Kinetic and Isotherm Study of Ammonium Sorption Using Natural Zeolites from Lampung

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Abstract. The aims of the study were to characterize and investigate the ammonium adsorption kinetic and isotherm of the natural zeolites from Lampung. Characterization of the natural zeolite was performed by using X-Ray Diffraction (XRD), nitrogen-physisorption, Scanning Electron Microscope (SEM) and X-Ray Fluorescence (XRF). According to XRD analysis, the natural zeolites were identified as clinoptilolite dominant phase with some impurities i.e. mordenite and quartz. The surface area calculated by BET model was 45 m²/g. The SEM images showed the irregular morphology shape. The XRF analysis revealed that the ratio Si/Al was 6.2. Ammonium sorption experiment was performed by using 100 ppm of ammonium solution in the batch reactor with variation on natural zeolite mass loading and adsorption time. Ammonium adsorbed onto the zeolites was increased with the adsorption time and mass loading. The kinetic models, i.e. Lagergren’s 1st order, Pseudo 2nd order, Elovich, Intraparticle diffusion, and isotherm models, i.e., Langmuir, Langmuir-Vageler, Freundlich, Temkin were fitted with the ammonium adsorption kinetic data by using non-linear regression analysis in MATLAB.

1. Introduction

Human activities produce wastewater containing ammonium with high concentration. There are some sources of ammonium from domestic activities such toilets, kitchen, and laundry [1]. Ammonium waste could harm the environment because it promotes the eutrophication along with phosphate. The eutrophication leads to decreasing oxygen concentration in the lake, death of fish, and high sedimentation rate. Ammonium also gives detrimental effects to the human health. The standard limit of ammonium concentration in potable water is 0.5 mg/L according to European Union Standard [2].

Zeolite is a porous material built of three-dimensional silica and alumina framework. The alumina has an extra electron charge which stabilized by a cation. The cations are easily to exchange with other cations in a solution. Zeolites potentially applicable for ammonium elimination by utilizing its ion exchange property. Mordenite and clinoptilolite are the commons zeolites framework found in Indonesia [3]. Zeolites are cheap and abundant sorbent materials that available worldwide. Lampung province is well-known as one of the natural zeolite producers in Indonesia. However, the study of characterization, kinetic and isotherm ammonium sorption is rarely found in the literature. Hence, the objectives of present research were to characterize and study the kinetic and isotherm aspect of ammonium adsorption on the natural zeolites from Lampung.
2. Experimental Section

2.1. Natural Zeolites Characterization
Natural zeolites were obtained from Lampung, West Java, Indonesia. X-Ray Diffraction (XRD) was performed to determine crystalline phase of the natural zeolites using Cu-Kα. Scan speed was 0.2°/min with step size 0.2°. The angle of 2θ was set from 0 to 90°. Elemental composition was analysed using X-Ray Fluorescence (XRF). Morphology of crystalline phase was captured using Scanning Electron Microscope (SEM). The SEM was performed using a Zeiss. Textural properties of the natural zeolites were determined using a TriStar II 3020. Nitrogen was used as a probe in liquid nitrogen at -195°C. The degassing procedure was applied at temperature 350°C for 6 h under vacuum. The Brunauer-Emmett-Teller (BET) was used to estimate the surface area.

2.2. Kinetic Study
Lagergren’s first order, pseudo second order, Elovich, and Intraparticle model were used to analyze the kinetic data. The Lagergren’s 1st order equation is presented below.
\[ \frac{dq_t}{dt} = k_L(q_e - q_t) \]  
(1)
Where \( q_e \) is the milligram amount of ammonium adsorbed per gram of zeolites at equilibrium (mg/g), \( q_t \) (mg/g) is the milligram amount of ammonium adsorbed per gram of zeolites at time t (min) and \( k_L \) (L/mg) is the rate constant of Lagergren’s equation. The solution of equation 1 is obtained by separating variable method with initial condition at t = 0, \( q_t = 0 \) and at t=t, \( q_t = q_e \). The solved equation is rewrite into a non-linear equation below.
\[ q_t = q_e - \frac{q_e}{\exp(k_Lt)} \]  
(2)
The pseudo 2nd order is written as follows:
\[ \frac{dq_t}{dt} = k_s(q_e - q_t)^2 \]  
(3)
where \( k_s \) is the rate constant of pseudo second order equation. The equation 3 can be solved by separating variable technique using initial condition at t = 0, \( q_t = 0 \) and at t=t, \( q_t = q_e \). The solved equation is presented as follows:
\[ q_t = q_e - \frac{q_e}{1-(k_s q_e t)} \]  
(4)
The Elovich equation is stated in equation 5.
\[ \frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \]  
(5)
where \( \alpha \) and \( \beta \) are the kinetic parameters of Elovich equation. The solution of Elovich equation can be obtained by separating variable method with initial condition at t = 0, \( q_t = 0 \) and at t=t, \( q_t = q_e \). The solved equation is presented below.
\[ q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \]  
(6)
The Intraparticle model is described in equation 7.
\[ q_t = k_i t^{1/2} + C \]  
(7)
where \( k_i \) is the rate constant and \( C \) is the intercept of the linear equation.

2.3. Ammonium Isotherm Study
Isotherm was fitted using several models such as Langmuir, Freundlich, and Temkin. The Langmuir equation is as follows.
\[ q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \]  
(8)
where \( q_{max} \) is the monolayer maximum capacity (mg/g) and \( K_L \) is the equilibrium constant of Langmuir model.
The Freundlich equation is written below.
\[ q_e = K_F C_e^{1/n} \]  
(9)
where \( K_F \) is the Freundlich capacity factor.
The Temkin equation is as follows:
\[ q_e = B \ln(K_t C_e) \tag{10} \]

where \( B \) is the heat of adsorption parameter and \( K_t \) is an equilibrium binding constant.

Non-linear least squared (NLLS) method was applied to fit the experimental data with models which generated more accurate results as compared to the linearization method [4]. Error analysis was performed based on the sum of squared error (SSE).

\[ SSE = \sum_{i=1}^{n} (q_e - q_{e,calc})^2 \tag{11} \]

where \( q_{e,calc} \) is the milligram amount of ammonium adsorbed per gram mass of zeolites at equilibrium calculated by the model (mg/g).

3. Results and Discussion

3.1 Characteristics of Natural Zeolites from Lampung

The XRD pattern of Lampung natural zeolites showed that the dominant phase was clinoptilolite (card no: 010791462), with impurities phase mordenite (card no: 000110155) and quartz (card no: 010773162) as presented in Figure 1. This is in agreement with literature that reported the Lampung natural zeolites were clinoptilolite major phase [5]. Natural zeolites from other provinces in Indonesia such as Central Java, West Java, and Banten typically consist of various crystalline phase, i.e., clinoptilolite, mordenite, and quartz [6-8]. It was observed that the peaks intensities were relatively low which suggested a low crystallinity phase of the Lampung natural zeolites. It most likely that the amorphous phase content of silica was high in the natural zeolites.

Elemental composition of the Lampung natural zeolites is presented in Table 1. The natural zeolites were high in silicon element which was most probably appeared in both of crystalline and amorphous phase. The cations compensated the extra electron on the aluminium framework were \( \text{Ca}^{2+} \) and \( \text{K}^+ \). Those cations could be exchanged with other cations such as \( \text{NH}_4^+ \), \( \text{Na}^+ \), \( \text{Cu}^{2+} \), etc. The metal impurities were detectable in the natural zeolites, i.e., \( \text{Fe}, \text{Ti}, \text{Mg}, \text{Ba}, \text{Sr}, \text{and Mn} \). Those metal impurities might block the pore of clinoptilolite. The ion exchange property of natural zeolite has been exploited in ammonium water treatment over decades. The ratio of Si to Al was 6.4 which suggested that the HEU framework of zeolite was clinoptilolite. The international mineralogical association define that the clinoptilolite has HEU framework with Si to Al \( \geq 4 \) while heulandite has the same HEU framework with Si to Al \( \leq 4 \) [9].
Table 1. Elemental composition of Lampung natural zeolites according to XRF analysis

| Major component | % Atom | Minor component | % Atom |
|-----------------|--------|----------------|--------|
| Si              | 59.4   | S              | 0.801  |
| Al              | 9.22   | Ti             | 0.5    |
| Ca              | 9.21   | Mg             | 0.42   |
| K               | 8.1    | Ba             | 0.23   |
| Fe              | 8      | Sr             | 0.21   |
| P               | 3.6    | Mn             | 0.09   |

Figure 2 presents SEM images of the Lampung natural zeolites. The morphology of crystalline phase was irregular. One may see the flaky trapezium shape as pointed by the arrow in Figure 2b. It is most likely the crystal of clinoptilolite. This flaky shape of clinoptilolite was also observed in SEM image of natural clinoptilolite from Sardinia, Italy [10]. The surface area calculated by BET model from the nitrogen physisorption analysis was 37 m$^2$/g. This low surface area indicated the low micropore area because of low crystalline phase of zeolites. For comparison, the surface area of natural zeolites from Klaten, Central Java, Indonesia, was reported 133 m$^2$/g which is larger than the Lampung natural zeolites [6].

Figure 2. SEM images of Lampung natural zeolites with different magnifications (a) 5k x (b) 10k x.

3.2 Kinetic Model of Ammonium Adsorption
Figure 3 shows the fitted kinetic models with experimental data. The data is well fitted with Lagergren’s first order, Pseudo second order, and Intraparticle diffusion. However, the pseudo second order model gives the smallest error which suggested that the effect of the difference concentration was enormous in the kinetic adsorption. The predicted ammonium adsorbed from the Pseudo second order was 0.43 mg/g which was in agreement with experiment data 0.46 mg/g (Table 2). This is supported the kinetic model of pseudo second order as the best fitted model.
Figure 3. NLLS fitted kinetic model of (a) Lagergren’s first order, (b) Pseudo-second order, (c) Elovich and (d) intraparticle diffusion for ammonium adsorption onto Lampung natural zeolites.

Table 2. Kinetic parameters of ammonium adsorption

| Kinetic models          | Parameters | Error   |
|------------------------|------------|---------|
| Lagergren’s first order| $k_L$      | $q_e$ [mg/g] | SSE* |
|                        | 0.0038     | 0.36    | 0.0027 |
| Pseudo second order    | $k_S$      | $q_e$ [mg/g] | SSE  |
|                        | -0.01      | 0.43    | 0.0025 |
| Elovich                | $\alpha$   | $\beta$ | SSE   |
|                        | 0.00316    | 10.16   | 0.0035 |
| Intraparticle diffusion| $k_i$      | C       | SSE   |
|                        | 0.0085     | 0.00712 | 0.0079 |

*SSE = Sum of Squared Error

3.3 Isotherm Model of Ammonium Adsorption

Figure 4 is presented the fitted data with various isotherm models, i.e. Langmuir, Langmuir-Vageler, Freundlich and Temkin. The Langmuir-Vageler showed the best fitted model with SSE 0.12. The maximum ammonium adsorbed monolayer predicted by the Langmuir-Vageler model of Lampung zeolites was 4.64 mg/g (Table 3). This value was lower as compared with the natural zeolites from literature which reached 13.32 mg/g [4]. However, the Lampung natural zeolites ammonium capacity was still in the range of the value reported in the literature ca. 4-20 mg/g [4]. The low adsorption monolayer capacity was most likely because of the low crystallinity, low surface area, and high metal impurities of the Lampung natural zeolites. The adsorption capacity might be improved by using acid or basic solution in order to remove the impurities [8, 11]. The recrystallization technique of the natural zeolites was reported improved the crystallinity and textural properties [6].
Figure 4. NLLS fitted model of (a) Langmuir, (b) Langmuir-Vageler, (c) Freundlich and (d) Temkin for ammonium adsorption onto the Lampung natural zeolites.

Table 3. Parameters of isotherm models for ammonium adsorption

| Isotherm models        | Parameters                        | Error |
|------------------------|-----------------------------------|-------|
| Langmuir               | $q_{\text{max}}$ [mg/g]           | $K_L$ [L/mg] | SSE    |
|                        | 7.88                              | 0.01   | 0.31   |
| Langmuir-Vageler       | $q_{\text{max}}$ [mg/g]           | $K_{LV}$ [L/mg] | SSE   |
|                        | 4.64                              | 3.83   | 0.12   |
| Freundlich             | $K_F$ [L$^{0.3}$/(g.mg$^{0.36}$)] | $n$ [-] | SSE    |
|                        | 0.16                              | 1.36   | 0.46   |
| Temkin                 | $B$ [mg/g]                        | $A$ [L/mg] | SSE   |
|                        | 1.45                              | 0.14   | 0.44   |

4. Conclusion
We have successfully characterized and studied the ammonium adsorption onto the Lampung natural zeolites. The natural zeolites were characterized by using XRD, XRF, nitrogen physisorption, and SEM. The Natural zeolites from Lampung were identified as clinoptilolite with impurities phase quartz and mordenite. The metal impurities were also observed in the Lampung zeolites. The X-ray fluorescence reveal that the Si to Al ratio was 6.4. The clinoptilolite morphology was flaky shape. The surface area was low. The kinetic model best fitted by pseudo second order with error 0.0025. The isotherm model best fitted by Langmuir-Vageler with error 0.12.

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