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Removal of Fluoride from Wastewater by Natural and Modified Nano Clinoptilolite Zeolite

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ABSTRACT
In this study adsorption of fluoride ion from high-fluorine solutions (<2000 ppm) using the natural and modified ground clinoptilolite is investigated. These low-cost adsorbents are carefully characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), thermos-gravimetry (TGA) and differential scanning calorimeter analysis (DSC). In order to enhance the fluoride removal capacity of natural zeolite, it is milled into nano-powders and modified using hexadecyltriammoniumions ($HDTMA^+$). The kinetic, equilibrium, and thermodynamic of fluoride adsorption are measured and described by the well-known mathematical models. The Langmuir model is fitted to the experimental data of nano HDTMA-clinoptilolite with the average relative error (ARE) of 1.57%. According to Langmuir isotherm, the maximum adsorption capacity of nano clinoptilolite and nano HDTMA-clinoptilolite are determined 25.26 and 32.40 mg/g, respectively. The heat of fluoride adsorption onto the nano-clinoptilolite and nano HDTMA-clinoptilolite is calculated to equal to -82.57 and -60.46 kJ/mol, respectively. Kinetic studies indicated that fluoride adsorption rate on nano HDTMA-clinoptilolite is higher than unmodified zeolite and it is modeled by the pseudo-second kinetic model.

Keywords: *Adsorption, Clinoptilolite, Fluoride, $HDTMA^+$, Nanopowder, Surface Modification*

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INTRODUCTION

In recent decades, the excessive discharge of domestic, agricultural, and industrial wastewater containing various organic and inorganic pollutants had become a serious threat to natural resources. During various industrial activities including glass and ceramic production, semiconductor manufacture, electroplating, coal-fired power stations, beryllium extraction, brick and ironworks, aluminum smelters, and UF_6 production, fluoride ions could pollute the groundwater [1]. Pollution of groundwater with fluoride ions has adverse effects on human health and the environment. The presence of fluoride anions over 1.5 ppm in drinking water could be harmful [2-4]; therefore, the removal of fluoride ions from industrial wastewater is extremely important. In order to eliminate fluoride from aqueous solutions, various chemical and physical methods were developed [3-4]. Chemical precipitation and adsorption, ion exchange, and membrane-based methods such as nano-filtration, reverse osmosis, and electrodialysis was utilized in the defluoridation process [3-4]. Among these methods, adsorption as a significant method for wastewater treatment is broadly utilized [5-6]. Finding cheap, efficient, and green adsorbents are the subject of many research activities [7-8]. One of the natural adsorbents is zeolite. Natural zeolites are extensively utilized in the treatment of wastewater

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containing heavy metals [9-11], anions [12-18], and organic components [19-20]. In addition, fluoride removal by various kinds of unmodified [21-24] and modified natural zeolites [25-28] was studied. Natural zeolite modified with Fe (III) [25-26], calcium chloride [27], and chitosan [28] indicated a good tendency towards the adsorption of fluoride from aqueous solution.

Zeolites are hydrated crystalline aluminosilicate compounds comprising alkaline and alkaline earth cations. Cations embedded in zeolites tend to exchange with positively charged species in solution [29]. In order to remove anions, it is necessary to alter the surface charge of zeolite. The easiest way to do this is to perform adsorption in the pH range below the pH_{PZC}. The pH point of zero charges (PZC) is the pH value at which the electrical charge density on a solid surface is zero. When the pH is lower than pH_{PZC}, the surface of the material is protonated by H^+ ions of water and is positively charged and therefore attracts anions [30]. Surface modification of zeolite is another way of making them suitable for anion attraction [13-20]. Modification of zeolite with the hexadecyltrimethylammonium ($HDTMA^+$) ions is an example of cationic surfactant modification [31, 32]. Although HDTMA-modified zeolites were not yet used for the defluoridation process, they were utilized in order to attract various anionic species from aqueous solution [13-20].

In the uranium conversion factory of Isfahan, Iran, wastewater with large amounts of fluoride was produced; thus, in this study, the adsorption of fluoride onto the natural Iranian clinoptilolite which was from a solution containing high concentrations of the anion (<2000 ppm) was investigated. In addition, clinoptilolite as the most abundant zeolite in Iran was modified with $HDTMA^+$ and used in the defluoridation process. Clinoptilolite is belonged to the HEU zeolitic group with the typical unit cell composition of Na_6 $[(AlO_2)_6(SiO_2)_{30}].24H_2O$ [29]. Moreover, in order to eliminate the mass transfer resistance and increase the external surface area of zeolite, the natural zeolite was mechanically milled by utilizing a planetary ball milled. The milling procedure for the production of nano-clinoptilolites has been described in our previous work [33]. In addition, through a careful investigation of the kinetic, equilibrium, and thermodynamic of fluoride removal, a mechanism was proposed for the defluoridation process by natural and modified clinoptilolite.

MATERIALS AND METHODS

Materials

Hexadecyltrimethylammonium bromide (HDTMABr), Ca $(NO_3)_2$, $NaNO_3$ and NaF were supplied from Merck company and Iranian clinoptilolite zeolite was obtained from Afrazand company. Nanopowder of natural clinoptilolite zeolite was prepared by using a planetary ball mill according to the optimum condition presented in our previous work [33].

Characterization method

The crystallinity of Iranian clinoptilolite was studied using an STOE STAD-MP X-ray diffractometer (XRD) using Cu (Kα) at 40 kV and 30 mA.

Fourier transforms infrared spectroscopy (FTIR) was also used for further structural analysis of clinoptilolite and HDTMA-clinoptilolite. IR spectrum was recorded using a Perkin-Elmer PE-2000 FTIR spectrometer. A mixture of the sample and KBr was pressed into a thin wafer for FTIR measurements.

Thermal behaviors of the samples were studied using simultaneous thermogravimetry and differential scanning calorimeter analysis (TGA–DSC) techniques using a Rheometric Scientific Analyzer. Samples were heated in an air atmosphere at a heating rate of 10 °C/min from room temperature up to 700 °C.

The morphology and particle size of the ground clinoptilolite were investigated by scanning electron microscopy (SEM, KYKY-EM3200).

The cation exchange capacity of ground Iranian clinoptilolite was determined through the batch adsorption method. In this method, 0.1 g of the adsorbent is added into 20 ml of a solution containing 1000 ppm of Ba^{2+} ions at neutral pH. The suspension was shacked for 24 h at 25°C. After separation of the adsorbent, the concentration of Ba^{2+} ion in the clear solution was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) method (Perkin-Elmer, USA). Moreover, in order to determine the exchange capacity of Ca^{2+} embedded in zeolite with Na^+ cations in the solution, the aforementioned procedure was carried out using a solution containing 1210 ppm of Na^+ that was prepared from $NaNO_3$ salt. The concentration of Ca^{2+} in solution was measured by ICP-OES.

In order to determine the point of zero charges (ZPC) of natural ground clinoptilolite, 0.1 g of

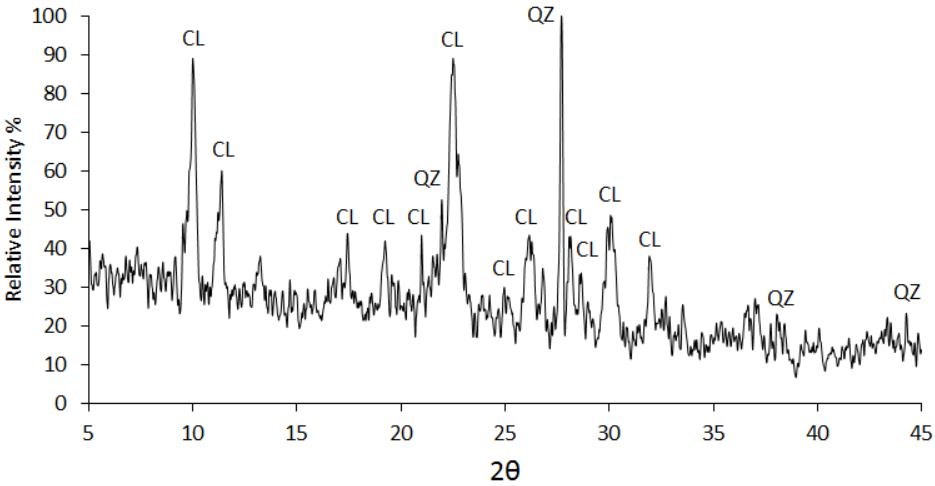


Fig. 1. The X-ray diffraction pattern of Iranian clinoptilolite

zeolite was added to a 50 ml solution of 0.1 M $NaNO_3$. The pH of solution was adjusted in the range of 2 to 12 by adding the appropriate amount of 0.01 M NaOH and 0.01 M HNO_3. The solution pH levels were measured after 24 h shaking at room temperature [24].

Modification of nano clinoptilolite

5 g of ground clinoptilolite powder was added to 250 ml of 0.2M HDTMBr solution in a polyethylene flask. The suspension was shaken at 25 °C and 160 rpm for 24 hours. Afterward, the modified sorbent was separated by centrifugation at 12000 rpm and was washed by redispersing in distilled water followed by recentrifugation for three times. Finally, the obtained powder was dried in air at 30 °C for 48 hours.

Fluoride adsorption measurement

Adsorption experiments were studied using a batch method. In order to calculate the adsorption isotherm, 0.1 g of adsorbent was added to 10 ml of NaF solutions with concentrations ranging from 150 to 2000 ppm. The samples were shaken at 160 rpm and 25°C for 24 hours. Afterward, the suspensions were centrifuged at 12000 rpm for 10 minutes and the concentration of fluoride ions in obtained clear solution was measured using a F^- selective electrode connected to an ion meter (USA, Van London Phonix).

In order to evaluate the adsorption kinetic, 0.1 g of sorbent was added to10 ml of 1000-ppm NaF solution. The suspensions were shaken at 25 °C and 160 rpm for various intervals of time ranging from 15 minutes to 24 h. Finally, the solution was separated by centrifugation and analyzed by F^- selective electrode in order to measure fluoride ions.

In order to find the effects of temperature on the fluoride adsorption, 0.1 g of adsorbent was added to the 10 ml of NaF solution with a concentration of 250, 1000, and 2000 ppm. The suspensions were shaken at 160 rpm for 24 h at various temperatures ranging from 25 to 60°C. In the end, the adsorbent separated from the suspension by centrifugation, and the concentration of fluoride ion was measured by F^- selective electrode.

RESULTS AND DISCUSSIONS

Characterization of adsorbent

The X-ray diffraction pattern of ground zeolites is shown in Fig. 1. The main crystalline phase of the sample is clinoptilolite zeolite. The main peaks which belong to clinoptilolite [34] have been identified by CL in Fig. 1. Otherwise stated, the strong peaks that were about 2q = 10°, 11°,° 22°, 27°, 30° and 32° could be attributed to the clinoptilolite structure.

In addition, the XRD pattern confirmed that the small amounts of quartz as impurities exist in the samples. The main peaks belonging to quartz are observed at 2θ of 21.94 and 27.17 degrees.

The Fourier transform infrared spectra of ground clinoptilolite and HDTMA-clinoptilolite are shown in Fig. 2. In the spectra of unmodified zeolite, peaks at 610-1060 cm^{-1}range are characteristic of clinoptilolite. The band at 1060 cm^{-1}could be attributed to the asymmetric internal

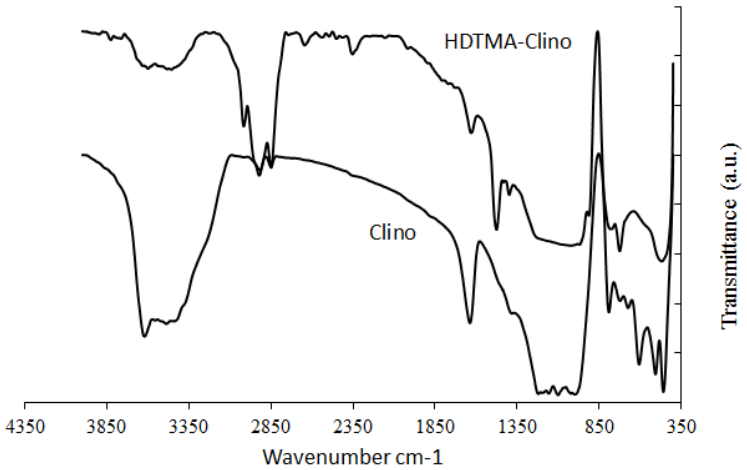


Fig. 2. Fourier transform infrared spectra of ground clinoptilolite and HDTMA-clinoptilolite

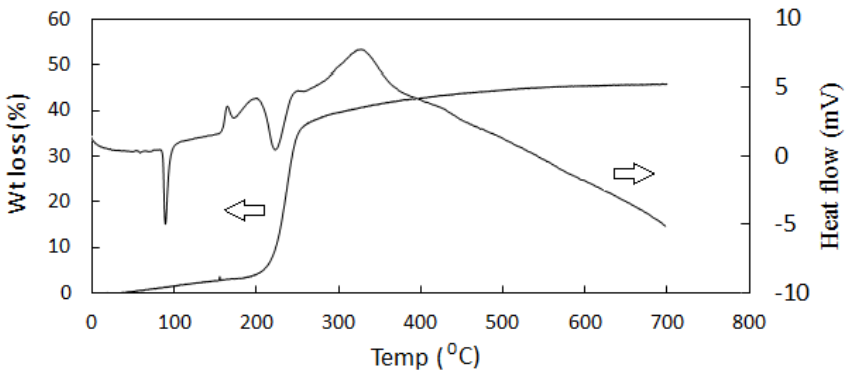


Fig. 3. TGA-DSC thermal analysis of modified ground clinoptilolite

tetrahedral bending [35-37]. The peak at 609 cm^{-1}could be attributed to the double rings in the framework structure [35-37]and The bands at 700 -1200 cm^{-1} range could be attributed to the asymmetric stretching modes of internal tetrahedra and symmetric stretching modes of external and internal tetrahedra [35-37].

The bands that appeared on the FTIR spectra of modified zeolite at 715–740, 1420–1480, and 2800–3000 cm^{-1} own it to HDTMA molecules [12, 31]. The bands at 2920 cm^{-1} and 2851 cm^{-1} belong to the asymmetric and symmetric stretching vibrations of CH_2, respectively [12, 31]. Therefore, it could be concluded that $HDTMA^+$ cations adsorbed on the surface of zeolite and the washing process has no reverse effects on the structure of the modified zeolite.

In order to determine the amount of adsorbed $HDTMA^+$ ions on the ground clinoptilolite surface, the TGA-DSC thermal analysis of samples was performed and the results are shown in Fig. 3. As shown in Fig. 3 two endothermic reactions occurred at 104 and 231°C that were related to the water elimination. At 332°C an exothermic reaction started that belongs to the elimination of $HDTMA^+$ ions and prolonged to the temperature above 540°C. Therefore, weight loss related to the elimination of $HDTMA^+$ has been estimated at 5.7wt%. This value is equivalent to the adsorption of 200.7mmol of $HDTMA^+$ ions per Kg of clinoptilolite. This value is in the range of what has been reported by other researchers [14, 18, 31, and 32].

The SEM image of milled natural clinoptilolite is shown in Fig. 4. SEM image indicated that the zeolite powders with particle size less than 100 nm agglomerate as the larger particles. Moreover, particles have lost their initial octahedral shape and converted into spherical, elliptical, or irregular

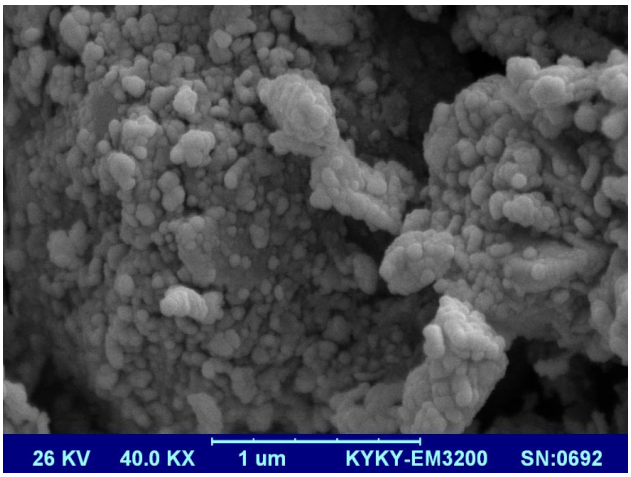


Fig. 4. the SEM image of milled clinoptilolite

Table 1. Chemical composition of Iranian clinoptilolite measured by XRF

Component	Al_2O_3	SiO_2	Na_2O	MgO	K_2O	CaO	Fe_2O_3	TiO_2	L.O.I	Others
mass ratio wt%	7.95	65.9	0.47	0.57	3.31	4.26	1.05	0.18	13.63	2.68

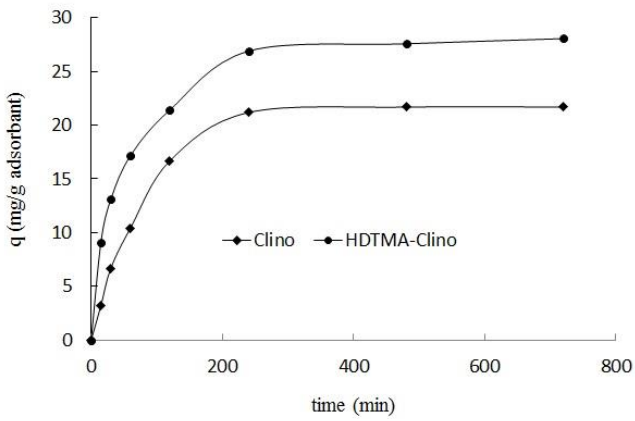


Fig. 5. adsorption kinetics of fluoride on modified and unmodified nano clinoptilolite

shapes.

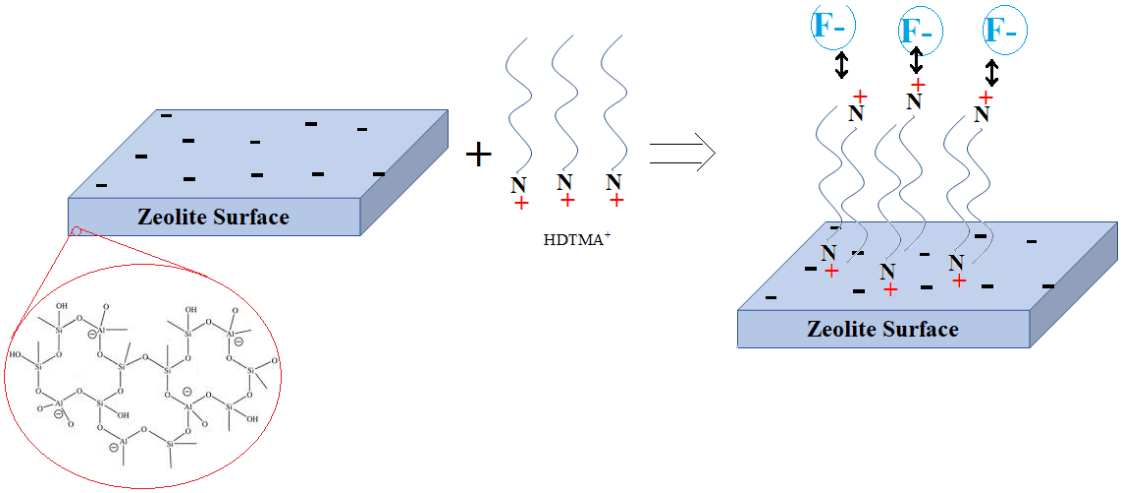
The chemical composition of Iranian clinoptilolite that was determined by XRF was given in Table 1. The results indicated that the Si/Al molar ratio of adsorbent is about 7 which is higher than the Si/Al ratio of a typical clinoptilolite. According to the XRD pattern, higher amounts of Si/Al ratio is related to the presence of quartz impurity. Moreover, the amounts of K^+ and Ca^{2+}cations in the sample are more than other cations. If Na^+, K^+, Ca^{2+}, and Mg^{2+} were considered as the exchangeable cations, the cation exchange capacity of clinoptilolite was estimated at around 1.14 meq/g.

Cation exchange capacity (CEC) of zeolite was also determined by the adsorption of Ba^{2+} cations. At this experiment, the CEC of clinoptilolite was measured equal to 1.318 meq/g.

Removal of fluoride

Effect of contact time and adsorption kinetic

The amount of sorbed fluoride ion on nano-clinoptilolite and nano HDTMA-clinoptilolite at various contact times is shown in Fig. 5. These data were measured at an initial concentration of 1000 ppm. It could be observed that the modification



Scheme1: Illustration of clinoptilolite modification with HDTM and fluoride ions uptake.

of clinoptilolite with $HDTM^+$ increases the fluoride adsorption capacity. Modification leads to the creation of the anionic adsorption site on the surface of zeolite. During the modification stage, $HDTMA^+$ cations attract bycolumbos bonds on the negative surface of zeolite [18]. As the concentration of $HDTMA^+$ becomes higher than critical micelle concentration (CSC), the attraction between hydrophobic tails could cause the formation of a bilayer or patchy bilayer with positive charge head groups [18]. Therefore, one appropriate mechanism for the removal of fluoride anions could be an electrostatic attraction with these positive head groups (scheme 1).

Although, in the presence of attracted barium anions on this positive heads, the anion exchange between barium and fluoride anions may be the exact mechanism. Moreover, Haggerty et al proposed the surface precipitation mechanism for the removal of chromate anions by HDTMA-clinoptilolite [18]. The presence of the hydrophobic tail of $HDTMA^+$ creates an organic solvent-like environment with lower dielectric constants than water. Therefore, anions and cations may precipitate in this media.

The reason for the fluoride removal by clinoptilolite is also described by Gomez et al. [21-22]. At pH levels below pH_{PZC}, the surface charge of zeolite is positive and appropriate for the attraction of anions through electrostatic forces. The PZC of clinoptilolite is related to its structure and it measured less than 6.8 [20-25]. In this study, the pH_{pzc} is measured equal to 6.25. At pH levels between 6.8 and 7.2 (which is the pH used in this study), the surface charge of zeolite was negative and according to the high adsorption capacity of clinoptilolite, there may exist another effective mechanism. The mechanisms proposed for the removal of anions by zeolite include: 1) interaction of the anions by the hydrated cations of zeolite through hydrogen bonding, 2) substitution of anions with OH^- bonded to Al or Si atoms, 3) attraction or substitution of anions onto the partial protonated sites of OH_2^+ and 4) occlusion mechanism [20-26]. Furthermore, the result of Na+-Ca^{2+} exchange experiment revealed that after 24 h the Ca^{2+} concentration in the solution with the initial Na^+ content of 1210 ppm was 34.8 ppm. If this amount of Ca^{2+} gets replaced with Na^+ in the NaF solution, 0.068 g of CaF_2 will precipitate. It means that about 26% of the fluoride adsorption capacity of nano clinoptilolite is related to the precipitation of CaF_2. In addition to the precipitation mechanism, the occlusion mechanism seems to be more probable than the others. Fluoride would be easily occluded in the zeolite cavity due to the Donnan effect, which is related to the associated cations in the solution [24]. Cai et al. showed that this mechanism is the predominant mechanism in defluoridation by natural zeolite [24].

Moreover, the initial kinetic rates of fluoride removal by nano-clinoptilolite are slower than nano HDTMA-clinoptilolite that may be related to the presence of an additional intra-crystalline diffusion resistance that was imposed because of the exchange between Na^+ existing in the solution

Table 2. parameters of the kinetic model

Absorbent	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
	K_I (1/min)	q_e (mg/g)	ARE %	K_{II} (g/mg.min)	q_e (mg/g)	ARE %
Nanoclinoptilolite	0.0115	21.76	2.47	0.0005	25.53	5.93
Nano HDTMA- clinoptilolite	0.026	26.93	8.48	0.0011	29.24	3.59

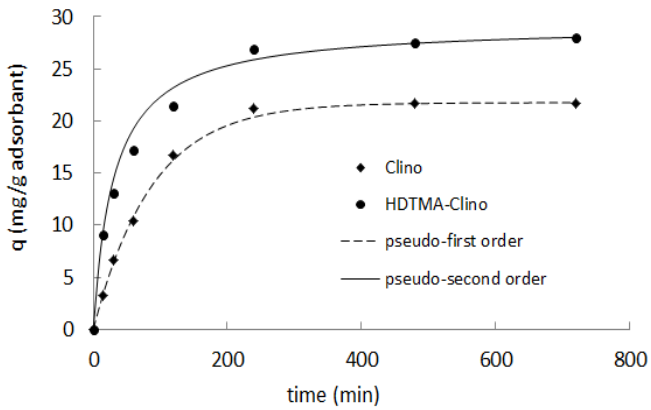


Fig. 6. Comparison between adsorbed fluoride capacities obtained from the theoretical model and experimental data

and Ca^{2+} embedding in the zeolite cages as well as the attachment of Na^+ to the internal surface of zeolite pores.

In order to present the appropriate expressions for describing the defluoridation kinetic rate, pseudo-first-order and pseudo-second-order kinetic models were fitted to the obtained data. These models are given in equations1 and 2, respectively [38, 39].

$$\frac{dq_t}{dt} = K_I(q_e - q_t) \quad (1)$$

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

Where, q_e and q_t are the sorption capacity (mg/g) at equilibrium state and time t, respectively. The kinetic rate constant (K_I and K_{II}) and q_e were determined through the minimization of the average relative error (ARE) given in the following equation. The optimization was performed using Matlab software.

$$ARE\% = \frac{1}{n}\sum_{j=1}^{n}\frac{\left|q_t^{\exp} - q_t^{cal}\right|}{q_t^{\exp}} \times 100 \quad (3)$$

Where, n is the number of experimental points and q_t^{cal} and q_t^{exp} are the calculated and experimental amounts of adsorbed fluoride at time t, respectively. The parameters of kinetic models were given in Table 2. According to the average relative error, pseudo-first-order was a better fit for the experimental data of clinoptilolite and the pseudo-second-order kinetic model has a good agreement with the adsorption kinetic data of HDTMA-clinoptilolite. Fig. 6 indicates the agreement between the theoretical and experimental kinetic data. The pseudo-second kinetic model proposed by Blanchard et al [40] is usually associated with situations similar to a chemical reaction [38]. Moreover, in some theoretical attempts, the pseudo-second-order kinetic model has been obtained by the assumption that a chemical reaction is occurring on the surface of sorbents [38]; thus, the surface ion-exchange mechanism may be a true assumption in the fluoride removal by nano HDTMA-clinoptilolite. Furthermore, obtained q_e is consistent with the Langmuir maximum adsorption capacity presented in the last section. As mentioned earlier, the initial adsorption rate of fluoride ions on nano HDTMA-Clinoptilolite is higher than nano clinoptilolite zeolite. The reason for this finding may be the elimination of internal diffusion resistance in nano HDTMA-clinoptilolite. The size of the $HDTMA^+$ ions is

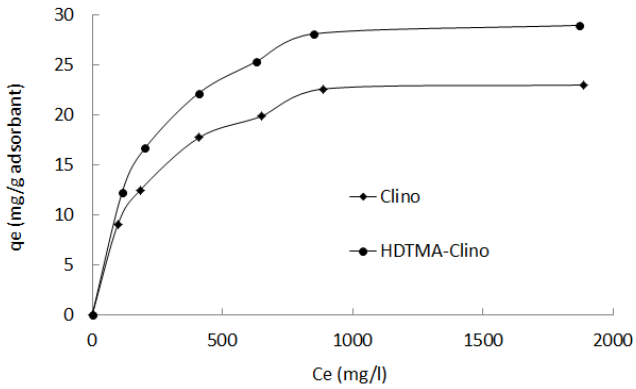


Fig. 7. Fluoride adsorption isotherm at T=25°C

Table 3. parameters of isotherm model

Models	Parameters	Adsorbent	
		Nano Clinoptilolite	Nano HDTMA-Clinoptilolite
Langmuir	K_L (L/mg)	5.60e-3	5.3e-3
	q_{max}(mg/g)	25.26	32.40
	ARE%	1.83	1.57
Freundlich	K_F	1.81	2.41
	N	2.71	2.74
	ARE%	7.38	7.23

too large to enter the zeolite channels. Thus, the bilayer of $HDTMA^+$ (adsorption sites) is formed on the external surfaces of zeolite; since the film diffusion and anion exchange rates are the rate-limiting factors. According to the precipitation and occlusion mechanism of nano clinoptilolite zeolite, the Na^+ ions penetrate the zeolite channel and get adsorbed on the internal surface or get replaced with Ca^{2+}ions. Therefore, intra-crystalline diffusion as well as the other rate-limiting factors influence the overall sorption rate. The pseudo-first kinetic model is used in situations that the diffusional transport of solute is the rate-limiting step [38, 41]. The solution for the partial differential equation obtained for the mass transport of species A into a porous solid plate has an exponential form, similar to the solution of the pseudo-first-order model [42]. Therefore, the agreement between the model and the experimental data may be an indication of the proposed mechanism.

Adsorption isotherm

Adsorption isotherm of fluoride on the nano clinoptilolite and nano HDTMA-clinoptilolite are shown in Fig.7. The adsorption capacity of nano HDTMA-clinoptilolite is greater than nano clinoptilolite. The reasons for this finding were described in the previous section.

In order to predict the adsorption isotherm of fluoride ions, Langmuir (equation (4)) and Freundlich (equation (5)) isotherm models [43] were fitted to experimental data.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{4}$$

$$q_e = K_F C_e^{1/n} \tag{5}$$

In order to obtain the parameters of these models, the average relative error presented in equation 3 was minimized by using MATLAB software. The parameters of models are given in Table 3. According to the ARE, the Langmuir model has a good prediction of experimental data. The results are shown in Fig. 8.

Effect of temperature on adsorption capacity

The effects of temperature on fluoride removal are shown in Fig. 8. Results indicated that the increase in temperature leads to the capacity adsorption decrease of both modified and unmodified nano clinoptilolite. Similar behavior has been reported for the adsorption of Chromate

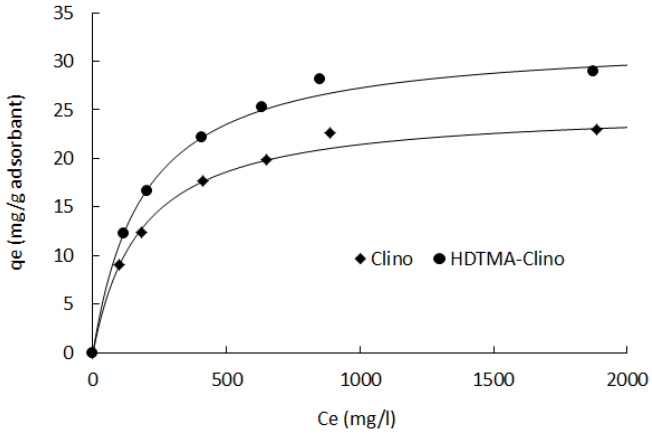


Fig. 8. Comparison between Langmuir model and experimental isotherm data

Table 4. the temperature dependency of Langmuir parameters

Models	parameters	Adsorbent	
		Nano Clinoptilolite	Nano HDTMA-Clinoptilolite
Langmuir	K_{L0}(L/mg)	2.99e-16	3.20e-12
	Q (kJ/mol K)	82.57	60.46
	q_{max}(mg/g)	25.26	31.91
	ARE%	2.70	3.09

[16] and arsenic [17] anionic species by HDTMA-clinoptilolite. An increase in temperature may lead to surfactant desorption. Besides, the adsorption capacity of HDTMA-Clinoptilolite was higher than the unmodified zeolite; this indicates that at a temperature of 333 k, $HDTMA^+$ cations have not been completely desorbed.

As illustrated in the previous section, the Langmuir isotherm model was in good agreement with the experimental data. Thus, in order to model the effects of temperature on adsorption capacity, temperature dependency of Langmuir constant (K_L) was assumed as the following equation [39].

$$K_L = K_{L0}\frac{1}{T^{0.5}}e^{Q/RT} \tag{6}$$

Where, Q, R, and K_{L0} are the heat of adsorption, universal gas constant and pre-exponential factor, respectively.

In order to find the K_{L0}, Q, and q_{max}, the ARE given in equation 3 was minimized by utilizing the MATLAB software. Results were given in Table 4. Additionally, the predicted data for the adsorption of F^- onto the selected adsorbents at various temperatures in the range of 297 to 333 K are shown in Fig. 9 and are compared with the experimental data.

Thermodynamic properties of Gibbs free energy change (ΔG^0)ΔG^0)), entropy change ((ΔS^0)(ΔS^0)), and enthalpy change (ΔH^0)ΔH^0)) could provide useful information for the design of an adsorption process. In order to calculate the parameters, equation (7) was used [44-47].

$$\ln K_a = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} \tag{7}$$

Where R is the gas universal constant and K_a is the thermodynamic equilibrium constant without unit. According to Eq. (7), (ΔH^0) and ((ΔS^0)(ΔS^0)) parameters could be individually calculated from the slope and intercept the plot of ln (K_a) versus 1/T. (ΔH^0) and ((ΔS^0)(ΔS^0)) values are dependent on the method selected for the estimation of K_a. According to the Langmuir model's assumption, adsorption of the species of A is performed by the following equation.

A+free-Site on adsorbent ↔A-Site on adsorbent (8)

Thus, the following formula gives a relationship between K_a and K_l [44].

$$K_a = \frac{K_L}{\gamma_e}(1mol\ L^{-1}) \tag{9}$$

Where, γ_e is the activity coefficient at adsorption equilibrium that could be calculated by

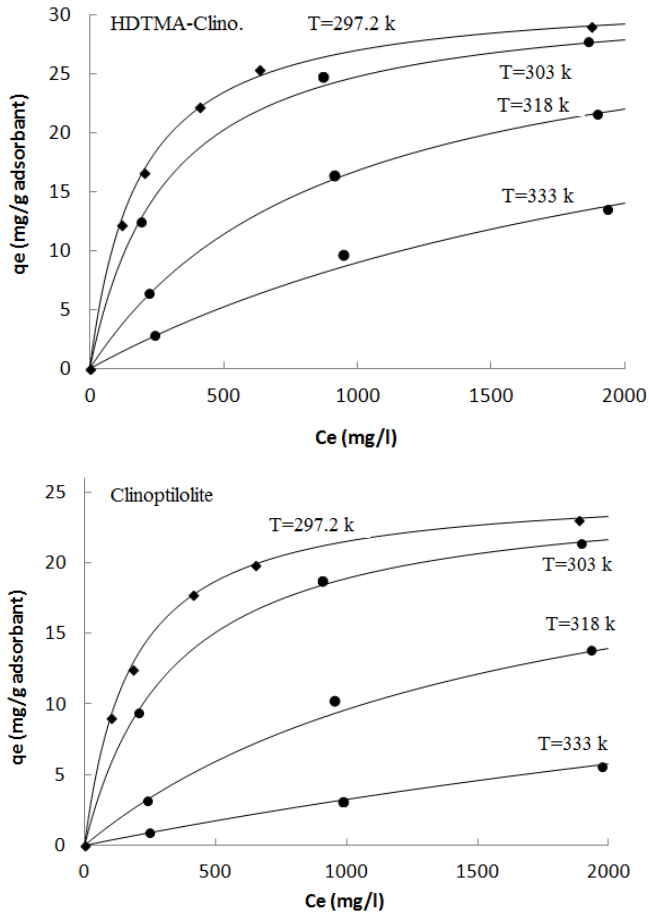


Fig. 9. the effect of temperature on adsorption capacity of nano clinoptilolite and nano HDTMA-clinoptilolite different temperatures

Table 5. Thermodynamic parameters

Absorbent	ΔS^0 (J/mol.K)	ΔH^0 (kJ/mol)
Nano Clinoptilolite	-318.68	-83.02
Nano HDTMA-clinoptilolite	-240.49	-58.82

the Debye-Huckel thermodynamic law [44]. In a dilute solution of charged adsorbates, the activity coefficient would be closed to unity. Thus, in equation 9, K_a could be replaced by K_t. Therefore, the calculated (ΔH^0) and ((ΔS^0)(ΔS^0)) parameters are given in Table 5. $\Delta H^0 \Delta H^0$ in the adsorption of F^- onto nano-clinoptilolite and nano HDTMA-clinoptilolite is negative indicating the exothermic nature of this process in a temperature range of 25-60 °C. Moreover, the results indicated that the value of $\Delta H^0 \Delta H^0$ in F^- adsorption on clinoptilolite is in the range of the heat of chemisorption (80-200 kJ mol^{-1}). Therefore, the mechanism proposed in section3.2.1 including the cation exchange of Ca^{2+} with Na^+ following by the precipitation of CaF_2 as well as occlusion mechanism is verified.

The negative values of ((ΔS^0)(ΔS^0)) also suggest a decrease in the degree of adsorbate freedom ions. In the case of F^- removal through precipitation and occlusion mechanism, the decrease in the entropy of the system is easily understood.

The values of Gibbs free energy (ΔG^0)ΔG^0)) were directly calculated according to Eq. 10.

$$\Delta G^0 = T\Delta S^0 - \Delta H^0 \quad (10)$$

The calculated Gibbs free energy showed in Fig.10. The negative values $\Delta G^0 \Delta G^0$ are an indication of the spontaneous nature of F^- removal in this study.

Table 6 shows the fluoride ions uptake ability

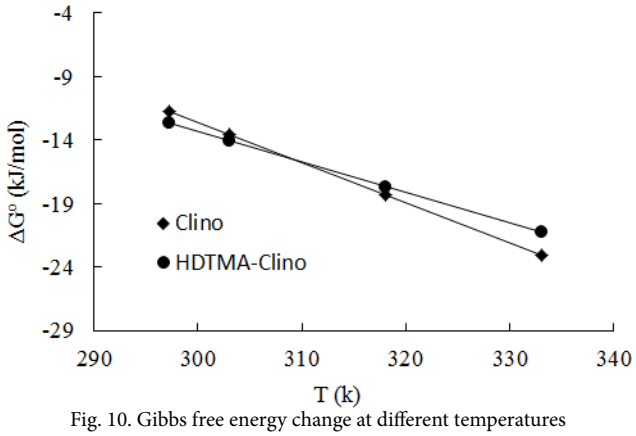


Fig. 10. Gibbs free energy change at different temperatures

Table 6. Comparison of the adsorption capacity of the HDTMA-clinoptilolite and some of the reported adsorbents

Adsorbent	Maximum Adsorption capacity (mg/g)	Reference
Activated carbon	18.9	[45]
Alginate	39.9	[46]
Aluminum modified zeolitic tuff	10.25	[47]
Aluminum (hydr)oxide coated pumice	7.87	[48]
Fe–Al–Ce nano-adsorbent	2.77	[49]
Fe-Ti oxide nano-adsorbent	47.0	[50]
Graphene	48.31	[51]
Hydrous bismuth oxides	1.93	[52]
Zirconium-iron oxide	9.80	[53]
PP@Fe3O4 nanocomposite	~23	[54]
Diatomite Modified with Aluminum Hydroxide	1.67	[55]
HDTMA-clinoptilolite	32.40	Current work

of the HDTMA-clinoptilolite compared with some reported adsorbents [48-58]. The results indicated that the modified zeolite has comparable and, in some cases, a greater affinity for fluoride ions adsorption.

CONCLUSION

In order to enhance the fluoride removal capacity of clinoptilolite zeolite, the zeolite was milled into nanopowders and modified by the $HDTMA^+$ surfactant. Kinetic, equilibrium, and thermodynamic properties of fluoride removal by the modified and unmodified clinoptilolite were carefully investigated. Results indicated the maximum adsorption capacity of clinoptilolite and HDTMA-clinoptilolite is 25.26 and 32.40 mg/g, respectively. The adsorption heat of modified and unmodified nano clinoptilolite was measured equal to -60.46 and -82.57 kJ/mol, respectively. The fluoride removal rate using nano HDTMA-clinoptilolite is faster than unmodified zeolite. The pseudo-second-order model was well fitted to the defluoridation rate of nano HDTMA-clinoptilolite. The defluoridation kinetic data using nano clinoptilolite was in good agreement with the first-order kinetic models indicating the internal mass transfer resistance is controlling the kinetics of the process. According to the obtained results, the salt precipitation and occlusion mechanism may be a predominant mechanism in defluoridation by nano clinoptilolite. In addition, anion exchange over nano HDTMA-clinoptilolite is the fluoride removal mechanism.

CONFLICT OF INTEREST

Author declares no conflict of interest.

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