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Removal of F^- from Water Using PPyCl/ATP Composites

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Abstract. Conducting polypyrrole(PPy) was found to possess potential efficiency to remove F^- from aqueous solutions. In this study doped with Cl^- PPyCl/ATP composites were prepared via in-situ polymerization and employed as adsorbent to remove from aqueous solutions. The ability of the adsorbent to remove F^- from aqueous solution was demonstrated in a batch sorption mode. External factors such as initial concentration of F^-, contact time, adsorbent dosage and pH value of solution how to influence the adsorption efficiency of composites were investigated. The results showed that the adsorption efficiency is strongly pH, initial concentration and adsorbent dose dependent. Experiment data fitted well to the Langmuir isotherm model. The adsorption kinetics is described by the pseudo-second-order model. Meanwhile, the adsorption may proceed by an ion exchange mechanism between Cl^- and F^-.

Introduction

Nowadays, fluoride is one of the most abundant constituents occurring in the groundwater in many parts of the world. Low levels of fluoride are required for humans and other animals and have beneficial effect on tooth and bone structures. 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]. However, an excessive fluoride in drinking water can give rise to a number of adverse effects. So, fluoride-related health hazards are considered to be a major environmental problem. It is suggested that the solution lies only in prevention; the fluoride should be removed from its source of entry using appreciate technologies.

During recent years, several technologies have been applied to remove fluoride from drinking water, such as adsorption, chemical treatment, ion exchange, membrane separation, electrolytic defluoridation and electro dialysis [2-8], etc. Most of the methods have distinct limitations and disadvantages, while adsorption is the most widely used method because it is simple, economical and efficient for producing high quality water.

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 [9]. Polypyrrole(PPy) is one of the most commonly investigated conducting polymer due to its high electrical conductivity and simple preparation. PPy can be applied in various fields such as microelectronics, composite materials, optics and biosensors and as adsorbent due to its ion exchange capacities [10-11].

During chemical polymerization of pyrrole, charge balance or electroneutrality of the polymer matrix is maintained by incorporation of anions from the reaction solution. It is revealed that PPy synthesized in solutions with small dopants such as Cl^-, ClO_4^-, NO_3^-, etc., mainly exhibits anion-exchanger behavior due to the high mobility of these ions in the polymer matrix[12]. As a result, polypyrrole can be used to remove fluoride ions from water.

Attapulgite (ATP) is a kind of crystalline hydrated magnesium aluminum silicate mineral with a fibrillar structure[13]. Presently, ATP and activated ATP, which is a natural, cheap, adsorbent clay mineral with exchangeable cations and reactive-OH groups on its surface[14], have been intensively used as adsorbents for the removal of heavy metal ions and organic pollutants[15]. However, adsorption capacities of ATP are too low to satisfy the effective demand. To enhance its adsorption capacity, organic modified ATP with small molecules or polymers, have been intensively investigated for the removal of harmful ions in groundwater [13].

Hence, it is noteworthy to make composites of two adsorbents (conducting polymer and natural

nanomaterials), which will be of eco-friendly in nature and to study their potential for the removal of fluoride ions from water. Therefore, in this work, using in-situ polymerization method PPy doped with Cl^- was carried on the surface of ATP, PPyCl/ATP composites were prepared to remove F^-. The batch sorption method was used to investigate adsorption equilibrium and kinetics of the adsorption process.

Experimental

Materials and characterization. The attapulgite used in the study was provided by Xuyu, Jiangsu Province, China. Pyrrole was purchased from Shanghai Zhongqin Chemical Reagent Co. Ltd. and was distilled prior to use. Anhydrous ferric chloride ($FeCl_3$), as oxidant and dopant for polymerization of pyrrole, was purchased from Yantai Shuangshuang chemical Co. Ltd.. Stock solutions of F^- were prepared by dissolving NaF in distilled water. All the reagents used were of analytical-reagents grade. The morphology of nanocomposites was examined using a JSM-670 scanning electron microscope (SEM) (Electronics optical Ltd., Japan). The concentration of fluoride ions and pH were measured using ion-selective meter (PXS—270, Shanghai, China).

Preparation of composites. 5g $FeCl_3$ was added into 100mL distilled water and stirred until totally dissolved. 1g ATP was added into the solution, then freshly distilled pyrrole (1mL) dropped into the mixture and black precipitation appeared. The reaction was allowed to continue for 4h, then the precipitation was filtered, washed with distilled water and acetone until the washing liquid was colorless, and dried at temperature about 60℃for 24h.

Batch experiments. Batch experiments were carried out by adding certain qualities of PPyCl/ATP composites and 20mL solution of NaF with desired concentration and appropriate pH into a flask and stirring at room temperature. After filtrating, the ion-selective meter was employed to analyse the residual quantity of F^- in order to calculate the adsorption efficiency and adsorption capability. Experimental variables considered were initial concentration of NaF 5~21mg/L; contact time between PpyCl/ATP and NaF solution 0.5–2.5 h; pH 1–12; dosage of composites 0.1-0.35g. The efficiency of adsorbent was calculated through the following equation:

$$E = \frac{c_0 - c}{c_0} \times 100\% \quad \text{(Eq.1)}$$

$$q = \frac{(c_0 - c_e)V}{m} \quad \text{(Eq.2)}$$

where E is the adsorption efficiency, c_0 (mg/L)and c_e (mg/L) are the initial and outlet concentration of F^- concentration in solution. V was the solution volume and m was the mass of PpyCl/ATP adsorbent.

Results and Discussion

Effect of contact time. The effect of contact time was depicted in Fig.2. As can be seen that adsorption efficiency changes little with contact time increased from o.5h to 2.5h, and after 1.5h the adsorption equilibrium was reached. This might be due to the fact that once certain amount of F^- gets adsorbed onto PPyCl/ATP within a given time, no more removal occurs afterwards, i.e. the removal level might have reached. So, 1.5h was selected as contact time in this study.

Effect of absorbent dose. The effect of adsorbent dose on the equilibrium uptake of F^- was investigated and the result was shown in Fig.3. It was observed that with the amount of adsorbent increasing the value of adsorption efficiency increased because more active adsorption sites can be available. However, the value of adsorption capacity of F^- decreased. Considered two factors (the adsorption efficiency and the adsorption capacity), 0.18g of adsorbent was selected for further study, which the adsorption efficiency is 74.71%.

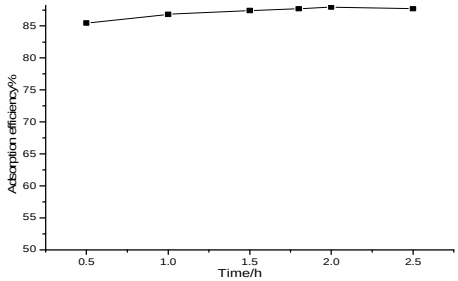

Fig.2 Effect of contact time

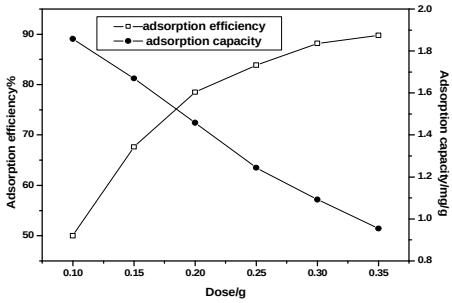

Fig.3 Effect of absorbent dose

Effect of initial concentration of F^-**.** The influence of initial concentration of F^- was investigated. It can be seen from Fig.4 that with the initial concentration of F^- improved from 5mg/L to 21mg/L the adsorption efficiency decreased from 93.32% to 74.88%, which means that there are no more adsorption sites for F^- due to fixed adsorbent dose. However, with the initial concentration of F^- improvement the adsorption capacity increased. Considered two factors the initial concentration of F^- was chosen as 12mg/L.

Effect of pH. The effect of initial pH of the solution on the removal of F^- by PPyCl/ATP is depicted in Fig. 5. The results implied that with an increase in pH the adsorption efficiency gradually increased and there was hardly any removal at pH 11. The decrease of solution pH values will increase the H^+ concentration and can lead to the selective adsorption of H^+ on the surface of the PPyCl/ATP[12] Thus low adsorption efficiency can be found at pH=1~2. However, F^- might be exchanged(because of the smaller size of the F^- ions) easily with Cl^- (as dopant in PPyCl/ATP)onto the surface of PPyCl/ATP, leading to enhanced removal of F^- from the aqueous solution at 5<pH< 7. Drinking water pH normally ranges from 6.5 to 8.5 and hence the nanocomposite is expected to perform optimally in drinking water defluoridation. In the alkaline pH range, there is a selective adsorption of OH^- (OH^- being physically smaller than Cl^-) [12], replacing Cl^-. For F^-, it is difficult to exchange with OH^- on the surface of PPyCl/ATP, adsorption efficiency of F^- decreased.

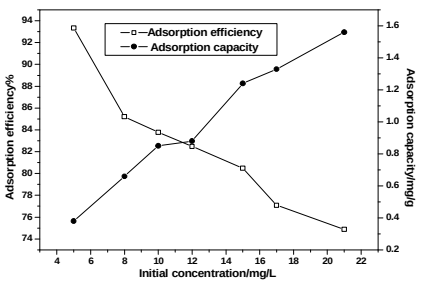

Fig.4 Effect of initial concentration of F^-

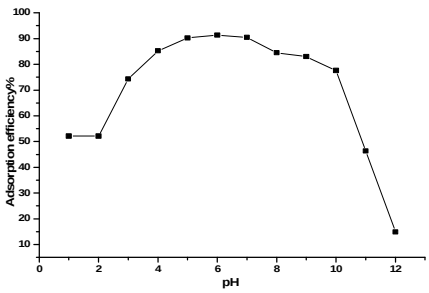

Fig.5 Effect of pH

Further, it is well suggested that these polymer, in the chloride ion doped form, remove fluoride ions from water via dopant-exchange mechanism[12]. Hence, in the present study the PPyCl/ATP composites remove fluoride ions from water through the ion-exchange mechanism using the N-atoms present in both the constituent polymers.

Adsorption isotherms. The distribution of sorbate between the solid and the solution interface at equilibrium has been described by the Freundlich and Langmuir equations. The two equations are presented by the following Eq.(3) and Eq.(4).

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \tag{3}$$

$$lnq_e = lnk_F + \frac{1}{n} lnc_e \tag{4}$$

Where q_m is the maximum adsorption capacity (mg/g) of the PPyCl/ATP nanocomposites; b is the free energy of dasorption (L/mg); k_F and n are the Freundlich isotherm parameters related to

adsorption capacity (mg/g) and intensity of adsorption. The linearized results and calculated values of Langmuir and Freundlich constants are listed in Table 1 and Table 2. The values of correlation coefficient reveal that Langmuir model fitted well the isotherm data compared to the Freundlich model, which indicates that the adsorption of F^- on the surface of PPyCl/ATP nanocomposites is a monolayer adsorption. It is also observed that there is an increase in the removal of F^- with an increase in temperature. This indicates that F^- adsorption by the PPyCl/ATP nanocomposite is endothermic in nature.

Table 1 Regression equation for Langmuir isotherms

Temperature/K	Regression equation c_e/qe	R^2	$qm/(mg\cdot g^{-1})$	$b/(L\cdot mg^{-1})$
298	$0.3879c_e+0.2699$	0.9953	2.5780	1.4372
308	$0.3828c_e+0.2445$	0.9924	2.6123	1.5656
318	$0.3782c_e+0.2244$	0.9976	2.6441	1.6854
328	$0.3739c_e+0.1930$	0.9979	2.6751	1.9369

Table 2 Regression equation for Freundlichr isotherms

Temperature/K	Regression equation ln qe	R^2	K	n^{-1}
298	$0.40779+0.62452\ln c_e$	0.9714	1.5035	0.62452
308	$0.46494+0.66686\ln c_e$	0.9501	1.5919	0.66686
318	$0.53199+0.63164\ln c_e$	0.9788	1.7023	0.63164
328	$0.67618+0.65713\ln c_e$	0.9837	1.9964	0.65713

Kinetics of adsorption. To understand the kinetic mechanism of the present adsorption process, various kinetics models, namely pseudo-first-order kinetics and pseudo-second-order kinetics model have been used for their validity with the experimental adsorption data. These kinetic equations can be linearly expressed as follows:

$$ln(q_e - q_t) = lnq_e - k_1 t \qquad \text{(Pseudo-first-order kinetics equation)}$$

$$\frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{(Pseudo-second-order kinetics equation)}$$

where q_e and q_t are the adsorption capacity (mg/g) of the adsorbent at equilibrium and at time t (s), respectively, $k_1(min^{-1})$ is the pseudo-first-order rate constant, k_2 (g/mg/min) is the pseudo-second -order rate constants. The linearizing results are shown in Table 4. According to the correlation coefficient (R^2), the kinetic data indicate that the adsorption process is controlled by pseudo-second-order model, which implies that the F^- uptake process is due to chemisorptions. The assumption behind the pseudo-second-order model is that the rate-limiting step may be chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

Table 4 Parameters for kinetic models of F^-adsorption onto PPyCl/ATP

$c_0/(mg\cdot L^{-1})$	pseudo-first order kinetics		Pseudo-second order kinetics	
	k_1/min^{-1}	R^2	$k_2 \times 10^6$ (g/mg/min)	R^2
19	0.0280	0.9801	13289.797	0.9998
15	0.0528	0.9901	7084.369	0.9999
13	0.0467	0.9827	2668.563	0.9999
9	0.0414	0.9816	2484.967	0.9999
7	0.0383	0.9735	861.115	0.9996

Conclusions

The PPyCl/ATP composites were performed via in-situ polymerization and the composites showed considerable potential for the removal of F^- from aqueous solutions. The various factors, such as adsorbent dose, contact time, initial concentration of F^- and pH were investigated. The optimum conditions of sorption were found: a sorbent dose of 0.18g, contact time of 1.5h, initial concentrate

of 12mg/L, a pH value of 5~7. The equilibrium data gained from this study fitted well to Langmuir models. The adsorption kinetics was described by the pseudo-second-order kinetic model. The adsorption may proceed by an ion exchange mechanism.

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