

Bentonite and montmorillonite nanoparticles effectiveness in removal of fluoride from water solutions

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ABSTRACT

The aim of this study was to evaluate the effectiveness of montmorillonite and bentonite nanoparticles in removal of fluoride from water solutions. This experimental study has been conducted in batch condition in which the effects of different parameters such as contact time, pH, initial concentration of fluoride and amount of adsorbent mass have been investigated. Finally thermodynamics, isotherm and kinetics of the both adsorbents have been studied. The maximum adsorption capacity for both adsorbents occurred at fluoride concentration of 20 mg/L, contact times of 60 minutes, pH = 3 and adsorbent mass of 0.25 g/L. The adsorption process was exothermic and the result of the Langmuir and Freundlich isotherm study show that bentonite nanoparticles behave more similar to the Langmuir isotherm model and montmorillonite nanoparticles behave according to the both isotherms. Furthermore, the adsorption of fluoride by bentonite in all studied fluoride concentrations and montmorillonite in higher fluoride concentrations followed pseudo second-order kinetics.

Key words | adsorption, bentonite, fluoride, montmorillonite, nanoparticles

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INTRODUCTION

Water is a vital part of human life and has a critical role in our health, and water pollution is an important environmental issue (Ashtari & Gharbani 2014). Fluorine has an oxidation state of -1 , is a corrosive gas, pale yellow and has high toxicity (3). Fluorine is highly reactive and can be found as CaF_2 in nature (Bishnoi & Arora 2007; Tahaik *et al.* 2007). In north and west countries of Africa and India there are large amounts of CaF_2 and $\text{Ca}_{10}\text{Po}_4\text{F}_2$ and this can cause higher concentration of fluoride (more than 20 mg/L) (Li *et al.* 2003; Shen *et al.* 2003; Annouar *et al.* 2004; Chubar *et al.* 2005).

Fluoride can be found in soil, water and atmosphere. Fluorine is one of the elements that can be found in earth's crust in amounts of 3 g/kg and exists beside other minerals in forms such as ceriolite, fluoroapatite and fluor-spars (WHO 2008). In many surface water supplies, there

is a small amount of fluorine but ground waters have higher concentrations of fluoride.

Fluoride enters the food chain through drinking water, vegetables, and cereal. Fluoride and its compositions are widely used in industries including semiconductors, coal power plants, glass, ceramics, uranium enrichment and others. Fluoride enters the environment via wastewater and this wastewater enters surface waters which causes pollution of ground waters (Tripathy *et al.* 2006). Fluoride is among the important anions that enter water resources through the environment and human activities, and has hygienic importance. Fluoride can be seen in high concentrations in ground water resources. Advantages and disadvantages of fluoride in the human body are related to its concentration in water. If the concentration of fluoride in drinking water is in the standard range (1–1.5 mg/L),

then it can prevent tooth decay, but if its concentration exceeds that level, then it affects the potassium metabolism and if fluorine amounts exceeds 2.5 mg/L, then it causes formation of fluorosis and teeth becomes brown (Kawamura 2000; Qasim *et al.* 2002; Devi *et al.* 2008). Higher concentrations of fluoride are poisonous and can cause great harm to endocrine glands, thyroid, liver, normal growth and intelligence (Dobaradaran *et al.* 2009). The standard amount of fluoride is 1 to 1.5 mg/l; however this amount is dependent on parameters such as temperature of environment, amount of drinking water used and diet (Fomon *et al.* 2000).

Until now, many methods have been used for the removal of fluoride from aqueous solution such as adsorption by activated aluminum oxide and alum, ash, ion-exchange resins, membrane processes like nanofiltration, reverse osmosis (Fan *et al.* 2003), electrodialysis and other methods (Çengelöglu *et al.* 2002; Tripathy *et al.* 2006; Wu *et al.* 2007; Kumar *et al.* 2009).

Most of these methods have a lot of problems such as high operation and maintenance costs (Mahvi *et al.* 2006; Derakhshani & Naghizadeh 2014; Naghizadeh 2015), high production of sludge, high consumption of coagulant aids, creation of secondary pollution, complexity of treatment method, formation of sulfate anion and aluminum cation (Jamhour 2005; Tor 2007).

In contrast to all of these methods, the adsorption process is usually low cost and is simple so that it can be used for decentralized water treatment equipment. This method is being considered because it has many advantages such as high effectiveness, simple operation, availability and low sludge production (Örnek *et al.* 2007; Xue *et al.* 2009).

In recent years, the adsorption process has been considered for removal of many elements. The operation of adsorption process is dependent on many parameters such as pH, the kind of adsorbent and the kind of pollutant. For this purpose, many adsorbents for removal of fluoride have been used such as activated carbon, brick powder, activated alumina, and charcoal (Garg & Malik 2004).

Application of many adsorbents for fluoride removal from aqueous solution was investigated. In a study performed by Bazrafshan *et al.* (2015), efficiency of ZnCl₂ treated Eucalyptus leaf as a natural adsorbent for removal of fluoride from water environment was evaluated. In

another research, Daifullah and colleagues studied the application of KMnO₄-modified activated carbon derived from steam pyrolysis of rice straw for removal of fluoride from aqueous solution (Daifullah *et al.* 2007). Teutli-Sequeira *et al.* (2014) performed the comparison of aluminum modified natural materials in the removal of fluoride ions.

In recent years, a large number of studies have been done on the usage of clay for removal of various pollutants from the environment. Clays are generally classified under the family of silicates. These materials unlike zeolites have a layer structure and have negative charges (Shokouh *et al.* 2011). It is because of this negative charge that clays are being used for removal of cations and heavy metals from aqueous solutions. Nanoclay is one of the low cost nano materials. It has some positive characteristics such as not being poisonous for the environment, a high adsorption capacity and a high specific surface area (Litchfield & Baird 2008). In the present study, the efficiency of bentonite and montmorillonite nanoparticles in fluoride removal from aqueous solution was investigated.

MATERIALS AND METHODS

In this experimental study that has been conducted in batch conditions, the effects of various parameters such as contact time, pH, initial concentration of fluoride and amounts of bentonite and montmorillonite in the removal of fluoride were examined. Bentonite and montmorillonite nanoparticles were obtained from the Iranian Nanosany Corporation and were used without further purification.

Adsorption experiments

The 1,000 ppm stock solution of fluoride was prepared by dissolving 0.221 grams of NaF powder (Merck Company) in one liter of distilled water. In the present study, Laboratory Erlenmeyer flasks were used for adsorption experiments. The volume of fluoride solution in all stages of adsorption studies was 100 mL. Also different concentrations of fluoride (5, 15, 10, 20 mg/L) at 3 different pH (3, 7, 9) as well as various dosage of nano adsorbents (0.25, 0.5, 0.75 and 1 g/L) at different reaction times were studied for the optimization of the

fluoride removal process with bentonite and montmorillonite nanoparticles. After that, the solutions were filtered through a 0.2 μm filter and finally fluoride concentrations were measured with a spectrophotometer (HACH DR 5000) at 580 nm wavelength.

The adsorption capacity of bentonite and montmorillonite nanoparticles in the removal of fluoride was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)}{M} \times V \quad (1)$$

where C_0 is initial concentration of fluoride (mg/L), C_e is final concentration of fluoride (mg/L), M is mass of adsorbent (g) and V is volume of solution (L).

For determination of the point of zero charge (pH_{PZC}), two series of 30 mL deionized water in conical flasks were prepared with initial pH values in the range of 2–12. These pH values were adjusted by addition of hydrochloric acid (1 N) for the acidic range and sodium hydroxide (0.1 N) for the basic range, using a pH meter. Then 20 mg of either bentonite or montmorillonite were placed in each conical flask of the series and left overnight to reach equilibrium at 25 °C. The final pH was then measured and plotted against the initial pH for each series. The pH_{PZC} can be readily obtained from the point at which the initial pH versus final pH curve crossed the $y = x$ line on the graph.

To verify the desired structure of the synthesized sorbents, a scanning electron microscopy (SEM) image was taken with a Camscan MV2300 Microscope. Structural features were investigated by Raman spectroscopy (JobinYvon T-64 000), and X-ray diffraction (XRD) (Philips Analytical PC-APD) was used for characterization of the sample.

Adsorption isotherms

To study the adsorption isotherms the experimental data were analyzed using Freundlich and Langmuir isotherm models. The linear forms of Langmuir (Equation (2)) and Freundlich (Equation (3)) can be expressed as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}K_L} + \frac{C_e}{Q_{\text{max}}} \quad (2)$$

$$L_n Q_e = \left(\frac{1}{n}\right) L_n C_e + L_n K_f \quad (3)$$

where Q_e is the equilibrium concentration of fluoride in the solid phase (mg/g), Q_{max} is the maximum adsorption (mg/g), K_L is the Langmuir adsorption equilibrium constant (L/mg), K_f is the Freundlich constant representing the adsorption capacity ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$), and n is the Freundlich constant representing the intensity of adsorption.

Adsorption kinetics

Kinetic equations examine the transfer of particles of adsorbed material in time and determine the speed of the reaction. In this study pseudo first- and pseudo second-order kinetic models were examined. The linear equations of these two models are shown in following equations:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (4)$$

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (5)$$

where q_e (mg/g) is the adsorbed fluoride at equilibrium, q_t (mg/g) is the adsorbed fluoride at the time t (min^{-1}), K_1 is the constant of pseudo first-order equation, and K_2 is the constant of pseudo second-order equation.

Adsorption thermodynamics

For this stage of the study, all optimized parameters obtained from previous stages such as pH, contact time, adsorbent dosage and fluoride concentration were kept constant and the test was conducted using incubator shakers device (COMBI-SHAKER, Model NB-101MT) at temperatures of 288, 298, 308 and 318 K. Then, thermodynamic parameters of adsorption including Gibbs free energy (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) were studied. The following equations (Equations (6)–(8)) were used to calculate the thermodynamic constants. In these equations, R (8.314 J/mol K) is the universal gas constant, T (K) is absolute temperature and K_e is

thermodynamic equilibrium constant,

$$\ln Ke = \frac{\Delta S^\circ}{R} - \left(\frac{\Delta H^\circ}{R.T} \right) \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T . \Delta S^\circ \quad (7)$$

$$\ln Ke = \frac{qe}{Ce} \quad (8)$$

RESULTS AND DISCUSSION

Characteristics of the adsorbents

The SEM images give information about the surface morphology. Figure 1 shows the SEM images of bentonite and montmorillonite nanoparticles. According to SEM images, bentonite and montmorillonite nanoparticles are stacks of multi-layers with a sheet structure. Regarding this figure, these nanoparticles consist of irregular morphology with a size of a few micrometers. Furthermore, the heterogeneous surface of the particles is clear.

The XRD patterns of the bentonite and montmorillonite nanoparticles in Figure 2 show a medium peak at $2\theta = 6.05^\circ$ and $2\theta = 5.97^\circ$ for both nanoparticles, respectively, and also a sharp peak at $2\theta = 27.80^\circ$ and $2\theta = 27.81^\circ$ that corresponds to the nanostructures of the adsorbents.

Figure 3 shows the Fourier transform infrared spectroscopy (FTIR) (scanning electron microscope) image, taken of montmorillonite and bentonite nano particles. The FTIR spectra of the bentonite and montmorillonite fractions were measured in transmittance between 400 and 4,000 cm^{-1} . The absorption band at 3,622 cm^{-1} is due to stretching vibrations of structural OH groups of bentonite. Water in bentonite gives a broad band at 3,435 cm^{-1} corresponding to the H₂O-stretching vibrations, with a shoulder near 3,250 cm^{-1} , due to an overtone of the bending vibration of water observed at 1,637 cm^{-1} . A sharp band at 791 cm^{-1} with inflexion near 779 cm^{-1} confirms quartz admixture in the sample. The band at 696 cm^{-1} is due to the deformation and bending modes of the Si-O bond. The band at 530 cm^{-1} is due to Al-O-Si and Si-O-Si bending vibrations in the montmorillonite and bentonite, respectively (Wang *et al.* 2009).

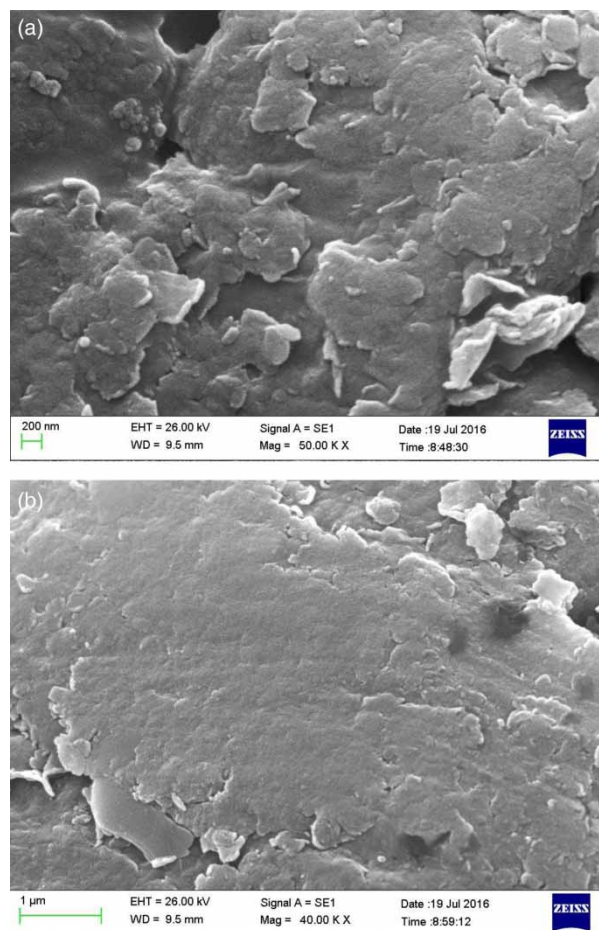


Figure 1 | SEM images of (a) bentonite and (b) montmorillonite nanoparticles.

Effect of pH and determination of pH_{zpc}

The results of the effect of pH on the removal of fluoride by bentonite and montmorillonite are shown in Figure 4.

Figure 4 shows that the maximum adsorption capacity of the two adsorbents occurred at the $\text{pH} = 3$. According to the Figure 4, for both the studied adsorbents, when the pH reached 3, the maximum adsorption of fluoride takes place and with increasing pH, adsorption capacity decreases. The adsorption capacities of bentonite and montmorillonite nanoparticles at $\text{pH} = 3$ are 4.45 and 3.85 mg/g, respectively. As both of these adsorbents have positive charge in acidic pH and the fluoride anion has negative charge, the removal process increases markedly in acidic pH.

When the pH is increased, due to the repulsive force of opposite charges, fluoride molecules are pressured less and

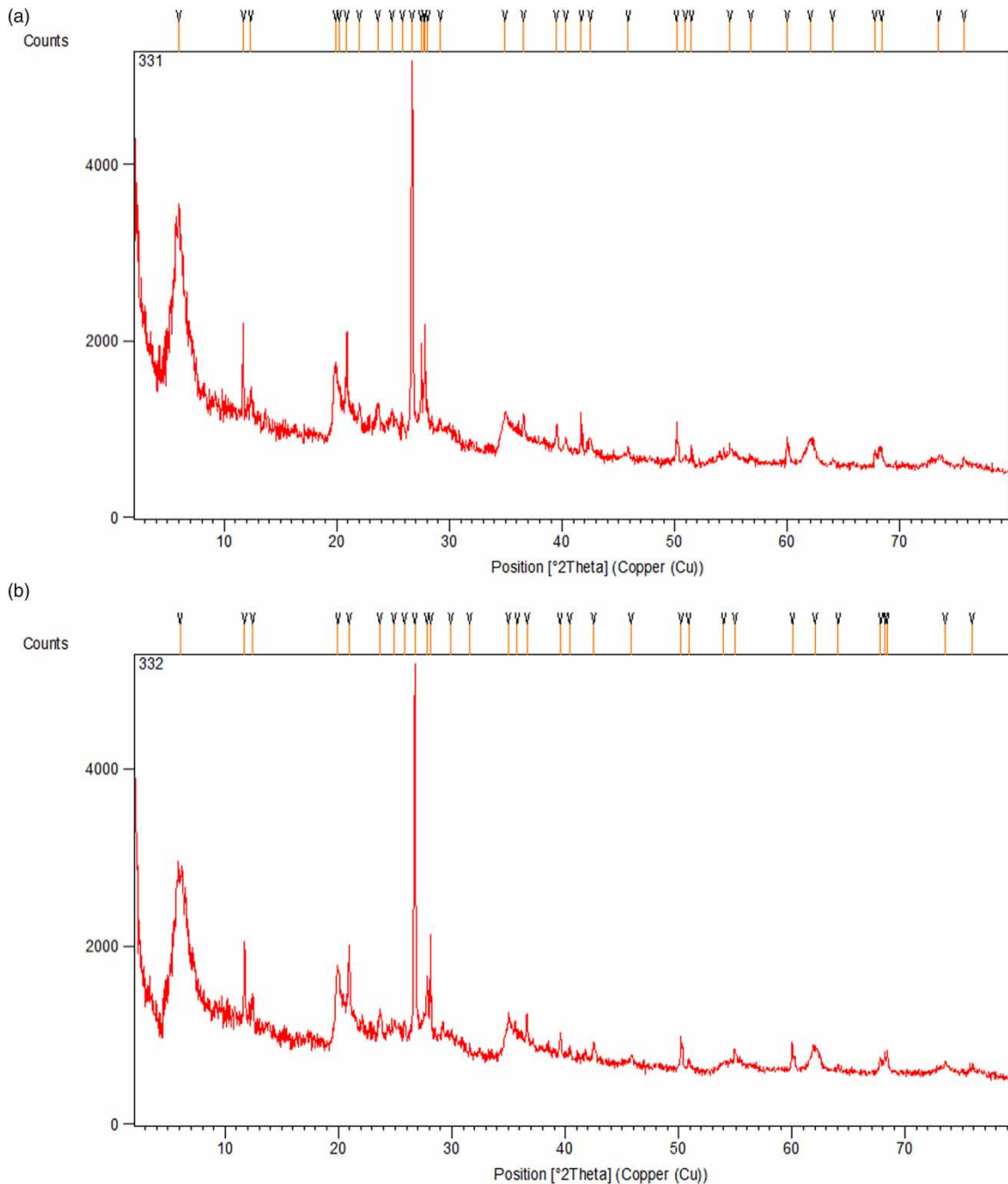


Figure 2 | (a) XRD spectra that were taken from (a) nano-montmorillonite and (b) nano-bentonite.

possibly adsorption capacity will be reduced as well. In addition, at higher pH, due to the abundance of hydroxyl radicals, the possibility of creating a repulsive force between the adsorbent surface and fluoride (both have negative charge), is higher.

In a study conducted by Yuxin Ma and his colleagues in 2011, it was shown that the maximum removal of fluoride at pH 4.95 and time of 40 minutes reaches equilibrium (Ma *et al.* 2011). In another study by Young Ku and his colleagues, the pH level for removal of fluoride by activated

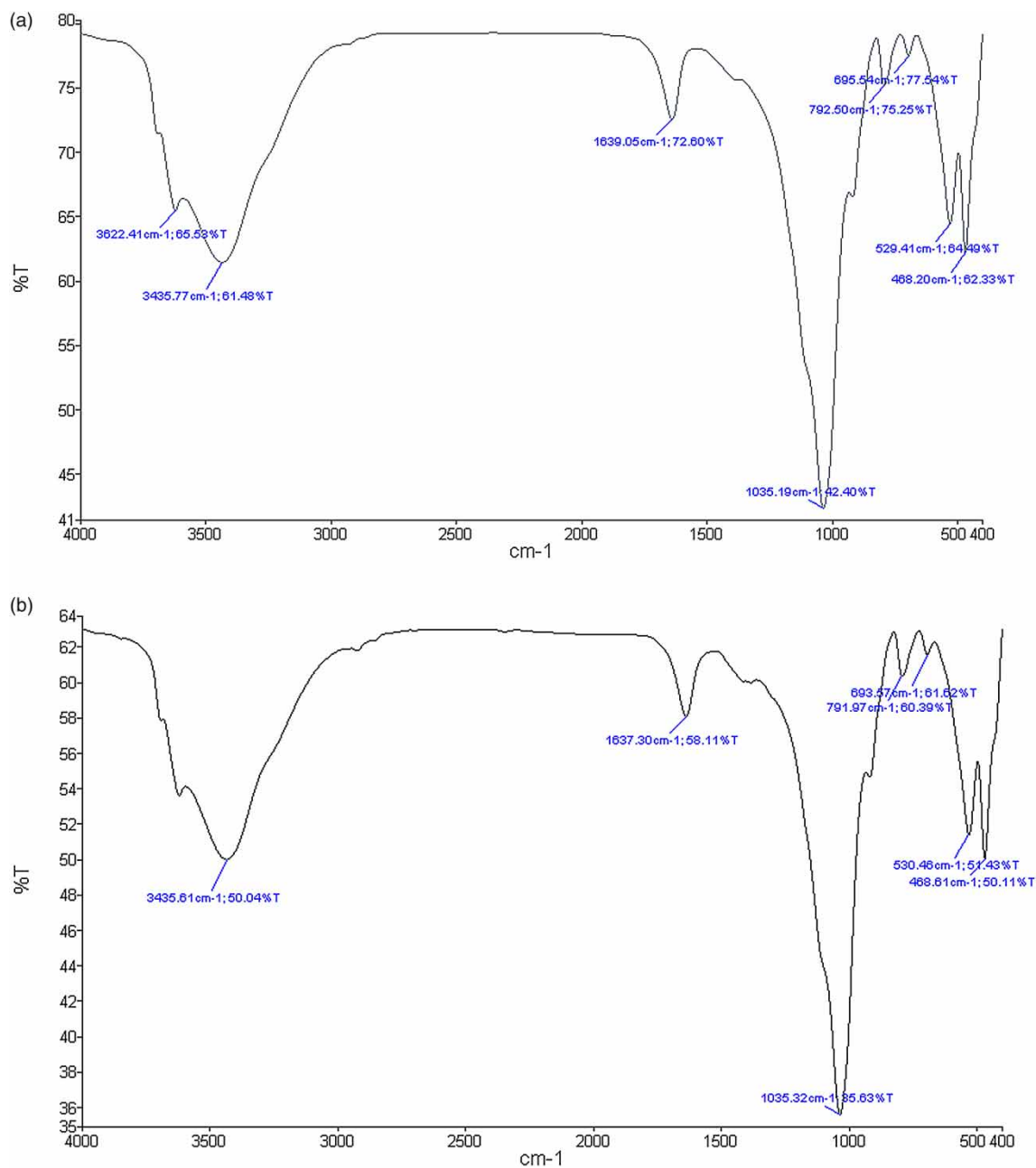


Figure 3 | FTIR spectra of (a) montmorillonite nanoparticles and (b) bentonite nanoparticles.

alumina was determined to be between 5 and 7 (Ku & Chiou 2002). The results of the study of Wajima *et al.* (2009), with two adsorbents of titanium hydroxide and saturated zirconium showed that the maximum amount of fluoride removal occurred at pH 3 (Wajima *et al.* 2009; Shengjuet *al.* 2010).

The results of measuring pH_{zpc} for humic acid adsorption by adsorbents are shown in Figure 5.

According to Figure 5, it becomes clear that pH_{zpc} for bentonite and montmorillonite nanoparticles is 7.4 and 7.8, respectively. These results indicated that the surface of bentonite nanoparticles in pHs lower than 7.4 and the

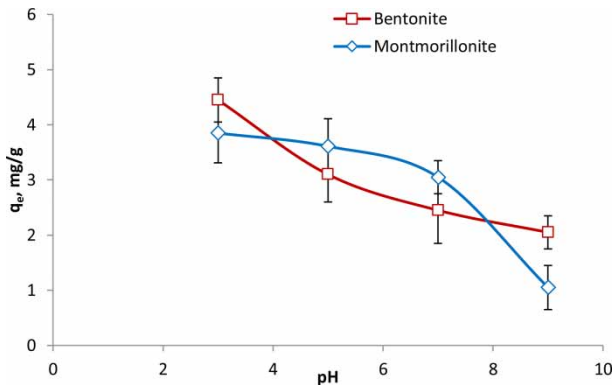


Figure 4 | Effects of pH on the removal of fluoride by both adsorbents ($C_0 = 10$ mg/L, adsorbent dosages = 1 g/L, $V = 0.1$ L).

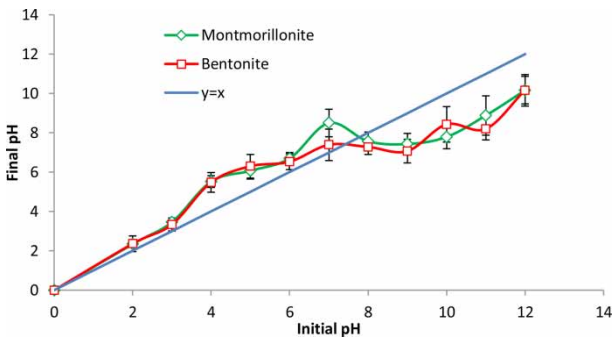


Figure 5 | Determination of the pH_{zpc} for bentonite and montmorillonite nanoparticles.

surface of montmorillonite particles in pHs lower than 7.8 are positively charged. So in acidic pHs, the adsorption of substances like fluoride that have negative surface charges, will increase. In a study done by Shirzad-Siboni and his colleagues about the removal of a pesticide by CTAB-modified nanoclay, the researchers concluded that pH_{zpc} of this adsorbent was 4.4 (Shirzad-Siboni *et al.* 2015).

The effects of initial concentration of fluoride on its removal by both adsorbents at various times

The results of the initial concentration of fluoride on its adsorption onto bentonite and montmorillonite nanoparticles at different reaction times are shown in Figures 6 and 7, respectively.

As can be seen in Figures 6 and 7, the maximum adsorption capacities occur at concentrations of 20 mg/L and contact times of 60 min.

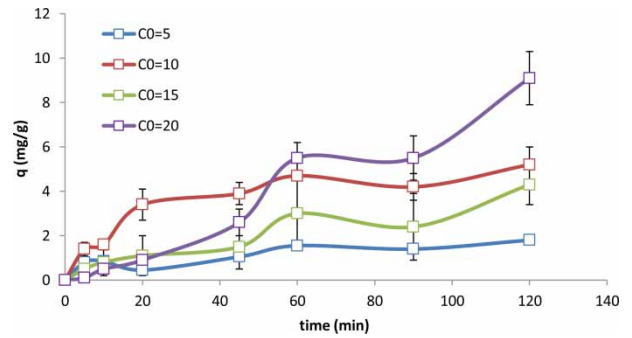


Figure 6 | Effect of contact time and initial fluoride concentration on efficiency of fluoride adsorption onto bentonite nanoparticles.

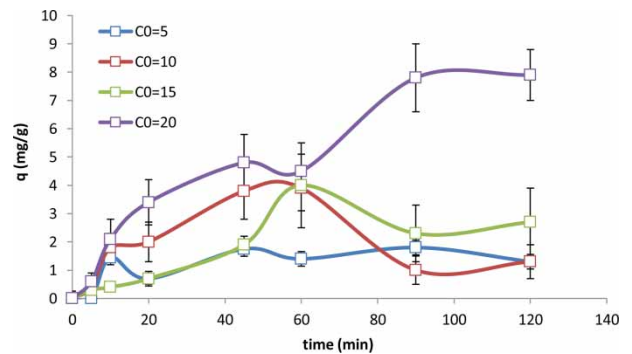


Figure 7 | Effect of contact time and initial fluoride concentration on efficiency of fluoride adsorption onto montmorillonite nanoparticles.

According to these figures, the maximum adsorption capacities, for both adsorbents, after passing 60 minutes has approximately reached equilibrium. For bentonite nanoparticles at fluoride concentrations of 5, 10, 15, 20 mg/L, the amounts of adsorption capacity at contact time of 60 minutes were 1.55, 4.7, 3.0 and 5.5 mg/g, respectively. For montmorillonite adsorbent at fluoride concentrations of 5, 10, 15, 20 mg/L, the adsorption capacities at contact time of 60 minutes were 1.4, 3.9, 4.0 and 4.5 mg/g, respectively. Therefore it is obvious that with increasing the initial fluoride concentration, the adsorption capacity of both adsorbents increases. That is because of more contact between the fluoride molecules and adsorbents. In a study conducted by Shirmardi and his colleagues in 2012 it was shown that with increasing the contact time and initial concentration of fluoride, the removal process becomes more effective (Shirmardi *et al.* 2012). In another study conducted by Asgari and his colleagues in 2012, it was shown that the maximum amount of fluoride removal was at pH 3,

adsorbent dose of 5 g/L, contact time of 30 minutes and initial fluoride concentration of 5 mg/L (Asgari *et al.* 2013).

Effect of adsorbent dosages

Figure 8 shows the amounts of fluoride adsorption on both adsorbents with dosages of 0.25, 0.5, 0.75 and 1 g/L.

Figure 8 shows that with increasing the adsorbent masses, the adsorption capacities of the adsorbents decreases. So the maximum amount of adsorption with these two adsorbents occurred when the adsorbent mass was 0.25 g/L. As can be concluded from the results, due to greater availability of the exchangeable sites or surface area at higher concentrations of the adsorbent, with increasing of adsorbent dosage from 0.25 g/L to 1 g/L, the removal efficiency of fluoride increased. This was due to increasing collisions and also free bond on adsorbent surfaces (Naghizadeh & Nabizadeh 2016; Naghizadeh *et al.* 2016).

Adsorption isotherm

The results of two types of the most commonly used isotherms, Langmuir and Freundlich, are presented in Figures 9 and 10, respectively, and summarized in Table 1. Regarding these figures and table, it is obvious that both Freundlich and Langmuir isotherms describe well the adsorption of fluoride by montmorillonite (R^2 equal to 0.99) and the Langmuir isotherm was found to be more suitable for adsorption of fluoride onto bentonite nanoparticles as evidenced from the value of the regression coefficients ($R^2 = 0.90$), confirming the results of a

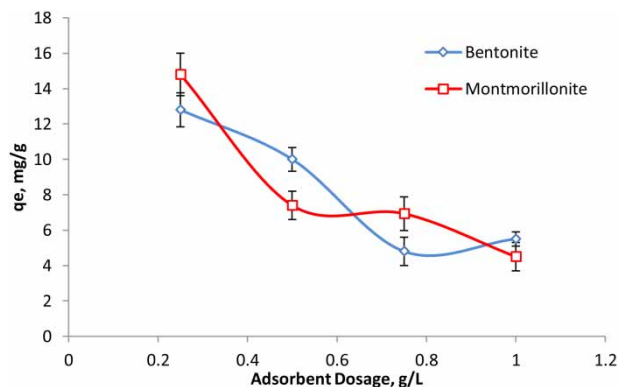


Figure 8 | Effect of adsorbent dosage on the removal of fluoride by bentonite and montmorillonite nanoparticles.

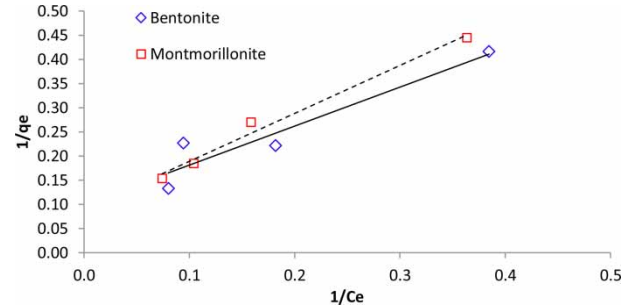


Figure 9 | Langmuir isotherm for bentonite and montmorillonite nanoparticles.

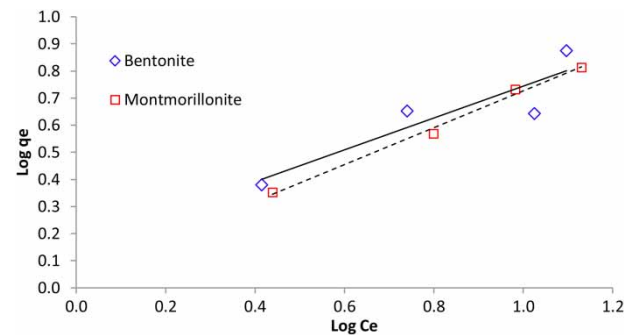


Figure 10 | Freundlich isotherm for bentonite and montmorillonite nanoparticles.

Table 1 | Freundlich and Langmuir isotherms constants

Isotherm	Constants	Values	
		Bentonite	Montmorillonite
Freundlich	R^2	0.81	0.99
	k_f (mg/g)	1.43	1.11
	n	1.70	1.47
	$1/n$	0.59	0.68
Langmuir	R^2	0.90	0.99
	R_L	0.22	0.50
	K_L (L/mg)	0.12	0.73
	q_{max} (mg/g)	9.95	11.15

study conducted by Kagne and his colleagues in which they studied hydrated cement as a potential adsorbent for removal of fluoride from aqueous solutions (Kagne *et al.* 2008).

Effect of temperature and thermodynamic parameters on fluoride adsorption onto bentonite and montmorillonite nanoparticles

Thermodynamic parameters studies included enthalpy changes (ΔH°), entropic changes (ΔS°) and Gibbs free

energy (ΔG°). In this study thermodynamic parameters were conducted at different temperatures (288, 318, 298 and 308 K). In Figure 11 and Table 2, the results of temperature effect on the fluoride adsorption process by both adsorbents are shown.

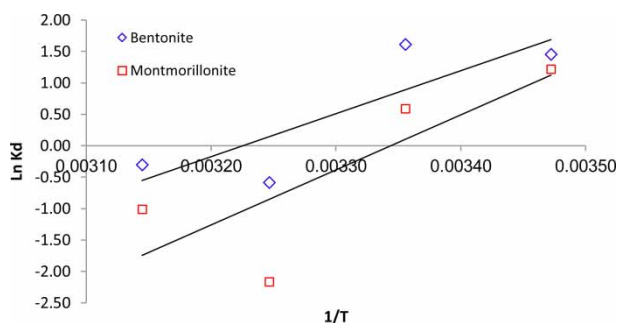


Figure 11 | The effects of temperature on the adsorption of fluoride onto bentonite and montmorillonite nanoparticles.

Table 2 | The results of effects of temperature on the removal of fluoride by bentonite and montmorillonite nanoparticles

Adsorbent	T (K)	qe (mg/g)	Thermodynamics parameters		
			ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
Bentonite	288	37.2	-3.48	-74.16	-242.18
	298	40	-3.99		
	308	8.8	1.50		
	318	11.2	0.81		
Montmorillonite	288	33	-2.92	-124.01	-417.46
	298	22.4	-1.47		
	308	2	5.55		
	318	6	2.67		

The results from Table 2 show that the adsorption process of fluoride by both adsorbents is exothermic (ΔH is negative). Also, the negative amount of ΔG shows the adsorption process to be spontaneous. The negative standard entropy change (ΔS°) indicates that the degree of freedom decreases at the solid-liquid interface during the adsorption of fluoride on to bentonite and montmorillonite nanoparticles. Similar results have been previously published by Takaaki *et al.* (2009) about adsorption behavior of fluoride ions using a titanium hydroxide-derived adsorbent. They found that rising temperature led to a reduction in fluoride removal.

Adsorption kinetics

In Table 3, the results of adsorption kinetics of the removal process by the two adsorbents are shown.

Surveying the kinetics of the adsorption process is useful for predicting the speed of adsorption in order to design models for the process. According to the results of the kinetic studies for fluoride adsorption by bentonite and montmorillonite nanoparticles at concentrations of 5, 10, 15 and 20 mg/L that are shown in Table 3, it can be seen that the kinetics of fluoride adsorption by bentonite nanoparticles can be better described by pseudo second-order kinetics (as the correlation coefficients are compatible with this model), and kinetics of fluoride adsorption by montmorillonite nanoparticles in lower fluoride concentrations (5 and 10 mg/L) can be better described by pseudo first-order model of kinetics but in higher fluoride concentration (15 and 20 mg/L) can be better described by pseudo second-order model of kinetics.

Table 3 | Results of the kinetic models of pseudo first- and second-order kinetics in removal of fluoride by two adsorbents

Adsorbents	C ₀ (mg/L)	Pseudo first-order			Pseudo second-order			
		K ₁ (min ⁻¹)	q _{e, cal} (mg/g)	R ²	K ₂ (g/mg min)	q _{e, cal} (mg/g)	R ²	q _{e, exp} (mg/g)
Montmorillonite	5	0.07	1.36	0.73	0.06	1.79	0.65	1.80
	10	0.06	3.02	0.69	0.01	5.97	0.33	3.90
	15	0.00	2.34	0.01	0.01	2.71	0.33	4.00
	20	0.01	3.31	0.01	0.01	7.25	0.45	7.90
Bentonite	5	0.01	1.15	0.64	0.04	1.58	0.78	1.80
	10	0.01	2.31	0.37	0.02	4.80	0.96	5.20
	15	0.00	2.54	0.05	0.02	2.97	0.80	4.30
	20	0.00	4.90	0.00	0.00	-9.64	0.05	9.10

CONCLUSION

In the present study, bentonite and montmorillonite nanoparticles were used for adsorption of fluoride from aqueous solution. Maximum adsorption process occurred at pH equal to 3. It was also observed that the increase in the initial concentration of fluoride increases the efficiency of the adsorption process. Increasing temperature led to reducing the adsorption capacity that is indicative of an exothermic adsorption reaction. Furthermore the adsorption of fluoride by bentonite in all the studied fluoride concentrations and montmorillonite in higher fluoride concentrations followed pseudo second-order kinetics. According to the results of this study bentonite and montmorillonite nanoparticles have good performance in the removal of fluoride, therefore could be used as a natural adsorbent for removal of fluoride from aqueous solutions.

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First received 3 March 2017; accepted in revised form 8 April 2017. Available online 26 May 2017