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Conducting polymer/alumina composites as viable adsorbents for the removal of fluoride ions from aqueous solution

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ABSTRACT

The polyaniline/alumina (PANi–AlO) and polypyrrole/alumina (PPy–AlO) composites were prepared and characterized by FT-IR, SEM and X-ray diffraction studies and were employed as adsorbents for the removal of fluoride ions from aqueous solution by the batch sorption method. The amount of fluoride ions adsorbed per unit mass of the adsorbents was observed to be higher than that by the individual constituents. The maximal amount of adsorption is 6.6 mg/g for PANi–AlO and for PPy–AlO it is 8 mg/g. The Langmuir and Freundlich isotherms were used to describe adsorption equilibrium. The kinetics of the adsorption process was investigated using Natarajan–Khalaf equation and intraparticle diffusion model. FT-IR and XRD pattern of the adsorbent, before and after the adsorption is recorded to get better insight into the mechanism of the adsorption process. The results of equilibrium and spectral investigations revealed that the mechanism of fluoride ion removal by these composites involve both the formation of aluminium–fluoro complexes on the alumina surface and doping/dopant-exchange of fluoride ions in the polymer.

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1. Introduction

Fluoride is an essential micronutrient in preventing the dental carries and for mineralization of hard tissues. The optimum fluoride level in drinking water for general good health set by WHO is considered to be between 0.5 and 1.5 mg/l [1]. Concentration higher than this can lead to fluorosis, which causes a serious health problem for the population.

During recent years, several methods have been developed to remove fluoride ions from water, namely, adsorption [2–7], chemical treatment [8,9], ion exchange [10], membrane separation [11,12], electrolytic defluoridation [13], and electro dialysis [14,15], etc. Among these methods, adsorption is still one of the most extensively used methods for the defluoridation of water due to its low cost and viability.

The important feature of the present study is to investigate the possibility of using conducting polymer composites such as polyaniline/alumina and polypyrrole/alumina composites for the removal of fluoride ions from aqueous solution. Conducting polymer/inorganic hybrid composites have attracted more attention, because they combine the merits of conducting polymers and inorganic materials. They have unusual hybrid mechanical, thermal, physical and chemical properties. They also have large surface area, which makes the polymer composite as good adsorbent as the pure polymer and inorganic host. Also, they have wide potential applications in areas such as chemistry, electronics, optics, materials and biomedical sciences, etc. [16]. Alumina is one of the most effective adsorbents identified for removing fluoride ions from water. So for various grades/forms of alumina have been tested and reported for this purpose [17–21]. Recently we have reported that conducting polymers like polyaniline [4] and polypyrrole [7] exhibited appreciable capacity for removing fluoride ions from water and the defluoridation capacities were found to be 0.77 and 2.66 mg/g, respectively. Hence, it is noteworthy to make composites of these two materials with alumina, possessing appreciable defluoridation capacities, for the removal of fluoride ions from water.

2. Experimental procedure

2.1. Materials

All the reagents used were of commercially available high purity Analar grade (Merck or Aldrich, India). Aniline and pyrrole were purchased from Sigma–Aldrich Ltd., India and were distilled prior to use. Stock solutions of fluoride were prepared by dissolving sodium fluoride in doubly distilled water.

2.2. Preparation of composites

Polyaniline/alumina composite (PANi–AlO) was prepared by reported method [22]. In a typical experiment, about 1 ml of

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aniline (0.1 M) was dissolved in 1 ml hydrochloric acid solution and then about 2 g of alumina was added. This mixture was stirred thoroughly for 10–15 min using a magnetic stirrer. To this stirred mixture, ammonium peroxydisulphate (4.4 g, 0.1 M) was added at 0–5 °C. After completion of the addition, stirring is continued for 6 h. The greenish black powder obtained was washed with deionised water followed by methyl alcohol until the filtrate become colourless and then the powder was dried in an oven at 60–80 °C for 24 h.

Polypyrrole/alumina composite (PPy–AlO) was prepared by the method adopted for the preparation of polypyrrole/montmorilonite composite [23]. About 2.1 ml of pyrrole was dissolved in 50 ml of methyl alcohol and then alumina (2 g) was added in a 100 ml beaker. This mixture was stirred for 10–15 min using magnetic stirrer. To this stirred mixture, 7.18 g of anhydrous ferric chloride was added. The colour of the solution gradually changes from dark brown to black. The reaction was allowed to proceed for 16 h at about 0–5 °C with stirring. The resulting black product was filtered and washed thoroughly with methyl alcohol until the filtrate is colourless. Finally, the product was dried in an oven at 60 °C for 24 h. The conducting polymer/alumina composites were characterized using FT-IR, XRD and SEM techniques.

2.3. Methodology

The concentration of fluoride ions and pH was measured using ion-selective meter (Eutech Cyberscan 2100). The XRD (X' Pert PRO PANalytical, Netherlands) patterns of the composites before and after adsorption were recorded at the National Institute for Science and Technology, Thiruvananthapuram. The SEM (HITACHI-S-3400H) images and EDAX patterns of the composites were recorded at Pondicherry University, Pondicherry. The FT-IR spectra were recorded using KBr disc on a JASCO FT-IR 460 Plus spectrometer.

2.4. Batch adsorption experiments

Adsorption experiments were performed, as reported earlier [2,4], by agitating 25 mg of the composites with 50 ml of fluoride ion solution of desired concentration at 30 ± 0.5 °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 sorbate was filtered and the concentration of fluoride ions was measured. All experiments were carried out twice and the adsorbed fluoride ion concentrations reported were the means of duplicate experimental results. Experimental variables considered were initial concentration of fluoride ions 2–10 mg/l; contact time between composite and fluoride ion 5–30 min; pH 3–9; dosage of composites 25–200 mg/50 ml; temperature 30–50 °C and common co-ions viz. chloride, nitrate, sulphate, and bicarbonate ions.

3. Results and discussion

3.1. Effect of initial fluoride ion concentration and contact time

The amount of fluoride ions adsorbed from different initial fluoride ion concentrations and at three different temperatures is given in Table 1. The results revealed that, the amount of fluoride ions adsorbed per unit mass of the adsorbent is increased with an increase in concentration. This is due to the availability of higher number of fluoride ions per unit mass of adsorbent. Increase in temperature also increases the fluoride ion uptake suggesting the endothermic nature of the process. Further, the experimental results (figure not shown) indicated that initially the adsorption process is very fast and most of the fluoride ion is adsorbed within 10 min and equilibrium was established about 20 min. It is interesting to compare the time taken for the attainment of equilibrium, in the present study, with that for the constituents reported earlier. In the case of the polymers equilibrium was established within 10 min [4,7]. While in the case of alumina it was 20 min [20]. From the time taken in the present study it is presumed that both the constituents may participate in the fluoride ion removal process.

Table 1
The amount of fluoride ions adsorbed (Q_e, mg/g) by the polymer composites.

[F] (mg/l)	PANi–AlO			PPy–AlO		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
2	1.6	1.8	1.9	2.0	2.1	2.2
4	3.1	3.2	3.3	3.8	4.1	4.4
6	4.1	4.3	4.5	4.9	5.1	5.5
8	5.3	5.4	5.6	5.5	5.7	5.9
10	5.8	6.2	6.6	6.7	7.3	8.0

The Q_e values for PANi, PPy and alumina at [F] = 4 mg/l and 30 °C are 0.77, 2.66 and 1.04 mg/g, respectively.

3.2. Effect of dosage

The effect of adsorbent dose on the amount of fluoride ion removed was studied at 30 °C and at initial fluoride ion concentration of 4 mg/l by allowing a contact time of 30 min. The results are presented in Fig. 1. It is evident from the figure that the amount of fluoride ion uptake per gram of adsorbent increased with a decrease in adsorbent dose. This increase in fluoride ion removal is due to the availability of higher number of fluoride ions per unit mass of polymer composites, i.e., higher fluoride/composite ratio. Thus, further experiments were carried out using 25 mg of adsorbent per 50 ml of fluoride ion solution, as it exhibits appreciable removal capacity, for the optimization of adsorption parameters.

3.3. Adsorption isotherm

Adsorption isotherms are important for the description of how adsorbate interacts with adsorbent surface and also are critical in

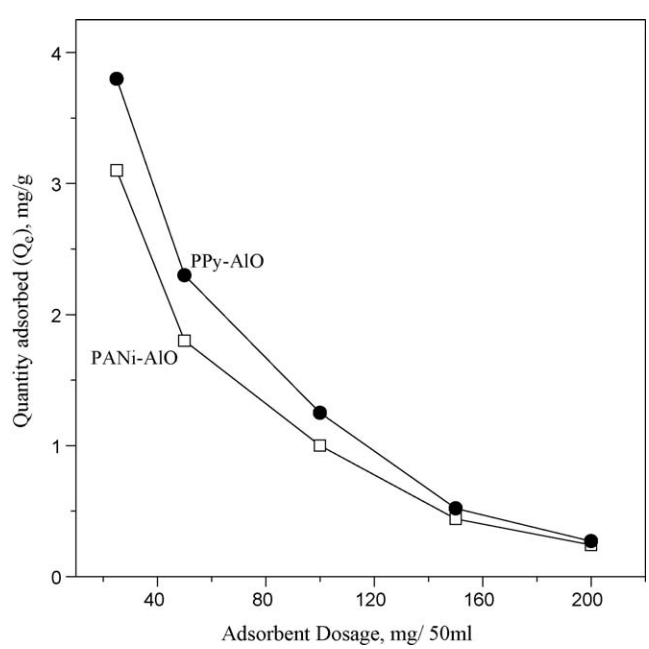


Fig. 1. Effect of dose on the removal of fluoride ions by conducting polymer composites.

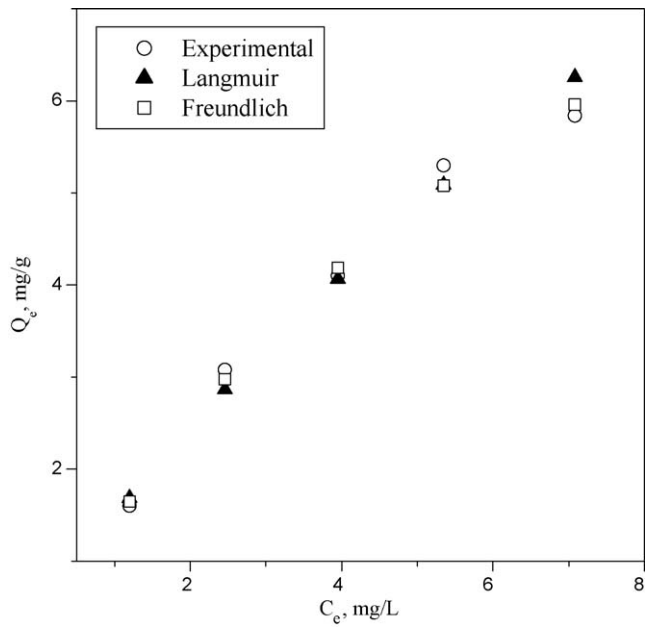


Fig. 2. Adsorption isotherms for PANi–AlO composites.

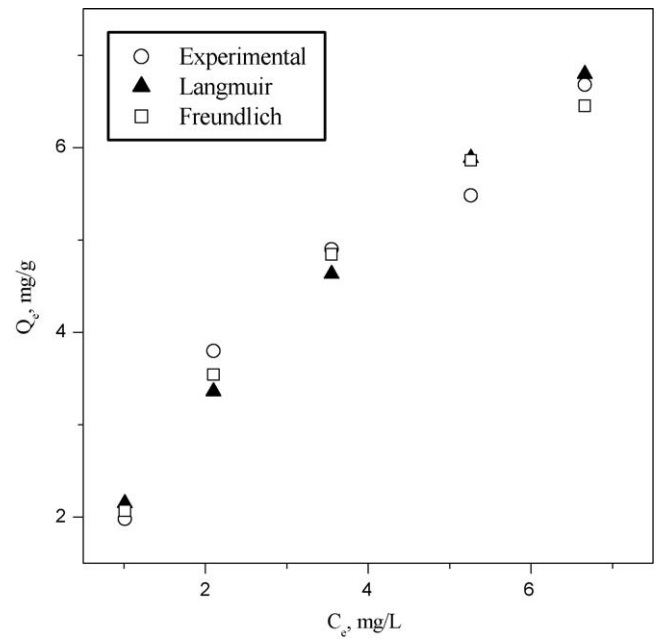


Fig. 3. Adsorption isotherms for PPy–AlO composites.

optimizing the use of an adsorbent. Hence, in the present study, two well known isotherm equations viz. Langmuir [24] and Freundlich [25] isotherms have been applied for deeper interpretation of the adsorption data obtained. The adsorption isotherms for the adsorption of fluoride ions onto PANi–AlO are shown in Fig. 2 and for PPy–AlO in Fig. 3. The calculated values of the Langmuir and Freundlich constants are given in Table 2. The results showed that both the isotherms fit well with the experimental values suggesting a physico-chemical interaction of fluoride ions with the adsorbents [5]. The adsorption capacity, K, increased with rise in temperature suggesting that the uptake of fluoride ions by the composites is an endothermic process. Further, the values of intensity of adsorption (n) are greater than unity indicating that the process is favourable [26].

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (1)$$

where C_0 is the initial concentration and b is the Langmuir isotherm constant. The values of R_L thus computed are given in Table 3. The R_L values were found to be between 0 and 1 which confirms that the ongoing adsorption process is favourable [2,5].

3.4. Thermodynamic parameters

The thermodynamic parameters such as standard free energy, enthalpy and entropy changes were calculated from the temperature dependence of equilibrium constant as explained earlier [2] and are collected in Table 4. The endothermic nature of the adsorption process is indicated by an increase in the equilibrium constant, K_o, values with rise in temperature and the positive ΔH° values. The positive ΔG° values indicated the reversible nature of the adsorption of fluoride ions onto the composites under present experimental conditions. From the magnitude of the enthalpy changes, fluoride ion sorption by both the adsorbents could be a physical process [27]. The positive ΔS° values indicate the prevalence of a high degree of disorderliness at the solid solution interface during the adsorption of fluoride ions onto PANi–AlO and PPy–AlO. This may be due to the fact that adsorbed water molecules which are displaced by the adsorbate species gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system [27].

3.5. Effect of pH

Generally the pH is an important variable affecting defluoridation at solute/solid interface. Therefore, the removal of fluoride ions by both the adsorbents were examined at different pH values

Table 2
Langmuir and Freundlich isotherm constants for the removal of fluoride ions by polymer composites.

Isotherm	Statistical parameter/constants	PANi–AlO			PPy–AlO		
		30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Langmuir	r	0.985	0.993	0.991	0.982	0.980	0.971
	sd	0.04	0.03	0.03	0.05	0.07	0.09
	Q_0 (mg/g)	12.8	12.2	13.0	10.4	11.1	12.0
	b (l/mg)	0.12	0.15	0.15	0.250	0.253	0.254
Freundlich	r	0.993	0.998	0.999	0.98	0.98	0.97
	sd	0.03	0.01	0.006	0.04	0.05	0.07
	n (mg/g)	1.35	1.43	1.44	1.63	1.64	1.7
	K (g/l)	1.47	1.66	1.76	2.1	2.3	2.5

Table 3
Equilibrium parameter R_L.

[F] (mg/l)	PANi–AlO			PPy–AlO		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
2	0.80	0.77	0.77	0.67	0.66	0.66
4	0.67	0.63	0.63	0.51	0.50	0.49
6	0.57	0.54	0.53	0.40	0.39	0.39
8	0.50	0.46	0.46	0.34	0.33	0.33
10	0.49	0.42	0.41	0.29	0.28	0.28

Table 4
Equilibrium constants and thermodynamic parameters for the removal of fluoride by polymer composites.

[F] (mg/l)	K_0			ΔG°			ΔH°	ΔS°
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C		
PANi–AlO								
2	0.67	0.79	0.85	1.02	0.63	0.43	10	30
4	0.63	0.65	0.69	1.18	1.14	1.0	4	9
6	0.52	0.55	0.59	1.65	1.57	1.43	5	11
8	0.49	0.51	0.54	1.77	1.74	1.68	3	5
10	0.41	0.44	0.49	2.23	2.12	1.94	7	15
PPy–AlO								
2	0.98	1.08	1.13	0.05	−0.20	−0.32	6	19
4	0.90	1.05	1.19	0.25	−0.13	−0.48	11	37
6	0.69	0.73	0.85	0.93	0.80	0.41	9	26
8	0.52	0.55	0.58	1.64	1.53	1.46	4	9
10	0.50	0.57	0.66	1.74	1.44	1.11	11	31

ΔG° = (kJ mol^{-1}); ΔH° = (kJ mol^{-1}); ΔS° = (J K^{-1} mol^{-1}).

ranging from 3 to 9 and the results are shown in Fig. 4. The pH of the medium was adjusted using required quantities of decimolar hydrochloric acid and sodium hydroxide solutions. It is evident from the figure that the amount of fluoride ions adsorbed (Q_e) in this pH range varied from 3.96 to 2.64 mg/g for PANi–AlO and 4.7 to 3.16 mg/g for PPy–AlO. The observed variation in the Q_e values with change in pH is similar to that observed with the constituents [7]. In acidic pH range the higher quantity adsorbed may be due to the combined effect of both the polymer and alumina where the positively charged adsorbent moiety attracts fluoride ions electrostatically [7,20]. It is well known that in the alkaline range the hydroxide ions compete effectively with the fluoride ions leading to a lower defluoridation in this range [2,4]. Further, the adsorbent exhibits a commendable defluoridation capacity in a wide range of pH and particularly around the neutral pH which would make the adsorbents more suitable for practical applications.

3.6. 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 removed (mg/g) is given in Table 5. The results indicated that the addition of these common co-ions does not have any marked effect on the removal of fluoride ions by these composites under the present experimental conditions. Parallel observations were also made with the constituent materials [4,20].

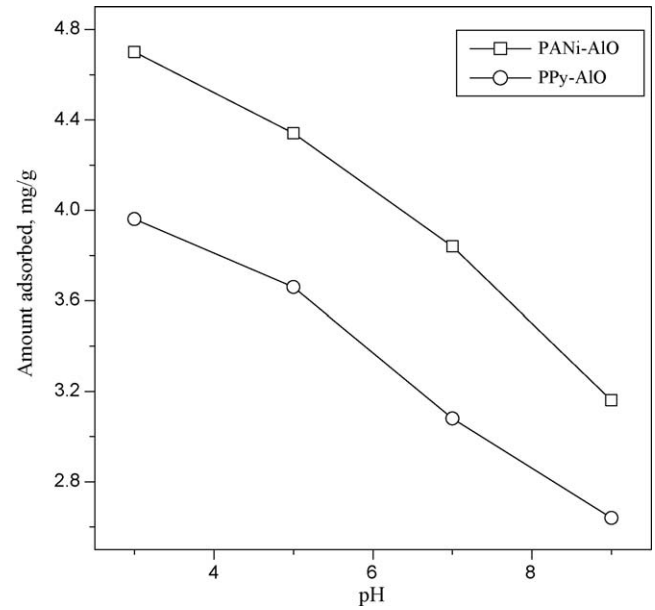


Fig. 4. Effect of pH on the removal of fluoride by PANi–AlO and PPy–AlO composites.

Table 6
Rate constants (K_{ad}, min^{-1}) for the adsorption of fluoride and the rate constants for forward (k_1, min^{-1}) and reverse (k_{-1}, min^{-1}) processes.

[F] (mg/l)	10^3k_{ad}			10^3k_1			10^3k_{-1}		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
PANi–AlO									
2	2.9	4.8	8.8	1.3	2.1	4.1	1.6	2.7	4.7
4	2.8	4.8	8.6	1.0	1.9	3.4	1.8	2.9	5.2
6	2.8	4.7	5.8	9.7	1.7	2.1	1.9	3.1	3.6
8	1.2	2.6	2.3	4.0	8.7	8.0	8.1	1.7	1.5
10	1.0	2.2	2.0	2.8	6.8	6.6	6.7	1.5	1.4
PPy–AlO									
2	2.9	13.3	16.1	1.4	6.9	8.5	1.5	6.4	7.6
4	2.7	5.6	10.9	1.3	2.7	4.9	1.4	2.9	6.0.
6	2.4	3.1	3.9	1.0	1.3	1.8	1.4	1.8	2.1
8	1.9	2.7	3.2	0.6	1.0	1.2	1.3	1.7	2.0
10	1.7	2.1	3.1	0.6	0.8	1.2	1.1	1.3	1.9

3.7. Kinetic modeling

The sorption of fluoride ions form liquid phase to solid phase may be expressed as

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \tag{2}$$

Table 5
Effect of co-ions on the amount of fluoride ions removed (mg/g) by PANi–AlO and PPy–AlO composites.

Co-ion	Amount adsorbed (mg/g)											
	PANi–AlO						PPy–AlO					
	0	100	200	300	400	500	0	100	200	300	400	500
Chloride	3.08	3.04	3.02	3.08	3.10	3.06	3.80	3.72	3.68	3.76	3.74	3.66
Bicarbonate	3.08	3.08	3.02	2.98	3.06	2.96	3.80	3.58	3.66	3.70	3.78	3.54
Sulphate	3.08	2.96	3.00	2.98	3.06	2.92	3.80	3.64	3.68	3.70	3.52	3.56
Nitrate	3.08	2.92	2.96	2.93	2.98	2.95	3.80	3.52	3.58	3.54	3.64	3.66

[F] = 4 mg/l; temp. = 30 °C; pH 7; contact time = 30 min.

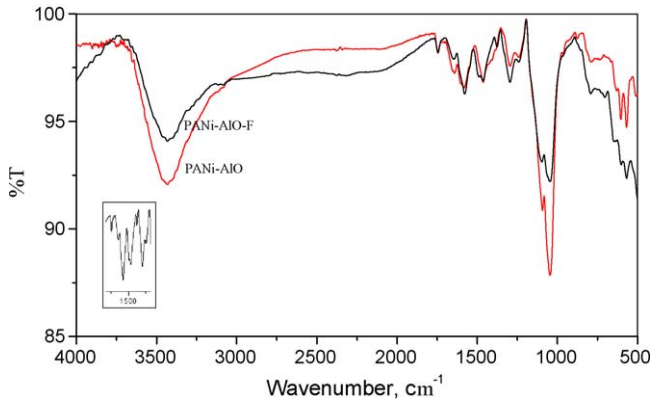


Fig. 5. FT-IR spectra of PANi–AlO composite before and after the treatment with fluoride.

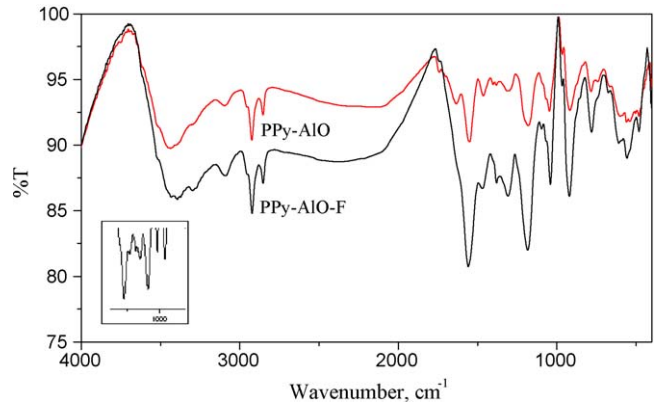


Fig. 6. FT-IR spectra of PPy–AlO composite before and after the treatment with fluoride.

where k_1 is the forward rate constant and k_{-1} is the backward rate constant. *A* represents fluoride ions remaining in the solution and *B* represents fluoride ions retained on the surface of the adsorbent. The reaction in the both directions is of first order. The rate constant for the adsorption, k_{ad} was determined using the Natarajan–Khalaf equation as described elsewhere [2]. The rate constants for the adsorption, forward process and reverse process are collected in Table 6. The results indicated that the k_{ad} values increased with an increase in temperature suggesting endothermic nature of the adsorption process. Further, an examination of the

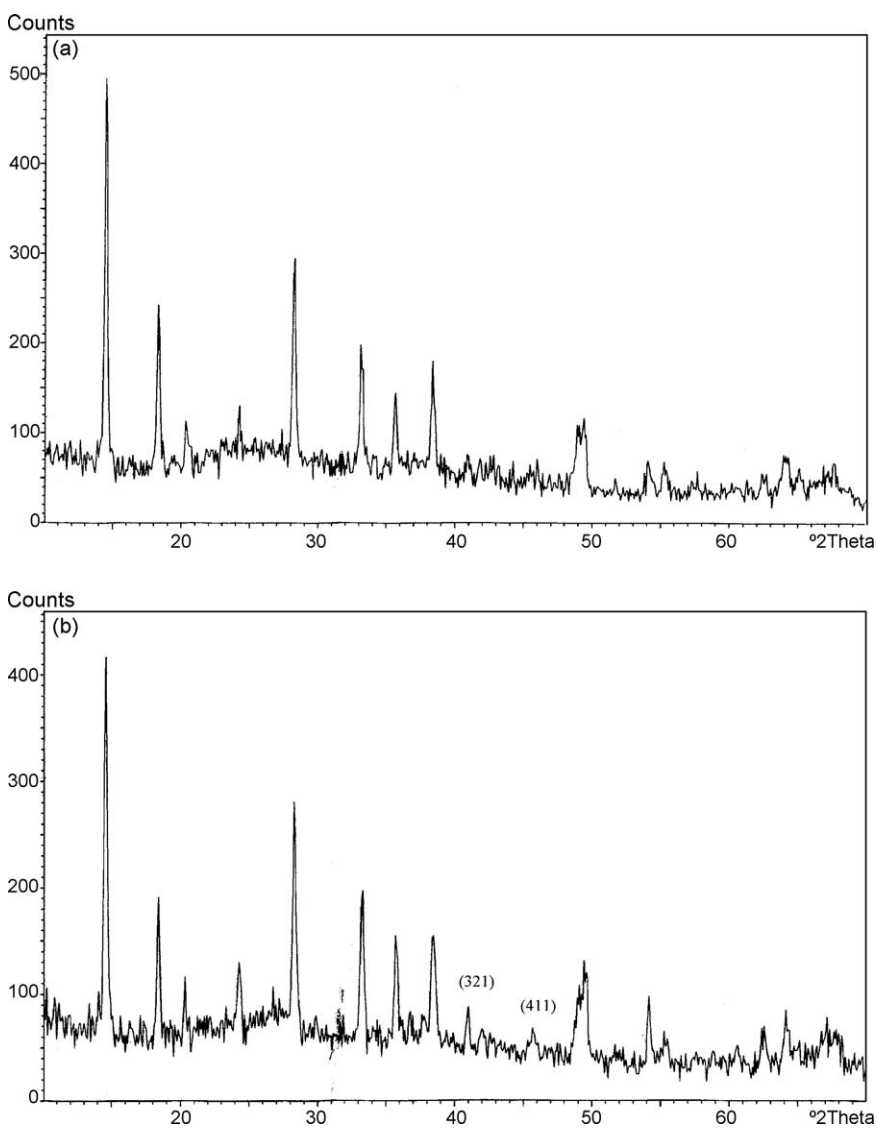


Fig. 7. XRD patterns of (a) PANi–AlO composite and (b) fluoride doped PANi–AlO composite.

Table 7
Infrared band assignment of alumina and PANi–AlO and PPy–AlO composites before and after adsorption.

Sample	Wavenumber (cm^{-1})	Band assignment
Alumina	1638 (s)	H–O–H bending of water
	1451 (w)	H stretching
	1050 (s)	Al–O stretching
	2099–3400 (m)	Hydroxyl group
PANi–AlO composite before adsorption	3433 (s)	N–H stretching
	1573 (m)	Stretching quinoid ring
	1483 (m)	C=C stretching benzenoid ring
	1463 (m)	Al–O stretching
	1288 (w)	C–N bending
	791 (w)	C–N stretching
	1045 (s)	Charge delocalization
PANi–AlO composite after adsorption	3429 (s)	N–H stretching
	1577 (m)	C=C stretching quinoid ring
	1481 (w)	C=C stretching benzenoid ring
	1376 (w)	Al–F stretching
	1046 (s)	Charge delocalization
PPy–AlO composite before adsorption	3436 (s)	N–H stretching
	1300 (m)	C=C stretching benzenoid ring
	1040 (s)	C=C stretching Quinoid ring
	1304 and 1180 (m)	C–H in-plane vibration
	1463 (m)	Al–O stretching
	924 (s)	2,5 coupling
PPy–AlO composite after adsorption	3393 (s)	N–H stretching
	1308 (m)	C=C stretching benzenoid ring and C–H in-plane vibrations
	1040 (s)	C=C stretching quinoid ring
	1463 (m)	Al–O stretching
	1383 (w)	Al–F stretching

effect of fluoride ion concentration on the k_{ad} values helps to describe the mechanism of removal taking place. In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial solute concentration and the rate of reaction will not be linear. Hence, it seems likely that in the present study pore diffusion also limits the rate of fluoride ion adsorption [28].

3.8. Intraparticle diffusion

Intraparticle diffusion studies helps to determine the rate-limiting step. In order to show the existence of intraparticle diffusion in the adsorption process, the amount of fluoride adsorbed (Q_e) was plotted versus square root of time, $t^{0.5}$. The k

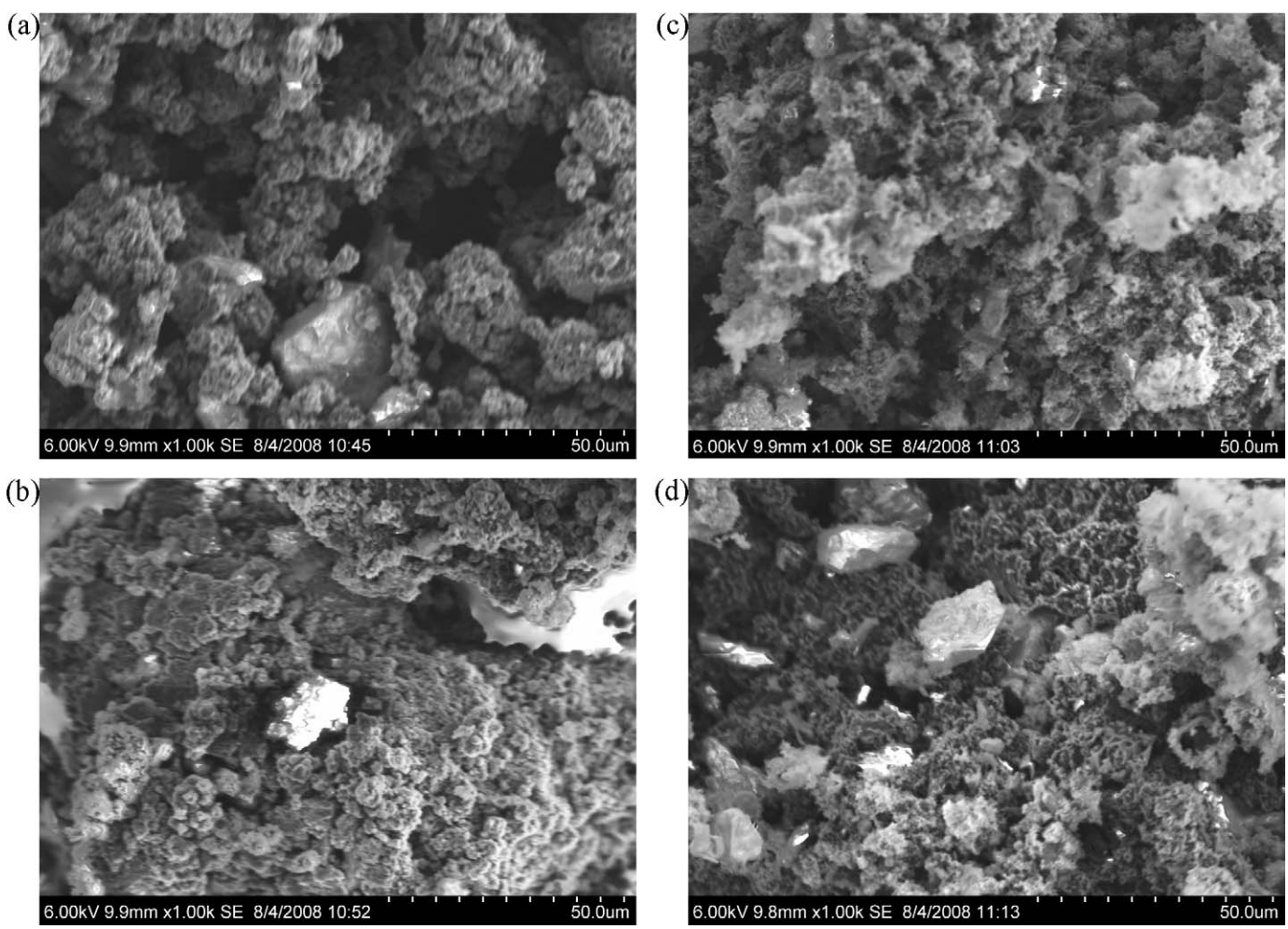


Fig. 8. SEM images of (a) PANi–AlO composite, (b) after the treatment with fluoride ions, (c) PPy–AlO composite and (d) after the treatment with fluoride ions.

values obtained from the slope of the linear portions of the curves and were found to be 0.098, 0.285 and 0.422 mg/g $min^{0.5}$ for PANi–AlO and 0.163, 0.283 and 0.295 mg/g $min^{0.5}$ for PPy–AlO at an initial fluoride ion concentration of 4 mg/l. Further, the linear portions of the curves do not pass through the origin (figure not shown). This indicated that in the mechanism of fluoride ion removal by the composites, both surface adsorption as well as intraparticle diffusion contributed to the rate determining step [27,29].

3.9. Analytical techniques

To get a better insight in to the mechanism of removal of fluoride ions by these composites various analytical techniques such as FT-IR, SEM, XRD and EDAX were employed. The FT-IR spectra of PANi–AlO and PPy–AlO composites are shown in Figs. 5 and 6, respectively and the band assignments are collected in Table 7. The characteristic bands (Fig. 5) at 1573 cm^{-1} arises mainly from both C=N and C=C stretching for quinoid form, while the band near 1483 cm^{-1} is attributed to the C–C aromatic ring stretching of the benzenoid unit. The peaks at 1288 cm^{-1} and 791 cm^{-1} can be assigned to C–N stretching of the secondary aromatic amine and aromatic C–H out-of-plane bending vibration, respectively. The absorption bands at 1549, 1304 and 1180 cm^{-1} are attributed to the polyaniline chain [22]. In Fig. 6, the band at 1542 cm^{-1} is assigned to pyrrole ring, i.e., the combination of C=C and C–C stretching vibrations. The peak at 1463 cm^{-1} is associated with Al–O stretching vibration. The peaks at 1304 and 1180 cm^{-1} are attributed to the in-plane vibrations of C–H. A sharp and intense peak at 924 cm^{-1} shows the 2,5 coupling between the monomer molecules of pyrrole in polypyrrole [30]. In both cases, the strong peaks at 1050 and 1451 cm^{-1} are the characteristic vibrations of alumia [22,31]. Further, Table 7 revealed that after adsorption of fluoride ions the intensity of the peak at 1463 cm^{-1} which corresponds to Al–O stretching in the composites decreased and in both the cases a new peak corresponds to Al–F stretching appeared. This indicated the involvement of Al–O bond in interaction with the adsorbed fluoride ions and formation of aluminium–fluoro complex on the surface [22]. As reported earlier the peak corresponds to N–H stretching of the polymer exhibited slight change while other peaks showed no appreciable change, as a result of adsorption of fluoride ions [4]. Hence, in the present study, the removal of fluoride ion by the composites may occur through the same mechanism followed by the constituents present in it [4,7].

The XRD patterns of the composites before and after adsorption of fluoride ions were also recorded. Representative XRD patterns for PANi–AlO composites are shown in Fig. 7a and b. The XRD pattern before adsorption (Fig. 7a) shows the characteristic peaks for the emeraldine structure of PANi [22]. After the adsorption of fluoride ions the XRD pattern (Fig. 7b) shows two new peaks with *h k l* parameters (3 2 1) and (4 1 1). These two new peaks which correspond to aluminium fluoride [32], confirms the formation of Al–F on the surface of the composite. However, as reported earlier, after the adsorption of fluoride ions the peaks corresponds to the polymer showed no marked variations [32].

The SEM images of the composites before and after adsorption of fluoride ions are shown in Fig. 8a–d. Fig. 8a and c corresponds to PANi–AlO and PPy–AlO composites before adsorption. In these images polymer are seen as spongy like structures and alumina as crystalline particles. After adsorption (Fig. 8b and d), the bright spots on the crystalline particles indicate the presence of fluoride ions on the surface of alumina. This may be due to the adsorption of fluoride ions on the surface of the alumina. However, there is no noticeable change in the SEM images of the polymer moieties after adsorption [7]. Energy dispersive analysis of X-ray (EDAX) was employed to analyze the elemental constituents of PANi–AlO composites (as a representative case) before and after adsorption of fluoride ions. The EDAX patterns of PANi–AlO composite before and after adsorption are shown in Fig. 9a and b, respectively. The EDAX pattern after adsorption (Fig. 9b) indicated the presence of fluoride ions along with other principal elements. This provides a direct evidence for the adsorption of fluoride ions onto the composite [33].

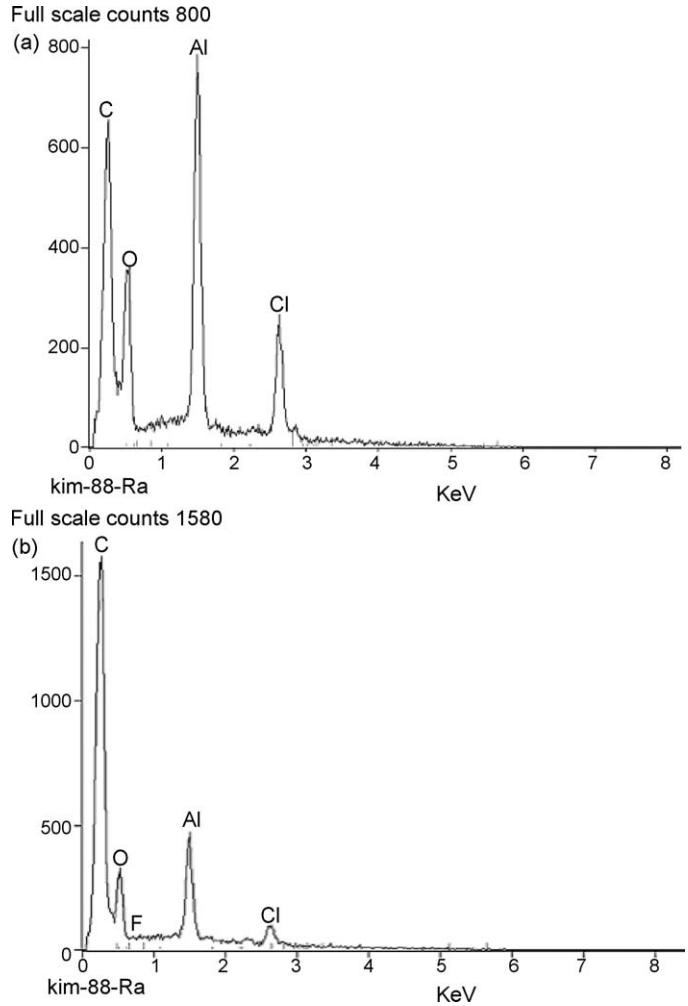
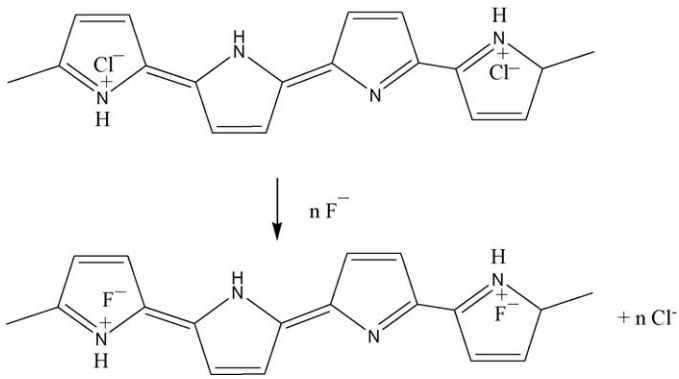


Fig. 9. EDAX spectra of (a) PANi–AlO composite and (b) after the treatment with fluoride.

3.10. Mechanism of fluoride removal

Based on the enhanced amount of fluoride ions adsorbed per unit mass of the composites, foregoing results and discussions on isotherm and spectral studies, it is evident that both the constituents present in these composites contributes to the removal of fluoride ions from aqueous solution. Zhang [34], in the study of preparation, spectral characterization and corrosion protection of alumina–polyaniline composite, established that there is no chemical interaction between the polyaniline and the alumina surface. However, its morphological and peel off studies indicated the good adhesion of the polyaniline layer on the alumina particles forming a composite with enhanced surface area, mechanical and thermal properties, etc. which is of great importance in applications of the composite particles. Hence, it is presumed that, in the present study, there is a synergistic effect in the defluoridation capacity of the constituents in the form of a



Scheme 1.

composite. Thus, the mechanism of fluoride ion removal by the composites involves the interaction of fluoride ions with both the polymer and alumina moieties. It is well established that removal of fluoride ions by alumina occurs through the formation of aluminium–fluoro complexes as given below [20].

$$Al_2O_3 + nF^- \xrightarrow{m\,H_2O} AlF_n{}^{3-n} + Al(OH)_{3-m}F_m$$

The removal of fluoride ions by polyaniline, in the form of emaraldine base, occurs via doping [4]. In the case of polypyrrole which is employed in the form of chloride ion doped polymer, fluoride ions were removed from aqueous solution through the replacement of doped ionizable chloride ions present in it, i.e., by ion-exchange mechanism [7] as depicted in Scheme 1. In the present study chloride ion doped polypyrrole was used because it is more stable than the base form. Therefore, in the present study, removal of fluoride ions by the conducting polymers/alumina composites is a combination of both the mechanisms followed by constituents present in it.

4. Conclusion

The polymer composites showed considerable potential for the removal of fluoride ions from aqueous solutions. Lower and neutral pH and higher temperature ranges were found as the favourable conditions for maximum fluoride removal. The results gained from this study were well described by the theoretical Freundlich and Langmuir models. The thermodynamics of the system pointed out the system was endothermic. The results of the equilibrium, FT-IR, XRD, SEM and EDAX studies revealed that the defluoridation of water occurs via the combination of both the mechanism followed by the constituents leading to enhanced fluoride ion uptake.

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