Nitrate Removal from Drinking Water using Organo-Silane Modified Natural Nano-Zeolite

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Abstract

Nitrate-containing compounds are considered as groundwater contaminants, the concentration of which has been growing in these resources during recent years. As a result, it seems necessary to use effective methods to remove nitrate from water and wastewater. Adsorption is generally considered more economical in water treatment compared to other feasible alternative techniques. Natural Clinoptilolite zeolite is one of the best absorbents because of its high capacity and low cost. Surfactants such as hexadecyl trimethyl ammonium (HDTMA) are usually used for modification but they are not stable and removed as a result of subtle temperature variations. In this research, zeolite nanoparticles are chemically modified by 3-aminopropyl triethoxysilane. The advantage of this modification method is its stability at different environmental conditions. Adsorbent properties have been analyzed by PSA, FTIR, XRD, FESEM and CHN elemental analysis. Also, nitrate adsorption capacity of modified zeolite was examined by UV-Vis spectroscopy. NH_2 groups are developed on the zeolite surface as a result of organo-silane modification, which must be converted to NH_4^+ so that nitrate adsorption becomes possible in acidic conditions. Based on the results, the best nitrate removal capacity is achieved at the lowest concentration and pH values. 80.12 % nitrate removal was obtained at pH=3, nitrate concentration = 50 mg/l and adsorbent concentration = 4 g/l.

Keywords: Nitrate removal, Zeolite, Surface modification, Organo-silane, Adsorption.

1. INRODUCTION

Application of nitrogen-containing fertilizers in agricultural applications and their final introduction into wastewaters, have led to the intensification of nitrate contamination in surface and ground water resources [1, 2]. Nitrate is possibly the most widespread groundwater contaminant, imposing serious threats to drinking water supplies causing ecological disturbances. High nitrate content in drinking water can be hazardous to human health causing problems such as liver damage, cancer and Methhemoglobinemia [3, 4]. The US environmental protection agency (U.S. EPA) has set the nitrate standard level as 10 mg/l for drinking water [5].

Various methods have been used for nitrate removal from water and wastewater [6], such as catalytic reduction [7], biological denitrification [8], reverse osmosis [9], electrodialysis [10] and adsorption [11] among which adsorption is more preferred because of lower expenses and simple equipment requirements. Materials used for nitrate adsorption have been ion-exchange resins [12, 13], phosphoric acid ester type [14], Sepiolite and its HCl activated type (a kind of fibrous silicate clay mineral formed as both tetrahedral and octahedral sheets) [15], activated carbon [14], bamboo powder charcoal [16] and amine-modified coconut coir [17]. Recently, SiO_2-FeOOH-Fe core-shell nanostructures have also been applied for nitrate removal from drinking water [18]. Zeolites with a negative charged framework (especially Clinoptilolite), have

already been widely used for environmental remediation as cation exchangers and heavy metal removal [19-21] and also as catalysts [22].

Zeolites are unable to remove anions from aqueous solutions through anion exchange, although it can be made feasible using surface modification techniques [23].

Surfactants such as hexadecyl trimethyl ammonium (HDTMA) are usually used for modification but they are not stable on the zeolite surface and will be removed due to subtle temperature variations [24]. So, chemical modification can be used to improve the stability of the adsorbent characteristics. Surface hydroxyl groups are convenient sites for modification. In the majority of cases, functionalization of zeolite external surface is achieved by reacting surface silanols by organo-silanes of $R_n Si X_{(4-n)}$ type. X is the reactive group (typically halogen or alkoxy) and R is a non-hydrolysable moiety possessing the desired functionality [25]. Zhan et al. (2003) modified the external surface of nanometer-sized zeolite-X crystals using amino groups (by reaction with 3-aminopropyltriethoxysilane, APTS) and vinyl groups (by reaction with vinyl triethoxy silane (VTS)) [26]. Based on Raman and solid-state NMR spectra, it was proposed that reaction with APTS leads to a dipodal grafting $RSi (OSi\text{-}Zeolite)_2$, whereas tripodal grafting $RSi (OSi\text{-}Zeolite)_3$ is obtained in the case of VTS. The difference in podality between the two modification techniques can be attributed to different hydrolytic activities of organo-silane reagents. Reactive surface-anchored groups promote the possibility for further functionalization also.

Reaction of zeolite-grafted amino groups with isothiocyanates [27], chlorides [26, 28], epoxides [29], and fullerenes [28] have also been reported. As a result, amino-silane compounds are suitable for modification, being able to graft to the surface through stable covalent bonding [25, 26 & 33]. The present research is thus aimed at the investigation of nitrate sorption on Clinoptilolite-based adsorbents at room temperature based on batch experiments.

2. EXPERIMENTAL SECTION

2.1. Materials

Natural zeolite Clinoptilolite (Semnan region, Iran) was used in this study with the chemical composition given in Table 1. Sodium nitrate, toluene, 3-aminopropyltriethoxysilane, ethanol and HCl were purchased from Merck. Co. used without further purification.

Table 1. *Composition of natural zeolite.*

Material	Mass %
SiO_2	68.95
Al_2O_3	11.4
Fe_2O_3	0.97
CaO	4.83
Na_2O	0.95
K_2O	0.9
MgO	0.97
TiO_2	10.64

2.2. Modification of Zeolite

Natural zeolite was ball-milled to obtain zeolite nanoparticles, at the first step. The as-produced zeolite particles were then washed by de-ionized water to remove any impurities, centrifuged, dried and dehydrated at 373 K inside a vacuum oven to remove surface-adsorbed water molecules. Then, a suspension of 1 g nanozeolite and 50 cc of toluene and 2 cc of APTS (amino propyltriethoxysilane), was refluxed in a flask in an oil bath at 110 ºC for 24 h. The modified nanozeolite powder was washed using ethanol to remove any surface-adsorbed APTS and its hydrolytic products and then centrifuged and dried at 70-75 ºC [26, 31-33]. NH_2 groups are thus formed on the surface which should be converted into ammonium (NH_4^+) to become able and become capable of anions removal. Thus, zeolite powder was stirred in l00 ml of 0.5 M HCl for 6 h.

3. Results and discussion

3.1 Characterization

Zeolite particle size distribution was determined using dynamic light scattering (DLS) particle size analyzer (JAPA Horiba LB550). The FT-IR spectra were recorded by a RX-1 PerkinElmer spectrometer. Periodic structure of the framework was confirmed by XRD (Holland Philips) with a Cu Kα radiation. FESEM micrograph of zeolite powder is also given.

### Nitrate Adsorption Experiments

Various adsorbent contents were stirred in 50 ml of nitrate solution for 24 h. The solution was centrifuged to remove solids and analyzed by UV-Vis spectrophotometer at $\lambda_{max} = 300$ nm. Several parameters such as pH, temperature, adsorbent dosage, nitrate concentration and contact time were studied.

pH and Kinetic Studies

In order to investigate the effect of pH on nitrate removal, pH of nitrate solutions was varied in the range of 1-9. First of all, the solution initial pH was adjusted using 1 N HCl or 1 M NaOH and the modified zeolite was added to a 50 mL solution. The rate of nitrate removal was studied at different time intervals (30 min to 6 h). At first, sampling was performed every 30 min till 6 h, and every 1 h thereupon. Then, the samples were taken once every 24 h to test the stability of the sorption process.

Adsorbent Content

The experiments were performed using different amounts of modified zeolite added to a 50 mL solution. 1-5 g/L of modified zeolite was used in the experiments.
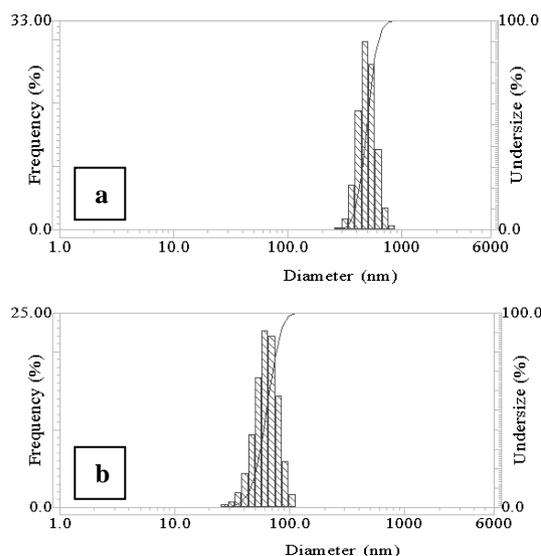
Figure 1. *PSA analysis for zeolite before (a), after (b) ball milling.*
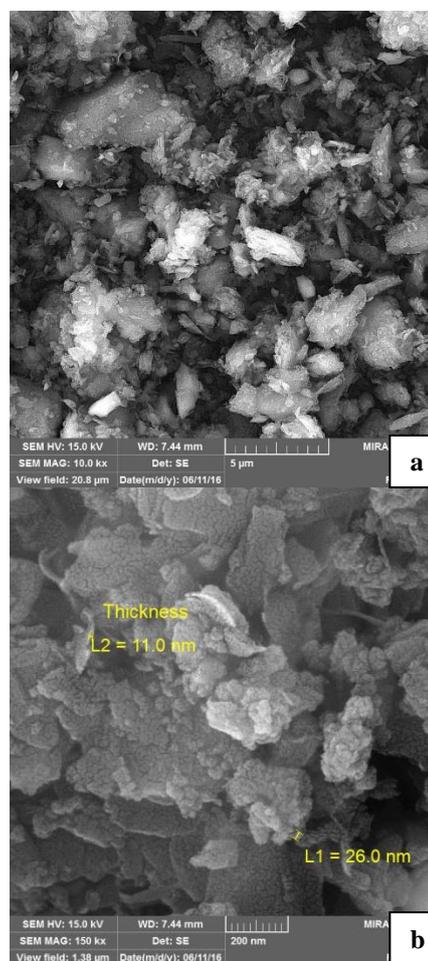
Figure 2. FESEM micrographs of zeolite powder with (a) 10 kx (b) 150 kx magnifications.

Table 2. *CHN analysis.*

Nitrogen %	Carbon%	Hydrogen %
٠.٣٢	١.٤٠٢	٠.٨٥

Nitrate Concentration and Temperature

To investigate the role of nitrate concentration, 5 experiments at 5 concentrations of 20, 50, 100, 150 and 200 mg/L were carried out. These concentrations are chosen over the maximum nitrate concentration standard in drinking water. The mixtures were then shaken in a thermostatic water-bath shaker at 150 rpm and fixed temperatures (30, 40 and 50°C).

According to PSA analysis before and after ball milling, the average zeolite particle size is ~ 493 nm before ball milling which is reduced to 62.9 nm upon ball milling for 8 h (Figure1). FESEM results also confirmed these observations (Figure 2a & b).

Figure 3 shows the FTIR spectrum of nanozeolite before and after chemical modification. FTIR spectra of raw Clinoptilolite shows a broad band at 3348 cm^{-1} due to OH stretching vibration of water and defective OH groups. Also, the band at 1642.53 cm^{-1} is due to the bending vibration of OH groups. Defective Si-OH stretching vibration gives a peak at 976 cm^{-1}. In the modified zeolite spectrum, CH_2 vibrations of APTS give peaks close to 2845 cm^{-1} and 1470cm^{-1}. The NH stretching vibration of APTS has occurred close to 334 cm^{-1}. The most important evidence for APTS functionalization is the complete removal of Si-OH stretching vibration close to 976 cm^{-1}. The peaks due to OH stretching and bending vibrations also show decreased intensity due to APTS functionalization [34].

According to CHN analysis, the percentages of carbon, hydrogen and nitrogen are given in Table 2. Since there is no nitrogen in the raw zeolite structure,

this trace can be attributed to APTS molecules chemically modifying the zeolite.

Figure 4 compares the XRD patterns of Clinoptilolite zeolite before and after functionalization with APTS. It is obvious that the intensity of the peak at 10 and 22 degree for raw zeolite is higher than that of the APTS-modified zeolite, but peak sharpness at 26 and 42 degrees is obviously increased upon modification. Also, a 40.4 nm crystal size is calculated for zeolite using Debye-Sherrer correlation given as:

$$\tau = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

where, τ is the mean size of crystalline domains, K shape factor with a value close to 1, λ x-ray Wavelength, β the line broadening at half maximum intensity (FWHM) and θ also Bragg diffraction angle.
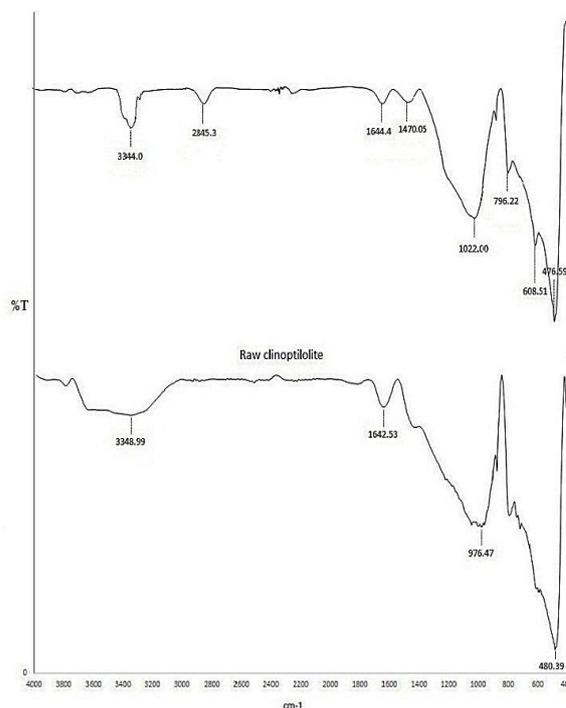
Figure 3. *FTIR analysis before and after APTS modification.*

3.2. Nitrate Sorption Experiments

3.2.1. Effect of pH

Based on the results, the effective conditions of the adsorbent for nitrate removal is in the acidic range.

In order to determine the optimum pH, the equilibrium nitrate removal point over a 1-9 pH range was investigated. Figure 5 shows that nitrate removal by modified zeolite is strongly pH dependent. The removal of nitrate is increased by decreasing pH, reaching a maximum at equilibrium pH=3 and there is no significant increase in the removal percentage at pH= 1. During adsorption using APTS-zeolite, H^+ is necessary to convert NH_2 to NH_4^+ in order to remove anions which is possible in acidic conditions only. Also, the OH^- present in basic mediums as a competitive anion for nitrate can reduce removal. 80.78 %, 80.12%, 72.04 %, 54.71 % and 4.52 % percentage removals at 50 mg/L initial concentration of nitrate and 4 mg/L adsorbent were achieved at initial pH of 1, 3, 5, 7 and 9, respectively.
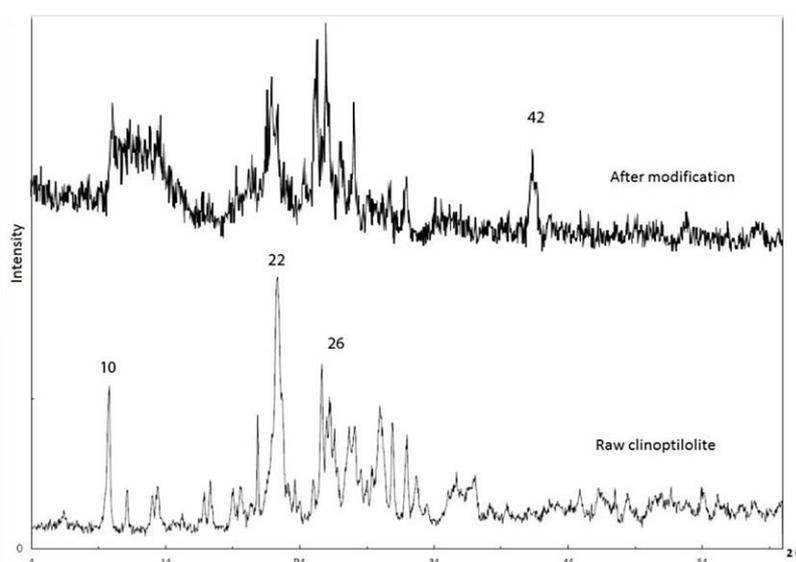

Figure 4. XRD patterns of the Clinoptilolite zeolite before and after functionalization with APTS.
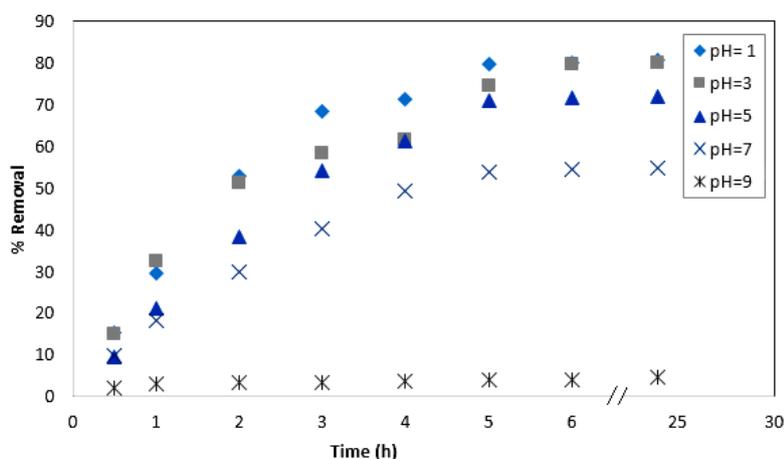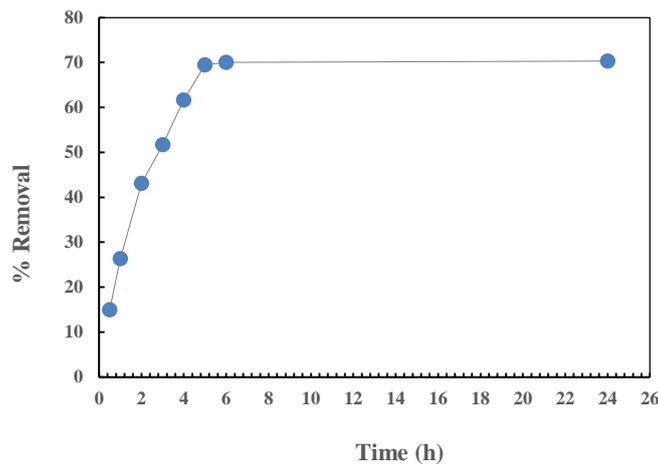

Figure 5. Effect of pH on nitrate removal, (nitrate concentration = 50 mg/L, adsorbent amount= 4 g/l).

Figure 6. The adsorption kinetic curve at pH=3, adsorbent amount = 4 g/l and nitrate concentration = 100 mg/L.

3.2.2 Effect of contact time

Nitrate removal was also investigated as a function of contact time. Figure 6 exhibits that the rate of nitrate removal is rapid in the beginning followed by a slower rate that gradually reaches a plateau. The maximum removal percentage is achieved within 5 h and equilibrium within 6 h.
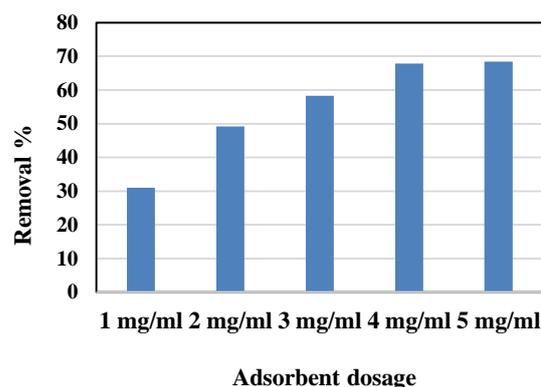
3.2.3 Effect of adsorbent amount

Experimental investigation shows that the percentage removal by APTS-zeolite is increased by increasing the concentration. Figure 7 shows the nitrate removal efficiency over time vs. different amounts of adsorbent contents. Under similar conditions (nitrate concentration = 100 mg/L, pH=3), nitrate removal was investigated using various nanostructure loadings during 6 h. Based on Figure 7, there is no obvious distinction in removal between 4 and 5 mg/ml adsorbent loadings and 4 mg/ml is thus considered as the optimum amount.

3.2.4 Effect of Nitrate Concentration

The experiments were performed at 5 different nitrate concentrations, selected based on standard values (20, 50, 100, 150 and 200 mg/l are over the standard limit). Percentage removal by APTS-zeolite is decreased by increasing the initial nitrate concentration from 20 to 200 mg/L (Figure

8) at a 4 mg/mL concentration and initial pH=3. The reduction of removal by raising the nitrate concentration can be explained by the increase in nitrate ion/active sites ratio on the adsorbent surface.


Figure 7. Nitrate removal efficiency over time vs. amount of adsorbent loading under similar conditions (nitrate concentration = 100 mg/L, pH=3).

3.2.5. Effect of Temperature

Figure 9 displays the temperature effect on nitrate sorption. At the beginning of sorption, nitrate uptake is increased by increasing the temperature because temperature is known to increase the rate of adsorbate diffusion (physical adsorption) across the external boundary layer. Attractive forces between the adsorbent surface and ions are weakened resulting in decreased adsorption by increasing the temperature.

228 **Meftah and Zerafat**
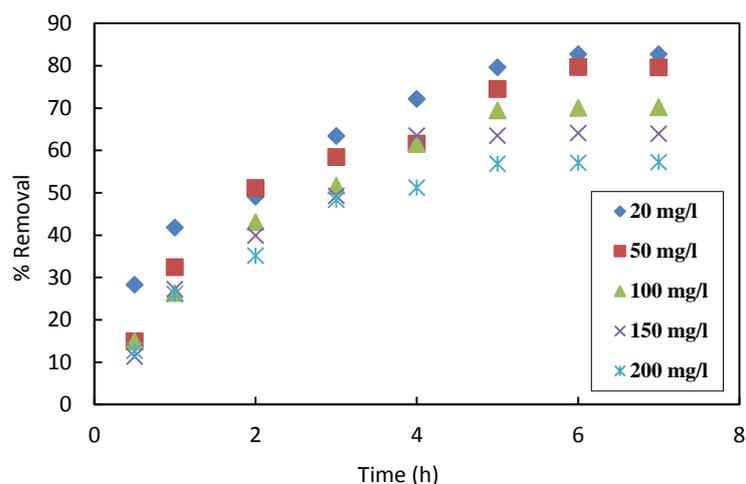
Figure 8. *Adsorption kinetic curves at pH=3 and adsorbent dosage= 4 g/L at different nitrate concentrations.*
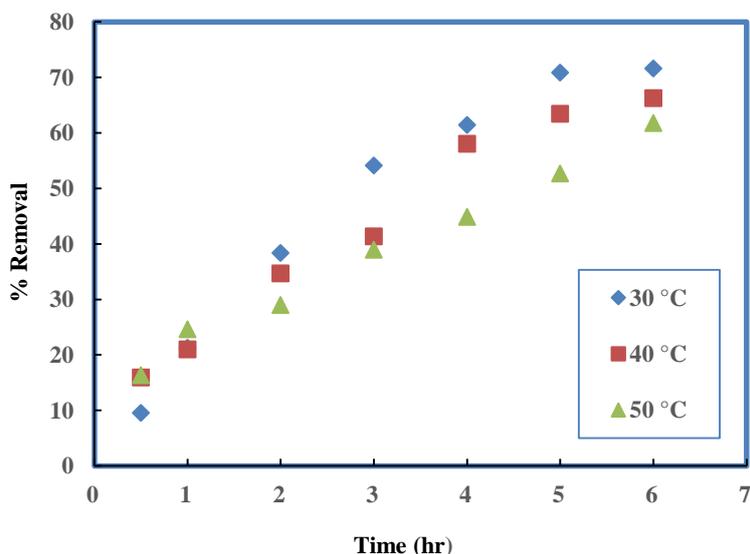
Figure 9. *Adsorption kinetic curves at pH=3 and adsorbent dosage = 4 g/L and nitrate concentration = 50 mg/L at various temperatures.*

3.3. Adsorption kinetics

Figure 6 shows the effect of contact time on the adsorption of nitrate onto the zeolite-APTS nanostructure. Nitrate adsorption was increased by increasing the reaction time until equilibrium was attained. In order to investigate the adsorption process, pseudo-1st-order and pseudo-2nd-order kinetic models were used to fit the experimental data. Kinetic modeling not only allows the estimation of sorption rate but also leads to suitable rate expressions characteristic of possible

adsorption mechanisms. The pseudo-1st-order kinetic equation of Lagergren is given as follows [35]:

$$\log (q_e - q_t) = \log (q_e) - \frac{k_1}{2.303} t \quad (2)$$

where q_t (mg/g) and q_e (mg/g) are the amounts of nitrate adsorbed at time t and at equilibrium, respectively; $k_1 \, (min^{-1})$ is the pseudo-1st-order rate constant for the adsorption process. Since, the experimental data after equilibrium does not influence the adsorption kinetics, the experimental data before adsorption equilibrium were

used to evaluate the adsorption kinetics. q_e, k_1 and the correlation coefficient were determined from linear plot of log ($q_e - q_t$) vs. t as shown in Table 3. The correlation coefficient for the pseudo-1st-order kinetic model was relatively low ($R_2 = 0.969$) and the calculated q_e does not agree with the experimental data. Therefore, the pseudo-1st-order kinetics model cannot reasonably describe nitrate adsorption process. The pseudo-2nd-order kinetic equation is expressed as follows [36]:

$$t/q_t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (3)$$

where, k_2 (g/mg min) is the pseudo-2nd-order rate constant for the adsorption process. In this model, the rate limiting step is surface adsorption that involves chemi-sorption, where the removal from solution is due to physicochemical interactions between the two phases [37]. q_e, k_2 are correlation coefficients determined from a linear plot of t/q_t vs. t (Table 3). The correlation coefficient for the pseudo-2nd-order kinetic model was higher ($R_2 = 0.986$), and the calculated q_e was closer to the experimental value. Therefore, the adsorption of nitrate onto zeolite-APTS adsorbent follows the pseudo-2nd-order kinetic model.

3.4. Nitrate Adsorption Isotherms

Adsorption isotherm models are commonly used to describe the adsorption mechanism. In this study, Langmuir and Freundlich isotherms were used to analyze the experimental data. The linearized Langmuir isotherm is as follows [38, 39]:

$$\frac{C_e}{q} = \frac{1}{K q_m} + \frac{C_e}{q_m} \qquad (3)$$

where, q_e (mg/g) is the equilibrium amount of nitrate adsorption; C_e (mg/L) the equilibrium nitrate concentration in the solution; q_m (mg/g) the maximum nitrate adsorption capacity and K_L (L/mg) the Langmuir adsorption equilibrium constant related to the adsorption energy. In order to determine whether the adsorption is favorable, a dimensionless constant separation factor (R_L) is defined as follows [39]:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (4)$$

where, C_0 (mg/L) is the initial nitrate concentration. R_L is considered as a more reliable indicator of the adsorption. There are four probabilities for the R_L value [39]:

(i) Favorable adsorption, $0 < R_L < 1$;

(ii) Unfavorable adsorption, $R_L > 1$;

(iii) Linear adsorption, $R_L = 1$; and,

(iv) Irreversible adsorption, $R_L = 0$.

q_m and K_L were determined from the slope and intercept of the C_e/q_e vs. C_e plots (Table 4). The relatively high correlation coefficient ($R_2 = 0.979$) for the adsorbent indicates that the Langmuir isotherm model fits better with the experimental data. Based on the Langmuir isotherm, the predicted maximum monolayer nitrate adsorption capacity for adsorbent was found to be 12.547 mg/g (202.37 mmol/kg). The linear form of Freundlich equation is given as [39, 40]:

$$\ln q = \ln K_F + \left(1/n\right) \ln C_e \qquad (5)$$

where, K_F is the Freundlich constant related to the adsorption capacity and n an empirical parameter related to the adsorption intensity varying with the heterogeneity of the adsorbent. For a favorable adsorption process, the value of 1/n should be between 0.1-1 [37]. The values of K_F and 1/n were determined from the slope and intercept of the ln (q_e) vs. ln (C_e) plots. The high correlation coefficient ($R^2 = 0.941$) reflect that the experimental data agree well with the Freundlich isotherm model. The value of 1/n (0.334) is between 0.1-1, indicating the favorable adsorption of nitrate. Totally, according to the higher correlation coefficient for Langmuir model, it can be a more appropriate alternative for the adsorption of nitrate onto Zeolite-APTS.

Meftah and Zerafat

Table 3. Kinetic model rate constants for adsorption of nitrate onto zeolite-APTS.

q_e (Experimental)	Pseudo-1st-order kinetic model			Pseudo-2nd-order kinetic model		
	K_1	q_e	R^2	K_2	q_e	R^2
$10.015\ ^{mg}/_g$	$0.55\ min^{-1}$	$6.119\ ^{mg}/_g$	0.9693	$0.159\ ^{g}/_{mg\ min}$	$12.468\ ^{mg}/_g$	**0.986**

Table 4. Results of Langmuir isotherm for adsorption of nitrate onto zeolite-APTS

$q_m(\dfrac{mg}{g})$	K_L (l/g)	R_L	R^2
۱۲٬۵۴۷	0.0293	۰٬۴۰۵	۰٬۹۷۹۹

4. Conclusions

In this study, a suitable chemical modification method is applied to improve the adsorbent stability. Surface hydroxyl groups are convenient targets for modification. Functionalization of zeolite external surface is achieved through the reaction of surface silanols with APTS organo-silane, which will result in the development of NH_2 groups on the zeolite surface. The conversion of NH_2 groups into NH_4^+ is necessary for nitrate adsorption, only possible in acidic conditions. Totally, nitrate uptake increases by increasing the adsorbent content and contact time and decreasing pH, temperature and nitrate concentration. The optimum conditions were determined to be: adsorbent amount = 4 g/l, nitrate concentration = 50 mg/l, pH=3 and contact time = 6 h resulting in a maximum uptake of 80.12 % at these conditions.

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