

Adsorption dynamics and the effect of temperature of fluoride at alumina-solution interface

G. Karthikeyan*, A. Shunmuga Sundarraj, S. Meenakshi and K. P. Elango

Department of Chemistry, Gandhigram Rural Institute-Deemed University, Gandhigram-624 302, India

E-mail : drg_karthikeyan@rediffmail.com Fax : 91-451-2454466

Manuscript received 24 April 2003, revised 14 October 2003, accepted 14 January 2004

The defluoridation efficiency of the commercially available grades of activated alumina were determined. The various factors which influence the defluoridation efficiency of the material were studied. There was a marked dependence of pH on the defluoridating capacity. The adsorption of fluoride ions on activated alumina was studied in the temperature range of 303–333 K by the batch equilibration method. The experimental adsorption data fitted well to the Langmuir isotherm indicating that the forces of adsorption are governed mainly by chemisorption. The equilibrium parameters and activation parameters were calculated and reported. The results indicate that the adsorption process is endothermic and occurs spontaneously which substantiate the proposed mechanism for the adsorption of fluoride at the alumina-solution interface.

Fluorosis, an endemic public health problem, prevails in 22 nations around the globe. It is a crippling disorder/condition known to occur due to the entry of fluoride into the body. The excessive ingestion of fluoride through drinking water causes this debilitating condition^{1,2}. It is a slow, progressive, crippling malady that affects every organ, tissue and cells in the body and results in health complaints that overlap with several other disorders. The extent of affectation may vary depending upon the chemical constitution of the tissue/organ. Drinking water is reported to be the major cause of dental, skeletal and non-skeletal fluorosis in human beings. If alternative water sources are difficult to be located in a region and the provision of piped water supply is impracticable, chemical treatment of the available water sources to reduce the fluoride level seems to be the only viable alternative. A number of methods have been suggested for the defluoridation of water, each having its own merits and demerits. Depending upon their mode of action they are classified into three major types, viz., those based on chemical addition, based on adsorption process and based on ion exchange process. The method, to be implemented should be effective, inexpensive and replicable. It should also be simple and socially and ethically acceptable by the users. Activated alumina has been found to be a promising material among all the available defluoridating agents. It is a porous material with the surface comprising of active sites^{2,3}. The main component of activated alumina is Al₂O₃ and it is prepared by dehydration of Al(OH)₃ in

the temperature range of 300–700°.

Detailed study on the adsorption of fluoride ion on activated alumina has been carried out in our laboratory by varying initial concentrations of fluoride, particle size of activated alumina, pH, etc. The influence of other ions like bicarbonate, chloride and sulphate on the defluoridation capacity of the activated alumina has also been experimentally verified. Based on the results, a probable mechanism has been proposed for the adsorption of fluoride ion at alumina-solution interface. Dayaram and Chitranshi⁴ reported the kinetics of defluoridation using activated alumina as an adsorbent. However, none of the earlier reports deal with the effect of temperature on the defluoridation capacity of activated alumina. Such a study and computation of thermodynamic and equilibrium parameters will provide a comprehensive understanding of the nature of defluoridation capacity of activated alumina. The results of the detailed investigations are reported here.

Results and discussion

The defluoridation efficiency of activated alumina was studied under different experimental conditions like particle size of the adsorbent, pH of the medium, contact time of the adsorbent for maximum defluoridation and also the effect of other ions like bicarbonate, chloride and sulphate on defluoridation.

Effect of contact time : The defluoridation capacity of activated alumina was determined by varying the contact

time between the adsorbent and the adsorbate, till the adsorbent got exhausted. A plot of defluoridation capacity versus contact time (Fig. 1) indicates that the defluoridation capacity reached saturation after 20 min. Hence in all the experiments the time of contact of the adsorbent and adsorbate was fixed at 20 min, i.e., equilibrium was allowed to be attained.

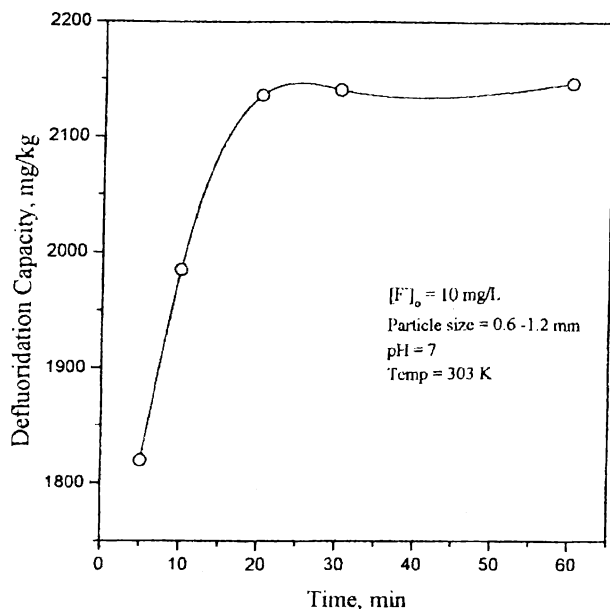


Fig. 1. Effect of contact time on the defluoridation capacity of activated alumina

Effect of particle size : The experiments were carried out with six different particle sizes of the adsorbent, five grades supplied by M/s R. V. Corporation, Mumbai and one grade prepared in the laboratory by pulverizing the G-87 sample obtained from M/s IPCL, Thane, while keeping all other factors constant. The results presented in Table 1 indicate a significant increase in defluoridation capacity with a decrease in particle size of activated

Table 1. Effect of particle size on the defluoridation capacity of activated alumina

Sl. no.	Particle size (mm)	Defluoridation capacity (mg/kg)
1.	0.6 -1.2	2136
2.	1-3	1795
3.	3-5	1070
4.	5-8	590
5.	8-10	550
6.	G-87 (0.6-1.2)	2200

Initial fluoride concentration, $[F]_0 = 10 \text{ mg dm}^{-3}$; pH = 7; contact time = 20 min; temp. = 303 K.

alumina. This is obvious, because any adsorption process depends upon the number of active surface sites. The activated alumina with particle size 0.6–1.2 mm, supplied by M/s R. V. Corporation, Mumbai possessed comparable defluoridation efficiency (2136 mg/kg).

Effect of pH : The defluoridation capacity of activated alumina was determined at five different pH levels, viz. 3, 5, 7, 9 and 11 and the results are given in Table 2. The results indicate that there was a marked dependence of

Table 2. Effect of pH of the medium on the defluoridation capacity of activated alumina

Sl. no.	pH	Defluoridation capacity (mg/kg)
1.	3	7911
2.	5	3747
3.	7	2136
4.	9	1345
5.	11	1110

Initial fluoride concentration, $[F]_0 = 10 \text{ mg dm}^{-3}$; contact time = 20 min; particle size = 0.6–1.2 mm; temp. = 303 K.

defluoridation capacity of activated alumina on pH of the medium. Fig. 2 gives the plot of defluoridation capacity versus pH. There was a four-fold increase in the defluoridation capacity of the material from pH 7 to 3. On the other hand, it decreases in the alkaline range. Due to experimental difficulty, it is not possible to obtain more adsorption data outside the pH range 3–11.

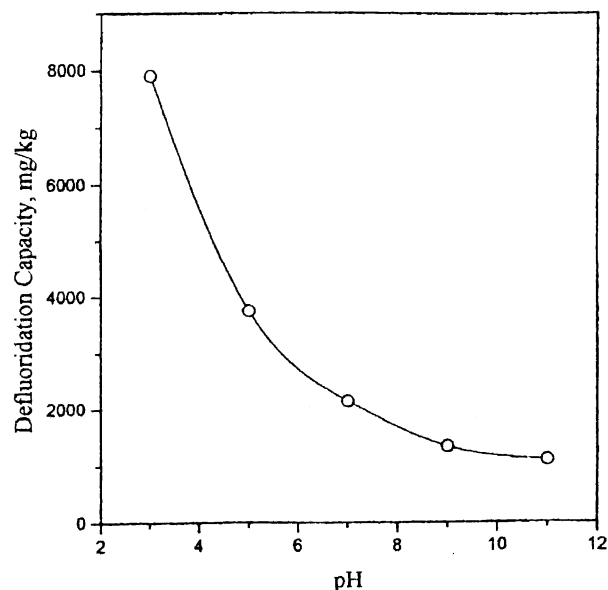


Fig. 2. Effect of pH on the defluoridation capacity of activated alumina.

Effect of temperature : Adsorption studies were carried out at four different temperatures (303–333 K) keeping all other factors constant. It has been observed that the defluoridation capacity of activated alumina is independent of temperature.

Effect of fluoride ion concentration : The defluoridation capacity of activated alumina was determined at different initial concentrations of fluoride ion. The results are given in Table 3. With an increase in initial fluoride ion concentration of the solution from 2 to 20 mg dm⁻³, the

Table 3. Effect of fluoride ion on the defluoridation capacity of activated alumina

Sl. no.	[F] ₀ (mg dm ⁻³)	Defluoridation capacity (mg/kg)
1.	2	650
2.	5	1345
3.	10	2136
4.	15	2540
5.	20	2590

Particle size = 0.6–1.2 mm; pH = 7; emp. = 303 K; contact time = 20 min.

defluoridation capacity of activated alumina increased from 650 to 2590 mg/kg. It is clear from the plot of defluoridation capacity versus initial fluoride ion concentration (Fig. 3) that the defluoridation capacity of activated alumina increases with increase in fluoride ion concentration and reached saturation beyond 15 mg dm⁻³.

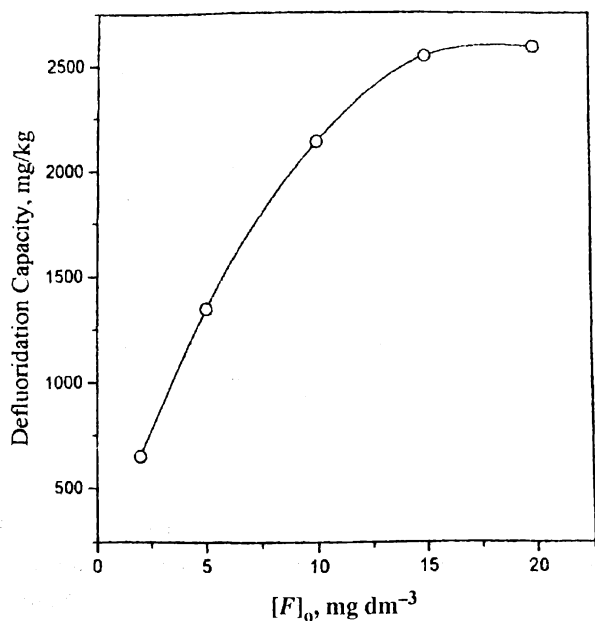


Fig. 3. Effect of fluoride concentration on the defluoridation capacity of activated alumina.

Effect of chloride and sulphate ions : The dependence of the defluoridation capacity of activated alumina on the presence of chloride and sulphate ions in the medium was investigated with varying initial concentrations of the two ions. The results indicate that both the ions do not have any effect on the defluoridation capacity of activated alumina under the experimental conditions.

Effect of bicarbonate ions : The effect of bicarbonate ion concentration on the defluoridation capacity of activated alumina was studied by keeping all other factors constant. The results (Table 4) indicate a significant reduction of defluoridation efficiency of activated alumina

Table 4. Effect of bicarbonate ion concentration on the defluoridation capacity of activated alumina.

Sl. no.	[HCO ₃] ₀ (mg dm ⁻³)	Defluoridation capacity (mg/kg)
1.	0	2136
2.	200	1620
3.	400	1367
4.	600	1220
5.	800	1200

Initial fluoride concentration, [F]⁻₀ = 10 mg dm⁻³; pH = 7; contact time = 20 min; particle size = 0.6–1.2 mm, temp. = 303 K.

at higher concentrations of bicarbonate ions upto 600 mg dm⁻³, beyond which it remains constant (Fig. 4). Therefore, it is presumed that activated alumina adsorbs bicarbonate ions also to some extent and as a consequence

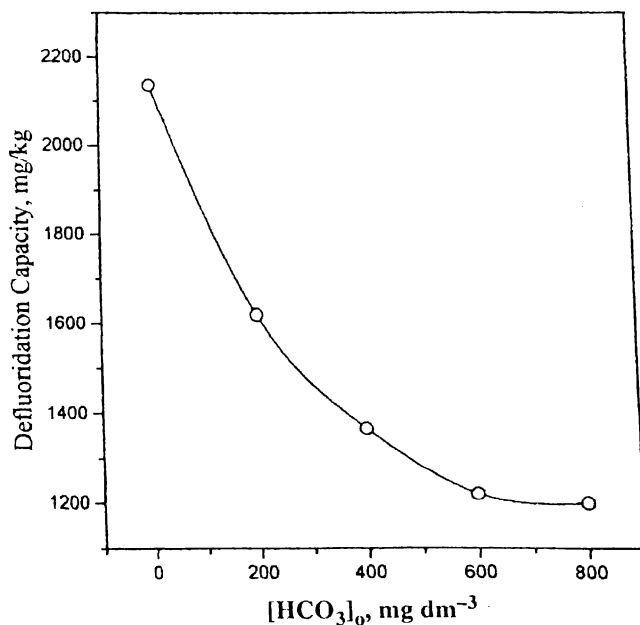
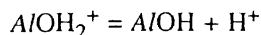


Fig. 4. Effect of bicarbonate on the defluoridation capacity of activated alumina.

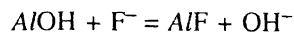
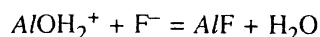
there is a decrease in the defluoridation efficiency with increase in the concentration of bicarbonate ions. In the presence of bicarbonate ions there may be a competition among four species viz., fluoride, hydroxyl, bicarbonate ions and water dipoles, for sites on activated alumina. The concentration of water dipoles is always very high because we are dealing with extremely dilute fluoride solutions here. Only the concentrations of the other three ions are comparable to each other and the competition among these three species is of greater significance in deciding the defluoridation capacity.

Mechanism of adsorption : The results of the systematic study on the influence of various factors on the defluoridation capacity of activated alumina indicate that the effectiveness of activated alumina for removing fluoride is predominantly governed by solution pH. This observation is in line with the earlier reports on the adsorption of fluoride on different varieties of alumina⁵. The adsorption reaction may be described using conceptually simple surface complex formation model⁶. Upon hydration, hydroxo groups develop at the alumina surface. These hydroxo groups behave amphotericly.



where $AlOH_2^+$, $AlOH$ and AlO^- are positive, neutral and negative surface hydroxo groups respectively. The underline indicates the activated alumina solid surface. Thus the total number of surface hydroxo groups is pH dependent. Further it is seen that at $pH < pH_{zpc}$ (where pH_{zpc} is pH of zero point charge and for alumina the value is 9), the total number of surface hydroxo groups is sum of $AlOH_2^+$, $AlOH$ while at $pH > pH_{zpc}$ it depends only on $AlOH$.

Therefore at pH lesser than 9 the adsorption of fluoride onto activated alumina can be described by the following equation i.e. with the formation of alumina-fluoro complexes on the surface.



Further at $pH < pH_{zpc}$ the potential determining hydrogen ion render the activated alumina surface positive^{7,8}, consequently the adsorption of fluoride ion becomes more pronounced (Fig. 5). Thus, the mechanism of the exchange of fluoride ion for the activated alumina surface hydroxide is generally called adsorption through ligand exchange and chemisorption which are more appropriate terms for the highly specific surface reactions involved.

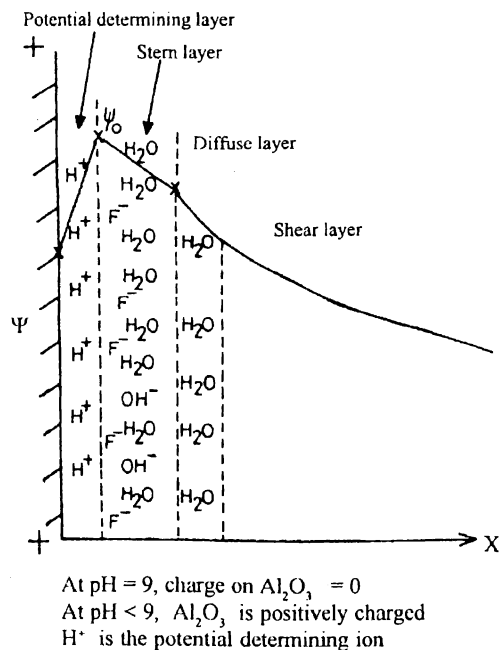


Fig. 5. Model of the double layer between alumina/solution interface.

At pH greater than 9 fluoride removal by activated alumina may be purely governed by physisorption. In fact, adsorption through van der Waals type of forces may be taking place to some extent throughout the pH range. This argument is supported by the fact that the defluoridation capacity is reached only after a minimum contact time of 20 min⁹.

Thus it may be concluded that the adsorption of fluoride ions at the alumina-solution interface is a spontaneous endothermic process and the forces which are responsible for the adsorption to occur are physisorption and/or chemisorption depending upon the pH of the medium in addition to other intermolecular forces of attraction.

Adsorption isotherm : To quantify the adsorption capacity of activated alumina for the removal of fluoride ions from the solution, Langmuir adsorption equation was applied in the form

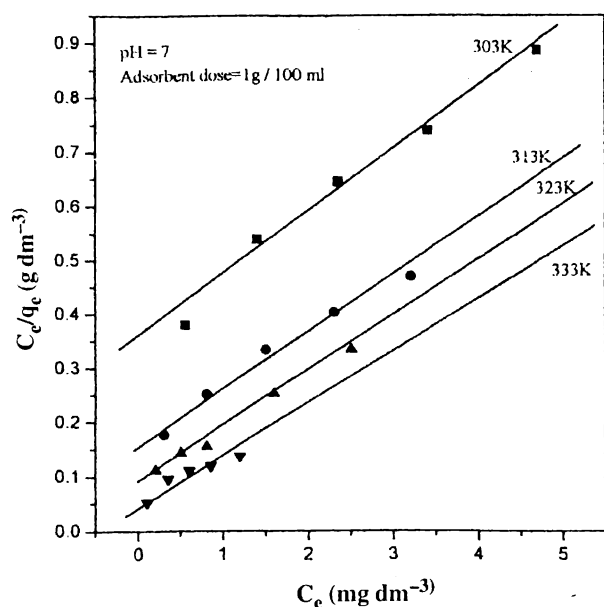
$$C_e/q_e = 1/Qb + C_e/Q$$

where Q and b are the Langmuir constants, indicating the adsorption capacity and energy of adsorption respectively and C_e and q_e have their usual significance. The equilibrium parameters for fluoride adsorption by activated alumina at different temperatures are given in Table 5.

Table 5. Effect of temperature on equilibrium parametes for the fluoride adsorption on activated alumina

Concentration of fluoride ion (mg dm ⁻³)	C _e (mg dm ⁻³)				C _e /q _e (mg dm ⁻³)			
	303	313	323	333 K	303	313	323	333 K
2	0.55	0.30	0.20	0.10	0.3793	0.1769	0.1111	0.0526
4	1.40	0.80	0.50	0.35	0.5385	0.2500	0.1429	0.0959
6	2.35	1.50	0.80	0.60	0.6438	0.3333	0.1539	0.1111
8	3.40	2.30	1.60	0.85	0.7391	0.4035	0.2500	0.1189
10	4.70	3.20	2.50	1.20	0.8868	0.4706	0.3333	0.1364

The linear plots ($0.939 < r < 0.997$ and $0.009 < sd < 0.028$) of C_e/q_e versus C_e at different temperatures (Fig. 6) indicate the applicability of Langmuir adsorption isotherm. Further, such linear plots indicate that the forces


Fig. 6. Langmuir plots for the adsorption of fluoride on activated alumina.

of adsorption of fluoride on activated alumina are governed by chemisorption as depicted in the mechanism. The values of Q and b at different temperatures were determined from the above plots and are given in Table 6. The results showed that the energy of adsorption (b) for fluoride adsorption on activated alumina increases with increase in temperature indicating that fluoride ion adsorption takes place more readily with increase in temperature.

Equilibrium parameter : The dimensionless equilibrium parameter R_L is defined by $R_L = 1/(1 + bC_0)$ where b is the Langmuir constant and C_0 is the initial concentra-

Table 6. Langmuir and thermodynamic parameters for the fluoride ion adsorption on activated alumina

Temp. K	Langmuir constants		Thermodynamic parameters			
	$10^2 b$ dm ³ mg ⁻¹	Q mg g ⁻¹	K_0	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° J mol ⁻¹ K ⁻¹
303	33.75	8.54	1.22	-0.50	-	-
313	60.80	9.99	2.02	-1.83	23.97	81.52
323	110.78	10.20	2.61	-2.58	-	-
333	116.24	14.37	2.88	-2.93	-	-

tion¹⁰. The R_L values for the initial concentrations of fluoride ion at different temperature studied were calculated and are given in Table 7. The R_L values between 0 and 1 indicate favourable adsorption for all the initial concentrations and temperatures studied.

The thermodynamic equilibrium constant K_0 for the sorption reaction was determined by plotting $\ln q_e/C_e$ vs q_e and extrapolating to zero q_e (Fig. 7) as described in the literature¹¹. The K_0 values at different temperatures are also given in Table 6. The endothermic nature of adsorption is indicated by an increase in K_0 with rise in the temperature.

Effect of temperature : The effect of increase in temperature on the adsorption of fluoride at the alumina-solution interface has been studied in the temperature range of 303–333 K. The thermodynamic parameters associated with the adsorption viz., standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using the following equations as reported earlier¹².

$$\Delta G^\circ = -RT \ln K_0$$

$$\ln K_0 = \Delta S^\circ/R - \Delta H^\circ/RT$$

A plot of $\ln K_0$ vs $1/T$ was found to be linear. ΔH° and ΔS° were determined from the slope and intercept of the plot. The standard free energy changes (ΔG°) were negative suggesting that the adsorption of fluoride on activated

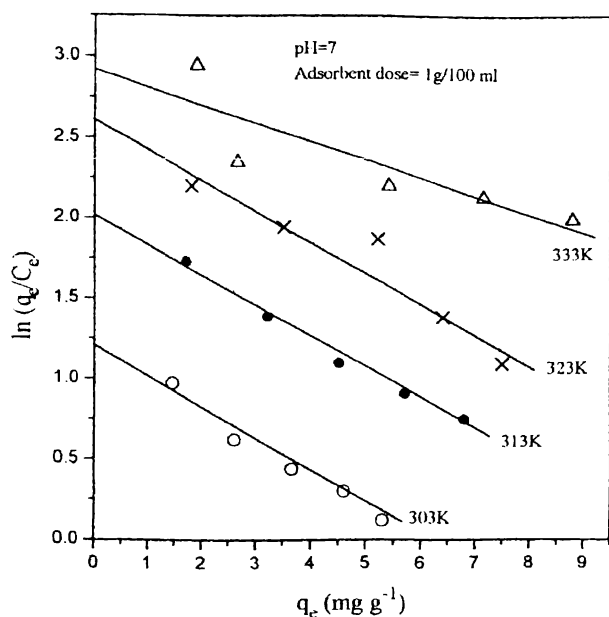


Fig. 7. Plots of $\ln q_e/C_e$ versus q_e for the adsorption of fluoride on activated alumina.

alumina was spontaneous. The value of ΔH° is positive ($23.97 \text{ kJ mol}^{-1}$). This indicates that the adsorption process is endothermic. The value of entropy change (ΔS°) was positive being $81.52 \text{ J K}^{-1} \text{ mol}^{-1}$ suggesting a higher degree of disorderliness at the solid-solution interface during the adsorption of fluoride on activated alumina.

Experimental

Commercially available activated alumina (M/s R. V. Corporation, Mumbai) of particle size 0.6–1.2 mm was used for the study. All other chemicals employed were AnalaR or other high purity grade and were used without further purification. Water was deionized and double-distilled, the second distillation was made from alkaline potassium permanganate using an all glass distillation still. All the solutions, including sodium fluoride solution were prepared using double-distilled water.

Defluoridation experiments were carried out by batch equilibration method as follows: The adsorption of fluoride ions (NaF) on activated alumina was studied at different initial concentration ($2\text{--}10 \text{ mg dm}^{-3}$) and in the temperature range of 303–333 K. In a typical case, 1 g of the adsorbent was added to 100 ml of the sodium fluoride solution of concentration 10 mg dm^{-3} . The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 120 rpm. The solution was then filtered and

the residual fluoride ion concentration was measured using ion expandable analyzer (All Orion, U.S.A) as reported earlier⁹. The adsorbent was dried in an oven at 110° and then reused with another sample of 100 ml of fluoride solution of the same concentration. The experiments were repeated till the adsorbent was unable to remove fluoride ion any further. The defluoridation capacity of the adsorbent was calculated as follows:

Defluoridation capacity =

$$\frac{\text{Total amount of fluoride removed in all the cycles (mg)}}{\text{Amount of adsorbent taken (g)}}$$

Computations were made using Microcal Origin (version 3.5) software. The goodness of the fit was discussed using correlation coefficient (r) and the standard deviation (sd).

References

1. S. P. S. Teotia and M. Teotia, *J. App. Polymer Sci.*, 1984, **32**, 347; E. S. McKay, *Dental Cosmos*, 1925, **67**, 847; A. K. Susheela, A. Kumar, Madhu Bhatnagar and Rashimi Bahadur, *Fluoride*, 1993, **26**, 94.
2. S. Meenakshi, Ph.D. Thesis, Gandhigram Rural Institute, Gandhigram, 1992.
3. K. R. Bulusu and W. G. Nawlakhe, *Indian J. Environ. Health*, 1990, **32**, 197; S. Meenakshi, Anitha Pius, G. Karthikeyan and B. V. Appa Rao, *Indian J. Environ. Protection*, 1991, **11**, 511; Frederick Rubel (Jr.) and R. Dale Woosely, *J. Am. Wat. Wks. Assn.*, 1979, 45.
4. Daya Ram and U. B. Chitranshi, *Indian J. Environ. Protection*, 1997, **17**, 594.
5. W. W. Choi and K. Y. Chen, *J. Am. Wat. Wks. Assn.*, 1979, **71**, 562; Y. C. Wu and A. Nitya, *J. Env. Engg. Div. ASCE*, 1979, **105**, 357; E. A. Savinelli and A. P. Black, *J. Am. Wat. Wks. Assn.*, 1958, **70**, 105.
6. Oliver J. Hao, A. M. Asce, C. P. Huang and M. Asce, *J. Env. Engg. Div. ASCE*, 1986, **112**, 1054.
7. D. W. Fuerstenau, *Chem. Biosurfaces*, 1976, **1**, 143.
8. Adamson, "Physical Chemistry of Surfaces", 3rd. ed., John Wiley and Sons, New York, 1976, 415.
9. G. Karthikeyan, B. V. Appa Rao and S. Meenakshi, "Proceedings of the 2nd. International Workshop on Fluorosis and Defluoridation of Water", Nazareth, Ethiopia, 1997, 78.
10. G. McKay, H. S. Blair and J. R. Garden, *J. Appl. Polymer Sci.*, 1982, **27**, 3043.
11. A. A. Khan and R. P. Singh, *Colloid Surface*, 1987, **24**, 33.
12. G. N. Manju, C. Raji and T. S. Anirudhan, *Wat. Res.*, 1998, **32**, 3062.