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Fluoride removal from aqueous solution by acid-treated clinoptilolite: isotherm and kinetic study

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ABSTRACT

For removing the fluoride contamination as a serious threat to human health, the adsorption process has shown an appropriate performance among several treatment methods applied in the past. Therefore, the present study investigated the removal of fluoride using the low-cost adsorbent of clinoptilolite treated with acid from aqueous solution. The adsorbent was characterized by various techniques, that is, scanning electron microscopy, X-ray diffraction, XRF and BET. In this lab-scale study, the effect of contact time (1–240 min), pH (3–11), initial concentration (2–8 mg/L) and adsorption dose (1–20 g/L) on the fluoride removal efficiency was evaluated in a batch system. In addition, the isotherm and kinetic studies were applied to describe the data obtained from the adsorption process. The results showed that the highest fluoride removal efficiency (87%) was obtained in the condition of pH = 3 and equilibrium time of 2 h. In addition, it is observed that the pseudo-second-order kinetic model and both the Freundlich and Langmuir isotherm models appropriately describe the obtained data during fluoride adsorption onto the studied adsorbent. Based on the results of this study, acid-treated clinoptilolite indicated an affordable and promising potential for the removal of fluoride from aqueous solution.

Keywords: Fluoride; Clinoptilolite; Adsorption; Isotherm; Kinetics

1. Introduction

The high concentration of fluoride ion in drinking water has the harmful influence on human health and long-term human exposure to the high concentration of fluoride through the drinking water brings some problems, especially fluorosis which is known as a chronic disease. In mild cases, it is revealed by the creation of mottling on teeth, whereas, in severe cases, the problems including neurological damage and softening the bones ossification of tendons and ligaments manifest fluorosis diseases is observed [1–4]. So that, with respect to health aspect, the recommended guideline level of

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fluoride concentration in drinking water was recommended to be 1.5 mg/L by WHO [5].

In general, water pollution by fluoride occurs through two pathways of natural source and human activities. In the structure of many of minerals, fluoride usually exists which is normally leached out due to minerals erosion by rainwater, and consequently contaminates both ground and surface waters [6,7]. Moreover, in the type of the pollutions arising from human activity, the fluoride was introduced into drinking water by the wastewaters discharged to the environment through the various industries, such as aluminum and steel production, metal finishing and electroplating and glass and semiconductor manufacturing. It can be also occurred by ore beneficiation and fertilization operation [8,9]. It is worth noting that even fluoride compounds as the precursors releasing fluoride are extensively applied in some industry. For instance, a number of fluoride compounds are applied in high-purity graphite production and nuclear industry [10].

It is reported that more than 200 million people in the world have received the concentrations of fluoride higher than the value recommended by WHO [11]. Plenty of studies have been implemented to evaluate the health risks caused by the exposure to high levels of fluoride [12–14] and also to investigate the different methods used to treat fluoride contaminated water. Up to date, various methods such as adsorption [11,15], electrocoagulation [16,17], reverse osmosis [18], nano-filtration [19], electrodialysis [20] and ion exchange [21] have been employed to remove the extra fluoride from aqueous environments. Among these processes, membrane and ion exchange processes are not very common due to their high installation and maintenance cost [22]. Some of these methods could be used for simultaneous removal of multiple pollutants from aqueous solution [17,23,24].

In last decades, the adsorption process to remove the fluoride from water has been investigated in a number of studies and various adsorbents, such as activated alumina, modified Azolla, Lemna minor, red mud and fly ash have employed in this process [25–28]. In recent years, some researches have been carried out on low-cost materials, such as local mineral adsorbents in order to investigate their ability on the elimination of some pollutants from aqueous environment. Natural zeolite is one of such low-cost materials, which has been investigated in various studies. The crystalline aluminosilicates form the main structure of natural zeolites. Zeolites with tetrahedron building blocks have composed of four oxygen atoms surrounding the relatively small atom of silicon or aluminum. Because the charge of aluminum is fewer than that of silicon, the framework of the zeolite has usually a negative charge and this negative charge is balanced by the exchangeable cation (K^+, Na^+, Mg^{2+} and Ca^{2+}). Therefore, the properties of the zeolite such as ion-exchange capability and cheapness have led to increase the attentions to use this substance for removing the unwanted ions from water supplies. In order to promote the qualitative properties of zeolite as a catalyst or adsorbent, the modification processes must be considered as one of the main parts of preparing the zeolite. The modification of surface, skeleton element and non-skeleton element is done by three methods that are usually employed for modifications of zeolite. Among them, non-skeleton element modification is the procedure which is widely utilized for modifications of zeolite, and is generally carried out under mechanisms of ion exchange or impregnation by treatment in the solutions of inorganic acids or some specific metals-derived salts [8]. One of the most well-known natural zeolites is the clinoptilolite and it is widely used in adsorption processes. Clinoptilolite has been widely spread over the most continents of the world, thus this expansiveness leads to that clinoptilolite known as a suitable candidate in adsorption process for the removal of many pollutants available in water and wastewater.

The main aim of the present study was to investigate the ability of the acid-treated clinoptilolite in removal of the fluoride from synthetic solutions in a batch system. In this study, the effects of variables, that is, contact time, pH of the solution, initial fluoride concentration and adsorbent dose on the adsorption efficiency were also studied. In addition, the isothermal studies were conducted using both Langmuir and Freundlich isotherm models to determine the adsorption capacity and equilibrium time of fluoride adsorption onto clinoptilolite. Furthermore, the kinetic studies using the pseudo-first order kinetic and pseudo-second order kinetic models were performed to explain the adsorption process and to determine kinetic coefficients.

2. Materials and methods

2.1. Materials

The clinoptilolite was purchased from Afrazand mineral Co., Semnan, Iran. All the chemicals including sodium fluoride, sodium hydroxide, hydrochloric acid, and sulfuric acid were of analytical grade and were obtained from Merck Co. (Germany).

2.2. Adsorbent preparation

First, the clinoptilolite was crushed up and was sieved to the particle size with a mesh in the range 30–40 [29]. Prior to treatment, the clinoptilolite was washed with deionized water for several times, and then it was impregnated with a solid to solution ratio of 1:10 in 5% solution of H_2SO_4 for 24 h. After being washed, the acid-treated clinoptilolite was dried in an oven at 105°C for 24 h. Finally, the obtained sample was calcinated at the temperature of 300°C for 2 h and was cooled in a desiccator before use. The pH_{pzc} (the point of zero charge) value of adsorbent was determined by pH-metric titration method as described by Chutia et al. [30]. The specific surface area of adsorbent was determined by BET method based on N_2 gas (Belsorp mini II, Japan). The mineralogy of clinoptilolite was also characterized by powder X-ray diffraction (XRD) techniques (RINT2200, Rigaku, Japan), and the surface morphology properties of acid-treated clinoptilolite were determined using the scanning electron microscope (SEM) technique (model KYKY EM3200, Japan). Finally, the chemical composition of acid-treated clinoptilolite was identified using XRF technique (model PW 2404 Philips, Holland).

2.3. Adsorption experiments

For preparing a stock solution with 100 mg/L concentration of fluoride, 221 mg of anhydrous NaF was dissolved in 1 L distilled water. The stock solution was then utilized to prepare desired working concentrations. All of fluoride adsorption experiments were carried out in a batch system using the constant volume of 100 ml in a 250 ml conical flask. NaOH (0.1 M) and HCl (0.1 M) solutions were used to adjust the pH of the fluoride solution to the desired level. Each sample was continuously shaken by a shaker at 180 rpm at the temperate of laboratory and for a desired time. It was then filtrated by the cellulose acetate membrane with a pore size of 0.45 µm. The amount of adsorbed fluoride was calculated as follows:

$$q = \frac{\left(C_o - C_e\right)V}{M} \tag{1}$$

where q is the mg of adsorbed fluoride per unit weight of adsorbent in equilibrium time (mg/g), C_0 and C_e are the initial concentration (mg/L) and concentration (mg/L) in the equilibrium time of fluoride, respectively, V is the volume of sample (L), and M is the used adsorbent dosage (g). By studying the previous studies, the variables and their ranges in the study were selected as follows [31–33]: the variables, which their effect was investigated on the adsorption efficiency, were contact time (1–240 min), pH (3–11), initial fluoride concentration (2–8 mg/L) and adsorbent dosage (1–20 g/L). After determining the optimum condition, the isotherm and kinetic studies of the adsorption process were carried out. The detection of the remaining concentration of fluoride in each sample was carried out using the DR.5000 spectrophotometer (Hach Co., Germany) at 590 nm wavelength according to SPADNS [34].

2.4. Regeneration

The exhausted acid-treated clinoptilolite was regenerated using 0.01 M NaOH [35,36]. In this way, the exhausted adsorbent was shaken with 50 mL of 0.01 M NaOH solution for 12 h, and then was impregnated into 5% solution of H_2SO_4 for 24 h, in a solid-to-solution ratio of 1:10 (w/v). After being washed, the adsorbent was dried in an oven at 105°C for 24 h. Finally, the obtained sample was calcinated at the temperature of 300°C for 2 h and was cooled in a desiccator before being used as regenerated adsorbent. Similar regenerated procedures were carried out in three consecutive adsorption–desorption experiments.

3. Results and discussion

3.1. Adsorbent characterization

Fig. 1 shows the XRD pattern of the acid-treated clinoptilolite. The XRD analysis revealed that the adsorbent is mainly composed of sodium aluminosilicates and other amorphous minerals reported in the previous study [37]. The chemical composition of this adsorbent based on XRF analysis is represented in Table 1, and it was observed to be similar to the previous study. The micrograph of SEM analysis was used to exhibit the acid-treated clinoptilolite morphology as is shown in Fig. 2. The image of the adsorbent indicates that the clinoptilolite has a porous surface. As can be observed in Table 2, the analysis of BET illustrated that the specific surface area of acid-treated clinoptilolite is 20.33 m^2/g.

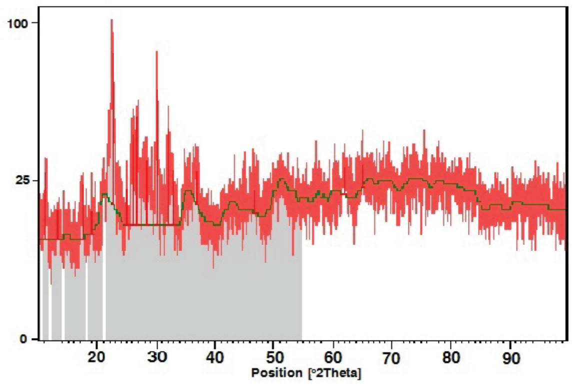

Fig. 1. XRD pattern of clinoptilolite.

Table 1
Chemical composition of clinoptilolite

	wt%
SiO_2	70.90
Al_2O_3	12.40
Fe_2O_3	1.21
CaO	2.54
K_2O	4.46
Na_2O	0.28
MgO	0.83

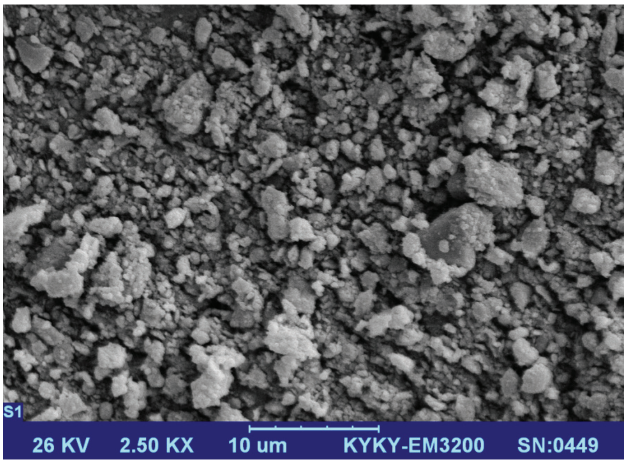

Fig. 2. SEM image of acid-treated clinoptilolite.

Table 2
Surface area and pore volume determining analyses of acid-treated clinoptilolite

Property	Acid-treated clinoptilolite
BET surface area (m^2/g)	20.33
BJH pore volume (cm^3/g)	0.1488
BJH average pore diameter (nm)	29.62

3.2. Effect of pH

The survey of pH effect on adsorption process is known as one of most important experiments, because its variations obviously influence on the net charge of an adsorbent, so that it is essential to recognize the effect of solution pH on the adsorption process of fluoride [2]. Fig. 3 displays influence of pH factor on fluoride adsorption efficiency of the raw clinoptilolite and acid-treated clinoptilolite in the range pH of 3–11, at the constant values of adsorbent dose = 10 g/L, initial fluoride concentration = 4 mg/L and contact time = 60 min. In the comparison between both the adsorbent in adsorption efficiency, acid-treated clinoptilolite was shown to be obviously more efficient than row clinoptilolite, for example, at pH = 3, adsorption percentage was achieved to be 73.5% for acid-treated clinoptilolite, while it was observed as 25% for raw clinoptilolite. The rest experiments were only conducted for the acid-treated clinoptilolite. It is apparent from Fig. 3 that the adsorption of fluoride onto the acid-treated clinoptilolite strongly is affected by solution pH. It is observed that fluoride removal would decrease when pH value enhances, and the efficiency reached the highest level when the pH of sample was adjusted to 3. Similarly, the same results were observed for fluoride adsorption onto the adsorbents of aluminum-impregnated activated carbon, acid-treated spent bleaching, and low-cost materials [10]. This result could be explained with regards to the obtained pH_{pzc} value of the acid-treated clinoptilolite. As seen in Fig. 4, the pH_{pzc} value of the adsorbent was 8, so that, at the pH values lower than pH_{pzc}, the surface charge would be positive; at the pH values equal to pH_{pzc}, the surface charge would be neutral; and at pH values higher than pH_{pzc}, the surface charge would be negative. As a result, the acid-treated clinoptilolite would acquire positive charge at the pH values lower than pH_{pzc}, and this charge would be more positive by further reduction of pH. Therefore, high efficiency in acidic condition can be attributed to presence of opposite charges between clinoptilolite and fluoride, and this efficiency would increase more if the pH of solution was further lowered. In contrast, the lower efficiency in alkaline condition can be explained by this fact that the presence of the same charge between clinoptilolite and fluoride led to the domination of repulsive forces, and consequently, to repel fluoride from clinoptilolite surface.

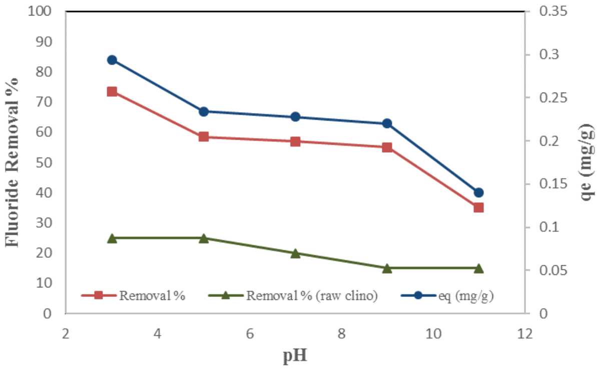

Fig. 3. Effect of initial pH (adsorbent dose 10 g/L, initial fluoride concentration 4 mg/L and contact time 60 min; ■ acid-treated clinoptilolite, ▲ raw clinoptilolite, ● adsorption capacity).

3.3. Effect of contact time

The second variable investigated in terms of its influences on the fluoride adsorption by acid-treated clinoptilolite was contact time. Fig. 5 shows efficiency variations as a function of contact time. Results illustrate that with increasing contact time until 10 min, the fluoride removal showed a rapid increasing trend, but when it reached 64%, there appeared a slow increasing trend until 120 min and after that equilibrium was reached. Obviously, the equilibrium time could be introduced as 2 h because, after this time, a significant increase is not observed in the adsorption of fluoride. Similar results have been previously reported for the adsorption of fluoride by natural zeolites [32]. This result could be interpreted by the fact that in initial contact time, especially up to 10 min, the adsorbent vacant sites exposed to fluoride is abundant, so it would lead to increment of adsorption efficiency. In contrast, due to the occupation and reduction of vacant sites at higher contact times, it is expected that the fluoride removal efficiency declines. On the other hand, since, in higher contact time, the fluoride concentrations exposed to clinoptilolite surface have been reduced, the number of collisions between adsorbent and adsorbate would decrease, and consequently the removal efficacy declines. In a study by Sun et al. [32], the maximum contact time was reported to be 2 h for fluoride removal using Fe^{3+}-modified zeolite.

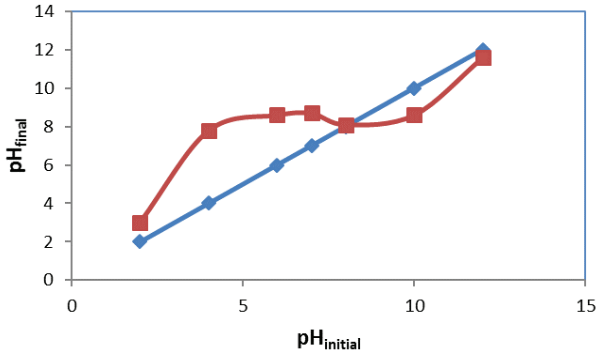

Fig. 4. Plots of pH_{final} as a function of $pH_{initial}$ for determination of pH_{PZC}.

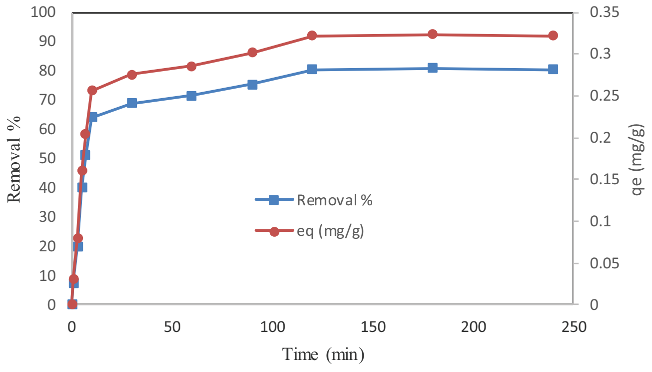

Fig. 5. Effect of contact time (adsorbent dose 10 g/L, initial fluoride concentration 4 mg/L and pH 3: ■ removal, ● adsorption capacity).

3.4. Effect of initial concentration

The effect of initial concentration of fluoride on adsorption efficiency is depicted in Fig. 6. Results showed that the adsorption capacity increased with increasing the initial concentration of fluoride. This phenomenon represents that, in high concentration of fluoride, the possibility of the collision between adsorbent and adsorbate increases, and then the higher amounts of fluoride would be adsorbed on clinoptilolite surface; so that the fluoride adsorption capacity would enhance. Similar results were observed in the study of Kamble et al. [31] so that increasing the initial concentration of fluoride has led to increasing the adsorption capacity of modified bentonite clay. Additionally, it is observed that equilibrium concentration enhances by increasing the initial concentration of fluoride. However, in the present study, the highest detected equilibrium concentration in the sample with an initial fluoride concentration of 8 mg/L was around 1.5 mg/L, which provides the guideline level of fluoride concentration in drinking water.

3.5. Effect of adsorbent dose

The influence of adsorbent dose on fluoride removal was investigated at the optimum condition, for example, initial concentration of 6 mg/L, pH of 3 and temperature of 25°C. This result showed that the removal percentage of fluoride enhanced from 34% to 87% when the dose of adsorbent increased from 1 to 20 g/L, respectively. However, after dosage of 10 g/L, there is no significant change in the removal percentage of fluoride, as observed in Fig. 7. It should be noted that, unlike the increase of removal efficiency, adsorption capacity indicated a declining trend. This decrease may be explained as follows: when the dosage of adsorbent increases, whereas initial fluoride concentration is fixed, a great portion of adsorbent sites would remain unsaturated, thus, this phenomenon leads to drop in adsorption capacity [10]. Moreover, reducing the adsorption capacity could be attributed to overlapping the active sites of clinoptilolite at its higher dosages [38]. Kamble et al. [31] in their study on defluoridation of drinking water by bentonite clay found similar results that confirm the results of current study in terms of adsorbent dosage.

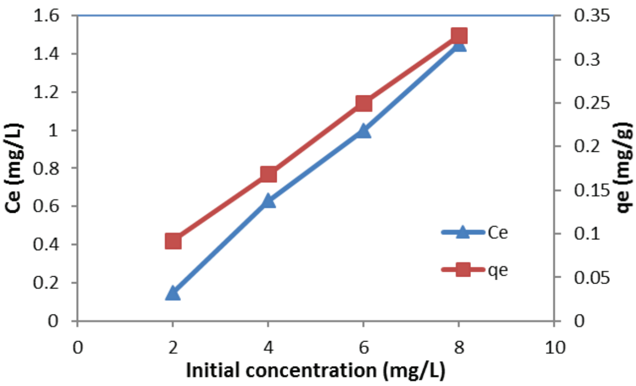

Fig. 6. Effect of initial concentration (contact time 2 h, adsorbent dose 20 g/L and pH 3: ▲ equilibrium concentrations, ■ adsorption capacity).

3.6. Adsorption isotherms

Because of design purposes, the survey and study of adsorption isotherms are taken into consideration. Langmuir and Freundlich, two well-known sorption isotherms, were the isotherms used in this study to analyze the experimental data [36].

Langmuir isotherm reveals that the adsorption on the surfaces of an adsorbent is of the type of monolayer coverage and assumes that the adsorption occurs at the homogenous surface of the adsorbent. Eq. (2) was employed to develop the linear form of Langmuir model as follows:

$$\frac{1}{q_e} = \frac{1}{q_{\max} b c_e} + \frac{1}{q_{\max}} \tag{2}$$

where C_e is the equilibrium concentration (mg/L), q_e is the adsorption capacity (mg/g), $q_{\max}$ is the maximum theoretical adsorption capacity, and b (L/mg) is the constant related to the enthalpy of adsorption process. By drawing the plot of $1/q_e$ vs. $1/C_e$, straight line and line equation were obtained and the values of $q_{\max}$ and b can be calculated by the slope and intercept of the line equation, respectively. The calculated values of these parameters are represented in Table 3.

Freundlich isotherm was developed to model the multilayer adsorption, and it represents that adsorption occurs on heterogeneous surfaces. Eq. (3) is the linearized form of Freundlich model as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

Both coefficients of K_F and $1/n$, which are indicative of the adsorption capacity and adsorption intensity, respectively,

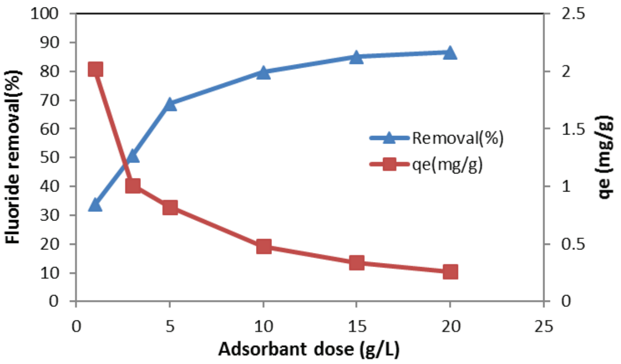

Fig. 7. Effect of adsorbent dose (contact time 2 h, fluoride concentration 6 mg/L and pH 3: ▲ removal, ■ adsorption capacity).

Table 3
Langmuir and Freundlich isotherm constant for the adsorption of fluoride on acid-treated clinoptilolite

Langmuir isotherm		Freundlich isotherm	
$q_{\max}$ (mg/g)	1.19	$1/n$	0.76
b (L/mg)	0.21	K_F (mg/g)	0.71
R^2	0.98	R^2	0.99

are empirical constants. The values of K_F and $1/n$ as shown in Table 3 were calculated by the obtained slope and intercept from the linear Freundlich plot developed by plotting $\log q_e$ vs. $\log C_e$.

It was observed from the linear equations that the coefficient of determination of Freundlich model ($R^2 = 0.99$) was higher than that of Langmuir model ($R^2 = 0.98$) and consequently is better obeyed by the adsorption process; however, the difference is not of appreciable amount. So that, it can be concluded that both the Freundlich and Langmuir models are potentially able to explain the adsorption behavior of fluoride onto acid-treated clinoptilolite, the active sites of which are distributed in both homogenous and heterogeneous form.

The study conducted by Wang and Reardon [39] to remove the fluoride using the activated soil clarified that the experimental data were more consistent with the Freundlich model. Moreover, Zhang et al. [40] reported that adsorption process of fluoride from wastewater onto calcium chloride modified natural zeolite corresponded to both Freundlich and Langmuir models, however R^2 value is calculated to be higher for Freundlich model than Langmuir models but the observed difference was little. In the following, a number of studies conducted on the adsorption of fluoride were investigated in terms of isotherm models, and the maximum adsorption capacity of fluoride is represented in Table 4.

3.7. Adsorption kinetics

Study on adsorption kinetics is important in terms of the determination of adsorbates uptake rate by adsorbent [44]. In this study, the pseudo-first-order model and the pseudo-second-order model as two most common types of adsorption kinetic models were employed to analyze the experimental data related to equilibrium time in optimum condition.

The linear form of pseudo-first-order kinetic model is given by the following equation:

$$\log\left(q_1 - q_t\right) = \log q_1 - \left(\frac{k_t}{2.303}\right)t \tag{4}$$

where q_1 and q_t are mg of adsorbed fluoride per unit mass of adsorbent (mg g^{-1}) at equilibrium and t time (min), respectively, and k_1 is kinetic constant (min^{-1}) for pseudo-first-order kinetic model. Typical plot of pseudo-first-order model for adsorption of fluoride on acid-treated clinoptilolite is shown in Fig. 8. The values of k_1, q_1 and the coefficient of determination (R^2) calculated from the linear equation are listed in Table 5.

The pseudo-second-order kinetic model is usually expressed by the following equation:

$$\frac{1}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2}t \tag{5}$$

where q_2 and q_t are mg of adsorbed fluoride per unit mass of adsorbent (mg g^{-1}) at equilibrium and t time (min), respectively, and k_2 is the kinetic constant of pseudo-second-order adsorption model in g mg^{-1} min^{-1}. The typical pseudo-second-order model for adsorption of fluoride on acid-treated clinoptilolite is plotted in Fig. 9. The values of k_2, q_2 and the coefficient of determination (R^2) obtained from linear equation are listed in Table 5.

As can be observed in Table 5, the equilibrium adsorption capacity ($q_{1,\mathrm{cal}}$) calculated using the pseudo-first-order kinetic model is higher than the adsorption capacity obtained experimentally ($q_{e,\exp}$), whereas $q_{2,\mathrm{cal}}$ value calculated by the pseudo-second-order kinetic model is close to the value of $q_{e,\exp}$. This result indicates that the adsorption of fluoride onto the acid-treated clinoptilolite is better described by the pseudo-second-order kinetic model compared with the pseudo-first-order kinetic model. Moreover, as it is seen in Table 5, the coefficient of determination (R^2) value obtained by the pseudo-second-order kinetic model is higher than that in the pseudo-first-order type; so that it is considered as further confirmation that the fluoride adsorption onto the acid-treated clinoptilolite follows the pseudo-second-order kinetic model. Similar results have also been observed in previous studies conducted to adsorb the fluoride onto nano sodalite zeolite and acid-treated bentonite [36,45].

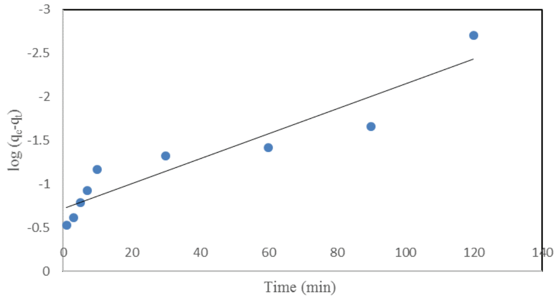

Fig. 8. Pseudo-first-order kinetic plot for fluoride removal (adsorbent dose 10 g/L, initial pH 3, fluoride concentration 6 and contact time 2 h).

Table 4
Comparison of the adsorption capacity of different adsorbents for fluoride adsorption

Adsorbent	Maximum adsorption capacity ($q_{\max}$) (mg/g)	Adsorption isotherm	Ref.
Acid-activated mud	2.8	Langmuir and Freundlich	[41]
$CaCl_2$-modified zeolite (CZ)	1.766	Langmuir and Freundlich	[40]
Bentonite/chitosan beads	0.895	Freundlich	[42]
Granular acid-treated bentonite (GHB)	0.278	Redlich–Peterson and Freundlich	[36]
Montmorillonite	0.263	Freundlich and Redlich–Peterson	[43]
Acid-treated clinoptilolite	1.19	Langmuir and Freundlich	This study

Table 5
Kinetic parameters estimated for fluoride adsorption onto acid-treated clinoptilolite

q (exp)(mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	k_1 (1/min)	q (cal)(mg/g)	R^2	k_2(g/(mg.min))	q (cal)(mg/g)	R^2
0.32	0.014	0.48	0.884	0.43	0.33	0.995

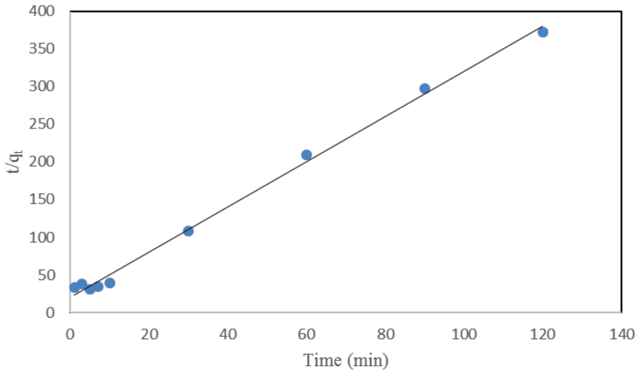

Fig. 9. Pseudo-second-order kinetic plot for fluoride removal (adsorbent dose 10 g/L, initial pH 3, fluoride concentration 6 and contact time 2 h).

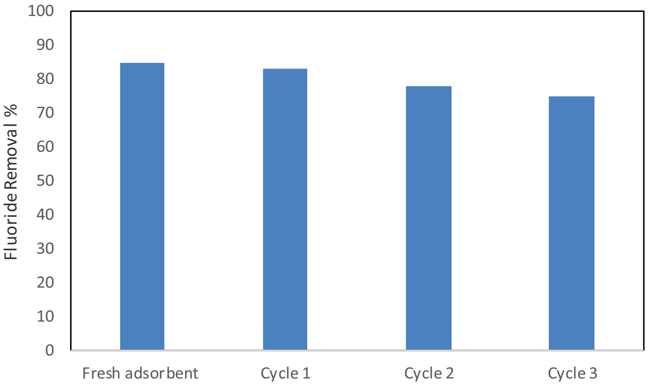

Fig. 10. Comparison of removal of fluoride by using fresh adsorbent and regenerated adsorbent (contact time 2 h, fluoride concentration 6 mg/L, pH 3 and adsorbent dose 15 g/L).

3.8. Desorption and regeneration of adsorbents

An adsorbent is known to be economically viable when it can be regenerated and reused in many cycles of operation. The selection of a desorbing agent largely depends on the influence of pH on fluoride adsorption and the strength of adsorption [46]. At higher pH conditions, acid-treated clinoptilolite has little sorption of fluoride (Fig. 3). Therefore, alkali (NaOH) can be used as a regenerant to adjust the pH in the solution to realize the fluoride desorption and regeneration of exhausted adsorption (as described in section 2.4). As can be seen from Fig. 10, the regenerated sample indicates no obvious reduction in adsorption efficiency after three cycles, where the desirable reusability of acid-treated clinoptilolite is revealed. The related results also indicate that used adsorbent can be regenerated by the alkali treatment.

4. Conclusions

The natural clinoptilolite treated by acid exhibited a considerable potential in the fluoride removal from the aqueous solution. This batch-adsorption study in laboratory scale revealed that fluoride concentration can be reduced to the lower level of 1.5 mg/L under the optimum condition. The optimum values of the parameters affecting the fluoride adsorption onto the acid-treated clinoptilolite were observed to be as follows: pH = 3, contact time = 2 h, adsorbent dosage = 10 g/L and fluoride concentration = 6 mg/L. Moreover, it is identified that the fluoride adsorption on acid-treated clinoptilolite is well described by both Freundlich and Langmuir adsorption model, and the kinetic results also indicated that the adsorption follows the pseudo-second-order kinetic model. Since clinoptilolite as an environment-friendly adsorbent has a lower chemical consumption and waste release, it could be proposed to test clinoptilolite in real scale.

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