SYNTHESIS OF NANOCHITOSAN FOR THE REMOVAL OF FLUORIDE FROM AQUEOUS SOLUTIONS: A STUDY OF ISOTHERMS, KINETICS, AND THERMODYNAMICS

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ABSTRACT: *Background:* Fluorine can be a harmful element for human health. High concentrations of the fluoride ion (F) are poisonous and can damage the endocrine glands, thyroid, and liver. It can also hinder human growth, decrease intelligence, and cause digestive problems and fluorosis. *Objective:* The main objective of this study was to evaluate the effectiveness of nanochitosan for the removal of F from the aquatic environment. *Method:* The effects of various parameters such as pH, adsorbent dosage, initial concentration of F, temperature, and contact time on the removal of F were examined in a batch system. *Results:* The maximum adsorption capacity of the nanoparticles (9 mg F/g nanochitosan) occurred with pH=3, adsorbent dosage=0.25 g/L, and F concentration=20 mg/L. The adsorption process for the removal of F by nanochitosan was an exothermic reaction and followed the BET isotherm and the pseudo-second-order kinetic model. *Conclusion:* Nanochitosan has a relatively good capacity for the removal of F from aqueous solutions.

Keywords: Fluoride; Isotherm; Kinetic; Nanochitosan; Thermodynamic.

INTRODUCTION

Fluorine is one of the major elements in the earth's crust where it is found in minerals and rocks at concentrations of 0.06–0.09%. Fluorine occurs as the fluoride ion (F) at different concentrations in water supplies.[1,2] When the concentrations of F in drinking water are high they must be artificially decreased as a high intake F may be a perilous for human health.[3,4] With the development of human civilization, industrial activities have increased and more F may enter the ecosystem. Aluminum production, plating, glassblowing, metal working, production of semiconductors, chemical fertilizer production, and other industries may use compounds containing F and lead to waste products containing F being discharged to the environment.[5] If high amounts of F enter the human body, it can cause many diseases such as dental fluorosis, skeletal fluorosis, infertility in women, and brain diseases including cognitive impairment.[6,7,8,9] The F concentration in drinking water has also been significantly related to impaired intelligence in children and to death from uterine cancer.[10, 11] Other negative consequences of a high F intake are an increased risk of bone fracture, skeletal fluorosis, negative effects on the blood vessels, and impaired fertility.[12] Some studies have measured the amount of F in milk, bottled water, and groundwater in Iran[13,14,15,16] while others have investigated the correlation of F with hypertension, low birth weight, IQ, and childhood dental caries.[17, 18, 19, 20]

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In tropical areas, these negative effects increase because of increased water consumption and, with higher temperatures, increased evaporation leading to an increased water F concentrations. The recommended range for F in drinking water of 0.7–1.2 mg F/L, based on the outdoor air temperature of geographic regions, has now been replaced in the USA with an optimal F concentration of 0.7 mg/L.[21,22] The WHO "desirable" upper limit set of 1.5 mg/L, set in 1984 and reaffirmed in 1993, has been seen to be unsuitable in some countries and lower country standards have been set of 1 mg/L in India and 0.6 mg/L in Senegal, West Africa.[22] The USA EPA has set a maximum contaminant level (MCT) of 4 mg/L to protect against crippling skeletal fluorosis and a secondary maximum contaminant level (SMCL) of 2.0 mg/L to protect against objectionable dental fluorosis.[23]

Different methods for the removal of F from water solutions have been investigated including chemical sediment,[24] ion exchange,[25] adsorption,[26,27] electrodialysis, [22] and nanofiltration.[28] The ion exchange and membrane processes are very effective for the removal of F and can lower the concentration of F to the standard levels, but since these processes are expensive and complex impoverished areas cannot afford to use them.[25] Among the aforementioned processes, the adsorption process is an economical, simple, and practical process that can be used in impoverished areas. This process is an effective method for decreasing F.[29,30] Polymeric chitosan is a hydrophilic and cation and can be derived from the removal of chitin steel groups from water environments. After cellulose, chitosan is the most prevalent biological polymer in the nature. This natural polymer can be derived from various sources (cell membrane of some fungi, crust of crabs, shrimps, and the cuticle of insects).[31] Chitosan can be modified by some chemical and physical processes to change the structure of the polymer producing membrane, nanoparticles, and powder, and the derivatives of chitosan can be modified in order to get new active bondage groups.[32, 33, 34]

Among adsorbent materials, nanochitosan is a relatively new material that are used in many fields such as medical, pharmaceutical, wastewater treatment, and biotechnology. Nanochitosan is a deacetylated derivative of the polysaccharide of chitin and has important characteristics such as high abundance, lack of toxicity, and the ability to be degraded.[35, 36] Although many studies have been conducted on the removal of F from aqueous solution by various adsorbents, few studies have been performed on the removal of F by nanoparticles.

OBJECTIVES

In the present study, the use of nanochitosan for the removal of F in water treatment was investigated by studying, in a batch system, the effects of various parameters on the adsorption process including pH, the initial concentration of F, the adsorbent dosage, the isotherms, the kinetics, and the thermodynamics.

METHOD

The research was a practical study conducted in a batch stream at the laboratory scale using nanochitosan as the adsorbent. An examination was made of the effects of F removal of various parameters such as pH, contact time, initial concentration of F, and mass of adsorbent. For preparing the stock solution of F with concentration of 100 mg/L, 0.221 g of NaF powder was solved in 1L of distilled water. At first, the optimal pH for the removal of F by nanochitosan was determined and then, according to the adsorption capacity of nanochitosan for the removal of F, the optimal concentration of F was determined as well. Laboratory Erlenmeyer flasks were used for the adsorption experiments. Five different pHs and(3, 5, 7, 9, and 11) and seven different contact time periods (2, 5, 10, 15, 30, 45, and 60 minutes) were studied. In order to detect the initial and final concentration of F, 10 mL of the filtrate sample was put into the specific cell of spectrophotometer and then 2 mL of SPADNS reagent was added to it. Finally, after 2 minutes, the remaining concentration of F was read by a spectrophotometer (HACH DR5000) at wavelength of 580 nanometers. The adsorption capacity of nanochitosan was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)}{M} \times V$$

where: C_0= initial concentration of fluoride
C_e= final concentration of fluoride
M= mass of adsorbent (g)
V= volume of solution (L).

RESULTS

Characteristics of nanochitosan: Figure 1 shows the scanning electron microscope (SEM) image of nanochitosan.

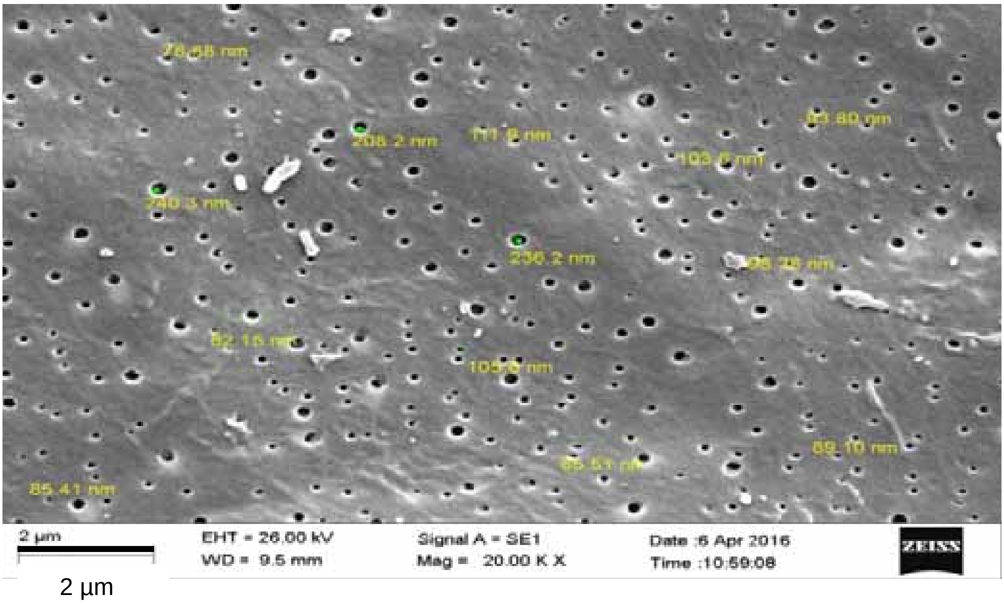

Figure 1. SEM image of nanochitosan.

The nanochitosan was analyzed in order to measure the size of the nanoparticles and their surface distribution.

Figure 2 shows the x-ray diffraction (XRD) patterns for nanochitosan particles.

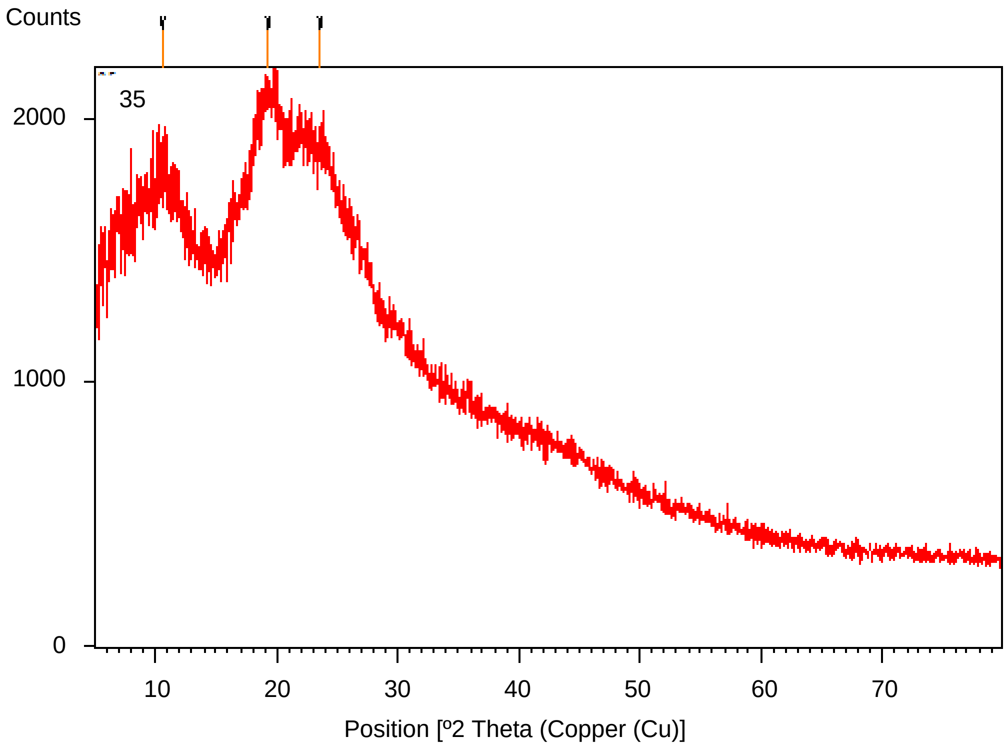

Figure 2. XRD spectrum for nanochitosan.

Effects of pH on the removal of fluoride by nanochitosan: Effect of pH on the removal of F by nanochitosan is shown in Figure 3.

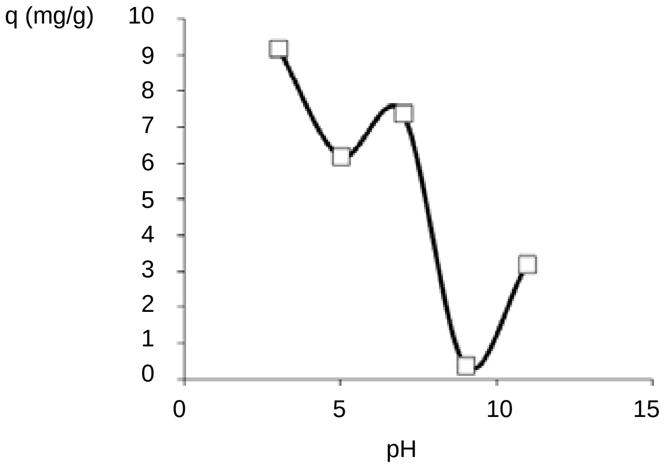

Figure 3. pH effect on fluoride adsorption onto nanochitosan.

The adsorption process occurs mostly on the surface of adsorbents, so in adsorption studies, the surface characteristics of the adsorbents and the factors that affect the surface of the adsorbents and their quality for the removal of the pollutants should be considered.

Effects of initial concentration of fluoride and different times on adsorption process: The effects of the initial concentration of F are shown in Figure 4.

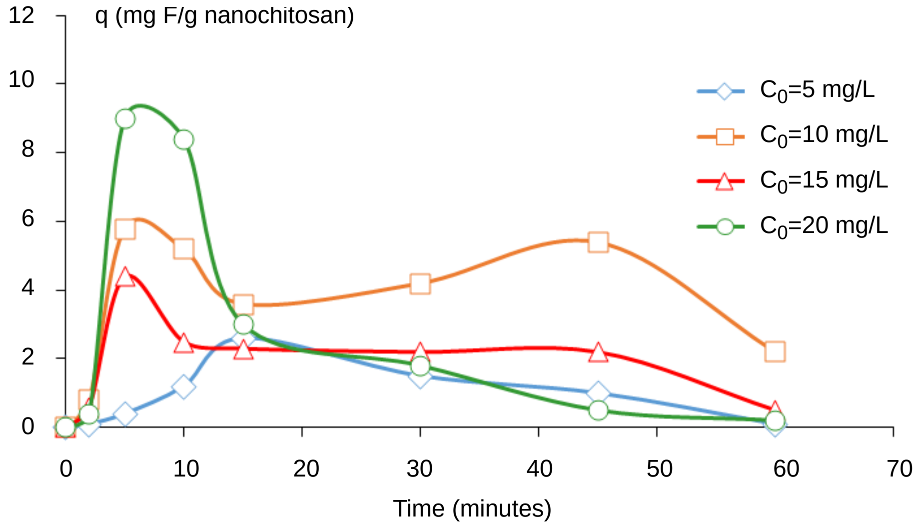

Figure 4. Fluoride concentration effect on fluoride adsorption by nanochitosan.

The maximum adsorption of fluoride occurred when the time reached 5 min and the F concentration was 20 mg/L. The adsorption capacity with these conditions was 9.4 mg/g. After 5 min, the adsorption capacity decreased. At 5 minutes, the adsorption capacities of nanochitosan for initial F concentrations of 10, 15, and 20 mg/L were 5.8, 4.4, and 9.4 mg/g, respectively.

Effects of adsorbent dosage on the removal of fluoride by nanochitosan: The results of this effect of adsorbent dosage are shown in Figure 5.

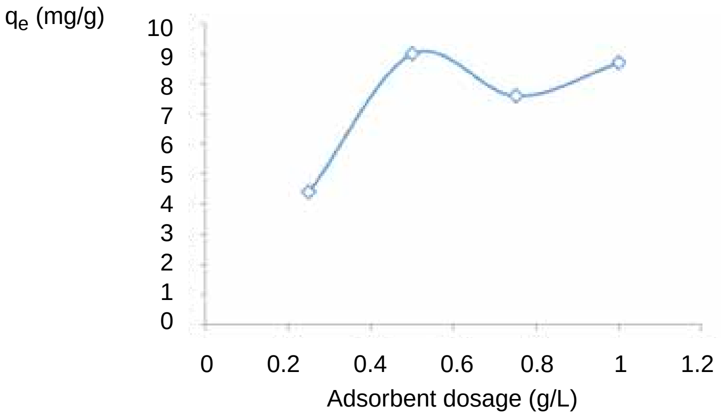

Figure 5. Effect of the adsorbent dosage on fluoride adsorption by nanochitosan.

The adsorption capacity of nanochitosan for adsorbent dosages of 0.25, 0.5, 0.75, and 1 g/L were 4.4, 9, 7.6, and 8.7 mg/g, respectively. It was concluded that as the mass of adsorbent increases until it reaches 0.5 g/L, the adsorption capacity increases as well, but the adsorption capacity decreases when the mass of adsorbent is between 0.5 and 0.75 g/L.

The adsorption isotherm models: In this section, the results of three prevalent isotherms (Freundlich, Langmuir, and BET) are presented. The results are summarised in Table 1.

Table 1. The results of the isotherms (Freundlich, Langmuir, and BET)

Isotherm	Constants	Values
Freundlich	R^2	0.23
	k_f (mg/g)	2.62
	n	1.95
	1/n	0.40
Langmuir	R^2	0.36
	R_L	0.19
	K_L (L/mg)	0.162
	q_{max} (mg/g)	10.33
BET	R^2	0.72
	A	10.2
	X_m(mg/g)	3.0
	$1/A.X_m$	2.26
	$(A-1)/(A.X_m)$	4.08

In order to define the adsorbed mass of pollutant per unit of adsorbent dosage, adsorption isotherms were used. Isotherms describe how the adsorbent and the pollutant react with each other.

Effects of temperature on the adsorption process and thermodynamic parameters: The effect of temperature on the removal process of F by nanochitosan is shown in Figure 7 and Table 2.

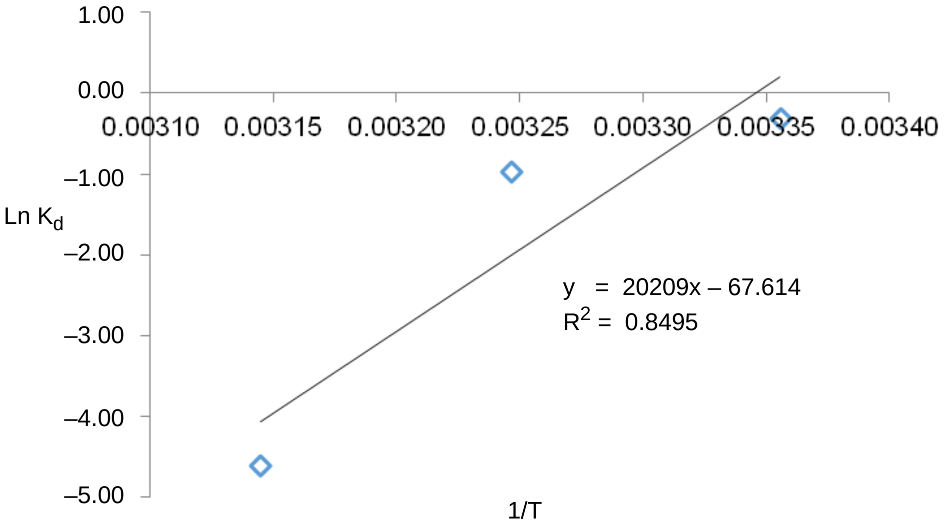

Figure 7. Effects of temperature on the adsorption of fluoride by nanochitosan.

Table 2. Effects of temperature on the removal of fluoride by nanochitosan

T(K)	q_e (mg/g)	Nanochitosan			
		ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	R^2
288	10.8	0.75	–562.14	–168.01	0.85
298	6.4	2.47			
308	0.2	12.16			

The thermodynamic parameters include entropy changes (ƒSX), enthalpy changes (ƒHX), and changes in Gipps free energy (ƒGX). These parameters must be calculated in order to determine whether the adsorption process is spontaneous or not. When ƒGX is negative, the adsorption process is spontaneous.

Study of the kinetics of adsorption: The kinetics of the F adsorption process by nanochitosan are shown in Figures 8 and 9 and Table 3.

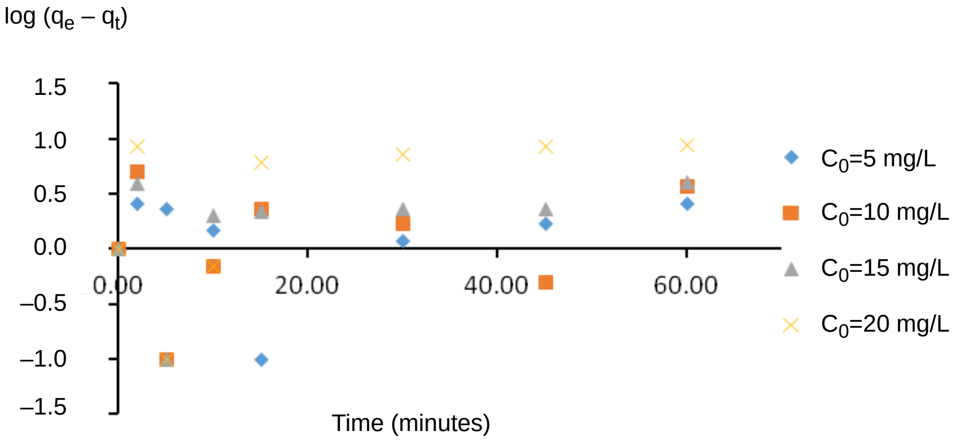

Figure 8. Pseudo-first-order kinetic for adsorption of fluoride onto nanochitosan.

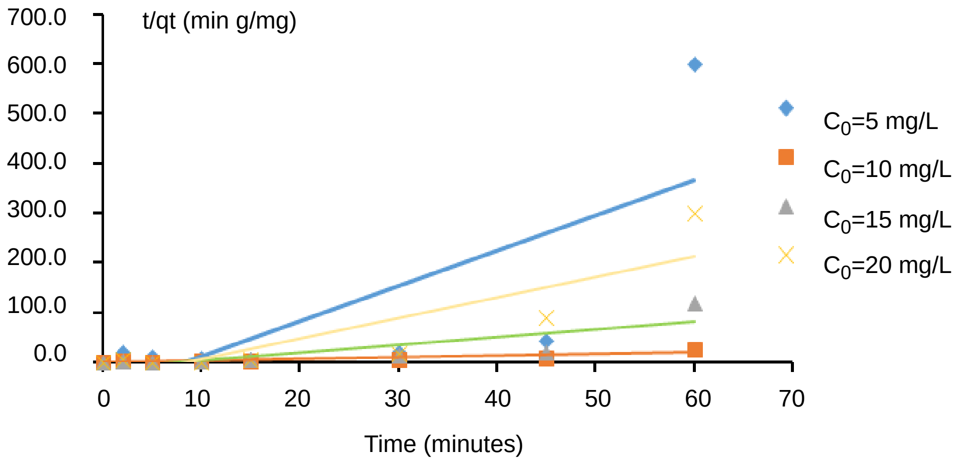

Figure 9. Pseudo-second-order kinetic for adsorption of fluoride onto nanochitosan.

Table 3. The results of studying the pseudo-first-order and pseudo-second-order kinetic models for the adsorption of fluoride by nanochitosan.

Adsorbent	C_0 (mg/L)	Pseudo-first-order			Pseudo-second-order			q_e,exp (mg/g)
		K_1 (min^{-1})	$q_{e,}$ cal (mg/g)	R^2	K_2 (g/mg min)	q_e,cal (mg/g)	R^2	
Nanochitosan	5	0.01	1.01	0.03	0.85	0.14	0.78	2.70
	10	0.01	0.86	0.05	0.13	2.77	0.79	5.90
	15	0.02	0.95	0.19	0.22	0.66	0.80	4.50
	20	0.04	1.07	0.32	0.50	0.24	0.93	9.10

According to the results, it is clear that the adsorption of F by nanochitosan follows the pseudo-second-order kinetics. In addition, the correlation coefficients for the pseudo-second-order kinetics were higher than the correlation coefficients for the pseudo-first-order kinetic model.

DISCUSSION

As shown in Figure 1, the smallest size of the pores on the surface of these nanoparticles was 62 nm and the range was 62–236 nm. As can be seen in Figure 2, the nanostructure of nanochitosan is represented by two flat peaks at $2\theta=11^{o}$ and $2\theta=20–25^{o}$.

One of the most important environmental factors that affects the potential of adsorbents to remove pollutants is the distribution of the negative and positive charges on the surface of the adsorbent, and this factor is a function of the pH of the reaction environment. The balance between the negative and positive charges may have huge effects on pollutant removal by the surface of the adsorbent and it is necessary to determine he effects of this parameter on the removal of various pollutants by adsorbents.[37] As depicted in Figure 3, the maximal F removal by nanochitosan, 9.4 mg/g, occurred at pH=3 and as the pH increased the adsorption decreased. These findings are consistent with the results of the 2016 study by Dehghani et al.[38] Similarly, Vijaya et al. and Naghizadeh et al. found that an acidic pH was a better operation for the removal of F than a neutral pH.[39,40] An acidic pH is best for the removal of F. With an alkaline pH, the OH ion operates as a competitor for the removal of fluoride ions by occupying some of the places on the adsorbent and consequently decreases the adsorption of F.[41,42]

As illustrated in Figure 4, the amount of adsorption increased up to a contact time of 5 min and after this time the adsorption capacity decreased. This is probably because initially there are many active sites on the surface of adsorbent, and as time increases these sites are filled. Huang et al. also found that F removal of fluoride increased with increasing contact time and that the maximal adsorption occurred in the first 40 min.[43] Tang and Zhang (2016) and Naghizadeh et al. (2017) showed that F removal reached a state of equilibrium after 40 min.[44,45]

Increasing the mass of the adsorbent increases the adsorption capacity because that the active surface of the adsorbent for the removal of a certain amount of pollutant increases. The results show that although the efficiency increases with increasing the mass of adsorbent, the amount of adsorbed F per g of adsorbent decreases because the active sites for the removal of pollutant are not saturated. When the mass of the adsorbent is increased, the capacity of all the active sites on the surface of adsorbent is not fully used thus leading to a decrease in adsorption per unit of adsorbent mass.[41,42] On the other hand, determining the effects of adsorbent mass on the removal process is very important because this factor has great impacts on the economic aspects of adsorption, and, in designing large industrial-commercial systems, this factor must be studied carefully. Therefore, in order to prevent the adsorbent from being wasted, it is very important to determine the optimal dosage of adsorbent. Cai et al. found that increasing the mass of adsorbent resulted in a decrease in the adsorption per unit of mass of adsorbent.[46] Imran et al. in 2015[47] and Naghizadeh et al.[48,49] showed that with increasing the adsorbent dosage until it reached 2.5 mg/L, the adsorption capacity increased and if the mass of adsorbent exceeded 2.5 mg/L, adsorption decreased and this effect continued until equilibrium was reached.

The type of isotherm can provide information on factors such as the quality and type of the adsorbed matter and the surface of adsorbent. In addition, information about the isotherms can be useful in describing the adsorption capacity and helpful for designing and analyzing the adsorption systems.[50] Three isotherm models (Freundlich, Langmuir, and BET) were used at equilibrium time and, according to the correlation coefficient, it became clear that nanochitosan followed the BET isotherm. Mourabet et al, in 2015, showed that removal of F by hydroxyapatite followed the Langmuir isotherm model.[51] Liu et al., in 2015, it was also found that F removal followed the Langmuir model.[52]

In the present study, the thermodynamic parameters were determined at different temperatures (298, 308, and 318 K). When the amounts of ƒHX are negative, the reaction is exothermic. In our study the ƒHX value for the adsorption of F by nanochitosan was negative and, therefore, the removal process of F by nanochitosan was exothermic. On the other hand, since the ƒSX was negative, the adsorption process is reversible. These findings contradict the findings by Pandi et al. in 2015.[53]Lin et al., in 2016, also showed that the removal process of F was exothermic.[54]

Kinetic studies, in which the relationship between the contact time and adsorption capacity is examined, are among the most important studies related to adsorption.[55] Studying the kinetics is important in order to predict the speed of the adsorption process and the data from these predictions can be used for the designing and modeling of an adsorption process. The results of the present study confirm the findings by Zazouli et al. on F adsorption by modified biomass of *Lemna minor*.[41] Asgari et al. also found that the adsorption of F by snail shell followed the pseudo-second-order kinetic model. [37] The results of our study were also consistent with the finding by Zhang et al., in 2016, that the adsorption kinetics for F adsorption using a micro-sized magnetic adsorbent (MMA) followed a quasi-second order model.[56]

CONCLUSIONS

We found that nanochitosan had a maximum capacity of 9 mg/g which occurred with pH=3, mass of adsorbent=0.5 g/L, and F concentration=20 mg/L. The adsorption process followed the BET isotherm. The thermodynamic parameters showed that the removal process of F by nanochitosan was exothermic and followed pseudo-second-order kinetics. Nanochitosan has a relatively good capacity for the removal of F from aqueous solutions.

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