



Fixed-bed study of ammonia removal from aqueous solutions using natural zeolite

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Abstract

Purpose – The purpose of this paper is to investigate the performance of natural Jordanian zeolite tuff to remove ammonia from aqueous solutions using a laboratory batch method and fixed-bed column apparatus. Equilibrium data were fitted to Langmuir and Freundlich models.

Design/methodology/approach – Column experiments were conducted in packed bed column. The used apparatus consisted of a bench-mounted glass column of 2.5 cm inside diameter and 100 cm height (column volume = 490 cm³). The column was packed with a certain amount of zeolite to give the desired bed height. The feeding solution was supplied from a 30 liter plastic container at the beginning of each experiment and fed to the column down-flow through a glass flow meter having a working range of 10-280 ml/min.

Findings – Ammonium ion exchange by natural Jordanian zeolite data were fitted by Langmuir and Freundlich isotherms. Continuous sorption of ammonium ions by natural Jordanian zeolite tuff has proven to be effective in decreasing concentrations ranging from 15-50 mg NH₄-N/L down to levels below 1 mg/l. Breakthrough time increased by increasing the bed depth as well as decreasing zeolite particle size, solution flow-rate, initial NH₄⁺ concentration and pH. Sorption of ammonium by the zeolite under the tested conditions gave the sorption capacity of 28 mg NH₄-N/L at 20°C, and 32 mg NH₄-N/L at 30°C.

Originality/value – This research investigates the performance of natural Jordanian zeolite tuff to remove ammonia from aqueous solutions using a laboratory batch method and fixed-bed column apparatus. The equilibrium data of the sorption of Ammonia were plotted by using the Langmuir and Freundlich isotherms, then the experimental data were compared to the predictions of the above equilibrium isotherm models. It is clear that the NH₄⁺ ion exchange data fitted better with Langmuir isotherm than with Freundlich model and gave an adequate correlation coefficient value.

Keywords Diffusion, Science, Ammonium removal, Breakthrough curve, Natural zeolite, Isotherm

Paper type Research paper



1. Introduction

Nitrogen in any soluble form (NH_3 , NH_4^+ , NO_2^- , and NO_3^-) is a nutrient and needs to be removed from wastewater to help the control of algae and plankton growth in receiving water bodies like groundwater, rivers, lakes, and large reservoirs of water supply systems. The biological oxidation of NH_4^+ to NO_3^- consumes large quantities of dissolved oxygen leading to dramatic effects on life in aquatic ecosystems. Therefore, increasing legislative pressures have caused wastewater-producing industries to utilize the best available technology for the protection of the environment (Eddy *et al.*, 2003).

The oil refining industry is a major source of ammonia in the industrial wastewater, which is known as sour water. Other industrial sources include fertilizing industries, phosphate and refinery processes. Usually the purpose of treating sour water is water re-use, particularly in countries with arid and semi-arid climates (Kmet, 2002).

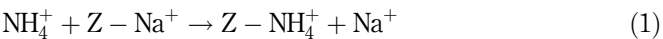
The cation-exchange process using a fixed-bed is widely used due to the affordability of both raw materials and operating costs. Natural zeolite, such as clinoptilolite, has been successfully employed to remove ammonia in the form of NH_4^+ from the streams of industrial wastewater. This raw material used as natural case to save the most adsorption properties without any advance treatment by using acids, which affect the iron oxides inside the pore if the pH decreases by 4.0 or below. This natural material was discovered and is produced in the Artin area, which is 120 km in the northeast of Amman, the capital city of Jordan. There are many uses for this material as natural source of fertilizer particularly through the addition of ammonia and/or additional additives. Indeed companies in Jordan produce it at an industrial scale and export this to some Arabian Gulf states to be used in the agricultural projects in desert or salty regions. When used in adsorption tests, the exhausted clinoptilolite column can be regenerated using a brine solution of NaCl (Booker *et al.*, 1996; Cooney *et al.*, 1999). Wang *et al.* (2011) developed fixed zeolite bioreactor and bioreactor without zeolite for the anaerobic digestion of ammonium-rich swine wastes. They found that the zeolite-containing reactor is more effective for ammonium removal. (Guo *et al.*, 2013) developed highly efficient regeneration of natural zeolite in conjunction with the removal of high concentrations of ammonia and potassium from the reverse osmosis effluent of anaerobic-digested wastewater by fixed-bed ion exchange.

Zeolite is a mineral having considerable ion exchange capacities for various cations in aqueous solutions including NH_4^+ and metal ions. Phillipsite, chabazite, and faujasite are the most abundant zeolite minerals found in the Jordanian zeolitic tuff. The zeolite content in these tuffs varies from 20 to 65 per cent. Using simple mineral processing routes, zeolite concentrations with grades up to 90 per cent were achieved[1].

Recently, many researchers studied the removal of ammonia from aqueous solutions using different types of zeolite such as natural Chinese zeolite (Huang *et al.*, 2010), natural zeolite (Karapinar, 2009), ion exchange on natural and modified chabazite (Leyva-Ramos *et al.*, 2010), natural Iranian zeolite (Malekian *et al.*, 2011; Marañón *et al.*, 2006), volcanic tuff (Marañón *et al.*, 2006), zeolite synthesized from fly ash by a fusion method (Zhang *et al.*, 2011a), zeolites synthesized from low-calcium, and high-calcium fly ashes (Zhang *et al.*, 2011b). Li *et al.* (2011) studied the removal of ammonia from drinking water using modified natural zeolite, and Widiastuti *et al.* (2011) studied the removal of ammonia from grey water using natural zeolite.

The unique physical and chemical properties of natural zeolites, in combination with their abundance in sedimentary deposits and in rocks derived from volcanic materials, have made them useful in many industrial applications (Mumpton, 1978). Natural zeolites have found wide applications in various industrial and agricultural

fields. Clinoptilolite was used in several sectors including removal of ammonia from the streams of domestic and industrial wastewater (Booker *et al.*, 1996), soil conditioner, and animal nutrition. Ion exchange using a fixed-bed column containing clinoptilolite has been successfully employed. Clinoptilolite is used as an independent ion exchange treatment or as a polisher after a biological treatment while the spent clinoptilolite is utilized in agricultural lands deficient of nitrogen. The use of natural zeolite for ammonia removal was mainly due to its availability, high selectivity and cation-exchange capacity for NH_4 ions. The sodium homo-ion form is usually used in zeolite ion exchangers. The reaction is as follows:



The clinoptilolite zeolite from the Aritain area in the northeastern part of Jordan is the product of alteration of volcanic basaltic glass, available in commercial-scale and rich in phillipsite tuff. Published studies on this mineral have reported that it has promising potential in wastewater treatment, especially for removing NH_4^+ as well as toxic heavy metal ions (Al-Haj-Ali and El-Bishtawi, 1997; Dwairi, 1993).

Fixed-beds are used due to the affordability of both raw materials and operating costs while it is easily regenerated using a brine solution of NaCl upon exhaustion (Booker *et al.*, 1996; Cooney *et al.*, 1999). There is a gap in the literature studies using fixed-bed column for polluted water using zeolite.

The main objective of the present work is to optimize the sorption of ammonia from the contaminated water by natural zeolite in a continuous fixed-bed column. In order to achieve this the capacity of the natural zeolite as an ion exchange material for ammonia removal using equilibrium isotherm should be tested. The effect of particle size, bed depth, feed flow-rate, initial ammonia concentration, and solution pH on the removal of ammonia by the zeolite using fixed-bed column are discussed. The ammonia removal capacity of natural Jordanian zeolite tuff is compared with zeolites from other locations as well as other sorbents.

2. Materials and methods

2.1 Materials

Natural Resources Authority, Amman, Jordan, supplied the zeolite. It is a phillipsite-rich tuff mined from Aritain area in the northeastern part of Jordan. The chemical composition of the zeolite is given in Table I. The mineral was crushed using jaw crusher, sieved using standard ASTM sieves to obtain size fractions in the range 355-1,000 μm , treated with a salt solution of NaCl (Arab Potash Company with purity of

Table I.
Chemical composition
of zeolite

| Chemical compound | Weight (%) |
|-------------------------|------------|
| Fe_2O_3 | 11.18 |
| TiO_2 | 2.61 |
| CaO | 8.33 |
| K_2O | 1.61 |
| P_2O_5 | 0.43 |
| SiO_2 | 37.17 |
| Al_2O_3 | 12.41 |
| MgO | 7.25 |
| Na_2O | 2.06 |

99.7 per cent of 25 g/l) for 24 hours (to convert the natural zeolite form to the sodium form (Na-Zeolite)) and then washed by distilled water twice to remove physical impurities. The aqueous ammonia solutions were prepared by dissolving analytical-grade NH_4Cl (Aldrich-UK) into distilled water.

2.2 Experimental setup

2.2.1 Equilibrium (batch) experiments. Equilibrium experiments for the zeolite- NH_4Cl system were conducted at 20° and 30°C. Samples were left for 48 hours in a water-bath shaker with temperature control to ensure that equilibrium was attained. The saturation (sorption) ammonium capacity of the zeolite was determined by using constant initial ammonia concentration (25 and 50 mg/L) or constant zeolite weight (1.0 and 4.0 g).

The procedure of the equilibrium experiments was as follows:

- (1) first series of experiments: the zeolite samples of particle size 500-710 μm weighing (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 g zeolite) were added to solution of constant ammonia concentration (25 mg/L); and
- (2) second series of experiments: constant weight of zeolite samples (4 g) each was added to different ammonia concentrations (15, 25, 50, 75, 90, 100, 150, 200, 250, and 500 mg/L).

2.2.2 Column experiments. Column experiments were conducted in packed bed column. The used apparatus consisted of a bench-mounted glass column of 2.5 cm inside diameter and 100 cm height (column volume = 490 cm^3). The column was packed with a certain amount of zeolite to give the desired bed height. The feeding solution was supplied from a 30 l plastic container at the beginning of each experiment and fed to the column down-flow through a glass flow metre having a working range of 10-280 ml/min.

The tested variables were the particle size, the bed depth or amount of zeolite, the flow-rate, the initial ammonium concentration, and the pH of the solution as shown in Table II.

2.2.3 Analysis. Samples from equilibrium experiments and continuous column effluent were withdrawn at pre-determined time intervals and the NH_4^+ ions were analysed by colorimetry. The solution containing ammonium was first reacted with Nessler reagent and then tested by a spectrophotometer (Bausch & Lomb Spectronic) at 20°C. Concentrations were then expressed as nitrogen ($\text{NH}_4^+\text{-N}$). Details are found elsewhere (APHA, 1995; Mashal *et al.*, 2002).

3. Results and discussion

3.1 Equilibrium study for ion exchange isotherms

The results were fitted to the Langmuir and Freundlich isotherm. Equation (2) represents Langmuir isotherm:

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

where K_L is the adsorption equilibrium constant, C_e the equilibrium aqueous concentration, q_e the amount adsorbed, and q_{\max} the maximum monolayer adsorption capacity (per unit mass of adsorbent) for a given system at given temperature.

Table II.
Column study
experiments

| Particle size fraction Dp in (μm) | Bed depth (cm) or zeolite weight (g) | Solution flow rate Fin (ml/min) | Ammonia initial conc. Co in (mg/L) | pH of solution at $T = 19^\circ\text{C} \pm 1^\circ\text{C}$ |
|---|---|------------------------------------|---------------------------------------|---|
| 500-710 710-850 850-1,000 | 20 cm or 106 g | 100 | 25 | 5.5 |
| 500-710 | 10 cm or 53 g 20 cm or 106 g 30 cm or 156 g 40 cm or 206 g | 100 | 25 | 5.5 |
| 500-710 | 20 cm or 106 g | 100 150 200 250 | 25 | 5.5 |
| 500-710 | 20 cm or 106 g | 100 | 15 25 35 50 | 5.5 |
| 500-710 | 20 cm or 106 g | 100 | 25 | 5.5 7.0 9.0 |

Langmuir equation (Equation (2)) can be linearized using Langmuir linear regression as follows:

$$C_e/q_e = C_e/q_{max} + 1/q_{max}K_L \quad (3)$$

Therefore, by plotting C_e/q_e vs C_e at different operating temperatures, a straight line is obtained with a slope equal to $1/q_{max}$ and an intercept, which is equal to $1/q_{max}K_L$ as shown in Figures 1(a) and 2(a). It is clear that the NH_4^+ ion exchange data fitted to the linear Langmuir model.

The Freundlich isotherm has the following form:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is a capacity factor, the amount adsorbed at unit concentration, that is, at 1 mg/L. and n is an intensity parameter (Weber, 1972).

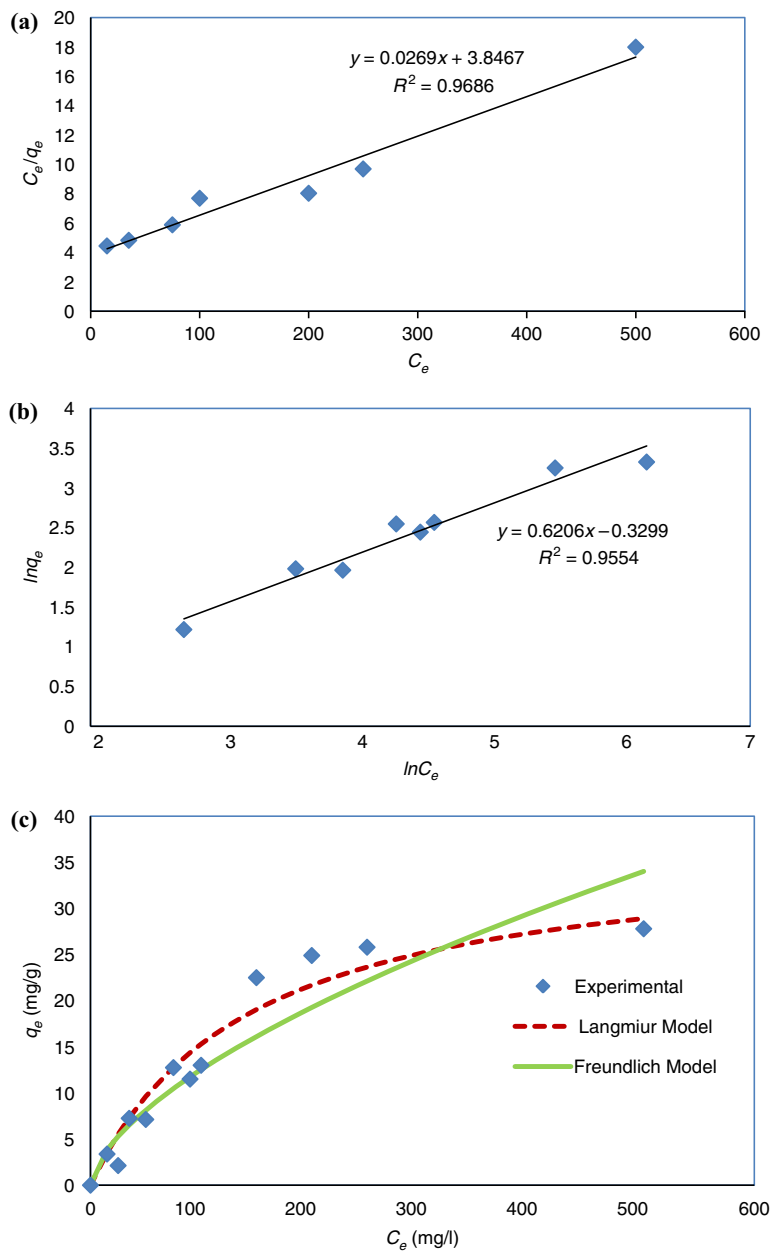
By plotting $\ln q_e$ vs $\ln C_e$ at different operating temperatures, a straight line is obtained with a slope equal to $1/n$ and an intercept equal to $\ln K_F$ as shown in Figures 1(b) and 2(b). It is clear that the NH_4^+ ion exchange data fitted to the linear Freundlich model.

The equilibrium isotherm for the sodium-saturated zeolite in ammonium chloride solutions was constructed from the batch equilibrium tests. The equilibrium relationships for Na-zeolite in NH_4Cl solutions are represented by the following equations.

Langmuir model at 20°C , Equation (5), and at 30°C , Equation (6):

$$q_e = \frac{0.26C_e}{1 + 6.99 \times 10^{-3}C_e} \quad (5)$$

$$q_e = \frac{1.27C_e}{1 + 0.0347C_e} \quad (6)$$



Notes: (a) Linearized Langmuir isotherm; (b) Linearised Freundlich isotherm; (c) Comparison of the Freundlich and Langmuir adsorption isotherms

Figure 1.
Adsorption isotherms for
ammonium removal by
Jordanian zeolite at 20°C

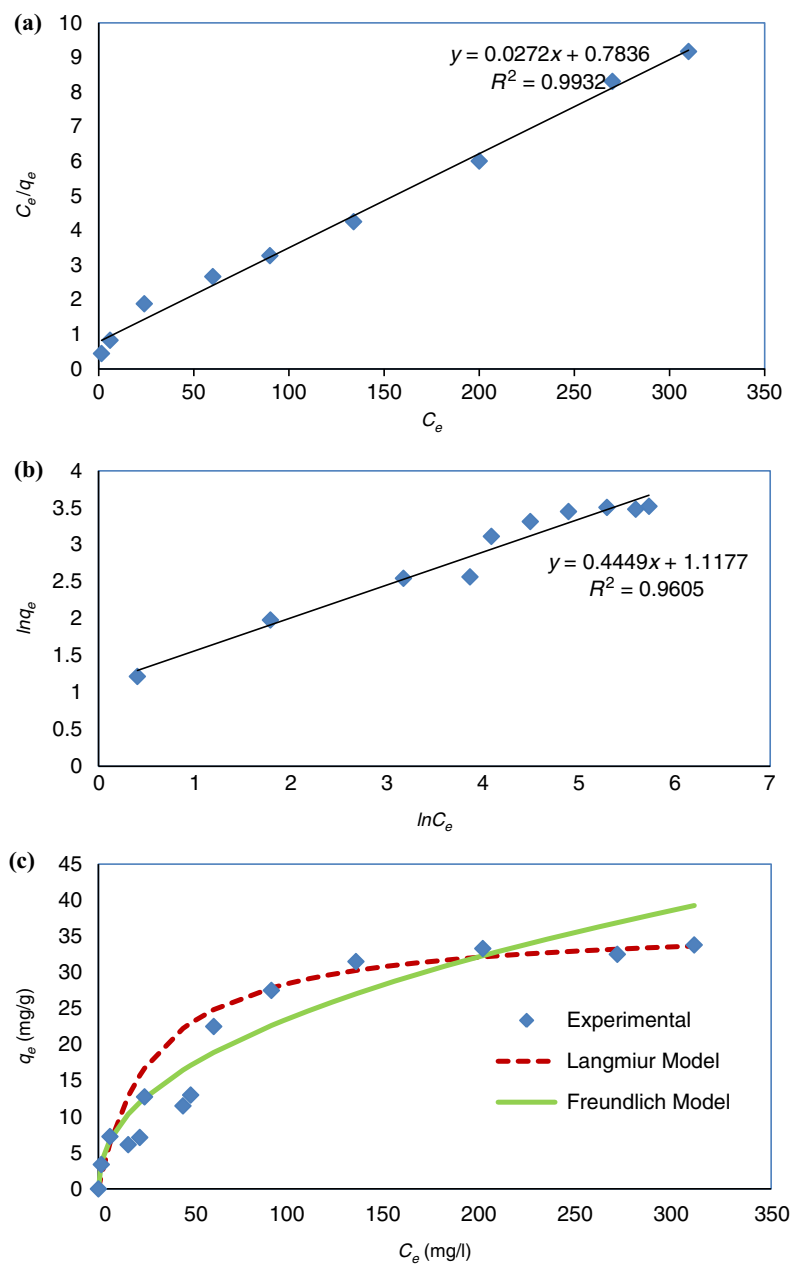


Figure 2.
Adsorption isotherms for
ammonium removal by
Jordanian zeolite at 30°C

Notes: (a) Linearised Langmuir isotherm; (b) Linearised Freundlich isotherm;
(c) Comparison of the Freundlich and Langmuir adsorption isotherms

Freundlich model at 20°C, Equation (7), and at 30°C, Equation (8):

$$q_e = 0.719C_e^{0.621} \tag{7}$$

$$q_e = 3.058C_e^{0.445} \tag{8}$$

Fixed-bed study
of ammonia
removal

The values of the Langmuir and Freundlich constants for ammonium removal using Jordanian zeolite are given in Table III.

In Figures 1(c) and 2(c), the experimental data are compared to the predictions of the above equilibrium isotherm models. It is clear that the NH_4^+ ion exchange data fitted Langmuir and Freundlich models, but the Langmuir isotherm gives an adequate correlation coefficient value compared to the Freundlich isotherm correlation isotherm. This agrees with results of Saltali *et al.* (2007) who investigated the removal efficiency of ammonium (NH_4^+) ion from aqueous solution using the natural Turkish zeolite. They found that the equilibrium modelling data fitted to linear Langmuir and Freundlich models.

Table IV presents the sorption capacity of some zeolites from different locations. It appears that the Jordanian zeolite presents promising exchange capacity for ammonium ion compared to some commercial zeolites from several locations around the world. The ultimate sorption capacity of zeolite obtained from the equilibrium isotherm experiments under operating conditions tested in this study is 28 mg $\text{NH}_4\text{-N/L}$ (2.0 meq/g) at 20°C, and 32 mg $\text{NH}_4\text{-N/L}$ (2.28 meq/g) at 30°C.

| | | | |
|-------------------|------------------------|-----------------------|----------------------|
| <i>Langmuir</i> | | | |
| <i>T, °C</i> | <i>q_{max}</i> | <i>K_L</i> | <i>R²</i> |
| 20 | 37.175 | 6.99×10^{-3} | 0.969 |
| 30 | 36.765 | 0.0347 | 0.993 |
| <i>Freundlich</i> | | | |
| <i>T, °C</i> | <i>K_F</i> | <i>1/n</i> | <i>R²</i> |
| 20 | 0.719 | 0.621 | 0.955 |
| 30 | 3.058 | 0.445 | 0.961 |

Table III.
Langmuir and Freundlich
parameters for NH_4 on
Jordanian Zeolite

| Type of zeolite | Country | Equilibrium sorption capacity | |
|---|-----------|---------------------------------|---------------------------------|
| | | ($\text{NH}_4\text{-N}$ meq/g) | Reference |
| Zeolitic-rich tuff (clinoptilolite and mordenite) | Chile | 0.87 | Englert and Rubio (2005) |
| Clinoptilolite tuff | Mexico | 1.53-2.38 | Leva-Ramos <i>et al.</i> (2004) |
| Clinoptilolite tuff (untreated) | Croatia | 1.54 | Rozic <i>et al.</i> (2002) |
| Montmorillonite tuff (untreated) | Croatia | 0.69 | Rozic <i>et al.</i> (2002) |
| Clinoptilolite (raw) | Turkey | 0.68 | Demir <i>et al.</i> (2002) |
| Clinoptilolite (untreated) | Australia | 1.20 | Cooney <i>et al.</i> (1999) |
| Clinoptilolite (Na form) | Australia | 1.50 | Cooney <i>et al.</i> (1999) |
| Clinoptilolite tuff (55% Zeolite) | Hungary | 1.17 | Dwairi (1993) |
| Pure Phillipsite | Jordan | 3.30 | Dwairi (1993) |
| Phillipsite tuff (62% Zeolite) | Jordan | 1.98 | Dwairi (1993) |
| Phillipsite tuff (Na-form) | Jordan | 2.00 | This study |

Table IV.
Ammonium sorption
capacities of zeolites from
different sources at 20°C

3.2 Fixed-bed column study

The breakthrough and the exhaustion times were used mainly to evaluate the performance of the zeolite bed for sorption of ammonium ions. Breakthrough time (t_B) is defined as the time at which the effluent solution from column contains 5 per cent of the initial NH_4 ions ($C_t/C_o=0.05$), which is usually the maximum allowable concentration of pollutant ions in the effluent. Exhaustion time (t_E) is taken as the time at which the effluent contains 95 per cent of the initial NH_4 ions, that is $C_t/C_o=0.95$.

3.2.1 *Effect of particle size.* The plots of breakthrough curves (BTCs) using three different particle size fractions (500-710, 710-850, and 850-1,000 μm) are shown in Figure 3. For any given particle size, ammonium ions concentration in the effluent solution increased steadily approaching $C_t/C_o=1.0$ more rapidly in the case of larger particle sizes. The time needed to reach the break point is longer for a smaller particle size fraction indicating higher sorption capacity of the zeolite bed. This result is because the total surface area increases as particle size decreases. The pore-diffusion resistance also decreases.

For size fraction 500-710 μm , ammonium ions start to appear in the effluent solution after 75 min. Breakthrough and exhaustion times were 90 and 195-min, respectively. For the size fraction 710-850 μm , NH_4 ions start to appear in effluent after 75 min. The t_B and t_E were 85 and 190 min, respectively. For the size fraction 850-1,000 μm , NH_4 ions start to appear in effluent after 60 min. The t_B and t_E were 60 and 165-min, respectively.

This result is in agreement with those of Booker *et al.* (1996), and Demir *et al.* (2002) for NH_4^+ sorption by natural Australian and Turkish zeolites, respectively. The trend is also consistent with the results of Al-Haj-Ali and Al-Hunaidi (2004) for sorption of lead ions by Jordanian zeolite. Huang *et al.* (2010) studied the removal of ammonium ion from aqueous solutions using natural Chinese zeolite. Their kinetic analysis showed that the adsorption of ammonium on zeolite at different ranges of particle size followed the pseudo-second-order model and followed the intra-particle diffusion model only during the initial 60 min of the adsorption process.

3.2.2 *Effect of bed depth.* BTCs obtained for different bed heights (10, 20, 30, and 40 cm) are shown in Figure 4. For any bed depth, ammonium ion concentration in the effluent approaches $C_t/C_o=1.0$ more rapidly in the case of low bed depths, indicating column exhaustion. The time needed for the fixed-bed of zeolites to reach the saturation

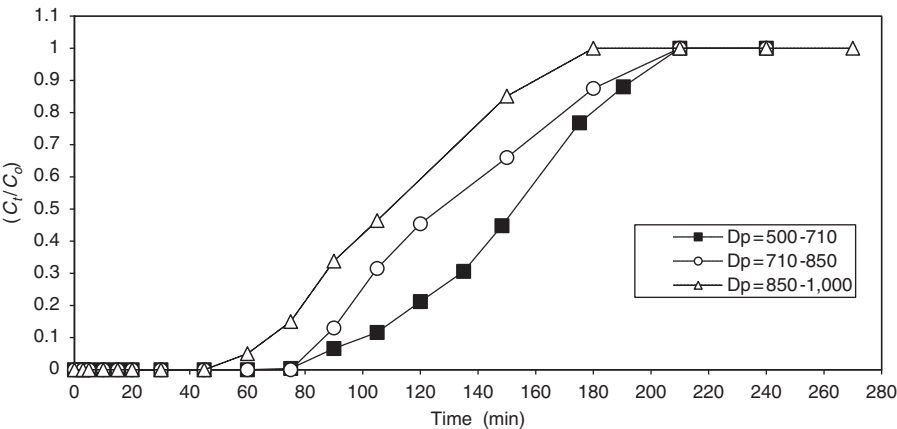
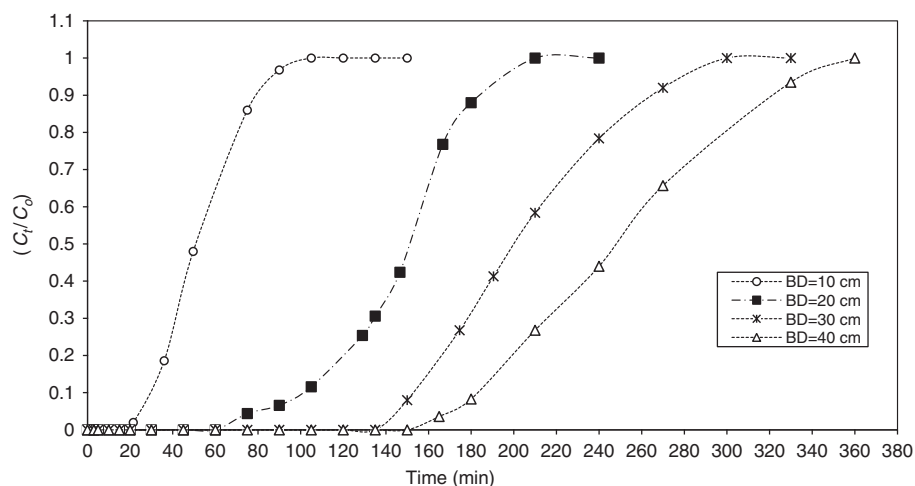


Figure 3.
Breakthrough curve for
 NH_3 sorption on Jordanian
natural zeolite for different
particle sizes

Notes: $F=100\text{ mL/min}$, $\text{BD}=20\text{ cm}$, $C_o=25\text{ mg/L}$, $\text{pH}=5.5$, $T=20^\circ\text{C}$



Notes: $F=100$ ml/min, $C_0=25$ mg/l, $\text{pH}=5.5$, $T=20^\circ\text{C}$

Figure 4.

Breakthrough curve for NH_3 sorption on Jordanian natural zeolite for different bed depths

concentration increased with bed depth, which is proportional to the amount of zeolite in the column. For the lowest bed depth of 10 cm, ammonium ions start to appear in the effluent solution after 15 min. Break-through and exhaustion times were 25 and 90 min, respectively. For a bed depth of 20 cm, NH_4 ions start to appear in the effluent after 75 min. Here break-through and exhaustion times were 90 and 195 min, respectively. As for bed depth of 30 cm, the NH_4 ions start to appear in effluent after 135 min with break-through and exhaustion times increasing to 145 and 280 min, respectively. For the highest bed depth of 40 cm, NH_4 ions start to appear in effluent after 150 min with the times further increasing to 165 and 340 min (5.7 hours), respectively.

3.2.3 Effect of flow. Figure 5 shows the BTCs obtained at different solution flow-rates (100, 150, 200, and 250 ml/min). It can be noted that as the flow-rate decreases, the BTC became drawn-out indicating better sorption capacity. The time required to reach the breakpoint increases with the decrease of feed flow-rate.

The best performance was obtained using the lowest flow-rate of 100 ml/min. This is explained by the greater contact time between ammonium ions and zeolite particles in the bed, which leads to higher removal of NH_4 ions. At this flow-rate, NH_4 ions start to appear in the effluent solution after 75 min. Here break-through and exhaustion times were 90 and 195 min, respectively.

At low flow-rates, the sorption rate is controlled by external diffusion. By increasing the flow-rate, the time needs for the liquid to transfer to the surface decreased, the controlling step of sorption becomes internal diffusion within the pores so to eliminate internal diffusion limitations in all flow experiments, particle size of $500\text{--}710\ \mu\text{m}$ were used. For flow-rate of 150 ml/min, NH_4 ions appear in effluent solution after 30 min with break-through and exhaustion times of 40 and 90 min, respectively. For flow-rate 200 ml/min, NH_4 ions appear in effluent after 15 min. The t_B and t_E are 20 and 70 min, respectively. For highest flow-rate 250 ml/min, NH_4 ions appear very rapidly in the effluent. The t_B and t_E are 15 and 50 min, respectively, which is a short breakpoint for the bed. This trend is consistent with the findings of other researchers in similar studies (Booker *et al.*, 1996; Lin and Wu, 1996).

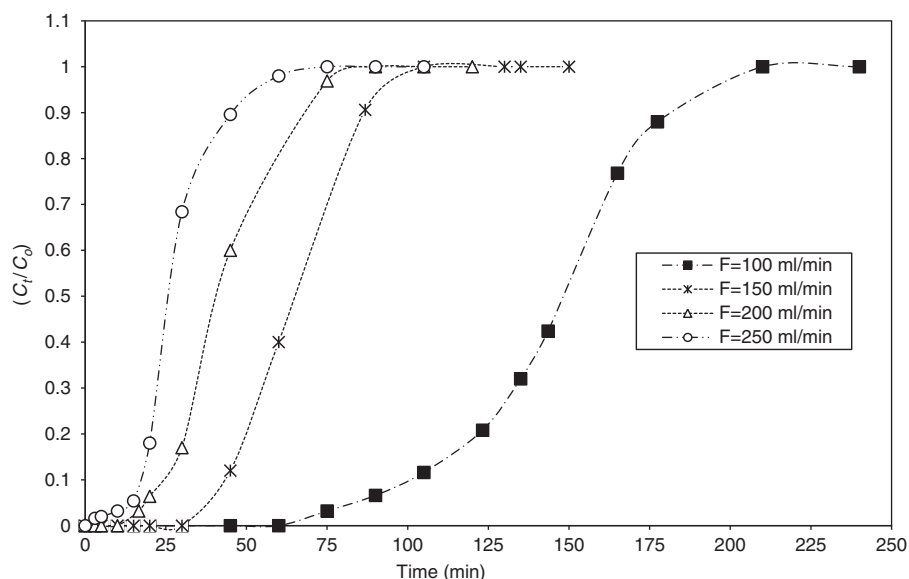


Figure 5.
Breakthrough curve for
 NH_3 sorption on Jordanian
natural zeolite for different
flow-rates

Notes: BD=20 cm, $D_p=500-710 \mu\text{m}$, $C_o=25 \text{ mg/l}$, $\text{pH}=5.5$, $T=20^\circ\text{C}$

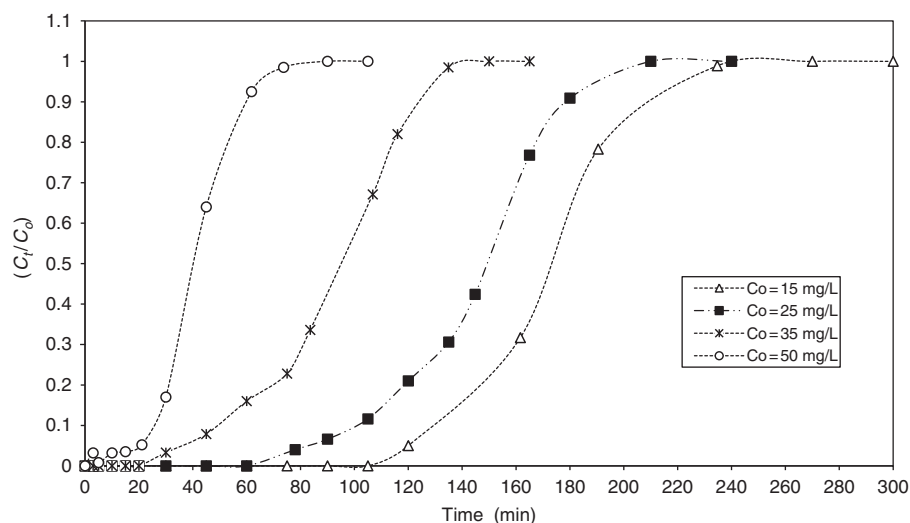
3.2.4 Effect of initial ammonia concentration. Figure 6 shows the BTCs at different initial ammonium concentrations (15, 25, 35, and 50 mg/l). When the initial NH_4^+ concentration decreased from 50 to 15 mg/l, the BTC shifted to the right indicating higher sorption capacity. When a high initial concentration of ammonia is used, the BTC is sharp and steep indicating fast exhaustion of the bed. The time needed to reach the breakpoint increased with decreased initial ammonia concentration in the solution.

For the initial NH_4^+ concentration of 15 mg/l, ammonium ions start to appear in the effluent solution after 100 min. Break-through and exhaustion times were 120 and 220 min, respectively. For initial NH_4^+ concentration of 25 mg/l, NH_4 ions start to appear in effluent after 75 min. Break time and exhaustion times are 90 and 195 min, respectively. For the initial concentration of 35 mg/l, ammonium ions start to appear in the effluent after 20 min. The t_B and t_E are 35 and 130 min, respectively. For initial concentration of 50 mg/l, ammonium ions start to appear in effluent immediately after contact. The t_B and t_E are 20 and 65 min, respectively. This also agrees with the results of Lin and Wu (1996) on uptake of ammonium ions by commercial ion exchange resins.

3.2.5 Effect of pH of the solution. The column experiments were conducted at different pH (5.5, 7, and 9). The pH of the solution was adjusted to the required value by controlling the amount of hydrochloric acid to decrease the pH or sodium hydroxide to increase the pH.

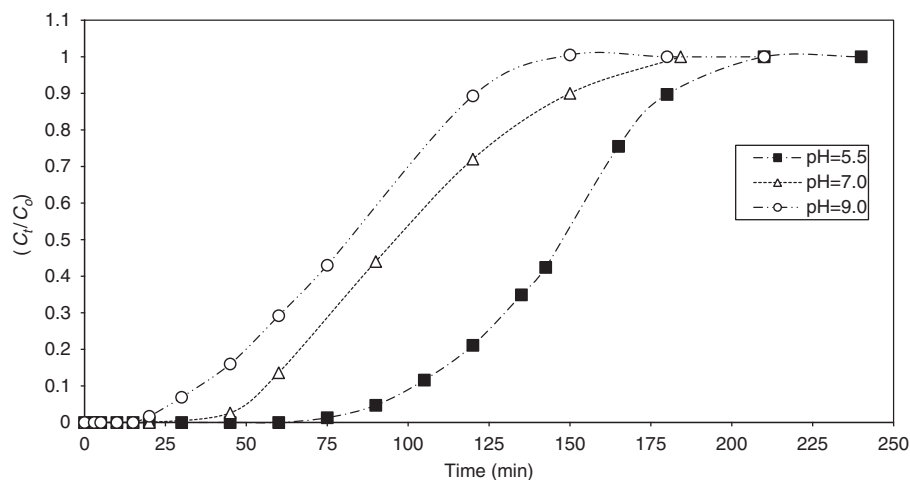
The zeolite adsorption is affected by the acidity of the media. As shown in Figure 7 as the pH decreases, the BTC shifts further to the right indicating higher sorption capacity. At a higher pH, BTCs become sharp and steep S-shape, which is characteristic of rapid exhaustion of the bed. This can be attributed to a decrease of acid sites density in which decrease the acid adsorption site.

The break and exhaustion times at different pH are presented in Table V. For pH 5.5, NH_4 ions appear in effluent solution after 75 min. Break and exhaustion times were 90 and 195 min, respectively. For pH 7.0, NH_4 ions appear in the effluent



Notes: $F = 100$ ml/min, $BD = 20$ cm, $D_p = 500-710 \mu\text{m}$, $\text{pH} = 5.5$, $T = 20^\circ\text{C}$

Figure 6.
Breakthrough curve for
 NH_3 sorption on Jordanian
natural zeolite for different
ammonia concentrations



Notes: $F = 100$ ml/min, $BD = 20$ cm, $D_p = 500-710 \mu\text{m}$, $C_0 = 25$ mg/l

Figure 7.
Breakthrough curve for
 NH_3 sorption on Jordanian
natural zeolite for different
pH

| pH | NH_4 ions appearing time | Break time | Exhaustion time |
|-----|-----------------------------------|------------|-----------------|
| 5.5 | 75 | 90 | 195 |
| 7.0 | 30 | 50 | 165 |
| 9.0 | 15-20 | 25 | 130 |

Table V.
The break and exhaustion
time at different pH

solution after 30 min. Break and exhaustion times were 50 and 165 min, respectively. At the high pH of 9.0, NH_4 ions appear in effluent solution rather quickly (after 15-20 min). Break and exhaustion times were 25 and 130 min, respectively. This result is in agreement with the findings of Lin and Wu (1996) who reported that the optimum ion exchange operation for ammonia removal by a commercial ion exchange resin requires an initial pH of the aqueous solution at or below 7.

4. Conclusions

Ammonium ion exchange by natural Jordanian zeolite data were fitted by Langmuir and Freundlich isotherms. Continuous sorption of ammonium ions by natural Jordanian zeolite tuff has proven to be effective in decreasing concentrations ranging from 15 to 50 mg $\text{NH}_4\text{-N/L}$ down to levels below 1 mg/l. Breakthrough time increased by increasing the bed depth as well as decreasing zeolite particle size, solution flow-rate, initial NH_4^+ concentration and pH. Sorption of ammonium by the zeolite under the tested conditions gave the sorption capacity of 28 mg $\text{NH}_4\text{-N/L}$ at 20°C, and 32 mg $\text{NH}_4\text{-N/L}$ at 30°C.

The equilibrium data of the sorption of Ammonia were plotted by using the Langmuir and Freundlich isotherms, then the experimental data were compared to the predictions of the above equilibrium isotherm models. It is clear that the NH_4^+ ion exchange data fitted better with Langmuir isotherm than with Freundlich model and gave an adequate correlation coefficient value.

For the design purpose at the industrial scale, the following parameters are the best values that are recommended: the zeolite particle size fraction (500-710 μm), solution flow-rate (100 ml/min), initial NH_4^+ concentration (25 mg/l) and pH (5.5).

More industrial scale experiments with different additives are recommended to be done and full design of filter unit of zeolite to be used as a sample model in the real world. We were specifically investigating synthetic aqueous wastewater than the industrial. The fact that this is essentially a waste and the treatment improves the environmental aspects for the refinery industry.

Note

1. www.nra.gov.jo/index.php?option=com_content&task=view&id=41

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