ISOTHERM AND KINETIC STUDIES ON FLUORIDE BIOSORPTION FROM AQUEOUS SOLUTION BY USING CUTTLEBONE OBTAINED FROM THE PERSIAN GULF

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ABSTRACT: Biosorption is considered to be one of the favored treatment technologies for fluoride ion (F) removal from aqueous solutions. The aim of this study was to determine the efficiency of cuttlebone (cuttlefish bone) obtained from the Persian Gulf in the removal of F from aqueous solutions. The biosorption experiments were studied in batch systems at room temperature. The effects of experimental parameters biosorbent dose, contact time, pH, and initial F concentration were studied. The highest removal biosorption was observed at 100 g/L of biosorbent, at 120 min contact time and an initial F concentration at 12 mg/L (88.52%). The Langmuir model fitted better than the Frendlich model and showed a homogeneous biosorption surface with the possibility of a monolayer biosorption of F by the biosorbent. The biosorption kinetic was controlled by the pseudo-second order and pore diffusion models. The results showed that cuttlebone can be used as an environmentally friendly, cheap, and effective biosorbent of F from aqueous solutions, particularly in the coastal areas of the Persian Gulf with high-F levels in the drinking water.

Keyword: Biosorption; Cuttlebone; Cuttlefish bone; Defluoridation; Kinetic and isotherm models; Persian Gulf.

INTRODUCTION

The fluoride ion (F) is widely distributed in the environment and occurs naturally in the earth's crust as well as being the result of anthropogenic activities such as the aluminum, steel, brick, fertilizer, ceramic, nuclear, and glass industries. These industrial activities play an important role in increasing water contamination by F.[1] Excess F intake by drinking water or food can cause a wide range of adverse health effects.[2-5] In Iran, studies have been made on the F concentration levels in drinking water, air, fish, tea, and sea water.[6-14] Various technologies have been developed for the defluoridation of water, such as adsorption, precipitation, ion exchange, membrane filtration, and electrodialysis. Among these techniques, adsorption, particularly biosorption, is arguably regarded

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as one of the most suitable techniques.[15-20] The advantages of biosorption over conventional treatment methods include low cost, simplicity, high efficiency, less sludge production, and easy handling.[21]

The objective of the present study was to determine the F biosorption capacity of cuttlebone as a biosorbent. The effect of the parameters of pH, contact time, biosorbent dose, and initial F concentration were investigated. The biosorption capacity, isotherm and kinetics were also determined.

MATERIAL AND METHODS

The cuttlebone was collected along the Persian Gulf in the Bushehr seaport coastal area (N 28º 58’ 21.5” and E 50º 49’ 22.8”, Figure 1).

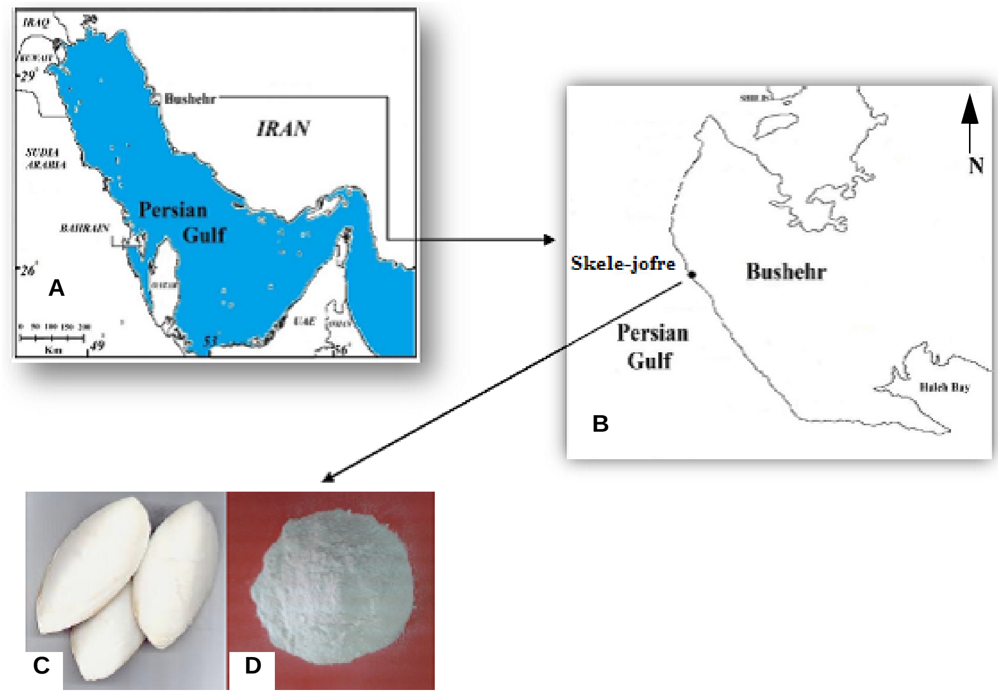

Figure 1. A and B: location of the site for the collecting of the cuttlebone at Skele-Jofre, Bushehr port, in the Persian Gulf; C: cuttlebone before preparation as a biosorbent; D: cuttlebone after preparation as a biosorbent.

The biosorbent was transferred to the laboratory and thoroughly washed twice with tap water and then with distilled water in order to remove all the impurities such as sand and clay. The washed cuttlebone was subsequently dried in an oven (Memmert, Germany) at 105ºC for 24 hr and finally powdered and sieved through a 0.71 mm screen. A stock solution of 100 mg F/L was prepared by dissolving sodium fluoride (Merck, Germany) in ultrapure water. F solutions with concentration levels of 3, 5, 8, and 12 mg F/L were prepared individually by dissolving the appropriate amounts of sodium fluoride. At each run, 100 mL of F solution with a particular initial F concentration was agitated at 120 rpm. The effect of five different contact times (5, 25, 60, 90, and 120 min), four initial F concentrations (3, 5, 8, and 12 mg/L), and five different pH values (4, 5, 7, 9, and 10) were studied in the batch systems at room temperature (25±1ºC). The standard SPADNS method was used by using a Spectrophotometer (HACH, USA, model CAM Spec M501) for analysis of the remaining F concentration in the aqueous solution after each run and the efficiency was calculated by using the following equation:

$$\text{Biosorption yield} = \frac{(C_i - C_e)}{C_i} \times 100$$

where C_i and C_e are the concentrations of F (mg/L) before and after the experiment.

The equilibrium biosorption capacity of cuttlebone at different F concentration levels was also calculated by using the following equation:

$$q_e = \frac{(C_i - C_e)\,V}{m}$$

where q_e is the equilibrium biosorption capacity (mg/L), C_i is the initial F concentration (mg/L), C_e is the F concentration in solution at equilibrium (mg/L), V is the solution volume (L), and m is the biosorbent dosage (g).

RESULTS AND DISCUSSION

As pH plays a key role in the biosorption process, the effect of pH on F biosorption by cuttlebone was investigated in the pH range from 4 to 10 (Figure 2).

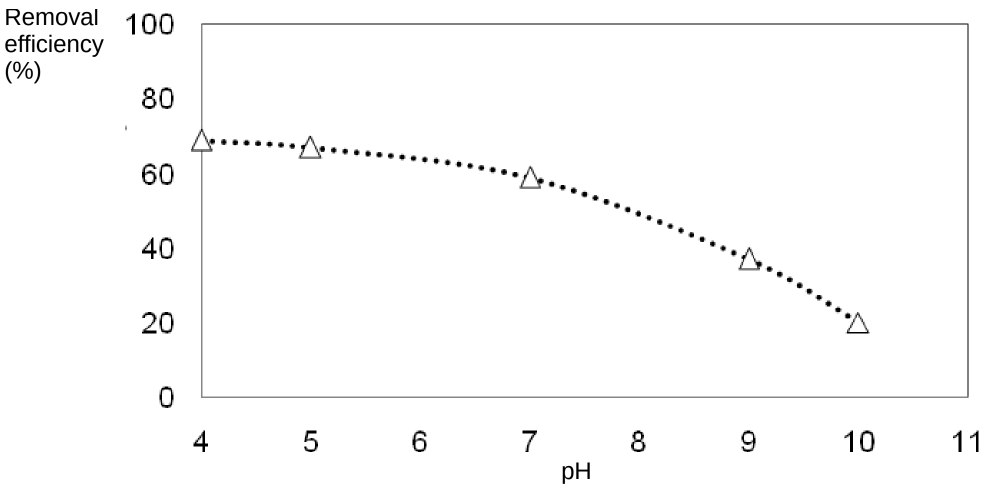

Figure 2. F biosorption as a function of pH (biosorbent dose: 50 g/L; initial F concentration: 8 mg/L).

The highest removal efficiency was at a pH value of 4 and the biosorption efficiency decreased with increasing pH values from 4 to 10. The decrease of F removal at an alkaline pH can be attributed to competition by hydroxyl ions with F for biosorption sites because of the similarity in F and OH^- ions in charge and ionic radius.[22] Similar results have been reported with the removal of F from a solution using granular ferric hydroxide.[16] Xu et al. showed that removal of F by using magnesia-loaded fly ash cenospheres decreased with increasing pH values from 3 to 11.[23] However, in other studies Dobaradaran et al. and Chen et al. examined the removal efficiency of F by using *Moringa oleifera* ash and Kanuma mud respectively and reported the highest F adsorption at neutral pH values.[20, 24] For shrimp shell waste, the removal efficiency for F biosorption increased with increasing pH values from 3 to 11.[19] In contrast, Kermer et al. and Nigussie et al. found that pH had no effect on F removal by waste residues from waste mud and the alum manufacturing process.[25-26]

The effect of the biosorbent dose on the removal of F is shown in Figure 3.

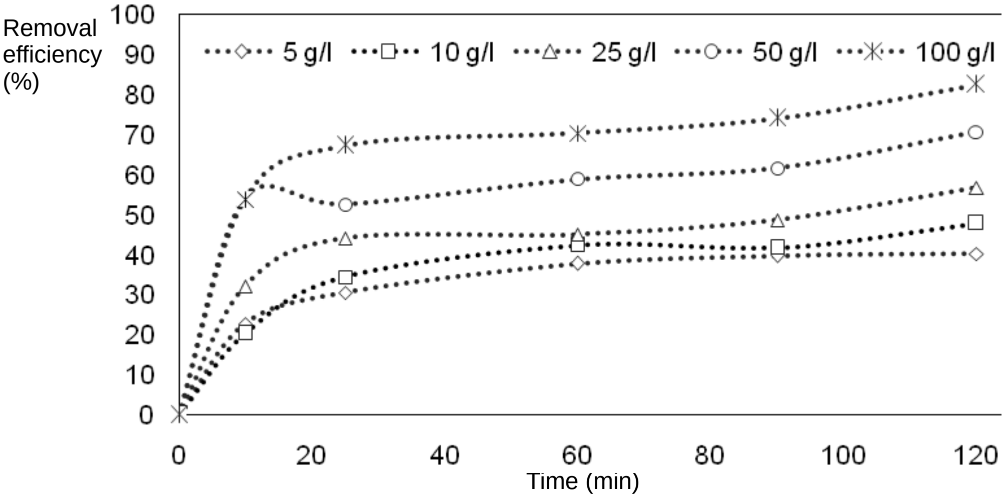

Figure 3. F biosorption as a function of biosorbent dose (initial F concentration: 12 mg/L; pH=7).

The amount of biosorbent significantly influenced the extent of F biosorption. As shown in Figure 3, when the biosorbent dose increased from 5 to 100 g/L, the F removal increased from 30% to 85%, respectively. This can be attributed to the additional number of biosorption sites resulting from the increase in the biosorbent dosage. Similar results have been reported in the defluoridation of aqueous solutions by using shrimp shell waste and *Moringa oleifera* seed ash.[19-20] In another study, Mourabet et al. reported that by increasing the biomass doses of apatitic tricalcium phosphate, the adsorption rate increased.[27] In contrast, Thakre et al. used lanthanum incorporated chitosan beads (LCB) for the removal of F from drinking water and reported that variations in the quantity of LCB in the dosage range from 0.2 to 2 g/L had no significant F removal capacity.[28] The effect of the initial F concentration on the F biosorption is shown in Figure 4. We found that by increasing the initial F concentration levels from 3 to 12 mg/L, at a fixed biosorbent dosage, the removal efficiency decreased (Figure 4). Similarly, Ramanaiah et al. performed F adsorption experiments by using waste fungal biomass derived from the Laccase fermentation process and found that the adsorption efficiency of F by adsorbent decreased with increasing initial F concentrations.[29] In contrast, in two other studies, when the F concentration levels were increased from 2 to 8 mg/L, the efficiency of seed *Moringa oleifera* ash and shrimp shell waste for removing F from aqueous solutions increased from 33.14% to 80.84% and 33% to 81%, respectively.[19-20]

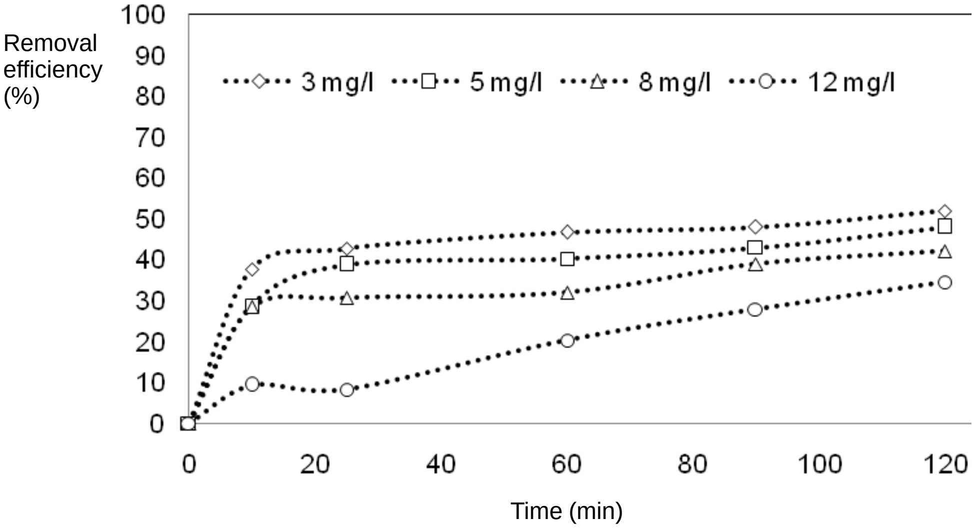

Figure 4. F biosorption as a function of the initial F concentration (biosorbent dose: 10 g/L; pH= 7).

To quantify the bisorption capacity of cuttlebone in the removal of F from aqueous solutions, the isotherm parameters of F onto cuttlebone were calculated for two frequently used isotherms, the Freundlich and Langmuir models. The Langmuir model fitted the data better than the Freundlich model (Table 1).

Table 1. Biosorption isotherm parameters for F biosorption onto cuttlebone

Langmuir parameters				Freundlich parameters		
b (L/mg)	q (mg/g)	R_L	R^2	K_F (L/g)	n	R^2
0.0797	0.0479	0.5111	0.9771	0.0022	0.5704	0.9083

The biosorption kinetics were also examined in order to perceive the mechanism of F biosorption onto cuttlebone. For this, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were applied and the constants and parameters for the biosorption kinetics for these models calculated (Figure 5a-c and Table 2)

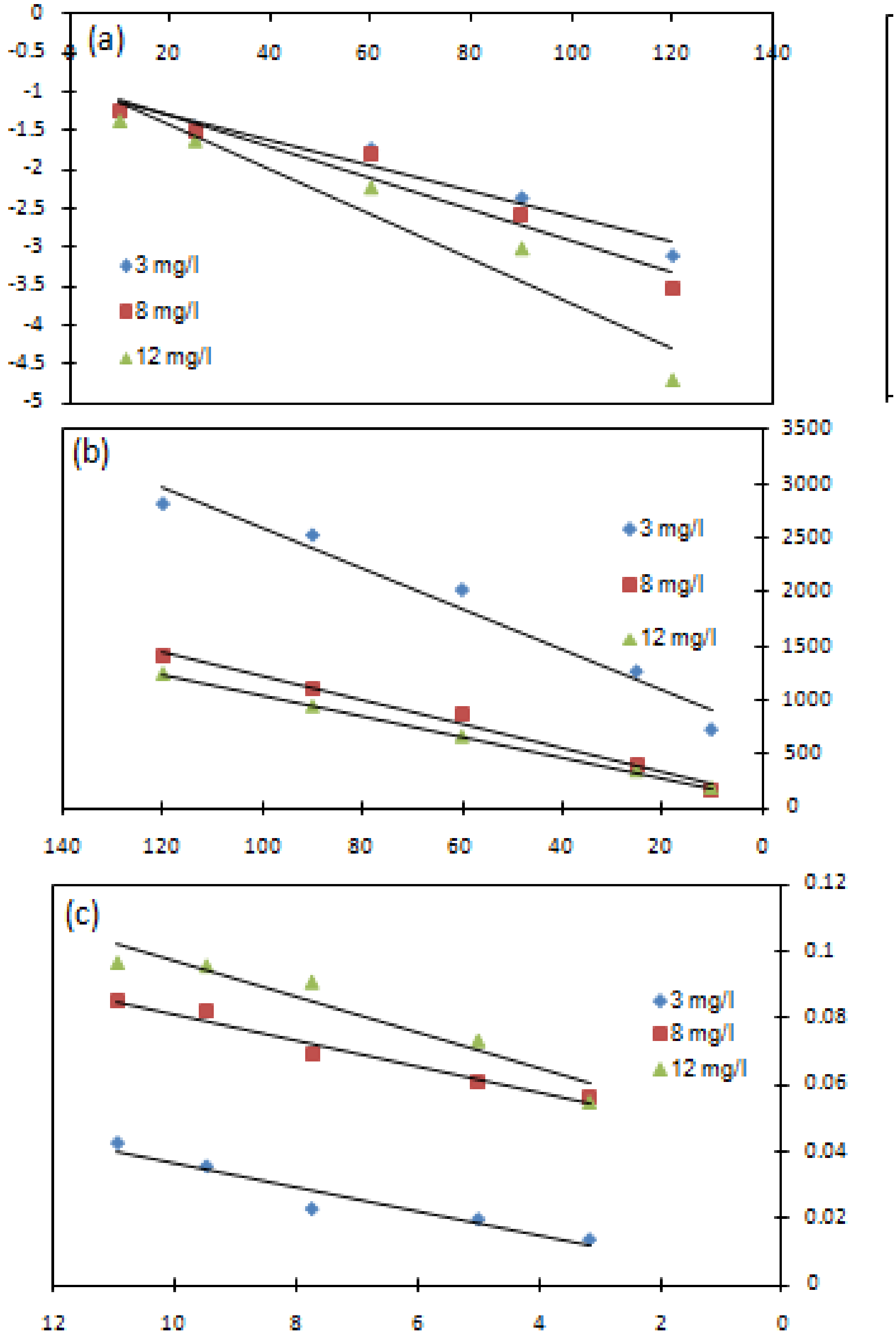

Figure 5. The biosorption kinetics of F biosorption by cuttlebone: (a) pseudo-first-order model, (b) pseudo-second-order model, and (c) intraparticle diffusion model.

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Table 2. Biosorption kinetic parameters for F biosorption onto cuttlebone

C_0 (mg/L)	q_{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion model		
		q (mg/g)	K_1	R^2	q (mg/g)	K_2	R^2	K_d	C	R^2
3	0.042	0.1062	0.0375	0.9565	0.053	0.4846	0.9648	0.0054	0.0431	0.9173
8	0.085	0.1218	0.0458	0.9448	0.0909	0.979	0.9881	0.0039	0.0421	0.9659
12	0.096	0.1387	0.0656	0.9276	0.1048	0.9899	0.9996	0.0036	0.0008	0.9244

The plots were found to be linear with good correlation coefficients indicating the applicability of the pseudo-second-order model to the present study (Figure 5a-c). Based on the drawn plots, the pseudo-second kinetic model had the highest correlation coefficient and this model fitted the experimental data best (Table 2).

The kinetics of F biosorption by cuttlebone followed the pseudo-second model, indicating that the biosorption limiting step may be chemisorption. This suggests that the biosorption of F may occur via surface complexation reactions at specific biosorption sites on the cuttlebone.[30] In addition, the plots showed that the intraparticle diffusion model was not the only rate controlling step because the line did not pass through the origin ($C \neq 0$). This showed that both intraparticle diffusion and boundary diffusion affected the F biosorption onto cuttlebone.

CONCLUSIONS

In this study we used cuttlebone, obtained along the Persian Gulf in Bushehr Province, as a local biosorbent for the removal of F from aqueous solution. The operating parameters of solution pH, biosorbent dosage, contact time, and initial F concentration effected the F biosorption efficiency. Our results showed that increasing the contact time and the biosorbent dose increased the removal efficiency and that the biosorption efficiency was higher at lower pH values. By increasing the initial F concentration levels at a fixed biosorbent dosage, the removal efficiency decreased. The Langmuir model fitted the data better than the Freundlich model indicating that there was a homogeneous biosorption surface and the possibility of a monolayer biosorption of F by biosorbent. The kinetic data signified that the biosorption of F ions onto cuttlebone best followed the pseudo-second-order kinetic model. Finally, according to present findings, it can be stated that cuttlebone is an effective, relatively inexpensive with a good cost-benefit ratio, and environmental friendly biosorbent for F removal from aqueous solutions, particularly in remote, coastal areas where cuttlebone is available such as in the Persian Gulf.

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