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Study of Ammonium Adsorption Mechanism in Hydrothermalized Pahae Natural Zeolites: Kinetic and Isotherm Adsorption, and Thermodynamics

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Abstract

This paper focuses on the effectiveness of hydrothermalized natural zeolite from Pahae, North Sumatera to remove ammonium ion and analysis the kinetics models of the zeolite adsorption ability, such as isothermic and kinetics adsorption; thermodynamics as well as desorption-regeneration studies. Our findings have demonstrated that natural zeolite shows good performance in terms of for ammonium removal up to 97 % depending on contact time, zeolite loading, initial ammonium concentration and pH. The adsorption kinetics is best estimated by the pseudo-second-order model, whereas the adsorption isotherm results indicated that Freundlich model provides the best fit for the equilibrium data. Furthermore, with regard to thermodynamic parameters, Gibbs free energy change (ΔG°), −19.52 kJ/mol at 25 °C, −20.45 kJ/mol at 35 °C and −22.91 kJ/mol at 45 °C, is negative due to the spontaneous nature of the adsorption process, whereas the enthalpy change (ΔH°), the energy of 30.96 kJ/mol is positive, suggesting endothermic adsorption process. The entropy change (ΔS°), 0.169 kJ/(mol/K) at 25 °C is also positive, indicating an increase of randomness at the solid-solution interface during adsorption. In addition, the desorption-regeneration studies demonstrated that desorption of ammonium on zeolite is sufficiently high using NaCl solutions.

Keywords: Adsorption, Hydrothermal, Ammonia, Zeolite

Introduction

Greywater, originating from bathrooms and laundry in households, contains significant levels of ammonium. This contaminant is present in bathroom wastewater due to urine[1], in kitchen wastewater from the use of ammonium salts as acidity regulators [2], and in laundry wastewater due to cationic surfactants like quaternary ammonium salts [2], [3], [4].

While ammonium serves as a vital nutrient for algae, its excessive presence in water streams can lead to eutrophication, posing environmental challenges such as algae blooms and corrosion in industrial water systems. Current methods for ammonium removal include biological nitrification-

denitrification, air-stripping, and ion-exchange [5], [6]. Among these, ion-exchange stands out due to its effectiveness, small space requirements, simplicity, and environmental friendliness, especially when using low-cost materials [7]. With the increasing emphasis on water reuse, the removal of ammonium, especially from bathroom and swimming pool wastewater, is essential for addressing health concerns.

Natural zeolites contain abundant cation exchange material that is economically feasible for water and wastewater treatment. They have a high selectivity toward water contaminants such as heavy metals reached up to 1,800 mg/g and ammonium ion reached up to 90 % [8], [9]. In addition, natural zeolites have advantages over other cationic-exchange materials such as organic resins Kokol *et al.* [8] due to low-cost usage, excellent selectivity at low temperatures, non-toxic exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) to the environment Sim *et al.* [10], compact size in a relatively small space, uncomplicated operation and maintenance in full-scale applications [11], [12]. Natural zeolites, therefore, gained significant interest over the last 2 decades, especially in eliminating or reducing water pollution problems. The 3-dimensional frameworks of aluminosilicate tetrahedral where the aluminum and silicon structure atoms are bound by covalent bonds via oxygen atoms to form interconnected cages and channels [13]. Substituting each aluminum (Al^{3+}) atom for silicon (Si^{4+}) within the zeolite framework generates a negative charge to the framework. The degree of aluminum directly influences the magnitude of this negative charge in the zeolite [14]. To balance this internal negativity, the pores of the zeolite host is positively charged ions (cations) such as Na^+, K^+, Ca^{2+}, Mg^{2+} on its external surface [15]. These cations form relatively weaker electrostatic bonds with the aluminosilicate framework, enabling them to be replaced by specific cations present in solutions [16]. Thus, it is necessary to modify the natural zeolites with high cation-exchange capacity, adsorption and molecular sieve capabilities.

Various studies have explored ammonium removal using natural zeolites, considering factors such as zeolite type, cation exchange capacity, contact time, zeolite loading, initial anion concentration, pH, and temperature [17], [18], [19]. Structural characteristic of the zeolite used (e.g., mordenite, clinoptilolite, erionite, chabazite) affects cation exchange capacity of natural zeolites to remove ammonium from aqueous solution [20]. Furthermore, cation exchange capacity depends upon the nature of the cation (size, load, etc.), contact time, zeolite loading, initial anion concentration, pH and temperature [21], [22], [23], [24]. To do so, some efforts have been done, and one of which is hydrothermal which induces changes in structural rearrangement, which often results in increased mesoporosity and microporosity, allowing improvements in adsorption capacity [25]. Additionally, the hydrothermal stability of zeolites can vary significantly their Si/Al ratios via the tendency to degrade some amorphous phase as well as influencing the crystallization under hydrothermal conditions, and these changes, significantly increase the ion-exchange mechanism, improving the adsorption capacity too [26], [27]. Unfortunately, adsorption capacity and performance of zeolite for ammonium removal cannot be predicted by a single zeolite chemical-physical parameter. A lab scale study, hence, is a need to evaluate the influence of variables on Pahae natural zeolite performance when ion-exchange is used for the practical application of ammonium removal. Based on our literature study, few research of ammonium removal has been conducted using Pahae natural zeolite, particularly regarding adsorption isotherm, kinetics, and thermodynamics, considering greywater characteristics, using Pahae natural zeolite to remove ammonium with consider greywater characteristics. The main purpose of this study is to investigate the ammonium adsorption capacity of both natural and hydrothermally treated Pahae zeolite, focusing on adsorption kinetics, isotherms, and thermodynamics. In addition, the desorption behaviour of ammonium exchanged on the zeolite was also examined. Theoretical models of adsorption, including isotherms, kinetics, and thermodynamics, via pseudo-second-order Kinect model and Bangham kinetic plots, were applied to determine the best-fitting equations for the experimental data.

Materials and methods

Materials

The Natural Zeolite (NZ) used in this study was from Pahae, North Tapanuli, North Sumatera. The natural zeolite was collected from the local mining sites at Pahae, North Tapanuli, North Sumatera Province, Indonesia. After being collected, the NZ was directly transported from Pahae to Medan without any further physical and chemical treatments.

The analytical-grade chemical reagents, including ammonium chloride (NH_4Cl, purity ≥ 99.8 %), sodium chloride (HCl, purity ≥ 99.5 %), sodium hydroxide (NaOH, purity ≥ 96.0 %), were purchased from Merck. Deionized water was used in all experiments.

Preparation of natural zeolite

The collected NZ then was grounded by hand via mortar. Then, the grounded zeolite was then sieved within a 10 - 20 mesh grain size range. Afterwards, the obtaining powder was then washed with deonized water to remove any impurities, such as dirts and dust. Finally, the wet powder of zeolite was dried in an oven at 100 °C for 3 h, prior the experiment.

Preparation of hydrothermal zeolite

A 2.50 g dried sample of NZ was impregnated with 50 mL of distilled water solution for 1, 3, 5 and 10 h at 30, 50, 80, and 100 °C. Then, the hydrothermal NZ was collected, followed by filtration. This hydrothermal NZ then was washed with deionized water. All samples were dried at 100 °C to remove free surface water.

Batch adsorption experiments

Batch ion-exchange experiments were carried out using stopper conical flasks (250 mL) in a shaking water bath and shaken at 260 rpm at 25 °C with zeolite/liquid ratio of 1 g/100 mL. In this study, evaluation of contact time, ammonium concentration, pH solution, adsorbent dosage was carried out. First, the effect of contact time on ammonium removal by natural zeolite (NZ) and hydrothermally treated zeolite (SNZ) was evaluated. A weighed quantity of zeolite (1 g) was added to a solution with an initial ammonium concentration of 80 mg/L and stirred for 10 - 250 min at 5-min intervals for NZ, and 5 - 40 min at 5-min intervals for SNZ, at a fixed pH of 7. Subsequently, batch ion exchange experiments were conducted to assess the effect of initial ammonium concentration, using concentration ranges of 10 - 200 mg/L for NZ over 120 min and 10 - 250 mg/L for SNZ over 20 min. Finally, the effect of pH was investigated by varying the pH between 2 and 10 in 1-unit intervals at an initial ammonium concentration of 80 mg/L and a temperature of 25 °C. The solution pH was adjusted by 1 M HCl or NaOH solution. The batch ion exchange was conducted for 120 and 20 min of NZ and SNZ, respectively. Afterwards, the adsorbent dosage was carried out via the determination of zeolites mass effect, zeolite amount was varied from 0.2 to 2.0 g/100 mL at initial ammonium concentration of 80 mgL^{-1}. The suspension was then stirred for 120 and 20 min of NZ and SNZ, respectively at temperature 25 °C.

Finally, to investigate the effect of temperature, in our batch adsorption experiments, the ammonium adsorption isotherms for 25, 35 and 45 °C were studied at pH 7 by varying the initial concentration of ammonium (10 - 250 mgL^{-1}). After ion exchange, samples were filtered through a 0.45 μm filter membrane, and the Nesslerization method to determine the NH_4^+ concentration in solution. Quality control testing includes experiments with blanks and duplicates. Each of filtered solutions were optimally investigated based on contact time, ammonium concentration, pH, and adsorbent dosage. The adsorption capacity of ammonia at equilibrium (qe, $mg.g^{-1}$) and the removal (R, %) were calculated using the following equations:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where C0 is the initial ammonia concentration (mgL^{-1}), Ce is the equilibrium concentration of ammonia after adsorption (mgL^{-1}), V is the volume of ammonia solution (L) and m is the mass of adsorbent (g). Each experiment was repeated in

triplicate under identical conditions and the results are reported as average.

Nomenclature

C_0 the initial ammonia concentration (mgL^{-1})

C_e the equilibrium concentration of ammonia after adsorption (mgL^{-1})

V the volume of ammonia solution (L)

m the mass of adsorbent (g)

Regeneration of adsorbent

The amount of ammonia desorbed (D, %) was determined using the following equation:

$$D = \frac{C_{des}}{C_{ads}} \times 100 \quad (3)$$

where Cdes and Cads are the concentrations (mgL^{-1}) of ammonia desorbed and adsorbed, respectively.

Results and discussion

Hydrothermalized-natural zeolite (SNZ)

The first stage of the equilibrium study focused on the improved ion-exchange capacity which will be achieved through hydrothermal modification of the zeolite. Parameters, such as hydrothermal time and temperature had to be investigated to obtain optimum modification conditions for the natural zeolite (NZ).

At the temperature of 100 °C, hydrothermal time of 10 h was most effective in the ion exchange capacity of the Pahae natural zeolite (NZ) for ammonium ion removal. Subsequently, any impurities that can block pore channels and active sites can be removed, freeing up more sites for ion exchange. Presented in **Table 1**, as the sodium ion has higher electropositivity behaviour than most common alkali metals, other alkali metals such as Ca and K, it can easily perform ion exchange mechanism towards the lower behaviour, indicating alterations at the pore structure of zeolite [28], [29]. Based on **Table 1**, after the hydrothermal modification, the content of Na_2O in SNZ was higher (4.06 %) compared to NZ (1.08 %), while the content of K_2O was lower in SNZ (2.66 %) than in NZ (3.68 %). In contrast, the CaO content was higher in SNZ (3.68 %) compared to NZ (2.38 %). These changes suggest that during the hydrothermal treatment, Na ions may have replaced some of the original cations, such as K^+, through ion exchange, resulting in a higher sodium content in SNZ. Furthermore, the Si/Al ratio showed a slight increase, indicating partial dissolution of the alumina framework during hydrothermal treatment. The ion-exchange mechanism of zeolite would be evaluated in the following section. The results showed that SNZ had a higher NH_4^+ ion-exchange capacity than NZ.

Table 1 XRF Result.

%	SiO_2	Al_2O_3	K_2O	CaO	TiO_2	Na_2O	MnO	Fe_2O_3	P_2O_5	MgO
NZ	63.00	12.00	0.73	2.38	1.20	1.08	0.18	5.10	0.08	0.17
SNZ	63.76	11.82	2.66	3.68	1.18	4.06	0.23	5.03	0.08	0.09

Ammonium ion exchange

Effect of parameters

Contact time

As shown in **Figure 1**, It is seen that 120 and 20 min are required for the equilibrium ion exchange to be attained for NZ and SNZ, respectively. Based on **Figure 1**, the rate of ion exchange initially occurred in a relatively quick reaction. About, 39 and 86 % of NH_4^+ removal was achieved within 10 min for NZ and SNZ respectively, thus confirming the higher ion exchange capacity of SNZ relative to NZ.

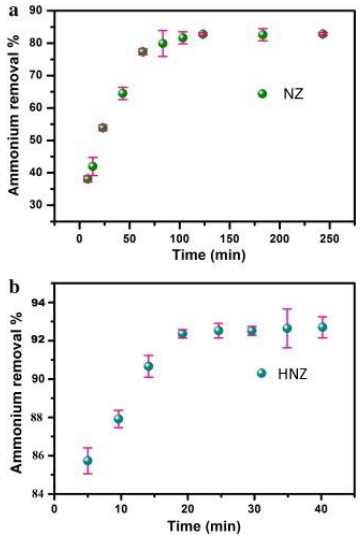

Figure 1 Influence of contact time on NH_4^+ removal capacity of natural zeolite (NZ) (a) and hydrothermal zeolite (SNZ) (b) (initial NH_4^+ concentration: 80 mgL^{-1}, 25 °C and pH 7).

The experimental data show that ammonium removal by NZ exceeded 80 % after 120 min but exceeded 92 % after 20 min by SNZ before attaining equilibrium. This suggests that the hydrothermal modification of zeolite enhances its ion-exchange capacity, leading to faster adsorption (**Figure 1**). During the initial stage, the adsorbing sites on the zeolite surface attract and hold ammonium ions, with the adsorbed ions rapidly moving to the available adsorption sites. In this study, the ammonium ions dispersed in the liquid phase were able to move quickly to the surface of the powder-zeolite. When the ion exchange of the exterior surface of the adsorbent reached the saturation point, the NH_4^+ enters the adsorbent pores and are adsorbed by the interior surface of the particles [30], [31], [32].

Ammonium concentration

The experimental results, shown in **Figure 2**, indicate that the removal efficiency ofNH^{4+} ion ions increased within the concentration range of 10 - 30 mg/L for both NZ and SNZ. The hydrothermal treatment applied to SNZ likely enhanced its ion-exchange capacity by modifying its surface properties. This treatment can lead to the creation of additional active sites for cation exchange, which contributed to the increased removal efficiency observed in the range of 8 - 50 mg/L. The higher initial ammonium concentrations increased the mass transfer driving force, facilitating a more efficient ion exchange process, as seen in both NZ and SNZ[1], [20]. This can increase the rate at which NH_4^+ moved from the bulk solution onto the adsorbent [33], [34] as generally expected in clinoptilolite that have micropores and macropores [7]. Above 30 mgL^{-1} ammonium concentration, the removal efficiency of both zeolites decreases due to saturated and a consequent decrease in the driving force required for further ion exchange mechanism of NH_4^+ ion onto the zeolite [22], [35]. As a result, the NH_4^+ could migrate from the external surface to the internal micro-pores of the zeolite within a given shaking time [33]. Equilibrium was achieved when all the exchangeable ammonium ions on the external and internal surfaces of the zeolite are replaced [2]. **Figure 2** shows that the ion exchange capacity of the modified zeolite was higher than that of natural zeolite at each initial ammonium concentration. The NH_4^+ sorption is generally enhanced by the increase of exchangeable ions on sorbent material. This is attributed to the fact that, high Na^+ concentration during treatment essentially places exchangeable ions onto sites which are in relatively homogenous areas of the zeolite or enhances access to relatively inaccessible sites [35].

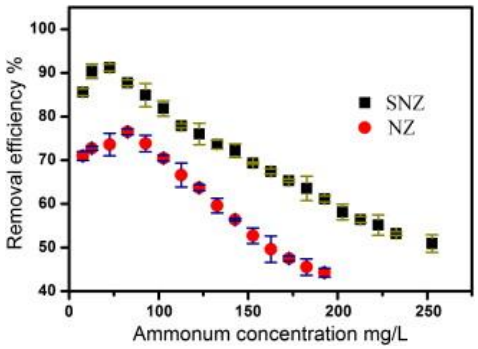

Figure 2 Influence of initial ammonium concentration on NH_4^+ removal capacity of the SNZ and NZ (contact time: 20 and 120 min for SNZ and NZ, respectively, at 25 °C and pH 7).

The investigation of adsorption behaviour within pH

The pH of the bulk solution significantly contributes to ammonium adsorption by SNZ and NZ, as illustrated in **Figure 3** As solution pH increased in the range of 2 - 8, the removal efficiency of NH_4^+ ion increased gradually and reached a maximum value (97.4 and 84 % for SNZ and NZ, respectively); thereafter, it decreased steadily towards pH 10. Hydrothermal treatment can shift the balance between hydrophilic and hydrophobic sites on the zeolite surface. The treatment can modify the pore size distribution and accessibility of internal and external surface areas in zeolites. This structural change can affect how molecules are adsorbed, especially under varying pH conditions, and this change can be crucial in adsorption processes, as it influences the interaction with polar or nonpolar molecules, which can be pH-dependent, such as NH_4^+. Similar observations reported by previous studies for ammonium adsorption onto zeolite from different regions [8], [9], [22]. This behavior is probably due to the fact that at pH above 8 partial dissolution of the natural zeolite occurs, and NH_4^+ is likely converted into NH_3 [1], [8], [22]. However, the increase in the removal efficiency of NH_4^+ ion by zeolites as pH increases from 2 to 8, can be attributed to decrease in hydrogen ions of solution corresponding to increase of pH. This indicated a reduction on hydrogen ions with ammonium ions on adsorption/exchanging sites onto zeolite particles [22], [29], [33].

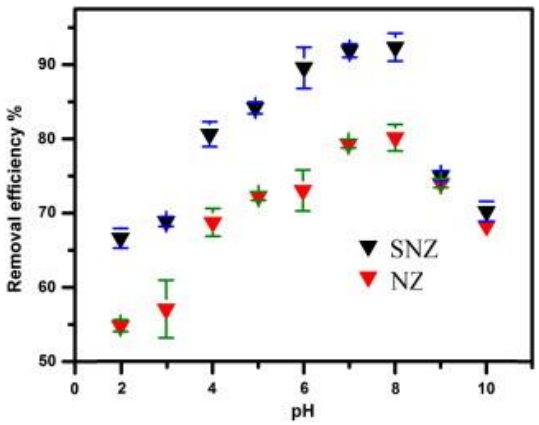

Figure 3 Influence of pH on the removal of NH_4^+ ions (adsorbent mass: 1 g/100 mL; contact time: 20 min and 120 min for SNZ and NZ, respectively; initial NH_4^+ concentration: 80 mgL^{-1} at 25 °C).

Mass of hydrothermal natural zeolite

As depicted in **Figure 4**, the removal efficiency of NH_4^+ by both zeolites increased linearly to the mass of both zeolites and peaks occurred at 1.2 g and 1.8 g for SNZ and NZ, respectively. A mass of 1.2 g and 1.8 g were thus selected as the optimum value for the subsequent adsorbent experiments. This effect is likely due to

the availability of more ion exchange sites as the amount of adsorbent mass increased, leading to higher removal efficiency [33], [35] . As can be seen in **Figure 4**, the NH_4^+ removal was negligible at higher adsorbent mass. This is because a large adsorbent amount effectively reduces the unsaturation of the ion exchange sites, and the number of such sites per unit mass correspondingly comes down resulting in comparatively lesser ion exchange at higher adsorbent amount [33], [35], [36]. Hence, when the ammonium is exchanged completely with cations on the zeolite surface, the NH_4^+ removal reaches equilibrium at a certain amount of zeolite loading [2].

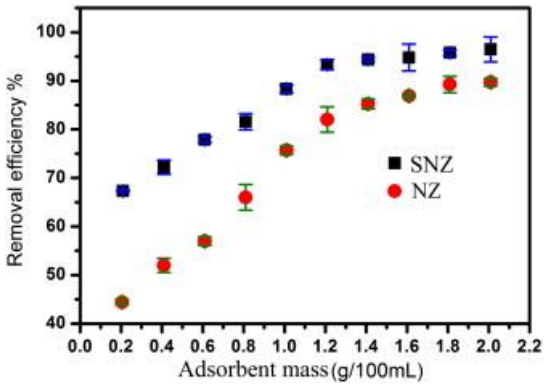

Figure 4 Influence of adsorbent mass on the removal of NH_4^+ ions (contact time: 20 and 120 min for SNZ and NZ, respectively; initial NH_4^+ concentration: 80 mgL^{-1} at 25 °C and pH 7).

Effect of temperature

Temperature has a pronounced effect on the removal capacity of zeolite. Ammonium removal capacity was examined as 25, 35 and 45 °C as shown in **Figure 5(a)**. The NH^{4+} removal capacity was at its maximum at 35 °C. The removal capacity decreased when the temperature was increased from 35 to 45 °C. The ammonium exchange capacity (Q) for the SNZ and NZ were 11.18 and 8.29 mg/g, respectively.

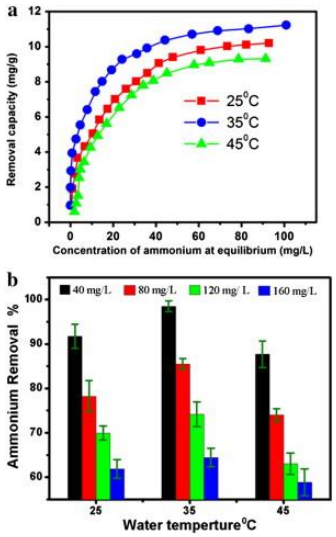

Figure 5 Influence of temperature on the removal capacity (a) and on NH_4^+ removal (b) for modified zeolite (SNZ) at equilibrium conditions.

Figure 5(b) also shows that increase of temperature from 25 to 35 °C resulted by an increase of ammonium removal from 92 to 99 % with ammonium concentration of 40 mgL^{-1}, and from around 77 to 86 % with ammonium concentration of 80 mgL^{-1}. Meanwhile, in the presence of 120 mgL^{-1}

of ammonium concentration, the removal efficiency of ammonium has increased from around 70 to 75 %. Similar results have been reported for the exchange of ammonium by zeolite 13X [35]. The ion exchange rate is slow in the process of chemical adsorption of ammonium. Relatively high temperature (35 °C) is favorable to improving the ion exchange rate. However, higher temperature is unfavorable to exothermic process once equilibrium is attained. Therefore, there is a tendency for the ammonium ion to desorb from the solid phase to the bulk phase with an increase in the temperature of the solution [22], [35], [36].

Some literature reported inconsistent findings on the effect of temperature on the adsorption of ammonium. For instance, the adsorption capacity of ammonium increased with a rise in temperature, including Australian zeolite [35] as well as in Mongolian zeolite [18]. In contrast, a decline in the ammonium adsorption capacity with increasing temperature has been reported several studies [5], [6], [11]. Consequently, by comparing findings of the present study with those of other literatures, the effect of temperature on the ion exchange of ammonium conclusively depends on both the nature of the adsorbent and the selected experimental conditions [34]. The increase in the exchange capacity can be explained by considering a linear increase of the kinetic energy of NH_4^+ ions increases and adsorption temperature. Therefore, a larger quantity of NH_4^+ ions can be exchanged on the zeolite since more NH_4^+ ions have enough energy to be bound to the sites of the zeolite [23]. Such example can be favoured in Yemen zeolite, in which a decrease in ammonium exchange capacity at temperatures above 35 °C was due to the weakening of the attractive forces between NH [7] and adsorbent sites. Similarly, when the temperature increases, solubility of ammonium increases and its ion-exchange decreases [34].

Ion exchange kinetics

The ion exchange kinetics of ammonium by SNZ and NZ are presented in **Figures 6(a)** - **6(e)**. The kinetic data were better fitted by the pseudo second order model than by the pseudo first order model and Bangham model as indicated by higher R2 values (**Table 2**). Also, the figure shows a higher sorption rate for SNZ than NZ.

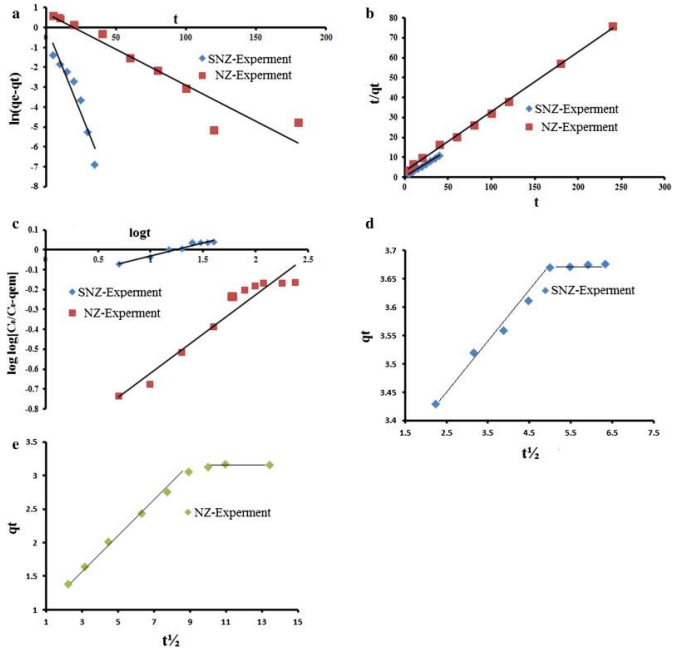

Figure 6 Pseudo-first order (a), pseudo-second-order (b), Bangham kinetic plots (c), and intra-particle diffusion of both zeolites, SNZ (d) and NZ (e) for NH_4^+ removal.

Table 2 Kinetics parameters for NH_4^+ ion exchange using various kinetic models.

Kinetic model	**Parameters**	**Empty cell**	**Empty cell**
Pseudo-first order	k1(min^{-1})	qe(mg/g)	R2
	Absorbent		
SNZ	0.1767	0.1001	0.911
NZ	0.0362	0.7206	0.907
Kinetic model Pseudo-second order	Parameters		
	h(mg/g min)	qe(mg/g)	R2
	Absorbent		
SNZ	8.5012	3.724	0.999
NZ	0.3394	3.336	0.997
Kinetic model Bangham model	Parameters		
	k0	α	R2
	Absorbent		
SNZ	200.859	0.1316	0.966
NZ	24.625	0.3944	0.942
Kinetic model Intraparticle diffusion	Parameters		
	kid	C	R2
	Absorbent		
SNZ	0.0623	3.3195	0.9258
NZ	0.1763	1.2053	0.9089

The pseudo second order model indicates that chemisorption dominated in the ion exchange process [37]. The difference in the adsorbed concentration of adsorbate at equilibrium (qe) and at time t (qt) is the key driving force for the ion exchange, and the ion exchange capacity is proportional to the number of active ion exchange sites, presented on the adsorbent [38]. There are 3 steps involved in the pseudo second order kinetic model; (i) the ammonium ions diffuse from liquid phase to liquid-solid interface; (ii) the ammonium ions move from liquid-solid interface to solid

surfaces; and (iii) the ammonium ions diffuse into the particle pores[39], [40]. Herein, the diffusion of NH_4^+ in aqueous phase was faster on the surface of the zeolite than inside the zeolite particles (intraparticle diffusion) because shaking conditions enhanced the mass transfer between the solution and the solid [38].

Intraparticle diffusion is assumed to be the sole rate-controlling step if the regression of qt versus t1/2 is linear, and the plot passes through the origin [40]. Our fitting results showed that the regression was linear, but the plot did not pass through the origin ($C \neq 0$).

Therefore, the ion exchange kinetics of NH_4^+ on zeolite was regulated by both surface and intraparticle diffusion processes. As can be seen from **Figures 6(d)** and **6(e)**, ammonium exchange by both zeolites involved within 2 stages. These 2 stages suggest that the ammonium exchange process proceeded on surface sorption and intraparticle diffusion. It has been suggested that the first one can be attributed to the instantaneous occupation of most available surface sites on the zeolite's particles by the exchange of ammonium ions. The surface of zeolites is negatively charged at solution pH below 8 (**Figure 6**) thus making the rate of ion exchange of the NH_4^+very fast. The latter is due to the gradual ion exchange of the NH_4^+ into zeolite particle by intraparticle diffusion through pore. The values of intercept C provide information about the thickness of the boundary layer, the resistance to the external mass transfer increases as the intercept increases. The constant C was found to increase from 1.2053 to 3.3195 mg/g after modification as shown in **Table 2**, which indicates the increase of the thickness of the boundary layer and decrease of the chance of the external mass transfer and hence increase of the chance of internal mass transfer [41], [42]. **Table 2** presents the results of fitting experimental data to the pseudo-first, pseudo-second-order, Bangham and intraparticle diffusion models. It can be seen from **Table 2** that the coefficient of determination R2 decreases in the order: pseudo-second order > Bangham > intraparticle diffusion > pseudo-first order model under all experimental conditions, which indicates that the pseudo-second-order model is the most suitable in describing the ion exchange kinetics of NH_4^+ on zeolite.

Ion exchange isotherms

The isotherms for $Na^+ \rightarrow NH_4^+$ in the SNZ and NZ zeolites are given in **Figure 7(a)**. The exchange isotherm lies above the diagonal which indicates a good selectivity of SNZ and NZ for NH_4^+. However, SNZ has a higher selectivity than NZ at ambient temperature (25 °C). As can be seen from **Figure 7(a)**, the ion exchange for SNZ climaxed at 35 °C and ebbed at 45 °C.

Table 3 Values of the Langmuir coefficients for NZ and SNZ at different temperatures.

Isothermal model langmuir model	**Langmuir coefficients**		
	b (L/mg)	**K (mg/g)**	**R^2**
SNZ			
25 °C	1.053	3.682	0.984
35 °C	1.025	4.480	0.996
45 °C	1.082	3.156	0.993
NZ			
25 °C	1.208	2.833	0.998

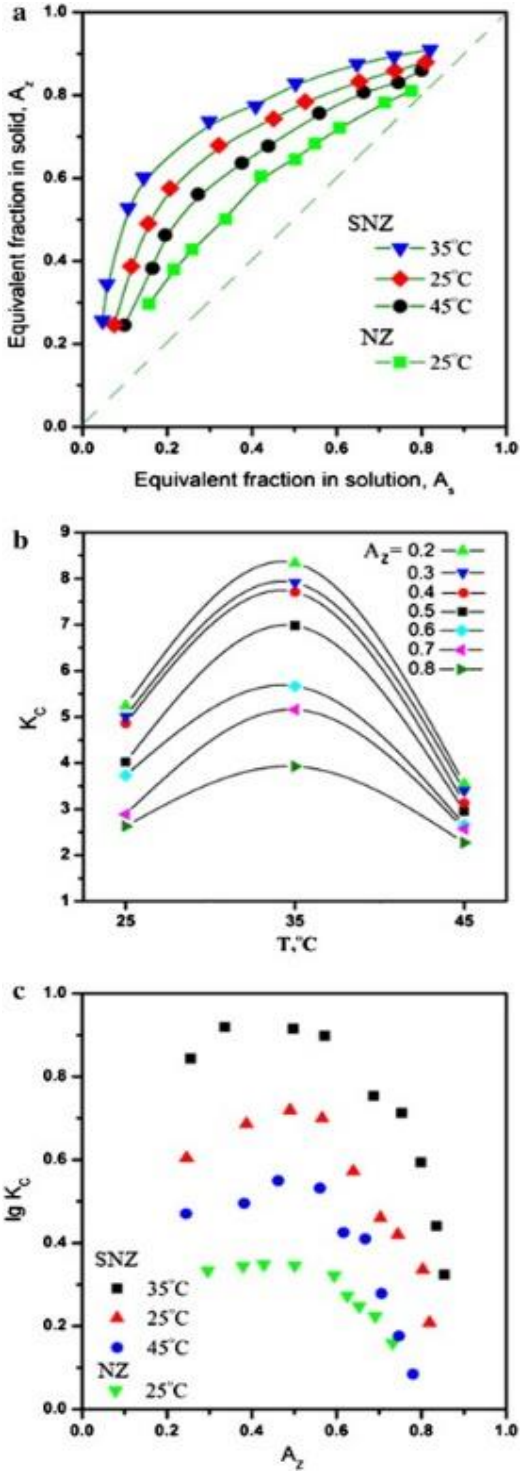

Figure 7 Na+/ NH_4^+ cation exchange isotherms (a), relation of Kc and T (25, 35 and 45 °C) (b) Na^+/ NH_4^+ Kielland plots (c) a.

Thermodynamics studies

Effect of temperature on the kielland constant Kc

Figure 7(b) describes the relation of Kc and temperatures. It is clear that the value of Kc was at its maximum at 35 °C. The Kc decreased when the temperature was increased from 35 to 45 °C. This attributed to the hydrated ionic radius of NH_4^+ and Na^+ at higher temperature close to the effective ionic radius aperture of clinoptilolite, and then the competition of NH^{4+} and Na^+ came into being. So, the selectivity of SNZ for NH_4^+ reduced.

Kielland plots and thermodynamic parameters

Figure 7(c) shows the Kielland plots for the NH_4^+ exchange. The curves have been fitted to polynomials and the values of ln Ka have been calculated from Eq. (13), as shown in **Table 5**. Thermodynamic function ΔGO was obtained from Eq. (14) (**Table 4**). As seen from the results, the ion-exchange of ammonium on zeolite was spontaneous as indicated by the negative value of ΔGO (−2.221, −2.849 and −4.328 kJ/mol). Furthermore, it is interesting to note that the temperature of 35 °C has more negative value which means that the temperature of 35 °C is the most favorable for ion exchange.

Table 4 Thermodynamic parameters for Na^+/NH^{4+} ion exchange in the zeolite at various temperatures.

T (K)	lnKa	Ka	ΔG0 (kJ/mol)	ΔH0 (kJ/mol)	ΔS0 (kJ/mol K)
298	1.15	3.2	−2.849		−11.444
308	1.69	5.4	−4.328	−3413.24	−11.068
318	0.84	2.3	−2.221		−10.726

Some literatures have reported similar trends for other zeolites (natural and synthetic) [17], [43].

They reported that the high Si/Al ratio of clinoptilolite generated in a typical low anionic field provided a rise in good selectivity towards cations with lower charge. As a monovalent ion, NH_4^+ prefers the high Si/Al ratio [14]. This is in agreement to the result obtained in this study where the Si/Al ratio for SNZ and NZ were obtained as 5.3 and 5.1 respectively.

Ammonium exchange is an exothermic process as indicated by the negative change in the standard enthalpy ΔH0. Likewise, the negative value of the standard entropy change ΔS0 suggests the decreasing randomness at the solid/liquid interface during the exchange of ammonium on the SNZ.

Conclusions

The findings of this study indicated that the optimum modification conditions for Pahae natural zeolite were; 1 mol/L of NaCl, stirring time of 1 h and a temperature of 80 °C. As evident in the experimental results, the SNZ has a higher selectivity for NH_4^+ than that for NZ and the maximal exchange for NH_4^+ was up to 99 %. The pH of solution, contact time, temperature and adsorbent mass had a significant effect on the removal of NH_4^+. The highest ion-exchange capacity was obtained rapidly within 20 and 120 min for modified and natural zeolite respectively. While the optimum pH was 8 for both zeolites and the NH^{4+} removal rate and Kielland constant Kc increased when the temperature rose from 25 to 35 °C. The pseudo-second-order kinetic model agreed positively to the ion-exchange of NH_4^+ on zeolite, and the ion-exchange isotherm was accurately described by the Langmuir model. In addition, thermodynamic studies revealed that the ion exchange of NH_4^+ by zeolite was spontaneous and exothermic in nature. Based on these results, it was demonstrated that Pahae zeolite is highly selective for NH_4^+ and therefore, an efficient and cost effective alternative adsorbent material. Thus, it can be recommended for water treatments and has potential for application in controlled-released of (NH_4^+)-based fertilizer.

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