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Ammonia removal from water using sodium hydroxide modified zeolite mordenite

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Abstract

Natural and modified mordenite zeolites were used to remove ammonium ions from aqueous solution and Koi pond water. The zeolite modification was conducted using sodium hydroxide solutions of different strengths at 75^{o}C for 24 h. Langmuir, Freundlich, Sips, and Toth equations with their temperature dependent forms were used to represent the adsorption equilibria data. The Langmuir and its temperature dependent forms could represent the data better than the other models. The pseudo-first order has better performance than pseudo-second order in correlating the adsorption kinetic data. The controlling mechanism of the adsorption of NH_4^+ from aqueous solution onto the natural zeolite and the one treated with 6M sodium hydroxide solution was dominated by physical adsorption. The competition with other ions occurred through different reaction mechanisms so it decreases the removal efficiency of ammonium ions by the zeolites. For the treated zeolite, the removal efficiency decreased from 81% to 66.9%. A Thomas model can represent the experimental data for both adsorption of ammonia from aqueous solution or from Koi pond water.

Keywords: Zeolite; Mordenite, Sodium hydroxide; Ammonium removal; Adsorption isotherm; Kinetic; Breakthrough

INTRODUCTION

The presence of ammonia in aquatic environments causes a serious problem for aquatic biota, especially fish. In water, the ammonia can be present in the ionized form (NH_4^+) and un-ionized form (NH_3), and both of these substances are present in equilibrium condition according to the following equation [1]:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (1)$$

The total concentration of the ionized ammonia (NH_4^+) and un-ionized ammonia (NH_3) in water is defined as the total ammonia nitrogen (TAN), and at a certain concentration the un-ionized ammonia (NH_3) is lethal for fish. The equilibrium concentration of ammonia in the water is affected by both the pH and temperature. At high pH, the equilibrium condition (equation 1) will shift towards the formation of ammonia, while at low pH the formation of ammonium ion (NH_4^+) is dominant. For aquatic biota such as fish, the ammonium ion is relatively non-toxic compared to the ammonia. Ammonia also predominates when temperature is high while the ammonium ion predominates at low temperature.

In the aquaculture industry the quality of water is the most important parameter for the continuation of the industry. One of the important parameters for the quality of water is TAN as it is the major nitrogenous waste product of fish and also results from the decomposition of organic matter. As a natural byproduct of fish metabolism, ammonia can accumulate easily in an aquatic system and it has the tendency to block the transfer of oxygen from gills to the blood nerve system and cause gill damage. The excess ammonia in water also destroys the mucous producing membrane in fish and damages the internal intestinal surfaces. The presence of excessive amounts of ammonia in the aquatic environment causes eutrophication.

A number of processes are currently available for the removal of TAN from the aquatic environment, and the most widely used process is the adsorption process. This process offers several advantages over other available processes, such as high removal efficiency, the adsorbent can be re-used, it can be applied for a wide range of concentrations, and is a cost effective process. One of the available natural adsorbents which is widely employed for the removal of ammonia from aquatic environment is a zeolite. A zeolite is a microporous aluminosilicate mineral which possesses a structure like a three-dimensional honeycomb with an overall negatively charged framework. The presence of hydrated alkali and/or alkaline earth cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) in the pores of the aluminosilicate framework stabilizes the structure, and in the aquatic condition, these cations are also exchangeable with other cations from the solution [2,3].

The disadvantage of using a natural zeolite as an adsorbent for the removal of NH_4^+ ion from aqueous solution is a low adsorption capacity; most have a value less than 10 mg/g [4-10]. The low adsorption capacity and removal efficiency are still the main problem for industrial application of natural zeolites in aquaculture, water and wastewater processes. In order to improve the adsorption capacity, a modification using a chemical treatment processes is necessary such as using an acid, alkali or salt [11-14]. Microwave irradiation [15] and heat treatment [16] methods have also been employed to increase the adsorption capacity of natural zeolites. Leyva-Ramos *et al.*[14] modified natural zeolite chabazite with sodium chloride to remove ammonium from aqueous solution and the result clearly indicates that chabazite enriched with Na^+ is more preferentially exchanged by NH_4^+ than the other alkali cations. The modification using acid solution is seldom used because acid treatment causes de-alumination, the removal of Al^{3+} ions from the zeolite structure degrades it and decreases the ion exchange capacity [1].

In this study a modification of natural mordenite with sodium hydroxide combined with a thermal treatment is investigated. To the best of our knowledge, this is the first of the use of such a modified zeolite as the adsorbent for removal of the ammonium ion from aqueous solution in an aquaculture system (Koi pond). Since the final goal of this study was to treat the ammonia from the Koi pond, therefore all of the adsorption experiments were conducted at a pH similar to the water of Koi pond system (6.5). The adsorption isotherms of ammonium ion onto natural and modified mordenite were obtained at three different temperatures (303.15, 308.15, and 313.15 K). The temperature-dependent forms of the Langmuir, Freundlich, Sips, and Toth equations were used to correlate the experimental adsorption data. The adsorption kinetics of ammonium ions onto the natural and modified zeolite was also studied. Well known pseudo first- and second-order kinetic models were employed to represent the kinetic data. The removal of ammonium ion from the Koi pond system was conducted in dynamic mode. The breakthrough adsorption performances were correlated by a Thomas equation.

MATERIAL AND METHOD

Materials

The natural zeolite used in this study was obtained from Ponorogo, East Java, Indonesia. The zeolite was crushed in a mortar and sieved using a Retsch Haan vibrator screener to particle size of about 0.85 - 1.70 mm (- 12 + 20 US mesh). All of the chemicals used in this study were obtained as pure analysis reagents from Sigma Aldrich Singapore and used without any further treatment or purification.

Modified zeolite preparation

The modification of the natural zeolite was performed under alkaline condition using sodium hydroxide solution at concentrations of 1 M, 3 M, and 6 M at 75^{o}C for 24 h. Subsequently the modified zeolite was washed using tap water to remove excess sodium hydroxide solution. Then, the solid sample was dried at 110^{o}C for 24 h.

Characterization of solid samples

The characterization of the natural (NatZ) and modified zeolites (1M-Z, 3M-Z, and 6M-Z) used scanning electron microscopy (SEM), X-ray diffraction (XRD), and nitrogen sorption. The SEM analysis was conducted to study the surface topography and texture of the adsorbents. The SEM analysis was conducted on a JEOL JSM-6390 field emission SEM operated at an accelerating voltage of 15 kV. Prior to analysis the samples were coated with ultra-thin layer of conductive platinum on the specimens using an auto fine coater (JFC-1200, JEOL, Ltd., Japan) for 120 s in an argon atmosphere. The X-ray diffraction analysis was conducted on a Philips PANalytical X'Pert powder X-ray diffractometer with monochromated high intensity Cu Kα_1 radiation (λ = 0.15406 nm). The diffractograms were obtained at 40 kV, 30 mA and with a step size of 0.05^{o}/s. The elemental compositions of the adsorbents were analyzed using a Bruker S8 Tiger X-ray fluorescence spectrophotometer.

The pore structures of NatZ, 1M-Z, 3M-Z, and 6M-Z were characterized by nitrogen sorption method. The nitrogen sorption measurements were carried out at boiling point of liquid nitrogen (77 K) on automated Micromeritics ASAP2010 sorption equipment. Prior to the analysis, the solid samples were degassed at 473.15 K for 24 h. The specific surface area of the samples were calculated by the Brunauer–Emmett–Teller (BET) method at a range of relative pressure of 0.05 to 0.3, while the total pore volume was determined at a relative pressure of 0.995.

Adsorption isotherm study

The adsorption isotherm study was conducted in batch mode at three different temperatures (303, 308, and 313 K) and pH of 6.5. A known amount of adsorbent (0.1 to 1.0 g) was added in a series of Erlenmeyer flasks containing 100 mL ammonium chloride solution with a concentration of 10 mg/L. The flasks were moved to a Memmert type WB-14 thermostatic shaker water bath. The temperature of the thermostatic shaker water bath was adjusted to a desired temperature and then the system was shaken at 100 rpm for 24 h (equilibrium condition). The equilibrium condition was determined at temperature of 303 K, pH of 6.5, and initial solution concentration of 10 mg/L. After the equilibrium time was reached, the solid adsorbent was removed from the solution by centrifugation. The concentration of ammonium in the solution was measured quantitatively at maximum wavelength (699.5 nm) based on Nessler method [17] using Shimadzu UV/VIS-1700 Pharma Spectrophotometer. The amount of ammonium ion adsorbed by the adsorbent at equilibrium condition was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)}{m} V \qquad (2)$$

Where q_e is the equilibrium condition (mg/g), C_o (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of ammonium in the solution, respectively. The amount of adsorbent (g) and the volume of solution (L) are represented by symbols m and V. The adsorption isotherm experiments were conducted in triplicate.

Adsorption kinetic study

The adsorptions kinetic of ammonium from aqueous solutions onto natural and modified zeolites were also conducted isothermally at three different temperatures (303, 308, and 313 K) and pH of 6.5. A similar procedure to the adsorption isotherm study was employed for the

kinetic study. In the kinetic study, the fixed amount of adsorbent (1 g) was added to each Erlenmeyer containing 100 mL ammonium solution (10 mg/L). At a certain interval of time (1 h) one of the available flasks was taken from the thermostatic water bath. The amount of the ammonium adsorbed by the adsorbent at time *t* was determined by the following equation

$$q_t = \frac{(C_o - C_t)}{m} V \quad (3)$$

Where C_t is the concentration of ammonium in the solution at time interval of *t*. The adsorption kinetic experiments were conducted in triplicate.

Continuous adsorption experiment

Continuous adsorption of ammonium ion from aqueous solution and Koi pond onto modified zeolites were conducted as follow: The modified zeolites were packed in glass columns of 1 cm diameter and 16.5 cm height. Synthetic ammonium chloride solution and fish pond wastewater were pumped into the column using a Masterflex 7550-62 peristaltic pump. This experiment was performed to obtain breakthrough curves of ammonium from aqueous solution and real aquaculture system (in this case Koi pond). The flowrate of the solution entering the column was 6.5 mL/min and the height of modified zeolite in the column was 5 cm. The solution was collected at the outlet of the column after certain intervals of time and the concentration of ammonium was measured spectrophotometrically using the Nessler method[17].

RESULTS AND DISCUSSION

Characterization of natural and modified zeolite

The SEM micrographs of the surface morphology of NatZ and 6M-Z are depicted in Figure 1. It can be seen that the modification using a strong sodium hydroxide solution (6 M) did not affect the surface topography of the zeolite. The breakdown of some of the particles from a

189 needle-like shape into smaller and less uniform particles is attributed to the mechanical force
190 used during the grinding of the zeolite.
191
192 The XRD patterns of NatZ and 6M-Z are given in Figure 2. The identification of the mineral
193 content by comparing to the standard of JCPDS 80-0642 indicates it consists mainly of
194 mordenite. The modification of the natural zeolite using sodium hydroxide solution did not
195 change or degrade the mordenite as seen in the XRD patterns in Figure 2. This evidence
196 clearly indicates that the sodium hydroxide modification exerted little or no influence on the
197 crystallinity of the mordenite. The chemical composition of the natural zeolite and its
198 modified form obtained from XRF analysis are summarized in Table 1. The increase of Na_2O
199 composition in modified zeolite indicates that the incorporation of exchangeable sodium ions
200 to the natural zeolite occurred during the modification process. Partial exchange of several
201 cations such as Ca^{2+}, K^+ and, to a lesser extent, Mg^{2+} with Na^+ was observed. With increasing
202 NaOH concentration, the amount of CaO decrease from 2.43 to 0.11%, while the composition
203 of Na_2O increase from 1.87 to 3.85%. The modification using 6M NaOH almost completely
204 transformed the Ca-zeolite into a Na-zeolite with, as stated earlier, no obvious change in
205 crystallinity.
206
207 As illustrated in Figure 3, the modification of the natural zeolite using sodium hydroxide
208 solution improved the porosity. The hysteresis loops in NatZ, 1M-Z, 3M-Z, and 6M-Z
209 confirms the presence of mesopores in the pore structure. The BET surface area, micropore
210 volume and total pore volume of the zeolites are summarized in Table 2. It can be seen that
211 the micropores did not have significant contribution to the total pore since the values were
212 almost equal to zero. The modification of zeolite using sodium hydroxide at 75^{o}C brought the
213 formation of more mesopores due to the clearing of the pore channels and voids of the natural

zeolite. The increased NaOH concentration also increased the formation of pores, leading to the increase of BET surface area and total pore volume as indicated in Table 2 and Figure 3.

Effect of sodium hydroxide concentration to adsorption capacity

Initial adsorption experiments showed that the adsorption of ammonium ions had reached equilibrium after 24 h. For subsequent adsorption experiments, 24 h was chosen as the equilibrium time. Figure 4 shows the removal efficiency of NH_4^+ from the solution using natural and NaOH modified zeolites as the adsorbents. This figure clearly indicates that NaOH modification effectively improved the adsorption capability of the zeolite for removal of NH_4^+ from aqueous solution. According to Table 1, the removal efficiency of NH_4^+ is closely related to the content of Na and Ca; the zeolite with higher Na and less Ca content removed more NH_4^+. Since the 6M-Z has the highest removal efficiency; this modified zeolite was used for subsequent adsorption experiments.

Adsorption equilibria

The equilibrium relation between the ammonium ion on the surface of the adsorbent and in the solution could be related through an adsorption isotherm. Different kind of adsorption models have been developed and are currently used for the interpretation of liquid phase adsorption experimental data. The adsorption of chemical compounds onto the surface of adsorbents is affected by temperature. For physical adsorption, the temperature gives a negative effect on the adsorption capacity of adsorbent, while for chemical adsorption the uptake increases with the increase of temperature. The influence of temperature on the amount uptake can be represented in the adsorption models through the inclusion of temperature dependent forms [18-20]. In this study, the Langmuir, Freundlich, Sips, and Toth

models with their temperature dependent forms were employed to correlate the adsorption equilibria of NH_4^+ onto NatZ and 6M-Z.

The Langmuir equation is one of the most widely used adsorption equations to correlate liquid phase adsorption experimental data of various systems. Based on the theory of the adsorption on a flat surface, Langmuir developed an adsorption model which has the form as follows

$$q_e = q_{\max}\left(\frac{K_L C_e}{1 + K_L C_e}\right) \quad (4)$$

Where $q_{\max}$ is the maximum amount of adsorbate adsorbed by the adsorbent to achieve complete monolayer coverage of the adsorbent surface (mg/g), and K_L is the adsorption affinity (L/mg). The parameters $q_{\max}$ and K_L are affected by temperature, and the mathematical forms of these parameters as function of temperature are as follow:

$$q_{\max} = q^o_{\max} \exp\left(\delta\left(T_o - T\right)\right) \quad (5)$$

$$K_L = K_L{}^0 \cdot \exp\left(\frac{-E}{R \cdot T_0}\right) \quad (6)$$

Parameter $q^o{}_{\max}$ represents the maximum adsorption capacity at a reference temperature T_o, while temperature coefficient of expansion of the adsorbate is represented by parameter δ. The affinity constant of Langmuir equation at reference temperature and heat of adsorption are given by symbols $K_L{}^o$ and E, respectively.

The second equation used in this study to represent the adsorption equilibria data is the Freundlich isotherm. This equation is the earliest known empirical adsorption equation and widely used for heterogeneous systems and reversible adsorption processes. The Freundlich isotherm has the form

$$q_e = K_F \cdot C_e^{1/n} \quad (7)$$

Where K_F ((mg/g)(mg/L)$^{-n}$) and n are parameters represent adsorption capacity and the adsorption intensity, respectively. Parameter n also indicates the heterogeneity of the system. The temperature dependent forms of Freundlich equation are

$$K_F = K_F^{\,0} \cdot \exp\left(\frac{-\alpha \cdot R \cdot T}{A_0}\right) \quad (8)$$

$$\frac{1}{n} = \frac{R \cdot T}{A_0} \quad (9)$$

Where K_F^o is the adsorption capacity at the reference temperature, α/A_o is a constant.

The Sips equation was developed for predicting adsorption in heterogeneous systems, and this model is a combination of the Langmuir and Freundlich adsorption isotherm. The advantage of Sips equation is it has a finite limit. The Sips equation can be written as follows:

$$q_e = q_{\max} \cdot \left[\frac{(K_s \cdot C_e)^{1/n}}{1 + (K_s \cdot C_e)^{1/n}}\right] \quad (10)$$

Where K_s (L/mg)^n is the adsorption affinity of Sips model, and n characterizes the heterogeneity of the system. When the value of n become unity, Eq (10) reduces to Eq (4). The temperature dependent forms of Sips equation are represented by parameter $q_{\max}$, K_s and n. The temperature dependent of $q_{\max}$ follows Eq (5) while for K_s and n are as follow

$$K_S = K_S^{\,0} \cdot \exp\left[\frac{E}{R \cdot T_0}\left(1 - \frac{T_0}{T}\right)\right] \quad (11)$$

$$n = \frac{1}{\frac{1}{n_0} + \eta \cdot \left(1 - \frac{T_0}{T}\right)} \quad (12)$$

The parameter K_s^o is a measure of the affinity between the adsorbate and the adsorbent at the reference temperature, while n_o characterizes the heterogeneity of the system at reference temperature. The parameter η is a constant of Sips temperature dependent form.

The last model used in this study is the Toth equation. This equation was developed on the basis of potential theory and provides a good description of many systems with sub-monolayer coverage[21]. Similar to Langmuir equation, Toth equation has finite saturation limit for high concentration and follows Henry's law at very low concentration[19].

$$q_e = \frac{q_{\max} \cdot C_e}{(K_{Th} + C_e^{\,t})^{1/t}} \tag{13}$$

The adsorption affinity of the Toth equation is given by parameter K_{Th} (mg/L)^t, and t is a parameter represents the system heterogeneity. Both of these parameters are affected by temperature and can be written as:

$$K_{Th} = K_{Th}^{\,0} \cdot \exp\left[\frac{E}{R \cdot T_0}\left(\frac{T_0}{T} - 1\right)\right] \tag{14}$$

$$t = t_0 + \eta \cdot \left(1 - \frac{T_0}{T}\right) \tag{15}$$

Where K_{Th}^o and t_o are adsorption affinity constant and parameter characterizes system heterogeneity at reference temperature, respectively.

Temperature has a pronounced effect on the removal capacity of the zeolite as shown in Figure 5 for NatZ and 6M-Z. The uptake of NH_4^+ ions by both of the adsorbents decreased as the temperature increased. The main mechanism of the adsorption of NH_4^+ ions by the zeolite is ion exchange and the process can be written as

$$Na_xZ + x\ NH_4^+ \leftrightarrow (NH_4)_xZ + x\ Na^+ \tag{16}$$

In most cases, ammonium exchange onto a zeolite is an exothermic process [5,8,22], therefore the increase of temperature will shift the equilibrium condition towards endothermic, and less NH_4^+ ions adsorbed by the NatZ and 6M-Z.

Figures 6 and 7 depict the adsorption equilibria of ammonium ions onto NatZ and 6M-Z at three different temperatures. The experimental data were fitted by temperature dependent forms of Langmuir, Freundlich, Sips, and Toth equations. The parameters of each model were obtained by the non-linear least-squares method, and the fitting was conducted for all the experimental data at various temperatures simultaneously using T_o = 298 K. The Toth equation with its temperature dependent forms failed to correlate the adsorption equilibria data of ammonium onto NatZ. The values of parameters of Langmuir, Freundlich, Sips, and Toth equations obtained from the fitting of the adsorption experimental data are summarized in Table 3. Since the Toth equation failed to represent the adsorption equilibria data of ammonium onto NatZ, it will be excluded for further discussions of the validity of the adsorption equations in representing the adsorption experimental data.

Visually (Figures 6 and 7), Langmuir, Freundlich, and Sips isotherm equations could represent the experimental data well with good value of R^2 (Table 3). However, the decision of the suitability of the models in representing the experimental data should not be based on the visual appearance of the model or the value of R^2 but should be based on the physical meaning of the parameters obtained through the fitting of the data. The parameter q^0_{max} in the Langmuir and Sips models and the parameter K_F^0 in the Freundlich model represent the adsorption capacity of the adsorbent at 298 K. Since the values of adsorption capacity of NatZ and 6M-Z were in the range of the adsorption capacity of common zeolites [15,23],

therefore, the value of parameter q^0_{max} and $K_F{}^0$ of those models were physically consistent and reasonable.

The affinity parameter in the Langmuir and Sips models is expressed as $K_L{}^0$ and $K_S{}^0$, respectively. This parameter measures how strong the adsorbate (ammonium ion) is attracted to the adsorbent (zeolite) surface. A higher value of the affinity parameter means more adsorbate molecules cover the adsorbent surface. The experimental results revealed that 6M-Z zeolite has better adsorption capability than NatZ as seen in Figures 6 and 7. It indicates that 6M-Z zeolite had higher affinity value than NatZ. Based on the affinity parameter values listed in Table 3, all of three model used still capable to correlate the adsorption experimental data.

The parameter δ in the Langmuir and Sips equations is the temperature coefficient of adsorbate expansion. The value this parameter is specific for different component and independent with type of adsorbent [24]. From Table 5, the fitted values of parameter δ of ammonium ion obtained from both adsorbents and equations were essentially constant and consistent with the value of most liquids and independent on the type of adsorbent. Therefore, the Langmuir and Sips models still had plausible reason for further discussion.

In the Freundlich and Sips models, the heterogeneity of a given system is represented by A_0 (Freundlich) and n_0 (Sips). The attachment and exchange of the sodium ion into the zeolite framework would increase the system heterogeneity, and therefore increase the A_0 and n_0 value. The inconsistency of the heterogeneity parameter values with the physical meaning of this parameter is observed as indicated in Table 3. Since both of the Freundlich and Sips

models failed to predict a correct value, both of these are excluded in the subsequent discussion.

Figures 6 and 7 show that the temperature had a negative effect on the amount of ammonium ion uptake by both of NatZ and 6M-Z. This phenomenon indicates that physical adsorption is more dominant than chemisorption. Comparing the heat of adsorption value (E) with adsorption bonding type is necessary to verify the adequacy of Langmuir isotherm model. An adsorption process can be classified into physical adsorption if the adsorption energy is less than 40 kJ/mol and chemisorption when the adsorption energy is between 40-80 kJ/mol. In physical adsorption, increasing temperature would weaken the interaction between adsorbate and adsorbent therefore less amount of ammonium ion adsorbed onto zeolite. The fitted adsorption heat value in Langmuir model was found to be consistent with the theory. Accordingly, Langmuir model can represent the adsorption data better than any other models.

Adsorption kinetic study

The adsorption kinetic information is important for the design of an adsorption system. The rate of ammonium ion adsorbed into NatZ and 6M-Z are represented by pseudo-first order [25] and pseudo-second order [26-28] models. The pseudo-first order has the form

$$q(t) = q_e \cdot (1 - \exp\ (-k_1 \cdot t)) \quad (17)$$

While the pseudo-second order has the following form

$$q(t) = q_e \cdot \left(\frac{q_e \cdot k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t}\right) \quad (18)$$

While k_1 (1/hour) and k_2 (g/mg.hour) are time scaling factor for pseudo-first and pseudo second order, respectively. Time scaling factor describes how fast the system reaches the equilibrium.

The adsorption kinetic data of NH_4^+ onto NatZ and 6M-Z are given in Figures 8 and 9. Figure 8 depicts the experimental data and plots of pseudo-first order while the plots of pseudo-second order are given in Figure 9. The fitted parameters of pseudo-first and pseudo-second order are given in Table 4. From Figures 8 and 9 and Table 4, it can be seen that pseudo-first order gave better performance in representing the experiment kinetic data than pseudo-second order. The deviation of q_e obtained from the fitting and experimental data in the pseudo first order is smaller than the pseudo-second order. Based on this evidence, the controlling mechanism of the adsorption of NH_4^+ from aqueous solution onto NatZ and 6M-Z was dominated by physical adsorption.

Depending on the adsorption mechanism, the time scaling parameter k_1 in pseudo-first order and k_2 in pseudo-second order is also as a function of temperature. At a temperature higher than 30^{o}C, the physical adsorption gave a quite dominant effect in the adsorption of NH_4^+ onto NatZ and 6M-Z. In both kinetic models, the value of this time scaling parameter decreased with increasing of temperature, obviously, the higher temperature of the system, the longer time was needed for the system to reach equilibrium state.

Adsorption of ammonia from real aquaculture water

In order to test the effectiveness of the modified zeolite for removal of NH_4^+ from an aquatic environment, an adsorption study using a real aquaculture system, a Koi pond, was also conducted. The water capacity of the Koi pond was 2 m^3 and it was equipped with a filtering and biological system. The number of Koi in the pond was 45 Koi carp with an average weight of 2.0 kg/Koi. With this high density of Koi, the average ammonia concentration in the Koi pond after 1 h feeding was 4.2 mg/L. The pH in the Koi pond was 6.5. The zeolites used for

the adsorption of NH_4^+ from the Koi pond were NatZ, 1M-Z, 3M-Z, and 6M-Z. The adsorption experiments were conducted at 30°C in a batch mode.

The water analysis of the Koi pond before and after zeolite adsorption is given in Table 5. It can be seen that the adsorption in this real system also involved the adsorption of other ions. The competition with other ions occurred through different reaction mechanisms so it decreases the removal efficiency of ammonium ions by the zeolites. For 6M-Z zeolite, the removal efficiency decrease from 81% to 66.9%. The comparison of the adsorption capacity of sodium hydroxide modified zeolite mordenite with other zeolite adsorbents toward the ammonium ion is given in Table 6. From this table it can be seen that the sodium hydroxide modified zeolite mordenite has better ammonium adsorption capacity than other zeolites.

Continuous adsorption experiment

A breakthrough curve for ammonium provides the performance of adsorption in a packed bed column system. A number of models with different kinds of assumptions have been developed and tested for various adsorption systems. One of the models is the Thomas equation:

$$\frac{C_t}{C_o} = \frac{1}{1 + \exp\left[\left(\frac{K_{Th} \cdot q_{max} \cdot x}{Q}\right) - K_{Th} \cdot C_o \cdot t\right]} \quad (19)$$

Where K_{Th} is Thomas rate constant (mL/min.mg) and q_{max} is maximum adsorption capacity (mg/g).

The zeolite used for the breakthrough curve experiments was 6M-Z. The breakthrough curves of the adsorption of NH_4^+ from aqueous solution and from Koi pond water are given in Figure 10. The symbols represent the adsorption data while the solid lines represent the

Thomas model. From this figure it can be seen that the Thomas model can represent the experimental data well for both system. The values of parameters K_{Th} and q_{max} for adsorption of NH_4^+ from the aqueous solution are 0.0082 mL/min.mg and 45.47 mg/g, respectively, while for the real system (Koi pond water) the values are K_{Th} and q_{max} of 0.0080 mL/min.mg and 38.40 mg/g, respectively.

The Thomas parameter K_{Th} for both systems is essentially the same, this parameter represents the interaction between adsorbent and adsorbate in a dynamic system. Since the breakthrough experiments for both systems were conducted at the same operating conditions (temperature, initial concentration, column diameter, and amount of adsorbent) it is not surprising that the parameter of K_{Th} for both systems should be the same. As mentioned before, the parameter q_{max} represent the adsorption capacity of the adsorbent, the fitted value of q_{max} for adsorption of NH_4^+ from aqueous solution is higher than from the Koi pond water. As seen in Table 5, the Koi pond water contains other ions besides NH_4^+. During the adsorption of NH_4^+ in the packed bed column the competition for active sites or for exchangeable cations (especially Na^+) occurred; therefore less NH_4^+ could be adsorbed/exchanged on the surface of 6M-Z. The breakthrough condition was achieved after 800 min.

CONCLUSIONS

The modification of natural zeolite from Ponorogo, predominantly mordenite, using NaOH as a modifying agent has been successfully conducted. The natural zeolite and its modified forms were used for the removal of ammonium ions from aqueous solution and Koi pond water. The adsorption and kinetic experiments were conducted at three different temperatures at static mode conditions. Temperature-dependent forms of Langmuir, Freundlich, Sips, and Toth adsorption equations were used to analyse the experimental data and among these

models the Langmuir model could best represent the data with reasonable values of the fitted parameters. For the kinetic study, well-known pseudo-first order and pseudo-second order equations were used to represent the kinetic data. Pseudo-first order gave better performance than pseudo-second order model. The Thomas model also successfully represents the dynamic adsorption data.

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Table 1. Chemical composition of natural and NaOH modified zeolites as determined by XRF.

Element	% weight			
	NatZ	1M-Z	3M-Z	6M-Z
SiO_2	60.85	60.14	62.05	58.47
Al_2O_3	11.78	12.03	12.6	13.41
CaO	2.43	1.92	0.93	0.11
Fe_2O_3	2.07	2.02	2.01	1.78
Na_2O	1.87	2.34	3.05	3.85
K_2O	1.05	0.95	0.92	0.51
MgO	0.52	0.51	0.51	0.42
Other	19.43	20.09	17.93	21.45

Table 2. The pore characteristics of natural and modified zeolites

Sample	S_{BET}, m^2/g	V_{micro}, cm^3/g	V_{Total}, cm^3/g
NatZ	30.2	0.002	0.116
1M-Z	38.9	0.002	0.138
3M-Z	49.5	0.002	0.153
6M-Z	58.6	0.002	0.182

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561 **Table 3**. The parameters of Langmuir, Freundlich, Sips and Toth equations as fitted to the

562 adsorption of ammonium onto NatZ and 6M-Z

Isotherm Model	Parameters	NatZ	6M-Z
Langmuir	q^0max (mg/g)	7.9462	53.9169
	δ (K^{-1})	0.00203	0.00218
	$K_L{}^0$ (L/mg)	0.1111	0.4044
	E (kJ/mol)	1.575	18.234
	R^2	0.9851	0.9882
Freundlich	$K_F{}^0$ (mg/g)(mg/L)$^{-n}$	1.2505	1.676
	α/A_0	0.029	-0.0412
	A_0	37.82	36.63
	R^2	0.9835	0.9925
Sips	$q^0{}_{max}$ (mg/g)	0.1166	0.5633
	δ (K^{-1})	0.00251	0.00243
	$K_S{}^0$ (L/mg)	4.0834	7.0279
	E (kJ/mol)	0.8499	10.36
	n_0	1.4735	1.333
	η	-0.3281	-1.8641
	R^2	0.9835	0.9724
Toth	q^0max (mg/g)	-	528.567
	$K_{Th}{}^0$ (L/mg)		5.3859
	E (kJ/mol)		31.327
	t0		0.4155
	η		-2.6879
	R^2		0.929

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571 **Table 4.** Fitted parameters for pseudo-first order and pseudo-second order for adsorption
572 kinetic of NH_4^+ onto NatZ and 6M-Z

	Pseudo-first order			Pseudo-second order		
T (K)	k_1 (1/h)	q_e (mg/g)	R^2	k_2 (g/mg.h)	q_e (mg/g)	R^2
Using natural zeolite as adsorbent						
303	0.2399	2.9457	0.9785	0.0485	4.0609	0.9691
308	0.1929	2.9243	0.9602	0.0335	4.2665	0.9525
313	0.1837	2.7522	0.9656	0.0326	4.0744	0.9580
Using modified zeolite as adsorbent						
303	0.4102	20.7974	0.9796	0.0167	25.6145	0.9644
308	0.3764	20.3851	0.9733	0.0147	25.5650	0.9568
313	0.3480	20.1977	0.9698	0.0130	25.7437	0.9550

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586 **Table 5.** Water analysis report of Koi pond before and after adsorption using zeolites

	Original	NatZ	1M-Z	3M-Z	6M-Z
pH	6.5 ± 0.0	6.5 ± 0.0	6.5 ± 0.0	6.5 ± 0.0	6.5 ± 0.0
Alkalinity total as $CaCO_3$, mg/L	121 ± 4.1	121 ± 3.2	120 ± 5.5	121 ± 3.8	119 ± 2.1
CO_3^{2-} as $CaCO_3$, mg/L	1.21 ± 0.04	1.21 ± 0.06	1.18 ± 0.05	1.11 ± 0.05	1.05 ± 0.03
Fe^{2+}, mg/L	0.12 ± 0.01	0.11 ± 0.01	0.11 ± 0.02	0.08 ± 0.01	0.06 ± 0.0
Mn^{2+}, mg/L	0.01 ± 0.0	0.01 ± 0.0	-	-	-
Cl^-, mg/L	4.50 ± 0.08	4.42 ± 0.05	4.34 ± 0.07	4.24 ± 0.09	4.14 ± 0.21
SO_4^{2-}, mg/L	3.74 ± 0.14	3.69 ± 0.10	3.61 ± 0.09	3.43 ± 0.11	3.11 ± 0.23
NO_3^-, mg/L	0.09 ± 0.0	0.08 ± 0.0	0.07 ± 0.01	0.02 ± 0.0	-
Total ammonia, mg/L	4.20 ± 0.17	3.91 ± 0.13	3.25 ± 0.20	2.61 ± 0.05	1.39 ± 0.06
NO_2^-, mg/L	0.01 ± 0.0	-	-	-	-
PO_4^{3-}, mg/L	0.15 ± 0.01	0.14 ± 0.02	0.12 ± 0.01	0.11 ± 0.01	0.08 ± 0.01

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589 **Table 6.** Adsorption capacity of sodium hydroxide modified zeolite mordenite and several

590 zeolites samples toward ammonium ion

Sample	Adsorption capacity, mg/g	References
zeolite mordenite	7.94	This study
sodium hydroxide modified zeolite mordenite	53.91	This study
New Zealand mordenite	8.70	7
Natural calcium rich zeolite	9.72	15
Sodium salt modified zeolite	15.44	
NaA zeolite from halloysite	44.30	29
Zeolite 13X	8.61	30

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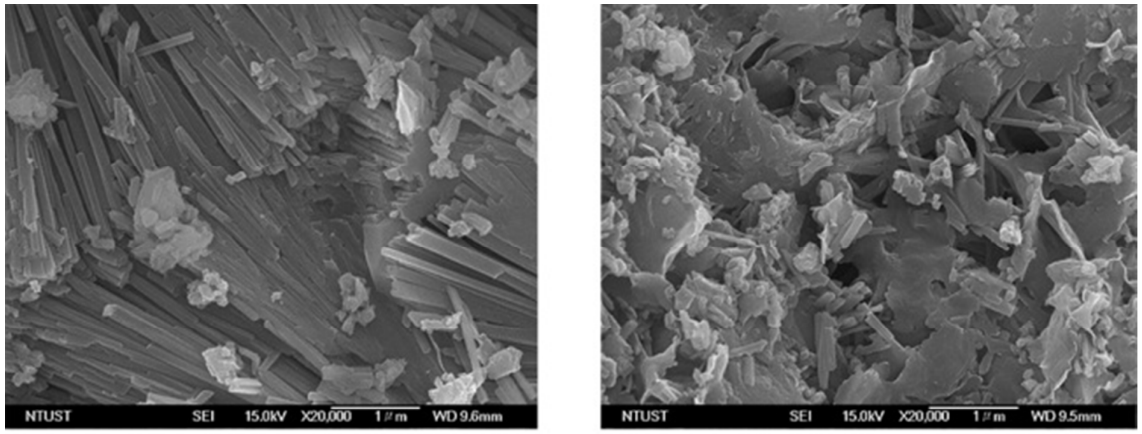

(a) (b)

Figure 1. Surface topography of (a) natural zeolite (NatZ), and (b) modified zeolite (6M-Z)

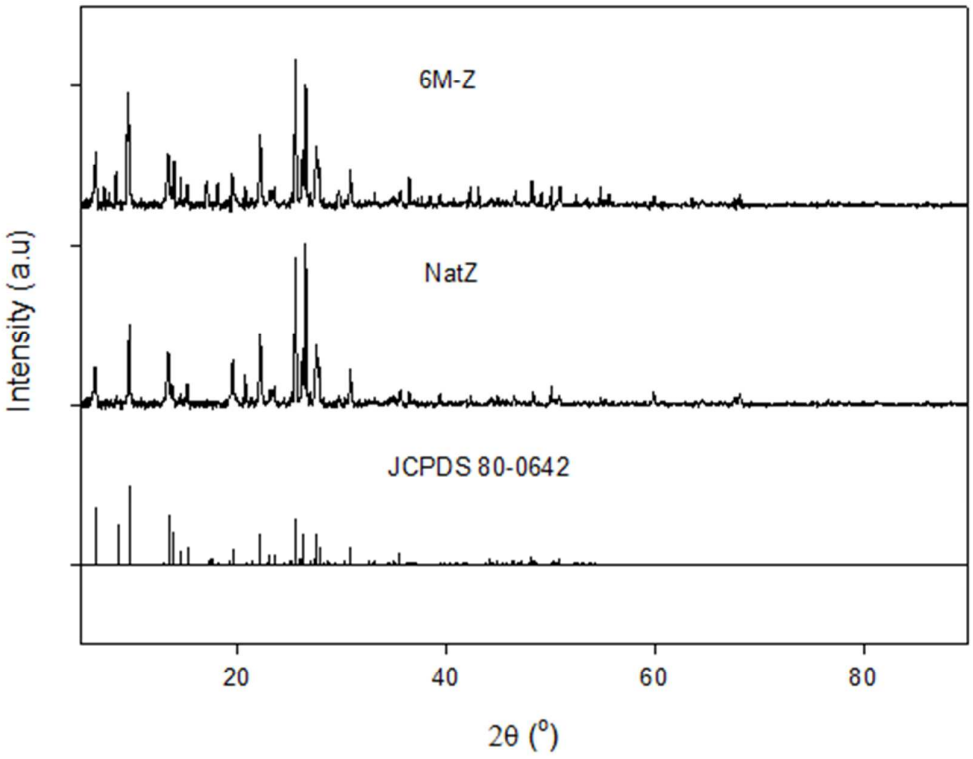

Figure 2. XRD diffractograms of natural zeolite (NatZ) and its modified form (6M-Z) with the pattern reported for mordenite in the ICSD JCPDS database.

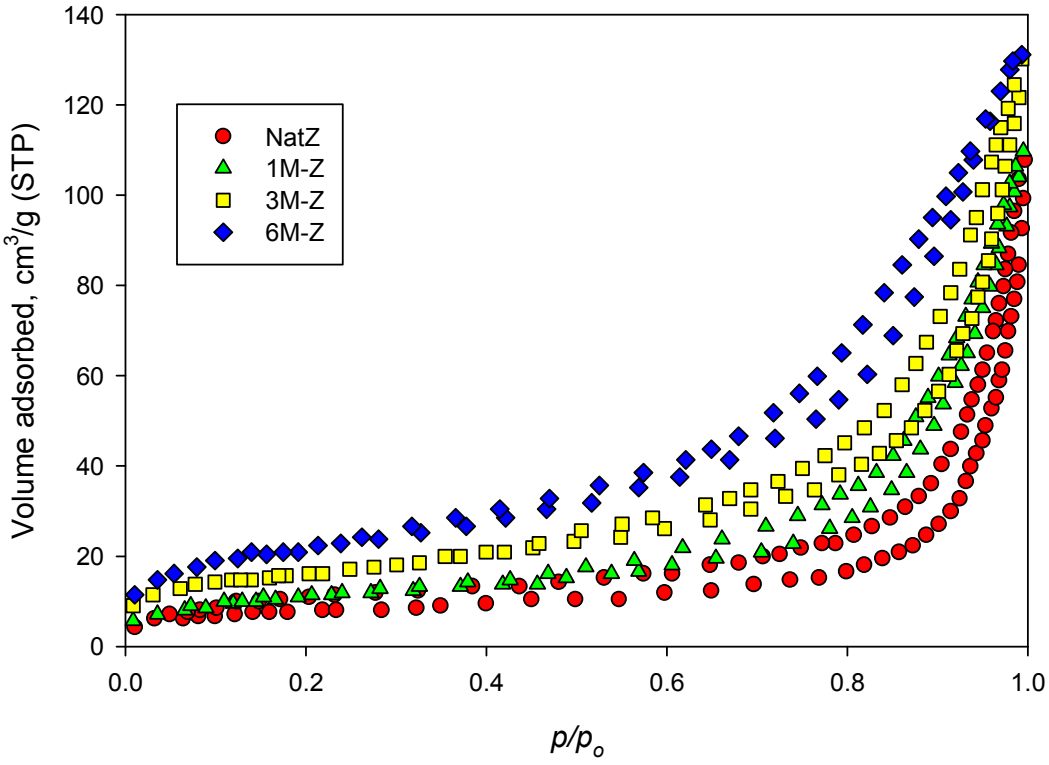

Figure 3. Nitrogen sorption isotherms of natural and modified zeolites

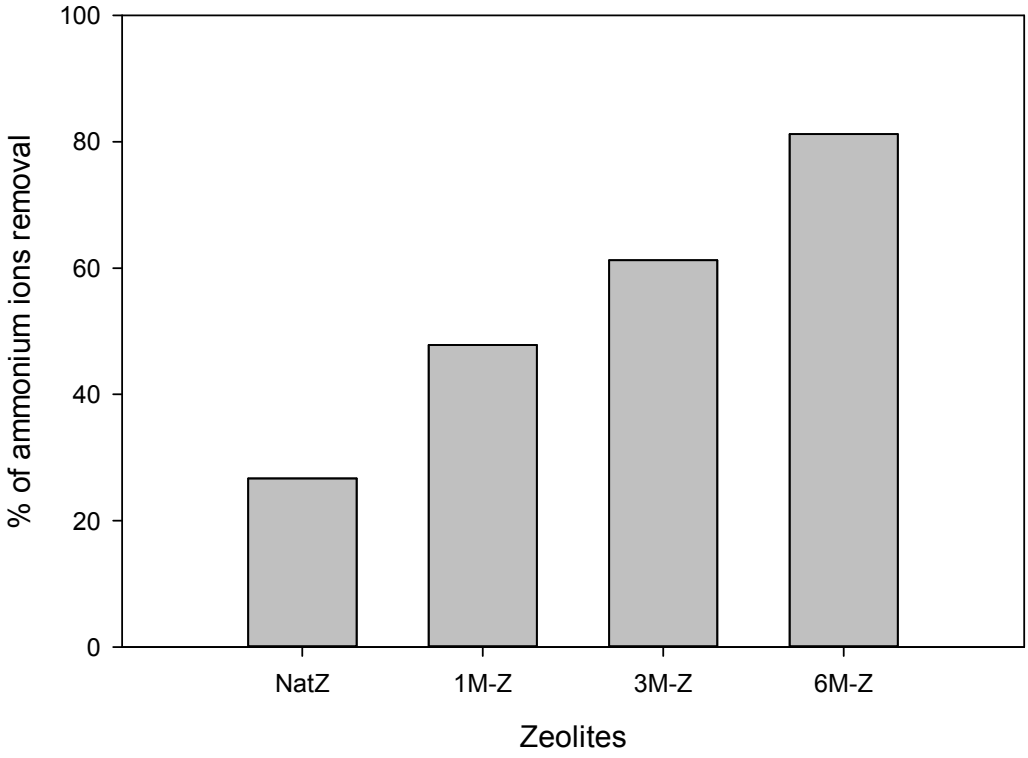

Figure 4. Removal efficiency of natural and modified zeolites

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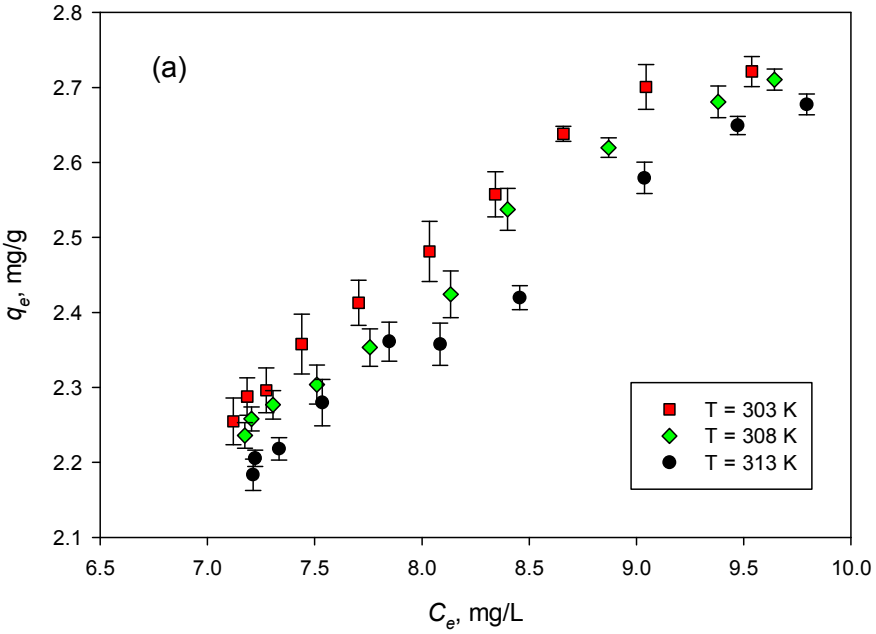

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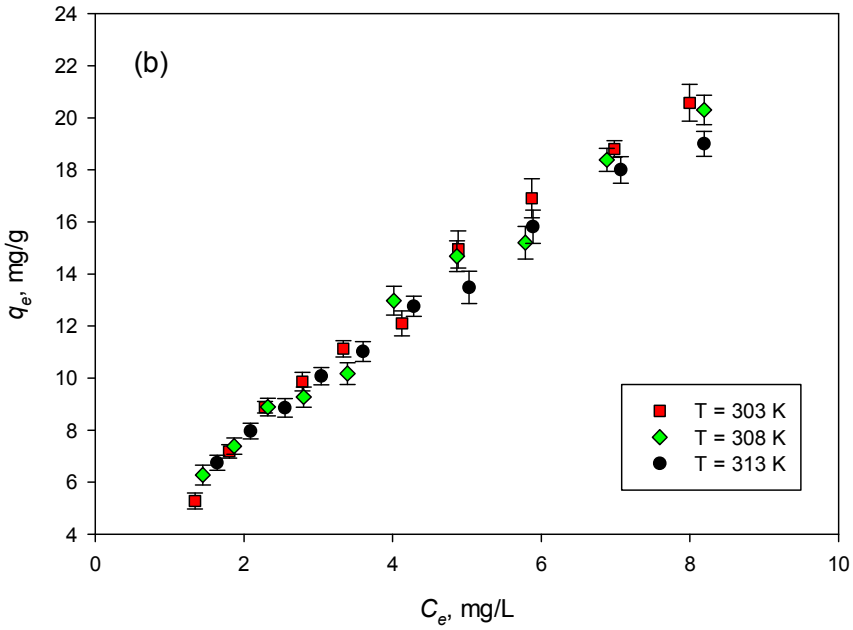

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663 **Figure 5.** Effect of temperature on ammonium removal using: a) NatZ, b) 6M-Z

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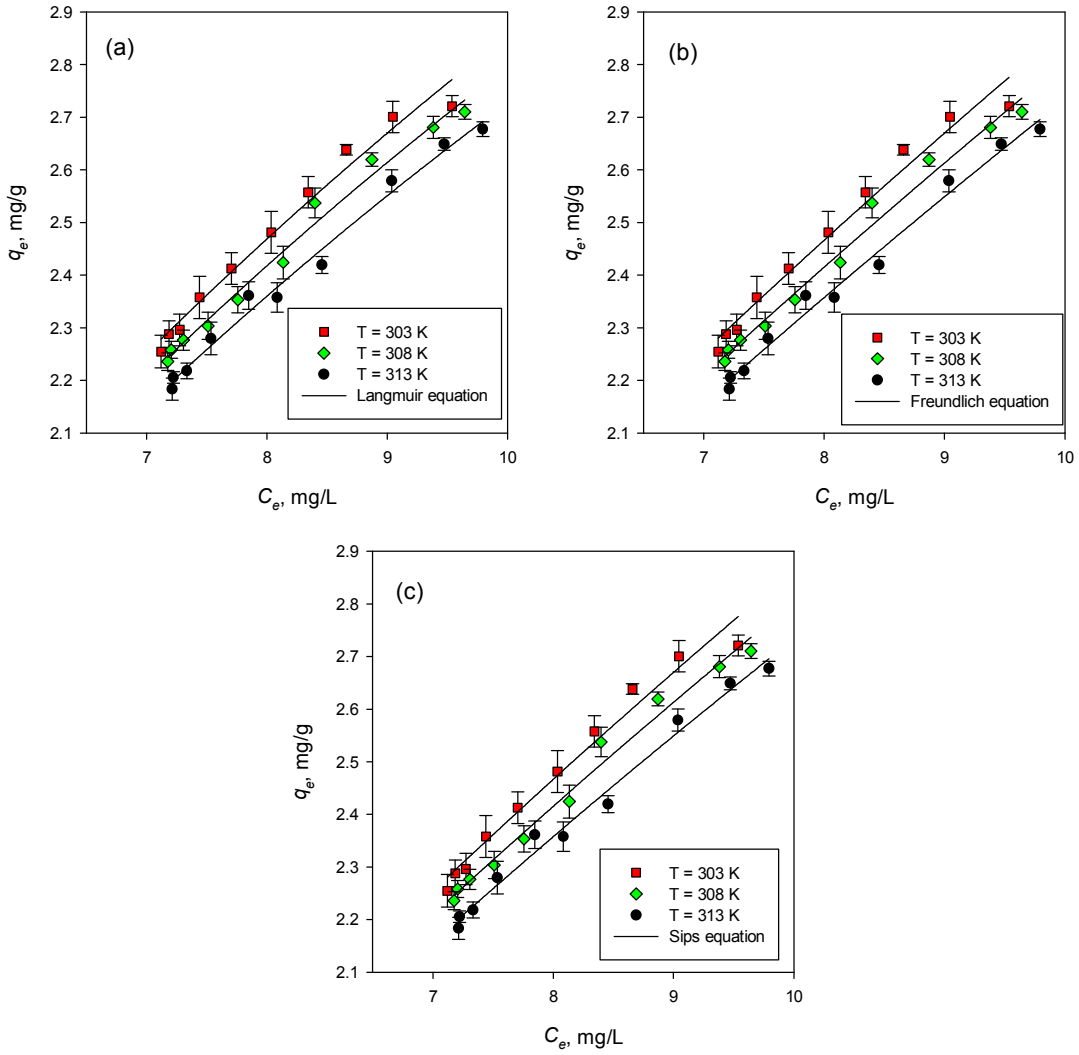

Figure 6. Adsorption experimental data of ammonium ion into NatZ and the model fitted by: (a) Langmuir, (b) Freundlich, and (c) Sips.

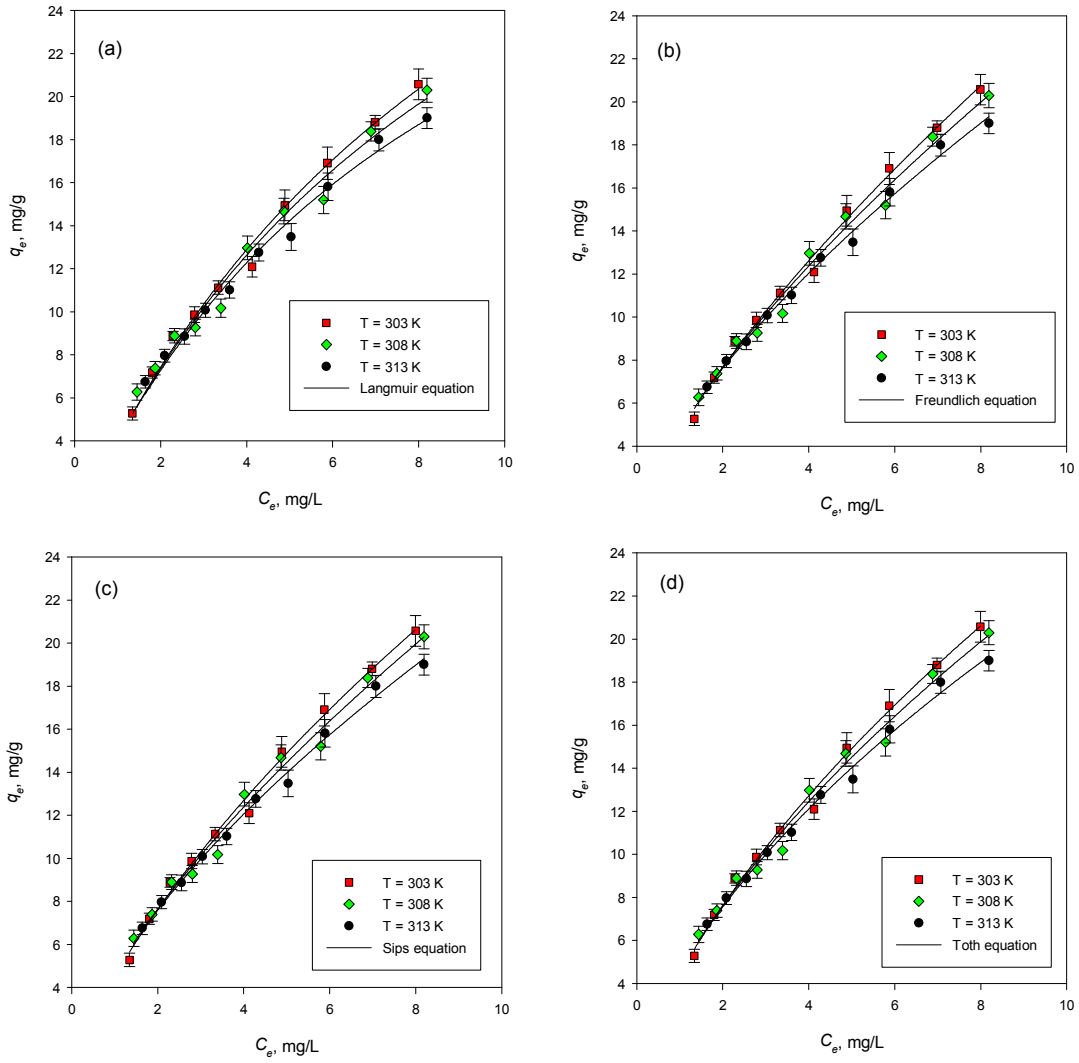

Figure 7. Adsorption experimental data of ammonium ion into 6M-Z and the model fitted by: (a) Langmuir, (b) Freundlich, (c) Sips, and (d) Toth.

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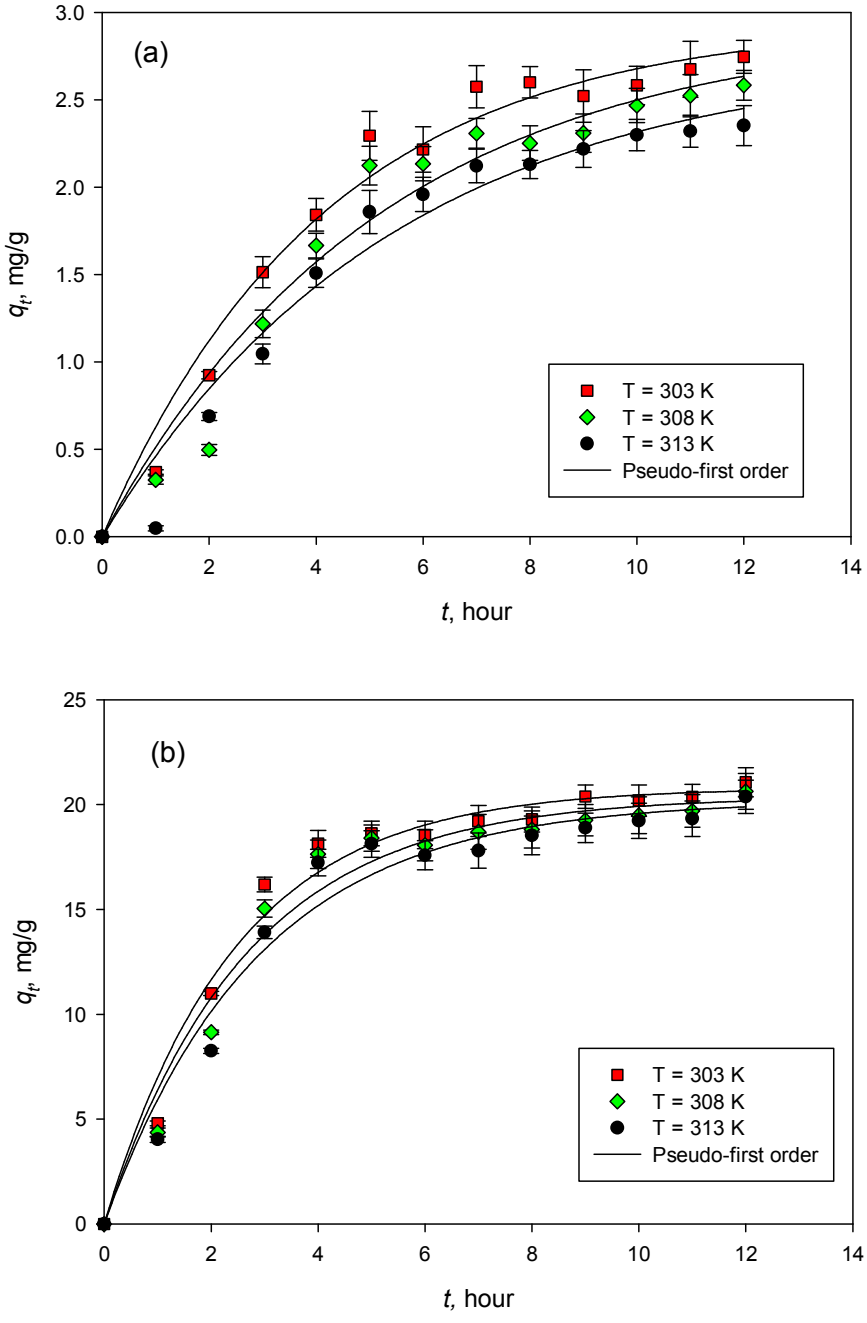

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690 **Figure 8.** Pseudo first order reaction kinetics for the adsorption of NH_4^+ ion on (a). NatZ and

691 (b). 6M-Z

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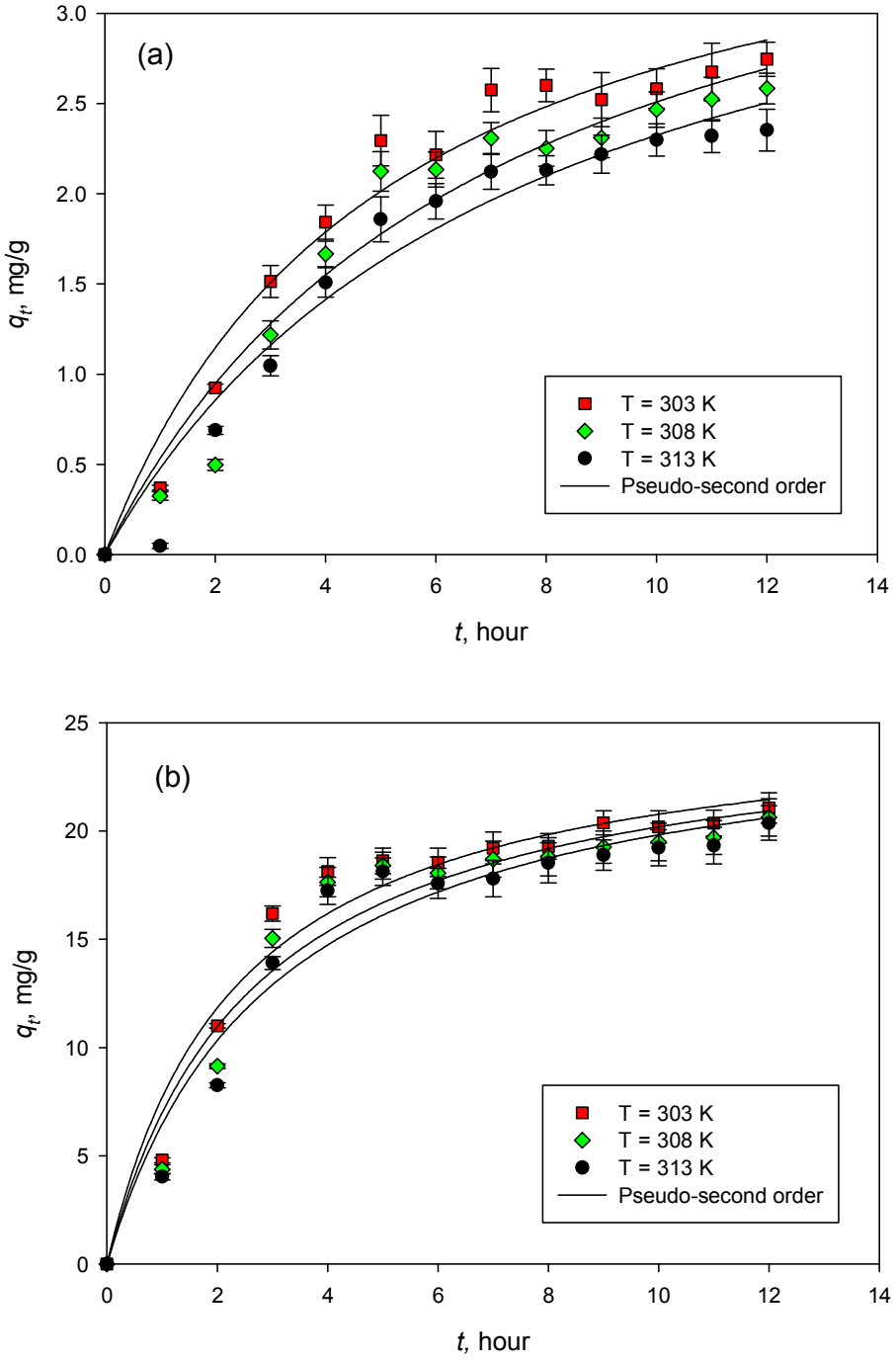

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695 **Figure 9.** Pseudo second order reaction kinetics for the adsorption of NH_4^+ ion on (a) NatZ

696 and (b) 6M-Z

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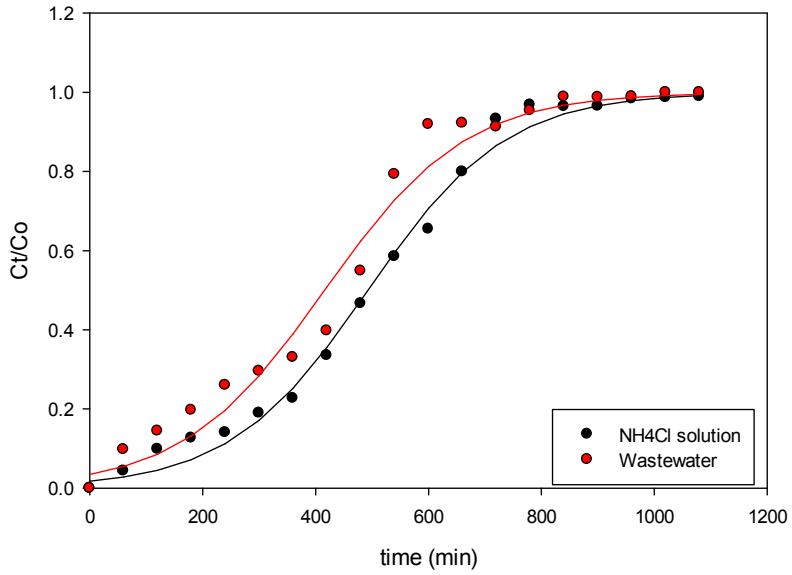

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700 **Figure 10.** Breakthrough curve for NH_4^+ adsorption from aqueous solution and Koi pond

701 water

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