Removal of fluoride from water using aluminium containing compounds

M. Karthikeyan, K. P. Elango[*]

Department of Chemistry, Gandhigram Rural University, Gandhigram 624302, India. E-mail: nmkarthic@yahoo.com

Abstract

Batch adsorption studies were undertaken to assess the suitability of aluminium titanate (AT) and bismuth aluminate (BA) to remove fluoride ions from water. The effect of pH, dose of adsorbent, contact time, initial concentration, co-ions and temperature on fluoride removal efficiency were studied. The amounts of fluoride ions adsorbed, at 30°C from 4 mg/L of fluoride ion solution, by AT and BA were 0.85 and 1.55 mg/g, respectively. The experimental data fitted well to the Freundlich and Langmuir isotherms. Thermodynamic parameters such as ΔH^0, ΔS^0 and ΔG^0 indicated that the removal of fluoride ions by AT was exothermic and non-spontaneous while that by BA was endothermic and spontaneous. Fourier transform infrared (FT-IR) analysis and X-ray diffraction (XRD) patterns of the adsorbent before and after adsorption indicated that fluoride ions were chemisorbed by these adsorbents.

Key words: adsorption; defluoridation; isotherms; aluminium titanate; bismuth aluminate

DOI: 10.1016/S1001-0742(08)62448-1

Introduction

Fluoride ion is potentially toxic for human, therefore, its ingestion in food or drinking water must not exceed a narrow range of concentrations. According to the World Health Organization the maximum acceptable concentration of fluoride ions in drinking water lies below 1.5 mg/L (WHO, 2004). Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electro-negativity which results in dental, skeletal and non-skeletal forms of fluorosis, in children as well as adults (WHO, 1984). To encounter this fluoride menace, the quantification of fluoride ions in environment is important, followed up with suitable adaptation of an effective defluoridation methodology.

The current techniques applied for defluoridation are precipitation, membrane and adsorption processes. Precipitation process accomplished with the use of calcium and aluminium salts (Saha, 1993). Reverse osmosis, nanofiltration, electro dialysis and Donon dialysis fit into the category of membrane process which has disadvantages in terms of economic viability and maintenance cost (Ruiz et al., 2003). Adsorption from solution is widely used for fluoride ion removal from drinking water. Many adsorbents have been reported in literature (Subhasini and Pant, 2005; Fan et al., 2003; Karthikeyan et al., 2009; Gopal and Elango, 2007; Aravind and Elango, 2006; Elango and Gopal, 2007; Das et al., 2005; Nordin et al., 1999; Kraemer et al., 1998).

Aluminium salts have been conventionally used for the

removal of fluoride ion due to the high affinity for fluoride ions, where Al-F complexes of varying compositions have been proposed (Saha, 1993). This work reports the results of the equilibrium, thermodynamic and kinetic investigations on the adsorption of fluoride ions onto aluminium titanate (AT) and bismuth aluminate (BA). The choice of these two compounds is based on the fact that AT has some special properties such as high refractivity, low thermal conductivity, insoluble in water and low thermal expansion coefficient etc. (Zhareslu et al. 2003), and BA is antacid, nontoxic, water insoluble material etc., which makes them more suitable to be an adsorbent. Hence it is worth attempting to use AT and BA as adsorbents for the removal of fluoride ions from aqueous solution.

1 Experimental

All chemicals used were of analytical reagent grade (Sd-fine/Merck, India). The adsorbents, AT nano powder and BA hydrate were purchased from Aldrich, India and were used as received. Doubly distilled water was used throughout the study. The point of zero charge (pH_{ZPC}) of the adsorbents was determined by reported method (Jia et al., 2002) and are found to be 7.4 for AT and 7.1 for BA.

The adsorption experiments have been carried out by batch sorption method under varying conditions as reported earlier (Gopal and Elango, 2007; Aravind and Elango, 2006). In a typical experiment, adsorption was performed by agitating 100 mg of the adsorbent with 50 mL of fluoride ion solution of varying concentrations (2–10 mg/L) at 30, 40 or 50°C in different stoppered bottles

---

in a shaking thermostat machine. The shaking speed was 120 strokes/min throughout the study. At the end of predetermined time intervals, the sorbet was filtered and the concentration of fluoride ion was determined using an ion-selective electrode (Eutech Cyberscan 2100, Singapore). All experiments were performed in duplicates and the adsorbed fluoride ion concentrations given were the means of experimental results.

The Fourier transform infrared (FT-IR) spectra of the adsorbents were recorded in a JASCO FT-IR 460 Plus spectrometer (Japan). The X-ray diffraction (XRD) patterns (X' Pert PRO PANalytical, the Netherlands) of the adsorbents were recorded at the National Institute for Interdisciplinary Science & Technology, Thiruvananthapuram, India.

2 Results and discussions

2.1 Adsorption isotherms

Adsorption isotherms help in determining the feasibility of the adsorbents for treating fluoride ion in water. Freundlich and Langmuir isotherms were employed to provide a deep insight into the mode of adsorption of fluoride ions onto AT and BA. These isotherms not only provide general idea of the effectiveness of the adsorbents in removing fluoride ions, but also indicate the maximum amount of fluoride ions that will be adsorbed by the adsorbents.

The linearity of the plots (Table 1) for both AT and BA indicated the applicability of the Freundlich adsorption isotherm. The results indicated that the values of the intensity of adsorption, n, were greater than unity, indicating a favourable adsorption and formation of relatively stronger bond between adsorbate and adsorbent (Gopal and Elango, 2007; Mehrotra *et al.*, 2003). Further, the observed variation in the adsorption capacity values (K) with temperature suggested that the adsorption process is exothermic in AT while endothermic in BA. The high values of correlation coefficient (Table 1) showed that the Langmuir equation

Table 1   Langmuir and Freundlich isotherm constants

	Isotherm	Constants	Temperature (°C)		
			30	40	50
Adsorption onto aluminium titanate (AT)	Freundlich	r	0.99	0.99	0.99
		sd	0.02	0.02	0.04
		n	1.56	1.54	1.30
		K	0.52	0.46	0.35
	Langmuir	r	0.97	0.98	0.96
		sd	0.20	0.20	0.21
		Q^0	3.01	2.83	3.35
		b	0.19	0.18	0.11
Adsorption onto bismuth aluminate (BA)	Freundlich	r	0.98	0.99	0.98
		sd	0.06	0.05	0.06
		n	1.30	1.12	1.11
		K	1.52	1.67	1.85
	Langmuir	r	0.93	0.96	0.99
		sd	0.07	0.03	0.01
		Q^0	7.09	9.43	9.01
		b	0.29	0.24	0.30

r: correlation coefficient; sd: standard deviation; n: intensity of adsorption; K: adsorption capacity; Q^0: quantity adsorbed; b: energy of adsorption.

provides an accurate description of the experimental data. Comparing with AT, the relatively larger values of b for BA suggest a stronger bonding of fluoride ions to BA than AT. The equilibrium parameter, R_L, values between 0 and 1 indicated favorable adsorption for all the initial concentrations and temperatures studied (Manju *et al.*, 1998). The applicability of both Freundlich and Langmuir isotherms to AT and BA, in the present study, implies that both monolayer adsorption and heterogeneous surfaces conditions exist under the experimental conditions. The adsorption properties of AT and BA are thus likely to be complex involving more than one mechanism (Yadav *et al.*, 2006; Gulnaz *et al.*, 2005).

2.2 Effect of contact time and initial fluoride ion concentration

The results of equilibrium studies are shown in Table 2. Contact time experiments showed that, the removal of fluoride ions increased with time up to 40 min, and after which the increase in agitation time did not alter the fluoride ion uptake due to the attainment of equilibrium. Fluoride ion uptake by the adsorbents at pH 7 indicated that the process was rapid with typically 0.85 and 1.55 mg/g for AT and BA, respectively, being the amount of fluoride ions adsorbed per unit weight of the adsorbent within 40 min of contact time from 4 mg/L fluoride solution at 30°C. This initial rapid adsorption subsequently gave a way to equilibrium and saturation at about 40 min, which was considered as equilibrium time. Further, the results in Table 2 indicated that the amount of fluoride ion adsorbed increased with an increase in the initial fluoride concentration as expected.

2.3 Effect of adsorbent dose

The amounts of fluoride ions removed by 25, 50, 100, 250 and 500 mg/50 mL of AT are 1.52, 1.26, 1.01, 0.51 and 0.33 mg/g and that by 100, 250, 500 and 1000 mg/50mL of BA are 1.69, 1.12, 0.56 and 0.19 mg/g, respectively. The increase in the amount of fluoride ions adsorbed with a decrease in the dose of the adsorbents was due to the availability of higher fluoride/adsorbent ratio. Further experiments were carried out using 100 mg/50 mL as the dose of both the adsorbents, as it exhibits appreciable removal capacity for optimizing of adsorption parameters.

2.4 Thermodynamic parameters

The thermodynamic parameters such as standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) changes were calculated from the temperature dependence of equilibrium constant as explained earlier (Gopal and Elango, 2007) (Table 3). In the case of AT, the exothermic nature of adsorption is indicated by a decrease in equilibrium constant, K_0, with a rise in temperature and the positive ΔG^0 values indicated non-spontaneous reactions. However, in the case of BA, the adsorption process is endothermic and spontaneous. The values of enthalpy of adsorption depend on various factors such as the effect of temperature on pH_{ZPC}, solubility of the adsorbents, surface functional groups etc. Hence, in the present study, it is presumed

Table 2　Equilibrium parameters for the adsorption of fluoride ion by AT and BA

	C^0_F (mg/L)	C_e (mg/L)			Q_e (mg/g)		
		30°C	40°C	50°C	30°C	40°C	50°C
Adsorption onto	2	0.97	1.05	1.24	0.52	0.48	0.38
AT	4	2.30	2.38	2.50	0.85	0.81	0.75
	6	3.64	3.68	3.84	1.18	1.16	1.08
	8	4.92	5.37	5.51	1.54	1.32	1.25
	10	6.64	6.76	7.09	1.68	1.62	1.46
Adsorption onto	2	0.48	0.46	0.44	0.76	0.77	0.78
BA	4	0.91	0.84	0.74	1.55	1.58	1.63
	6	1.44	1.31	1.21	2.28	2.35	2.40
	8	2.16	2.04	1.83	2.92	2.98	3.09
	10	3.36	2.57	2.39	3.32	3.72	3.81

C^0_F: initial fluoride ion concentration; C_e: equilibrium concentration; Q_e: amount of fluoride adsorbed.

Table 3　Equilibrium constants and thermodynamic parameters for the adsorption of fluoride ion

	C^0_F (mg/L)	K_0			ΔG^0 (kJ/mol)			ΔH^0 (kJ/mol)	ΔS^0 (J/(k·mol))
		30°C	40°C	50°C	30°C	40°C	50°C		
Adsorption onto	2	1.1	0.9	0.6	−2	3	13	−22	−72
AT	4	0.7	0.7	0.6	8	10	14	−8	−30
	6	0.7	0.6	0.6	11	12	16	−6	−22
	8	0.6	0.5	0.4	12	19	21	−13	−48
	10	0.5	0.5	0.4	17	19	24	−9	−33
Adsorption onto	2	3.1	3.3	3.5	−2.9	−3.1	−3.4	5	25
BA	4	3.4	3.8	4.4	−3.1	−3.5	−4	11	45
	6	3.2	3.6	4	−3	−3.3	−3.7	91	39
	8	2.7	2.9	3.4	−2.5	−2.8	−3.3	9	37
	10	2	2.9	3.2	−2	−2.8	−3.1	20	70

that the observed values may be due to the combination of these effects. Both positive (Islam and Patel, 2007; Aravind and Elango, 2006) and negative (Valdivieso *et al.*, 2006; Mohapatra *et al.*, 2004) enthalpy values were reported for the removal of fluoride ions by similar materials. From the magnitude of enthalpy changes, the adsorption of fluoride ions onto AT and BA could be a physical process (Doula *et al.*, 2000).

As indicated in Table 3, ΔS^0 values for the adsorption process were negative for AT which may be due to the fact that during adsorption the degree of internal freedom of the system were decreased (Doula *et al.*, 2000). While, the ΔS^0 values for BA were positive indicating the prevalence of a high degree of disorderliness at the solid solution interface during the adsorption of fluoride ions. This may be due to the fact that adsorbed water molecules which were displaced by the adsorbate species gain more translational entropy than lost by the adsorbate molecules and thus allowing the prevalence of randomness in the system (Doula *et al.*, 2000).

2.5 Effect of pH

Generally pH is an important variable affecting the quantity and mode of defluoridation at water/adsorbent interfaces. The amount of fluoride ions adsorbed in pH range 3–9 varies from 0.92 to 0.74 mg/g for AT and from 1.64 to 1.53 mg/g for BA. The results indicated that the adsorbents exhibit relatively a larger defluoridation capacity in the acidic range. This observation can conveniently be explained with the help of zero point charge of the adsorbents. The pH_{ZPC} value of 7.4 for AT and 7.1 for BA suggested the presence of some weakly basic groups

on the surface of the adsorbents. Below this pH value the surface of the adsorbents will be positively charged which will attract the fluoride ions electrostatically and consequently enhance the amount of fluoride ions adsorbed per unit mass. While above this point the reverse is true. Further, it is well known that in the alkaline pH range the hydroxide ions compete with fluoride ions leading to a lower removal of fluoride ions (Karthikeyan and Elango, 2007; Karthikeyan *et al.*, 2004).

2.6 Effect of co-ions

The effect of added co-ions viz. Cl^-, NO_3^-, SO_4^{2-} and HCO_3^- on the amount of fluoride ions adsorbed by AT and BA indicated that the addition of the chosen common co-ions did not have any marked effect on the defluoridation capacity of AT.

2.7 Intra particle diffusion

The possible occurrence of intra particle diffusion, in the present study, has been examined by adopting the model developed by Webber and Morris (1963). Both the plot of amount of fluoride adsorbed per unit mass of the adsorbent versus square root of time (figure not shown) have the same general features indicating the operation of similar type of adsorption onto AT and BA. The plots showed multi-linearity with three steps. The first, sharper portion represents the adsorption on external surface, which is almost instantaneous. The second portion indicates a comparatively slower adsorption when the fluoride ions diffuse gradually into the interior surfaces of the particles and the adsorption becomes intra-particle diffusion controlled. The third portion is attributed to the final equilibrium stage
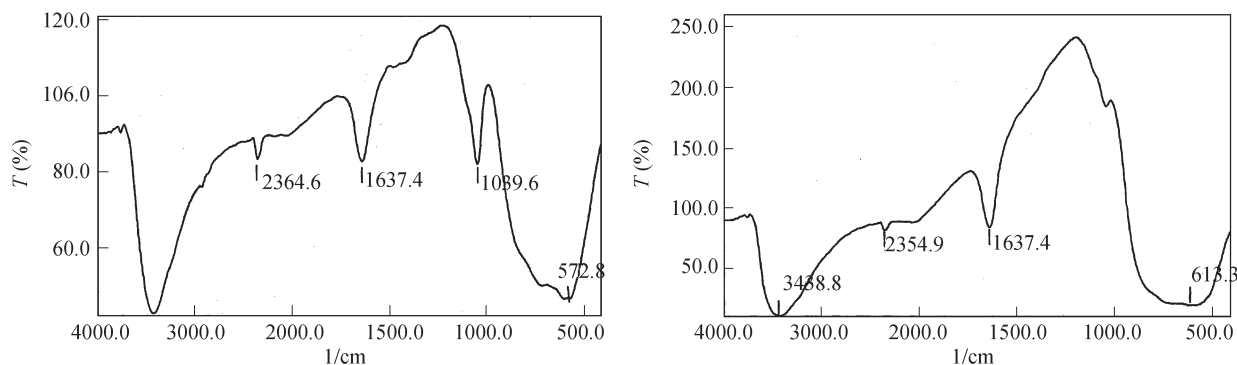
Fig. 1 FT-IR spectra of AT before (a) and after (b) adsorption of fluoride ions.

when the intra-particle diffusion starts slow down due to the saturation of most of the adsorption sites.

Further, the linear portions of the curves do not pass through the origin indicating that the mechanism of removal of fluoride ions by AT and BA are complex and both the surface adsorption as well as intra-particle diffusion contributes to the rate-determining step (Weber and Morris, 1963). The intra particle diffusion rate constant, k_p, was calculated from the linear portion of the curves as described earlier (Gopal and Elango, 2007; Kamble *et al.*, 2007) and the values are found to be 0.099, 0.049 and 0.042 mg/(g·min$^{0.5}$) for AT and for BA the values are 0.066, 0.109 and 0.124 mg/(g·min$^{0.5}$) at 30, 40 and 50°C, respectively. The k_p values, in general, with BA are larger than that with AT, indicating that BA possess more micropores for intra-particle diffusion. The variations of the k_p values with rise in temperature are in agreement with the results of the effect of temperature on the adsorption process as described earlier.

2.8 FT-IR spectral studies

The foregoing results suggested that the adsorption of fluoride ions onto AT and BA may be a complex one involving both physi- and chemi-sorption. To get a better insight into the nature of the mechanism, the FT-IR spectra of the adsorbents before and after adsorption were recorded and representative spectra are given in Fig. 1a and 1b, respectively. In FT-IR spectrum of AT before adsorption the peaks at 2364.6–3419 cm^{-1} and 1637.4 cm^{-1} were attributed to the stretching vibrations of hydroxyl and molecular water respectively. The peak at 1039.6 cm^{-1} corresponds to the Al–O and Ti–O stretching vibrations (Zhareslu *et al.*, 2003). After adsorption of fluoride ions, the peaks corresponding to hydroxyl and molecular water are not much affected. However, the peak intensity at 1039.6 cm^{-1} is decreased and a new broad peak has appeared at 613.3 cm^{-1}. The decrease in the intensity of 1039.6 cm^{-1} peak indicated the involvement of the Al–O/Ti–O bonds in the interaction with fluoride ions. The new peak appeared at 613.3 cm^{-1} is due to Al-F stretching vibrations (Kleist *et al.*, 2006). Hence, it is presumed that the uptake of fluoride ions by AT is due to the complexation of fluoride ions with aluminium. In other words, fluoride ions are chemisorbed onto AT. Parallel observations, i.e., complexation of aluminium

with fluoride ions, were earlier been reported in literature related to the defluoridation of water using aluminium salts (Saha, 1993; Subasini and Pant, 2005; Valdivieso *et al.*, 2006). However, none of these publications report the FT-IR spectral evidence for the same. Likewise, in the FT-IR spectrum of BA after the adsorption of fluoride ions new intense peaks at 660 and 760 cm^{-1} were observed which are corresponds to the Al-F bond (Kleist *et al.*, 2006; Valdiveso *et al.*, 2006). This observation suggested that the removal of fluoride ions by BA is also by chemisorption.

2.9 X-ray diffraction studies

The XRD patterns of the adsorbents before and after treatment with fluoride ion were also recorded to confirm the mechanism of adsorption process. Representative XRD patterns of AT before and after adsorption are shown in Figs. 2a and 2b, respectively. It is evident from the pattern that the adsorbent possessed predominantly amorphous character and to a very lesser extent crystalline character
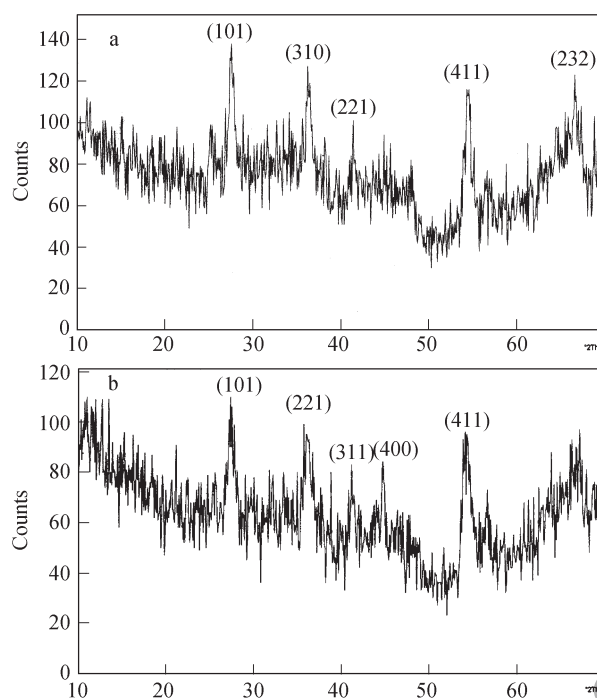

Fig. 2 XRD pattern of AT before (a) and after (b) adsorption of fluoride ions.

also. The XRD pattern of AT loaded with fluoride ions (Fig. 2b) showed significant changes when compared to that of AT before adsorption. This suggested that the uptake of fluoride ions by AT is by chemisorption which consequently alters the structure of the adsorbent (Venkata Mohan *et al.*, 2001; Roshenberg, 1988). The complexation between fluoride ions and aluminium to yield Al–F bonds is evident from the appearance of characteristic new peaks with (hkl) values (311) and (221) in the XRD pattern of AT after adsorption (Roshenberg, 1988). Similar changes were also observed in the XRD pattern of BA after adsorption of fluoride ions when compared to that before adsorption. The new peaks with (hkl) values (311) and (221) were due to Al–F bonds. Hence, it is confirmed that, in the present study, fluoride ions are adsorbed by the adsorbents through chemisorption via the formation of Al–F complexes.

2.10 Comparison with other adsorbents

The adsorption isotherms for the removal of fluoride ions from aqueous solution obtained in the present study were compared with those reported earlier in literature. Although direct comparison of AT and BA with other adsorbents is difficult, owing to the different applied experimental conditions, it was found, in general, that the adsorption capacity of AT and BA for fluoride ions is comparable with that of other adsorbents and in fact greater than certain adsorbents reported earlier.

3 Conclusions

In batch adsorption studies, data show that AT and BA have considerable potential for the removal of fluoride ions from aqueous solutions. Wide range of pH was found to be the optimum condition for maximum fluoride ions adsorption by the adsorbents. The results gained from this study were well described by the theoretical Freundlich and Langmuir isotherms. Values of equilibrium parameter, R_L, indicated that the F$^-$/AT or F$^-$/BA systems were favorable. The amount of fluoride ions adsorbed by BA was found to be almost twice that by AT. The thermodynamics of the systems pointed out the adsorption of fluoride ions onto AT is exothermic while that onto BA in endothermic. The foregoing results and discussions indicated that the adsorption occurs through chemisorption i.e., via the formation of Al–F complexes.

References

Aravind V, Elango K P, 2006. Adsorption of fluoride onto magnesia-equilibrium and thermodynamic study. *Indian Journal of Chemical Tecnology*, 13: 476–483.

Das N, Pattanaik P, Das R, 2005. Defluoridation of drinking water using activated titanium rich bauxite. *Journal of Colloid and Interface Science*, 292: 1–10.

Doula M, Ioannou A, Dimirkou A, 2000. Thermodynamics of copper adsorption, desorption by Ca-kaolinite. *Adsorption*, 6: 325–335.

Elango K P, Gopal K P, 2007. Adsorption of fluoride onto activated newspaper carbon: An equilibrium, kinetic and thermodynamic study. *Environmental Science: An Indian Journal*, 2: 75–83.

Fan X, Parker D J, Smith M D, 2003. Adsorption of fluoride on low cost materials. *Water Research*, 37: 4929–4937.

Gopal V, Elango K P, 2007. Equilibrium, kinetic and thermodynamic studies of adsorption of fluoride onto plaster of Paris. *Journal of Hazardous Materials*, 141: 98–105.

Gulnaz O, Saygideger S, Kusvuran E, 2005. Study of Cu(II) biosorption by dried activated sludge: effect of physicochemical environment and kinetics study. *Journal of Hazardous Materials*, 120: 193–200.

Islam M, Patel R K, 2007. Evaluation of removal efficiency of fluoride from aqueous solution using quick lime. *Journal of Hazardous Materials*, 143: 303–310.

Jia Y F, Xiao B, Thomas K K, 2002. Adsorption of metal ions on nitrogen surface functional groups in activated carbon. *Langmuir*, 18: 470–478.

Kamble S P, Jagtap S, Lobhsetwar N K, Thakare D, Godfrey S, Devotta S *et al.*, 2007. Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan. *Chemical Engineering Journal*, 129: 173–180.

Karthikeyan G, Shunmugasundarraj A, Meenakshi S, Elango K P, 2004. Adsorption dynamics and the effect of temperature of fluoride at alumina-solution interface. *Journal of Indian Chemical Society*, 81: 461–466.

Karthikeyan M, Elango K P, 2007. Defluoridation of water using aluminium impregnated activated newspaper carbon. *Environmental Science: An Indian Journal*, 2: 187–193.

Karthikeyan M, Satheeshkumar K K, Elango K P, 2009. Defluoridation of water via doping of polyanilines. *Journal of Hazardous Materials*, 163: 1026–1032.

Kleist W, Haebner C, Storcheva O, Kohler C, 2006. A simple aqueous phase synthesis of high surface area aluminum fluoride and its bulk and surface structure. *Inorganica Chemica Acta*, 359: 4851–4854.

Kraemer S M, Chiu W Q, Hering J G, 1998. Influence of pH and competitive adsorption on the kinetics of ligand promoted dissolution of aluminium oxide. *Environmental Science and Technology*, 32: 2876–2882.

Mohapatra D, Mishra D, Mishra S P, Ghaudhury G R, Das R P, 2004. Use of oxide minerals to abate fluoride from water. *Journal of Colloid and Interface Science*, 275: 355–359.

Manju G N, Raji C, Anirudhan T S, 1998. Evaluation of coconut husk carbon for the removal of arsenic from water. *Water Research*, 32: 3062–3070.

Mehrotra R, Kapoor B S, Narayan B, 2003. Defluoridation of drinking water using low cost adsorbent. *Indian Journal of Environmental Health*, 41: 53–58.

Nordin J P, Sullivan D J, Phillips B L, Casey W H, 1999. Mechanisms for fluoride-promoted dissolution of bayerite [β-Al(OH)$_3$(s)] and boehmite [γ-AlOOH]: 19F-NMR. *Geochimca Cosmochimca Acta*, 63: 3513–3524.

Oguz E, 2005. Adsorption of fluoride on gas concrete materials. *Journal of Hazardous Materials B*, 117: 227–233.

Rengaraj S, Arabindoo B, Murugesan V, 1999. Preparation and characterization of activated carbon from agricultural waste. *Indian Journal of Chemical Technology*, 6: 1–4.

Roshenberg P E, 1988. Aluminium fluoride hydrates, valcanogenic salts form Mount Erebus, Antartica. *American*

Mineralogy, 73: 855–560.

Ruiz T, Persin F, Hichor M, Sandeux J, 2003. Modelization of fluoride removal in Donon dialysis. *Journal of Membrane Science*, 212: 113–121.

Saha S, 1993. Treatment of aqueous effluent of fluoride removal. *Water Research*, 27: 1347–1350.

Subhasini G, Pant K K, 2005. Equilibrium kinetics and break through studies for adsorption of fluoride on activated alumina. *Separation and Purification Technology*, 42: 265–271.

Valdivieso A L, Reyes Bahena J L R, Song S, Urbina R H, 2006. Temperature effect on the zeta potential and fluoride adsorption at the α-Al_2O_3/aqueous solution interface. *Journal of Colloid and Interface Science*, 298: 1–5.

Venkata Mohan S, Krishna Mohan S, Karthikeyan J, 2001. IR, XRD, SEM studies to evaluate the mechanism of azo dye sorption interaction with coal based adsorbents and activated carbon from aqueous phase. *Journal of Scientific and Industrial Research*, 60: 410–415.

Weber W J, Morris J C, 1963. Kinetics of adsorption on carbon from solutions. *Journal of Scientific and Engineering Division*, 89: 31–60.

WHO (World Health Organization), 1984. Environmental Health Criteria, 36 International Programme on Chemical Safty, Fluorines and Fluoride Geneva.

WHO (World Health Organization), 2004. Guidelines for Drinking (3rd ed.). Geneva. Volume 1.

Yadav A K, Kaushik C P, Haritash A K, Kansal A, Rani N, 2006. Defluoridation of groundwater using brick powder as an adsorbent. *Journal of Hazardous Mater*, 128: 289–293.

Zhareslu M, Crisan M, Preda M, Fruth V, Preda S, 2003. Al_2TiO_5 – Based ceramics obtained by hydrothermal process. *Journal of Optoelctro Advanced Materials*, 5: 1411–1416.