



## Defluoridation of water via doping of polyanilines

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### ABSTRACT

The potentiality of polyaniline and poly (*m*-methyl aniline) to remove fluoride from water via doping was investigated. The influence of pH, dosage of polyanilines, initial fluoride concentration and temperature on the amount of fluoride removed by the polyanilines were studied. The amount of fluoride removed at pH 7.0 by 50 mg/50 ml dose was found to be 0.78 mg/g. The data of fluoride removal fitted well with Langmuir and Freundlich isotherms. Thermodynamic parameters computed show that the adsorption process is endothermic in nature. FT-IR, X-ray and EDAX patterns of the polyanilines before and after exposure to fluoride ions suggest that the defluoridation occurs via doping of fluoride ions onto these polymers.

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### 1. Introduction

The health impact of ingesting water containing a fluoride concentration outside the permitted limits is a subject that has been studied very extensively. Consumption of water with fluoride concentrations below the permitted limit accompanied by poor dental hygiene has been shown to cause cavities while ingesting water with fluoride concentrations exceeding the limit causes dental fluorosis, but long-term ingestion of water that contains more than a suitable level of fluoride causes bone disease and mottling of the teeth. The permissible limit of fluoride in drinking water specified by the World Health Organization (WHO) is 1.5 mg/l [1].

The methods reported for the removal of excess fluoride from drinking water includes, adsorption [2,3], chemical treatment [4,5], ion exchange [6], membrane separation [7,8], electrolytic de-fluoridation [9], and electro-dialysis [10–12], etc. Among these methods, adsorption is still one of the most extensively used methods for defluoridation of water due to its cost and viability.

Polyaniline, a conducting polymer, has received considerable interest in recent years because of its applications in a variety of technological fields, such as electro chromic devices [13], chemical sensors [14], charge storage systems [15], protection against corrosion [16], etc. Polyaniline is considered as an organic metal. Although its specific conductivity and the temperature dependence of its conductivity are semi-metallic, all other properties such as its thermo power, must be classified as clearly metallic. The conduc-

tivity mechanism of polyaniline is of an unmistakably electronic nature, but is quantum mechanically limited by the very small size of its primary particles (~10 nm), which results in a macroscopically observable reduction in conductivity. Further, polyanilines are high molecular weight (typically 100,000) polymers and are capable of doping large number of anions [17]. These properties prompted us to make an attempt to investigate the removal of fluoride from water using such a significant material, polyaniline, which we thought that it would add a new dimension to this organic metal.

### 2. Experimental procedure

#### 2.1. Materials

All the reagents used were of commercially available high purity Analar grade (Merck or Aldrich, India). Stock solutions of fluoride were prepared by dissolving sodium fluoride in doubly distilled water.

#### 2.2. Preparation of polyaniline (Emeraldine base)

Polyaniline, P(ANI), is prepared by the reported method [17]. Ice cooled 0.1 M aqueous solution of ammonium peroxydisulphate is added drop wise to a stirred solution of ice cooled 0.1 M solution of aniline dissolved in 1 M HCl pre-cooled to 0–5 °C. Ammonium peroxydisulphate solution is added very slowly to prevent the warming of the solution. After completion of the addition (2–4 h), stirring is continued for further 2 h to ensure completion of the reaction. The precipitated Emeraldine salt is filtered and washed repeatedly with distilled water until the filtrate is colourless. The precipitate is then

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transferred to a beaker and stirred with methyl alcohol and filtered. Methyl alcohol washing is desirable to remove oligomeric impurities. The so obtained Emeraldine salt is suspended in 0.1 M  $\text{NH}_4\text{OH}$  solutions and stirred for 6 h. The pH of this solution should be kept around nine by adding drops of 1 M  $\text{NH}_4\text{OH}$ . The blue Emeraldine base obtained after filtration is dried under dynamic vacuum for 12 h.

### 2.3. Methodology

The concentration of fluoride and pH were measured using ion-selective meter (Eutech Cyberscan 2100). The XRD patterns of polyanilines before and after adsorption were recorded at the Regional Research Laboratory, Thiruvananthapuram. The EDAX patterns were recorded at Anna University, Chennai. The zero point charge ( $\text{pH}_{\text{ZPC}}$ ) of the polyaniline was determined by pH drift method [18].

### 2.4. Batch adsorption experiments

Adsorption experiments were performed by agitating 50 mg of P(ANi) with 50 ml of fluoride solution of desired concentration at  $30 \pm 0.5^\circ\text{C}$  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 was determined. All experiments were carried out twice and the adsorbed fluoride concentrations given were the means of duplicate experimental results.

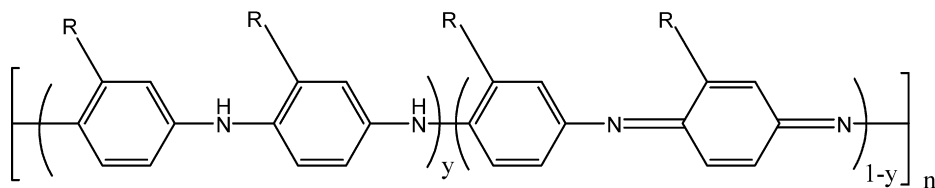
Experimental variables considered were initial concentration of fluoride ions 2–10 mg/l; contact time between P(ANi) and the fluoride solution 5–360 min; pH 3–10; dosage of P(ANi) 25–1000 mg/50 ml; temperature  $30\text{--}50^\circ\text{C}$  and co-ions viz. chloride, sulphate, and bicarbonate ions.

### 2.5. Data analysis

All computations were made using Microcal Origin (version 6.0) computer software. The goodness of fit was discussed using correlation coefficient,  $r$ , and standard deviation, S.D.

## 3. Result and discussions

Two polyanilines were chosen for the present study so as to investigate the effect of an electron-donating group such as methyl group on the doping process. The structure of these polyanilines is as shown below.



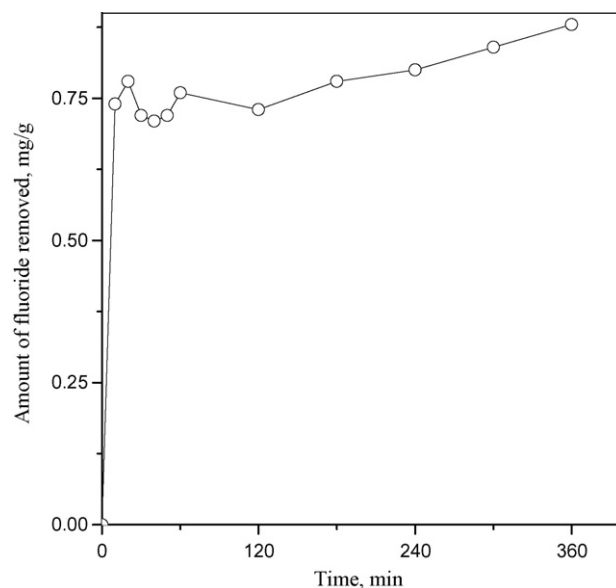
The zero point charge,  $\text{pH}_{\text{ZPC}}$ , of the polyanilines determined by the pH drift method are 6.89 and 6.92, respectively for  $\text{R}=\text{H}$  and  $\text{R}=\text{Me}$ .

### 3.1. Effect of contact time and initial concentration

The amount of fluoride removed ( $Q_e$ , mg/g) by both the polyanilines are collected in Table 1. The results reveal that, the amount of fluoride adsorbed per unit mass of the P(ANi) increased with increase in concentration and rise in temperature. The variation of  $Q_e$  with temperature indicates that the process is endothermic in

**Table 1**  
Equilibrium parameters for the removal of fluoride (mg/g) by polyanilines

[F] mg/l	R=H			R=Me		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
2	0.47	0.49	0.52	0.56	0.68	0.71
4	0.77	0.78	0.89	0.78	0.85	0.89
6	0.80	0.83	0.87	0.89	0.94	0.98
8	0.87	0.89	0.96	0.97	1.01	1.05
10	0.94	1.02	1.05	0.94	1.02	1.08



**Fig. 1.** Effect of contact time on the removal of fluoride by polyaniline ( $\text{R}=\text{H}$ ).

nature. The effect of contact time between the P(ANi) and adsorbate is depicted in Fig. 1. It is evident from the figure that 0.74 mg/g of fluoride was removed within 5 min and the same remains almost unaltered even up to 6 h. This may be due to the fact that once certain amount of fluoride ions gets doped onto the P(ANi) within a given time, no more doping occurs afterwards, i.e., the doping level might have reached [19]. Further, the attainment of maximum doping level within 5 min suggests that a very minimum contact time is sufficient enough for the removal of fluoride from water by P(ANi).

### 3.2. Effect of dose

The effect of dose of P(ANi) on the removal of fluoride is shown in Fig. 2. It was observed that the amount (mg/g) of fluoride removed is decreased with the increase in dose. The maximum removal of fluoride was found to be 0.78 mg/g at a P(ANi) dose of 25 mg/50 ml. This increase in fluoride removal is due to the availability of higher number of fluoride ions per unit mass of P(ANi), i.e., higher fluoride/P(ANi) ratio. Further experiments were carried out using 50 mg

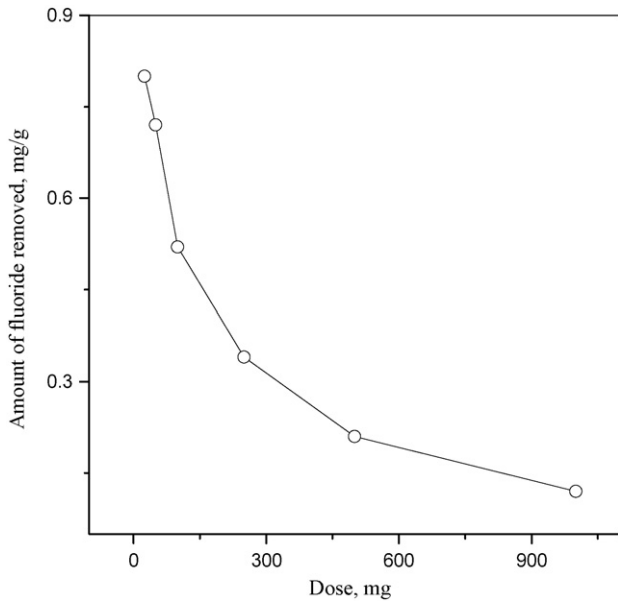


Fig. 2. Effect of dose on the removal of fluoride by polyaniline (R=H).

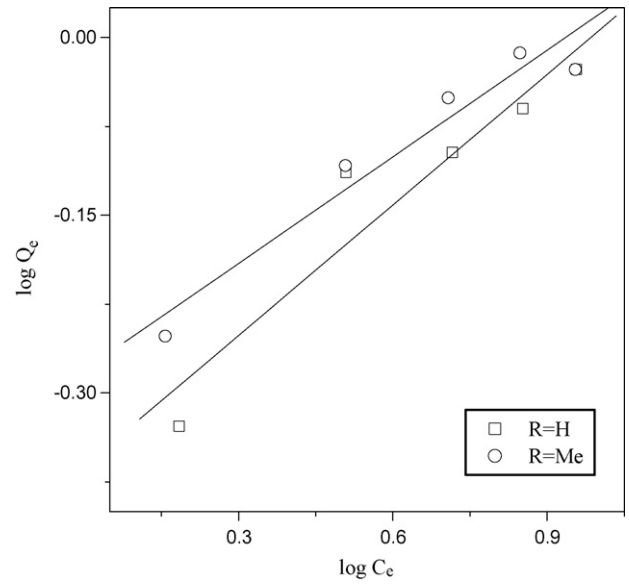


Fig. 4. Freundlich isotherms for the removal of fluoride by polyanilines.  $T=30\text{ }^{\circ}\text{C}$ ; contact time = 30 min; pH 7.

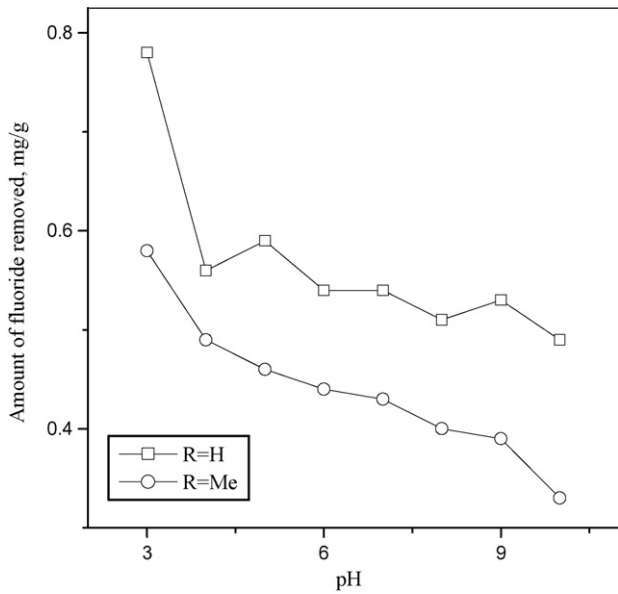


Fig. 3. Effect of pH on the removal of fluoride by polyanilines.

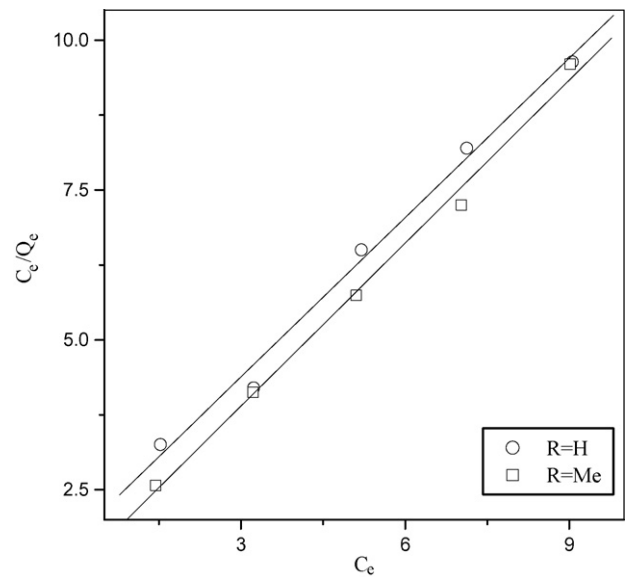


Fig. 5. Langmuir isotherm for the removal of fluoride by polyanilines.

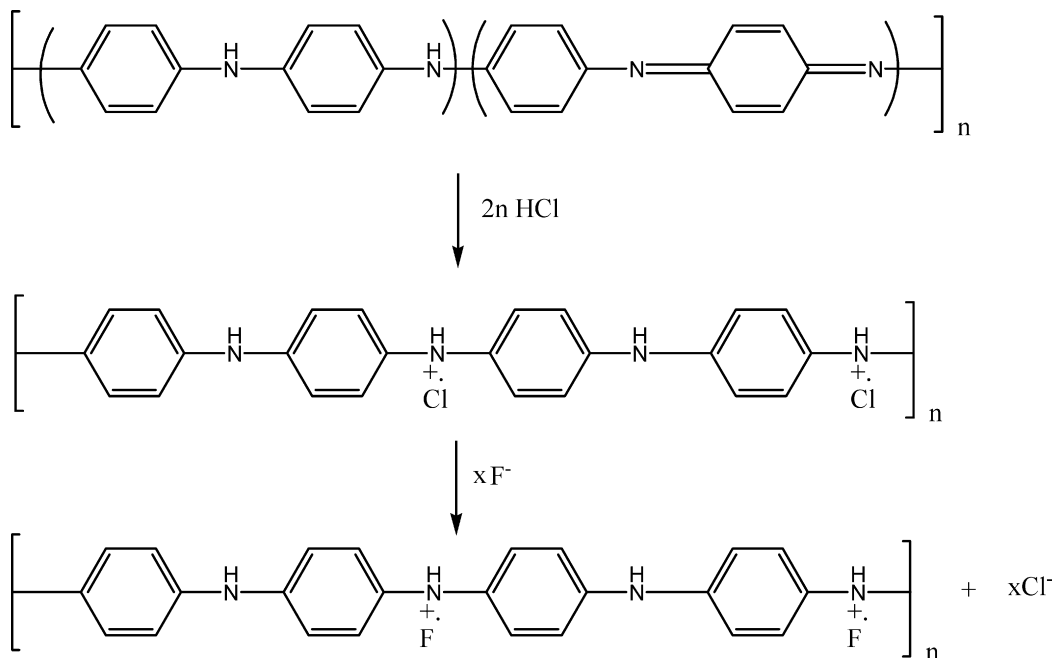
**Table 2**  
Langmuir and Freundlich isotherm constants for the removal of fluoride by polyanilines

Isotherm	Statistical parameter/constants	R=H temperature			R=Me		
		30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Freundlich	<i>r</i>	0.95	0.97	0.97	0.97	0.99	0.99
	S.D.	0.04	0.03	0.05	0.03	0.01	0.01
	<i>n</i>	2.72	2.63	2.82	3.34	4.54	4.54
	<i>K</i>	0.43	0.44	0.49	0.52	0.65	0.68
Langmuir	<i>r</i>	0.99	0.99	0.99	0.99	0.99	0.99
	S.D.	0.29	0.36	0.37	0.23	0.09	0.08
	$Q^0$	1.13	1.23	1.82	1.10	1.13	1.19
	<i>b</i>	0.51	0.45	0.55	0.76	1.05	1.02

of P(ANi) per 50 ml of fluoride solution, as it exhibits appreciable removal capacity, for optimization of adsorption parameters.

### 3.3. Effect of pH

The increase in pH of the solution drastically decrease the fluoride uptake from 0.78 to 0.49 mg/g when the pH increasing from 3 to 10 (Fig. 3). This is due to the fact that in acid medium (HCl) the polymer undergoes full protonation with doping of chloride ions yielding a radical cation structure as shown below [20].



But the chloride ion is a more fleeting dopant [21] and is might have been replaced by fluoride ion when agitated with sodium fluoride solution leading to higher fluoride removal in acidic medium. Further, the point of zero charge of the polyanilines suggests the presence of some weakly acidic groups in the polymer which would attract fluoride ions electrostatically [22]. However, with increase in pH, the OH<sup>-</sup> ion may compete with fluoride ion in doping and consequently the efficiency of fluoride removal is decreased [22].

### 3.4. Adsorption isotherms

The distribution of sorbate between the solid and the solution interface at equilibrium has been described by the Freundlich [23] and Langmuir [24] 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.

The Freundlich equation is commonly presented as

$$\log Q_e = \log K + \frac{1}{n \log C_e} \quad (1)$$

where  $K$  and  $n$  are temperature dependent constants, adsorption capacity and intensity of adsorption respectively,  $C_e$  and  $Q_e$  have the usual meanings. Linear plots of  $\log Q_e$  against  $\log C_e$  (Fig. 4) indicate the applicability of the Freundlich isotherm. The statistical parameters of these plots along with the Freundlich constants are given in Table 2. The results indicate that the adsorption capacity,  $K$ , increases with rise in temperature suggesting that the uptake of fluoride by P(ANi) is an endothermic process. Further, the values of intensity of adsorption ( $n$ ) are greater than unity indicating that the process is favourable.

To quantify the adsorption capacity of the P(ANi) for the removal of fluoride from aqueous solutions, Langmuir equation is applied. The Langmuir adsorption isotherm can be written as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (2)$$

where  $C_e$  and  $Q_e$  have the usual meanings and  $Q^0$  and  $b$  are the Langmuir constants related to the capacity and energy of adsorption, respectively. The linear plots of  $C_e/Q_e$  versus  $C_e$  (Fig. 5) indicate the applicability of Langmuir adsorption isotherm. By comparing

the results presented in Table 2, it can be seen that the Langmuir model is the best fitting model for isotherm data of fluoride removal by P(ANi) than the Freundlich model. Additionally, the values of  $Q^0$  calculated by the Langmuir equation were close to those determined experimentally. These facts suggest that the removal of fluoride by polyanilines involves a monolayer coverage of fluoride on the surface of the polymer [2,25,26].

### 3.5. Thermodynamic parameter

The standard free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were calculated from the variation of equilibrium constant,  $K_0$ , with temperature. The values of  $K_0$  and other thermodynamic parameters for the defluoridation process were determined by the reported method [2] and are summarized in Table 3. The values of enthalpy change are positive indicating the endothermic nature of the process. The positive  $\Delta G^0$  values indicate that the process is nonspontaneous. The negative or low positive values of  $\Delta S^0$  reveal that during the doping of fluoride ions onto the polymers the degree of internal freedom of the system are decreased [27].

### 3.6. Effect of co-ions

The effect of added co-ions viz. Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> on the amount of fluoride removed (mg/g) is given in Table 4. The results indicate that addition of these common co-ions, except bicarbonate, does not have any significant effect on the defluoridation capacity of P(ANi). This behaviour shows that P(ANi) can

**Table 3**  
Equilibrium constants and thermodynamic parameters for the removal of fluoride by polyanilines

[F] mg/l	$K_0$			$\Delta G^0$ (kJ mol <sup>-1</sup> )			$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (kJ <sup>-1</sup> mol <sup>-1</sup> )
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C		
R = H								
2	0.307	0.325	0.351	2.97	2.92	2.81	5.4	8
4	0.238	0.242	0.286	3.61	3.68	3.36	7.4	12
6	0.154	0.161	0.170	4.71	4.76	4.76	3.9	2.4
8	0.122	0.125	0.138	5.29	5.41	5.35	4.5	2.6
10	0.104	0.114	0.117	5.7	5.68	5.75	5.0	2.2
R = Me								
2	0.389	0.515	0.550	2.38	1.72	1.60	14	39
4	0.242	0.270	0.286	3.57	3.41	3.35	6.8	11
6	0.174	0.186	0.195	4.40	4.38	4.38	4.6	0.8
8	0.138	0.144	0.151	4.98	5.03	5.07	3.7	-4.3
10	0.109	0.114	0.121	5.59	5.66	5.67	4.4	-3.9

effectively remove fluoride in the presence of other such common anions. In the case of bicarbonate ions, there is a very slight reduction in the amount of fluoride adsorbed with increase in its concentration. Parallel interference of bicarbonate ions on the defluoridation has been cited earlier [2,22].

### 3.7. FT-IR and XRD studies

The FT-IR spectra of the undoped polyaniline (R = H) and that of after doping with fluoride ions are shown in Fig. 6a and b. The FT-IR spectrum (Fig. 6a) of the undoped P(ANI) resembles that the one reported earlier in literature [17,28,29]. The peak around 3400 cm<sup>-1</sup> corresponds to the characteristic N–H stretching vibrations which further indicates that the polymer linkage were not at the N-group and thus likely on the aromatic ring. It was observed that (Fig. 6b)

the heavily doped states of these polyanilines yield a band around 1566–1581 cm<sup>-1</sup>, corresponding to the N–H bending of the amine salts and strong band in the 1100 cm<sup>-1</sup> region corresponding to the dopant [17,28–30]. These observations strongly suggest that the removal of fluoride by these polyanilines is via doping mechanism.

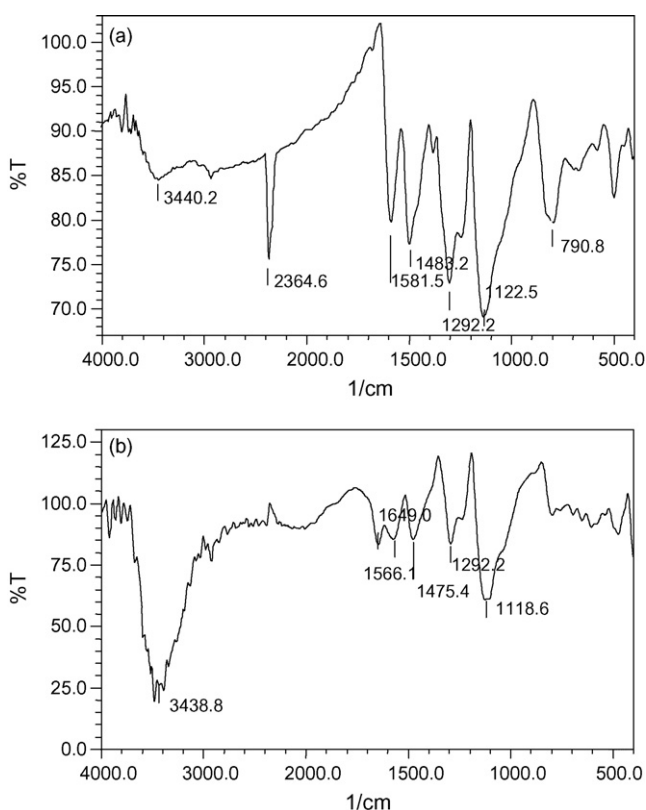
The XRD patterns of the polyanilines before and after doping are shown in Figs. 7a–d. It is evident from the figures, Fig. 7a and c that the polyanilines in the undoped form exist in the amorphous form which remains unaltered after doping (Fig. 7b and d). This is due to the fact that the P(ANI) prepared in the undoped form show poor or no crystallinity, which does not improve even with doping [17].

### 3.8. EDAX analysis of fluoride-P(ANI)

Energy-dispersive analysis of X-rays was used to analyze the elemental constituents of the P(ANI) before and after doping of fluoride ions are shown in Fig. 8a and b, respectively. It shows that the presence of fluoride appears in the spectrum after doping (Fig. 8b) along with other principal element C and minor elements O, Cl and Au. The signal found for Au is due to the spattering of gold chloride during the analysis. EDAX analysis provides direct evidence for the doping of fluoride ions onto P(ANI) [33].

### 3.9. 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. For different adsorbents the values of Langmuir isotherm constants for the adsorption of fluoride ions are summarized in Table 5. Although direct comparison of P(ANI) and methyl substituted P(ANI) with other adsorbents is difficult, owing to the different applied experimental conditions, it was found, in general, that the adsorption capacity of the adsor-

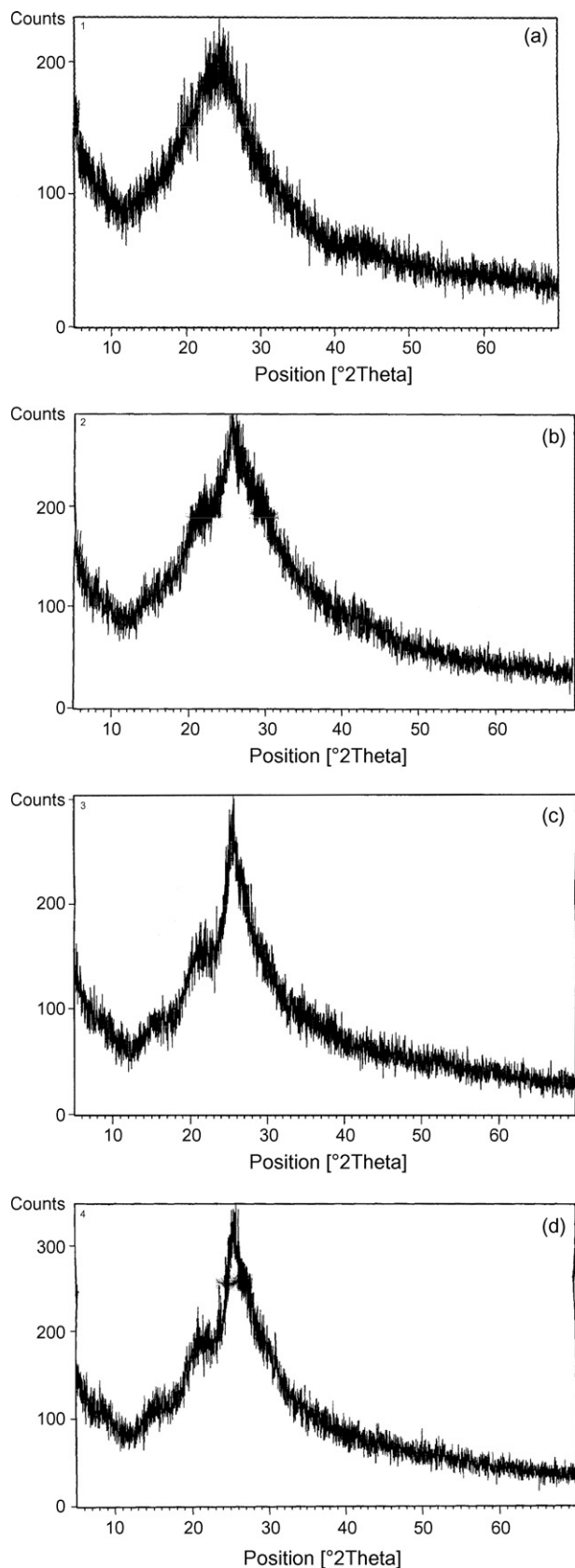


**Fig. 6.** (a) FT-IR spectrum of polyaniline (R = H) and (b) FT-IR spectrum of fluoride doped polyaniline (R = H).

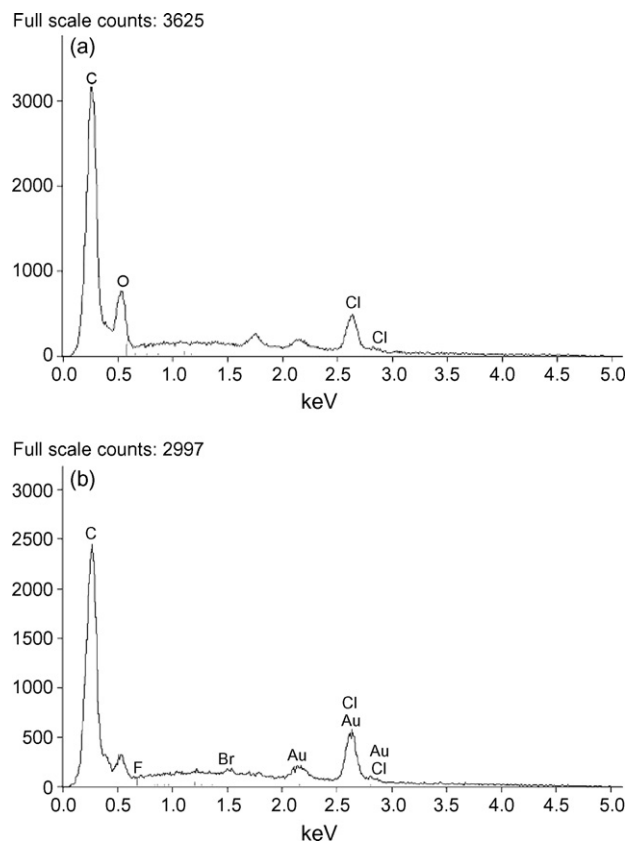
**Table 4**  
Effect of co-ions on the amount of fluoride adsorbed (mg/g) by polyanilines

Co-ion	Concentration (mg/l)					
	0	100	200	300	400	500
R = H						
Chloride	0.78	0.74	0.76	0.75	0.81	0.84
Sulphate	0.78	0.72	0.73	0.69	0.74	0.76
Bicarbonate	0.78	0.72	0.72	0.68	0.64	0.51
R = Me						
Chloride	0.78	0.82	0.79	0.85	0.83	0.77
Sulphate	0.78	0.79	0.68	0.72	0.86	0.69
Bicarbonate	0.78	0.77	0.75	0.69	0.66	0.68

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



**Fig. 7.** (a) XRD pattern of polyaniline (R=H), (b) XRD pattern of fluoride-doped polyaniline (R=H), (c) XRD pattern of polyaniline (R=Me) and (d). XRD pattern of fluoride doped polyaniline (R=Me).



**Fig. 8.** (a) EDAX spectra of polyaniline (R=H) and (b) EDAX spectra of fluoride doped polyaniline (R=H).

bents for fluoride ions is comparable with that of other adsorbents and in fact greater than certain adsorbents reported earlier.

### 3.10. Test with field samples

The utility of the adsorbent has been tested by treating water samples collected from water sources located at Gopalpatti (sample 1) and Theppakulathupatti (sample 2) of Dindigul District, Tamil Nadu, S. India. Compositions (all in mg/l except pH) of the water samples are, respectively, pH: 7.98, 7.62; total alkalinity: 452, 310; total hardness: 325, 740; total dissolved solids: 588, 1190;  $\text{Cl}^-$ : 60, 310;  $\text{F}^-$ : 1.92, 2.88;  $\text{SO}_4$ : 13, 50. The amount of fluoride adsorbed (mg/g) by the adsorbent from samples 1 and 2 were found to be 0.38 and 0.68, respectively which is in close agreement with the results mentioned above.

**Table 5**

Langmuir isotherm parameters for the adsorption of fluoride ion from aqueous solution by different adsorbents

Adsorbent	Langmuir constants		Reference
	$Q^0$ (mg/g)	$b$ (l/mg)	
Activated alumina	2.41	0.31	[31]
Fluorspar	1.79	0.091	[32]
Activated quartz	1.16	0.086	[32]
Calcite	0.39	0.023	[32]
Quartz	0.19	0.12	[32]
Plaster of Paris	0.366	0.830	[2]
NPC	2.732	0.028	[25]
P(ANi)	1.82	0.55	Present work
Substituted P(ANi)	1.19	1.02	Present work

### 3.11. Regeneration studies

The regeneration of the spent adsorbent has been carried out by stirring it with 0.1 M NH<sub>4</sub>OH solutions for 6 h followed by treating with hydrochloric acid which yielded the Emeraldine salt, as many times as we require.

## 4. Conclusion

The polyanilines show considerable potential for the removal of fluoride ions from aqueous solutions. Lower 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 and EDAX studies reveal that the defluoridation of water occurs via doping of fluoride ions onto the polyanilines which may be depicted as



## Acknowledgement

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## References

- [1] World Health Organization (WHO) Guidelines for drinking, 1993 45–46.
- [2] V. Gopal, K.P. Elango, Equilibrium, kinetic and thermodynamic studies of adsorption of fluoride onto plaster of Paris, *J. Hazard. Mater.* 141 (2007) 98–105.
- [3] E.J. Reardon, Y. Wang, Limestone reactor for fluoride removal from waste waters, *Environ. Sci. Technol.* 34 (2000) 3247–3253.
- [4] S. Saha, Treatment of aqueous effluent for fluoride removal, *Water Res.* 27 (1993) 1347–1350.
- [5] G. Singh, B. Kumar, P.K. Sen, J. Maunder, Removal of fluoride from spent pot liner leach ate using ion exchange, *Water Environ. Res.* 71 (1999) 36–42.
- [6] A. Dieye, C. Larchet, B. Auclair, C. Mar-Diop, Elimination des fluorures parla dialyse ionique croisee, *Eur. Polym. J.* 34 (1998) 67–75.
- [7] Z. Amer, B. Bariou, N. Mameri, M. Taky, S. Nicolas, A. Elimidaoui, Fluoride removal from brackish water by electro dialysis, *Desalination* 133 (2001) 215–223.
- [8] N. Mameri, H. Lounici, D. Belhocine, H. Grib, D.L. Prion, Y. Yahiat, Defluoridation of Sahara water by small electro coagulation using bipolar aluminium electrodes, *Sep. Purif. Technol.* 24 (2001) 113–119.
- [9] M. Hichour, F. Persin, J. Sandeaux, C. Gavach, Water defluoridation by Donann dialysis and electro dialysis, *Sep. Purif. Technol.* 18 (2000) 1–11.
- [10] M. Hichour, F. Persin, J. Sandeaux, C. Gavach, Water defluoridation by Donann dialysis and electro dialysis, *Rev. Sci. Eau.* 12 (1999) 671–686.
- [11] S.K. Adikari, U.K. Tipnis, W.P. Harkare, K.P. Govindan, Defluoridation during desalination of brackish water by electrodialysis, *Desalination* 71 (1989) 301–312.
- [12] S. Venkata Mohan, N. Chandrasekhar Rao, J. Karthikeyan, Adsorption removal of direct azo dye aqueous phase onto coal-based sorbents a kinetic and mechanistic study, *J. Hazard. Mater.* 90 (2) (2002) 189–204.
- [13] T. Kobayashi, H. Yoneyama, H. Tamura, Polyaniline film-coated electrodes as electrochemical display devices, *J. Electroanal. Chem.* 161 (1984) 419–421.
- [14] M.V. Deshpande, D.P. Malnerkar, Biosensor prepared from electrochemically synthesized conducting polymers, *Prog. Poly. Sci.* 18 (1993) 623–649.
- [15] A.G.M. Diarmid, S.L. Mu, N.L. Somasiri, W. Wu, Electrochemical characteristics of polyaniline cathodes and anodes in aqueous electrolytes, *Mol. Cryst. Liq. Cryst.* 121 (1985) 187–190.
- [16] R. Noufi, A.J. Nozik, J. White, L.F. Warren, Enhanced stability of photoelectrodes with electrogenerated polyaniline films, *J. Electrochem. Soc.* 129 (1982) 2261–2265.
- [17] P. Chandrasekhar, *Conducting Polymers: Fundamentals and Applications a Practical Approach*, Kluwer Academic Publishers, Hingham, USA, 1999.
- [18] Y.F. Jia, B. Xiao, K.K. Thomas, Adsorption of metal ions on nitrogen surface functional groups in activated carbon, *Langmuir* 18 (2002) 470–478.
- [19] M. Mahramanlioglu, I. Kizilcikli, I.O. Bicer, Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, *J. Fluorine Chem.* 115 (2002) 41–47.
- [20] B.J. Jhonson, S.M. Park, Electrochemistry of conductive polymers, *J. Electrochem. Soc.* 143 (4) (1996) 1277–1282.
- [21] A.G.M. Diarmid, A.J. Epstein, Polyanilines: a novel class of conducting polymers, *Faraday Discuss. Chem. Soc.* 88 (1989) 317–332.
- [22] V. Aravind, K.P. Elango, Adsorption of fluoride onto magnesia-equilibrium and thermodynamic study, *Indian J. Chem. Technol.* 13 (2006) 476–483.
- [23] H.M.F. Freundlich, Over the adsorption in solution, *Z. Phys. Chem. A* 57 (1906) 385–470.
- [24] I. Langmuir, Adsorption of gaseous on plane surface of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (9) (1918) 1361–1403.
- [25] K.P. Elango, V. Gopal, Adsorption of fluoride onto activated newspaper carbon: an equilibrium, kinetic and thermodynamic study, *Environ. Sci. Ind. J.* 2 (2007) 75–83.
- [26] M. Karthikeyan, K.P. Elango, Defluoridation of water using aluminium impregnated activated newspaper carbon, *Environ. Sci. Ind. J.* 2 (3) (2007) 187–193.
- [27] M. Doula, A. Ioannou, A. Dimirkou, Thermodynamics of copper adsorption, desorption by Ca-kaolinite, *Adsorption* 6 (2000) 325–335.
- [28] P. Chandrasekhar, R.W. Gumbs, Electrosyntheses, spectroelectrochemical, electrochemical, and chronovoltabsorptometric properties of family of poly (aromatic amines), novel processible conducting polymers, *J. Electrochem. Soc.* 138 (5) (1991) 1337–1346.
- [29] P. Chandrasekhar, J.R.G. Pthorne, R.M. Hochstrasser, Third-order nonlinear optical properties of poly(diphenyl amine) and poly(4-amino biphenyl), novel processible conducting polymers, *Appl. Phys. Lett.* 59 (1991) 1661–1663.
- [30] T. Fukuda, H. Takezoe, K. Ishikawa, A. Fukuda, IR and Raman studies in three polyanilines with different oxidation levels, *Synth. Metals* 69 (1995) 175–176.
- [31] G. Subhasini, K.K. Pant, Equilibrium kinetics and break through studies for adsorption of fluoride on activated alumina, *Sep. Purif. Technol.* 42 (2005) 265–271.
- [32] X. Fan, D.J. Parker, M.D. Smith, Adsorption of fluoride on low cost materials, *Water Res.* 37 (2003) 4929–4937.
- [33] S.S. Tripathy, J.L. Bersillon, K. Gopal, Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina, *Sep. Purif. Technol.* 50 (2006) 310–317.