration of fluoride (inset) upon varying the amount of the tree bark powder (TBP). The percentage removal increases sharply with increase in the dose amount and more than 90% removal was observed at around 10g/100ml thereafter no significant change was observed which may be attributed to the overlapping of active sites at higher dosage and there is decrease in the effective surface area resulting in the conglomeration of exchanger particles³⁹. This amount of dose was fixed for other study.

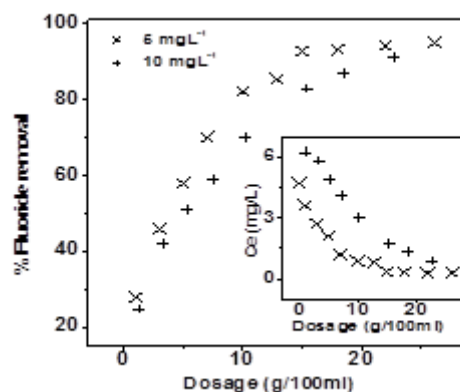


Figure 1. Plots showing percentage removal and equilibrium concentration c_e (inset) of fluoride as a function of adsorbent dose.

3.2. Effect of initial Fluoride concentration

Effect of initial fluoride concentration on fluoride adsorption was studied by varying the concentration of fluoride and keeping other parameters constant. Figure 2 shows that with increase in the initial concentration of fluoride, the percentage removal decreases sharply which can be explained considering that at high fluoride concentration, the concentration gradient will be more and hence the adsorption rate will be high and the number of active sites on the adsorbent surfaces is not enough to accommodate fluoride ions⁴⁰.

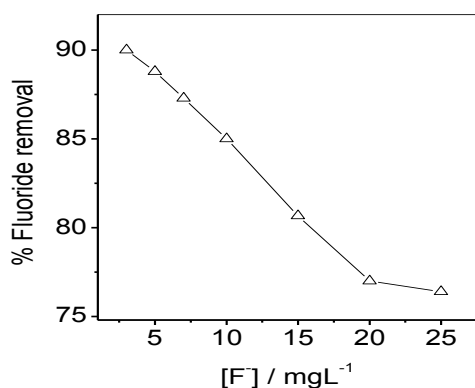


Figure 2. Effect of initial fluoride concentration (c_0) on the percentage removal of fluoride.

3.3. Effect of pH

The fluoride adsorption at different pH environment were also experimentally tested. In this investigation, the preselected pH values are from 3 to 12. The change in the pH greatly affects the adsorption of fluoride onto the adsorbent in solution. Figure 3 shows the effect of pH on the percentage removal of fluoride. The adsorption of fluoride is more at pH range in between 3 – 8 and decreases rapidly above pH 8. At acidic pH, the surface of the adsorbent appears to be highly protonated and this serve as a fluoride binding sites⁴¹. However in alkaline medium the removal of fluoride decreases sharply which may be due to strong competition from hydroxide ions on the active sites because of similarity in F^- and OH^- in charge and ionic radius⁴². Another possibility is that with increase in pH the concentration of protonated surface sites, which serve as fluoride binding sites, decreased significantly and hence fluoride adsorption decreased sharply above pH 8⁴³.

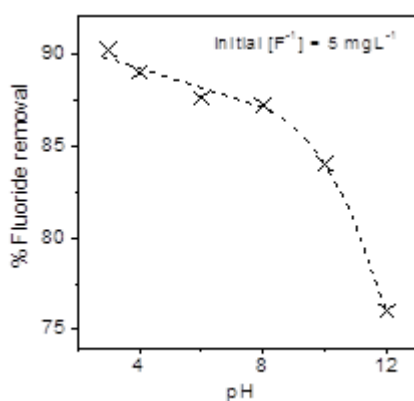


Figure 3. Plot showing the percentage removal of fluoride as a function of pH.

3.4. Zero Point Charge (ZPC) determination

The Zero Point Charge (ZPC) describes the condition when the electrical charge density on a surface is zero⁴⁴. To determine the ZPC, the initial pH of the working solution versus final pH is plotted and is given in Figure 4. The horizontal position of the graph determines the ZPC and for TBP is found to be 2.94. This shows that the experimental condition (pH 6.5 ± 0.1) is greater than the ZPC value, hence the acidic water donates more protons than hydroxide groups, and so the adsorbents surfaces are positively charged thus attracting the fluoride anions.

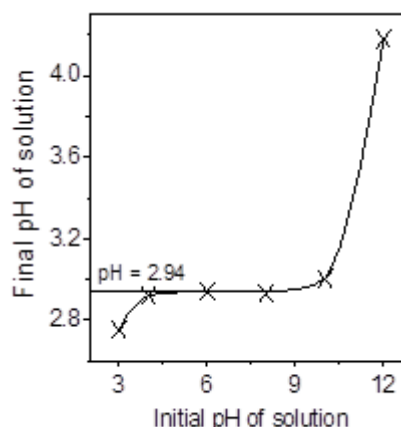


Figure 4. Initial pH vs final pH for determination of ZPC of TBP.

3.5. Effect of contact time

Figure 5(a) shows the effect of contact time on fluoride removal. It was observed that most of the removal took place during the first 120 min and reaches the pseudo-equilibrium slowly after 180 min. No appreciable removal of fluoride took place at higher contact time.

3.6. Adsorption kinetics

Rate of adsorption is an important factor in any adsorption process. To understand the dynamics of fluoride adsorption process, kinetic data were analysed using two mass transfer and one intraparticle diffusion models. These are the pseudo first-order equation⁴⁵, pseudo second-order equation⁴⁶ and intraparticle diffusion model⁴⁷. The mathematical representations (linear) of these models are as follows:

Pseudo-first-order equation :

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

Pseudo-second-order equation :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Intraparticle diffusion model :

$$q_t = k_{id} t^{0.5} \quad (3)$$

where q_e and q_t (mg g^{-1}) are the amounts of fluoride adsorbed per unit mass of adsorbent at equilibrium and time t , k_1 , k_2 and k_{id} are the rate constant for the pseudo-first-order equation (min^{-1}), the pseudo-second-order equation ($\text{g mg}^{-1} \text{min}^{-1}$) and the intraparticle diffusion model ($\text{g mg}^{-1} \text{min}^{-1/2}$) respectively.

The kinetic parameters and the determination coefficient (R^2) obtained linearly (Figure 5b,c) are summarized in Table 1. The higher values of the determination coefficient obtained for pseudo-second-order model indicates that the experimental data are well described by this model and that the nature of adsorption mechanism is a chemisorption process⁴⁸.

The intra-particle diffusion model can be utilized to understand the adsorption mechanism. If the intraparticle diffusion is the sole rate determining step, the plots of q_t vs. $t^{0.5}$ should be linear and pass through the origin⁵⁰. The plot of q_t vs. $t^{0.5}$ (Figure 5d) show multilinearity characterisations, indicating that more than one diffusion step takes place and that both intraparticle diffusion and surface adsorption contributes to the rate-limiting step.

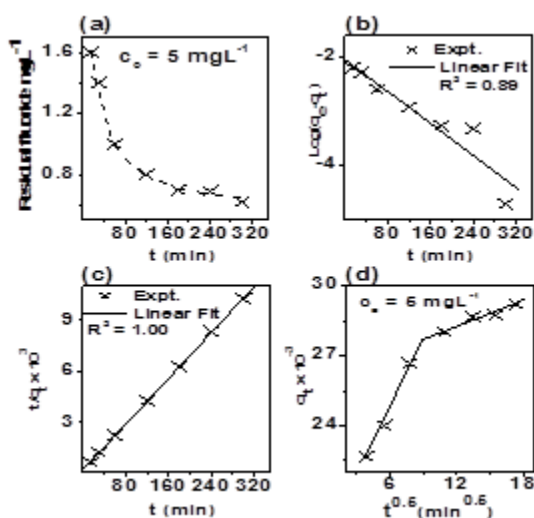


Figure 5. Plots showing (a) residual fluoride at various time interval, (b) pseudo-first-order kinetics, (c) pseudo-

second-order kinetics and (d) intraparticle diffusion model.

Models	Parameters	Values
Pseudo-first-order	k_1 (1/min)	0.0161
	q_e (mg/g)	0.1307
	R^2	0.8925
Pseudo-second-order	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	5.2694
	q_e (mg/g)	0.0297
	R^2	0.9999
Langmuir	q_m (mg/g)	0.1443
	K_L (L/mg)	0.4686
	R^2	0.9970
Freundlich	K_F ($\text{mg/g})(\text{l/mg})^{1/n}$)	0.0415
	n	1.5873
	R^2	0.9946

Table 1. Parameters of kinetic and isotherm model for the adsorption of fluoride on TBP.

3.7. Equilibrium isotherm

Langmuir isotherm. Adsorption isotherms help in determining the feasibility of tree bark powder for treating fluoride ion in water. Langmuir adsorption isotherm is commonly used to provide insight into the adsorption behaviour. We therefore used this adsorption isotherm to understand the adsorption of fluoride ion on tree bark powder. The isotherm not only provides general idea of the effectiveness in removing fluoride but also indicates the maximum amount of fluoride that will be absorbed by the TBP. Langmuir equation is given by

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

where q_e is the amount of fluoride adsorbed at equilibrium (mg/g), q_m is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), c_e is the concentration of the adsorbate at equilibrium (mg/L) and b is the Langmuir constant (L/mg). q_e is calculated according to the equation

$$q_e = \frac{(c_0 - c_e)v}{1000w} \quad (5)$$

where c_0 is the initial concentration (mg/L), v is the volume of aqueous solution (in ml) and w is the adsorbent weight.

Langmuir equation (4) can be linearized as

$$\frac{1}{q_e} = \frac{1}{q_m K_L c_e} + \frac{1}{q_m} \quad (6)$$

In Figure 6a, we plotted $1/q_e$ versus $1/c_e$ and linearity of this plot confirms the applicability of Eq. 6. Therefore, the adsorption of fluoride by TBP obeys Langmuir adsorption isotherm. The constants of Langmuir isotherm are given in Table 1. Although the value of q_m is low, it is comparable to other natural adsorbents for fluoride removal as reported in literature^{50,51}.

Separation factor. The essential feature of the Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called separation factor, R_L , also called the equilibrium parameter which is defined by the following equation,

$$R_L = \frac{1}{1 + b c_0} \quad (7)$$

The value of R_L indicates the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The calculated R_L values are in the range from 0.08 to 0.42, which reveal that adsorption of fluoride ion onto TBP is favourable. Also higher values of R_L at lower initial fluoride concentrations show that adsorption is more favourable at lower initial concentration (Figure 6c).

Freundlich isotherm. The adsorption of fluoride by TBP was also analysed by using the Freundlich isotherm, which is an empirical equation of the form

$$q_e = K_F c_e^{1/n} \quad (8)$$

where K_F is the Freundlich constant (mg/g)(L/mg)^{1/n} and $1/n$ is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms as follows

$$\ln q_e = \ln K_F + (1/n) \ln c_e \quad (9)$$

A plot of $\ln q_e$ versus $\ln c_e$ enables the determination of the constant K_F and $1/n$ which are given in Table 1. The value of n lying between 1 and 10 indicates the

condition for validity of the Freundlich adsorption isotherm.

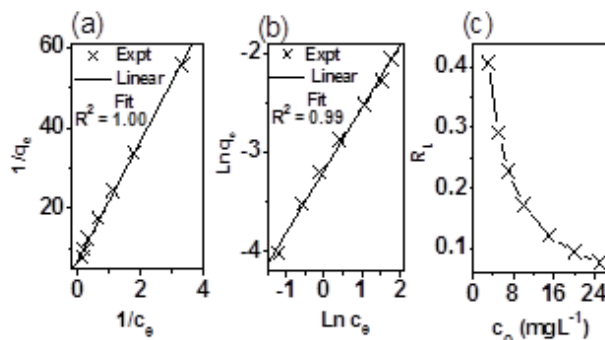


Figure 6. (a) Langmuir isotherm, (b) Freundlich isotherm and (c) Separation factor R_L for adsorption of fluoride by TBP at 25 °C

3.8. Characterization studies

The adsorbents before and after fluoride treatment were examined by Scanning Electron Microscope (SEM) and FTIR measurements. SEM photographs are given in Figure 7. It is clear that the surface morphology of these samples were different, which confirmed the fluoride adsorption.

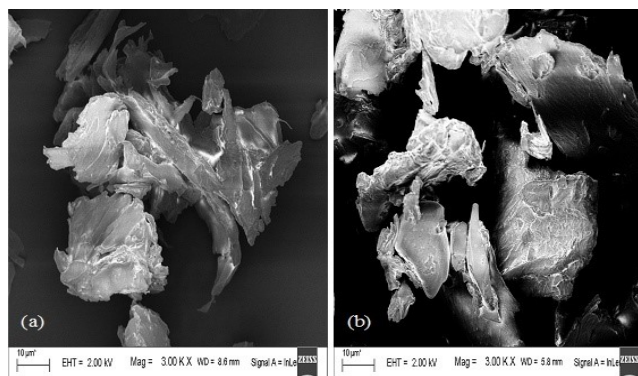


Figure 7. SEM Images of TBP (a) before and (b) after fluoride adsorption.

FTIR spectra are given in Figure 8. The spectra show a broadband at 3600-3200 cm^{-1} with a maximum at 3400 cm^{-1} which is characteristic of the stretching mode of the hydroxyl group (-OH) while broadening of the band is indicative of high degree of association through extensive hydrogen bonding. The weak peak around 2900 cm^{-1} is C-H stretching vibration in methyl and methylene groups⁵². A strong band at 1590-1600 cm^{-1}

can be assigned to C=C aromatic ring stretching mode indicating the existence of single or multiple aromatic rings. The absorption bands between 1300 and 900 cm^{-1} may be due to carbonyl groups, ethers, esters and phenol groups⁵³. It was observed there is an overall shift in the intensity after fluoride adsorption.

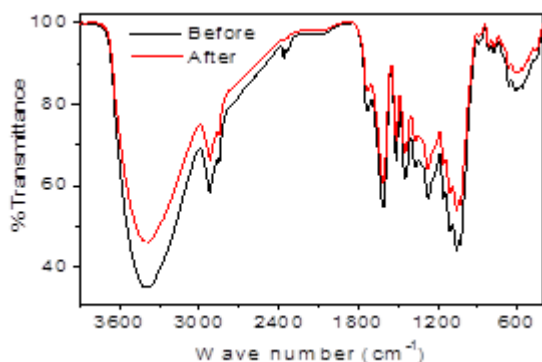


Figure 8. FT-IR spectra of TBP before and after fluoride adsorption.

IV. Conclusion

The present investigation for the fluoride removal from water using adsorbent prepared from bark of pine shows a removal efficiency of more than 90% well below the permissible limit prescribe by WHO. The removal varies over wide range of pH and is best in between pH 3-8. Most of the removal took place during the first 120 min and reaches pseudo-equilibrium after 180 mins. The equilibrium data is being described by the Langmuir and Freundlich, model. The determination coefficient, R^2 shows that the adsorption follows pseudo-second-order kinetics, and that the nature of adsorption mechanism is a chemisorption process. The surface adsorption as well as intra-particle diffusion contributes to the rate-limiting step. This natural material without further modification could prove to be a very useful and effective method for fluoride removal from water particularly where fluoride related problems exist.

V. REFERENCES

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