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Evaluation of natural zeolite clinoptilolite efficiency for the removal of ammonium and nitrate from aquatic solutions

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Abstract

Background: Surface water and groundwater pollution with various forms of nitrogen such as ammonium and nitrate ions is one of the main environmental risks. The major objectives of this study were to evaluate the capacity of natural zeolite (clinoptilolite) to remove NO_3^- and NH_4^+ from polluted water under both batch and column conditions.

Methods: The laboratory batch and column experiments were conducted to investigate the feasibility of clinoptilolite as the adsorbent for removal of nitrate (NO_3^-) and ammonium (NH_4^+) ions from aqueous solution. The effects of pH, clinoptilolite dosage, contact time, and initial metal ion concentration on NO_3^- and NH_4^+ removal were investigated in a batch system.

Results: Equilibrium time for NO_3^- and NH_4^+ ions exchange was 60 minutes and the optimum adsorbent dosage for their removal was 1 and 2.5 g/L, respectively. The adsorption isotherm of reaction (r > 0.9) and optimum entered concentration of ammonium and nitrate (30 and 6.5 mg/L, respectively) were in accordance with Freundlich isotherm model. The ammonium removal rate increased by 98% after increasing the contact time.

Conclusion: Our findings confirmed that natural Clinoptilolite can be used as one of effective, suitable, and low-costing adsorbent for removing ammonium from polluted waters.

Keywords: Ammonium, Nitrate, Adsorption, Clinoptilolite

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Introduction

Nowadays, one of the main environmental risks is surface and groundwater pollution with various forms of nitrogen such as ammonium and nitrate ions. In natural water large amounts of nitrogen exist as ammonium and often have a negative impact on the status of water quality and the surrounding objects. This may cause environmental problems such as eutrophication. In addition, high levels of nitrate in body increases the risk of liver cancer and methemoglobinemia, which is often called blue baby disease in children (1-3). So, according to USEPA standards the maximum concentration level of Nitrate and nitrite in drinking water must be less than 10 and 1 mg/L respectively (4).

Different methods have been reported to remove several forms of nitrogen from aqueous solutions. These methods involve using biological processes (nitrification and denitrification), reverse osmosis, electro dialysis, adsorption, and ion exchange (1,2). Each of these methods have some advantages and disadvantages. Biological processes such as denitrification are not effective in temperature less than 7°C and require specific bacteria, such as bacillus or thiobacillus denitrificans to reduce NO_3^- into N_2. Chemical processes require adding chemicals which may release toxic compounds into the environment. Reverse osmosis is an expensive method to treat large amounts of water. Ion exchange is simple and effective among these methods (2,5). It is a reversible chemical reaction in which an ion of a solution is exchange with a similar charged ion attached to solid particles. There are two forms of solid

ion exchanger particles involving the natural form such as inorganic zeolite and the synthetic form such as solid ion exchangers produced from organic resins (6). The natural zeolites, such as clinoptilolite are inexpensive and easily available in large quantities in most regions of the world like Iran (7,8). The most common and abundant zeolite is clinoptilolite with high silica which can remove ammonium from aqueous solutions by ion exchange. Furthermore, this zeolite is a natural form ($Na_6Al_6Si_30_{72}.24H_2O$) consisting SiO_4 and AlO_4 connected to oxygen atoms (9-12). On the other hand, most of the recent studies are conducted by laboratory grade clinoptilolite. So there is lack of studies on natural clinoptilolite ions removal efficiency. The purposes of this study were: 1) evaluating of natural zeolite clinoptilolite efficiency for the removal of ammonium and nitrate from aquatic solutions in laboratory and column scale; 2) assessing the effects of (a) exposure time, (b) the amount of used natural clinoptilolite; 3) assessing the effects of initial ammonium and nitrate concentrations on the efficiency of their removal by clinoptilolite; and 4) determining ammonium and nitrate ions adsorption isotherms.

Methods

In this study Iranian natural clinoptilolite was purchased and used as an adsorbent. Table 1 shows the structure of clinoptilolite which is localized in Iran. The structure and chemical composition of Iranian natural clinoptilolite was studied in another investigation (10), so there was no need for XRD examination. At first, clinoptilolite samples were ground by a grinder and screened by 60 mesh sieve, and then dried at 105°C for 24 hours before using. After preparing the clinoptilolite, preliminary experiments were performed to optimize the effective factors including contact time (10-120 minutes), initial concentration and the adsorbent dosage (1-2.5 g/L) to remove ammonium and nitrate from aqueous solution. Assessing ammonium and nitrate, an ion exchanging was conducted at both laboratory and column conditions using clinoptilolite. In this study distilled and deionized water were used the pH which was maintained at 9.5. One gram of sorbent was added to 1000 ml of solution containing ammonium and nitrate with the range of concentrations 6.5-52 mg/L and 5-40 mg/L, respectively. This range was selected according to the concentrations of ammonium and nitrate ions in polluted groundwater. Ammonium chloride (NH_4CI) and sodium nitrate ($NaNO_3$) salts and distilled water were used to prepare stock solutions of ammonium and nitrate. These stock solutions were diluted to prepare test solution, and then were mixed at the speed of 150 rpm 25°C ± 2°C. The pH of water was maintained at 9.5 during the experiment process. After obtaining the balance time, samples were filtered by Whatman filter papers (0.45 μm) and were immediately analyzed by UV spectrophotometer (HACH, Model DR5000) at the wave length of 220 and 275 nm for nitrate and 640 nm for ammonium. Am-

monium and nitrate adsorption equilibrium were carried out using ammonium and nitrate ion solutions at different concentrations and at optimized pH. Removal efficiency and the amount of ions exchanged by clinoptilolite were calculated by equation 1 and 2.

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

$$q = \frac{(C_o - C_e)V}{W} \tag{2}$$

In these equations, C_o and C_e are respectively the amount of initial and final concentration; V is the amount of aqueous solution and W is the amount of used clinoptilolite expressed as grams.

Continuous test (columns) was done in a glass column with aninternal diameter of 15 cm and length of 120 cm. At this stage, the column was filled by clinoptilolite up to 30 cm of height. The used feeding water was a synthetic solution consists of ammonium and nitrate with initial concentration of 30 and 6.5 mg/L respectively, which was passed through the column consisted of constant bed with initial concentration and flow velocity of 7.5 mg/min. The output samples containing ammonium were collected and analyzed at different times.

Results

Effect of adsorption time
The effect of contact time on the adsorption of both ammonium and nitrate species on the clinoptilolite was studied in the duration of 10 to 120 minutes (Figure 1). The rate of adsorption of ammonium as a function of time

Table 1. Features of clinoptilolite

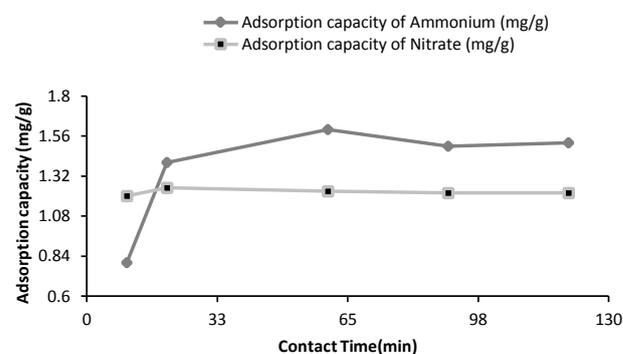| Quantity	Characteristic
1.11	Specific gravity (g/cm³)
2.10	Moisture content (%)
0.10	Ash (%)

Figure 1. Changes in the adsorption capacity of ammonium and nitrate (mg/g) by clinoptilolite over the time (min).

presented a biphasic pattern with a rapid initial uptake up to 60 minutes, which gradually reached equilibrium after a period of 60 minutes. About nitrate, results clearly indicated that clinoptilolite have a low adsorption capacity for nitrate. As the pH of water was maintained at 9.5 during the test, there was not the possibility of releasing any ammonia from water. Moreover, there is not the possibility of nitrate production because the process was not an oxidative process. So, it is assumed that there is not any possibility of ammonia and nitrate ion production along the process; however their concentration was not checked in this study.

Effects of the amounts of adsorbent
Figure 2 shows the effect of adsorbent dosage on the value of ammonium and nitrate removal at equilibrium conditions. So, it can be observed that removal efficiency of the adsorbent generally improved with increasing ammonium ion dose and decreased for nitrate ion gradually.

Effects of initial concentrations of nitrate and ammonium
Figure 3 illustrates that at a fixed adsorbent dose, the adsorbed amount increased with increasing concentration of solution, but the percentage of adsorption decreased.

Biosorption equilibrium and separation factor (R_L)
The calculated results of biosorption of ammonium on the clinoptilolite as a function of the initial concentration of ammonium are shown in Table 2. It is found that the biosorption of ammonium on the clinoptilolite were correlated well with the Freundlich equation as compared with Langmuir equation under the concentration range studied.
The calculated RL for concentrations of 5-40 mg/L for ammonium adsorption by clinoptilolite was between 0.116 and 0.512 which represents ideal processes of adsorption.

Column studies
Column experiments showed that clinoptilolite is able to remove ammonium from aqueous solutions, so the column study was carried out in order to investigate ammonium removal by clinoptilolite in an optimal condition obtained in continuous experiment. In this experiment, 30 g of 40 mesh-size clinoptilolite was transferred to a glass column. Data obtained from passing a solution containing ammonium at a flow rate of 7.5 ml/min at different times are shown in Figure 3. The results in Figure 4 indicate that much low ammonium was found in the effluent.
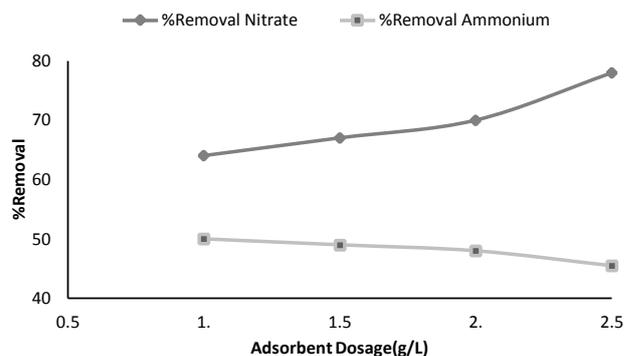
Figure 2. The changes in percentage of ammonium and nitrate removal relative to the clinoptilolite adsorbent dosage (g/L).
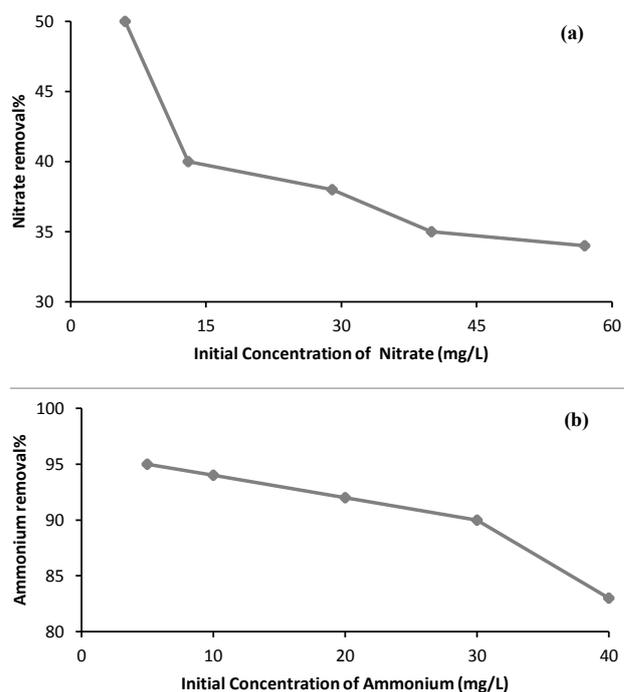
Figure 3. The changes in the initial concentration of (a) nitrate (mg/L) and (b) ammonium (mg/L) adsorption by clinoptilolite.

Discussion
Effect of contact time
The effect of contact time is one of the most important factors in the process of removing contaminants. This variable is an important factor because of its effect on determination of adsorption kinetics of an adsorbent at the initial concentration of adsorbent. So, tests using cl-

Table 2. The constants and ammonium adsorption isotherm models by clinoptilolite

Freundlich			Langmuir				Temkin
K_f	n	R^2	q_{max}	R_L	b	R^2	R^2
0.0405	8.77	0.9003	0.5843	0.116- 0.512	0.19	0.5088	0.872
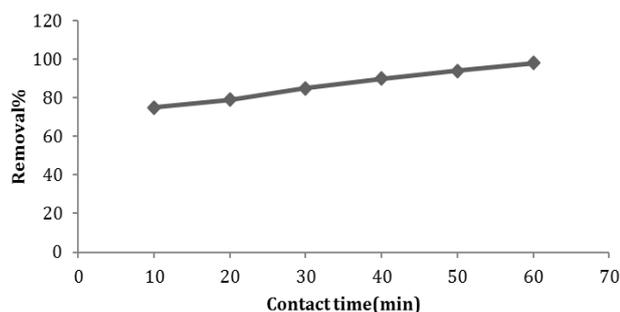
Figure 4. The changes in amount of ammonium (mg/L) removal by clinoptilolite over the time (min).

inoptilolite and a balance time of 10 to 120 minutes were conducted to find the balance time for nitrate and ammonium removal. Figure 1 shows the results of the effect of contact time on percentage of nitrate and ammonium removal with initial concentration of 20 mg/L. It seems that the rate of ammonium removal at the first 30 minutes was very fast. Then, the rate of removal decreased gradually and finally reached the balance point after 60 minutes. This reduction was resulted from adequate saturation of clinoptilolite sites of adsorbent [13]. Regarding the percentage of nitrate removal, the results clearly indicated that clinoptilolite has a low adsorption capacity for nitrate. The low nitrate adsorption was resulted from negative structural charge of adsorbent and nitrate [14]. These results are consistent with the findings of other researchers. Sprynskyy et al found that the ammonium removal rate increases with increasing contact time [12]. Moreover, Lebedynets et al [9] selected 30 and 60 minutes as an optimum time due to its high efficiency in ammonium removal and observed the similar results. Ugurlu [15] concluded that the ammonium removal rate increased at contact time of 30 minutes, but the concentration of nitrate did not change.

Effects of the Amounts of Adsorbent

The amount of used adsorbents is one of the variables affecting the adsorption equilibrium. So, the effect of clinoptilolite amount on nitrate and ammonium removal (Figure 2) was studied at constant pH. It is suggested that the adsorption rate of ammonium and nitrate from solution increases and decreases respectively with increasing the amount of adsorbent. The effects of adsorbents amount may be explained by adsorption sites and clinoptilolite structural charge. Clinoptilolite is a crystalline hydrated aluminosilicate formed by a tetrahedral extensive network of AlO_4 and SiO_4. Substitution of Al^{3+} and Si_4^+ will create negative charge network within the network framework. The negative charge can be balanced with the exchanger cations. This negative charge network caused by Al^{3+} ions increases due to increasing the adsorbent amount and results in increasing and decreasing the adsorption and exchange of ammonium and nitrate in solution [14,16,17]. Bhatnagar and Sillanpää [18] studied the nitrate removal

using modified natural zeolite and found that the nitrate removal rate increased with increasing the amount of adsorbent. Moreover, in this study it was shown that nitrate removal efficiency with the natural clinoptilolite zeolite was low. Mažeikiene et al [19] indicated that clinoptilolite has low nitrate removal efficiency due to negative charge network at its structure. Furthermore, Shoumkova [14] study shows that raw natural zeolites have no effect on anions removal such as nitrate from solution due to its own negative charge.

Effects of initial concentrations of nitrate and ammonium

Effects of initial concentrations of nitrate and ammonium on their removal using clinoptilolite application was studied by adding 1 g of clinoptilolite in 1000 ml of solution containing nitrate and ammonium at the same contact time as the equilibrium time (60 minutes). It was found that the adsorption capacity of ammonium and nitrate increases with enhancing initial concentration due to either further possible contact between ammonium and nitrate ions and adsorbent surface or elevation of repulsion force like concentration gradient. However, the adsorption percentage of nitrate and ammonium ions on clinoptilolite decreases from 95% to 85% and from 50% to 35% respectively. This reduction may be resulted from saturation of the adsorbent surface because the amount of ammonium and nitrate adsorption decreases at high concentrations due to the saturation of adsorption sites [13]. These results are consistent with the studies carried out by Zabochnicka and Malińska [11], Rahmani and colleagues [10], and Lebedynets and colleagues [9].

Adsorption Isotherm study

Adsorption isotherm is an important and essential factor for designing the adsorption systems as it shows the separation of pollutants ions from liquid phase by adsorbent in the equilibrium balance as a function of the pollutant concentration. According to the results of the present study, adsorption data followed Freundlich isotherm model because of a higher R2 value. Similar results were reported by Khan et al [20]. The results of their study indicated that adsorption of nitrate follows the Freundlich isotherm model for modified lignite granular activated carbon. Karadag et al [21] studied the removal of ammonium ion using natural Turkish clinoptilolite. In their study the adsorption plots fitted very well with Freundlich isotherm model in temperature of 25°C.

In this study, the RL value of the Langmuir isotherm was between 0 and 1 and the 1/n value of the Freundlich isotherm was less than 1, which indicates favorable adsorption of ammonium ion. Karadag et al [21] studied the removal of ammonium ion using natural Turkish clinoptilolite. The RL values were less than 1 and almost close to 0.2, and therefore, indicated favorable adsorption of ammonium ions by the clinoptilolite.

Conclusion

In this study, ion exchange was studied to remove ammonium and nitrate ions from aqueous solutions by Iranian natural zeolite clinoptilolite. The results of this study showed that ammonium removal efficiency increases due to an increase of the contact time and adsorbent dosage, and decreases due to an increase of the initial concentration of ions. Removal efficiency of nitrate declines by increasing the adsorbent dosage and increases by enhancing the contact time and reduces due to increasing the initial concentration of ions. Our findings show that the simultaneous removal of ammonium and nitrate, may not cause to increase the nitrate removal and cannot affect its adsorption by clinoptilolite. According to the other studies (22,23) negatively charged clinoptilolite decreases the nitrate removal efficiency due to the substitution of Al to Si, which concurs with our studies findings. For this reason, it is necessary to add cationic material such as cationic surfactants to modify the clinoptilolite to increase the nitrate removal efficiency. In addition, these results revealed that Freundlich isotherms may be a proper model to show the ammonium adsorption by natural clinoptilolite zeolite. We conclude that clinoptilolite is a suitable zeolite with a high performance for ammonium removal in laboratory and column scales.

Acknowledgments

Ethical issues

We certify that all data collected during the study is presented in this manuscript and no data from the study has been or will be published separately.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

NJHF conceived and designed the study. MN and MM did the lab work and MR and PB performed literature search and wrote the manuscript. All authors participated in the data acquisition, analysis, and interpretation. All authors critically reviewed, refined, and approved the manuscript.

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