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ADSORPTION OF FLUORIDE USING SIO₂ NANOPARTICLES AS ADSORBENT

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Abstract:

Presence of Fluoride in water is safe and effective when used as directed, but it can be harmful at high doses. In the present paper SiO2 nanoparticles as a adsorbent is used for removal of fluoride from aqueous solution. The effect of various operating parameters such as initial concentration of F-, Contact time, adsorbent dosage and pH were investigated. Equilibrium isotherms were used to identify the possible mechanism of the adsorption process. Maximum adsorption capacity of the SiO2 nanoparticles was 49.95 mg/g at PH=6, contact time 20 min, initial concentration of 25 mg/L, and 25±2 ◦C temperatures, when 99.4% of F- were removed. The adsorption equilibriums were analyzed by Langmuir and Freundlich isotherm models. It was found that the data fitted to Langmuir (R2=0.992) better than Freundlich (R2=0.943) model. Kinetic analyses were conducted using pseudo first-and second-order models. The regression results showed that the adsorption kinetics was more accurately represented by a pseudo second-order model. These results indicate that SiO2 nanoparticles can be used as an effective, low-cost adsorbent to remove fluoride from aqueous solution.

Keywords:
SiO2 nanoparticles, Fluoride removal, Equilibrium, Kinetics.

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1. INTRODUCTION

Fluoride pollution in the environment occurs through two different channels which are natural and anthropogenic sources(1). Low concentration of fluoride in drinking water is recognized as an essential micronutrient for both humans and animals to impede dental carries and facilitate the mineralization of hard tissues(2). Fluoride is beneficial especially to young children below 8 years of age when present within allowable limits for calcination of dental enamel and bone formation(3). On the contrary, when the fluoride concentration is high, it can act as a health hazards(4). The negatively charged fluoride ion is highly attracted by positively charged ions,

like calcium ions, of bones and teeth, which results in dental, skeletal and non-skeletal fluorosis(5). According to the World Health Organization (WHO) the maximum allowable concentration of fluoride is 1.5 mg L^{-1}.(6) For these reasons, the removal of the excess fluoride from waters and wastewaters is important in terms of protection of public health and environment(7). Many methods such as adsorption, ion exchange, precipitation, Donnan dialysis, electrodialysis, reverse osmosis, nanofiltration and ultrafiltration have been investigated to remove excessive fluoride from water(8, 9). For the treatment of water by adsorption, activated carbon is the most widely used adsorbent(10). However, it is very expensive and has high operating cost(11). Therefore, in recent years, considerable attention has been devoted to the study of different types of low-cost materials and high performance such as kaolinites, bentonite, charfine, lignites, lemna minor, calcite, amorphous alumina, red mud, azolla filiculidous and etc., for adsorption of fluoride from water(12, 13). In this paper, SiO_2 nanoparticles as sorbent was used to remove Fluoride from aqueous solutions for the first time. The nanometer material is a new functional material, which has attracted much attention due to its special properties. Most of atoms on the surface of the nanoparticles are unsaturated and can easily bind with other atoms. Nanoparticles have high adsorption capacity. Besides, the operation is simple, and the adsorption process rapid. So there is a growing interest in the application of nanoparticles as sorbents(14).

2. MATERIALS AND METHODS

CHEMICAL MATERIALS

Sodium fluoride (CAS No. 7681-49-4) with purity >99% was purchased from Merck (Darmstadt, Germany). All other chemicals were analytical grade and used without further purification. Synthetic fluoride solutions were prepared by adding appropriate amounts of sodium fluoride to distilled water.

Adsorbent Preparation: The SiO_2 nanoparticles (provided from Research Institute of Petroleum Industry (RIPI), Tehran, Iran) was selected as adsorbent to study the adsorption characteristics of F^- from aqueous solutions. The size of the outer diameter for the nano SiO_2 was 10-20 nm. Furthermore, specific surface area of SiO_2 nanoparticles was more than 210 m^2/g, and the mass ratio of the amorphous carbon of SiO_2 nanoparticles was less than 10%.

BATCH SORPTION STUDIES

A stock fluoride solution of 100 mg F $litre^{-1}$ was prepared by dissolving 220 mg of sodium fluoride in 1.0 liter of distilled water, and the test fluoride solution of 5 mg F $liter^{-1}$ was prepared from fresh stock fluoride solution by appropriate dilution. The pH of the distilled water was in the range of 6.8 to 7.1 and all the experiments were conducted at room temperature of 25 + 2°C. Batch adsorption tests were conducted to investigate the effect of controlling parameters like contact time, adsorbent dosage, initial F concentration and pH. Removal efficiency was measured at pH (3-11), the initial concentration of fluoride (1-20 mg/L), adsorbent dose (0.1-0.5 g/L) and contact time (5-90 min). The effect of pH on fluoride removal was found by adjusting the pH of the test solution to initial pH values of 3-11 using 0.1 NHC1 or 0.1 N NaOH; a fixed quantity (0.1 $litre^{-1}$) of adsorbent was added and mixed for the equilibrium sorption time, and analysed for pH and residual fluoride content.

To determine equilibrium sorption time, samples were withdrawn at 5, 10, 15, 20, 30, 40, 50, 60, 75 and 90 min, filtered through Whatman filter paper No. 42 and the filtrate was analysed for residual fluoride concentration by SPANDS method.

Fluoride analysis was measured according to SPADNS method and by using spectrophotometer at a wavelength of 570 nm(15). The SPADNS colorimetric method is based on the reaction between fluoride and zirconium Dye Lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}); and the dye. As the amount of fluoride increases, the produced color becomes progressively lighter. Standard curves were constructed for concentrations of 0 -1.40 mgF L^{-1}. All analysis methods were taken from Standard methods for examination of water and wastewater of the twentieth editing.

3. RESULTS AND DISCUSSION

Removal efficiency of F^- is strongly dependent on concentration of adsorbent dose in test sample. Removal of F^- increases as increasing dose of adsorbent in the sample as shown in Fig 1. At the starting, removal of fluoride increases as increasing the dose until a some extent after that very slightly change in the removal of fluoride it means, the curve lapse as flat indicating the higher fluoride adsorption occurs at their maximum dose and the removal remains constant. Adsorbents have a higher availability of surface and pore volume because of this adsorption increases after that adsorption of fluoride is constant at higher dose because of saturation of pore volume and surface(16). The efficiency was 99.8% for the dose range 0.5 g/L, but there are no significant changes in removal efficiency for fluoride from the dose 0.5 to 1 g/L. This is happened because of the overlapping of active sites at higher dosage, thus reducing of the net surface area(17).

The graphical representation is shown in Fig 2 it shows that as the contact time increased the adsorption of fluoride also increased. After 20 min the adsorption of fluoride was 95.2% and remaining fluoride concentration in water was 1.2 mg/L which was within permissible limit (1-1.5 mg/L). After this the adsorption of fluoride increased as the contact time increased but the remaining concentration of F^- range was below 1 mg/L, so optimum contact time of 20 min was selected for all further experiments. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The sorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface(18).

To find pH effect the study was conducted from pH 3 to11 in acidic and alkaline conditions respectively. The graphical representation is shown in Fig.3 found that the removal of fluoride was increased up to pH 6 and then decreases. Highest adsorption of fluoride was found to be 97.5% to 99.8 % in the pH range 3.0 to 6.0. It is seen that the sorption of fluoride is good in the pH range 3.0-6.0. This may be due to neutralization of the negative charge at the surface of adsorbent material by greater hydrogen concentration at lower pH values(19, 20). In the acidic pH range, the amount of fluoride adsorbed slightly decreased and this can be due to the formation of weak hydrofluoric acid(21). In the alkaline condition pH range there was sharply drop in adsorption which may be due to the competition of the hydroxyl ions with the fluoride for adsorption(22).

The efficiency of fluoride adsorption for different initial F concentrations ranging from 1 to 25.0 mg/L was investigated by carrying out adsorption experiments at the best experimental

conditions present in Figure 4. The percentage removal Increases with an increase in the initial concentration of fluoride and reached in equilibrium condition at higher concentrations. The effect of C_0 observed in this study suggests that the increase in C_0 enhances the interaction between F$^-$ and adsorbent. In another word, increasing in the initial F$^-$ concentrations cause to increase in the driving force to overcome the resistance of the mass transfer of F$^-$ between the solution and the adsorbent surface(23, 24).
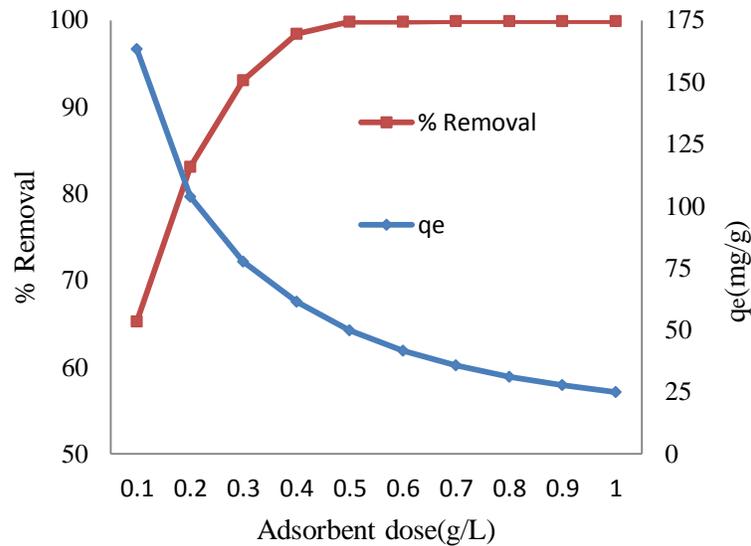

Figure 1: Effect of Adsorbent dose (Initial F concentration: 25 mg/L, pH: 6, time: 20 min, Temp: 25℃)
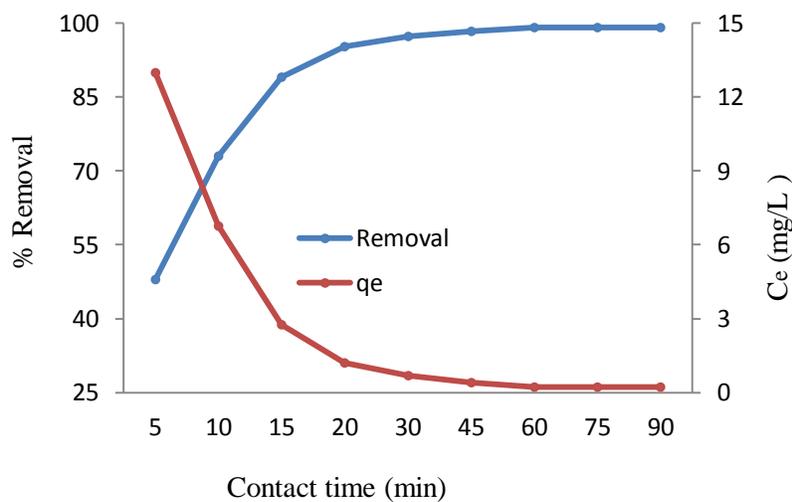

Figure 2: Effect of contact time on removal efficiency (pH = 3, dose 0.5 g/L, Con: 25 mg/L, Temp: 25 °C)
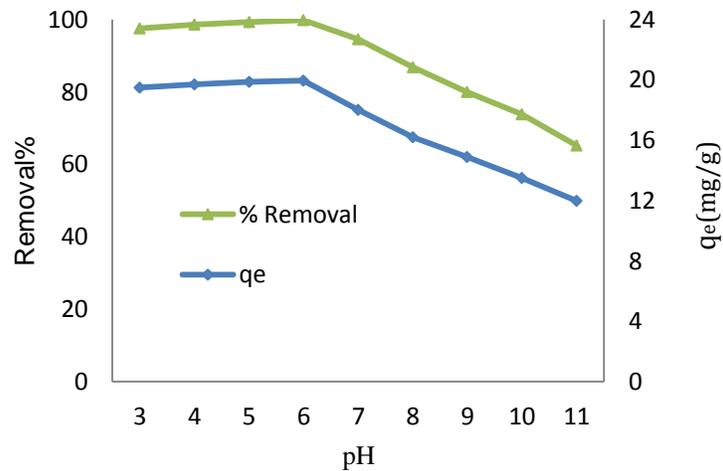
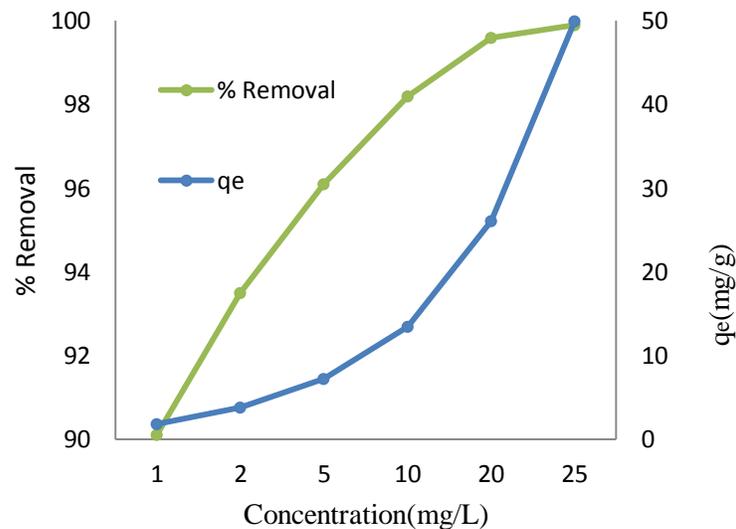**Figure 3:** Effect of pH on F removal efficiency (C_0 = 10 mg/L, dose of 0.5 g/L, time = 20 min and temp: 25 ℃)

Figure 4: Effect of initial F concentrations on the adsorption of F⁻ (dose: 0.5 g/L, Temp: 30 °C, time: 20 min, pH: 6)

KINETIC MODELING

According to the kinetic data obtained from the experiment, pseudo-first-order and pseudo-second-order and Intraparticle diffusion mechanisms have been used to elucidate the mechanisms of adsorption and potential rate controlling steps[25, 26,27].

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303}t \qquad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2.q^2} + \frac{t}{q_e} \qquad (2)$$

$$q_t = K\,t^{0.5} + C \qquad (3)$$

Where q_t and q_e are the amount of adsorbed fluoride (mg/g) at time t and at equilibrium time, respectively. k_1 and k_2 are first-order and second-order rate constants for adsorption. As well as C (mg/g) is the intercept and k is the intra-particle diffusion rate constant (mg g^{-1} min^{-1}),

Kinetic constants obtained from the pseudo-first-order, pseudo-second-order and intra-particle diffusion models are given in Table 1. The value of correlation coefficient for the pseudo-second-order sorption model is higher than obtained from the pseudo-first-order kinetic and intra-particle diffusion at all concentrations of fluoride. Additionally, theoretical and experimental q_e,exp value is in a good accordance with the calculated equilibrium adsorption capacity q_e,cal. Therefore, it is possible to suggest that the sorption of fluoride by N SiO_2 nanoparticles adsorbent followed the pseudo-second-order type reaction kinetics.

Table 1: The adsorption kinetic model constants for the removal F^-

C_o	Pseudo Second-order model			Pseudo First-order model			Intraparticle diffusion		
	K_2	R^2	q_e	K_1	R^2	q_e	K	C	R^2
1	0.0034	0.998	1.56	0.022	0.923	0.79	0.231	1.19	0.921
5	0.0045	0.999	7.45	0.041	0.941	4.51	0.654	2.45	0.932
10	0.0071	0.998	13.71	0.059	0.934	9.14	0.945	1.84	0.894
25	0.0082	0.998	48.61	0.078	0.956	25.81	1.22	3.17	0.904

ADSORPTION ISOTHERMS

Isotherms study can describe how an adsorbate interacts with adsorbent. The experimental data were correlated by Langmuir and Freundlich models. The related linear equations are shown in Equations (4) and (5) respectively(28, 28,30):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} \times \frac{C_e}{q_m} \qquad (4)$$

Where q_e = the amount of F^- adsorbed per unit mass at equilibrium (mg/g); q_m = the maximum amount of adsorbent that can be adsorbed per unit mass adsorbent (mg/g); C_e = concentration of adsorbent (in the solution at equilibrium (mg/L); k_L= adsorption equilibrium constant.

$$Ln\ q_e = ln\ K_f + \frac{1}{n} ln\ Ce \qquad (5)$$

Where Ce (mg/L) and q_e (mg/g) are the equilibrium concentration of adsorbent in the solution and the amount of adsorbent adsorbed at equilibrium respectively; K_F (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}) and n

are the Freundlich constant which show the adsorption capacity for the adsorbent and adsorption intensity, respectively. If $1/n < 1$; then the adsorption is favorable. If $1/n > 1$ the adsorption bond becomes weak and unfavorable adsorption occurs.

At first, we correlated the adsorption data at different initial concentrations of F^- in terms of the Langmuir isotherm. Furthermore, we examined the data according to the Freundlich isotherm. The calculated parameters of the Langmuir and Freundlich models are given in Table 2. The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the Freundlich model. This suggests the monolayer coverage of the surface of SiO_2 nanoparticles by F^- molecules.

Table 2: The adsorption isotherms constants for the removal F^-

Langmuir Model			Freundlich model		
q_m	K_L	R^2	n	K_F	R^2
48.79	0.321	0.992	3.17	1.95	0.943

4. CONCLUSION

From the present result it is concluded that SiO_2 nanoparticles as a adsorbent are promising materials for F^- removal. Optimum dose of nanoparticles was found 0.5 g/L for removal of fluoride concentration of 25 mg/L. The remove increases with increasing contact time, adsorbent dose and initial F^- concentration. Adsorption capacity was more in the pH range of 3-6. Optimum time of contact was found 20 min. The present study on Defluoridation using nanoparticles shows that the equilibrium data fits better to Langmuir isotherm as compared with Freundlich isotherm and maximum absorption was 48.79 mg/g at 25 ◦C Kinetic study results indicate that the adsorption process followed a pseudo-second-order kinetic model.

5. ACKNOWLEDGEMENTS

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