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Adsorption characteristics and mechanisms of high-levels of ammonium from swine wastewater using natural and MgO modified zeolites

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ABSTRACT

This paper focuses on the effectiveness of removing ammonium by both natural and MgO modified zeolites and the theoretical aspects of adsorption including mechanisms. Results have demonstrated that the zeolite synthesized by integrated calcination with MgO at 400℃ performances a good ammonium adsorption capacity as high as 24.9 mg g^{-1}, an increase by 97.6 and 68.2% compared to that of natural zeolite itself and natural zeolite that heated in 400℃ for 4 h (12.6 and 14.8 mg g^{-1}, respectively), when its dose was adjusted at 27 g L^{-1} with solution pH of 8.3 and agitation speed of 280 r min^{-1} at 25℃. Negative Gibbs free energy change indicated the spontaneous nature of the adsorption. In addition, both ion-exchange and molecular adsorption being the main mechanisms, in which ion-exchange dominated the ammonium adsorption process near neutral pH, and the molecular adsorption was of secondary importance, and contributed less to the total ammonium removal according to the experimental results under neutral pH conditions.

Keywords: Zeolite; Modification; Ammonium; Ion-exchange; Molecular adsorption

1. Introduction

Nitrogen compounds are nutrients essential to all forms of life, but high concentration of them in ground and surface waters can lead to eutrophication, an intense accumulation of algae [1]. Hence, prevention of nitrogen pollution with ammonium removal from wastewater is required. Various methods such as air stripping, biological nitrification–denitrification, and ion-exchange have been used for the removal of ammonium [2,3], in which ion-exchange has attracted much attention for nutrient removal/recycling operations with the advantages of high reaction rate, no sensitivity to ammonium loads and well controlling of effluent quality [4].

Being microporous aluminosilicate minerals with an average diameter of 0.6–1.5 nm (larger than that of NH_4^+, 0.29 nm), zeolites can provide adsorption sites with exchangeable ions for NH_4^+ and porosity for free ammonia (NH_3) with ion-exchange and molecular adsorption being the main mechanisms [5]. Substitution of silicon by aluminum atoms in the crystal framework leads to extra negative charge to be balanced by surrounding counterions (such as Na^+, K^+, Ca^{2+}, and Mg^{2+}), and these counterions are easily exchanged by other surrounding cations (like NH_4^+) in a contact solution. Thus, the utilization of zeolite for the removal of NH_4^+ has been considered as an efficient way for environment applications for decades [6,7]. Nevertheless, current studies on ammonium

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adsorption onto zeolite are usually conducted at low ammonium levels (<200 mg L^{-1}), due to the limited potential of ammonium adsorption (9–16 mg g^{-1}) of natural zeolite [8,9]. Hence, it is always need to be treated by chemical or physical methods frequently before using for ammonium removal from landfill leachate, livestock wastewater, and effluents from anaerobic digestion tanks of livestock manure, which contain ammonium greater than 1,000 mg L^{-1} [10]. For example, several modification methods have been tried to enhance the ammonium adsorption capacity of zeolite, including acid, alkali and hydrothermal treatments, and others. The ammonium uptake values of NaOH-treated zeolite (7.5 g of the natural zeolite powder was placed in a Ni crucible and fused with 9 g of NaOH powder at 550℃ for 2 h), HCl-treated zeolite (natural zeolite was treated with 10% HCl at 25℃ over a period of 24 h), and hydrothermally treated zeolite were 19.3, 21.2, and 12.2 mg g^{-1}, respectively, higher than that of the selected natural zeolite (10.5 mg g^{-1}) [11–13].

It is reported that the adsorption capacity of zeolites can be improved with the increasing contents of alkaline cations with large charge and low ionic radius [11]. Magnesium oxide, microporous minerals with a large specific surface area, contains a considerable amount of Mg^{2+} (ionic radius of 78 pm), which could broaden the effective pore space of zeolite and enhance the ion-exchange capacity (IEC) of NH_4^+ by replaced Na^+ (98 pm) and K^+ (133 pm) contain in zeolite. Thus, MgO modification can effectively increase ammonium adsorption capacity.

In this study, a novel zeolite was synthesized by integrated calcination with MgO for ammonium removal from swine wastewater in this study. Characteristics and the equilibrium removal of NH_4^+ onto natural and MgO modified zeolites were investigated and compared. Accordingly, the rate-limiting steps for adsorption kinetics on both zeolites were identified, and contributions of ion-exchange and molecular adsorption mechanisms during ammonium adsorption onto the MgO modified zeolite were clarified at ammonium concentration of 1281.3 mg L^{-1}.

2. Materials and methods

2.1. Materials

Two kinds of zeolites, natural, and MgO modified zeolites were used in this study. The natural zeolite was obtained from Jingyun Mining Processing Plant, Zhejiang province, China, and was prepared through crushing, sieving, washing with deionized water, and air-drying at 105 ± 1℃ for 12 h until a constant weight. The modified zeolite was obtained by calcining the mixture of the above natural zeolite and MgO (analytical grade) with a mass ratio of 6:1 at 400℃ for 4 h in a muffle. The feed solution, swine wastewater, was taken from an anaerobic digestion tanks of livestock wastewater treatment plant located in Fuhua pig farm, Hunan Province, China. The concentration of ammonium in this case was 1,281.3 mg L^{-1}. The concentrations of K^+, Na^+, Ca^{2+}, and Mg^{2+} of the wastewater were 0.031, 0.026, 0.025, and 0.007 mg L^{-1}, respectively. The pH of the wastewater was 7.5–8.5.

2.2. Experimental methods

Preliminary conditional experiments were first conducted the effects of agitation speed and solution pH on the removal of ammonium from swine wastewater. Subsequently, experiments were performed to determine the equilibrium kinetics and thermodynamics of ammonium adsorption by the two zeolites. For each batch adsorption experiment, 3 g of zeolite was firstly added into the flask containing 100 mL of swine wastewater at desired pH level (adjusted using 0.1 mol L^{-1} HCl or NaOH solution) [14]. Then the zeolite liquid was shaken at specified agitation speed and temperature controlled in the thermostatic shaker (HZQ-X3000, China). The suspension was finally filtered via 0.45 μm filter and the filtrate was analyzed for the target compound(s). Table 1 lists the detailed conditions for each batch experiment.

The adsorption performance was evaluated by the amount of ammonium absorbed on per unit mass of zeolite (q_e in mg g^{-1}) and the ammonium removal efficiency (η), which could be calculated according to the following equations:

Table 1
Experimental conditions for ammonium adsorption

	Experimental conditions					
Main factors	Zeolite type	Ammonium (mg L^{-1})	Temperature (℃)	Agitation speed (r min^{-1})	Time (min)	pH
Agitation speed	Modified zeolite	1,281.3	25	0, 100, 200, 300, 400	210	Original
Temperature	Modified zeolite	1,281.3	25, 35, 45	100	210	Original
pH	Modified and natural zeolites	1,281.3	25	100	210	3–11

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

where C_0 and C_e are the initial and equilibrium ammonium concentrations (mg L^{-1}), respectively. V is the volume of the working solution (L) and m is the mass of zeolite used (g).

Following the ammonium adsorption experiment, the central composite design (CCD), which is the standard response surface methodology (RSM), was selected to investigate the interactions of parameters including the modified zeolite dose (x_1), solution pH (x_2), agitation speed (x_3), and experimental temperature (x_4), respectively. The response variable (y) that represented ammonium adsorbed (q_e) was fitted by a second-order model in the form of quadratic polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{m} \beta_i x_i + \sum_{i<j}^{m} \beta_{ij} x_i x_j + \sum_{i=1}^{m} \beta_{ii} {x_i}^2 \tag{3}$$

where y is the response variable to be modeled, x_i and x_j are independent variables which determine y, β_0, β_i, and β_{ii} are the offset term, the i linear coefficient and the quadratic coefficient, respectively. β_{ij} is the term that reflect the interaction between x_i and x_j. The actual design ran by the statistic software, Design-expert 7.1.3 (Stat–Ease Inc., USA), is presented in Table 2.

2.3. Analysis of kinetics and thermodynamics data

To identify the key step controlling the adsorption rate, intra-particle diffusion model was applied to reveal the relative contribution of surface and intra-particle diffusion to the kinetic process. Intra-particle diffusion is assumed to be the sole rate-controlling step if the regression of q_t versus $t^{1/2}$ is linear, and the plot passes through the origin [15], and the formula of intra-particle model is represented by using the following equation:

$$q_t = k_d t^{1/2} + C \tag{4}$$

where q_t and k_d are amount of ammonium adsorbed onto per unit mass of zeolite (mg g^{-1}) at an instant t (min) and intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$).

In order to investigate the effect of adsorption temperature on removal of ammonium on the two zeolites, the thermodynamics data such as enthalpy (ΔH°), free energy change (ΔG°), and entropy (ΔS°) can be calculated by Eqs. (5)–(8) [16]:

$$\Delta G^\circ = -RT \ln K \tag{5}$$

$$\mathrm{d}\left(\frac{\Delta G^\circ}{T}\right) = -\frac{\Delta H^\circ}{T^2}\mathrm{d}T \tag{6}$$

$$\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = -\frac{\Delta H^\circ}{RT^2} \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

where K is the equilibrium constant.

2.4. Analytical methods

The main functional groups of the zeolites related to molecular adsorption were determined by Fourier transform infrared spectroscopy (IRAffinity-1, Japan). The concentrations of Na^+, K^+, Ca^{2+}, and Mg^{2+} in solution were measured by atomic absorption spectroscopy (AAS, Hitachi-Z 5000, Japan). The concentration of ammonium in solution was determined with the Neslerization method [17]. The solution pH was determined by a pH Meter (Hach-HQ11d, USA). All tests were done in duplicate with average data reported.

Table 2
Coded levels for five variables framed by the CCD

Factors	Codes	Codes levels		
		−1	0	1
MgO modified zeolite (g L^{-1})	x_1	20	30	40
Solution pH	x_2	5.0	8.5	12.0
Agitation speed (r min^{-1})	x_3	100	200	300
Experimental temperature (℃)	x_4	25	35	45

3. Results and discussions

3.1. Adsorption property of MgO modified zeolite

3.1.1. Effects of agitation speed and temperature on ammonium removal

Agitation speed had no noticeable effects on ammonium adsorption capacity after 150 min testing, but it had great impact on adsorption kinetics, especially during the initial 30 min of adsorption.

As presented in Fig. 1(a), the equilibrium ammonium adsorption rate increased from 0.13 to 0.27 mg g^{-1}·min^{-1} when agitation speed was increased from 0 to 300 r min^{-1} with the increasing trend leveled off at higher agitation speeds. This observation indicated that the external mass transfer resistance from the solution phase to zeolite surface was diminished at >300 r min^{-1} agitation speed. By considering the above facts, the adsorption was not equilibrated with ion transfer rates at external boundary layers and the role of surface reaction dominated the process, which was in accordance with the findings of Alkan et al. [18] and Erdoğan and Ülkü [16]. Additionally, 51.3% of NH_4^+ removal was completed within 30 min for MgO modified zeolite, and the ammonium removal rate exceeds 58.3% at 90 min, and there is no noticeable increase in the adsorption beyond this level (at 300 r min^{-1}). Ammonium adsorption on zeolite proceeded fast, particularly during the initial 30 min (which might be a result of vacant adsorption sites on the zeolites), and the equilibrium began to establish itself after just a short time (30 min). It can be said that there was a fast diffusion of NH_4^+ adsorbed onto external surface of the adsorbent followed by a relatively slow intra-particle diffusion process, in which NH_4^+ enter the adsorbent pores and are adsorbed by the adsorption/exchange sites to attain equilibrium.

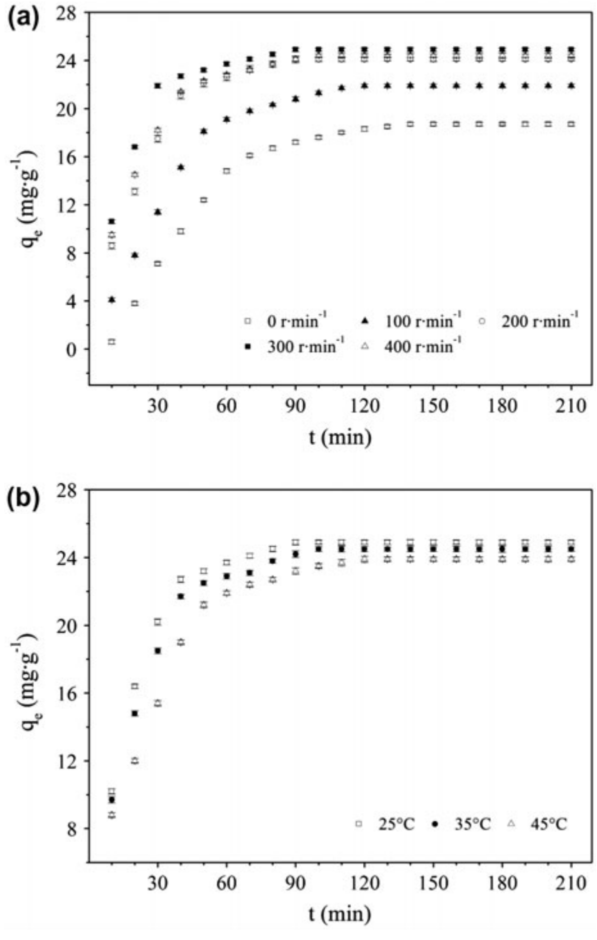

Fig. 1. Effects of agitation speed and temperature on ammonium adsorption by MgO modified zeolite under 1,281.3 mg L^{-1} of initial ammonium concentration condition. (a) Effect of agitation speed under 25℃ and (b) effect of temperature under 100 r min^{-1}.

Fig. 1(b) shows the effects of temperature on removal of ammonium by MgO modified zeolite. It seemed that the equilibrium adsorption capacity was decreased slightly (from 24.9 to 23.9 mg g^{-1}) by increasing temperature from 25 to 45℃. A similar trend was also observed of some adsorbents, including activated zeolite (ActZ) [19], Turkish zeolite [20], and NaA zeolite [21]. This indicated that the adsorption process of ammonium onto zeolite is exothermic reaction. Probably during this process the effective adsorption sites on zeolite remained unchanged, a tendency for the ammonium molecules to escape from the solid phase to the bulk phase with the solution temperature increase. Furthermore, ammonium exchange capacity decreases with increasing temperature due to a weakening of the attractive forces between NH_4^+ and adsorption/exchange sites [22] and when the temperature increases, solubility of ammonium increases and its adsorption decreases [23].

3.1.2. Effects of solution pH on ammonium removal

Solution pH affects ammonium adsorption by zeolite significantly, since it can influence both the ammonium diffusion process and the vigor of the adsorption sites on zeolite itself. As shown in Fig. 2, the adsorption capacities of both natural and MgO modified zeolites increased gradually with increasing pH from 2 to 8 and then decreased from pH 9–11 with the maximum values (12.6 and 24.8 mg g^{-1}, respectively) achieved at pH 8, and an almost similar trend has been reported for ammonium adsorption onto zeolites by different researchers [24,25]. For ammonium adsorption, the behavior of ammonium as a function of water's pH can be explained by considering the change in density of hydrogen ions (H^+), the dominant ionic species of ammonium, and the surface charge of zeolite. Variation in zeolite performance in the ammonium removal at various pH reported that the ammonium in aqueous solution can be found as dissociated form (NH_4^+) in solution at pH value of below 7, while a molecular form or as "free" ammonia, NH_3, is dominant at alkaline pH value, and their formation depend upon solution pH. To the best of

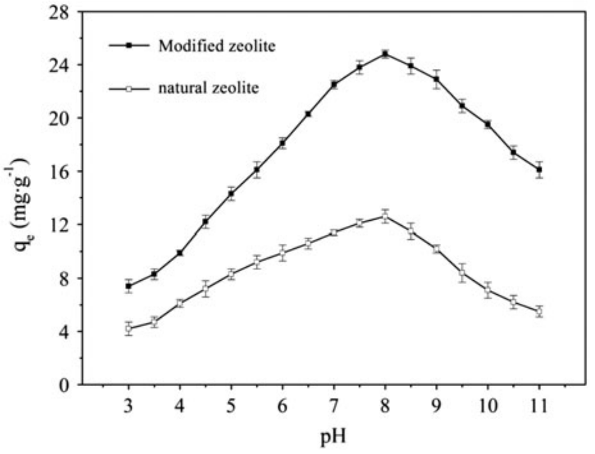

Fig. 2. Effects of pH on ammonium adsorption by natural and MgO modified zeolite under 1,281.3 mg L^{-1} of initial ammonium concentration condition.

our knowledge, the ionic radius (0.24 nm) of H^+ is lower than that of NH_4^+ (0.29 nm), which resulting an easier transfer to pore channel of zeolite and be adsorbed than NH_4^+; and hence, the increased H^+ concentration with the decreasing in water's pH value of below 7 promoted the competition for adsorption/exchange sites with NH_4^+, which results a decline of the ammonium adsorption. Thus, the increase in adsorption of ammonium with the increasing water's pH up to the maximum point (pH 8) can be attributed to a decrease of H^+ corresponding to an increasing solution pH, and eventually a reduction of the competition between H^+ and NH_4^+ for adsorption/exchanging sites onto zeolite. This observation correlates with the findings by Huang et al. [2] and Erdoğan, and Ülkü [16]. NH_4^+ exists in part as $NH_3{\cdot}H_2O$ when it is in alkaline solution, which is impossible to adsorb by ion-exchange. Higher the aqueous solution pH, higher the concentration of $NH_3{\cdot}H_2O$ will be. The decrease of ammonium adsorption with the increase of solution's pH value of above 8 is likely owing to the increasing percentage of molecular ammonium, which resulted in a reduction of ion-exchange potential. By considering the above facts, a low exchange amount obtained at higher pH (>8) value due to the conversion of NH_4^+ into $NH_3{\cdot}H_2O$.

Attempts were made to monitor pH change during adsorption/ion-exchange measurements; Fig. 3 depicts a decreased solution pH during ammonium adsorption/ion-exchange process by natural and modified zeolites. NH_4^+ was adsorbed rapidly by the most readily available adsorption sites of the zeolites' exterior surface that leads to a fast diffusions, especially during the initial 30 min of adsorption, and then entered into the adsorbent pores and are adsorbed by the interior surface of the particles or exchanged by the exchangeable ions (like Mg^{2+}, Ca^{2+}, and Na^+) after the adsorption of exterior surface of the adsorbent reached the saturation point. Exchangeable ions released into solution phase that decreased the pH values of the solution. The decreasing in water's pH below 7 through adsorption/ion-exchange increased H^+ concentrations and promoted the competition for adsorption/exchange sites with NH_4^+, there eventually leads to a slow equilibrium attainment.

3.2. Response surface and selection of optimum conditions

Following equation represents empirical relationship in the form of quadratic polynomial between the ammonium adsorbed (y) and the other four factors (x_1–x_4).

$$\begin{aligned} y = 24.6 &- 3.34x_1 + 1.12x_2 - 0.04x_3 + 0.21x_4 + 0.62x_1x_2 \\ &+ 10.24x_1x_3 + 2.49x_1x_4 - 1.19x_2x_3 + 5.43x_2x_4 \\ &- 2.97x_3x_4 - 8.45{x_1}^2 + 1.21{x_2}^2 - 0.46{x_3}^2 + 5.98{x_4}^2 \end{aligned} \tag{9}$$

Statistical testing of this model was performed with the Fisher's statistical method for analysis of variance (ANOVA). The result of ANOVA for ammonium adsorbed indicates that the second-order equation fitted well. Because model value of $F_{\text{statistic}}$ (the ratio of mean square due to regression to mean square to real error) of 4.23 was greater than $F_{0.01}(20, 29)$ of 2.57, values of "Prob > F" < 0.0001 less than 0.05, and the

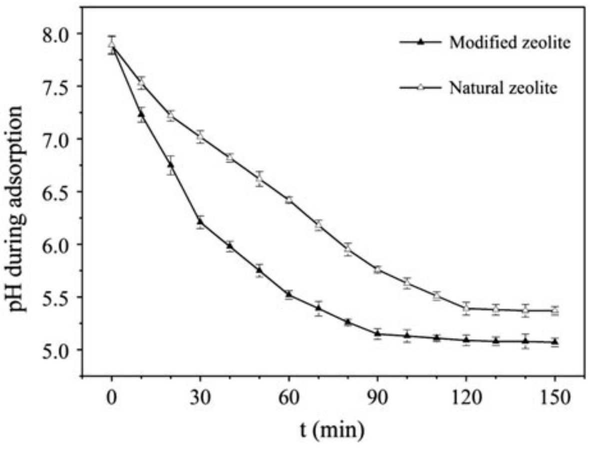

Fig. 3. Change of solution pH during ammonium adsorption/ion-exchange process by natural and MgO modified zeolites under 1,281.3 mg L^{-1} of initial ammonium concentration condition.

total correlation coefficient R reached 0.9451. Moreover, the value of the determination coefficient ($R^2 = 0.8933$) indicates that only 11.67% of the total variation could not be explained by the empirical model.

The significance testing for the coefficient of Eq. (9), whose variables are in terms of coded factors are listed in Table 3. As seen from Table 3, in the linear terms, agitation speed and MgO modified zeolite doses were significant. Zeolite dose was significant and unique for the reason that NH_4^+ could be adsorbed by pore adsorption, ion-exchange, and complexation with some functional groups such as alkyl, carboxyl, and hydroxyl groups on both external surfaces and internal pores of the zeolite. Furthermore, agitation speed was significant based on the reasoning that a higher speed creates greater turbulence and greater turbulence leads to better mixing [26]. Therefore, agitation speed was significant. Among the higher order effects, the quadratic terms of pH were significant and unique. In acidic environment, H^+ concentration rises with the decreasing pH and increases competition for exchange sites (active sites) with NH_4^+, as the concentration of ammonium (NH_4^+ form) also rises with the decreasing pH, there eventually results a decline in the amount of ammonium adsorbed onto the MgO modified zeolite. While in the strong alkaline environment ($pH > 10$), it is likely that ammonium was converted into “free” ammonia (NH_3), which cannot be exchanged. The interaction terms with significant effects are shown in Fig. 4. Fig. 4(a) shows that ammonium adsorption is enhanced with the advance of solution pH and the MgO modified zeolite dose, while the agitation speed and the experimental temperature are kept at central level. This indicated that the MgO modified zeolite makes an obviously positive effect on ammonium removal in alkaline environment. Fig. 4(b) shows that the adsorption is enhanced to vary with the MgO modified zeolite dose and agitation speed, while solution pH and experimental temperature are kept at central level. And it is predicted that, at a low speed of stir, ammonium adsorbed enhances as the MgO modified zeolite added and gets to the peak ultimately. However, this target obviously becomes more difficult when the agitation speed is kept at a high level.

According to the target value of ammonium removal rate of 100%, the optimal condition calculated from the regression equations was MgO modified zeolite of 27 g L^{-1}, pH 8.3, and agitation speed of 280 r min^{-1} at 25℃. Under this optimal condition, the amount of ammonium adsorbed onto the clinoptilolite was appeared as 24.9 mg g^{-1}.

3.3. Mechanisms of ammonium adsorption onto zeolite

3.3.1. Ion-exchange

According to the fundamental of ion-exchange between solid and liquid phases [27], the ion-exchange process between NH_4^+ and zeolite frame can be expressed by using the following equation:

$$\text{Zeolite} - M^{n+} + nNH_4^+ \leftrightarrow \text{Zeolite} - nNH_4^+ + M^{n+} \quad (10)$$

where M represents the exchangeable ions in zeolite and n is the number of electric charge.

Assuming that the exchangeable ions in the zeolites are Ca^{2+}, Mg^{2+}, Na^+, and K^+, the IEC can be defined as the sum of exchanged cations as:

$$\text{IEC} = [N^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] = [NH_4^+] \quad (11)$$

Fig. 5 shows the variation of equivalent concentrations of Mg^{2+}, Ca^{2+}, Na^+, and K^+ into solution under different initial ammonium concentrations. The sum of these four cations (IEC) was almost equal to the ammonium adsorption capacity at equilibrium, demonstrating the predominant role of ion-exchange in ammonium adsorption to zeolite. The equilibrium IEC was 0.83 meq g^{-1}, lower than the theoretical IEC [28], 2.86 meq g^{-1} from chemical composition of zeolite if all alkaline and alkaline earth cations in zeolite were replaced. About 29% of the exchangeable sites were available for ammonium adsorption, probably owing

Table 3
Significance of quadratic model coefficient of ammonium adsorbed (q_e)

Independent variables	Regression coefficients	Degrees of freedom	Standard error	Prob > F
x_1	0.04008	1	0.70	<0.0001
x_3	10.8234	1	0.70	0.0047
x_1x_2	1.5330×10^{-3}	1	1.41	0.0291
x_1x_3	-2.2857×10^{-3}	1	1.41	0.0245
x_2^2	−0.8649	1	0.95	<0.0001

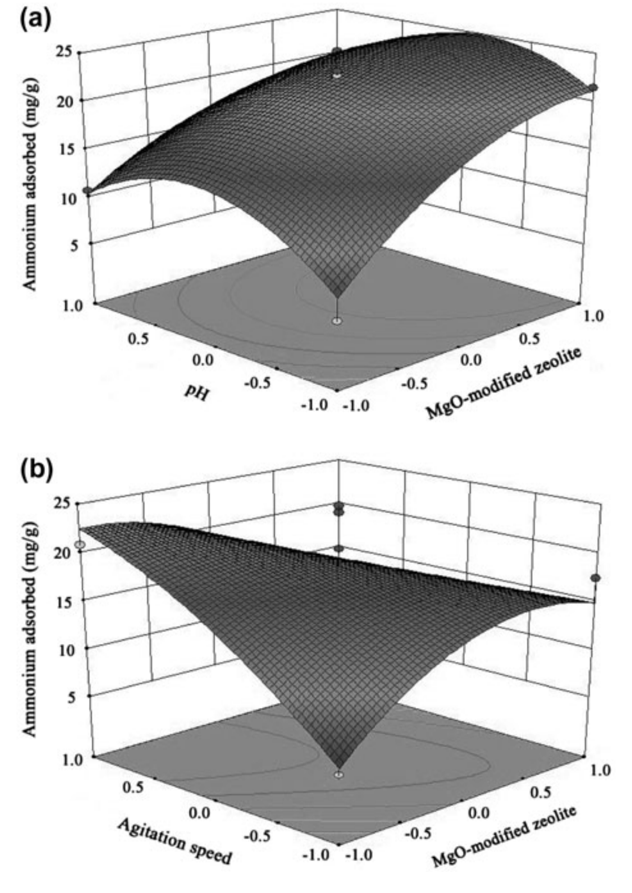

Fig. 4. Surface graphs of ammonium adsorbed showing the effect of variables: (a) pH-MgO modified zeolite and (b) Agitation speed-MgO modified zeolite.

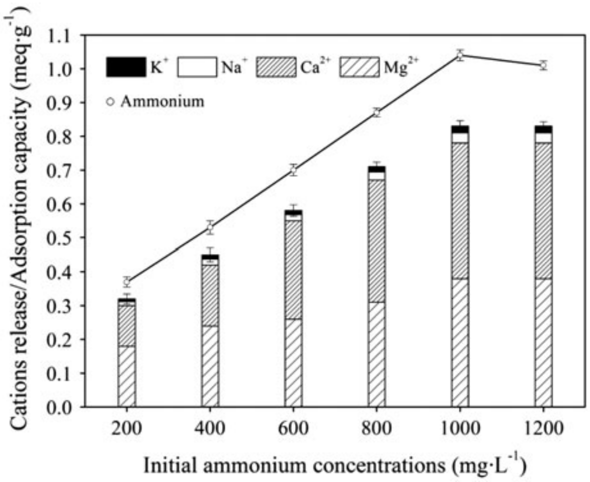

Fig. 5. The ions release and ammonium adsorption capacity of MgO modified zeolite under different initial ammonium concentration conditions.

to limited access of NH_4^+ to interior sites of zeolites. From Fig. 5, the order of ion-exchange selectivity for cations in the MgO modified zeolite was determined as $Mg^{2+} > Ca^{2+} > Na^+ > K^+$, different from results of Lin et al. [27] ($Na^+ > Ca^{2+} > Mg^{2+} > K^+$), this inconsistency is attributed to the difference in chemical compositions of the tested zeolites: rather low Mg content in their NaCl modified zeolite. Mg^{2+} and Ca^{2+} were the dominant ion exchanged with NH_4^+, whose exchange equivalent were 42–47% and 36–51% of the total ion-exchange equivalent, respectively. The exchange equivalent capacity of other metal cations such as Na^+ and K^+ was only 3–8%. Mg^{2+} was the dominant cation under lower initial ammonium concentration conditions (<400 mg L^{-1}). With the increase of initial ammonium concentration, Ca^{2+} started to dominant the ion-exchange process after most Mg^{2+} being released, especially at higher initial ammonium concentrations (>800 mg L^{-1}). In present tests, K^+ and Na^+ were low in concentration, K^+ is preferred than NH_4^+ in ion-exchange sequence for zeolite, owing to the strong affinity of K^+ with zeolite, the released K^+ might be re-adsorbed back via exchange with NH_4^+, Na^+, Ca^{2+}, or Mg^{2+}. After most available sites were covered by NH_4^+, the released K^+ could not be easily re-adsorbed back, so its concentration was slightly increased with initial ammonium concentration in solution. The low content in MgO modified zeolite hindered the exchange of Na^+ with NH_4^+.

Furthermore, the equivalence of ammonium adsorbed and summations of equivalences of released exchangeable ions were compared at different initial ammonium concentrations, and approximately 12.5–20.1% excess equivalence of NH_4^+ is adsorbed over its stoichiometric equivalence. If only ion-exchange is the controlling mechanism in the sorption process, the equivalence of the major ions (Ca^{2+}, Mg^{2+}, Na^+, and K^+) released to the wastewater should be equal to those of NH_4^+ adsorbed by the MgO modified zeolite. This indicated that apart from ion-exchange there was also molecular adsorption involved in the removal of the ammonium by the MgO modified zeolite.

3.3.2. Molecular adsorption

Ammonium in bulk solution exists in both ionized (NH_4^+) and molecular (NH_3) forms, and their formations depend upon solution pH and temperature. The relationship between pH, temperature (T), concentrations of NH_4^+, NH_3, and total ammonium (TAN) can be expressed by using the following equations.

$$\left[NH_4^+\text{-N}\right](\text{mg L}^{-1})/[\text{TAN}](\text{mg L}^{-1}) = (10^{\text{pH}} + e^{0.06344(T+273)})/10^{\text{pH}} \tag{12}$$

$$[\mathrm{NH_3\text{-}N}](\mathrm{mg\ L^{-1}})/[\mathrm{TAN}](\mathrm{mg\ L^{-1}}) = 10^{\mathrm{pH}}/(10^{\mathrm{pH}} + \mathrm{e}^{0.06344(T+273)}) \tag{13}$$

$$[\mathrm{TAN}](\mathrm{mg\ L^{-1}}) = [\mathrm{NH_4^+\text{-}N}](\mathrm{mg\ L^{-1}}) + [\mathrm{NH_3N}](\mathrm{mg\ L^{-1}}) \tag{14}$$

The distributions of the ionized (NH_4^+) and molecular (NH_3) forms of ammonium were calculated based on Eqs. (12)–(14) at 100 mg L^{-1} and 1,281.3 mg L^{-1} of initial ammonium concentrations (25℃). More than 94% of the ammonium existed in ionized form (NH_4^+) when solution pH was adjusted to below 7, whereas only about 0.2% of ammonium was left in ionized form when pH approached 11. The ammonium adsorption onto zeolite is a pH-dependent process and the increasing in ammonium adsorption capacity at increased pH suggests the interplay of molecular adsorption mechanism. The significance of molecular adsorption was negligible at pH < 8. At pH 10, 84.1%, and 98.2% of ammonium removal were contributed by free ammonia (NH_3) adsorption under 400 and 1,281.3 mg L^{-1}, respectively (Fig. 6). Anyway, the molecular adsorption was of secondary importance and contributed less to the TAN removal according to the experimental results under neutral pH conditions.

3.3.3. Formation of complexes between NH_4^+ and functional groups

To determine the functional groups involved in adsorption of ammonium by the modified zeolite, a comparison between the FTIR spectra before and after adsorption was done. The FTIR spectra confirmed changes in functional groups and surface properties of the modified zeolite, illustrated by the shift of some functional group's bands due to ammonium adsorption (Table 4). These shifts may be attributed to the changes in NH_4^+ associated with carboxyl and hydroxyl groups, suggesting that these groups are predominant contributors in the complexation of ammonium. The changes in peaks observed on the spectrum between 3,200 and 3,550 cm^{-1}, may be attributed to complexation between NH_4^+ and –OH groups. The changes in peaks observed between 1,740 and 1,710 cm^{-1} are indicative of stretching vibration of C–O bonds due to non-ionic carboxyl groups (–COOH, –$COOCH_3$) [29]. The changes in peaks observed between 1,660 and 1,500 cm^{-1}, caused by stretching vibration of the asymmetric and symmetric –COO^- [30]. The changes in peaks observed between 1,375 and 1,300 cm^{-1}, which reflect stretching vibrations of symmetrical or asymmetrical ionic carboxylic groups. This information indicated that the surface or intra-particle sharing between NH_4^+ and functional groups (such as alkyl, carboxyl and hydroxyl groups) was also in importance.

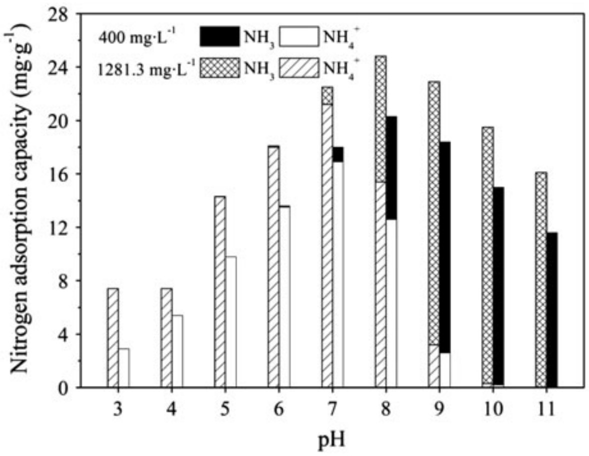

Fig. 6. Contributions of ion-exchange and molecular adsorption mechanisms during ammonium adsorption onto MgO modified zeolite under initial ammonium concentration of 1,281.3 and 400 mg L^{-1}, respectively.

3.4. Adsorption kinetics and thermodynamics

Fig. 7 depicts that the ammonium adsorption/exchange by both zeolites involves two stages, surface sorption (film diffusion) followed by intra-particle diffusion. It has been suggested that the first one can be attributed to the instantaneous occupation of most available surface sites by exchanging NH_4^+ onto zeolite's particles, and the second region is due to a gradual adsorption stage, where NH_4^+ enters into zeolites particle by intra-particle diffusion through the pores. For the case of MgO modified zeolite, the line with high slopes ($t^{1/2}$ between 0 and 5.7 $min^{1/2}$) is the external surface adsorption or film diffusion, the line with lower slopes ($t^{1/2}$ between 5.7 and 9.5 $min^{1/2}$) represented the intra-particle diffusion, and the line with null slope ($t^{1/2}$ between 9.5 and 12.2 $min^{1/2}$) may be revealed the equilibrium attained by NH_4^+ absorbed onto adsorption sites or exchanged with exchangeable ions such as Mg^{2+} and Ca^{2+} by chemical reaction at interior surface of the zeolites. The intra-particle diffusion model fitted well the experimental data and there was a fast diffusion of ammonium adsorption onto the external surface of the zeolite followed by a slow intra-particle diffusion process. In addition, our fitting results showed that the regression was linearly, but the plot did not pass through the origin ($C \neq 0$). The values of intercept C provide information about the

Table 4
FTIR spectral characteristics of modified zeolite before and after ammonium adsorption

		Modified zeolite			
σ (cm^{-1})	Wavelength range (cm^{-1})	Before adsorption	After adsorption	Differences	Assignment
3,500–3,400	3,550–3,200	3,430	3,223	207	–OH groups
1,740–1,600	1,740–1,720	1,620	1,740	−120	C–O bonds
	1,720–1,660	1,620	1,710	−90	C–O bonds
1,650–1,500	1,600–1,500	1,500	1,544	−44	Symmetric $-COO^-$
	1,600–1,500	1,500	1,640	−140	Asymmetric $-COO^-$
1,375–1,300	1,350–1,300	1,345	1,310	35	Ionic carboxylic groups

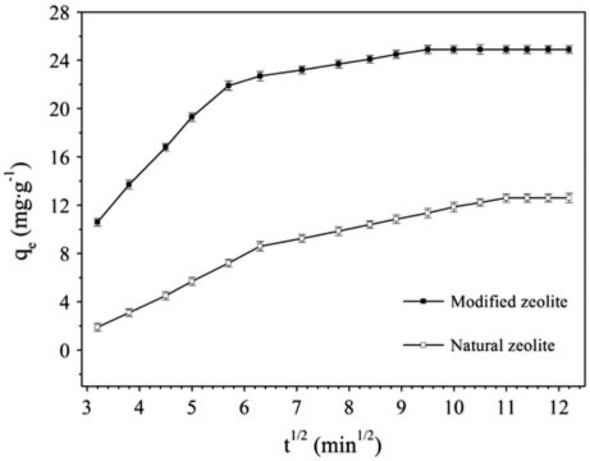

Fig. 7. Kinetic plots of intra-particle diffusion model for ammonium adsorption by natural and MgO modified zeolite under 1,281.3 mg L^{-1} of initial ammonium concentration condition.

thickness of the boundary layer and the resistance to the external mass transfer increases as the intercept increases. The constant C was found to increase from natural zeolite (3.71 mg g^{-1}) to MgO modified zeolite (5.12 mg g^{-1}), 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. Additionally, as shown in Table 5, it is noted that the intra-particle diffusion rate constant has higher value at a higher initial ammonium concentration, which leads to a higher driving force for adsorption, hence a higher diffusion rate of ammonium into the pores of the two zeolites. However, a slight reduction of the value of the intra-particle diffusion rate constant was obtained with the increasing agitation speed. This reduction may be attributed to the pore over filling due to the increase concentration of the released exchangeable ions. The pore blocking due to the competition between solute molecules for available sorption sites may also be effective.

The contribution of each rate controlling step in ammonium adsorption onto the two zeolites was further analyzed by calculating the coefficients of the film diffusion (D_f) and intra-particle diffusion (D_p) according to the corresponding models as Eqs. (15) and (16):

$$\ln\left(1-\frac{q_t}{q_e}\right) = -k_f t \tag{15}$$

$$\ln\left[1-\left(\frac{q_t}{q_e}\right)^2\right] = -2k_p t \tag{16}$$

where $k_f = D_f C_s / C_z h r$ and $k_p = D_p \pi^2 / r^2$ are the rate constants. C_s and C_z (mg kg^{-1}) are the concentrations of ammonium in wastewater and zeolite phases, respectively. r is the average radius of zeolite particles (44 μm in this study), t is the contact time (min), h is the thickness of film around the zeolite particle (10^{-5} m for poorly stirred solution).

The best-fit D_f and D_p values for ammonium adsorption onto the two zeolites were listed in Table 6. It is noted that D_p values for both natural and MgO modified zeolites were considerably lower than D_f values, this also indicated that the intra-particle diffusion was the rate-limiting step for ammonium adsorption, and the ammonium adsorption was mainly occurred at the surface of zeolites. Similar results were reported by Iranian zeolite [24] and morganite tests [31]. Compared with the natural zeolite, the D_f and D_p values of the modified zeolite increased by 127.5 and 2.5%, respectively, indicating that MgO modification could reduce the resistance for mass transfer in film diffusion, but have little effects on intra-particle diffusion. Namely, MgO modification could effectively improve the surface morphology of zeolite particles, but hardly alter the intra-particle structures.

Table 5
Kinetic parameters for ammonium adsorption using intra-particle diffusion model

Intra-particle diffusion model		Modified zeolite				Natural zeolite			
		First stage		Second stage		First stage		Second stage	
Parameters		k_{d1} (mg g^{-1} $min^{-1/2}$)	R^2	k_{d2} (mg g^{-1} $min^{-1/2}$)	R^2	k_{d1} (mg g^{-1} $min^{-1/2}$)	R^2	k_{d2} (mg g^{-1} $min^{-1/2}$)	R^2
Initial concentration (mg L^{-1})	200	0.0052	0.932	0.0014	0.893	0.0033	0.852	0.0006	0.794
	400	0.0074	0.946	0.0018	0.911	0.0052	0.894	0.0011	0.837
	600	0.0173	0.988	0.0036	0.937	0.0093	0.900	0.0018	0.852
	800	0.0336	0.999	0.0066	0.956	0.0126	0.921	0.0025	0.879
	1,000	0.0364	0.997	0.0073	0.949	0.0188	0.929	0.0039	0.884
Temperature (℃)	25	0.0054	0.979	0.0011	0.918	0.0038	0.923	0.0007	0.881
	35	0.0046	0.953	0.0009	0.903	0.0032	0.865	0.0007	0.811
	45	0.0037	0.893	0.0007	0.838	0.0021	0.799	0.0004	0.745
pH	5	0.0043	0.839	0.0008	0.794	0.0029	0.786	0.0006	0.732
	8	0.0054	0.979	0.0011	0.926	0.0041	0.922	0.0008	0.872
	11	0.0036	0.965	0.0007	0.911	0.0033	0.895	0.0007	0.845
Agitation speed (r/min)	100	0.0061	0.921	0.0013	0.877	0.0049	0.878	0.0011	0.836
	200	0.0056	0.934	0.0012	0.885	0.0042	0.892	0.0008	0.847
	300	0.0049	0.968	0.0011	0.925	0.0031	0.912	0.0006	0.863

Table 6
Kinetic constants of film and particle diffusion models for ammonium adsorption

	Film diffusion model		Particle diffusion model	
Kinetic constants	D_f (m^2 s^{-1})	R^2	D_p (m^2 s^{-1})	R^2
Modified zeolite	2.11×10^{-9}	0.972	8.55×10^{-10}	0.975
Natural zeolite	9.26×10^{-10}	0.925	8.33×10^{-10}	0.923

Thermodynamic parameters such as enthalpy (ΔH°), free energy change (ΔG°), and entropy (ΔS°) for the adsorption of ammonium by the two zeolites were calculated in this study at various temperatures (25, 35, and 45℃) using Eqs. (5)–(8) and were given in Table 7. Results showed that the ammonium adsorption process is feasible and spontaneous in nature indicated by the negative values of ΔG° (−23.4, −21.7, and −20.5 kJ mol^{-1} at 25, 35, and 45℃ for modified zeolite), and no energy input to the system is required. The negative value of ΔH° of −127.4 and −108.3 kJ mol^{-1} at 25℃ for the two zeolite's indicates that the ion-exchange/adsorption is an exothermic process, which supports the previous discussion that the adsorption amount of ammonium decreased with increasing temperature. The negative value of the standard entropy change ΔS° suggests that the randomness decreases the removal of NH_4^+ on the two zeolites. Furthermore, higher negative value reflects a more energetically favorable adsorption, for that reason, more energetically favorable adsorption occurs at 25℃.

Table 7
Thermodynamic parameters for ammonium adsorption by natural and modified zeolites

	MgO modified zeolite			Natural zeolite		
T (℃)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1})
25	−23.4	−127.4	−0.37	−16.5	−108.3	−0.35
35	−21.7	−124.8	−0.34	−14.8	−104.6	−0.31
45	−20.5	−121.6	−0.33	−12.4	−102.9	−0.28

4. Conclusions

Based on the results presented in this study, MgO modification enhanced ammonium adsorption capacity from 12.6 to 24.9 mg g^{-1}. Ion-exchange mechanism dominated the ammonium adsorption process with the order of exchange selectivity for cations: $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$, whereas the molecular adsorption was of secondary importance and contributed less to the TAN removal, especially in strong alkaline solutions. All in all, ammonium adsorption onto the MgO modified zeolite was partly controlled by ion-exchange, molecular adsorption, and the formation of complexes between NH_4^+ and functional groups of zeolite itself.

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