Retrieval of Fluoride Using Polyaniline Polypyrrole Composite

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Abstract - **This paper explains the possible use fo Polyaniline polypyrrole composite (PANi/PPy) as an adsorbent for the removal of the fluoride ions, from aqueous solution. The adsorption of the fluoride was appreciable around the natural pH of the aqueous solution of fluoride ions. This shows that adsorption of the fluoride ions could be carried out on the PANi/PPy composite without adjusting the pH of the medium. The experimental data yielded perfect fits with Freundlich isotherm equation. The values of the adsorption coefficients computed from the isotherms indicated the potential of the adsorbent for practical applications in defluoridation processes. Adsorption kinetics obeyed a first-order kinetic model. Diffusion of the fluoride ions into the micro pores and macro pores is the rate-determining step in the mechanism of the adsorption process. The adsorption of fluoride ions on the PANi/PPy composite was non-spontaneous and endothermic in nature with the defluoridation capacity increasing with increasing temperature due to increase in the rate of adsorption.The enthalpy change for the adsorption process was in the range of 25-67 kJ mol^{-1}, which did not, indicates very strong chemical forces between the adsorbed fluoride ion and the PANi/PPy composite surface. This observation was well supported by the XRD pattern studies. Hence, physisorption seems to be the major mode of adsorption.**
Keywords: **adsorption, removal, fluoride, PANi, PPy, composite, thermodynamics, kinetics**

I.INTRODUCTION

Water is one of the most essential commodities available on the earth. This is required for many human activities like drinking, cooking, bathing etc. it is very important to maintain good quality of water as it is directly linked with man's daily life. Water is susceptible to get contaminated by any natural or artificial foreign matter. "Any alteration in the physical, chemical and biological properties of water, as well as combination of any foreign substance that leads to a health hazard or decrease in the utility of water" can be termed as water pollution.

Fluoride falls into the category of soluble salts. In recent years, ever increasing population pressure, evolving industrial chemical society and advances in science and technology have resulted in many questions about the safety of drinking water. In countries like India, where the majority of population live in villages with bare infrastructural facilities, illiteracy, lack of awareness, poor sanitation and hygiene, the concept of safe potable water assumes greater significance. If water containing excess fluoride is consumed consistently, it is found to be highly harmful to health. In India, the problem of excess fluoride content is prevailing in the states of Anthra Pradesh, Rajasthan, Karnataka, Maharastra, Tamilnadu, Madhya Pradesh, Uttar Pradesh and smaller pockets of other states. The permissible level of fluoride in drinking water is 1.5 ppm as per WHO standards. Since many food materials that we consume everyday (like common salts, tooth paste, etc.) contain excess of fluoride.

Excess fluoride in drinking water can lead to fluorosis. Fluorosis is a crippling and painful disease caused by intake of fluoride (>1.5 ppm). Fluoride can enter the body through drinking water, food, toothpaste, mouth rinses and other dental products; drugs, and fluoride dust and fumes from industries using fluoride containing salt and or hydrofluoric acid. This means that the body may tolerate fluoride upto a certain limit of 1.5 ppm depending upon the nutritional standards and body physiology.

The methods of defluoridation of water are based on the principles of precipitation, adsorption, ion-exchange, adsorption and exchange, reverse osmosis, electro chemically stimulated coagulation and electro dialysis. Among these methods adsorption is still one of the most extensively used methods for removing fluoride from water due to its low cost and viability

During recent past good amount of work has been carried out by many researchers on the removal of fluoride ions from water. The literatures pertaining to the removal of fluoride ions that are closely related to the present study only are documented hereunder. Polyaniline [1], Polypyrrole [2], Carboxylated cross-linked chitosan beads [3], Fe(III) loaded chitosan beads [4], nano-hydroxyapatite/chitosan (n-HApC) composite [5], La(III) incorporated carboxylated chitosan beads [6], hardened alumina cement granules [7], nano-hydroxyapatite [8], kaolinites [9], cellulose supported layered double hydroxides [10], graphite [11], aluminium impregnated activated news paper carbon[12], Fe-Al-Ce trimetal oxide [13], Tunisian clays [14], chitin, chitosan and lanthanum-modified chitosan [15], quick lime [16], Spirogyra sp-IO2 [17], calcined MgAl-CO_3 layered double hydroxides [18], magnetic-chitosan [19], waste carbon slurry [20], zirconium impregnated coconut shell carbon [21], powdered corn cobs [22], bayerite/SiO_2/Fe_3O_4 [23], α-Al_2O_3 [24], brick powder [25], titanium rich bauxite [26], concrete materials [27], trivalent cation exchanged zeolite F-9 [28], activated

alumina[29], inexpensive leaf adsorbents [30], lanthanum (III)-loaded adsorbents with different groups and polymer matrices [31], hydroxyapatite, fluorspar, calcite, quartz and quartz activated by ferric ions [32], amended clay [33], Andosols [34], South African clays [35], iron-oxide-rich soils [36], natural materials such as red soil, charcoal, brick, fly-ash and serpentine [37], electrochemical generated aluminium sorbent [38], acid treated spent bleaching earth [39], brushite and calcite [40], activated carbons prepared from *prosopis jolifera* [41], alumina supported on carbon nanotubes [42], mixed rare earth oxides [43], geomaterials [44], granular calcite [45], aluminium-impregnated carbon [46], kaolinite, bentonite, charfines, lignite and nirmali seeds [47], kaolinite [48], activated alumina [49], Kenyan Ando soil [50], fired clay chips [51], and zirconium [52], alum-impregnated activated alumina [53], coconut carbon shell [54], non-viable algal spirogyra IO1 [55], manganese-oxide- coated alumina [56], aluminium hydroxide polymers [57], portlandite, calcium silicate hydrate and ettringite in the cement paste [58],carbons of palmyra endocarps (PEC), palmyra male inflorescences (PMIC), mango shells (MGSC) and Maize shells (MZSC) [59], carbons of morringa indica(MIC), moringa pubescence(MPC) [60], dolomite [61].

II.MATERIALS AND METHODS

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

A.Adsorbent Preparation

A typical experiment was done as follows: 1 g of aniline and 1 g of pyrrole were dissolved in 100 ml of carbon tetrachloride and Solution I was thus obtained. Solution II was made by dissolving 6 g of APS into 100 ml of HCl (1 M). Solution II was carefully added up to Solution I and a liquid-liquid interface was visible. The solution near the interface turned dark quickly, indicating the beginning of the polymerization. The reaction was carried out at room temperature for 12 h and finally the resulting polymer separated into Solution II (water phase), leaving Solution I (oil phase) transparent. Then the mixture was filtered and the precipitate was washed repeatedly with water and acetone until the acetone washings were colorless. The resulting product was dried in vacuum at room temperature for 48 h.

B.Methods

The concentration of fluoride was measured using a fluoride ion-selective electrode (Eutech, Cyberscan, Singapore). pH measurements were made with Eutech digital pH/Ion meter. The FT-IR spectra were recorded using KBr disc on a FT-IR spectrometer (JASCO 460 Plus, Japan).

C.Batch adsorption experiments

Adsorption experiments were performed by agitating 0.1g of adsorbent with 50 mL of fluoride solution of desired concentrations at 30 ± 1^oC in different stoppered bottles in a shaking thermostat machine. At the end of pre-determined time intervals, the sorbate was filtered and the concentration of fluoride was determined. All experiments were carried out twice and the average values are given. Adsorbed fluoride concentrations were the means of the duplicate experimental results. Experimental variables considered were: (i) initial concentration of fluoride ions: 2-10 mg L^{-1}; (ii) contact time between adsorbent and the fluoride solution: 10-60 min; (iii) pH: 3-11; (iv) dosage of the adsorbent: 0.1-2g/50 mL; (v) temperature: 30-50°C ; and (vi) co-ions: Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^-.

D.Data Analysis

The experimental data were analyzed using Microcal Origin (version 6) computer software. The goodness of fit was discussed using correlation coefficient, *r*, and standard deviation, sd.

III.RESULTS AND DISCUSSION

A.Effect of agitation time and initial concentration

The amount of fluoride adsorbed per unit mass of the adsorbent (Qe, mg/g) onto the polyaniline-polypyrrole conducting polymer composite was studied and are presented in Table 1. The results indicated that the amount of fluoride adsorbed increased with an increase in the initial sorbate concentration and also with rise in temperature. The variation of Qe with temperature suggested that the adsorption is an endothermic process. However, this increase is only marginal. This may be due to the fact that with rise in temperature the enlargement of pores in the adsorbent may be to a very lesser extent as it is crystalline in nature.

The variation of Qe with contact time for different initial concentrations of fluoride (Fig. not shown) shows that the amount of fluoride adsorbed per gram of the adsorbent increased with time up to 40 min and then the curve became flattened indicating the attainment of equilibrium. It is also seen that the equilibrium time was independent of the initial concentration of fluoride. The changes in the rate of removal of fluoride may be due to the fact that, initially, all adsorbent sites were vacant and solute gradient was high. A decreasing removal rate particularly towards the end of the experiment indicated possible monolayer of fluoride ions on the outer surface and/or pores of the adsorbent [62].

B.Effect of adsorbent dosage

The amount of fluoride removed as a function of adsorbent dosage at 4 mg/L of initial fluoride concentration at 30^0 C was shown in Fig. 1. Adsorbent dosage was varied from

0.05 g to 0.250 g per 50 ml and equilibrated for 60 min. From the result it is evident that optimum dosage of 0.1 g /50ml is required for maximum removal for fluoride

C.Adsorption isotherms

Adsorption isotherms are important for the description of how adsorbate interacts with adsorbent surface and also are critical in optimizing the use of an adsorbent. Hence, in the present study, two well known isotherm equations viz. Langmuir [63] and Freundlich [64] isotherms have been applied for deeper interpretation of the adsorption data obtained. The adsorption isotherms for the adsorption of fluoride ions onto PANi-PPy are shown 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 physio-chemical interaction of fluoride ions with the adsorbents [2]. 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 [5].

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation.
$R_L = 1/ (1+bC_0)$ (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].

D.Thermodynamic parameters

The standard free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated from the variation of the thermodynamic equilibrium constant K_o. The values of K_o for the adsorption process were determined by the reported method [65]. The thermodynamic parameters were calculated using the following equations.

$\ln K_o = (\Delta S^o/R) - (\Delta H^o/RT)$ (4)
$\Delta G^o = -RT \ln K_o$ (5)
ΔH^o and ΔS^o were determined from the slope and intercept of the plot of $\ln K_o$ versus $1/T$ (figure not shown).

The equilibrium constants were given in Table 4. The endothermic nature of adsorption is indicated by an increase in K_o with rise in temperature. The standard free energy change, enthalpy and entropy changes are given in Table 4. The ΔG^o values are positive which mean that the reaction is non-spontaneous. The values of enthalpy of a sorption process may be used to distinguish between chemical and physical sorption [66]. For chemical sorption, enthalpy values range from 83 to 830 kJ mol^{-1}, while for physical sorption they range from 8 to 25 kJ mol^{-1}. On the basis of
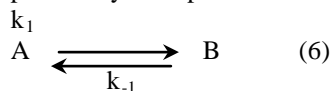
the above distinction, we conclude that fluoride ion sorption by PANi/PPy composite is a physical process. Positive values of ΔH^o suggest that the process is endothermic, so an increase of temperature encourages fluoride ion adsorption. Enhancement of adsorption capacity of PANi/PPy composite at higher temperatures may be attributed to the enlargement of the pore size and/or activation of the adsorbent surface and to the increase in the mobility of the fluoride ions. As indicated in Table 4, ΔS^o values for the adsorption process are positive. This observation suggests a high degree of disorderliness at the solid-solution interface during the adsorption of fluoride onto PANi/PPy composite. This may be due to the fact that the 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 [67].

E.Effect of pH

The effect of initial pH of the fluoride solution on the amount of fluoride ions adsorbed was studied. The percent removal of fluoride ion (by 0.1g of adsorbent per 50 mL of the solution at 4 mg L^{-1} of initial fluoride ion concentration) at pH values 3, 5, 7, 9, 11 and 0.90, 0.85, 0.92, 0.95 and 0.78 respectively. The results indicate that the adsorbent exhibits a commendable defluoridation capacity in wide range of pH.

F.Kinetics of adsorption

The sorption of fluoride ions form liquid phase to solid phase may be expressed as:
$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad (6)$$
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 PANi/PPy composite. 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 [68]. The rate constants for the adsorption (k_{ad}) and forward (k_1) and reverse (k_{-1}) processes are presented in Table 5, the values of k_1 were found to be lesser than that of k_{-1} suggesting desorption is dominant over adsorption.

G.FT-IR and XRD studies

The FT-IR spectra of the PANi/PPy is shown in figure 5. The FT-IR spectrum of the PANi/PPy resembles that the one reported earlier in literature for PANi and PPy [1,2]. The peak around 3400 cm^{-1} 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 (after doped with polymer composite, Fig not shown) the heavily doped sates of these polyanilines yield a band around 1566-1581 cm^{-1},

corresponding to the N-H bending of the amine salts and strong band in the 1100 cm^{-1} region corresponding to the dopant [1]. These observations strongly suggest that the removal of fluoride by these PANi/PPy composite is via doping mechanism.

The XRD patterns of the PANi/PPy before and after doping are shown in figures 6a and 6b. It is evident from the figure the Fig. 6a that the PANi/PPy composite exist in the amorphous form which remains unaltered after doping (Fig. 6b). This is due to the fact that the PANi/PPy prepared show poor or no crystallinity, which does not improve even with doping [1].

IV.CONCLUSION

PANi/PPy composite has demonstrated sufficient promise as an adsorbent for the removal of the fluoride ions, from aqueous solution. The adsorption of the fluoride was appreciable around the natural pH of the aqueous solution of fluoride ions. This shows that adsorption of the fluoride ions could be carried out on the PANi/PPy composite without adjusting the pH of the medium. The experimental data yielded perfect fits with Freundlich isotherm equation. The values of the adsorption coefficients computed from the isotherms indicated the potential of the adsorbent for practical applications in defluoridation processes. Adsorption kinetics obeyed a first-order kinetic model. Diffusion of the fluoride ions into the micro pores and macro pores is the rate-determining step in the mechanism of the adsorption process. The adsorption of fluoride ions on the PANi/PPy composite was non-spontaneous and endothermic in nature with the defluoridation capacity increasing with increasing temperature due to increase in the rate of adsorption.The enthalpy change for the adsorption process was in the range of 25-67 kJ mol^{-1}, which did not, indicates very strong chemical forces between the adsorbed fluoride ion and the PANi/PPy composite surface. This observation was well supported by the XRD pattern studies. Hence, physisorption seems to be the major mode of adsorption.

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