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Defluoridation using hybrid clay – influence of process conditions and modeling

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ABSTRACT

Fluoride contamination in groundwater is identified as a serious threat to the ecosystem due to its hazardous after-effects. In this experimental research, a hybrid clay was synthesized using clay and *Phoenix dactylifera* biochar and employed to remove fluoride under shaking conditions. Parametric experiments were conducted to study the effect of pH (2.0–9.0), initial fluoride concentration (10–40 mg/L), sorbent dose (0.25–8.0 g/L) and temperature (303–313 K) on defluoridation efficiency. At pH 3.0, the maximum fluoride removal efficiency of 90% was achieved with an equilibrium time of 180 min. Higher initial fluoride concentrations required more removal times due to the limitation of sorption sites availability. The following empirical equation relating fluoride uptake and clay dose was established as: $RE = 31.648\ln(w) + 34.424$. The kinetic data fitted well to pseudo-second-order model compared with power function model. The removal efficiencies increased with increase in temperature and confirmed the endothermic nature. The pseudo-second-order rate constant was determined as 0.0456 g/mg min at a temperature of 308 K and 30 mg/L fluoride concentration. Thermodynamic studies were conducted to verify the feasibility of sorption.

Keywords: Fluoride; Kinetics; Removal; Hybrid clay

1. Introduction

Fluoride pollution in groundwater caused by natural and man-made reasons has gained increased attention due to its toxic effects. Leaching of fluoride from rocks and soils is the natural sources of fluoride contamination in the ecosystem [1]. Industrial emissions from coal power plants, electroplating industries, semi-conductor manufacturing units, sewage system run-off and rubber industries are reported to be the main sources of fluoride pollution [2–5]. Fluoride is a nutritional requirement for humans, but reported to be acutely hazardous when exceeding its tolerance level. The WHO regulations recommended the maximum contaminant level of fluoride concentration as 1.5 mg/L and set a range of 0.5–1.0 mg/L as the desirable range [6]. Deficiency of fluoride in water causes dental caries and excess fluoride results in fluorosis, bone diseases, disorders in endocrine system, liver and thyroid glands [7,8]. The water should be made suitable and safe consumption in terms of fluoride levels. Removal of fluoride has been investigated using conventional methods such as ion-exchange, coagulation, adsorption, electrocoagulation and membrane separation techniques including reverse osmosis, nano-filtration and dialysis [2,7]. Conventional adsorbents such as activated carbon and resins have suffered limitations including excessive regeneration cost and limited adsorption capacity. Novel adsorbents based on biological origin, termed as biosorbents, are reported to be more effective and yield better uptakes. Nano-composite-based adsorbents using chitosan and polymer gelatin-based matrix [9] have been reported as potential techniques for removal of fluoride from aqueous medium. Clay minerals are identified as an equivalent replacement of any other adsorbent because of their increased surface area, beneficial surface properties and low cost. The cost of montmorillonite clay was reported to be 20 times lesser than the activated carbon [10]. Clays are identified to be natural scavengers and possess exchangeable

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cations and anions on their surfaces. Research studies on application of clay for the effective removal of boron [11], nickel and copper [12] and methylene blue [13] produced better removal efficiencies. In this background, this research study was aimed to synthesize a hybrid adsorbent made from naturally existing clay and biochar produced from date palm trees. The novelty of this research was to incorporate the beneficial surface properties of the biochar onto the clay surface in order to produce a composite adsorbent with superior surface properties. The parametric experiments were performed with respect to initial pH, initial fluoride concentration, clay dose and temperature. The experimental data were modeled using pseudo-second-order and power function models to verify the removal mechanisms.

2. Materials and methods

2.1. Chemicals

Sodium fluoride (NaF, Sigma-Aldrich) was utilized to prepare the stock solutions. All other chemicals used were of analytical grade.

2.2. Synthesis of hybrid clay

The natural form of clay, found commonly in Northern Oman, was used in this study and the characterization of the clay was reported in Rajamohan and Al-Sinani [11]. The clay identification was done based on X-ray diffraction analysis and the minerals were identified as kaolinite and illite. The clay received was in the form of bigger flocs and was ground and sieved to obtain particle size in the range of 0.85–1.70 mm. The barks of *Phoenix dactylifera* (date palm) tree, a native tree of Middle East countries, were used to produce the biochar. The tree barks were cut into small pieces and dried in sun for 5 d. The dried wood was pyrolyzed and converted into biochar using the given procedure [14]. The anionic surfactant, sodium oleate (20 mM), was dissolved in 1 L of deionized water. The Sarooj clay was dispersed in this surfactant solution and shaken for 2 h. The solution was centrifuged and the activated clay was separated and dried in an oven at 333 K. The activated clay was mixed with equal quantity of biochar (25 g each) and dissolved in 30 mL of acetone to improve the solubility. The mixture was agitated well for 1 h and the resultant solution was centrifuged in order to separate the solids. The solid residue was dried in an oven at 333 K. The oven dried product was sieve analyzed and the particle size in the range of 425–600 μm was chosen. The dried solid, a mixture of activated clay and biochar, is termed as hybrid clay and used throughout this experimental research.

2.3. Experimental studies

The experimental design consisted of parametric studies and kinetic modeling. The effect of operating variables, namely initial solution pH, initial fluoride concentration, dose of hybrid clay and temperature were studied. The performance evaluation parameters such as the removal efficiency and uptake capacities were evaluated. In the first set of experiments, the pH was varied in the range of 2.0–9.0 whereas the dose, fluoride concentration and temperature were fixed at 2.0 g/L, 30 mg/L and 308 K for an equilibrium time of 180 min. Initial pH was adjusted by adding either 0.1 N HCl or NaOH as the buffering agent. The initial concentrations of fluoride were varied at 10, 20, 30 and 40 mg/L and the removal performance was monitored at optimal pH and 308 K. The hybrid clay dose was varied in the range 0.25–8.0 g/L at fixed fluoride concentration of 30 mg/L under optimized pH. Studies were conducted in an environmental shaker to identify the effect of temperatures fixed at 303, 308 and 313 K with 30 mg/L fluoride concentration and 2.0 g/L of hybrid clay dose. All the experiments other than the effect of temperature studies were conducted at 308 K. Samples were withdrawn at predetermined intervals and filtered to remove the solids from fluoride solution. The filtrate was analyzed for residual fluoride concentrations using ion selective electrode [15]. The interference of co-existing ions was eliminated using the ionic strength adjustment buffer [1]. The experiments were repeated thrice and their relative standard deviations were in the acceptable range.

2.4. Kinetic modeling

The concentration–time dependence was studied by recording the fluoride removal profile at the selected fluoride concentrations. During the experimental period of 180 min, the samples collected in the periodic intervals were analyzed for residual fluoride concentration. Two popular models, namely pseudo-second-order model [16] and power function model [17] were employed. The linearized form of pseudo-second-order kinetic model is expressed as Eq. (1):

$$\frac{t}{q_t} = \frac{1}{k_2 {q_1}^2} + \frac{1}{q_1} t \tag{1}$$

where q_1 (mg/g) is the maximum adsorption capacity, q_t (mg/g) is the amount of fluoride adsorbed at time, t and k_2 (g/(mg min)) is the equilibrium rate constant for pseudo-second-order adsorption.

Power function model, represented by Eq. (2) was fitted to the experimental data:

$$q = k_p t^n \tag{2}$$

where k_p and n are model parameters.

The fluoride uptake was calculated by using the following Eq. (3):

$$q_t = (C_0 - C_e)V / w \tag{3}$$

where C_0 and C_e are the initial and equilibrium fluoride concentrations, respectively (mg/L); V is the volume of sample (L) and w is the hybrid clay dose (g).

The fluoride removal efficiency was evaluated by Eq. (4):

$$\text{Fluoride removal effeciency (RE)} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{4}$$

3. Results and discussion

3.1. Influence of pH

Separation processes do rely on the speciation of the ions present in aqueous solutions. The ions dispersed in solutions have tendency to form complexes at different pH values. In this study, the pH was varied at fixed fluoride concentration of 30 mg/L and its effect on fluoride removal efficiency was studied. Fig. 1 presents the effect of pH in the range of 2.0–9.0 and it was observed that the removal efficiency remained stable in the pH range of 2.0–3.0. The maximum removal efficiency of 90% was achieved at pH 2.0 and 3.0 and further increase in pH led to decrease in efficiency over the entire range of 4.0–9.0. The zeta potential (pHzc) for the hybrid clay was estimated to be 5.80. The surface is more positive when the pH values are less than the pHzc. At acidic pH values, higher positive charges prevail due to the protonation of the oxide groups present on the hybrid clay. The positivity of the surface decreased with increase in pH contributing to reduced removal of fluoride ions. Moreover, at pH values in the basic range, the competition between the negative fluoride ions and hydroxide ions could reduce the surface sorption. Similar observations on influence of pH for the removal of fluoride using red mud were reported [1]. The role of zeta potential on removal of fluoride ions was reported in related studies [7]. From this set of experiments, the optimal pH was confirmed as 3.0 and used for the experiments conducted hereafter.

3.2. Effect of initial fluoride concentration

The concentrations of the adsorbate are susceptible to variations depending on the external factors, either related to natural or industrial process. The influence of fluoride concentration was studied at 10, 20, 30 and 40 mg/L under optimized pH. Fig. 2 presents the change in removal efficiencies at different fluoride concentrations and fluoride remaining was found to increase with increase in initial concentrations. The fluoride removal rates were found to be faster during the initial 60 min due to the availability of the unoccupied active sites on the surface. Fluoride removal using polysulfone-red mud capsules reported similar observations and related to the free availability of sorption sites during initial period of sorbate–sorbent contact [1,11]. The removal efficiencies attained were higher at lower concentrations and tend to decrease at higher fluoride concentrations. The removal efficiency decreased from 94% to 65% when the concentration increased from 10 to 40 mg/L. Moreover, the time required to achieve the equilibrium removal was more at higher concentrations. Limited availability of surface active sites and competition between the excessive fluoride ions at higher concentration was reported as reasons for this phenomenon. Studies on removal of boron using clay reported similar observations and the time required for equilibrium removal increased from 50 to 80 min when the boron concentration increased from 25 to 100 mg/L [11].

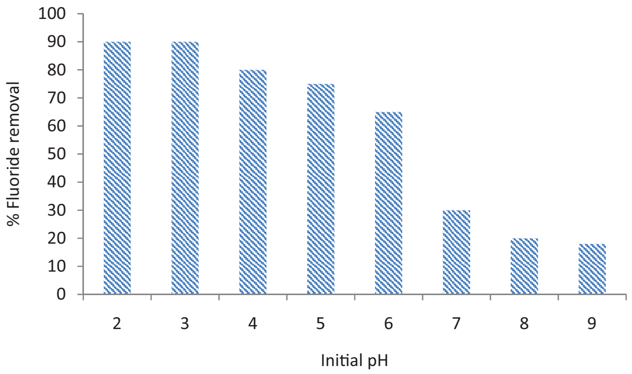

Fig. 1. Effect of initial pH on fluoride removal by hybrid clay (t = 180 min, C_0 = 30 mg/L, w = 2.0 g/L).

3.3. Effect of adsorbent dosage

Sorbent quantity is a measure of available surface area for contact with the sorbate ions dispersed in aqueous medium. The effect of hybrid clay dose was studied in the range of 0.25–8.0 g/L at fixed fluoride concentration (30 mg/L) and optimal pH (3.0). From Fig. 3, it was inferred that the removal efficiencies increased with increase in clay dose. The removal efficiencies attained varied from 31% at a dose of 0.25 g/L to 95% at a dose of 8.0 g/L. But, the variation was not linear without any proportionate change above dose of 2.0 g/L. The proportional increase in efficiency with dose in the initial

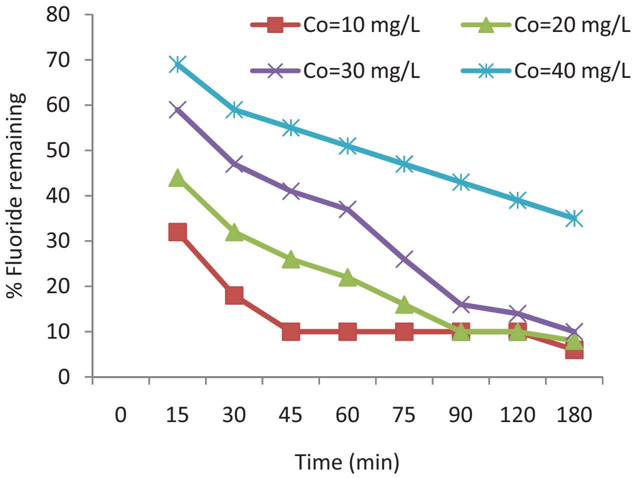

Fig. 2. Effect of initial fluoride concentration on percentage fluoride removal by hybrid clay (t = 180 min, pH = 3.0, w= 2.0 g/L).

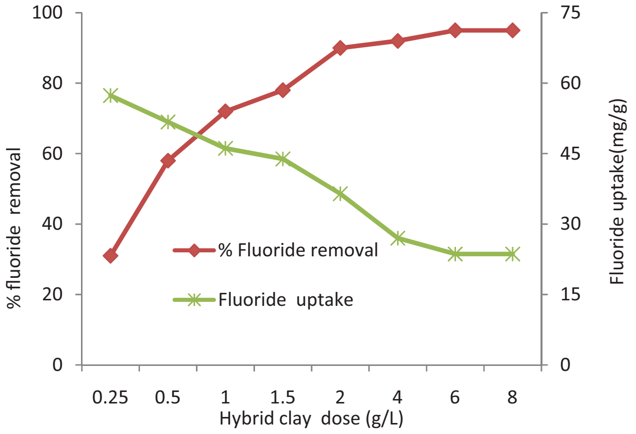

Fig. 3. Effect of hybrid clay dosage on percentage fluoride removal and uptake by hybrid clay (t = 180 min, C_0 = 30 mg/L, pH = 3.0).

phase was related to the availability of free sites and the flat pattern observed at higher doses was attributed to the saturation attained. Studied on removal of fluoride using activated carbon produced from *Ficus racemosa* reported similar results [18]. The fluoride uptake decreased with increase in sorbent dose and this phenomenon was attributed due to flux split and aggregation of sites. The fluoride uptake was found to reach the 57.37 mg/g at a dose of 0.25 g/L and decreased to 23.62 mg/g at a clay dose of 8.0 g/L. The optimal dose was identified as 2.0 g/L where the removal efficiency and uptake attained were 90% and 36.45 mg/g, respectively. An empirical relationship between removal efficiency and sorbent dose was proposed ($R^2 = 0.979$) and given by Eq. (5):

$$\mathrm{RE} = 31.648\ln(w) + 34.424 \tag{5}$$

3.4. Effect of temperature

Temperature variations are related to changes in kinetic energies of the dispersed molecules and affect their mobility and solubility. In this set of experiments, the operating temperatures were varied at 303, 308 and 313 K and the removal efficiencies were recorded over a period of 180 min with 30 mg/L fluoride concentration. As given in Fig. 4, the removal efficiency increased from 78% to 94% when the temperature increased from 303 to 313 K. Increased efficiency could be related to expansion of surface sites in the clay which in turn can adsorb more fluoride ions. But, breakdown of clay structure at temperatures higher than 773 K was reported to occur [10].

3.5. Kinetic studies

The experimental data were analyzed through correlative kinetic analysis to identify the relationship between removal rate and concentration of fluoride. The linearized form of pseudo-second-order model, based on solid phase sorption [16], was employed and the model constants, q_1 and k_2, were evaluated from the slope and intercept of the lines shown in Fig. 5. The values of the kinetic constants at different initial fluoride concentrations were tabulated in Table 1. The values of k_2 decreased from 8.38×10^{-3} to 3.84×10^{-3} g/(mg min) with increase in fluoride concentration from 10 to 40 mg/L. The uptake capacity at 30 mg/L fluoride concentration was found to be 40.49 mg/g and the pseudo-second-order model fitted to the entire range of data with comparatively higher values of R^2 (>0.997). The power function model constants were evaluated from the curves plotted in Fig. 6 and the specific sorption rate at unit time (represented by n) varied between 0.06 and 0.10. The model constant (k_p) increased with direct proportionality with change in fluoride concentration and presented in Table 1.

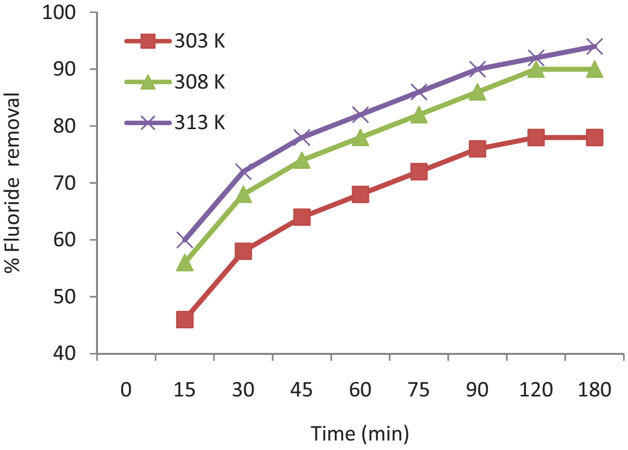

Fig. 4. Effect of temperature on fluoride removal by hybrid clay ($t = 180$ min, $C_0 = 50$ mg/L, $w = 2.0$ g/L, pH = 3.0).

3.6. Thermodynamic studies

The spontaneous nature and feasibility of the sorption process are essential to be studied through thermodynamic experiments. The Arrhenius equation representing the temperature dependence of rate constant (given by Eq. (6)) was plotted in a linear plot between the pseudo-second-order rate constants and temperature.

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{6}$$

where E_a (kJ/mol) is the activation energy, A (g/(mg min)) is the Arrhenius factor, R is the gas constant and T (K) is the solution temperature. The activation energy was estimated from the slope of Fig. 7 and found to be 29.53 kJ/mol. Thus, the endothermic nature of this removal process was confirmed.

3.7. SEM studies

The surface properties were studied by scanning electron microscopic (SEM) imaging (Jeol, Japan) with an accelerating voltage of 20 kV at high vacuum mode. From Fig. 8, it was observed that surface possessed better microstructure morphology favoring high removal efficiencies of fluoride ions.

3.8. Regeneration studies

From the effect of pH, the optimal value suitable for better fluoride removal was identified as 3.0. An alkaline

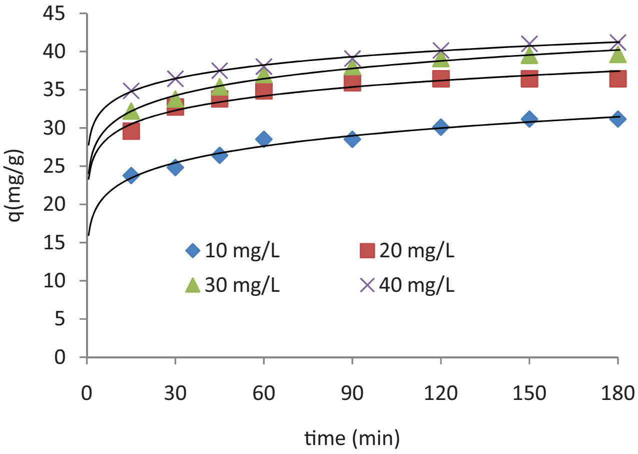

Fig. 5. Power function model for removal of fluoride at 308 K.

Table 1
Kinetic model constants for removal of fluoride

		Fluoride concentration (mg/L)			
		10	20	30	40
Pseudo-second-order model constants	q_1(mg/g)	31.54	37.45	40.49	42.37
	$k_2 \times 10^3$ (g/(mg min))	8.38	6.36	4.56	3.84
	R^2	0.997	0.999	0.999	0.999
Power function model constants	n	0.118	0.083	0.089	0.069
	k_p	17.03	24.39	25.26	28.85
	R^2	0.995	0.952	0.983	0.995

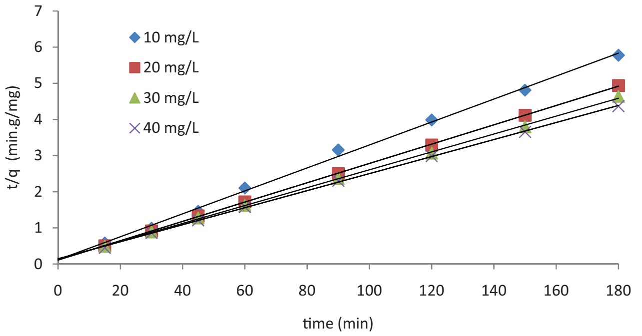

Fig. 6. Pseudo-second-order plot for the removal of fluoride at 308 K.

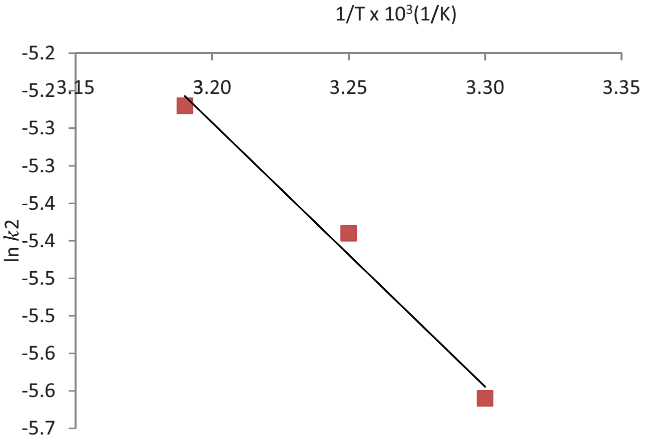

Fig. 7. Arrhenius plot for fluoride removal.

regenerating solution (namely NaOH) was used in three different concentrations 0.01, 0.05 and 0.10 M for a contact time of 60 min. The regeneration efficiencies attained were 59.4%, 78.6% and 80.2%, respectively. Hence, 0.05 M NaOH was proposed as suitable regenerating medium.

3.9. Comparison with other adsorbents

Table 2 presents the comparison of fluoride uptakes achieved using different adsorbents. The result obtained in this study was observed to be better than the other studies cited [1,7,9,18–20].

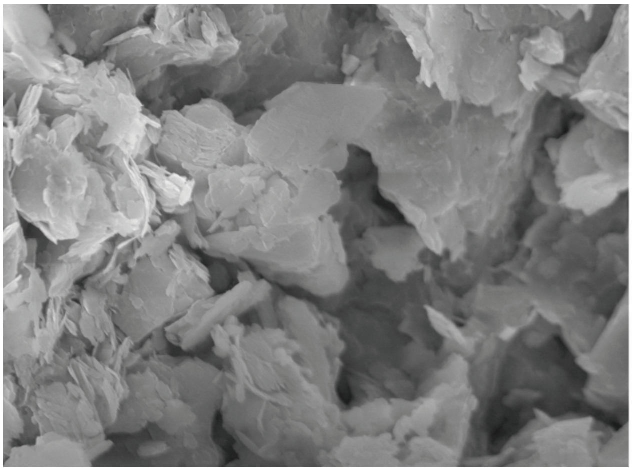

Fig. 8. SEM micrograph of the hybrid clay.

Table 2
Comparison with other studies

Adsorbent	Uptake capacity (mg/g)	Reference
Hybrid clay	36.45	This study
Red mud at polysulfone capsules	1.78	[1]
Nano-hydroxyapatite/ chitosan complex	1.56	[7]
n-Hap at gel composite	4.16	[9]
Activated carbon from *Ficus racemosa*	1.65	[18]
Alumina/chitosan composite	3.81	[19]
Magnesium bentonite clay	2.26	[20]

4. Conclusions

The feasibility of the application of hybrid clay, synthesized using clay and date palm biochar, was studied and the optimal conditions favorable for better fluoride removal were established. Acidic pH favored higher removal efficiencies and the selected clay sorbent successfully removed fluoride in the concentration range of 10–30 mg/L. The maximum uptake of fluoride at controlled conditions of pH (3.0), temperature (308 K) and clay dose (2.0 g/L), was found to be 36.45 mg/g. The results obtained in this study are comparable and better than the uptake capacities reported in other studies. Pseudo-second-order model represented the experimental data very well and the kinetic constants were evaluated. Thermodynamic studies confirmed the nature of sorption as endothermic and the activation energy was estimated. The surface characteristics of the clay were studied using SEM.

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