Studies on defluoridation of water by *Tamarind seed,* an unconventional biosorbent

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ABSTRACT

Tamarind seed, a household waste from the kitchen is used for the sorptive removal of fluoride from synthetic aqueous solution as well as from field water samples. Batch sorptive defluoridation was conducted under variable experimental conditions such as pH, agitation time, initial fluoride concentration, particle size and sorbent dose. Maximum defluoridation was achieved at pH 7.0. Defluoridation capacity decreases with increase in temperature and particle size. Further, defluoridation follows first order kinetics and Langmuir adsorption isotherm. Desorption was carried out with 0.1 N HCl and is 90 per cent. The surface and sorption characteristics were analysed using FTIR and SEM techniques. All these results indicate the involvement of energetic forces such as coulombic interaction in sorption. For domestic and industrial applications, defluoridation with 100% achievement and subsequent regeneration of adsorbent was performed with a household water filter and fixed bed column respectively.

Key words | batch adsorption, column adsorption, defluoridation, domestic application, *Tamarind seed*

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INTRODUCTION

Fluoride is known to be a natural contaminant for ground water resources globally. High fluoride content in groundwater has been reported from India, China, Sri Lanka, the West Indies, Spain, Holland, Italy, Mexico, North and South America. Groundwater is the prime source and meets the needs of 60 per cent of India's households. So the quality of ground water can potentially affect over 100 million households, rich and poor, urban dwellers and villagers alike (Susheela 1999).

According to the World Health Organisation (WHO 1984) the maximum acceptable fluoride concentration in drinking water is 1.5 mg/l. However, drinking water is considered to be safe for human consumption, if the concentration does not exceed 1.0 mg/l (Indian standard 1996). Excessive fluoride consumption causes many health hazards. For example, dental fluorosis, an initial stage disease by fluoride ion has been reported in many regions of India and elsewhere (WHO 1970; 1974). Chronic intake of excessive fluoride ion causes severe damage - bone stiffness, rheumatism and ultimately permanent crippling known as skeletal fluorosis (Waldbott 1973) and kidney damage (Odnnel 1973). Thus the removal of fluoride from potable water assumes significance and is given priority by chemists, environmentalists and public health engineers.

The conventional method of removal of fluoride includes ion-exchange, reverse osmosis and adsorption. The ion-exchange and reverse osmosis are relatively expensive. Therefore, still adsorption is the viable method for the removal of fluoride. Plant materials are reported to accumulate fluoride and hence application as defluoridating agents has been suggested. Examples of such biosorbents are *serpentine* (Maruthamuthu & Venkatanarayana Reddy, 1987a), *Tamarind gel* (Maruthamuthu & Venkatanarayana Reddy 1987b), *Duck weed Spirodela polyrrhiza* (Shirke & Chandra 1991), *Hydrilla Verticillata (l.f) Royale plants* (Sinha *et al.* 2000) *Aloe vera* (Murugan & Subramanian

2002). From the literature review it is learnt that the biosorptive defluoridation study is limited and hence in the present work, it is performed with the plant material *Tamarind seed*. *Tamarind seed* is a household material and is left as waste after removing *Tamarind pulp* for food preparation. It mainly consists of polysaccharides (Meltzer 1976) and is used as cattle feed. Since this material is familiar with all kinds of people, an attempt is made in the present study to use it for the removal of fluoride. Using both laboratory aqueous solution and ground water field samples, the study aims to devise a simple, cheap and viable defluoridation method that could be adopted easily by village communities and urban dwellers.

MATERIALS

Tamarind seed used in this study was collected from the kitchen as a waste material. It was soaked in water for an hour to remove the adhering pulp, washed well with tap water and then with double distilled water, dried in an air oven at 110 °C for an hour, micronised in a flour mill and sieved to get particles of sizes 75, 150 and 300 meshes ASTM. The powdered material was subjected to various physico-chemical parameters and used for sorption. A synthetic solution of fluoride was prepared from analytical reagent grade sodium fluoride (Fluka, Switzerland) and stored in polythene bottles. The pH of the solution was adjusted to the required level, using HCl ($0.1 \, \text{mol} \, l^{-1}$) and NaOH ($0.1 \, \text{mol} \, l^{-1}$) solutions.

METHODS

Batch studies

Batch sorption runs for different experimental variables were carried out by agitating 0.1 g of the sorbent with 50 ml of synthetic fluoride solution in 100 ml polythene bottles in a temperature-controlled water-bath-cum-shaker. At the end of predetermined time intervals, the contents were centrifuged and the supernatant was analysed for fluoride spectrophotometrically (Bellack & Schouboe 1968), using SPADNS reagent at $\lambda = 570 \, \text{nm}$ in a Perkin Elmer UV-visible spectrophotometer (Lamda 3B model).

Fluoride contaminated drinking water was collected from a bore-well by hand-pump in Pallikottai village (a fluoride prone area in Tirunelveli District, which comes under our university jurisdiction), and was analysed for physico-chemical characteristics according to the standard methods (APHA 1992). This field sample was also subjected to defluoridation by batch method.

Column study

Column study was also performed for defluoridation with *Tamarind seed*. 5 g of *Tamarind seed* powder was packed into a glass column (2 cm diameter and 45 cm height) for bed height of 8.2 cm. Synthetic fluoride solution was drawn into the column at a rate of 2 ml/min from a separating funnel fixed at a height of 1 m. Effluents were collected at regular intervals of time and analysed as described. The column flow was terminated when the ratio of the effluent to influent fluoride concentrations reached a value of 0.8. After column saturation, the adsorbed fluoride ion was eluted with $0.1 \, \text{mol} \, l^{-1}$ HCl.

Desorption studies were carried out by agitating 100 mg of fluoride-loaded *Tamarind seed* in 50 ml of $0.1 \, \text{mol} \, l^{-1}$ HCl for a period of 2 h.

Tamarind seed samples in the free and fluoride-loaded conditions were characterized by FTIR and SEM techniques. IR spectra were recorded (KBr pellet method) using JASCO FTIR 410 spectrophotometer. Scanning electron microscopic (SEM) pictures of free and fluoride-loaded *Tamarind seed* were taken using Hitachi S 450 instrument with 2000 times magnification, employing gold sputtering method (100 Å) for surface conductivity.
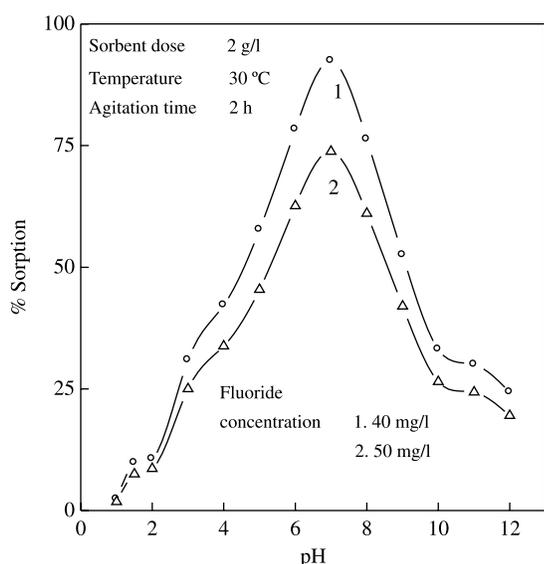
RESULTS AND DISCUSSION

The physico-chemical characteristics of micronised *Tamarind Seed* (particle size 75 micron) are given in Table 1. The surface characteristics make it suitable for sorptive defluoridation. The sorption is characterised under different experimental conditions systematically to obtain data relevant for applications.

Table 1 | Characteristics of the biosorbent *Tamarind seed* (75 micron)

Parameter	Value
pH	5.57
pH$_{ZPC}$	7.44
Mechanical moisture content % (W/W)	10.00
Surface area (m^2/g) (Nitrogen BET adsorption method)	0.99
Cation exchange capacity (meq/g)	2.76

Effect of pH

The effect of pH on fluoride ion removal at two different initial concentrations 40 and 50 mg/l is shown in Figure 1. It is seen that the sorption of fluoride is most appreciable in the pH range 6.0–8.0 with a peak value at pH 7.0. Hence in the present work, the studies were performed at pH 7.0. Since pH$_{ZPC}$ = 7.44, at pH 7.0 the surface will be positively charged. Consequently, there is a greater possibility of coulombic interaction between fluoride ion and *Tamarind seed* surface. Thermodynamic parameters (negative ΔH and ΔS; Table 3) for the sorption process, which will be discussed later, are consistent with this notion.

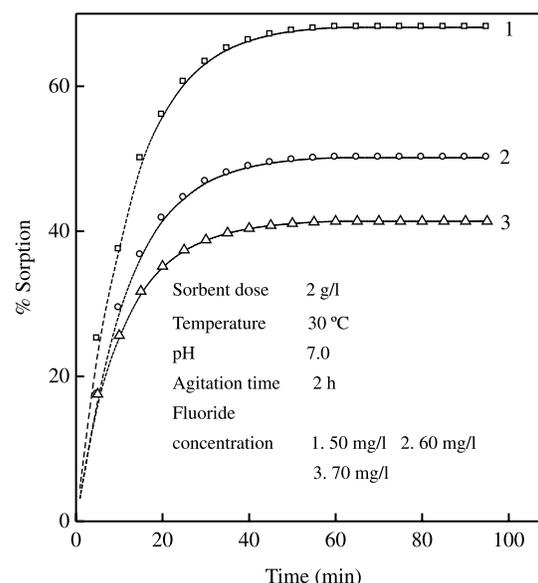## Effect of agitation time and initial fluoride ion concentration

Figure 2 shows the sorption profile, which clearly indicates that the sorption process attains equilibrium in less than 60 minutes. The per cent removal is found to be 68.1, 50.1, 41.3 at initial fluoride concentrations of 50, 60 and 70 mg/l respectively. Furthermore, the time curves are single, smooth and continuous leading to saturation and, therefore, suggest the possibility of monolayer coverage of fluoride ions on the surface of *Tamarind seed*.

Effect of temperature

As shown in Figure 3, increase in temperature, decreases the percentage sorption. This may be due to the weakening of adsorptive forces between *Tamarind seed* and fluoride ion (Ajmal 1998). These results obviously show that temperature is an unfavourable factor for fluoride sorption on *Tamarind seed*.

Effect of particle size and sorbent dosage

The effect of particle size on fluoride sorption is depicted in Figure 4. Increase in particle size from 75 to 300 micron reduces the sorption level from 92.1 to 38.4 per cent.

Figure 1 | Sorption of fluoride on *Tamarind seed* as a function of pH.

Figure 2 | Effect of agitation time and initial concentration on sorption of fluoride.
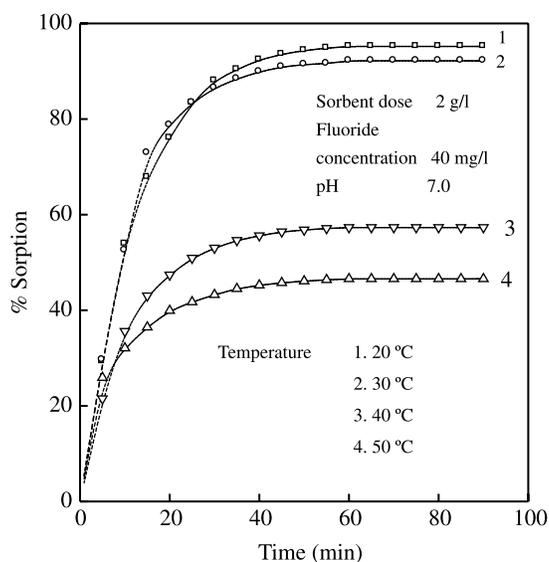
Figure 3 │ Effect of temperature on sorption of fluoride.

The breaking of larger particles tends to open tiny cracks and channels on the particle surface of the sorbent in smaller particles and provides more sorption sites and surface area leading to greater sorption.

The effect of sorbent dosage on sorption was studied with particles of 75 micron and fluoride of concentration 40 mg/l. This effect is illustrated in Figure 5. The extent of sorption increases with increase in dosage and levels off at a higher dosage; for the complete sorption of fluoride initially
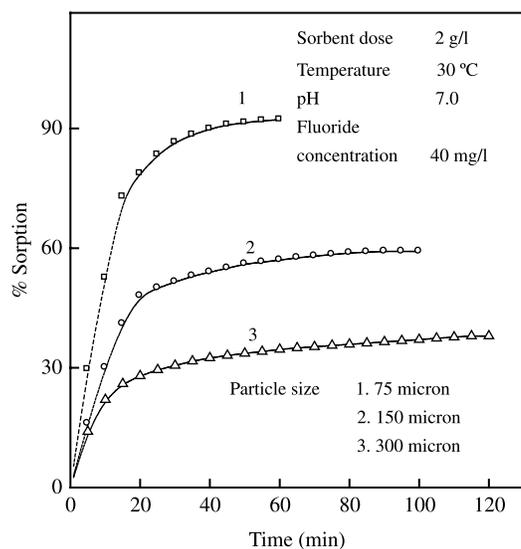

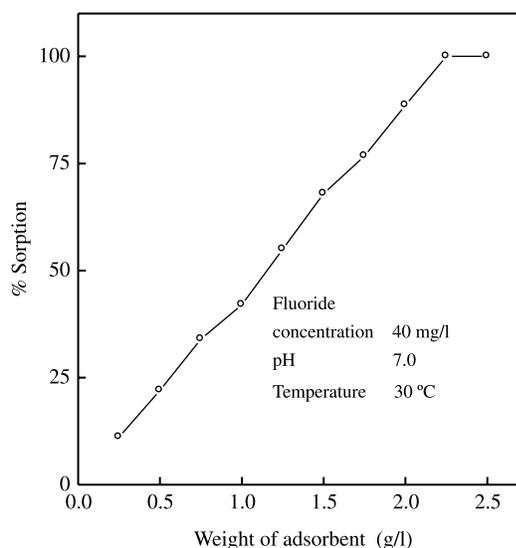**Figure 4** │ Effect of particle size on sorption of fluoride.

Figure 5 │ Effect of adsorbent dosage.

taken, 2.2 g of *Tamarind seed* is required. This amounts to a sorption capacity of 18.18 mg/g.

Sorption dynamics

The kinetics of fluoride sorption on *Tamarind seed* was examined by Lagergren model (Namasivayam & Ranganathan 1995), which is given by equation (1),

$$\log(q_e - q) = \log q_e - (k_{ad} \, t/2.303), \tag{1}$$

where, q_e and q are the quantity of fluoride adsorbed at equilibrium and at time t and k_{ad} is the adsorption rate constant. Figure 6 shows the Lagergren plot at different temperatures. The linear plots certainly show the obeyance of first order rate process in the sorption system. The k_{ad} values determined from the slope of the plots at 20, 30, 40 and 50 °C are 8.27×10^{-2}, 8.19×10^{-2}, 7.75×10^{-2} and $7.03 \times 10^{-2} \, min^{-1}$ respectively. The increase in temperature has slightly decreased the rate. This unfavourable thermal effect may be due to the fact that initially adsorbed fluoride ion via physisorption becomes desorbed at higher temperatures and this leads to a decrease in rate of sorption (Killedar & Bhargava 1993).

Adsorption isotherm

The sorption characteristics of *Tamarind seed* for defluoridation were determined using Langmuir adsorption
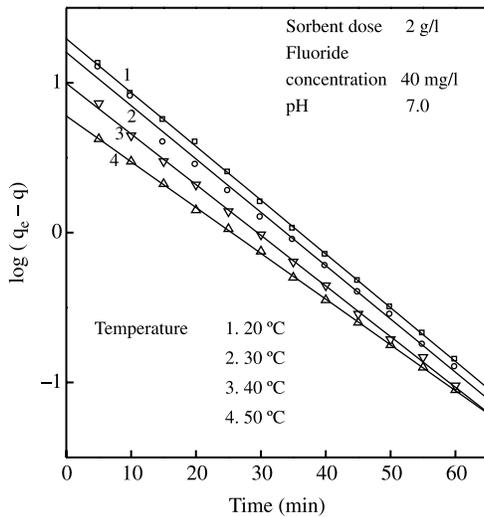
Figure 6 │ Lagergren plot at different temperatures.

isotherm (Langmuir 1918) and its reciprocal form is given in equation (2),

$$C_f/q = 1/Q_0 b + C_f/Q_0, \tag{2}$$

where, C_f and q are the free and sorbed concentrations of fluoride ion respectively at equilibrium; Q_0 and b are the Langmuir constants representing the sorption capacity and energy respectively. The linear plots of C_f/q versus C_f at different temperatures (Figure 7) point out the applicability
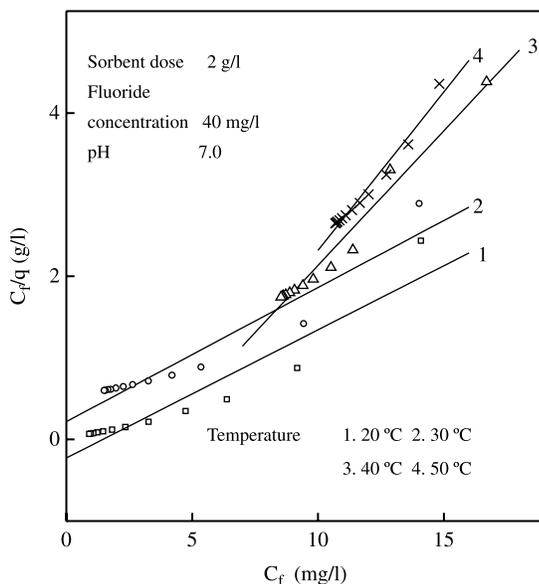

Figure 7 │ Langmuir plot at different temperatures.

of the Langmuir isotherm. The linearity of the plots further lends evidence to the formation of monolayer coverage on the surface of the *Tamarind seed* by the fluoride ion. The values of Q_0 and b (Table 2) were determined from the slope and intercept of the plots.

These decrease with increase in temperature and hence indicate a decline in adsorption capacity and energy. The unfavourable thermal effect observed earlier is, therefore, attributable to the weakening of sorptive forces between active sites and fluoride ions.

The essential characteristic of the Langmuir isotherm may be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter R_L (McKay *et al.* 1982). This parameter lies between 0 and 1 in the present case (Table 2), which indicates a favourable sorption towards *Tamarind seed* under the present experimental conditions.

The thermodynamic equilibrium constant values (K) were deduced (Khan & Singh 1987) by plotting ln (q/C_f) versus q and extrapolating to zero q. Further the changes in standard free energy ((G), enthalpy ((H) and entropy ((S) were also computed using equations 3 and 4 and from the corresponding linear plot of ln K versus 1/T.

$$\rho G = -RT \ln K, \tag{3}$$

$$\ln K = (\rho S/R) - (\rho H/RT), \tag{4}$$

As evident from the K values (Table 3) the sorption process is exothermic. The negative values of ΔG pinpoint the feasibility as well as the spontaneous nature of sorption. Furthermore, the values become less negative with increasing temperature, which shows that the sorption is favoured at low temperatures. This result is consistent with

Table 2 │ Langmuir constants and equilibrium parameters

Temperature (°C)	Langmuir constants		R_L
	Q_0 (mg/g)	b (l/mg)	
20	6.37	0.69	0.04
30	6.09	0.58	0.04
40	2.78	0.15	0.15
50	2.58	0.13	0.16

Table 3 | Thermodynamic parameters for the sorption of fluoride on *Tamarind seed*

Temperature (°C)	K	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})
20	2.95	2.63	2.04	4.85
30	2.63	2.43		
40	2.25	2.11		
50	2.16	2.07		

the effect of temperature and the trend in Langmuir constants Q_0 and b. Negative enthalpy values ($-\Delta H$) imply the involvement of energetic forces and hence the exothermic nature of sorption. The values of ΔS are also negative suggesting orderliness or lesser degree of freedom at the solid-solution interface and thereby indirectly indicate the predominance of energetic forces in sorption. Thus ΔH and ΔS substantiate the notion of involvement of coulombic forces in fluoride sorption proposed earlier.

Study with field drinking water sample

Field drinking water sample characteristics were determined by standard methods (APHA 1992) and are entered in

Table 4 | Physico-chemical parameters of field drinking water sample

Parameter	Value
Fluoride (mg/l)	2.7
pH	7.56
Specific conductance (µS/cm)	2160
Turbidity (NTU)	Negligible
TDS (mg/l)	2702
Total acidity (mg/l)	1.3
Total alkalinity (mg/l)	55.6
DO (mg/l)	7.0
BOD (mg/l)	0.75
Sulphate (mg/l)	9.38

Table 4. In batch sorption, it was found that 0.15 g of *Tamarind seed* powder is required for complete removal of fluoride of concentration 2.7 mg/l from the field sample of volume 1.0 l. This gives rise to a sorption capacity of 18 mg/g, which agrees well with the value observed for the laboratory solution.

With a view to making use of this finding in domestic applications, a simple method was developed. An ordinary household two-tier water tank (Figure 8) has a clay filter for water purification, for example, to remove sediments, but it does not have any defluoridating capacity. Hence it was loaded with 25 g of *Tamarind seed* powder and fluoride-containing water was stored in the upper tank as usual. When water passed through the clay filter column, with encapsulated powder, slowly at its own rate, the water becomes defluoridated and collected in the bottom tank. From the bottom tap the fluoride-free water is drawn out. Approximately 40 litres of water containing fluoride concentration of 5 mg/l is found to be treated in this filter in a household.

The results of the batch adsorption experiment could be extended for a household requirement of *Tamarind seed* powder for water treatment for a family (two adults and one child) consuming 10 litres of water per day for drinking and cooking purposes. The adsorption capacity of 18 mg/g/l of *Tamarind seed* means that for treating one litre of water of fluoride of concentration 1.0 mg/l, 0.055 g of *Tamarind seed* is required. This datum is linearly applicable for water of any volume and fluoride concentration. For the family in
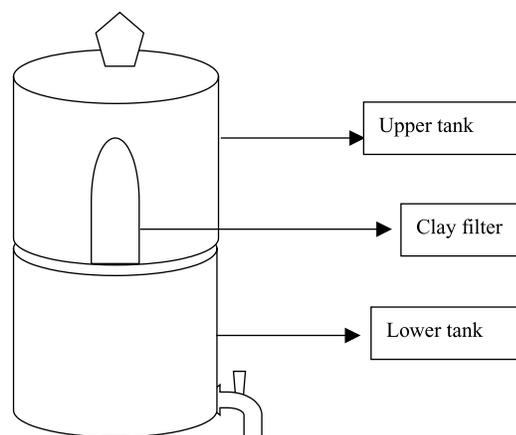
Figure 8 | Domestic water filter for defluoridation containing *Tamarind seed* within clay filter.

question, if the fluoride concentration of their water is 1 mg/l then for 10 litres of water treatment, 0.55 g of *Tamarind seed* is sufficient; on the other hand if the fluoride concentration is 5.0 mg/l, then 2.75 g of *Tamarind seed* is required per day.

Such an application, however, requires fresh *Tamarind seed* powder after each treatment. During water treatment, polysaccharides, the major constituent ($\approx 70\%$) of *Tamarind seed* powder responsible for fluoride binding, being hydrophilic, are leached out from the powder. This is also reported in the literature (Davidson 1980). Nevertheless, it is non-toxic and indeed, it is regarded as having a medicinal effect and is recommended for curing diarrhea and dysentery (Davidson 1980). No other leachate either from testa or kernel is found in the treated water. Though harmless, the slowly leaching polysaccharide may alter the aesthetic sense of the water. Hence it is our aim in our future study to immobilize/condition the polysaccharide in the *Tamarind seed* powder itself and to use *Tamarind seed* powder, free from pulverised testa, for defluoridation.

Desorption studies

Desorption studies are useful to elucidate the type of sorption and for regeneration of sorbent. In the present study, desorption was carried out for 0.1 g of fluoride loaded sorbent with 50 ml of 0.1 mol l^{-1} HCl. Desorption is 90%, which shows that both strong and weak forces are operating in the sorption of fluoride on *Tamarind seed*.

Column study for defluoridation

Continuous mode analysis (column study) was performed in order to make use of *Tamarind seed* for large-scale treatment of fluoride-contaminated water. The column data obtained from the experiment described earlier, were analysed using the Thomas model (Thomas 1948; Reynolds & Richards 1996), which is given in equation (5),

$$\text{Log}[(C_0/C_e) - 1] = Kq_0M/Q - KC_0V/Q, \tag{5}$$

where, C_0 and C_e are the influent and effluent fluoride concentrations respectively, K is the Thomas rate constant, q_0 is the maximum solid phase concentration of solute (mg/g), M is the mass of adsorbent (g), Q is the influent flow

rate (ml/min) and V is the through put volume (ml/min). Figure 9 displays the breakthrough curve for sorption of fluoride on *Tamarind seed*. Effluent fluoride ion concentration was found to be zero for the first 52 bed volumes; approximately 93% of fluoride is retained for 5 bed volumes; 74% for another 5 bed volumes and as evident from the curve, the retention of fluoride by the column gradually declines as the bed volume increases. The Thomas rate constant K and the maximum solid phase concentration of fluoride q_0 values are computed from the slope and intercepts of the linear plot of log $[(C_0/C_e) - 1]$ versus V and are found to be 26.68×10^{-2} ml/min/mg and 8.34 mg/g respectively. When the column was saturated with fluoride ion, it was eluted with 0.1 mol l^{-1} HCl and the recovery was 100%. These column analysis data are useful and provide a rough estimate of fluoride sorption in practical macro-level column treatment.

Mechanism of sorption of fluoride on *Tamarind seed*

The surface of *Tamarind seed* is positive at a neutral pH since its pH_{zpc} is 7.44. Hence, there may be electrostatic interaction between the fluoride ion and *Tamarind seed*. As reported (Meltzer 1976), *Tamarind seed* mainly contains polysaccharide with fats, tannins, proteins and amino acids in minimum proportion, which yield IR peaks at 1650 cm^{-1} (ketone moiety), 1445 cm^{-1} (OH in-plane bending) and
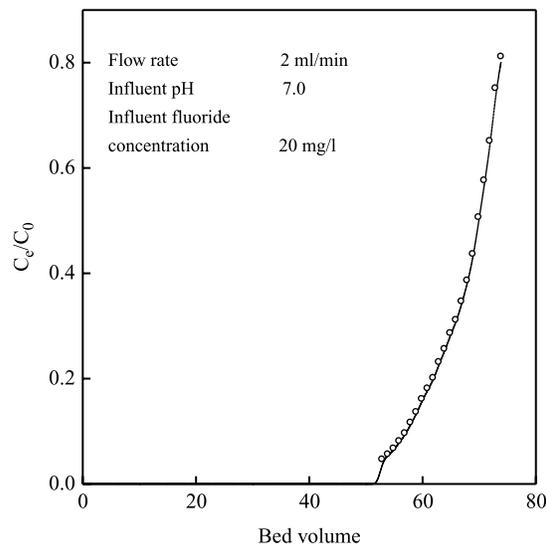
Figure 9 | Breakthrough curve for sorption of fluoride on *Tamarind seed*.

and is influenced by many experimental conditions. Remarkably, fluoride removal is favoured at low temperatures and at neutral pH. The decrease in sorption capacity at high temperatures is suggestive of an exothermic reaction caused apparently by electrostatic and hydrogen bonds between fluoride ions and the adsorbent. Desorption of fluoride to the extent of 90% from fluoride-loaded *Tamarind seed* with 0.1 mol l^{-1} HCl reveals the involvement of weak forces. Extension of sorption finding with the laboratory fluoride solution compared to the field water sample is quite agreeable and consistent. Further, household and column defluoridation methods have been developed. Therefore, from the present study it emerges that *Tamarind seed* has the potential to be an efficient defluoridating agent in its powder form, for application in domestic and macro level treatment systems. Future study is, however, required to immobilize/condition the leachable polysaccharide in *Tamarind seed* powder, although it is harmless, and to remove testa from *Tamarind seed* before the kernel is pulverised into powder.
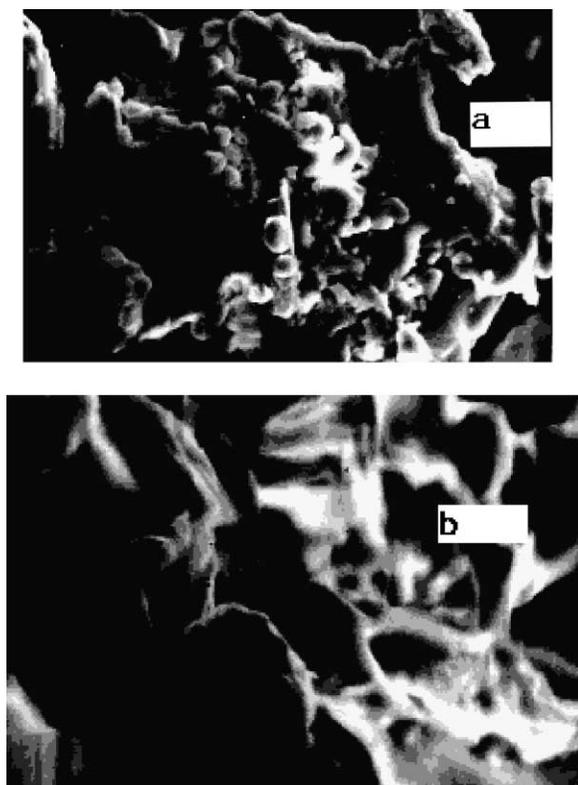

Figure 10 │ SEM images of (a) free *Tamarind seed* and (b) fluoride-loaded *Tamarind seed*. (x 2000 magnification).

$1032\,cm^{-1}$(C-O stretching). The peaks at $1650\,cm^{-1}$ and $1445\,cm^{-1}$ are blueshifted to 1667 and $1448\,cm^{-1}$ respectively while the peak at $1032\,cm^{-1}$ is redshifted to $1024\,cm^{-1}$ on fluoride uptake. Further in the SEM photographs (Figure 10), it appears clearly that the spongy particles of free *Tamarind seed* after fluoride binding are converted into large size, rough surface particles. All these spectral shifts and SEM study lend evidence to electrostatic bonding. Nevertheless, the hydrogen bonding of fluoride with the phenolic/hydroxyl groups of *Tamarind seed* is also a possibility. This type of hydrogen bonding is reported in the literature (Maruthamuthu & Venkatanarayana Reddy 1987b). Thus, from the above discussion one can conclude that the binding of fluoride to *Tamarind seed* may be due to both electrostatic attraction and hydrogen bonding.

CONCLUSIONS

The sorption process of fluoride ion on *Tamarind seed* does exhibit a first order kinetics and Langmuir type behaviour

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