Defluoridation of water using inexpensive adsorbents

A. V. JAMODE[1]*, V. S. SAPKAL[2] AND V. S. JAMODE[3]

[1]Chemical Engineering Department, Jawaharlal Darda Institute of Engineering and Technology, Yavatmal 445 001, Maharashtra, India.
[2]University Department of Chemical Technology, Amaravati University, Amaravati 444 602, Maharashtra, India.
[3]Pro-Vice Chancellor, Amaravati University, Amaravati 444 602, Maharashtra, India.
emails: [1]jamodeav@rediffmail.com; avjamode@sify.com; Phone: +91-232-321224 (R), 249378 (O), Fax: 249460.

Abstract

The study assesses the suitability of inexpensive leaf adsorbents to effectively remediate fluoride-contaminated water. The efficiency of the sorption of fluoride ion is affected by pH, contact time, adsorbent dose, type and size of adsorbents and initial fluoride ion concentration. The adsorption equilibrium is well correlated by Freundlich and Langmuir models. Treated leaf powder was studied at various pHs (2, 4, 6 and 8) with a series of aqueous solutions containing 2, 3, 5, 6, 8, 10, 12, and 15 mg F^-/l. At the highest F^- ion concentration (15 mg/l), the F^- ion level in the effluent gradually decreased to 0 mg/l within 180 min at $29 \pm 0.5°C$ when the dose of adsorbent is 10 g/l in a sample of 50 ml volume. With lower F^- ion concentrations (2 mg/l) in the feed solutions the fluoride ion concentration steadily decreased reaching 0 mg/l after 150 min. Langmuir isotherm fits well for defluoridation of water using leaf powder.

Keywords: Fluoride ion, adsorption, low-cost adsorbents, Langmuir and Freundlich Isotherm.

1. Introduction

Pure water is scarce and is not easily available to all. Deprived sections of the society consume contaminated water and take ill periodically, often resulting in epidemics. The water may be contaminated by natural sources or by industrial effluents. One such contaminant is fluoride. Fluoride is a salt of the element fluorine. Fluorine is the most highly reactive element of halogen family. Small amounts of it are found in seawater, bone, teeth and in ground water mainly as fluoride ion. Most fluoride associated with monovalent cations such as NaF and KF is water soluble, while the one formed with divalent cations such as CaF_2 and PbF_2 is generally insoluble.

Fluoride is "more toxic than lead and less toxic than arsenic" and is an accumulative toxin. Fluoride has dual significance; if its content is less then it may result in problems like dental caries. World Health Organisation (WHO) recommends it in the range of 0.1–0.5 ppm. The standard of the United States is between 0.6 and 0.9 ppm, and of India 1 and 15 ppm. Thus the requirement of fluoride content varies among countries and depends on the geography and the age of people involved.

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*Author for correspondence.

An intake of more than 6 mg of fluorine per day results in fluorosis. Fluorine being cumulative bone-seeking mineral, the resultant skeletal changes are progressive. Fluoride increases the stability of crystal lattice in bone, but makes the bone more brittle. Drinking fluoridated water will double the number of hip fractures. The International Society for Fluoride Research (ISFR) has reported studies implicating fluoride in the rising rates of Down's syndrome, chronic fatigue syndrome and sleep disorder.

Defluoridation is the process of removal of fluoride ion in drinking water. The process may be classified broadly into two categories, namely, i) Additive methods, and ii) Adsorptive methods. The different methods so far tried for the removal of excess fluoride from water can be broadly classified into four categories: A) Adsorption methods, B) Ion exchange methods, C) Precipitation methods, and D) Miscellaneous methods. Some defluoridation techniques developed to control fluoride content in water are reverse osmosis, adsorption using sunflower plant dry powder, steam of phytomass, Holly Oke, neem bark powder, activated cotton jute carbon, bagasse ash, burnt bone powder, phosphate-treated saw dust, bone char, etc. as adsorbents, Nalgonda technique, activated alumina process and ion exchange process. However, due to high cost or lower efficiency or nonapplicability on mass scale these techniques are not much in use.

This communication presents the findings of an investigation on the use of leaf powder from various trees for the defluoridation of water.

2. Materials and methods

All the reagents used were of AR grade. Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in 1000 ml distilled water in volumetric flask. Fluoride standard solution was prepared by diluting 100 ml stock solution to 1000 ml distilled water in volumetric flask. This 1 ml solution has 0.1 mg of fluoride.

2.1. *Equipment*

Fluoride ion was estimated by Orion ion meter as per standard methods. PH meter (Hanna portable), and Remi shaking machine for agitating the samples for the required period at a speed of 200 strokes/minute were used. The surface area of the adsorbent particle, porosity and density were measured by using surface area analyzer, mercury porosimetry and specific gravity bottles, respectively.

2.2. *Material development*

Fresh leaves chosen based on their crude fiber content and tress were obtained from neem (*Azadirachta indica*), pipal (*Ficus religiosa*) and khair (*Acacia catechu willd*) trees. The fresh leaves were sun-dried for 3–4 days, put in a cotton jute bag and crushed manually. (This process can save the energy expended in hot air oven drying and mechanical crushing.) The powder was sieved to get various particle sizes, viz. 600, 710, and 850 m, 1 mm, and 1.4 mm. Leaf powder biomass was further digested by chemical methods.

2.2.1. *Acid treatment*

Leaf biomass powder sample (40 gm) and 400 ml of 1N HNO_3 (nitric acid) were taken in a 1000-ml conical flask. The mixture was gently heated on burner for 20 min after boiling starts. Treated biomass was washed with distilled water. Washing was done until maximum colour was removed and clear water obtained.

2.2.2. *Alkali treatment*

Leaf biomass powder sample (40 gm) and 400 ml 0.5 N NaOH were taken in 1000-ml conical flask. Then mixture was gently heated on burner for 20 min after boiling started. Using distilled water, the treated biomass was washed which continued until maximum colour was removed and clear water obtained.

3. Results and discussion

3.1. *Sorption studies*

Successful application of the adsorption technique demands innovation of cheap, nontoxic, easily and locally available material. Bioadsorbents meet these requirements. Knowledge of the optimal conditions would herald a better design and modeling process. Thus, the effect of some major parameters like pH, contact, time, amount and particle size of adsorbent and concentration of fluoride ions of the uptake on adsorbent materials was investigated from kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the rate and equilibrium data. Experiments were carried out by shaking 10 g/l of adsorbent dose with 50 ml of aqueous solution containing known concentration of fluoride ions and by agitating the samples on Remi shaking machine at a speed of 200 strokes/min. Samples containing fluoride ions were maintained at a desired pH by adding 0.5 N HNO_3 or 0.1 M NaOH. All the experiments were conducted at room temperature ($29 \pm 0.5°C$).

3.2. *Effect of pH*

The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of hydrogen ion concentration was examined at pH values of 2, 4, 6, 8, and 10. This was adjusted by adding 0.5N HNO_3 or 0.1M NaOH with 50 ml of standard solution of 10 mg/l of fluoride for a contact time of 60 min with a dose of 10 g/l of treated bioadsorbent. The influence of pH on the sorption rate is shown in Fig. 1.

We have observed decrease in the extent of removal of fluoride ions with increase in the pH of the solution. This was investigated as 80% at pH 2 and 70% in the case of treated biosorbents. Hence further studies were conducted within these pH values. In the case of treated biosorbents, the percentage of adsorption increased almost linearly between 2.0 and 8.0, attaining a maximum removal at pH 2.0 in 60 min of contact time.

In this case, the result may be due to neutralization of the negative charges at the surface of the treated biosorbents by greater hydrogen ion concentration at lower pH values. This reduces hindrance to diffusion of the negatively charged fluoride ions on to the increased active surface of treated biosorbents. Bhargava and Killedar [8] observed similar results using fish bone charcoal.
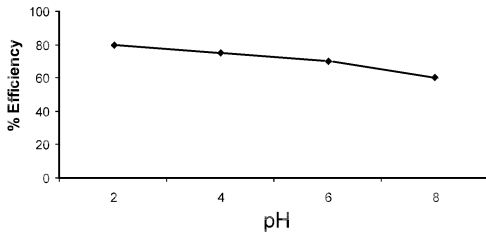
FIG. 1. Effect of pH on the percentage removal of fluoride ion. Adsorbent dose: 10 g/1, absorbent size: mixed, volume of sample: 50 ml, temp.: 29°C, initial adsorbate conc.: 10 mg/1, time of contact: 60 min.
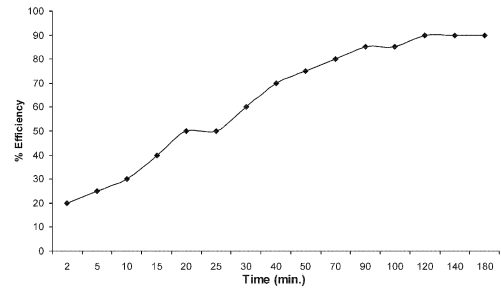

FIG. 2. Effect of agitation time on the removal of fluoride ion. Adsorbent dose: 10 g/1, adsorbent size: mixed, volume of sample: 50 ml, temp.: 29°C, initial adsorbate conc.: 10 mg/1, pH: 2.

3.3. *Effect of contact time*

It is found that the removal of fluoride ions increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material. Preliminary investigations on the uptake of fluoride ions on the adsorbent material at their optimum pH values indicate that the processes are quite rapid. Typically, 80% of the adsorption occurs within the first hour of the contact for fluoride ions with an initial concentration and adsorbent dose of 10 mg/l for treated biosorbents (Fig. 2).

This initial rapid adsorption subsequently gives way to a very slow approach to equilibrium and saturation is reached in 1.5 to 3 h. For further optimization of other parameters, this contact time was considered as the equilibrium time.

3.4. *Effect of adsorbent dose*

From Fig. 3, it is observed that the removal of fluoride ions increases with an increase in the amount of adsorbent. For all these runs, initial fluoride ion concentration was fixed at 10 mg/l. The amount of adsorbent dose was varied between 0.5 and 12 g/l in aqueous solution at their optimal pH values.

Results showed that treated bioadsorbent was efficient for 50% removal of fluoride ions, 55% at 5 g/l and maximum removal of 85%, and 80% was observed at 12 and 10 g/l, respectively, at a room temperature of 29 ± 0.5°C.

3.5. *Effect of initial adsorbate concentration*

For a strictly adsorptive reaction, in the optimized period of contact, the rate varies directly with the concentration of adsorbate. The capacity of the adsorbent materials gets exhausted sharply with increase in initial fluoride ion concentration (Fig. 4). The adsorption capacity of treated biosorbents was systematically studied by varying the initial concentration of fluoride ions between 2 and 15 mg/l. The per cent removal of fluoride ion is a function of initial concentration at different initial pH values.
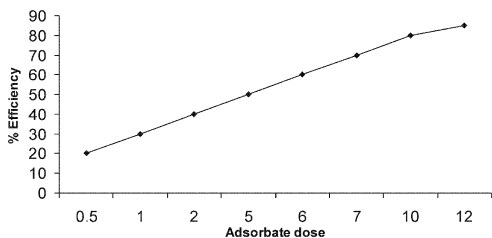
FIG. 3. Effect of adsorbent dose on the removal of fluoride ion. Temp.: 29°C, adsorbent size: mixed, volume of sample: 50 ml, initial adsorbate conc.: 10 mg/l, time of contact: 120 min, pH: 2.
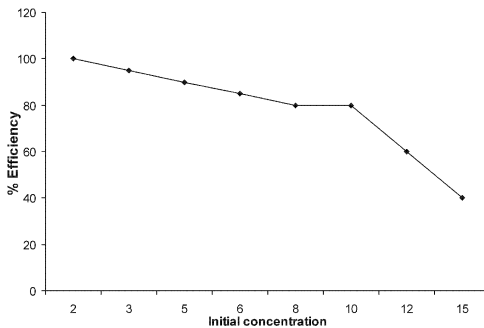
FIG. 4. Effect of initial concentration on the removal of fluoride ion. Temp.: 29°C, absorbent size: mixed, volume of sample: 50 ml, absorbent dose: 10 g/l, time of contact: 120 min, pH: 2.

Treated biosorbents may be seen fairly active in reducing fluoride ions from 100 to 40% when the initial concentration of fluoride ion concentration was increased from 2 to 15 mg/l with a constant sorbent dose of 10 g/l at pH of 2.0.

3.6. *Effect of adsorbent particle size*

Experiments were conducted to evaluate the influence of adsorbent particle size for a constant weight on the removal of fluoride ions. Particle size analysis was conducted on treated biosorbents and the percentage composition of particle size was investigated. The results obtained with the variation of adsorbent particle size and the per cent of the fluoride ions are graphically represented in Fig. 5. The uptake of fluoride ions at different adsorbent particle sizes increased with decrease in sorbent particle diameter. The presence of large number of smaller particles provides the sorption system with a larger surface area available for fluoride ion removal and it also reduces the external mass transfer resistance. Also, the time required for 50% of the total adsorption is less with the particles of smaller size. This also gives some idea of rate-limiting step of the adsorption process. The removal of fluoride ions has been studied at a room temperature of $29 \pm 0.5°C$.

With the largest particle size of 1.4 mm the amount of fluoride ions adsorbed was found to be 60 and 50% treated biosorbents, respectively, and 95 and 90% with smallest particle size of 600 ***m*** for an initial fluoride ion concentration of 10 mg/l, respectively. Small particle size provides more active surface area and hence such results were observed.

3.7. *Sorption mechanism*

The sorption data for the removal of fluoride ions have been correlated with Freundlich and Langmuir models.

3.7.1. *Freundlich equation*

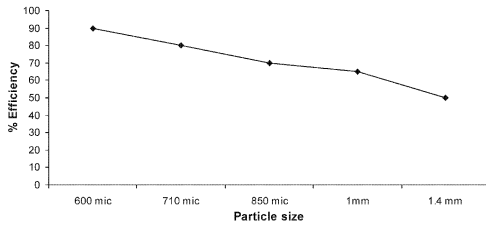It has the general form of

$$q_e = K_f C^{1/n}.$$

Fig. 5. Effect of particle size on removal of fluoride ion. Temp.: $29 \pm 10°C$, initial adsorbate conc.: 10 mg/l, volume of sample: 50 ml, adsorbent dose: 10 g/l, time of contact: 120 min, pH: 2.
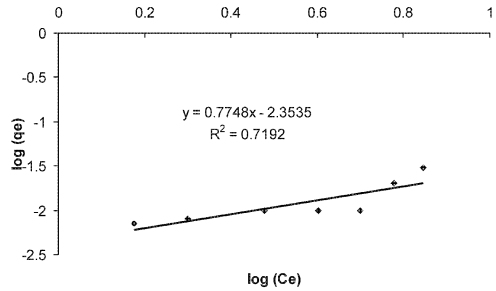
FIG. 6. Linear model of Freundlich isotherm.

The linearised Freundlich adsorption isotherm, which is of the form

$$\log (q_e) = \log K_f + 1/n \log C_e,$$

where q_e is the amount of metal ions adsorbed per unit weight of adsorbents (mg g^{-1}), K_f and $1/n$ are the Freundlich constants, if $1/n < 1$, bond energies with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$ all surface sites are equivalent.

C_e is the equilibrium concentration (mg/l). Linear plots of log $q_e(x/m)$ vs log C_e at different adsorbent doses are applied to confirm the applicability of Freundlich models as shown in Fig. 6. The calculations for Freundlich model for the removal of fluoride ions are shown in Table I.

3.7.2. *Langmuir isotherm*

Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as

$$q_e = Q_o b C_e / (1 + bCe),$$

where q_e is the amount adsorbed (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/l), Q_o and b are the Langmuir constants related to capacity and energy of adsorption, respectively.

The linear form of the Langmuir isotherm can be expressed as,

$$1/q_e = (1/Q_o) + (1/bQoC_e).$$

When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ_o$ is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Fig. 7. The Langmuir con-
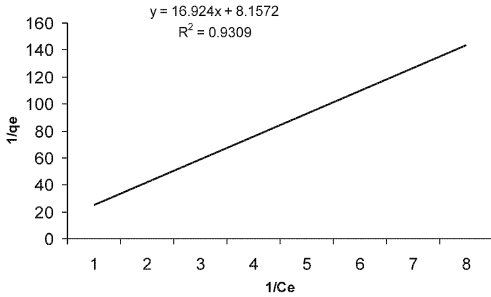
FIG. 7. Linear model of Langmuir isotherm.

stants b and Q_o are calculated from the slope and intercept with Y-axis. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and describe the type of isotherm defined by,

$$R = 1/(1 + bCo),$$

where b and Co are terms appearing in Langmuir isotherm. From Figs 6 and 7 it is found that the R^2 value for Langmuir model is near to unity and hence the process of defluoridation using treated biosorbents follows the Langmuir isotherm well. Table II gives the calculations of Langmuir model for the removal of fluoride ions and the various constants of this model.

3.8. Disposal of exhausted adsorbent materials

It is necessary to separate fluoride ion before its disposal. The exhausted adsorbent materials need to be dried and burned. The resultant product can be used in the manufacturing of bricks. Using various chemicals such as H_2SO_4, HCL, HNO_3, NaOH, EDTA, etc. desorption is possible.

3.9. Advantage of low-cost adsorbents over conventional adsorbents

- The efficiencies of removal of fluoride ions of various nonconventional adsorbents vary between 50 and 90% depending upon the characteristics and particle size of adsorb-

Table I
Calculation of Freundlich isotherm

Dose (mg/1)	C_e (mg/1)	Q_e (mg/mg)	$1/C_e$	$1/q_e$
50	8	0.04	0.9031	1.398
100	7	0.03	0.8451	−1.523
200	6	0.02	0.7782	−1.699
500	5	0.01	0.699	−2
600	4	0.01	0.6021	−2
700	3	0.01	0.4771	−2
1000	2	0.008	0.301	−2.097
1200	1.5	0.0071	0.1761	−2.15

Table II
Calculations of Langmuir isotherm

Dose (mg/1)	C_e (mg/1)	Q_e (mg/mg)	$1/C_e$	$1/q_e$
50	8	0.04	0.125	25
100	7	0.03	0.1429	33.333
200	6	0.02	0.1667	50
500	5	0.01	0.2	100
600	4	0.01	0.25	100
700	3	0.01	0.3333	100
1000	2	0.008	0.5	125
1200	1.5	0.0071	0.6667	141.18

ent(s). A combination of adsorbents can also be used effectively in defluoridation treatment.

- Nonconventional adsorbents are relatively cheaper compared to conventional ones and are easily available resulting in savings in cost.

- Nonconventional adsorbents require simple alkali or/and acid treatment for the removal of lignin before their application and to increase efficiency.

- Since the cost of these adsorbents is relatively low they can be used once and discarded.

- Nonconventional adsorbents require less maintenance and supervision. Separation is possible to segregate the nonconventional adsorbents from the effluents before their disposal.

- These nonconventional adsorbents can be disposed off easily and safely. Used adsorbents can be reused as a filler material in low-lying areas and hence their disposal does not pose any serious problem.

4. Conclusions

Results show that these low-cost bioadsorbents could be fruitfully used for the removal of fluoride over a wide range of concentrations. Treated biosorbents were observed to be efficient for the uptake of fluoride ions between 2.0 and 10.0 pH. Fluoride removal for a given bio-adsorbent size increased with time attaining equilibrium within 1.5 h.

The percentage of fluoride removal was found to be a function of adsorbent dose and time at a given initial solute concentration. It increased with time and adsorbent dose, but with higher initial solute concentration decreased with time and adsorbent dose. The process of adsorption by treated biosorbents follows Langmuir isotherm, which comprises statistical and empirical data estimated from Isotherm equation.

The adsorption capacity of treated biosorbents was studied by varying the initial concentration of fluoride ions between 2 and 15 mg/l. With the largest particle size of 1.4 mm, the amount of fluoride ions adsorbed was found to be 95. With smallest particle size of 600 m for an initial fluoride ion concentration of 10 mg/l, 90% adsorption was observed. Small particle size provides more active surface area and hence such results. Treated biosorbents can be disposed off safely by burning after use.

Treated biosorbents are locally available and hence involve no expenditure on transportation and have a very low cost for pretreatment. There is no need to regenerate the exhausted treated biosorbents as they are available abundantly, easily, cheaply and locally.

Our future work deals with the evaluation and performance of various biomasses for the removal of fluoride.

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