

Nitrate Removal from Aqueous Solution by Using Modified Clinoptilolite Zeolite

Ali Azari^a, Amir Hossein Mahvi^b, Simin Naseri^b, Roshanak Rezaei Kalantary^{c*}, Mohammad Saberi^d

^aDepartment of Environmental Health Engineering, Tehran University of Medical Sciences, Health Faculty, Tehran, Iran.

^bDepartment of Environmental Health Engineering, Tehran University of Medical Sciences, Tehran, Iran.

^cDepartment of Environmental Health Engineering, Iran University of Medical Sciences, Tehran, Iran.

^dDepartment of Environmental Health Engineering, Qom University of Medical Sciences, Health Faculty, Qom, Iran.

*Correspondence should be addressed to Ms. Roshanak Rezaei Kalantary; Email: r-rezaei@sina.tums.ac.ir

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Background & Aims of the Study: Nitrate is one of the most important pollutants that its reduced form, nitrite, can cause serious problems for human health and environment. Adsorption with cheap sorbents such as Zeolite is the best way for removal of this pollutant. So this study aimed to apply modified Clinoptilolite Zeolite for nitrate removal.

Materials & Methods: Firstly, Clinoptilolite zeolite was screened by 1-2 mm sieves for monolithic of it. Then zeolite was boiled in HCL 20% for 3 hours for removal of Carbonate and impurities present in zeolite structure and increase of porosity and purity of zeolite. Finally, the zeolite was dried in temperature of 300°C to evaporate the water present in zeolite structure and increase the absorbability. After the modification of the Zeolite, the effects of pH, time, strings speed, optimum amount of adsorbent in Nitrate removal were investigated and optimized by one factor at the time method. Also reaction kinetics and isotherms were determined.

Results: This study indicated that the optimum condition for Nitrate removal by means of modified zeolite as adsorbent is pH=5, contact time of 180 minutes and adsorbent amount of 16 g/l. The investigation of isotherm and kinetic equations indicated that Nitrate adsorption follows Langmuir and pseudo first order, respectively.

Conclusions: The zeolite modified by HCL and heat has a higher efficiency in Nitrate removal compared to simple zeolite, because of losing its hygroscopic water and having larger sites, although in total it doesn't have sufficient efficiency for Nitrate removal.

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Background

Much of the water on earth is salty and only 3 percent of these resources are fresh water and potable. Iran has a small proportion of this freshwater because Iran is located in desert and arid areas. Because of ascending trend of

population and industries and agricultural development (1), frequently application of chemical fertilizers for improving products quality (2,3) as well as increase of livestock and animal and human wastes (4), the groundwater pollution with Nitrate is increasing continuously, so that it has been raised as a problem even in advanced countries.

In our country, the risk of the pollution of groundwater and surface water in areas with high groundwater level and in areas active in agriculture and animal husbandry is more than other areas (5,6). Nitrate ion has a high solubility, so it couldn't be removed easily from water easily. This ion is relatively non-toxic but its reduction by microorganisms to Nitrite can cause serious health risks for human (7). If Nitrate concentration reaches to 45 mg/l in a baby's body, it causes a disease named methemoglobinemia. This disease results in a baby's body bruising that is idiomatically named blue baby (8-11). Also, the presence of Nitrate in water sources causes eutrophication (algal bloom) phenomenon that result in inefficiency of the water sources. For this reason, EPA and WHO set the maximum permissible concentration of Nitrate as 45 mg/l in terms of Nitrate or 10 mg/l in terms of Azote (12,13). The methods used for Nitrate elimination from water include ion exchange, reverse osmosis, denitrification and chemical reduction (7,14,15). Anionic and cationic resins are used in ion exchange method. These resins synthesis is very costly; furthermore the plants that produce these resins are themselves the cause of air pollution (16).

Denitrification process is more used for wastewater, and the biological sludge produced in this process, itself requires treatment and final disposal, which leads to extra problems and costs, so this process is taken into less consideration in water treatment (7,14,15). Totally, because of the problems and high costs of the mentioned methods, some countries are turning to the use of adsorption. Adsorption process has been more attractive in recent years because of its low cost, simplicity and easy operation (17). Many studies have been done in the world in this regard, in which Clinoptilolite zeolite was used as an efficient and inexpensive adsorbent (18). Clinoptilolite, crystalline and hydrated mineral Aluminosilicates of alkali metals and alkaline earth metals zeolites have a three-dimensional network.

Their open structure consists of channels and holes of cations and water molecules with 3 to 10 angstrom pores, the cations present in these types of zeolites are moving, that results in ion exchange in these types of adsorbents (19). Due to the abundance of Clinoptilolite zeolite mines in Iran and its very low price and high efficiency in removal of the ions such as Ammonium and Nitrate, it seems to be beneficial to use this adsorbent in treatment of the polluted water sources (16,18). The main problem of the use of natural zeolites such as Clinoptilolite is smallness of the pores of this adsorbent that limits catalytic adsorption of this substance (19). For this purpose in this study, modified Clinoptilolite zeolite was used to accelerate adsorption rate in addition to higher efficiency of Nitrate removal. In this regard, Guan (2010) compared the efficiency of four different natural zeolites in Nitrate removal that the highest removal was related to the American zeolite in temperature of 50 °C (11).

Also Schick et al (2010) showed that the zeolite modified with HDTMA (hexadecyltrimethyl ammonium) has a good performance in Nitrate removal (12).

Aims of the study: The aim of the present study was to investigate the feasibility of increasing the modified zeolite efficiency in Nitrate adsorption process and study of their isotherm and kinetic.

Materials & Methods

Materials used in this study include KNO_3 , $\text{C}_2\text{H}_5\text{OH}$, HCl , NaOH and Clinoptilolite zeolite. All materials of this study have been provided from a Merck company. In order to determine residual concentration of nitrate Spectrophotometer UV-Visible Model (7400CE CECIL) was used. Regulated temperature and stirrer speed with used Incubator-Shaker and pH of the solution were determined by using pH meter modeled HACH-HQ-USA.

Preparation of synthetic solution: The standard solution (stock) with a Nitrate concentration of 100 mg/l was prepared by use of Potassium Nitrate (KNO_3 , MERCK of Germany) compound according to the method 4500- NO_3^- -B of standard methods. Then it was used to prepare the dilutions of 1, 5, 10, 20, 30, 50, 100 mg/l in order to draw the calibration curve.

1. Zeolite conditioning:

At first, Clinoptilolite zeolite was screened by using of 1-2 mm sieves. Then, the screened zeolite washed with double distilled water till its turbidity in water was eliminated. In the next step, the washed zeolite boiled in 20% Chloridric acid for 3 hours that causes the removal of Carbonate and impurities present in zeolite structure and the increase of porosity and purity of zeolite. Finally, the purified zeolite put in 40% Chloridric acid for 24 hours in order to make the zeolite pores larger. The zeolite was brought out of acid after 24 hours and washed several times with double distilled water and then was dried in temperature of 300°C to evaporate the water present in zeolite structure and increase the absorbability (20). In the next step, the effects of pH, time, and optimum amount of adsorbent and different concentrations of Nitrate and different isotherms and kinetics were investigated in Nitrate removal process.

2. Carrying the experiments out in batch conditions:

2.1 investigation of pH effect on adsorption rate

In 4 similar containers pH was adjusted in range of 3-9. Then 10 g of adsorbent added to 50 ml Nitrate solution with a concentration of 100 ppm. Time and stirring revolution were set as 4 hours and 200 rpm, respectively. Nitrate was measured in different pH in order to obtain the optimum pH.

2.2 investigation of time effect on adsorption rate:

10 g adsorbent in 50 ml Nitrate solution of 100 ppm concentration, stirring revolution of 200 rpm and obtained optimum pH were used to determine the optimum contact time. Time range was selected between 0 to 240 minutes based on previous studies.

2.3 investigation of the effect of stirring revolution on adsorption rate:

In order to determine the optimum stirring revolution, erlens were shacked on a shaker with a speeds range of 50, 100, 200, 300 and 400 rpm in optimum pH and contact time.

2.4 investigation of the effect of zeolite amount on adsorption rate:

After determining optimum pH, contact time and stirring revolution, adsorbent was added to erlens in concentrations of 2, 4, 6, 8, 10, 12 and 16 g/l and the erlens were shacked while the obtained optimum conditions for each adsorbent were kept constant. Primary concentration of Nitrate was considered as 100 mg/l.

2.5 investigations of different concentrations of Nitrate on adsorption rate:

After determining optimum pH, contact time, stirring revolution and adsorbent dosage, the efficiency of adsorbents was studied in different concentrations of Nitrate (50, 100, 150, 200, 300, 400 mg/l) in optimum conditions.

3. Parameters measurement:

All parameters were read by spectrophotometer in wave length of 220 and 275 nm and Nitrate amount was calculated in terms of mg/l according to below equation:

$$NO_3^- = (abs\ 220nm - 2abs\ 275nm) \quad (1)$$

Then, by using the read adsorption amount of unknown samples, the concentrations of these samples were calculated from the standard curve. SPSS software was used for static analysis of data and results presentation and Excel software was used to draw diagram and $p\text{-value} < 0.05$ was considered for determining signification of results.

4. adsorption isotherm:

In this study Langmuir and Freundlich adsorption isotherms models were used for mathematical modeling of Nitrate adsorption process.

4.1 Freundlich adsorption isotherm model:

Linear formulation of Freundlich isotherm is show in equation 2:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (2)$$

Where:

q_e : adsorbate amount per solid weight unit (mg/g), C_e : equilibrium concentration of the substance in solution (mg/l), K , n : Freundlich constant. Linear equation of Freundlich isotherm is as follows:

4.2 Langmuir adsorption isotherm model:

Mathematical model of this isotherm is given in equation 4:

$$\frac{1}{q_e} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}} \quad (3)$$

Where:

b , q_{max} : experimental constant
 q_e and C_e parameters are similar to Freundlich isotherm(18).

5. adsorption Kinetic:

Adsorption kinetics is useful for predicted the sorption rate and determined Factors affecting the rate of reaction. In this study, first and second pseudo order Kinetic were evaluated that linear forms of them is expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where q_e , q_t , k_1 , and k_2 are equilibrium adsorbent concentration on adsorbent (mg/g), adsorbed concentration at time t (mg/g), Pseudo first-order rate constant (L/ min) and Pseudo second-order rate constant (mg/g.min), respectively.

Results

Optimum pH of Nitrate removal:

The effect of pH on Nitrate removal (in contact time of 4 hours, stirring revolution of 200 rpm, zeolite concentration of 10 g/l and Nitrate concentration of 100 mg/l) is shown in the figure 1. The highest efficiency of zeolite in Nitrate removal was in pH=5, so pH=5 used to continue testing.

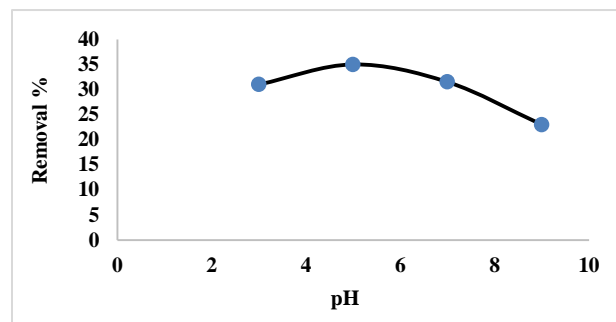


Figure 1) Nitrate removal efficiency in different pHs (contact time of 4 hours, stirring revolution of 200 rpm, zeolite concentration of 10 g/l, Nitrate concentration of 100 mg/l)

Optimum contact time of Nitrate removal:

The results of contact time effect on Nitrate removal in pH=5, zeolite concentration of 10 g/l and Nitrate concentration of 100 ppm, is shown in figure 2.

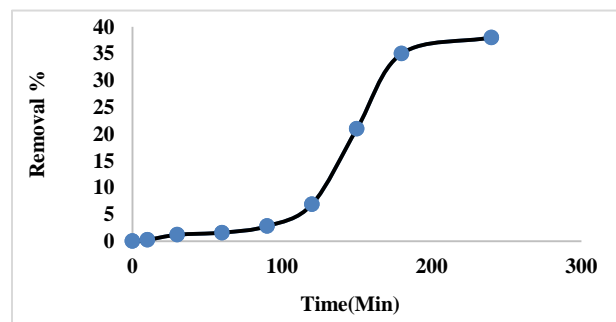


Figure 2) Nitrate removal efficiency in different contact times (pH=5, stirring revolution of 200 rpm, zeolite concentration of 10 g/l, Nitrate concentration of 100 (mg/l)

The highest efficiency of zeolite in Nitrate removal was at time of 240 minutes,

nevertheless since Nitrate removal efficiency at this time is not so different from the time of 180 minutes, so the time of 180 minutes was selected as equilibrium time to continue testing.

Optimum stirring revolution:

Figure 3 indicates that stirring revolution has no significant effect on Nitrate removal rate and stirring revolution was selected as 200 rpm to continue testing.

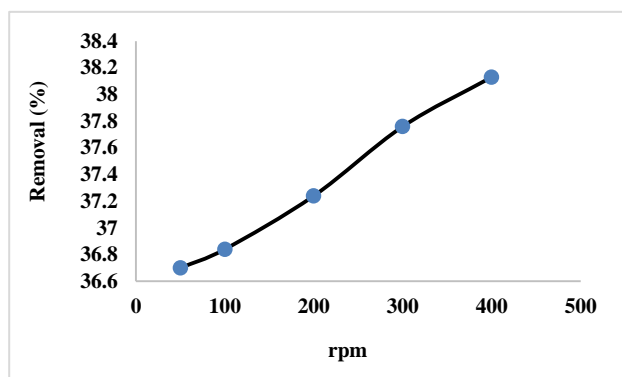


Figure 3) Nitrate removal efficiency in different stirring revolutions (pH=5, time of 180 minutes, zeolite concentration of 10 g/l, Nitrate concentration of 100 (mg/l))

Optimum concentration of adsorbent in Nitrate removal:

figure 4 shows the effect of zeolite dosage on Nitrate removal in pH=5, time of 180 minutes, stirring revolution of 200 rpm and Nitrate concentration of 100 mg/l.

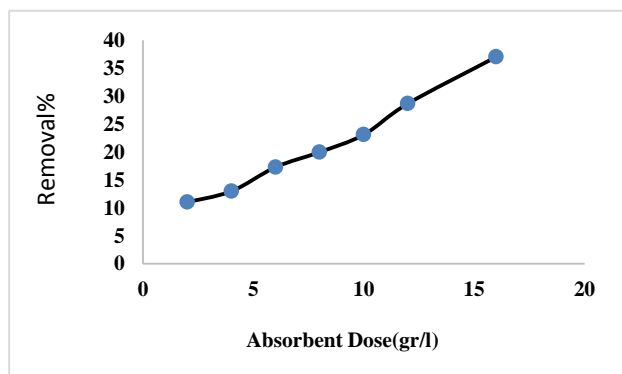


Figure 4) Nitrate removal efficiency in different concentrations of zeolite (pH=5, time of 180 minutes, stirring revolution of 200 rpm and Nitrate concentration of 100 (mg/l))

According to figure 4, the highest Nitrate removal efficiency of zeolite was related to optimum pH and contact time determined at adsorbent concentration of 16 g/l, which was used to continue testing.

Adsorption of different concentrations of Nitrate in optimum conditions:

The results of Nitrate removal efficiency in optimum conditions and different concentrations of Nitrate are presented in figure 5. maximum and minimum efficiency of Nitrate removal by Clinoptilolite adsorbent were investigated in concentration range of 50-400 mg/l and it was indicated that the highest and lowest adsorption were occurred in concentration of 50 and 400 mg/l, respectively.

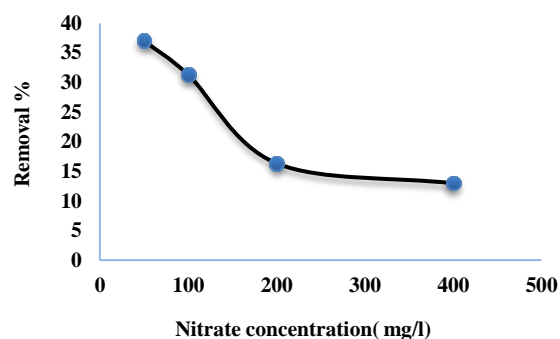
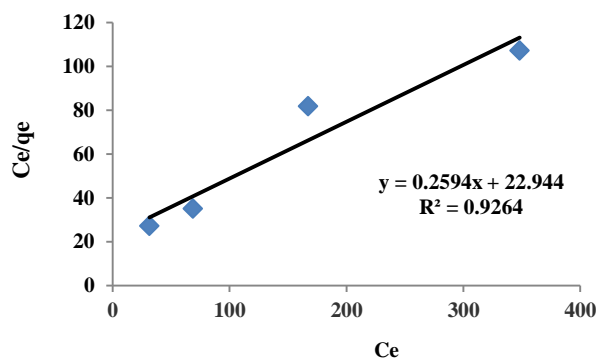


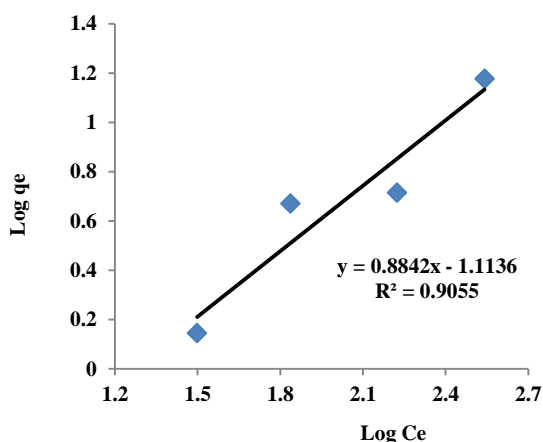
Figure 5) Nitrate removal efficiency in different concentrations of Nitrate (pH=5, time of 180 minutes, stirring revolution of 200 rpm and adsorbent amount of 16(g/l))

Adsorption isotherms:

Freundlich and Langmuir adsorption isotherms are shown in figure 6. curve of C_e/q_e versus C_e and diagram of $\text{Log}(q_e)$ versus $\text{Log}(C_e)$ indicate Langmuir and Freundlich isotherms, respectively. Langmuir and Freundlich constants values for Nitrate adsorption by modified Clinoptilolite zeolite are presented in table 1. B and q_m coefficients values in Langmuir isotherm for zeolite were determined as 0.38 and 21.66 mg/g, respectively with a correlation coefficient of 0.926.



(A)



(B)

Figure 6) (A)Langmuir isotherm, (B)Freundlich isotherm

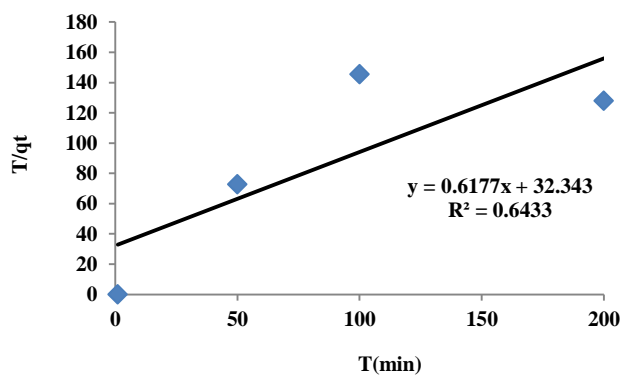
Table 1) Coefficients of isotherm models

adsorbent	Freundlich isotherm			Langmuir isotherm		
Modified zeolite	n	k	R ²	q _{max}	B	R ²
	0.385	1.334	0.905	2.66	0.38	0.926

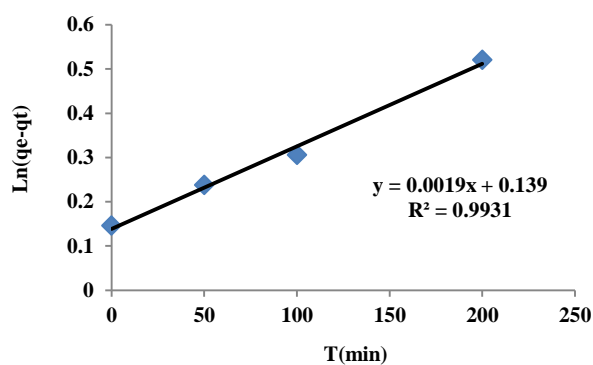
Adsorption kinetics:

The Results of various kinetics models for nitrate sorption onto modified Clinoptilolite zeolite are shown in table 2. As shown, calculated adsorption capacity for pseudo first order and pseudo second order models was 1.15 and 1.62 mg/g, respectively, whereas, adsorption capacity obtained from experiment

was 1.178 mg/g. The pseudo-first order and pseudo-second order are shown in Figures 7 (a, b), respectively.



(a)



(b)

Figure 7) adsorption kinetic models of (a) pseudo first order (b) pseudo second order

Table 2) Values of kinetic parameters for adsorption of nitrate

Pseudo first order			
q _{e,cal} (mg/g)	K ₁ (min ⁻¹)	R ²	
1.15	0.0019	0.993	
Pseudo first order			
q _{e,cal} (mg/g)	K ₁ (min ⁻¹)	R ²	q _{e,exp}
1.62	0.0196	0.643	1.178

Discussion

pH effect on Nitrate removal:

Data indicate that zeolite efficiency in Nitrate adsorption is decreased by changing pH from 3 to 9. The minimum and maximum efficiency of zeolite in Nitrate adsorption is in pH=9 and pH=5, respectively. In acidic pHs, production increase of available protons that are able to be added to zeolite surface has increased absorbability. However, in alkaline pHs, because of negative charge and OH⁻ ion, a repelling force is created between adsorbent and Nitrate that decreases the absorbability (17, 21). In a study of Chatterjee et al (2009) the maximum efficiency of Nitrate removal was 90% that was observed in pH=5 and Nitrate primary concentration of 500 mg/l. Chitosan modified with Sodium bisulphate was used as adsorbent in this study (7).

The effect of contact time on Nitrate removal:

The effect of contact time on Nitrate removal efficiency by zeolite adsorbent is shown in Figure 2. Nitrate removal by zeolite adsorbent was quick up to 180 minutes and it has been decreased gradually. Considering the highest efficiency of removal in this time and no significant changes in removal rate after this time, time of 180 min was selected as equilibrium time. In a similar study done by Soleimani et al (2008) on the efficiency of Firouzkouh and Semnan natural zeolites in removal of Nitrate with a primary concentration of 10 meq/l (60 mg/l), the equilibrium time was obtained 8 hours (20).

The effect of adsorbent concentration on Nitrate removal:

Equilibrium concentration of Nitrate was decreased by increasing the adsorbent mass, so that with increasing the zeolite adsorbent

amount from 2 to 16 g/l, output Nitrate concentration was decreased and adsorption efficiency was increased from 7 to about 37%. Modified Clinoptilolite zeolite can't be considered as a good adsorbent in Nitrate removal because of its Nitrate removal efficiency of 37%. In a study done by Oztork et al (2004) Nitrate removal rate with a primary concentration of 100 mg/l was increased from 75% to 100% by increasing the dosage of activated Sepiolite adsorbent from 2 g/l to 10 g/l (22).

The effect of stirring revolution on Nitrate removal:

As seen in Fig (3) with increasing stirring revolution from 50 to 400 in optimal condition removal efficiency of nitrate increased from 36.7 to 37.1%. This result indicated no effective significant for nitrate removal.

The effect of primary concentration of Nitrate on Nitrate removal:

The Nitrate removal rate of zeolite was decreased from 37.01% to 26.9% by increasing primary concentration of Nitrate from 50 mg/l to 400 mg/l. In a research done by Islam et al (2010) removal efficiency of Zn-Al-Cl-LDH adsorbent was decreased from 85% to 75% by increasing primary concentration of Nitrate from 10 mg/l to 100 mg/l (21). Adsorption efficiency decrease with increase of Nitrate concentration and constant adsorbent amount, can be related to the ratio of Nitrate concentration to adsorbent available surface, so that this ratio and so removal efficiency are decreased by increase of concentration (21,23). But due to adsorption of more amounts of substances per mass unit of adsorbent, adsorption capacity is increased.

Adsorption isotherm:

The results obtained from Langmuir and Freundlich isotherm models in nitrate removal

on modified Clinoptilolite zeolite showed that experimental data are following the Langmuir isotherm (The R^2 value for the Langmuir isotherm is higher than the Freundlich isotherm). This model expresses that distribution of nitrate sorption on modified Clinoptilolite zeolite are uniform and monolayer and this process are occurred in the homogeneous surface. According the Langmuir models the maximum of adsorption capacity for modified zeolite was calculated 2.66 mg/g. In a study by Demiral (2006) on Nitrate removal by zeolite, q_m value was obtained as 1.8 mg/g (24). K and n coefficients values in Langmuir isotherm for zeolite were determined as 1.334 and 0.385 respectively with a correlation coefficient of 0.903. R^2 values in these equations indicate that experiment data follow Langmuir isotherm.

Adsorption kinetics:

The results of various kinetics models for nitrate adsorption are illustrated in table 2. This table indicate that calculated adsorption capacity ($q_{e,cal}$) in the pseudo second order didn't match with experimental adsorption capacity ($q_{e,exp}$), so adsorption of nitrate onto modified Clinoptilolite zeolite isn't best fitted with pseudo second order model. In addition, the R^2 value in pseudo first order kinetic is higher than the pseudo second order models. This reasons indicated sorption nitrate on synthesis adsorbent is very good matching with pseudo first order kinetic. Liu H (2013) and Cho (2011) have reported similar results in nitrate removal using different sorbent (25, 26).

In this study modified Clinoptilolite zeolite as adsorbent was used for nitrate removal. Results showed that this adsorbent has a low efficiency in sorption of nitrate from aqueous solutions.

The optimum condition for this study obtained in acidic pH (pH=5), 180 min contact time and 16 g/l adsorbent dosage. The isotherm and kinetic studies indicated that NO_3^- adsorption process follows Langmuir isotherm and pseudo first order kinetic.

Footnotes

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Conflict of Interest:

The authors declare no conflict of interest.

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