Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1094422

57 (2016) 18992–19001
August

Taylor & Francis
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The dynamics and equilibrium of ammonium removal from aqueous solution by Na-Y zeolite

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Received 26 February 2015; Accepted 8 September 2015

ABSTRACT

The ammonium removal from aqueous solution using Na-Y zeolite was investigated. The Na-Y zeolite was selected from a group of Beta, A, X, and Y zeolites, which were first screened to identify the best candidate for the ammonium removal. Among the considered zeolites, Na-Y and Na-X zeolites had the highest adsorption efficiencies, presumably due to a combination of their qualifying characteristics such as low Si/Al ratio, high surface area, and large pore size. The order at which the different investigated Y zeolites showed affinity for ammonium uptake was Na-Y >> Cs-Y ≈ K-Y > Mg-Y = Ca-Y > H-Y. For the Na-Y zeolite, it was found that the ammonium removal dynamics followed a pseudo-second-order kinetic model while the Langmuir adsorption isotherm fitted the equilibrium data well. Furthermore, it was deduced that the ammonium removal proceeded through two mechanisms: ion exchange and molecular adsorption. Three regeneration methods for restoring the adsorption efficiency of the spent zeolites were examined, and the best approach was found to be a combination of two methods, namely washing by saline water followed by distilled water. In brief, Na-Y zeolite was found to be a promising adsorbent for the removal of ammonium from freshwater.

Keywords: Y zeolite; Ammonium removal; Ammonium ion exchange; Adsorption isotherm; Adsorption dynamics; Adsorbent regeneration

1. Introduction

Wastewater generated by industrial, commercial, agricultural, and domestic sources requires treatment before it can be discharged into the environment or reused [1]. Nitrogen compounds are among the pollutants that need to be removed when present in wastewater. Ammonium/ammonia are the more commonly encountered nitrogen compounds in wastewaters and groundwaters [2]. Dissolved ammonium ions and ammonia in water coexist in equilibrium according to the following equation [3]:

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$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+ \quad (1)$$

The sources of ammonium/ammonia in wastewaters and groundwaters are mainly ammonia/fertilizer production facilities, aquacultures, over fertilization and agriculture waste, and municipal sewage. Even low concentrations of ammonium/ammonia in water could be toxic to aquatic organisms [3,4], corrosive and have detrimental effect on processes [5,6], and result in undesired taste and odor in drinking water [6].

Techniques for ammonium/ammonia removal from water include biological treatments, air stripping, nanofiltration, adsorption/ion exchange, and breakthrough chlorination [7,8]. Adsorption is believed to be an effective and simple technique for water and wastewater treatment and its success depends, essentially, on the effectiveness of the adsorbent utilized [9]. Some zeolites were identified to be excellent candidates for adsorption due to their unique and favored adsorption properties, such as their cation exchanging and molecular sieving capabilities, suitable pore sizes and uniform pore distributions, large surface areas, and regeneration possibilities. For example, a vast number of natural zeolites, mainly clinoptilolite, from various sources have been evaluated as adsorbents/ion exchangers for ammonium removal from water [9]. Synthetic zeolites—such as A, X, and Y zeolites—were also prepared and evaluated for ammonium removal from aqueous solution [10–17]. Furthermore, due to their significant adsorption capability, Y zeolites have been assessed as adsorbents for several species removal, including ammonium, from aqueous and non-aqueous solutions. For instance, Y zeolites were considered for the removal of organosulfur compounds (e.g. dibenzothiophenes) from surrogate gasoline [18,19] and the removal of ammonium [10–12], organic compounds (e.g. benzene and toluene) [20], metal ions (e.g. Cr(VI) and Pb(II)) [21,22], and agrochemicals (e.g. simazine) [23] from aqueous solutions. Considering the number of research papers published concerning the use of natural zeolites for the removal of ammonium from aqueous solutions [9], those exploring the suitability of Na-Y zeolite for the same are very limited in the literature [12]. Three studies, conducted by Wang et al. [10], Yusof et al. [11], and Zhao et al. [12] revealed that Na-Y zeolites have capability and potential for ammonium removal from wastewater compared to many other zeolites, as will be highlighted later. This study aimed to further explore the suitability of Y zeolite for the application of ammonium removal from freshwater, its related kinetics, and regeneration methods.

In this study, the potential of a few zeolites, namely Beta, A, X, and Y zeolites, for ammonium removal from aqueous solution was investigated. For the best candidate, that proved to be the Y zeolite, the effect of the zeolite cation type on adsorption efficiency was also studied. Subsequently, more studies were conducted on the unsurpassed examined Na-Y zeolite. These studies included determining the time required for the ammonium adsorption to reach equilibrium, investigating the adsorption dynamics and isotherm, determining the maximum adsorption capacity of the zeolite, and finally finding the most effective regeneration method.

2. Materials and methods

2.1. Materials

The screened adsorbents were commercially available zeolites. The Beta and Y zeolites were obtained from Catal International Ltd, the 4A zeolite was obtained from Tosoh Corporation, while the 13X zeolite was obtained from Junsei Chemical Co. Ltd.

The modified zeolites—namely the K, Cs, Mg, and Ca-Y zeolites—were prepared from H-Y zeolite by ion-exchanging the H-form with the desired cation. First, a slurry of H-Y zeolite was prepared with small amount of distilled water. In another flask, a 0.1 M solution of the nitrate salt of the cation of interest (i.e. K^+, Cs^+, Mg^{2+}, or Ca^{2+}) was prepared at a ratio of 100 ml of solution per each gram of zeolite. The solution was heated to 80°C and then the zeolite slurry was slowly added to it. The resultant suspension was kept at 80°C for an hour with continuous stirring then cooled to room temperature and filtered. The collected solid was washed thoroughly with excess distilled water then dried overnight at 120°C. Finally, it was heated at a rate of $5^\circ C\ min^{-1}$ to 450°C and left to calcine for three hours.

The ammonium solution was prepared by dissolving a predetermined amount of ammonium chloride salt (NH_4Cl) in 1 l of distilled water to obtain a solution with the required concentration. The saline water, used for regeneration and Na-salt effect studies, was prepared from NaCl and distilled water, where they were mixed in a specific proportion to produce a 3.5 wt% salt concentration (seawater surrogate).

2.2. Experimental and analytical methods

X-ray diffraction (XRD) measurements were performed using a Bruker X-ray diffractometer in the 2θ range of 4°–80°, at a scan rate of $0.02^\circ\ sec^{-1}$, and by utilizing a monochromatized Cu Kα radiation

($\lambda = 0.154$ nm) from a broad focus tube operating at 45 kV and 30 mA.

Before using them in the batch adsorption experiments, the zeolites were dried by heating for an hour at 120°C. In each batch, 0.25 g of zeolite was added to 40 ml of ammonium solution with a specified initial concentration. The initial concentrations ranged from 40 to 615 mg NH_4^+-N L^{-1} (hereafter written as mg N L^{-1}). The flasks, containing the batches, were placed on a multi-stirrer plate operated at a specified stirring speed and room temperature. After a predetermined time, the flask of concern was removed from the multi-stirrer plate, and the zeolite and the solution were separated using a centrifuge (Heraeus™ Labofuge™ 200) operated at 4,000 rpm and for 3 min.

Based on the purpose of the experiment, the values of the operating parameters—namely the stirring speed, initial ammonium concentration, zeolite type, and contact time—were decided on. Unless otherwise stated, the standard operating parameters were as follows: 480 rpm stirring speed, 40 mg N L^{-1} ammonium initial concentration, Na-Y zeolite as the adsorbent, and 120 min contact time. The initial and final concentrations of ammonium in the solution were determined using Hanna Instruments' photometer (C 99 Multiparameter Bench Photometer) according to the described Neslerization method. The adsorption efficiency (i.e. the ammonium removal percentage) was calculated from the following equation:

$$\text{Adsorption efficiency} = \frac{C_{A0} - C_A}{C_{A0}} \times 100 \tag{2}$$

while the ammonium uptake by the zeolite (mg N g^{-1}) at time t, q_t, and that at equilibrium, q_e, were calculated according to Eqs. (3a) and (3b), respectively:

$$q_t = (C_{A0} - C_A) \times V/m \tag{3a}$$

$$q_e = (C_{A0} - C_{Ae}) \times V/m \tag{3b}$$

where C_{A0}, C_A, and C_{Ae} are the ammonium concentrations in the solution (mg N L^{-1}) at $t = 0$, at time t, and at equilibrium, respectively, V is the ammonium solution volume (L), and m is the mass of the zeolite used (g).

The regeneration of the used adsorbent was achieved either by heating the spent zeolite at 120°C overnight or by washing it with 40 ml volume of either distilled water, saline water, or saline water followed by the same volume of distilled water. To regenerate the adsorbent through washing, the used zeolite was first mixed with 40 ml of the washing water (distilled or saline) and stirred for 30 min. Then, the zeolite was filtered overnight using a 0.1-μm pore size filter.

3. Results and discussion

3.1. Modified zeolites characterization

To study the effect of the cation type on the ammonium removal, K, Cs, Mg, and Ca-Y zeolites were prepared from H-Y zeolite through ion exchange (see Section 2.1). Comparing the XRD diffractogram of each of the K, Cs, Mg, and Ca-Y zeolites with that of the H-Y zeolite revealed that no change in the zeolite structure had taken place. This indicated that the ion exchange procedure used for the adsorbents' preparation did not alter the zeolite structure. Fig. 1 illustrates a sample of this comparison between the K and H-Y zeolite.

3.2. Effect of mixing rate

Preliminary experiments were conducted to identify an optimum mixing rate at which mass transfer resistances are minimized. Adsorption experiments—using Na-Y zeolite and 40 mg N L^{-1} solutions—were carried out at four different stirring speeds, and the ammonium removal percentages achieved in 30 and 120 min were recorded. Fig. 2 shows that, for stirring speed of 480 rpm, equilibrium was reached in 30 min as the adsorption efficiencies were identical in 30 and 120 min. Even with lower stirring speeds, equilibrium was almost reached after 120 min. Nevertheless, mass transfer did improve with increasing the stirring speed, as could be seen by comparing the adsorption efficiency at 30 min to that at 120 min for each of the

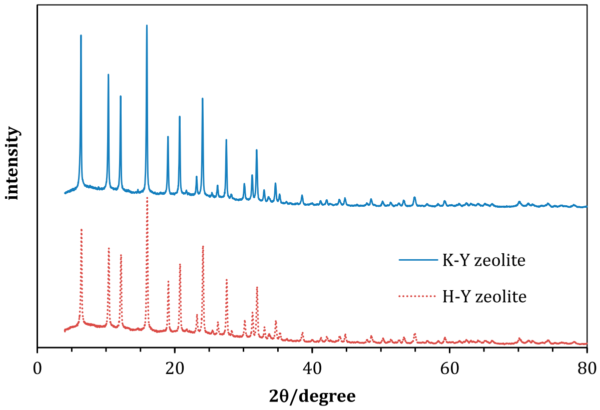

Fig. 1. XRD patterns of the original H-Y and the prepared K-Y zeolites.

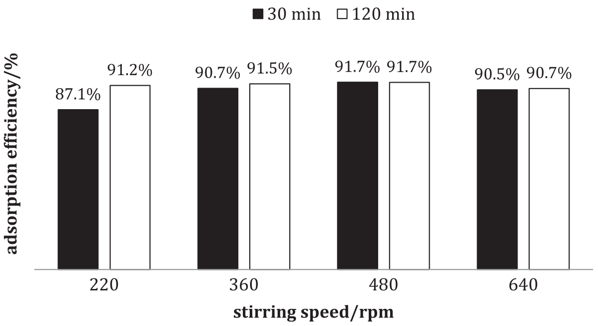

Fig. 2. The effect of the stirring speed on the adsorption efficiency of the Na-Y zeolite. $[NH_4^+]_0 = 40$ mg N L^{-1}; [Na-Y zeolite] = 6.25 g L^{-1}.

220, 360, and 480 rpm cases. However, increasing the stirring speed to 640 rpm had an adverse effect on the mixing effectiveness and, consequently, on the adsorption efficiency. This was apparently due to the vortex formation where the stirring resulted in fluid spinning rather than mixing. Therefore, the stirring speed of 480 rpm was deemed to be reasonable, and hence, all the experiments were carried out at this mixing rate. Although this set of experiments was conducted for Na-Y zeolite, this stirring speed (480 rpm) was used for all other experiments regardless to the type of the zeolites used. In addition, contact time of 120 min was considered suitable for adsorption efficiency comparison of different zeolites.

3.3. Screening the candidate zeolites

A number of commercial, synthetic zeolites were screened to determine the best candidate for ammonium removal from distilled water. The six investigated zeolites were as follows: H-Beta and Na-Beta zeolites, H-Y and Na-Y zeolites, Na-A zeolite, and Na-X zeolite. The candidacy of the examined zeolites was based on the percentage of ammonium removed from 40 mg N L^{-1} solutions after 120 min of contact time.

As demonstrated in Fig. 3, the ammonium removed by Na-Y zeolite was the highest, followed by Na-X zeolite. The best two zeolite candidates were from the Faujasite family and had Na^+ cation. It is well known that low Si/Al ratio results in high cation exchange capacity (CEC). Therefore, the zeolite that had the lowest Si/Al ratio was expected to be the one which would remove more ammonium. The Na-X zeolite had lower Si/Al ratio compared to Na-Y zeolite (1.24 vs. 2.9), but it also had lower surface area (527 vs. 980 m^2 g^{-1}). Since Na-Y zeolite performed better, this suggested that ammonium was not only removed by ion exchange with the zeolite cation (Na^+), but was also removed by molecular adsorption on the surface of the zeolite. In addition, Na-X and Na-Y zeolites have large pore sizes (7–8 Å). Therefore, among the investigated zeolites, Na-Y and Na-X zeolites performed better because of the suitable combination of low Si/Al ratio, high surface area, and large pore size. Note that in this study, the term "adsorption" was used to describe the ammonium removal by the solid phase, regardless of the mechanism by which it was removed.

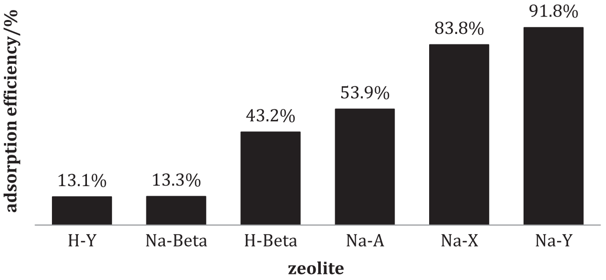

Fig. 3. The adsorption efficiencies of the different examined zeolites. $[NH_4^+]_0 = 40$ mg N L^{-1}; [zeolite] = 6.25 g L^{-1}; t = 120 min.

3.4. The effect of the Y zeolite cation

After the Na-Y zeolite had been determined to be the best candidate among the various types of zeolites investigated, the effect of the Y zeolite cation type on the ammonium removal was studied. H-Y zeolite was ion exchanged with K^+, Cs^+, Mg^{2+}, and Ca^{2+}, and the adsorption efficiencies of the resultant zeolites were compared to those of H and Na-Y zeolites tested earlier. Fig. 4 shows that Na-Y zeolite was still the best candidate among the studied Y zeolites. The higher adsorption efficiency of Na-Y zeolite compared to the other Y zeolites could be attributed to its higher

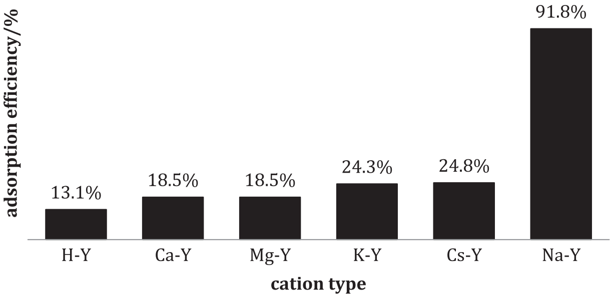

Fig. 4. The adsorption efficiencies of the ion exchanged H-Y zeolites with respect to the original H and Na-Y zeolites. $[NH_4^+]_0 = 40$ mg N L^{-1}; [Y zeolite] = 6.25 g L^{-1}; t = 120 min.

surface area ($980\,m^2\,g^{-1}$) compared to that of H-Y zeolite ($610\,m^2\,g^{-1}$)—which was the precursor of the prepared K, Cs, Mg, and Ca-Y zeolites—as well as to the known zeolites' preference of NH_4^+ over Na^+ [24]. The zeolite modification via exchanging H^+ with K^+, Cs^+, Mg^{2+}, and Ca^{2+} slightly improved the ammonium removal efficiency of the precursor zeolite, H-Y zeolite. For the prepared ion exchanged zeolites, the selectivity toward ammonium removal was as follows: Cs-Y ≈ K-Y > Mg-Y = Ca-Y > H-Y under the studied conditions. Nevertheless, the Na-Y zeolite remained by far the best adsorbent for ammonium removal among the compared Y zeolites based on the adsorption efficiency as illustrated in Fig. 4. Similar results were reported by Cooney et al. [25] when they examined natural Australian zeolite, clinoptilolite, for ammonium removal from wastewater, where it was found that the highest ammonium removal efficiency was achieved when the zeolite cations were first exchanged with sodium ion.

3.5. Dynamics of ammonium adsorption by Na-Y zeolite

The dynamics of ammonium adsorption was studied for the best performing zeolite—the Na-Y zeolite. The related experiments were conducted for the highest and the lowest initial ammonium solution concentrations considered in this study (615 and 40 mg N L^{-1}). Fig. 5 illustrates the approach to equilibrium curves for the mentioned two cases. It was observed that the dynamics of adsorption was very fast regardless of the initial ammonium concentration. In addition, less time was required for the solution with the lower C_{A0} to reach equilibrium ($t_e = 30$ min with $C_{A0} = 40$ mg N L^{-1} vs. 60 min with $C_{A0} = 615$ mg N L^{-1}). To demonstrate the adsorption rates ($r_{ad} = -dC_A/dt$) in the two C_{A0} cases in relation to each other, another figure was plotted—shown as an inset in Fig. 5—where C_A was plotted vs. t. The ordinates for the two cases were shifted to have their curves start at the same point in order for the comparison between the two slopes to be straightforward. The initial rate of adsorption, represented by the slope of the plotted curve in the inset figure, was found to be greater in the higher C_{A0} case, probably due to the higher concentration gradient between the ammonium concentration in the liquid phase and that in the solid phase.

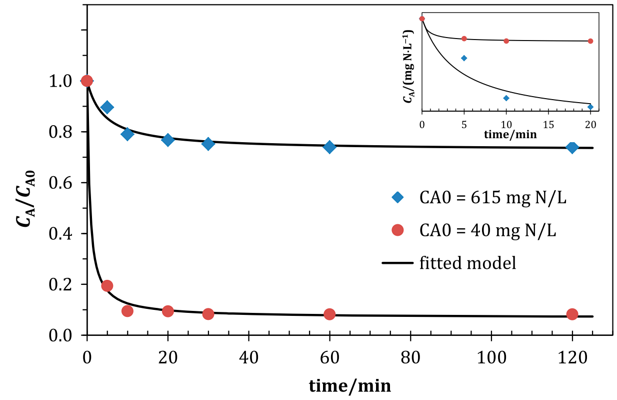

Fig. 5. The approach to equilibrium curves for a high and low initial ammonium concentration cases. [Na-Y zeolite] = 6.25 g L^{-1}.

Three models—namely pseudo-first-order, pseudo-second-order, and intraparticle diffusion models [26]—were tested to determine whether they described the adsorption dynamics data. Based on the coefficient of determination (R^2), the pseudo-second-order model was found to be the best fit to the adsorption dynamics data in both C_{A0} cases. The pseudo-second-order kinetic model is expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{4}$$

where q_t and q_e are as defined earlier and k is the adsorption rate constant (g mg N^{-1} min^{-1}). Integrating the above equation using the initial condition $q_t = 0$ at $t = 0$ gives the equation:

$$q_t = \frac{t}{a \cdot t + b} \tag{5a}$$

or upon linearization,

$$\frac{t}{q_t} = a \cdot t + b \tag{5b}$$

where $a = 1/q_e$ and $b = 1/kq_e^2$. Both forms of the equation were fitted to the experimental data and the goodness of fit was assessed by both R^2 and percentage error between the experimental and fitted q_e. The results of the linear regression (using Eq. (5b)) and the nonlinear regression (using Eq. (5a)) are listed in Table 1. The fitted model was manipulated to obtain $C_A(t)$, and for each of the C_{A0} cases, the simulated values were plotted in Fig. 5 as a continuous line along with the experimental values; for drawing the continuous lines, linear regression parameters were used in the C_{A0} 650 mg N L^{-1} case, and nonlinear regression parameters were used for the C_{A0} 40 mg N L^{-1} case. Yusof et al. [11] and Zhao et al. [12] also reported pseudo-second-order kinetic behavior for the

Table 1
Dynamic parameters of the pseudo-second-order model for the ammonium removal by the Na-Y zeolite

				Linear regression			Nonlinear regression					
C_{A0}	C_{Ae}	$q_{e,exp}$	R^2	k	q_e	q_e error[a]	R^2	k	95% conf.	q_e	95% conf.	q_e error[a]
40	3.29	5.87	1.000	5.09E−01	5.90	0.4%	0.998	2.59E−01	±8.83E−04	5.96	±9.46E−04	1.5%
615	454.73	25.64	0.998	8.74E−03	26.81	4.5%	0.967	6.29E−03	±8.52E−07	28.24	±6.97E−04	10.1%

Notes: Units: C_{A0} and C_{Ae} (mg N L^{-1}); q_e (mg N g^{-1}); k (g mg N^{-1} min^{-1}).
[a] q_e error = $(q_e - q_{e,exp})/q_{e,exp} \times 100$.

adsorption of ammonium from aqueous solution by their synthesized Y zeolites. Many other researchers also observed the same adsorption kinetic order with other zeolites [27–29].

3.6. Adsorption isotherm

An adsorption isotherm was constructed for the aqueous ammonium solution and Na-Y zeolite system, as illustrated in Fig. 6. As the ammonium concentration in the solution increased, the ammonium uptake by the zeolite increased as well until a limit was reached beyond which no more ammonium was adsorbed. This maximum ammonium uptake by the zeolite, also referred to as the adsorbent capacity (Q_0), was due to the limited sites that the ammonium chloride molecules could be adsorbed to, as well as the limited number of the Na$^+$ within the zeolite framework that could be accessed and exchanged with the NH$^+$ ions in the solution. The Na-Y zeolite adsorption capacity was found to be 25.7 mg N g^{-1}, as can be seen in Fig. 6. Based on stoichiometry, a typical Y zeolite that has CEC of 3 would have a maximum capacity for ammonium removal of 42 mg N g^{-1} through ion exchange only. Hence, the experimentally obtained capacity was of reasonable value. However, it was expected to be more due to the contribution of the molecular adsorption to the total capacity. Worth mentioning is that when the Na-Y zeolite was used for ammonium removal from a saline water (3.5 wt% NaCl) with high initial ammonium concentration, the adsorption capacity reduced by around 30%, owing to the competitive molecular adsorption of NH_4Cl and NaCl and to the shift in ion exchange equilibrium (Eq. (6)) to the left due to the high concentration of Na$^+$ in the solution:

$$\mathrm{Na^+ \cdot YZ + NH_4^+ \leftrightarrow NH_4^+ \cdot YZ + Na^+} \tag{6}$$

As a comparison to the adsorption capacity achieved in this study (25.7 mg N g^{-1}), Wang et al. [10] reported experimentally obtained ammonium uptakes as high as 15.0 mg N g^{-1} (19.29 mg NH$_4^+$ g^{-1}) and a fitted adsorption capacity of 17.61 mg N g^{-1} for their Na-Y zeolite which was synthesized from Chinese natural clinoptilolite. However, Yusof et al. [11] reported a higher adsorption capacity of 32 mg N g^{-1} (experimental value), which is 72.4% of the CEC of their synthesized rice husk ash-based Y zeolite. In addition, Zhao et al. [12] reported an adsorption capacity of 30 mg N g^{-1} (fitted value) at 25°C for their synthesized halloysite-based Y zeolite. On the other hand, Lie et al. [30] compared the adsorption capacities of many examined natural zeolites and found that their capacities ranged from 6.59 to 23.83 mg N g^{-1}, but noted that pretreated zeolites yielded significantly higher ammonium adsorption capacities compared to the non-pretreated natural zeolites. For example, they reported that their microwave-treated natural Chinese zeolite could potentially adsorb up to 23.83 mg N g^{-1} (fitted value).

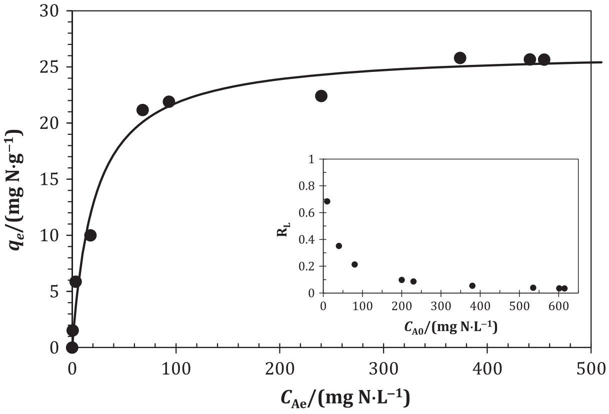

Fig. 6. The adsorption isotherm of the ammonium uptake onto the Na-Y zeolite fitted to Langmuir model. The inset shows the separation factor values at different C_{A0}.

Two isotherm models are traditionally used in the literature to describe the adsorption behavior at equilibrium: the Freundlich and the Langmuir models. The range of the ammonium concentration in the conducted equilibrium adsorption experiments was extended to cover values at which the adsorption capacity (i.e. the maximum uptake) of the N-Y zeolite was reached. Since the Freundlich model fails to describe this saturation phenomenon, only the validity of Langmuir model was verified. The Langmuir model is written as:

$$q_e = \frac{Q_0 K C_{Ae}}{1 + K C_{Ae}} \tag{7}$$

where Q_0 is the adsorption capacity or the maximum adsorbate uptake by the adsorbent (mg N g^{-1}), K is Langmuir adsorption equilibrium constant (L mg N^{-1}), and Q_0K is the relative affinity of the adsorbate toward the surface of the adsorbent. Nonlinear regression was used to fit Langmuir model to the experimentally obtained equilibrium data. The regression analysis results are shown in Table 2 and the fitted model is plotted in Fig. 6 as a continuous line. Both Table 2 and Fig. 6 indicate that the Langmuir isotherm is in a very good agreement with the experimental data. In addition to the R^2 value which was very close to one, the 95% confidence intervals which were smaller than the parameters values, and the absence of any trend in the residual plot (not shown here), the fitted adsorption capacity (26.49 mg N g^{-1}) was very close to the experimental value (25.70 mg N g^{-1}) with a 3.1% error. The Langmuir isotherm model was developed to describe the molecular adsorption phenomenon at equilibrium. Its ability to describe the ammonium uptake onto Na-Y zeolite, where both molecular adsorption and ion exchange mechanisms are involved, could be explained by the validity of the Langmuir model assumptions in both phenomena. In the ion exchange mechanism, NH_4^+ ions are exchanged with the exchangeable Na^+ ions at defined sites of the zeolite framework. Therefore, the Langmuir assumptions that are also valid in the ion exchange phenomenon include the following: (1) the monolayer adsorption assumption, where only one NH_4^+ ion is attached to the zeolite framework for each Na^+ ion replaced, and (2) the finite/limited number of definite localized sites assumption, where the ion exchange is constrained by the number of the exchangeable Na^+ ions (although in this case these sites are not identical). The Langmuir model has repeatedly been reported to describe the adsorption isotherm of the ammonium uptake onto different zeolites [28,31–33] including Na-Y zeolite [10–12].

Table 2
Langmuir isotherm parameters for the ammonium removal by the Na-Y zeolite

R^2	K	95% conf.	Q_0	95% conf.	$Q_{0,exp}$	Q_0 error[a]
0.982	0.046	± 0.024	26.49	± 2.52	25.70	3.1%

Notes: Units: K (L mg N^{-1}); Q_0 (mg N g^{-1}).

[a] Q_0 error = $(Q_0 - Q_{0,exp})/Q_{0,exp} \times 100$.

The calculated values of the separation factor (R_L), which is a dimensionless number proposed by Weber and Chakravorti [34] and determined from the following equation:

$$R_L = \frac{1}{1 + K C_{A0}} \tag{8}$$

showed that the adsorption of ammonium on the Na-Y zeolite was favorable. In effect, the adsorption was favorable over the entire examined ammonium initial concentration range, where R_L values were between 0 and 1 even at low concentrations, as illustrated in the inset plot in Fig. 6. However, the adsorption was substantially more favorable at initial concentrations higher than 200 mg N L^{-1}.

3.7. Na-Y zeolite regeneration

After illustrating that the Na-Y zeolite was a good candidate for ammonium removal from freshwater, it was necessary to determine a suitable regeneration method for recycling. Three regeneration methods were proposed and examined, namely regeneration by heating (120°C), by washing with distilled water, and by washing with saline water. The fresh Na-Y zeolite was first used with a 40 mg N L^{-1} ammonium solution, where 91.75% of the ammonium was removed. Next, the spent zeolite was regenerated with one of the three stated methods, then reused for another adsorption cycle. The recovery of the adsorption efficiency is shown in Fig. 7 for each of the regeneration methods. As explained in the following paragraphs, the recovery of the adsorption efficiency was most likely due to the release of the adsorbed ammonium without creating additional adsorption sites as all the applied regeneration methods were mild and would not alter the zeolite structure.

Regeneration by heating recovered 87.6% of the zeolite efficiency for ammonium removal. Heating presumably degassed the dissolved NH_3 that is in equilibrium with NH_4^+ in the presence of water, which in turn enabled getting rid of the adsorbed NH_4Cl ($NH_4^+Cl^-$) by shifting the equilibrium shown in Eq. (1) to the right. The same could have happened to the

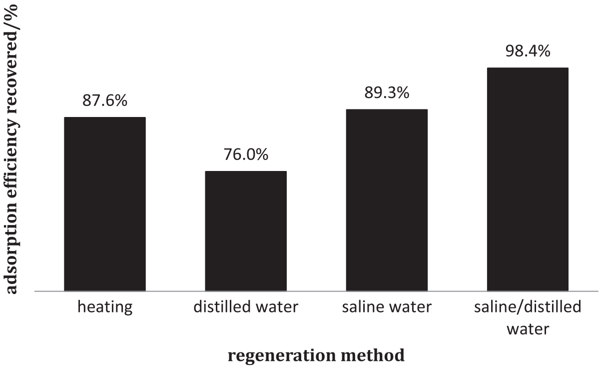

Fig. 7. Comparison of the adsorption efficiency recovery achieved by the investigated regeneration methods. $[NH_4^+]_0$ = 40 mg N L^{-1}; [Y zeolite] = 6.25 g L^{-1}.

exchanged NH_4^+. In the second regeneration method, washing the zeolite with distilled water recovered only 76.0% of its efficiency. Due to the absence of ammonium ions/salt in the distilled water, the washing process likely caused the adsorbed NH_4Cl molecules to be desorbed and diffused to the solution. Since the washing process lasted overnight, the spent zeolite could have slightly gone through hydrolysis as well, according to Eq. (9) (refer to Sherry [24] for zeolite hydrolysis). Therefore, it is believed that this method mainly regenerated the sites that were occupied by the ammonium that was molecularly adsorbed and, hence, the low adsorption efficiency recovery.

$$NH_4^+ \cdot YZ + 2HOH \leftrightarrow H_3O^+ \cdot YZ + NH_4OH \tag{9}$$

During the regeneration by saline water, it is believed that both the adsorbed and exchanged NH_4^+ ions were replaced with Na^+ ions due to the latter's very high concentration in the solution (3.5 wt% NaCl aqueous solution). The regeneration through ion exchange occurs, according to Eq. (6), in the reverse direction. Therefore, the zeolite was to some extent restored to its initial state, and an 89.3% efficiency recovery was obtained. This regeneration method was found to be the most promising among the three aforementioned regeneration methods. The spent adsorbent of the last case was regenerated—again using saline water—and reused in two more cycles and the adsorption efficiency was recorded after each regeneration. The following adsorption efficiencies were achieved after each regeneration: 81.97, 78.16, and 72.82%, compared to the 91.75% adsorption efficiency of the fresh adsorbent (i.e. the final recovery percentage in the adsorption efficiency was 79.4%). The reduction in the adsorption efficiency with every washing cycle using saline water was probably due the accumulation of Na^+ ions within the zeolite pores and channels. The presence of Na^+ ions near the exchangeable cation sites would shift the ammonium/sodium ion exchange equilibrium reaction (Eq. (6)) to the left, resulting in reduction in the ammonium removal from the solution. The accumulated Na^+ would also reduce the number of sites available for ammonium molecular adsorption. To get rid of the accumulated Na^+ ions within the zeolite pores, a combined saline/distilled water regeneration method was proposed, where the adsorbent was first regenerated using saline water then washed with distilled water to ensure that all the accumulated, non-exchanged Na^+ ions were removed by the end of the regeneration process. Fig. 7 shows that superior result was achieved when the adsorbent regeneration was carried out by saline water followed by washing with distilled water, where the adsorption efficiency was almost completely recovered. Other researchers also reported complete regeneration of their investigated clinoptilolite zeolites—used for ammonium removal—with the use of $Ca(OH)_2$ emulsion at 100–110°C [35], $Ca(OH)_2$ emulsion at pH 11–12 [35], or sodium chloride solution at pH 11–12 [36]. In this study, however, it was found that almost complete regeneration could be achieved with the spent Na-Y zeolite without the need for additional chemicals, heating, or pH alteration.

4. Conclusions

The study can be concluded with the following findings related to the ammonium removal from aqueous solution under the studied conditions:

(1) The order at which the examined zeolites showed competency for ammonium removal was as follows: Na-Y > Na-X > Na-A > H-Beta > Cs-Y ≈ K-Y > Mg-Y = Ca-Y > H-Y ≈ Na-Beta.
(2) Among the studied zeolites, the good candidates had a combination of the following characteristics: low Si/Al ratio, high surface area, large pore size, and Na^+ as the cation.
(3) The dynamics of ammonium removal by Na-Y zeolite was very rapid, where equilibrium was reached within an hour or less, and it followed a pseudo-second-order model with rate constants larger than 10^{-3} g mg N^{-1} min^{-1}.
(4) The adsorption isotherm followed Langmuir model with a maximum, experimentally achieved, adsorption capacity of 25.7 mg N g^{-1}.

(5) Ammonium removal presumably proceeded through two mechanisms: ion exchange and molecular adsorption.

(6) The adsorption efficiency of the spent Na-Y zeolite was almost completely recovered (98.4% recovery) when regenerated by washing with saline water then distilled water.

Concisely, the Na-Y zeolite was found to be a promising adsorbent for the ammonium removal from aqueous solution as it proved to have an adsorption capacity higher than many other zeolites'. Therefore, it is recommended to further explore the potential of Na-Y zeolite for such applications by improving its effectiveness through reducing its cost by synthesizing it from affordable materials and through increasing its adsorption capacity by different treatment methods.

Acknowledgments

The authors express their appreciation to the Deanship of Scientific Research at the University of Bahrain for its financial support of the work conducted at the University of Bahrain.

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