

## ADSORPTION OF FLUORIDE FROM AQUEOUS SOLUTIONS BY A CHITOSAN/ZEOLITE COMPOSITE

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**ABSTRACT:** This study examined the feasibility of removing the fluoride ion (F<sup>-</sup>) from aqueous solutions using a chitosan/zeolite composite. The effects of F<sup>-</sup> concentration, chitosan/zeolite composite dosage, and contact time on the adsorption of F<sup>-</sup> by chitosan/zeolite composite at a constant temperature (30°C) and pH (pH = 7) were also evaluated. Pseudo-first and second-order, intraparticle diffusion, and Bangham models were adopted to evaluate the experimental data and thereby elucidate the kinetic adsorption process. The adsorption percentage of F<sup>-</sup> increased as the chitosan/zeolite composite dosage and the contact time increased. Conversely, the adsorption percentage decreased as the F<sup>-</sup> concentration increased. The pseudo-second-order model best represented the adsorption kinetics. Based on the regressions of the intraparticle diffusion and Bangham models, the experimental data suggest that the adsorption of F<sup>-</sup> on to the chitosan/zeolite composite involved intraparticle diffusion, but that was not the only rate-controlling step.

**Keywords:** Adsorption kinetic; Chitosan/zeolite composite; Fluoride.

### INTRODUCTION

The presence of an excessive intake of fluoride in drinking water may provoke skeletal fluorosis with serious bone abnormalities, dental fluorosis, and non-skeletal fluorosis in which the morbidity may include hypertension and a lowering of IQ.<sup>1-4</sup> According to World Health Organization (WHO) norms, the upper limit of fluoride concentration in drinking water is 1.5 mg/L.<sup>5</sup> However, the measured fluoride concentrations in many regions are higher than the 1.5 mg/L prescribed by the WHO and could be hazardous for the health of humans.<sup>6-8</sup> In Iran there have been a number of studies concerning the F content of food, air, and, especially, water.<sup>9-14</sup> Therefore, many methods have been developed for fluoride removal from water such as adsorption, electrocoagulation, and membrane processes such as reverse osmosis and nanofiltration.<sup>15-17</sup> Among them, adsorption has peculiar advantages such as low cost, simplicity of design and operation, large sorbent availability, ability to treat a pollutant at a high concentration, insensitivity to toxic substances, and high effectiveness.<sup>18,19</sup> Recently, there has been a growing interest in biosorbents, such as chitosan, and using them for the effective removal of fluoride, nitrate, and heavy metals.<sup>20-22</sup> Chitosan is sensitive to pH and to resolve this problem different substances, such as bentonite, montmorillonite, and granular activated carbon have been successfully used in forming composites with chitosan. The aims of this study were (i) the preparation of chitosan/zeolite composites, (ii) the study of the adsorption of F<sup>-</sup> on to a chitosan/zeolite composite in batch experiments, and (iii) the investigation of the effects on F<sup>-</sup> removal of the initial F<sup>-</sup> concentration, the contact time, and the adsorbent dosage.

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## MATERIALS AND METHODS

All the chemicals used in the present study such as NaF, HCL, and NaOH were of analytical grade and were obtained from Merck Co.

To obtain chitosan, shrimp waste were washed several times with water to remove any contaminants and dried in an oven at 105°C for 5 hours. Then, briefly, dried material was fed into a grinder, ground, and submitted to successive steps of demineralization, deproteinization, and deacetylation. Demineralization and subsequent deproteinization were carried out at a ratio of 1:20 (w/v) for 24 hr at room temperature using 1.0 M HCl and 1.0 M NaOH, respectively. Chitin deacetylation to chitosan was done using 50% NaOH at a ratio of 1:20 (w/v) for 2 hr at 100°C. The resulting solids fraction was filtered and then washed with distilled water to obtain up to neutral pH and then the material was dried at room temperature for 24 hr. Finally, the residue was dried in an oven at 60 °C for 4 hr and then stored for further use.<sup>23</sup>

*Batch adsorption procedures:* A stock solution (1,000 mg/L) of F<sup>-</sup> was prepared by dissolving 0.221 g NaF into 1,000 mL of distilled water and diluting to different concentrations when necessary. Batch experiments were conducted at 30°C in a temperature-controlled shaker at a speed of 150 rpm. Twenty mL of F<sup>-</sup> solution was mixed with 20 mg of the chitosan/zeolite composite at different initial concentrations (10–100 mg/L) at pH = 7 in 100 mL stoppered conical flasks. The pH was adjusted to pH = 7 by 0.1 HCl and 0.1 M NaOH solutions. After equilibration, the suspension was separated and analyzed for F<sup>-</sup> by using by spectrophotometer in  $\lambda_{\max}=570$  nm. The adsorption capacity was calculated by using the following equation:<sup>24,25</sup>

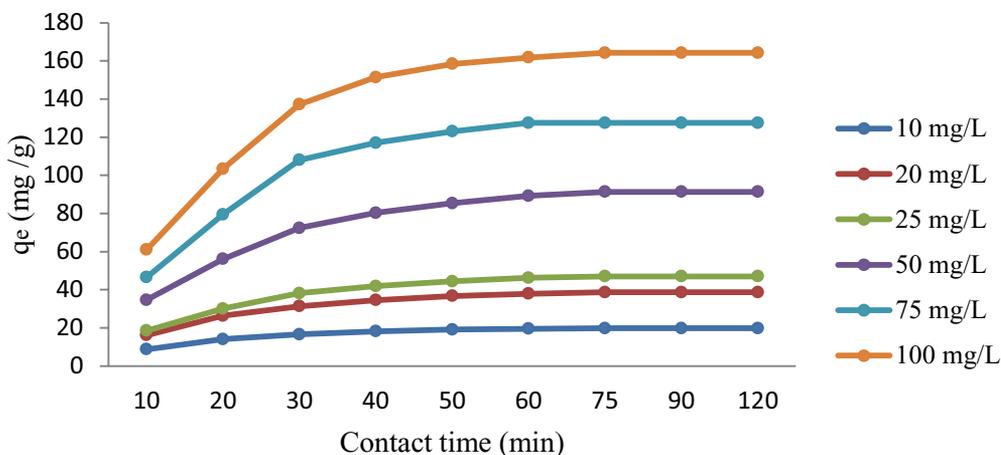
$$q_e = \frac{(C_0 - C_e)V}{M}$$

Where  $q_e$  (mg/g) is the adsorption capacity,  $C_0$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of F<sup>-</sup>,  $V$  (L) is the volume of the F<sup>-</sup> solution, and  $M$  (g) is the weight of the dried adsorbent.

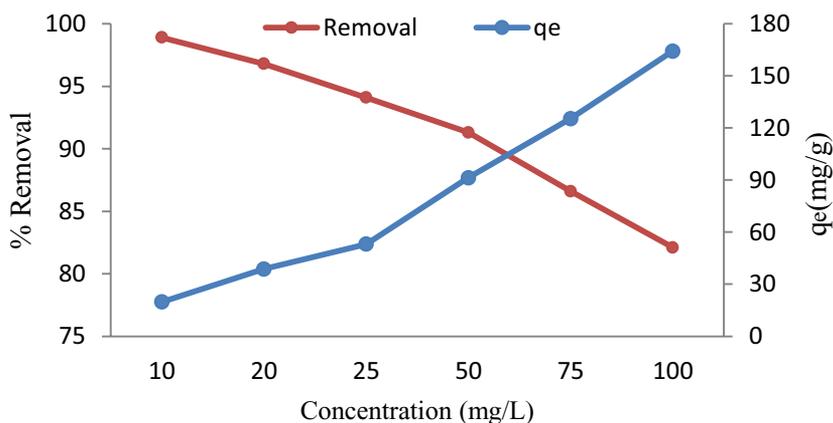
## RESULTS AND DISCUSSION

Figure 1 shows the effect of contact time on F<sup>-</sup> ion uptake by the selected adsorbent. This was achieved by varying the contact time from 10 to 120 min in separate experimental runs. Equilibrium contact time was found to be 60 min. The removal rate of F<sup>-</sup> gradually decreased with an increase in the contact time. Initially, the rate of F<sup>-</sup> uptake was higher because all sites on the adsorbent were vacant and the F<sup>-</sup> concentration was high, but then a decrease of sorption sites reduced the uptake rate.<sup>26,27</sup> Similar results were found in the study of Mahvi et al.<sup>28</sup>

The effect of the initial F<sup>-</sup> ion concentration on the adsorption efficiency is shown in Figure 2. Adsorption experiments were carried out at different initial F<sup>-</sup> concentrations ranging from 10 to 100 mg/L. It was observed, as a general trend, that there was a decrease of the removal percentage with an increase in the initial concentration from 10 to 100 mg/L. These results may be explained on the basis that the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the adsorbent at higher concentrations.<sup>29,30</sup>

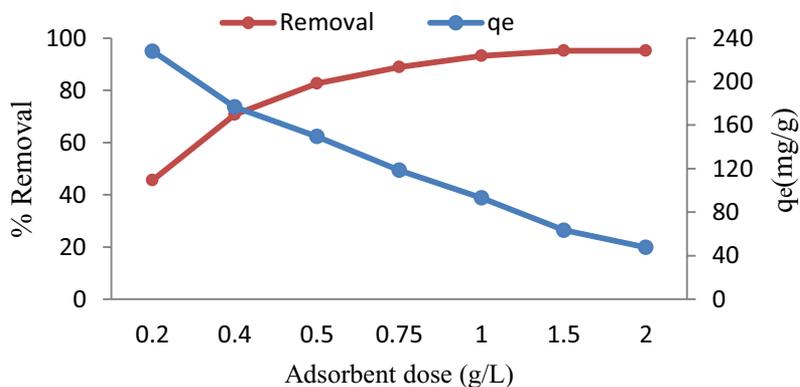


**Figure 1.** Effect of contact time on fluoride removal efficiency (pH = 7, adsorbent dose = 0.5 g/L, and temperature = 30°C).



**Figure 2.** Effect of initial fluoride concentrations on the adsorption (adsorbent dose = 0.5 g/L, temperature = 30°C, contact time = 45 min, and pH = 7).

Figure 3 plots the effects of the chitosan/zeolite composite dosage on the F<sup>-</sup> adsorption. The adsorption percentage increased from 45.6% to 95.2% at a concentration 100 mg/L, when the chitosan/zeolite composite dosage increased from 0.2 to 2 g/L. The increase in the percentage of F<sup>-</sup> removed with an adsorbent dosage can be attributed to an increase in the adsorbent surface, which increased the availability of adsorption sites.<sup>31,32</sup> By increasing the adsorbent dosage from 0.2 to 2 g/L, the capacity adsorption decreased from 228 to 47.6 mg/g. The reason for this result may be the overlapping of adsorption sites due to an overcrowding of adsorbent particles.<sup>33</sup>



**Figure 3.** Effect of adsorbent dose on the adsorption of  $F^-$  ( $F^-$  concentration = 100 mg/L, pH = 7, contact time = 45 min, and temperature = 30°C)

*Adsorption kinetics:* The pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to test the adsorption kinetics data to investigate the mechanism of adsorption. The pseudo-first-order rate expression of Lagergren is given as:<sup>34</sup>

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{K_1}{2.303}t$$

The linear form of pseudo-second order model is given by:<sup>35</sup>

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

Where  $q_e$  and  $q_t$  are the amounts of  $F^-$  adsorbed on the adsorbent (mg/g) at equilibrium and at various times ( $t$ ).  $K_1$  and  $K_2$  are the rate constants for the pseudo-first and pseudo-second order kinetic models, respectively.

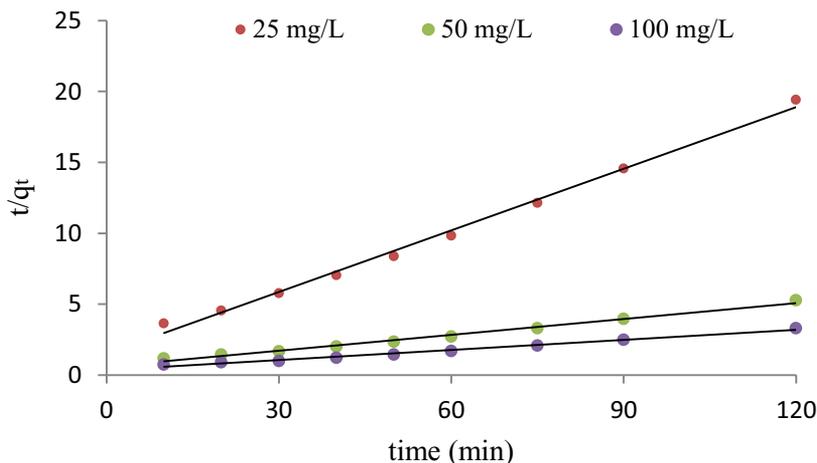
From Table 1, the values of the correlation coefficients obtained for the pseudo-first-order reaction were not appropriate to describe the adsorption of  $F^-$  on the chitosan/zeolite composite. On the contrary, the values of the correlation coefficients for the pseudo-second-order model were all greater than 0.99 and the adsorption capacities calculated by the model were close to those determined by the experiments.

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

| $C_o$<br>(mg/L) | Pseudo First-order |       |        | Pseudo Second-order |       |        | Intraparticle diffusion |      |       | Bangham's model |       |       |
|-----------------|--------------------|-------|--------|---------------------|-------|--------|-------------------------|------|-------|-----------------|-------|-------|
|                 | $K_1$              | $R^2$ | $q_e$  | $K_2$               | $R^2$ | $q_e$  | K                       | C    | $R^2$ | $\alpha$        | $k_0$ | $R^2$ |
| 25              | 0.049              | 0.876 | 44.12  | 0.0037              | 0.996 | 52.28  | 0.365                   | 2.89 | 0.961 | 0.474           | 0.024 | 0.912 |
| 50              | 0.036              | 0.891 | 72.34  | 0.0021              | 0.998 | 92.68  | 0.512                   | 2.44 | 0.974 | 0.689           | 0.018 | 0.904 |
| 100             | 0.017              | 0.905 | 116.74 | 0.0013              | 0.997 | 159.35 | 0.849                   | 1.56 | 0.869 | 0.731           | 0.011 | 0.909 |

Hence, the data was well correlated by the pseudo-second-order model as shown in Figure 4. Moreover, the  $q$  value ( $q_{ecal}$ ) derived from the pseudo-second-order model

was consistent with the experimental  $q$  values ( $q_{\text{exp}}$ ). Hence, this study suggests that the pseudo-second-order model best represents the adsorption kinetics.



**Figure 4.** Pseudo-second-order kinetics for  $F^-$  adsorption at different concentrations.

The adsorption process on porous adsorbents generally has four stages, namely, bulk diffusion, film diffusion, intraparticle diffusion, and, finally, adsorption of the solute on to the surface.<sup>35</sup> Typically, bulk diffusion and adsorption are assumed to be rapid and, therefore, not rate determining.<sup>36</sup> Since the pseudo-second-order model cannot identify the diffusion mechanism, the kinetic results were analyzed using the intraparticle diffusion model to elucidate the diffusion mechanism. For the intraparticle diffusion model, film diffusion was negligible and intraparticle diffusion was the only rate-controlling step.<sup>36,37</sup> The intraparticle diffusion model is expressed as:

$$q_t = K t^{1/2} + C$$

Where  $C$  is the intercept and where  $K$  is the intraparticle diffusion rate constant ( $\text{mg/gmin}^{1/2}$ ), which can be determined from the slope of the linear plot of  $q$  versus  $t^{1/2}$ . Kinetic data were further utilized to identify the slowness of the adsorption step in the present adsorption system based on Bangham's model.<sup>38,39</sup>

$$\text{Log} \left( \frac{C_0}{C_0 - q_m} \right) = \text{Log} \left( \frac{K_0 m}{2.303 V} \right) + \alpha \log t$$

Where  $q$  and  $t$  are defined as in the pseudo-second-order model,  $C_0$  is the initial  $F^-$  concentration in the solution ( $\text{mg/L}$ ),  $V$  is the solution volume ( $\text{mL}$ ),  $m$  is the mass of chitosan/zeolite composite per liter of solution ( $\text{g/L}$ ), and  $K_0$  and  $\alpha$  are constants.

If the regression of  $q$  versus  $t^{1/2}$  is linear and passes through the origin, intraparticle diffusion is then the sole rate-limiting step.<sup>40,41</sup> Although the regression was linear, the plot did not pass through the origin (Table 1), suggesting that adsorption involved intraparticle diffusion; however, that was not the only rate controlling step. Other kinetic mechanisms may control the adsorption rate, which is a similar finding to that

obtained from other studies of adsorption.<sup>42,43</sup> Also the double logarithmic plot according to the Bangham equation of the correlation coefficient ( $R^2 > 0.9$ ) for the removal of the  $F^-$  ion by the chitosan/zeolite composite yielded a perfect linear line, indicating that the diffusion of  $F^-$  into the chitosan/zeolite composite pores is not the only rate-controlling step.

### CONCLUSION

This study investigated the removal of  $F^-$  ion from aqueous solution by chitosan/zeolite composite. The amount of  $F^-$  adsorbed per unit of chitosan/zeolite composite mass increased with increases in the initial  $F^-$  concentration and the contact time. The adsorption of  $F^-$  revealed that the pseudo-second-order model best represented the adsorption kinetics. The results of the kinetics analyses imply that the adsorption of  $F^-$  onto the chitosan/zeolite composite involved intraparticle diffusion; however, that was not the only rate-controlling step.

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