Research Article

Kinetic and Isotherm Studies of Nitrate Adsorption in Salt Water Using Modified Zeolite

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Abstract

Nitrate is the main form of nitrogen species in natural waters. Excessive nitrate concentration in water is highly undesirable, so that removal of the excessive nitrates in waters is very important. However, the challenge is purposed to remove the excessive nitrates in sea waters by considering anions-rich sea water. Adsorption is a favorable method for the nitrate removal process. Therefore, this research was aimed to study the kinetics and isotherm of nitrates adsorption in salt water. The adsorbent preparation was done by modifying natural zeolite with iron oxide. The adsorbent characterization was carried out by FT-IR spectroscopy and Gas Sorption Analysis methods. The results showed that the modified zeolite have Fe−O group vibrations as indicated by a peak at a wave number of 1404.18 cm^{-1} and an increased specific surface area. The modified zeolite is capable of adsorbing nitrate ions. The adsorption isotherms studies indicated that the modified zeolite is appropriate to the Dubinin-Radushkevich model. The average adsorption energy value (ED), obtained based on the Dubinin-Radushkevich isotherm <2 kJ/mole, showed that the nitrate adsorption on zeolite surface occurred physically. The most suitable adsorption kinetics model is the pseudo second order with the rate constant of 1.80×10^{-2} g/mg.min.

1. Introduction

Nitrate (NO₃⁻) is salt of nitric acid and main form of nitrogen species in natural waters. Agricultural, industrial and household wastewaters are the major sources of nitrates in the surface and ground waters [1]. Excessive nitrate leads to rapid increase in the growth of plants and algae in waters. The increasing growth in these plants and algae in the water triggers, a competition for oxygen in the water body leading to tremendous deaths of these organisms which eventually results in a buildup in decaying matter. This buildup and may even lead to the filling up of ponds and lakes, thus destroying or creating an imbalance in the entire ecosystem, if not dealt with in time. It is also known to trigger the loss of diversity in the sea floor community (including seaweeds, sea grasses, and corals), and amongst planktonic organisms. Since planktonic algae are the basis of marine life, their absence affects the ecological food chain and food webs tremendously.

Excessive nitrate is among the most problematic surface water and groundwater pollutants. Removal of excessive nitrates in waters is very important. It becomes a challenge to it re-

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move excessive nitrates in sea waters, considering that sea water is rich in other anions such as sulfate, bicarbonate, bromide, borate and bromide. Various methods have been developed for nitrate removal up to date [2]. The most common methods are ion exchange [3,4], reverse osmosis [5,6], electrodialysis [7,8], denitrification using bacteria [9,10], and adsorption [11–14]. Even though these methods have their own advantages in removing nitrate, they have some major drawbacks such as high waste disposal, formation of disinfection by products, expensive cost and operation complexity. Adsorption, on the other hand, is a more favorable method for the nitrate removal process due to its simple of design, ease of operation, and less to no waste disposal.

Natural zeolite is an abundant mineral in Indonesia, with a hollow structure and large surface area. The abundance and availability of natural zeolite makes it a relatively low cost adsorbent, but because there is no positive charge on its surface, it is difficult for the anionic pollutants to adsorb. Iron modified zeolite is effectively used to remove anionic contaminant like cyanide from aqueous solutions [15], phosphate from river sediments [16], phosphate in rainwater runoff [17], arsenate aqueous medium [18], and sulfide from river sediments [16]. There have been limited studies concerned on nitrate adsorption in saltwater. Therefore, this research intends to study nitrate adsorption by iron modified zeolite. The objectives of this research are to study kinetics and isotherms of nitrate adsorption in salt water using natural zeolites coated with iron oxide.

2. Materials and Methods

2.1 Materials

This research used some research materials including distilled water and quality chemicals made of Merck including ammonium chloride, sodium chloride, magnesium chloride hexahydrate, potassium chloride, calcium chloride dehydrate, potassium nitrate, ferric chloride hexahydrate, chloroform, sodium hydroxide, chloric acid 37%, sodium salicylate, sulfuric acid 98% and natural zeolite (PT Brataco). The main mineral component of PT Brataco's natural zeolite is 66.78% quartz [19].

2.2 Adsorbent Preparation

In this study, natural zeolites of 250–500 µm were used. The adsorbent used was obtained by sieving natural zeolite using a 250 and 500 µm sieve. The 30 g of natural zeolite was then soaked with 25 mL of 1 M NH_4Cl salt solution for 24 h. Zeolites were washed using distilled water, then dried at 120 °C for 5 h. At this stage natural zeolite activation was obtained. Activated natural zeolite as much as 30 g was interacted with a solution containing 30 mL Fe^{3+} 0.5 M. The mixture was shaken for 15 min, then hydrolyzed by adding 1 M NaOH drops so that the pH reached 9. Next, the mixture is stirred for 15 min. The resulting precipitate was heated at 50 °C for 2 h. The result was then washed with distilled water until the pH of the solution was around 7. The suspension was decanted, then roasted at 70 °C for 5 h [19]. The adsorbent obtained in this stage was modified zeolite (MZ).

2.3 Adsorbent Characterization

The adsorbent used was characterized using the Shimadzu FT-IR-8201 PC infrared spectrophotometer with the solid method. The adsorbent to be analyzed was homogeneous with KBr powder, then pressed 2000 psi to become transparent thin pellets. The pellet was placed in the cell and spectra analysis was carried out at 300–4000 cm^{-1} wave number. The specific surface area and pore volume of adsorbents were measured by BET method on a Nova Win2 version 2.2 apparatus. Before measurement, the sample was heated and the degassing process is carried out at a temperature of 300 °C for 3 h under vacuum. Furthermore the sample was cooled with liquid nitrogen to form a single layer of nitrogen molecules on the surface of the sample. The volume of the gas or the mass of the gas adsorbed at liquid nitrogen temperature (77.3 K) was determined, by measuring changes in pressure and the volume or mass of gas adsorbed by the sample so the specific surface area, total pore volume, pore size distribution and adsorption isotherm of the sample analyzed could determined.

2.4 Solution Preparation

Salt water was made by dissolving 6.67 g NaCl, 0.18 g KCl, 2.82 g $MgCl_2.6H_2O$, and 0.45 g $CaCl_2.2H_2O$ in distilled water. The final volume of the solution was made to 250 mL to obtain salt water with concentration of Na^+, Mg^{2+}, K^+, and Ca^{2+} of 10.50, 1.35, 0.38, and 0.40 g/L, respectively.

2.5 Isotherm Studies

Adsorption isotherm of MZ were identified by batch experiments. Three different initial

nitrate concentrations, *i.e.* 2, 4, 6, 8 and 10 mg/L NO₃-N, were reacted with 150 mg of adsorbent during 24 h. The mixture was then filtered using Whatman-41 paper. The concentration of nitrate was determined using salysilate method [20]. This study used the isotherm model of the Langmuir, Freundlich, and Dubinin Radushkevich isotherms. Langmuir's equation [21] was represented in the Equation (1).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad (1)$$

C_e is the concentration of adsorbate in equilibrium (mg/L), q_e is the amount of adsorbate adsorbed at equilibrium by each gram of adsorbent (mg/g), K_L is the Langmuir constant (L/mg) and q_{max} is the maximum capacity of the adsorbent monolayer (mg/g). q_{max} and K_L values were calculated from slope and intercept of C_e/q_e graphs versus C_e.

Freundlich adsorption isotherms [22] are presented in Equation (2), where q_e is the amount of adsorbate adsorbed at equilibrium by each gram of adsorbent (mg/g), K_F is the Freundlich constant (L/g), C_e is the concentration of adsorbate in equilibrium (mg/L) and n is the adsorption intensity.

$$q_e = K_F.C_e^{1/n} \qquad (2)$$

Equation (2) if transformed into a linear equation into Equation (3) can be written as follows:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \qquad (3)$$

The linear form of the Dubinin-Radushkevich isotherm equation [23] is written in Equation (4):

$$\ln q_e = \ln Q_D - B_D\varepsilon^2 \qquad (4)$$

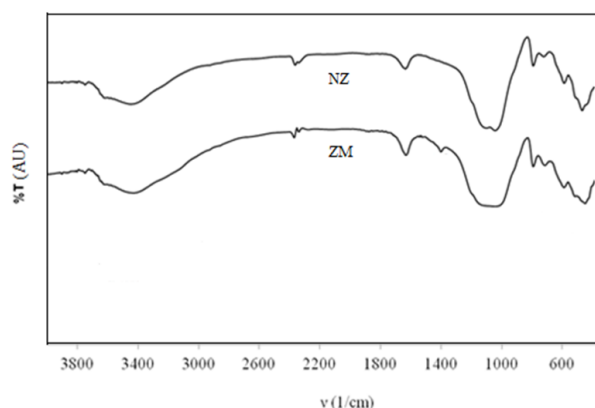Q_D is the maximum capacity (mmol/g), B_D is the Dubinin-Radushkevich constant (mol²./kJ²)

Figure 1. FT-IR spectra of natural zeolite (NZ) and modified zeolite (MZ).

and ε is the Polanyi potential obtained from Equation (5):

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \qquad (5)$$

Average adsorption energy (E_D) (kJ/mol) can be calculated from Equation (6):

$$E_D = \frac{1}{\sqrt{2B_D}} \qquad (6)$$

2.6 Kinetic Studies

The kinetics study was carried out using a solution containing 10 mg/L NO₃-N as much as 15 mL interacted with MZ as much as 150 mg. The time variations used were 60, 90, 120, 150, 180, and 210 min. In this study the kinetics of adsorption were studied using two models, namely pseudo-first-order Lagergren and pseudo-second-order. The pseudo-first-order kinetic model of Lagergren [24] was given by Equation (7).

$$\ln(q_e - q_t) = \ln q_e - kt \qquad (7)$$

q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at a certain time (mg/g), and k is the constant rate of the pseudo order reaction of one (1/min)). The pseudo-second-order kinetic model [25] is, presented in Equation (8).

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \qquad (8)$$

q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at a given time (mg/g), and k is the rate constant of the pseudo- second-order (g/mg.min).

3. Results and Discussion

3.1 Adsorbent Characterization

Figure 1 presents the FTIR spectrum of NZ compared to MZ. The coating of natural zeolites with iron oxide involves interactions be-
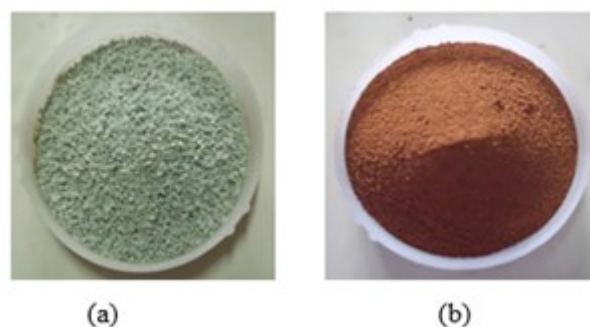

Figure 2. Change in the colour (a) NZ, (b) MZ.

tween the groups found in iron oxide and SiO_4. The vibration of the Fe−O group is shown by the appearance of a peak at the wave number of 1404.18 cm^{-1}. This result verifies that the modify carried out produced natural zeolites coated with iron oxide. Change in the colour of natural zeolite from grey to reddish brown was observed (Figure 2). This result indicates the presence of iron in the sample. Table 1 presents the functional groups of NZ compared to MZ. Modification of natural zeolite increase specific surface area and pore volume but decreases pore radius decreases (Table 2). This result indicates that the attached iron oxide closes the pores of natural zeolite, causing the pore radius to decrease.

Based on Figure 3 natural zeolites after being coated with iron oxide could increase micro-sized pores (<20 Å) and decrease meso-sized pores (20 to 500 Å). The decrease in pore radius was due to the attachment of iron oxide that increased the results of nitrate adsorption. The possible adsorption NO_3^- mechanism was controlled by electrostatic attraction and ion-exchange as shown in Figure 4. During adsorption, the nitrate ions in salt water were replaced by the hydroxyl (OH^-) ions present in MZ. The presence of positively charged Fe^{3+} and NH_4^+ ions in in the prepared natural zeolites shows a good tendency to attract negative-
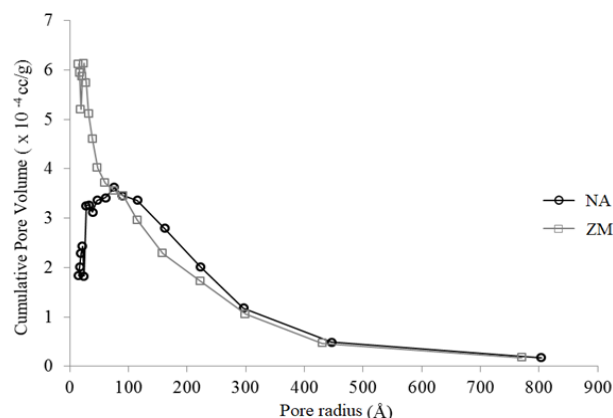

Figure 3. Distribution of adsorbent pore.

Table 1. Silica functional groups derived from the FTIR spectra recorded.

Functional Groups	Wavenumbers (cm^{-1})	
	NZ	MZ
Stretching vibration –OH from Si−OH	3749.62	3749.62
Bending vibration of –OH from water molecules	1635.64	1635.64
Vibration of Fe−O	−	1404.18
Asymmetric stretching vibration of ≡Si−O on ≡Si−O−Si≡	1041.56	1041.56
Symmetric stretching vibration of ≡Si−O on ≡Si−O−Si≡	794.67	794.67
Bending vibration Si−O−Si	470.63	447.49

Table 2. The results of the adsorbent analysis using GSA.

Description	NA	ZM
Specific surface area BET (m^2/g)	26.53	38.8
Total volume pore (mL/g)	0.1020	0.1052
Average of pore radius (Å)	76.89	54.14

Table 3. List of calculated parameters of Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherm models.

Models	Equation of isotherm	Constant	ZM
Langmuir	$\dfrac{C_e}{q_e} = -195.79 C_e + 1216.4$	R^2	0.6295
Freundlich	$\log q_e = 3.0286 \log C_e - 2.8959$	K_F	5.52×10^{-4}
		n	0.3302
		R^2	0.9634
Dubinin-Radushkevich	$\ln q_e = -5.4153 \varepsilon^2 - 0.4013$	Q_D (mmol/g)	9.7×10^{-2}
		B_D (mol^2.kJ^{-2})	0.1616
		E_D (kJ.mol^{-1})	1.76
		R^2	0.9801

ly charged species such as nitrate ions through electrostatic attraction.

3.2 Adsorption Isotherm

The equilibrium adsorption isotherms is primarily important to evaluate nitrate adsorption capacity. In order to determine the optimum isotherm model according to coefficient of determination values, Langmuir, Freundlich Dubinin-Radushkevich models were applied to the adsorption experimental results as given in Table 3. The Table 3 presents that the adsorption isotherms in the three systems are more likely to follow the Dubinin-Radushkevich isotherm. The value of E was used to determine the type of the adsorption process. It proceeded through a cation exchange when the value obtained was between 8 kJ/mol and 16 kJ/mol, while physisorption took place when it was less than 8 kJ/mol [23]. The energy value found with this equation application amounted to 1.78 kJ/mol. It indicates that the bonds between the nitrate anions and MZ can be attributed to physisorption. Batch adsorption isotherms indicated that the maximum multilayer adsorption capacity of

MZ for nitrate was 9.7×10^{-2} mmol/g which was higher than that of many other adsorbents reported in literature [1,9].

3.3 Adsorption Kinetics

The adsorption kinetics of MZ were studied using pseudo first order and pseudo second order reaction mechanisms. Based on the results shown in Table 4, the kinetic data could be best described by the pseudo second order kinetic equation. Experimental data correlate excellent to the pseudo second order reaction model with coefficient of determination value (R^2) as 0.9703. The rate constant was $k = 1.80 \times 10^{-2}$ g/mg.min. The data demonstrated the effect of nitrate concentration on the adsorption rate. Furthermore, based on the pseudo second order model, two reactions occurred; the first one was fast and reached equilibrium quickly, whereas the second one was a slow reaction that continued for an extended period. It is noted that diffusion control is the most consistent factor that is closely related to surface reactivity and porosity [26].
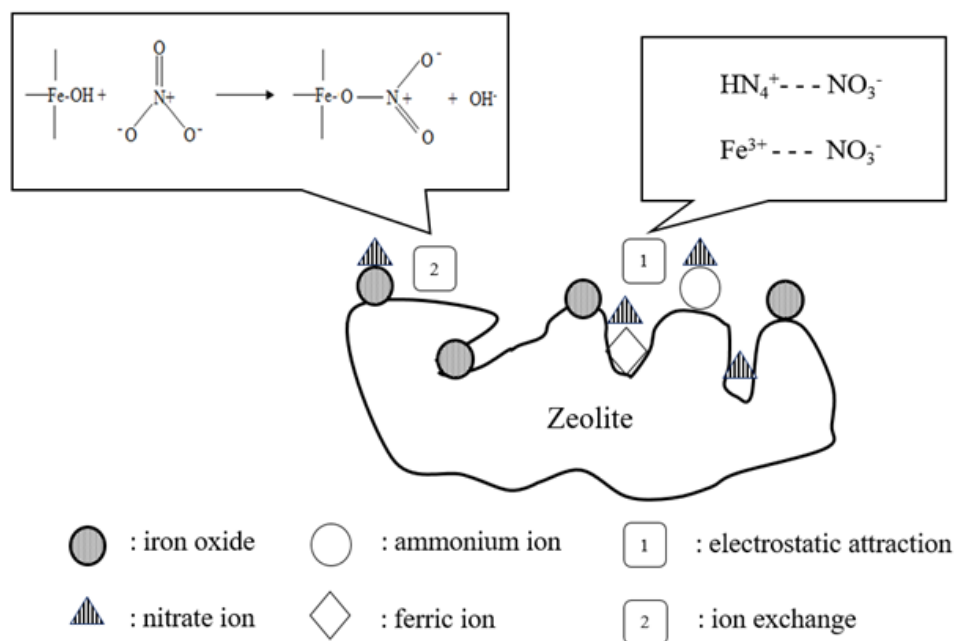

Figure 4. Proposed mechanism for the adsorption of nitrate on iron-oxide surface.

Table 4. The kinetic equation of nirate adsorption in saltwater on MZ.

Order of reaction	Equation of reaction	R^2
Pseudo first order	$\ln(q_e - q_t) = -0.0068t - 0.6948$	0.9557
Pseudo second order	$\dfrac{t}{q_t} = 0.7274t + 29.336$	0.9703

4. Conclusions

This study investigated the adsorption characteristics of natural zeolite coated with iron oxide as a potential adsorbent for the removal of nitrate from salt water. The energy involved in the adsorption process is calculated on the Dubinin-Radushkevich model. It was found equal to 1.78 kJ/mole verifying that physical adsorption of nitrate ions proceeds on the surface of modified zeolite. Pseudo second order model provides the best correlation of the experimental data, with rate constant of 1.80×10^{-2} g/mg.min.

Acknowledgments

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