

# Removal of Fluoride from Drinking Water By Natural Adsorbent

Dr. Sunita Goyal  
Department of Chemistry  
Jaipur Engineering College

Dr. Archana Sharma  
Department of Chemistry  
Jaipur Engineering College

## INTRODUCTION

Sustainability of good health of living organisms depends upon the quality of water. Pure water is scarce and it not easily available to all deprived sections of the society.

Water is a good solvent so that water picks up minerals and salts present in the earth crust during the run off and percolation processes.

Fluorine the most abundant element in the earth crust dissolves and contributes to fluoride in the water. Fluoride in drinking water may be beneficial or detrimental depending on its concentration and total amount ingested.

The chronic and toxic effects of excessive intake of fluoride are usually observed as dental fluorosis<sup>1</sup>, skeletal abnormalities that range stiffness and rheumatism to a permanent crippling skeletal rigidity. It is a recommended essential substance in water for building health teeth when present upto 1 mg/L. It is beneficial particularly to infants and young children (< eight year) for calcification of dental enamel when present upto the permissible range of 1.0-1.5mg. As the maximum acceptable level in drinking water is 1.5 mg/L<sup>2</sup>. World health organisation (WHO)<sup>3,4</sup> recommends it in the range of 0.1 mg/L -0.5mg/L. The standard of the United states is between 0.6 and 0.9 mg/L. In India 1.0 and 1.5 mg/L<sup>5</sup>. Thus the requirement of fluoride content varies among countries and depends on the geography and the age of people involved.

When fluoride concentration of the drinking water exceed 1.5mg/L then removal processes of fluoride ion in drinking water is known as defluoridation.

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 (D) miscellaneous methods.

A large number of plants and their wastes have been used to remove heavy metals and other contamination from water all over the world. Recently considerable attention has been devoted to develop better and suitable adsorbents for defluoridation purpose but adsorption process is the cheapest, simplest easily available and accessible process for

defluoridation in developing country. Materials like coconut shell carbon, activated carbon (Muthukumaran et al, 1995, Sivabalan et al 2002), bone char (Killedar and Bhargava 1993) and ion exchange resins (Shrivastava and Deshmukh 1994) have been used as adsorbents. Activated carbon prepared from various raw materials exhibits good capacity of removal of fluoride from drinking water.

## Material and methods

All the reagents used 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 100ml stock solution to 1000ml distilled water in volumetric flask. This 1ml solution has 0.1 mg of fluoride. Various characteristics of prepared adsorbent were studied by adopting the standard procedures<sup>5</sup>.

## Material development

Fresh leaves chosen based on their crude fiber content and trees were obtained from neem (*Azadirachta indica*), Pipal (*Ficus religiosa*) and kikar (*Accia catechu Willd.*) trees. The fresh leaves were sun-dried for 3-4 days, put in a cotton jute bag 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  $\mu$ m and 1.4mm leaf powder biomass was further digested by chemical methods. Prepared adsorbent were studied by adopting the standard procedures.

## Acid treatment

Leaf biomass powder sample (40g) and 400ml of 1N HNO<sub>3</sub> (nitric acid) were taken in a 1000ml conical flask. The mixture was gently heated on burner for 20 min after boiling starts. Then it was washed with distilled water. Washing done maximum colour was removed and clear water obtained.

## Alkali treatment

Leaf biomass powder sample (40g) and 400ml 0.5 N NaOH was taken in 1000ml conical flask. Then mixture was gently heated on burner for 20 min after boiling started. The treated

biomass was washed which continued until maximum colour was removed and clear water obtained.

## RESULT AND DISCUSSION

### Sorption studies

Successful application of the adsorption technique demands innovation of cheap, nontoxic, easily and locally available material. The effect of some major parameters like  $p^H$ , contact time amount and particle size of adsorbent and concentration of fluoride ions of the update on adsorbent materials was investigated from kinetic view point. Adsorbent were performed by batch technique to obtain the rate and equilibrium data.

Experiment were carried out by shaking 10g/l of adsorbent dose with 50 ml of aqueous solution containing known concentration of fluorides ions samples containing fluoride ion were maintained NaOH. All the experiment conduct at room temperature ( $29 \pm 0.5^\circ\text{C}$ ).

### Effect of $p^H$

The  $p^H$  of the aqueous solution is a controlling factor in the adsorption process. The role of hydrogen ion concentration was examined at  $p^H$  values of 2, 4, 6, 8 and 10. This was adjusted by adding 0.5 N HNO<sub>3</sub> or 0.1 M NaOH with 50 ml of standard solution of 10mg/l of fluoride for a contact time of 60 min. With a dose of 10g/l of treated bio adsorbent. The influence of  $p^H$  on the sorption is shown in fig (a). We have observed decreased in the extent of removal of fluoride ions with increase in the  $p^H$  of the solution. This was investigated as 80% at  $p^H$  2 and 70% in the case of treated bio sorbents. In the case of adsorption increased almost linearly between 2.0 and 8.0 attaining a maximum removal at  $p^H$  2.0 in 60 min of contact time.

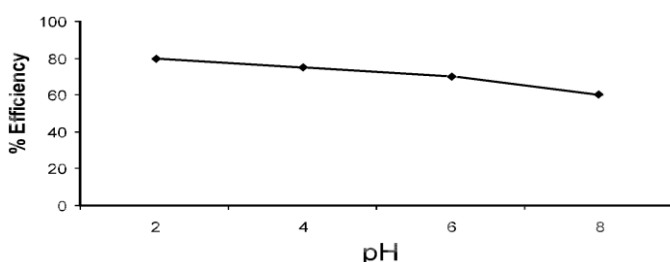


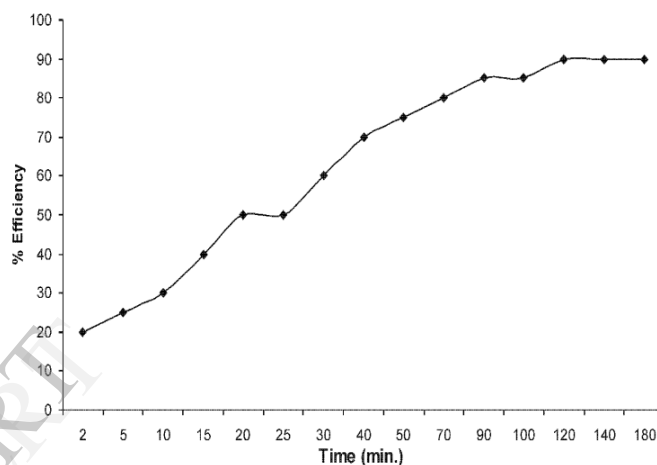
fig. a Effect of pH on the percentage removal of fluoride ion. Adsorbent dose: 10 g/l, adsorbent size: mixed, volume of sample: 50 ml, temp.:  $29^\circ\text{C}$ , initial adsorbate conc.: 10 mg/l, time of contact: 60 min.

In this case the result may be due to neutralization of the negative charge at the surface of the treated bio sorbents by greater hydrogen ion concentration at lower  $p^H$  values. This reduces hindrance to diffusion of the negatively charged fluorides ions on to the increased active surface of treated biosorbents<sup>8</sup> observed similar results using fish bone charcoal.

### Effect of contact time

It is found that the removal of fluoride ions increased with increase in contact time to some extent. Increased in contact time does not increase the uptake of fluoride ion the adsorbent material at their optimum  $p^H$  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 biosorbent Fig. (b). This initial adsorption subsequently gives way to a very slow approach to equilibrium and saturation is reached in 1.5 to 3h. For further optimization of other parameters, this contact time was considered as the equilibrium time.



- fig. b Effect of agitation time on the removal of fluoride ion. Adsorbent dose: 10 g/l, adsorbent size: mixed, volume of sample: 50 ml, temp.:  $29^\circ\text{C}$ , initial adsorbate conc.: 10 mg/l,  $p^H$ : 2.
- Effect of adsorbent dose
- Fig. (c) 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 10mg/l. The amount of adsorbent was varied between 0.5 and 12g/l in aqueous solution at their optimal  $p^H$  values. The treated bioadsorbent was efficient for 50% removal of fluoride ions 55% at 5g/l and maximum removal of 85% and 80% was observed at 12 and 10g/l respectively, at a room temperature of  $29 \pm 0.5^\circ\text{C}$ .

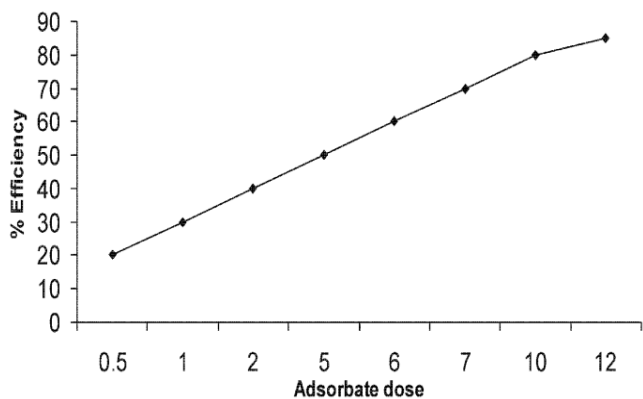


fig. c Effect of adsorbent dose on the removal of fluoride ion. Temp.: 29°C, adsorbent size: mixed, volume of sample: 50 ml, initial adsorbate conc. : 10 mg/l, time of contact: 120 min, pH: 2.

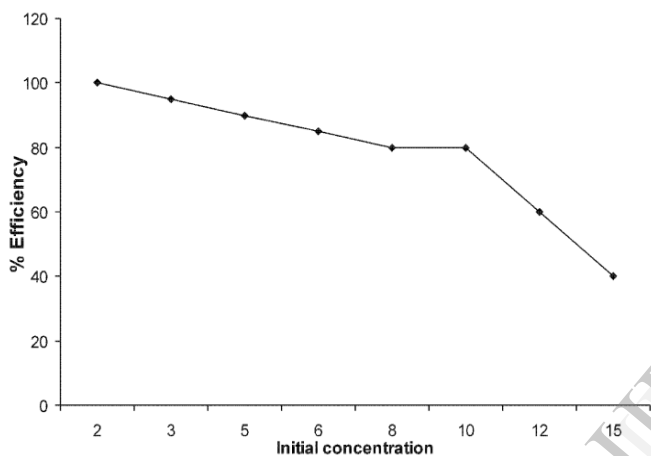


fig. d Effect of initial concentration on the removal of fluoride ion. Temp.: 29°C, adsorbent size: mixed, volume of sample: 50 ml, adsorbent dose: 10 g/l, time of contact: 120 min, pH: 2.

Effect of initial adsorbate concentration

In the optimized period of contact, the rate varies directly with the concentration of adsorbate . The capacity of the adsorbent material gets exhausted sharply with increase in initial fluoride ion concentration (Fig. d) .The adsorption capacity of treated biosorbents was systematically studied by varying the initial concentration of fluoride ions between 2 and 15 mg/l . The percent removal of fluoride ions is a junction of initial concentration at different initial pH values. Treated biosorbents may be seen active in reducing fluoride ions from 100 to 40% . when the initial concentration of fluoride ion concentration was increased from 2 to 15mg/l with a constant sorbent dose of 10g/l at pH of 2.0.

Effect of adsorbent particle size

The results obtained with the variation of adsorbent particle size and the % of the fluoride ions are graphically represented in Fig. (e) . The uptake of fluoride ions at different adsorbent particle size increased with decreased in sorbent particle diameter. The presence of large number of smaller particle

provides the sorption system with a large r surface area available for fluoride ion removal.

The time require for 50% of the total adsorption is less with the particles of smaller size . This gives some idea of rate – limiting step of the adsorption process . The removal of fluoride ion has been studied at a room temperature of 29±0.5 C.

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

Sorption mechanism

The sorption data for the removal of fluoride ions have been correlated with Freundlich<sup>10</sup> and Langmur modles<sup>11</sup>.

Frendlich equation

It has the general from of

$$q_e = KfC_1/n.$$

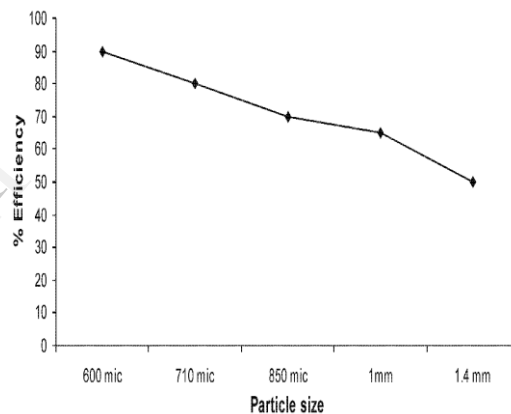


TABLE I.

TABLE II. FIG. E EFFECT OF PARTICLE SIZE ON REMOVAL OF FLUORIDE ION. TEMP.: 29 ± 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.

TABLE III.

TABLE IV.

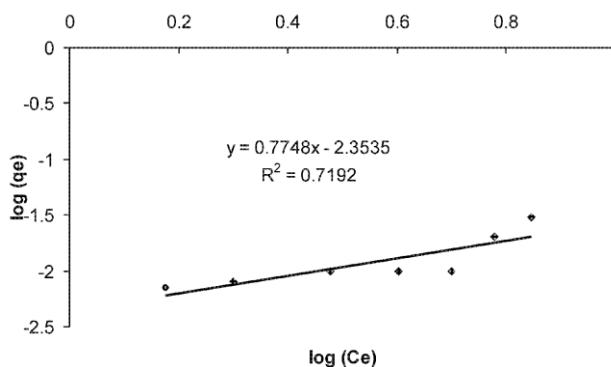


TABLE V.

TABLE VI. FIG. F. LINEAR MODEL OF FREUNDLICH ISOTHERM. THE LINEARISED FREUNDLICH ADSORPTION ISOTHERM WHICH IS OF THE FORM

TABLE VII.  $\text{LOG}(Q_E) = \text{LOG } K_f + 1/n \text{ LOG } C_E$ ,

TABLE VIII. TABLE STYLES

Where :

$q_e$  = Amount of metal ions adsorbent per unit weight of adsorbent (mg g / l).

$K_f$  = Freundlich constant .

$1/n$  = Freundlich constant.

$C_e$  = Equilibrium concentration (mg/l).

If  $1/n < 1$ , bond energies with surface density.

If  $1/n < 1$ , bond energies decrease with surface density and if  $1/n = 1$  all surface sites are equivalent.

Linear photos of  $\log q_e (x/m)$  vs  $\log C_e$  at different adsorbent doses are applied to confirm the applicability of Freundlich modles as shown in Fig. (f) . The calculations for Freundlich modle for the removal of fluoride ions are shown in table (a).

*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. The adsorbed layer will be one molecule thick.

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 desorption of molecules at an adjacent site.

*The Langmuir equation*

Dose 1/qe (mg/l)	Ce (mg/l)	Qe (mg/mg)	1/Ce
50	8	0.04	0.125
100	7	0.03	0.1429
200	6	0.02	0.1667
500	5	0.01	0.2
600	4	0.01	0.25
700	3	0.01	0.3333
1000	2	0.008	0.5
1200	1.5	0.0071	0.6667

$q_e = Q_0 b C_e / (1 + b C_e)$ ,

Where :

$Q_e$  = Amount adsorbed (mg/g)

$C_e$  = The equilibrium concentration of adsorbate (mg/ l)

$Q_0$  = Langmuir constant

$b$  = Langmuir constant

The leaner form of the Langmuir isotherm can be expressed

$1/q_e = (1/Q_0) + (1/b Q_0 C_e)$ .

Where :  $1/q_e$  is plotted against  $(1/ Q_0 b)$  is obtained which shows that the adsorption foffows the langmuir isotherm as shown Fig (i).

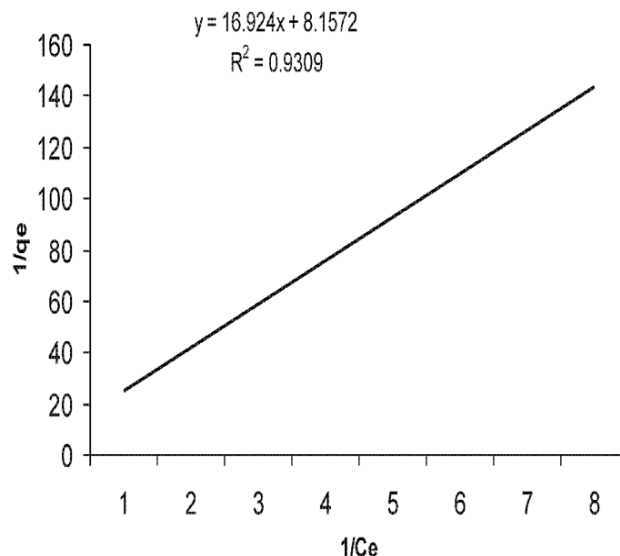


fig. i Linear model of Langmuir isotherm.

Table (a) Calculation of Freundlich isotherm

Dose (mg/l)	1/Ce	Qe (mg/mg)
50	8	0.04
100	7	0.03
200	6	0.02
500	5	0.01
600	4	0.01
700	3	0.01
1000	2	0.008
1200	1.5	0.0071

Table (b) Calculation of Langmuir isotherm

*Disposal of exhausted adsorbent material*

It is necessary to separate fluoride ion before its disposal. The exhausted adsorbent materials need to be dried and burned. Resultant product can be used in manufacturing of bricks.

## CONCLUSIONS

Results shows that these bio-adsorbent could be fruitfully used for the removal of fluoride over a wide range of concentrations .The treated bio-sorbent were observed to be efficient for the uptake of fluoride ions between 2.0 and 10.0 p<sup>H</sup>. Fluoride removal for a given bio-adsorbent size increased with time attaining equilibrium within 1.5h. The percentage of fluoride removal was found to be a junction of adsorbent dose and time at a given initial solute concentration .It increased with time and adsorbent dose. The process of treated bio-sorbents follows Langmuir isotherm.

The adsorption capacity of treated bio-sorbents 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 $\mu$  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 bio-sorbents can be disposed off safely by burning after use.

## REFERENCES

1. Yadav J. P. And Lata S, Indian J Med Sci. 57 (2003) 394.
2. Sivabalan R, Rengaraj S, Arabindo B and Murugesan V , J. Sci. Ind Res. , 61 (2002) 1039.
3. World Health Organisation : Industrial pollution Control Handbook, H. F. Lund , 1971, Mc GrawHill book (0) , New yark, P. 4/25-4/39 (1994).
4. WHO- world Health Organisation Fluoridein Drinking water , J. Fawell ,K. Bailey, J. Chitton , E. Dahi , L. Fewtrell, Y. (2006).
5. Bureau of India Standards , Drinking water specification (First revision ) 1991, IS 10500.
6. Muthukumar K, Balasubramanian N and Ramakrishna T V, Indian J. Environment Port 15 , (1995) 514.
7. Killedar j and bhargava D. S. , Indian J. Environ Helth, 35 (1993) 81.
8. Shrivastava P. K. and Deshmukh A. , JIPHE, 4(1994)531.
9. D. S. Bharava and D. J. Killedar, Batch studies of water defluoridation using fish bone charchole, Res. J. Waste Process, Chem. , Engrs, 63, 848-858 (1991).
10. Freundlich H. Z Phy Chem. , 57 (1985) 387.
11. Lagergren S. K. Sven Vetenskapskad Handl, 24 (1898).