Removal of fluoride ions from aqueous solution by conducting polypyrrole

M. Karthikeyan, K.K. Satheeshkumar, K.P. Elango*

Department of Chemistry, Gandhigram Rural University, Gandhigram 624 302, India

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ABSTRACT

Conducting polypyrrole was found to possess potential efficiency to remove fluoride ions from aqueous solutions. The amount of fluoride ions removed per unit mass of the adsorbent, at 30 °C from 10 mg/L fluoride ion solution, was estimated to be 6.37 mg/g. Batch sorption studies have been carried out to determine the effect of initial concentration of the sorbate, agitation time, adsorbent dose, pH, co-ions and temperature on the removal of fluoride by polypyrrole. The sorptive removal was found to be strongly pH and temperature dependent. The experimental data fitted well to the Freundlich and Dubinin–Radushkevick (D–R) isotherms. Thermodynamic parameters such as ΔH^0, ΔS^0 and ΔG^0 were calculated indicating that the adsorption process was spontaneous and exothermic. FT-IR spectral studies suggested that the mechanism of fluoride ions removal follow chemisorption.

1. Introduction

Environmental fluoride has received much attention on account of the fact that an optimum concentration was found to reduce the incidence of dental caries. Low levels of fluoride are required for humans and other animals and have beneficial effect on tooth and bone structures. However ingestion of excessive fluoride, mainly through drinking water, causes dental and skeletal fluorosis. According to WHO the acceptable limits of some chemical parameters in potable water are Cl (200–300 mg/L), hardness (500 mg/L), iron (0.3 mg/L), pH (6.5–8), total dissolved solids (<1000 mg/L), sulphate (1000 mg/L), calcium (100–300 mg/L), magnesium (<100 mg/L) and fluoride (1.5 mg/L) [1]. A maximum of 1.5 mg/L fluoride is recommended to protect human from fluorosis.

During recent past, several methods have been tried to remove fluoride ions from water, namely, adsorption [2–8], chemical treatment [9,10], ion exchange [11,12], membrane separation [13,14], electrolytic de-fluoridation [15], electro dialysis [16,17], etc. Among these methods, adsorption is still one of the most extensively used methods for defluoridation of water due to its low cost and viability.

Since the discovery of conducting polymers three decades ago, a large volume of research work has been performed associated with the physics and chemistry of conducting polymers. Polypyrrole is one of the most environmentally stable known conducting polymer and also one of the most commonly investigated conducting polymer due to its high electrical conductivity and ease of preparation [18]. Polypyrrole find applications in various fields such as microelectronics, composite materials, optics and biosensors [19] and as adsorbent [20,21]. The ion exchange capacities of conducting polymers were well understood and it was found to depend on the polymerization conditions, the type and size of the dopants incorporated during the polymerization process as well as on the ions present in the electrolyte solution, the polymer thickness and ageing of the polymer [22]. Review of the literature revealed that polypyrrole synthesized in solutions with small dopants such as Cl^-, ClO_4^-, NO_3^-, etc., mainly exhibits anion-exchanger behaviour due to the high mobility of these ions in the polymer matrix. While under certain conditions cation exchange was also found to take place with large dopants like polyvinylsulfonate and polystyrenesulfonate, due to immobility of these ions in the polymer matrix [22]. Furthermore, it was well established that polypyrrole prepared by both chemical and electrochemical polymerization reactions usually carries charges in the polymer, i.e. some of the nitrogen atoms in polypyrrole are positively charged. To maintain charge neutrality, some of the exchangeable counter anions present in the polymerization solution are incorporated into the growing polymer during the polymerization [21]. The existence of positively charged nitrogen atoms in polymer provides a good prospect for its applications in adsorption of anions such as fluoride ions. Therefore, in this study, an attempt was made to study the possibility of using conducting polypyrrole, with chloride ion as a dopant, for the removal of fluoride ions from aqueous solutions by batch sorption method.
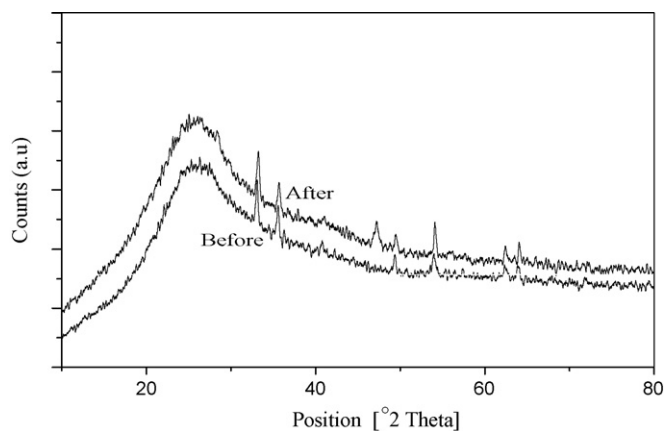
Fig. 1. XRD patterns of PPyCl before and after treatment with fluoride ions.

2. Experimental procedure

2.1. Materials

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

2.2. Preparation and characterization of polypyrrole

Polypyrrole was prepared by chemical polymerization as reported earlier [23]. The overall reaction is represented as
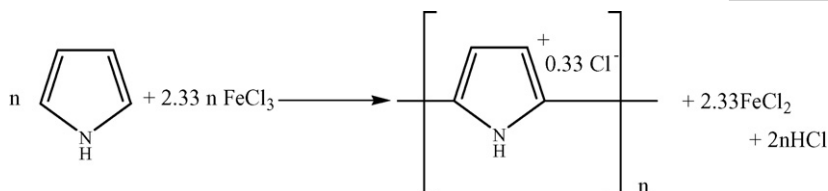
The doping density of Cl⁻ in polypyrrole prepared through chemical polymerization has often been reported to be at about 0.25–0.3 per pyrrole monomer unit [24]. The chloride doped polypyrrole are referred to as PPyCl in this paper. The pH of a solution of PPyCl was found to be 6.87. The FT-IR spectrum of PPyCl in the present study resembles that already reported [25]. The supporting figure is given in Fig. S1, the band at 1566 cm^{-1} is due to C–C and C–N stretching vibrations. The peak 790 cm^{-1} has been assigned to ring bending. The peak at 1566 cm^{-1} corresponds to C=C vibrations and contains contributions from both endocyclic and exocyclic double bonds. A sharp and intense peak at 924 cm^{-1} shows the 2,5 coupling between the monomer molecules of pyrrole in polypyrrole. The peaks at 1281 and 1043 cm^{-1} corresponds to the benzenoid and quinoid form of the polypyrrole. X-ray diffraction (XRD) pattern of PPyCl is shown in Fig. 1. The XRD pattern shows the PPyCl is amorphous in nature as indicated by the characteristic amorphous peak centered at $2\theta \approx 26°$ [21]. The scanning electron microscopic (SEM) image (Fig. S2a and b) of PPyCl, is also characteristic of the polymer and which resembles that of reported earlier [26].

2.3. Methodology

The concentration of fluoride and pH were measured using ion-selective meter (Eutech Cyberscan 2100). The XRD (X' Pert PRO PANalytical, Netherlands) patterns of PPyCl before and after

adsorption were recorded at the National Institute for Science and Technology, Thiruvananthapuram, S. India. The SEM (HITACHI-S-3400H) images were obtained from Pondicherry University, Pondicherry. 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 by agitating 50 mg of PPyCl 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 ion was determined. All experiments were carried out twice and the adsorbed fluoride ion concentrations given were the means of duplicate experimental results. Experimental variables considered were initial concentration of fluoride ions 2–10 mg/L; contact time between PPyCl and fluoride ion solution 5–30 min; pH 3–10; dosage of PPyCl 25–200 mg/50 mL; temperature 30–50 °C and co-ions viz. chloride, sulphate, and bicarbonate ions.

3. Results and discussion

3.1. Effect of contact time and initial concentration

The amount of fluoride ions removed per unit mass of PPyCl (Q_e, mg/g) at different initial fluoride ion concentrations and temperatures is collected in Table 1. The results revealed that, Q_e increased with an increase in concentration, as expected, and decreased with rise in temperature. The variation of Q_e with temperature indicated that the removal process is exothermic in nature. The results of the effect of contact time between PPyCl and adsorbate is depicted in Fig. 2. It is evident from the figure that the equilibrium was reached within 10 min. This might be due to the fact that once certain amount of fluoride ions gets adsorbed onto PPyCl within a given time (<10 min), no more removal occurs afterwards, i.e. the removal (or doping) level might have reached [2]. Further, the attainment of maximum doping level within 10 min suggested that a very minimum contact time is sufficient enough for the removal of fluoride ions from water by PPyCl. It is interesting to compare the time taken for the attainment of equilibrium in the present case with that reported, by us, using polyaniline [3] as an adsorbent for the removal of fluoride ions from aqueous solution. In the case of polyaniline, which was used as an Emerladine base, the removal of fluoride ions take place via doping and that occur within 2 min

Table 1
Equilibrium parameter for the removal of fluoride ions per unit mass (mg/g) of PPyCl.

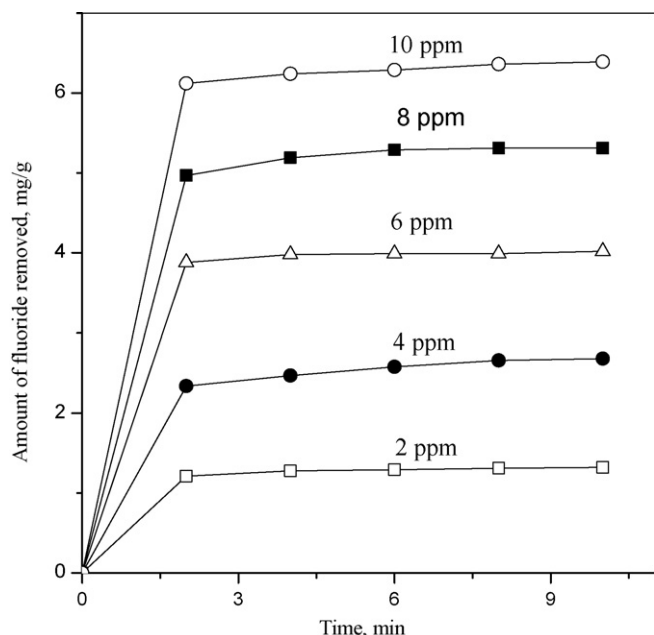| [F] (mg/L)	C_e (mg/L)			Q_e (mg/g)		
	30°	40°	50 °C	30°	40°	50 °C
2	0.68	0.76	0.93	1.32	1.24	1.07
4	1.34	1.42	1.56	2.66	2.58	2.44
6	1.99	2.03	2.37	4.01	3.97	3.63
8	2.69	2.71	2.88	5.31	5.29	5.12
10	3.63	3.88	4.43	6.37	6.12	5.57

Fig. 2. Effect of contact time on the removal of fluoride ions by PPyCl.

and after that no further adsorption was observed. However, in the present study, a relatively longer time taken for the equilibrium to reach may be due to the time taken for the exchange of chloride ions in the polymer matrix with fluoride ions present in the bulk.

3.2. Effect of PPyCl dose

The effect of dose of PPyCl on the removal of fluoride ions is shown in Fig. 3. It was observed that the value of Q_e increased with a decrease in dose. This increase in fluoride ion removal was due to the availability of higher number of fluoride ions per unit mass of PPyCl, i.e. higher fluoride ion/PPyCl ratio. Further experiments were carried out using 50 mg of PPyCl per 50 mL of fluoride ion solu-
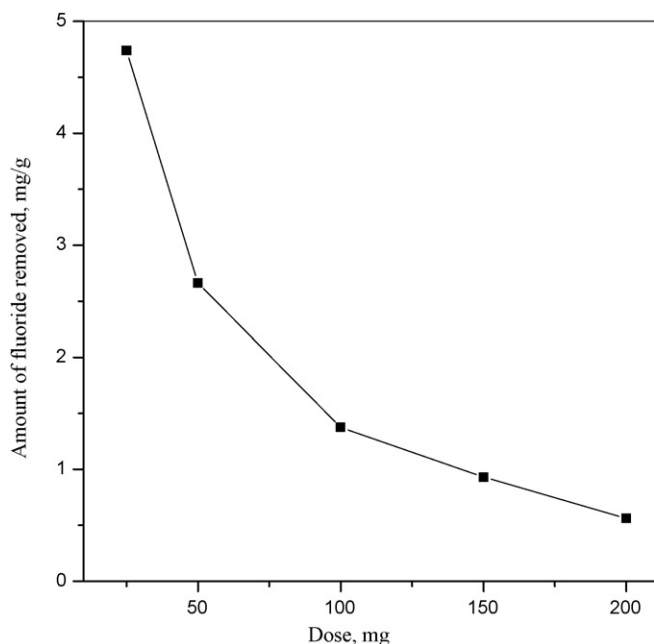
tion, as it exhibits appreciable removal capacity, for optimization of adsorption parameters.

3.3. Effect of pH

The effect of initial pH of the solution on the amount of fluoride ions removed by PPyCl is depicted in Fig. S3. The results indicated that the amount of fluoride ions removed decreased with an increase in pH and there was hardly any removal at pH 11. The decrease of solution pH values will exponentially increase the H^+ ion concentrations and can lead to the protonation of the nitrogen of the PPyCl or the selective adsorption of the H^+ ions on the surface of the PPyCl as shown below [21,27].

$$\text{\raisebox{0pt}{$\sim\!\!\sim\!\!\sim$}} \underset{Cl^-}{Py^+H} \text{\raisebox{0pt}{$\sim\!\!\sim\!\!\sim$}} + HCl \rightleftharpoons \text{\raisebox{0pt}{$\sim\!\!\sim\!\!\sim$}} \underset{2Cl^-}{Py^+HH^+}\text{\raisebox{0pt}{$\sim\!\!\sim\!\!\sim$}}$$

It was reported that polypyrrole with smaller ions as dopant exhibit largely anion exchanger behaviour [22] and also Zhang and Bai [21] reported, on the basis of the zeta potential measurements, that the doped chloride ion is ionizable and may transfer into the bulk solution. As a result, fluoride ions might be exchanged (because of the smaller size of the F^- ions) easily with chloride ions onto the surface of PPyCl, leading to enhanced removal of fluoride ions from the aqueous solution at pH < 7. This would decrease with an increase in pH of the medium. In the alkaline pH range, the surface charge of the PPyCl becomes negative due to deprotonation of the protonated nitrogen atoms on PPyCl and selective adsorption of hydroxide ions (OH^- being physically smaller than Cl^-), replacing chloride ions.

3.4. Adsorption isotherms

The distribution of sorbate between the solid and the solution interface at equilibrium has been described by the Freundlich and Langmuir equations. These two models are widely used, the former being purely empirical and the latter assuming that maximum adsorption occurs when the surface is covered by adsorbate. Linear plots of $\log Q_e$ against $\log C_e$ (Fig. 4) indicated the applicability of the Freundlich isotherm in the present study. The statistical parameters of these plots along with the Freundlich constants are given
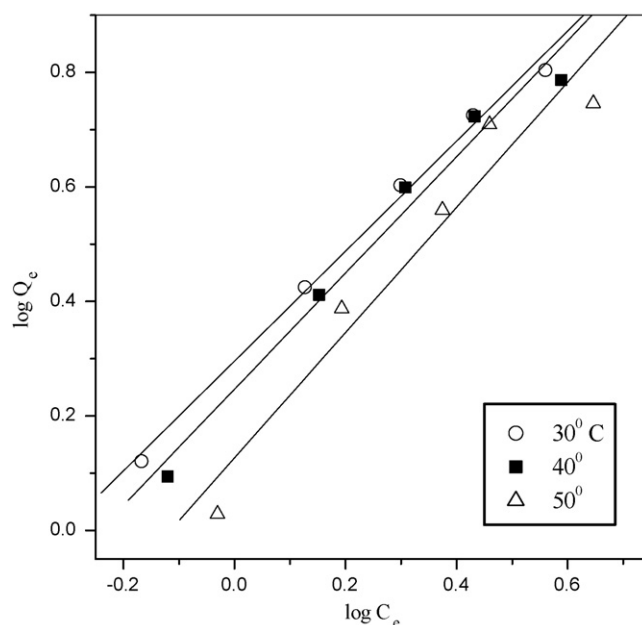

Fig. 3. Effect of dose on the removal of fluoride by PPyCl.

Fig. 4. Freundlich isotherm for the removal of fluoride by PPyCl.

Table 2
Equilibrium parameters and isotherm constants for the retrieval of fluoride ions by PPyCl.

Isotherm	Statistical parameter/constant	Temp. (°C)		
		30	40	50
Freundlich	r	0.997	0.988	0.968
	sd	0.03	0.05	0.08
	n	1.04	0.99	0.91
	K	1.98	1.77	1.34
Langmuir	r	0.664	0.164	0.111
	sd	0.026	0.064	0.144
D–R	r	0.970	0.979	0.989
	sd	0.175	0.151	0.113
	β ($\times 10^{-7}$)	−3.097	−3.516	−4.694
	E (kJ/mol)	1.27	1.19	1.03

in Table 2. The results indicated that the adsorption capacity, K, decreased with a rise in temperature suggesting that the removal of fluoride ions by PPyCl is an exothermic process. Further, the values of intensity of adsorption (n) are approximately unity indicating that the process is favourable.

The plots of C_e/Q_e versus C_e (Fig. 5) indicated that the Langmuir isotherm is not valid for the present study.

The Dubinin–Radushkevick (D–R) [8,11,28] isotherm was used to determine the nature of the adsorption process viz. physisorption or chemisorption. The linear form of this model is expressed by:

$$\ln Q_e = \ln Q_m - \beta \varepsilon^2 \tag{3}$$

where Q_e is the amount of fluoride ions adsorbed per unit dosage of the adsorbent (mg/g), Q_m the monolayer capacity, and β is the activity coefficient related to mean sorption energy and ε is the Polanyi potential described as

$$\varepsilon = RT \ln \left[1 + \left(\frac{1}{C_e} \right) \right] \tag{4}$$

The mean sorption energy, E (kJ mol^{-1}), can be calculated by using the following equation [29,30]:
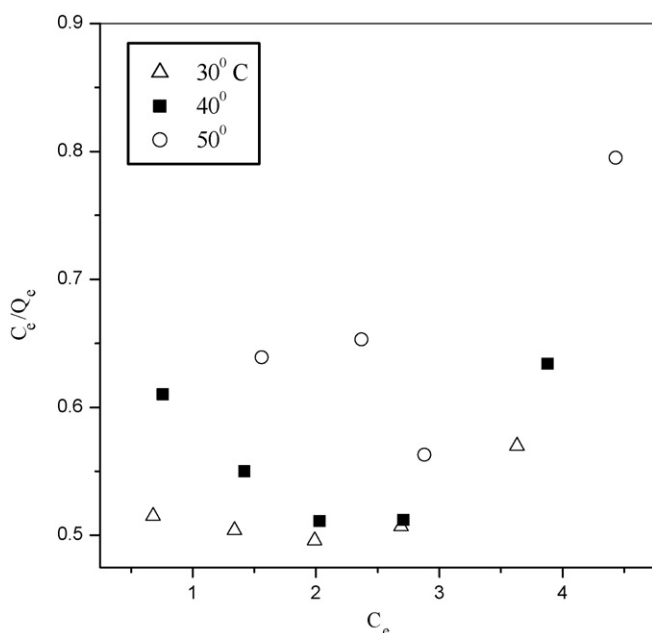
$$E = (-2\beta)^{-1/2} \tag{5}$$

A representative plot of D–R isotherm is depicted in Fig. 6. The statistical results along with the isotherm constants are also given in Table 2. The mean sorption energy values range from 0 to 8 kJ mol^{-1} is for physical adsorption and from 9 to 16 kJ mol^{-1} for chemical adsorption [29,30]. The observed low magnitude of mean sorption energy, in the present study, may be due to the fact that the fluoride ions are removed by the replacement of chloride ions from PPyCl and not by any chemical process.

3.5. Thermodynamic parameter

The thermodynamic parameter such as standard free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the temperature dependence of equilibrium constant as explained earlier [2] and are collected in Table 3. The endothermic nature of the adsorption is indicated by an increased equilibrium constant, K_0, with rise in temperature and also the negative values of enthalpy change. The entropy change showed that the adsorption process is more ordered. The negative values of ΔG^0 indicated that the removal of fluoride ions by PPyCl is a spontaneous process.

3.6. Kinetics of adsorption

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

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{6}$$
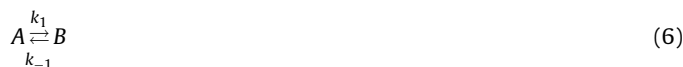
where k_1 is the forward rate constant and k_{-1} is the backward rate constant. A represents fluoride ions remaining in the bulk solution and B represents fluoride ions retained on the surface of PPyCl. The reaction in the both directions is of first order. The rate constant for the adsorption, k_{ad} was determined using the Natarajan–Khalaf equation as described earlier [2]. The rate constants for the adsorption (k_{ad}) and forward (k_1) and reverse (k_{-1}) processes are presented in Table 4. The results indicated that the k_{ad} values decreased with an increase in temperature suggesting exothermic nature of the adsorption process. Further, the values of k_1 were found to be larger than that of k_{-1} suggesting adsorption is
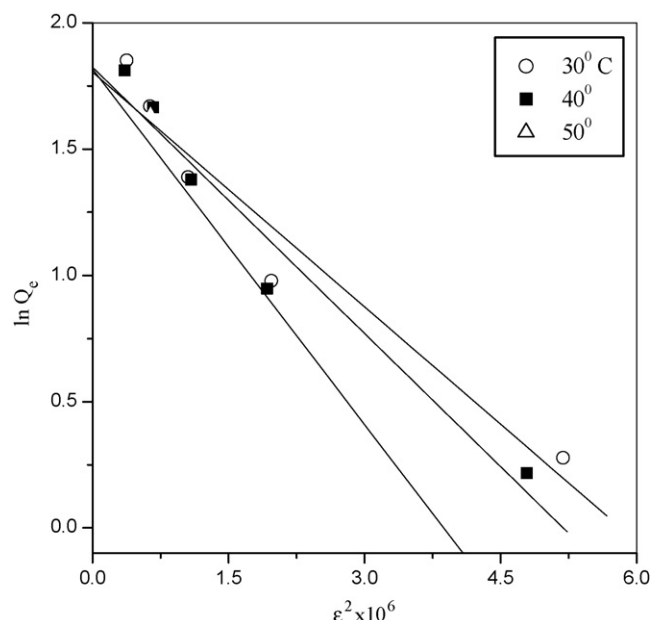

Fig. 5. Langmuir isotherm for the removal of fluoride by PPyCl.

Fig. 6. D–R plot for the removal of fluoride ions by PPyCl.

Table 3
Equilibrium constants and thermodynamic parameters for the removal of fluoride ions by PPyCl.

[F] (mg/L)	K_0			ΔG^0 (kJ mol^{-1})			ΔH^0 (kJ mol^{-1})	ΔS^0 (JK^{-1} mol^{-1})
	30°	40°	50 °C	30°	40°	50 °C		
2	1.94	1.64	1.15	−1.67	−1.28	−0.37	−21	−64
4	1.98	1.82	1.56	−1.73	−1.55	−1.20	−10	−26
6	2.01	1.96	1.53	−1.77	−1.75	−1.14	−11	−30
8	1.97	1.95	1.78	−1.71	−1.74	−1.55	−4	−8
10	1.75	1.58	1.26	−1.42	−1.19	−0.61	−13	−39

Table 4
Rate constants for the adsorption of fluoride (k_{ad}, min^{-1}), forward (k_1, min^{-1}) and reverse (k_{-1}, min^{-1}) processes.

[F] (mg/L)	k_{ad} ($\times 10^3$)			k_1 ($\times 10^3$)			k_{-1} ($\times 10^3$)		
	30°	40°	50 °C	30°	40°	50 °C	30°	40°	50 °C
2	21.2	4.4	2.2	14.0	2.7	1.2	7.2	1.7	1.0
4	35.9	21.7	10.4	23.9	14.0	6.3	12.0	7.7	4.0
6	10.5	5.3	7.6	7.0	3.5	4.6	3.5	1.8	3.0
8	20.7	25.3	6.2	13.8	16.8	4.0	6.9	8.6	2.2
10	7.9	8.7	10.6	5.1	5.3	5.9	2.9	3.4	4.7

dominant over desorption which lead to higher amount of fluoride ions retained by PPyCl, as observed.

3.7. FT-IR, XRD and SEM studies

It is evident from the spectrum that, the peak corresponding to the N–H stretching appeared at 3427 cm^{-1} for PPyCl shifted to 3399 cm^{-1} after treatment with fluoride ions. While all other peaks showed no significant variation in position. This might be due to the fact that the replacement of the Cl$^-$ by more electronegative F$^-$ might have caused the shift to a lower wave number. As the fluoride ions were removed by PPyCl through ion exchange (with Cl$^-$ ions) mechanism there is no visual change in the XRD pattern (Fig. 1) as well as in the SEM image of PPyCl after treatment with fluoride ions.

3.8. Comparison with other adsorbents

The capacity of PPyCl to remove fluoride ions from aqueous solution is comparable with other adsorbents reported earlier. Although direct comparison of PPyCl with other adsorbents is difficult, owing to the different applied experimental conditions, it was found, in general, that the adsorption capacity of PPyCl (6.37 mg/g) for fluoride ions is comparable with that of other adsorbents and in fact greater than certain adsorbents reported earlier. The amount of fluoride ions removed per unit mass by various adsorbents (in mg/g) is: zirconium impregnated coconut shell carbon, 0.94 [31]; lanthanum-modified chitosan, 3.1 [32]; waste carbon slurry, 4.5 [33]; magnetic chitosan, 3.0 [34]; neodymium-modified chitosan, 9.73 [35]; polyaniline, 0.77, [3]; poly(m-methyl aniline), 0.78 [3]; plaster of Paris, 0.158 [2]; and MgO, 0.052 [6].

4. Conclusion

The conducting polypyrrole showed considerable potential for the removal of fluoride ions from aqueous solutions. Lower pH and lower temperature ranges were found as the favourable conditions for maximum fluoride ion removal. The results gained from this study were well described by the theoretical Freundlich and D–R models. The thermodynamics of the system pointed out that the system was exothermic and spontaneous. The foregoing results indicated that the fluoride ions were removed from aqueous solution by PPyCl through the replacement of doped ionizable chloride ions present in PPyCl as shown below. It is interesting to compare the adsorption of fluoride ions from aqueous solution by polyani-

line [3], where the removal of fluoride ions occurs via doping of the polymer matrix, with polypyrrole where it is through ion exchange mechanism.
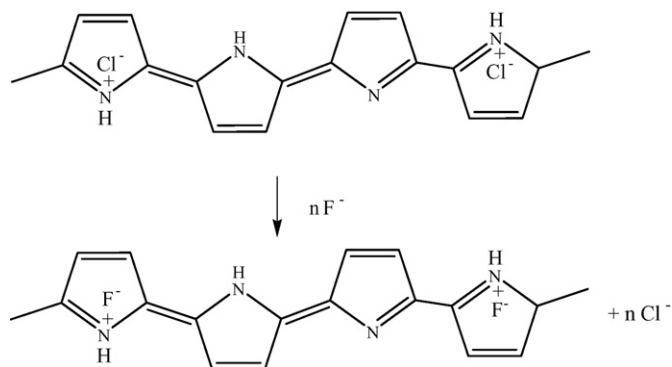
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.12.141.

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