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Defluoridation of water via doping of polyanilines

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

Department of Chemistry, Gandhigram Rural University, Gandhigram 624302, India

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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.

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 conductivity 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 made 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 (Emaraldine 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

* Corresponding author. Tel.: +91 451 2452371; fax: +91 451 2454466.
E-mail address: drkpelango@rediffmail.com (K.P. Elango).

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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 NH_4OH solutions and stirred for 6 h. The pH of this solution should be kept around nine by adding drops of 1 M NH_4OH. 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 (pH_{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 ± 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 was determined. All experiments were carried out twice and the adsorbed fluoride concentrations given were the means of duplicate experimental results.

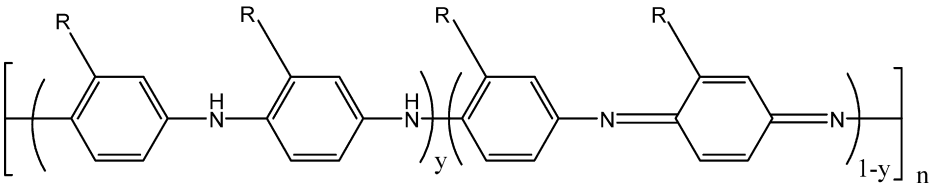
Experimental variables considered were initial concentration of fluoride ions 2–10 mg/l; contact time between P(ANi) and the fluoride solution 5–360 min; pH 3–10; dosage of P(ANi) 25–1000 mg/50 ml; temperature 30–50 °C and co-ions viz. chloride, sulphate, and bicarbonate ions.

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, pH_{ZPC}, of the polyanilines determined by the pH drift method are 6.89 and 6.92, respectively for R = H and R = 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 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).

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

[*F*] mg/l	Q_e (mg/g) 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

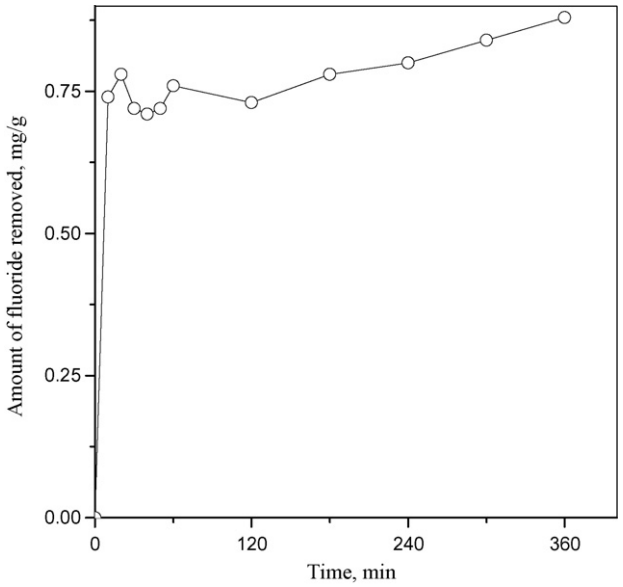


Fig. 1. Effect of contact time on the removal of fluoride by polyaniline (R = H).

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