546 Research report Fluoride 52(4):546-552 October 2019 Adsorption of fluoride from aqueous solutions by chitosan/zeolite composite 546 Mahvi, Kord Mostafapour, Balarak, Khatibi,

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

Amir Hossein Mahvi,^{a,b} Ferdos Kord Mostafapour,^c Davoud Balarak,^{c,*} Aram Dokht Khatibi,^{a,c}

Zahedan and Tehran, Iran

ABSTRACT: This study examined the feasibility of removing the fluoride ion (F⁻) from aqueous solutions using a chitosan/zeolite composite. The effects of F⁻ concentration, chitosan/zeolite composite dosage, and contact time on the adsorption of F⁻ 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⁻ increased as the chitosan/zeolite composite dosage and the contact time increased. Conversely, the adsorption percentage decreased as the F⁻ 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⁻ 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.¹⁻⁴ According to World Health Organization (WHO) norms, the upper limit of fluoride concentration in drinking water is 1.5 mg/L.⁵ 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.⁶⁻⁸ In Iran there have been a number of studies concerning the F content of food, air, and, especially, water.⁹⁻¹⁴ Therefore, many methods have been developed for fluoride removal from water such as adsorption, electrocoagulation, and membrane processes such as reverse osmosis and nanofiltration.¹⁵⁻¹⁷ 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.^{18,19} 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.²⁰⁻²² 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⁻ on to a chitosan/zeolite composite in batch experiments, and (iii) the investigation of the effects on F⁻ removal of the initial F⁻ concentration, the contact time, and the adsorbent dosage.

^aSchool of Public Health, Tehran University of Medical Sciences, Tehran, Iran; ^bCenter for Solid Waste Research, Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran; ^cHealth Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran; *For correspondence: Davoud Balarak, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan University of Medical Sciences, Zahedan, Iran; environmental Research Center, Zahedan University of Medical Sciences, Zahedan, Iran; *For correspondence: Davoud Balarak, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran; Email: dbalarak2@gmail.com.

547 Research report Fluoride 52(4):546-552 October 2019 Adsorption of fluoride from aqueous solutions by chitosan/zeolite composite 547 Mahvi, Kord Mostafapour, Balarak, Khatibi,

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.²³

Batch adsorption procedures: A stock solution (1,000 mg/L) of F⁻ 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⁻ 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⁻ by using by spectrophotometer in λ_{max} =570 nm. The adsorption capacity was calculated by using the following equation:^{24,25}

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

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

RESULTS AND DISCUSSION

Figure 1 shows the effect of contact time on F^- 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^- gradually decreased with an increase in the contact time. Initially, the rate of F^- uptake was higher because all sites on the adsorbent were vacant and the F^- concentration was high, but then a decrease of sorption sites reduced the uptake rate.^{26,27} Similar results were found in the study of Mahvi et al.²⁸

The effect of the initial F^- ion concentration on the adsorption efficiency is shown in Figure 2. Adsorption experiments were carried out at different initial $F^$ 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.^{29,30}

Fluoride 2019 Aug 21. www.fluorideresearch.online/epub/files/050.pdf [Epub ahead of print]

548 Research report Fluoride 52(4):546-552 Adsorption of fluoride from aqueous solutions by chitosan/zeolite composite 548 Mahvi, Kord Mostafapour, Balarak, Khatibi, October 2019



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 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⁻ removed with an adsorbent dosage can be attributed to an increase in the adsorbent surface, which increased the availability of adsorption sites.^{31,32} 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.³³

Research report Fluoride 52(4):546-552 Adsorption of fluoride from aqueous solutions by chitosan/zeolite composite 549 549 Mahvi, Kord Mostafapour, Balarak, Khatibi, October 2019



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:³⁴

$$Log (q_e - q_t) = log q_e - \frac{\kappa_1}{2.303}t$$

The linear form of pseudo-second order model is given by:³⁵

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

Where q_e and q_t are the amounts of F⁻ adsorbed on the adsorbent (mg/g) at equilibrium and at various times (t). K₁ and K₂ are the rate constants for the pseudofirst and pseudo-second order kinetic models, respectively.

From Table 1, the values of the correlation coefficients obtained for the pseudofirst-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												
Co	Pseudo First-order			Pseudo Second-order			Intraparticle diffusion			Bangham's model		
(mg/L)	K ₁	R ²	q _e	K ₂	R ²	q _e	K	С	R ²	α	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

550 Research report Fluoride 52(4):546-552 October 2019 Adsorption of fluoride from aqueous solutions by chitosan/zeolite composite 550 Mahvi, Kord Mostafapour, Balarak, Khatibi,

was consistent with the experimental q values (q_{eexp}). 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.³⁵ Typically, bulk diffusion and adsorption are assumed to be rapid and, therefore, not rate determining.³⁶ 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.^{36,37} The intraparticle diffusion model is expressed as:

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

Where C is the intercept and where K is the intraparticle diffusion rate constant $(mg/gmin^{1/2})$, 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:^{38,39}

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

Where q and t are defined as in the pseudo-second-order model, C_0 is the initial F-concentration in the solution (mg/L), V is the solution volume (mL), m is the mass of chitosan/zeolite composite per liter of solution (g/L), and K_0 and α 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.^{40,41} 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

551 Research report Fluoride 52(4):546-552 October 2019 Adsorption of fluoride from aqueous solutions by chitosan/zeolite composite 551 Mahvi, Kord Mostafapour, Balarak, Khatibi,

obtained from other studies of adsorption.^{42,43} 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.

REFERENCES

- 1 Mohammadi AA, Yousefi M, Yaseri M, Jalilzadeh M, Mahvi AH. Skeletal fluorosis in relation to drinking water in rural areas of West Azerbaijan, Iran. Scientific Reports 2017;7(1):Article number 17300.
- 2 Aghaei M, Karimzade S, Yaseri M, Khorsandi H, Zolfi E, Mahvi AH. Hypertension and fluoride in drinking water: case study from west Azerbaijan, Iran. Fluoride 2015;48(3):252-8.
- 3 Karimzade S, Aghaei M, Mahvi AH. Investigation of intelligence quotient in 9–12-year-old children exposed to high and low drinking water fluoride in west Azerbaijan province, Iran. Fluoride 2014;47(1):9-14.
- 4 Rahmani A, Rahmani K, Dobaradaran S, Mahvi AH. Mohamadjani R, Rahmani H. Child dental caries in relation to fluoride and some inorganic constituents in drinking water in Arsanjan, Iran. Fluoride 2010;43(3); 179-86.
- 5 WHO. Chemical fact sheets. In: WHO. Guidelines for drinking water quality Incorporating first addendum to third edition [electronic resource]. Vol 1. Recommendations. Geneva: WHO, 2006. pp. 375-77.
- 6 KheradPisheh Z, Ehrampoush MH, Montazeri A, Mirzaei M, Mokhtari M, Mahvi AH. Fluoride in drinking water in 31 provinces of Iran. Expo Health 2016;8:465-74. Available from: https://doi.org/10.1007/ s12403-016-0204-z.
- 7 Aghaei M, Derakhshani R, Raoof M, Dehghani M, Mahvi AH (2015) Effect of fluoride in drinking water on birth height and weight: an ecological study in Kerman Province, Zarand County, Iran. Fluoride 2015;48(2):160-8.
- 8 Kheradpisheh Z, Mirzaei M, Mahvi AH, Mokhtari M, Azizi R, Fallahzadeh H, Ehrampoush MH, Impact of drinking water fluoride on human thyroid hormones: a case-control study, Scient. Reports 2018;8:2674.
- 9 Mahvi AH, Ghanbarian M, Ghanbarian M, Khosravi A, Determination of fluoride concentration in powdered milk in Iran 2010. The British Journal of Nutrition 2010;107(7):1077-9.
- 10 Dobaradaran S, Mahvi AH, Dehdashti S. Fluoride content of bottled drinking water available in Iran. Fluoride 2008;41(1);93-4.
- 11 Mahvi AH, Zazoli MA, Younecian M, Esfandiari Y. Fluoride content of Iranian black tea and tea liquor. Fluoride 2006;39(4):266-8
- 12 Biglari H Chavoshani A, Javan N, Mahvi AH. Geochemical study of groundwater conditions with special emphasis on fluoride concentration, Iran. Desalination and Water Treatment. 2016; 57;12-8. [E-mail address for H Biglari: Biglari.h@gmu.ac.ir].
- 13 Nouri J, Mahvi AH, Babaei A, Ahmadpour E. Regional pattern distribution of groundwater fluoride in the Shush aquifer of Khuzestan County, Iran. Fluoride 2006;39(4):321-5.
- 14 Dobaradaran S, Fazelinia F, Mahvi AH, Hosseini SS. Particulate airborne fluoride from an aluminium production plant in Arak, Iran. Fluoride 2009;42(3);228-32.
- 15 Fan X, Parker DJ, Smith MD. Adsorption kinetics of fluoride on low cost materials. Water Research 2003;37:4929-37.
- 16 Bazrafshan E, Balarak D, Panahi AH, Kamani H, Mahvi AH. Fluoride removal from aqueous solutions by cupricoxide nanoparticles. Fluoride 2006;49(3);233-44.
- 17 Yousefi N, Fatehizedeh A, Ghadiri K, Mirzaei N, Ashrafi SD, Mahvi AH. Application of nanofilter in removal of phosphate, fluoride and nitrite from groundwater. Desalination and Water Treatment 2016;57:11782-8.
- 18 Chen N, Zhang Z, Feng C, Sugiura N, Li M, Chen R. Fluoride removal from water by granular ceramic adsorption. Journal of Colloid and Interface Science 2010;348:579-84.

- 552 Research report Fluoride 52(4):546-552 October 2019 Adsorption of fluoride from aqueous solutions by chitosan/zeolite composite 552 Mahvi, Kord Mostafapour, Balarak, Khatibi,
- 19 Hosseini SS, Pasalari H, Yousefi N, Mahvi AH. Eggshell modified with alum as low-cost sorbent to removal of fluoride from aquatic environments: isotherm and kinetic studies. Desalination and Water Treatment 2019;146:326-32.
- 20 Ma W, Ya FQ, Han M, Wang RJ. Characteristics of equilibrium, kinetics studies for adsorption of fluoride on magnetic-chitosan particle. J Hazard Mater 2007;143:296-302.
- 21 Srivastav AL, Singh PK, Srivastava V, Sharma YC. Application of a new adsorbent for fluoride removal from aqueous solutions. J Hazard Mater 2013;263:342-52.
- 22 Zazouli MA, Balarak D, Karimnezhad F, Khosravi F. Removal of fluoride from aqueous solution by using of adsorption onto modified *Lemna minor*: adsorption isotherm and kinetics study. Journal of Mazandaran University Medical Sciences 2014;23(109):208-17.
- 23 Zazouli MA, Mahvi AH, Dobaradaran S, Barafrashtehpour M, Mahdavi Y, Balarak D. Adsorption of fluoride from aqueous solution by modified *Azolla Filiculoides*. Fluoride 2014;47(4):349-58.
- 24 Sagheer FA, Al-Sughayer MA, Muslima S, Elsabee MZ. Extraction and characterization of chitin and chitosan from marine sources in Arabian Gulf Carbohydrate Polymers 2009;77;410-9.
- 25 Balarak D, Mahdavi Y, Bazrafshan E, Mahvi AH, Esfandyari Y. Adsorption of fluoride from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetic, and thermodynamic parameters. Fluoride 2016;49(1):71-83.
- 26 Zazouli MA, Mahvi AH, Mahdavi Y, Balarak D. Isothermic and kinetic modeling of fluoride removal from water by means of the natural biosorbents sorghum and canola. Fluoride 2015;48(1):15-22.
- 27 Boldaji MR, Mahvi AH, Dobaradaran S, Hosseini SS. Evaluating the effectiveness of a hybrid sorbent resin in removing fluoride from water. International Journal of Environmental Science and Technology 2009;6(4);629-32
- 28 Balarak D, Mostafapour FK, Bazrafshan E, Mahvi AH. The equilibrium, kinetic, and thermodynamic parameters of the adsorption of the fluoride ion on to synthetic nano sodalite zeolite. Fluoride 2017;50(2);17-25.
- 29 Haghighat GA, Dehghani MH, Nasseri S, Mahvi AH, Rastkari N. Comparison of carbon nonotubes and activated alumina efficiencies in fluoride removal from drinking water. Indian Journal of Science and Technology 2012;5(23):2432-5.
- 30 Li YH, Wang S, Cao A, Zhao D, Zhang X, Xu C, Luan Z. Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes, Chem Phys Lett 2001;350;412-6.
- 31 Balarak D, Mahdavi Y, Bazrafshan E, Mahvi AH. Kinetic, isotherms and thermodynamic modeling for adsorption of acid blue 92 from aqueous solution by modified *Azolla filicoloides*. Fresenius Environmental Bulletin 2016;25(5);1321-30.
- 32 Kumar E, Bhatnagar A, Kumar U, Sillanpaa M. Defluoridation from aqueous solutions by nano-alumina: Characterization and sorption studies. J Hazard Mater 2011;186(2–3):1042-9.
- 33 Tor A. Removal of fluoride from an aqueous solution by using montmorillonite. Desalination 2006;201:267-76.
- 34 Meenakshi D, Maheshwari RC. Fluoride in drinking water and its removal. J Hazard Mater 2006;137(1);456-63.
- 35 Balarak D, Joghataei A. Biosorption of phenol using dried rice husk biomass: Kinetic and Equilibrium Studies. Der Pharma Chemica 2016,8(6):96-103.
- 36 Deng S, Viswanathan V, Candelaria D. Sol-gel derived mesoporous alumina for fluoride and arsenic removal from drinking water. New Mexico Journal of Science 2006;44:183-202.
- 37 Camacho LM, Torres A, Saha D, Deng S. Adsorption equilibrium and kinetics of fluoride on sol-gel-derived activated alumina adsorbents. Journal of Colloid and Interface Science 2010;349(1):307-13
- 38 Kagne S, Jagtap S, Dhawade P, Kamble SP, Devotta S, Rayalu SS. Hydrated cement: a promising adsorbent for the removal of fluoride from aqueous solution. J Hazard Mater 2008;154:88-95.
- 39 Tembhurkar AR. Dongre S. Studies on fluoride removal using adsorption process. Journal of Environmental Science and Engineering 2006;48(3);151-6.
- 40 Balarak D, Mostafapour FK, Joghataei A. Adsorption of acid blue 225 dye by multi walled carbon nanotubes: Determination of equilibrium and kinetics parameters. Der Pharma Chemica 2016;8(8):138-45.
- 41 Tang Y, Guan X, Su T, Gao N, Wang J. Fluoride adsorption on to activated alumina: modeling the effects of Ph and some competing ions. Colloids and Surfaces A 2009;337(1-3);33-8.
- 42 Sun Y, Fang Q, Dong J, Cheng X, Xu J. Removal of fluoride from drinking water by natural stilbite zeolite modified with Fe(III). Desalination 2011;277(1–3):121-7.
- 43 Mourabet M, El Boujaady H, El Rhilassi A, Ramdane H, Bennani-Ziatni M, El Hamri R, Taitai A. Defluoridation of water using Brushite: equilibrium, kinetic and thermodynamic studies. Desalination 2011;278:1-9.