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Ammonium Removal From Water by Eight Natural Zeolites: A Comparative Study

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Abstract: Removal of low-concentration ammonium by eight commercial natural zeolites was studied in batch and continuous tests. In the batch and continuous tests, chabazite was superior to the other natural zeolites in removing low-concentration ammonium. In the batch tests, the ammonium adsorption capacity (up to 32.4 mg NH_4^+/g) decreased with increasing particle size (355 to 2500 µm), pH (7.5 vs. 9.0), and the temperature (279 vs. 295 K) and potassium ion concentration (20 and 100 mg K^+/l). In continuous column tests, the adsorption capacity of chabazite was 48.3 mg NH_4^+/g zeolite. Four clinoptiolites had an adsorption capacity of 15.7 to 25.0 mg NH_4^+/g zeolite. The zeolites were rapidly regenerated by an alkaline sodium chloride solution fed to the columns.

Keywords: Adsorption; Ammonium; Chabazite; Clinoptiolite; Natural zeolites

INTRODUCTION

The removal of ammonia by ion exchange on zeolites has been described by several authors (1–3), for a review, see e.g. (4). Natural zeolites are hydrated aluminiosilicates with a three-dimensional structure and high adsorption capacity. More than 50 different species of this mineral group have been identified (4). Some important zeolite minerals are clinoptilolite, chabazite, erionite, and mordenite. The substitution of Si^{4+} by Al^{3+} increases the negative charge of the mineral lattice. The negative charge is balanced by cations like Na^+, K^+, and Ca^{2+}, which are exchangeable

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with other cations such as NH_4^+. Theoretical cation exchange capacities (CEC) have been calculated for different zeolites, and these are used to estimate their ammonium exchange capacity (Table 1).

The removal of ammonium by ion exchange on zeolites is affected by the type of zeolites, the target and the competing cation concentration, pH, temperature, retention time, and particle size of the applied zeolites. Ames ranked the selectivity of different cations on clinoptiloite as follows (7–9):

$$Cs^+ > Rb^+ > \mathbf{K^+} > \mathbf{NH_4^+} > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$$

Breck (10) proposed a selectivity order for chabazite as follows:

$$Ti^+ > \mathbf{K^+} > Ag^+ > Rb^+ > \mathbf{NH_4}^+ > Pb^{2+} > Na^+ = Ba^{2+} > Sr^{2+} > Ca^{2+} > Li^+$$

Lahav and Green (11) proposed another selectivity order for chabazite:

$$\mathbf{K^+} > Ca^{2+} > \mathbf{NH_4}^+ >> Na^+ > Mg^{2+}$$

The selectivity series indicates that potassium cations are the most important competing ions compared to ammonium for ion exchange by clinoptiloites and chabazite. Thus the content of potassium cations in aqueous solutions will affect the ammonium removal by ion exchange.

The European Union has defined ammonium as an indicator parameter for drinking water at 0.5 mg/l (12) and recommends the monitoring

Table 1. Chemical formula and theoretical cation exchange capacities of some natural zeolite minerals

Zeolite	Chemical formula	CEC (meq/g)[a]	Theoretical cation exchange capacity (mg/g)[b]	
			NH_4^+	K^+
Chabazite	$(Na_6K_6)(Al_{12}Si_{24}O_{72}) * 40H_2O$	3.86	72.1	150.9
Clinoptilolite	$(Na_3K_3)(Al_8Si_{40}O_{96}) * 24H_2O$	2.22	41.5	86.4
Erionite	$(Na_3Ca_3K_2)(Al_9Si_{27}O_{72}) * 27H_2O$	3.16	59.0	123.4
Mordenite	$(Na_8)(Al_8Si_{40}O_{96}) * 24H_2O$	2.91	54.4	113.6

[a] CEC: cation exchange capacities [5].
[b] [6].

of ammonium in water (13). One source of ammonium in water bodies is the discharge of water from mines, where explosives based on ammonia nitrate are used (14–17). In a survey of mine waters at three operating mines the content of NH_4^+ and K^+ in water samples was 2–30 mg/l and 15–225 mg/l, respectively (unpublished results). The observed pH of 8 at the three mines is favorable for adsorption of ammonium (14), since at this pH the ammonium species make up 90% of the ammonia-nitrogen (18). Furthermore, the temperature of waste water is often low as it is in the case of mine water. Thus, the effect of temperature on ammonium exchange is of interest. So far, the results published on the temperature-dependence of ammonium removal by natural zeolites are ambiguous (1). In most water treatment processes the removal of ammonium will target dilute aqueous solutions, whereas many continuous ammonium adsorption studies have focused on high ammonium concentrations (19). Furthermore, adsorption studies in relation to mineralogical composition of zeolite samples are scarce (21,22). The aims of this study are to compare eight commercial natural zeolite based on their mineralogical composition and their ability to remove low concentrations of ammonium from water in the presence of competing potassium ions.

MATERIALS AND METHODS

Natural Zeolite Samples

Eight commercially available the natural zeolites of different particle size distribution were received from the suppliers. The chemical compositions of the samples were given in Table 2. Since natural zeolites were only to be used in the Na-form, the zeolites were conditioned in 3% NaCl for 3 hours on a shaking table at 200 rpm. The samples were rinsed with deionized water and dried at 105°C to reduce treatment time since the drying temperature has only slightly effect on ammonium adsorption capacity (19,23).

Batch Adsorption Tests

For the batch tests twelve synthetic aqueous solutions were prepared with 5, 50, or 500 mg NH_4^+/l, 10 or 200 mg K^+/l and a pH of 7.5 or 9.0. In batch tests 0.5 g of dry zeolite was put into glass bottles, with a volume of 1 l for 5 mg NH_4^+/l and 0.1 l for 50 and for 500 mg NH_4^+/l. The chosen potassium concentration and pH range were based on monitoring results of mine water (14). The bottles were placed in an orbital shaker and shaken at 150 rpm, overnight at temperatures of 279 and 295 K.

Table 2. Chemical composition of the eight natural zeolites as published by the supplier

Sample code	Mesh size[a]	Origin	Main zeolite mineral	Si/Al	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Fe_2O_3	MgO
1	14 × 40	USA	Clinoptilotie	5.6	67.4	10.6	2.23	4.19	0.59	1.7	0.45
2	8 × 14										
3	14 × 40	USA	Clinoptilotie	4.5	64.7	12.6	3.3	3.3	0.9	1.8	1.0
4	16 × 50	USA	Clinoptilotie	ng	ng	ng	ng	ng	ng	ng	ng
5	4 × 8										
6	20 × 35										
7	8 × 14	USA	Chabazite	3.7	69.5	16.6	4.49	1.32	2.40	4.33	0.89
9	8 × 14	USA	Clinoptilotie	5.6	66.03	10.47	1.55	1.81	3.25	1.12	0.58
11	14 × 40										
12	14 × 40	USA	Clinoptilotie	ng	ng	ng	ng	ng	ng	ng	ng
14	ng	Turkey	Clinoptilotie	5.3	71.0	11.8	3.4	2.4	0.4	1.7	1.4
15	ng	Europe	Clinoptilotie	5.1	70.78	12.34	2.80	2.41	1.48	0.92	0.67

ng: not given by supplier.

[a] mesh size indicated as by supplier.

Continuous Adsorption Tests

After the batch tests, the natural zeolites 1, 7, 11, 12, and 14 with sufficiently available mass of the particle size fraction 500 to 710 µm were further studied in continuous tests. The zeolites were put into in individual glass columns, with a length of 500 mm and diameter of 20 mm, and made up a bed volume of 140 ml (mass of fill from 73.9 to 135.4 g). The columns were fed in up-flow mode with a synthetic aqueous solution, containing 4.5 mg NH_4^+/l, made up with deionised water. The applied column flow rate of 5 ml/min ensured good resolution of the sorption kinetics. The pH and ammonium concentration were monitored. The columns were operated at 295 to 296 K over 107 days. The columns were regenerated by feeding a solution of 29.2 g/l NaCl at pH 9.3 and 25 ml/min to each column. The flow rate was chosen after initial flow tests to avoid fluidization of the bed.

Analyses

The zeolite samples were analysed by sieving for their particle size distribution (sieves 355, 500, 710, 1000, 1250, 1400, 2000, 2500, 2800, 3550, 4000, and 5600 µm). Sample 14 was received as coarse material and required crushing prior to sieve analysis. Since sample 15 was obtained as three different fractions of small amounts, the composite was used. The mineralogical analysis of the zeolite samples as-received was carried out by Mineral Liberation Analysis (MLA), which is an image analysis system based on Scanning Electron Microscopy (Quanta 600, FEI Ltd.) and double detector energy dispersive X-ray analysis (JKTech Pty Ltd.) (24). The elemental composition of the zeolites was determined by X-ray fluorescence spectrometer (Axios model, PANalytical Ltd.). The content of ammonium before and after the tests was analysed by standard colorimetric assays (LCK kits, HACH Dr. Lange Ltd.).

RESULTS

Characterization of the Natural Zeolites

The particle size d80 of the samples as received was between 910 and 1950 µm (Table 3), excluding sample 14 which had to be crushed prior to use. The particle size distribution of the zeolites was as shown in Fig. 1. The measured elemental composition of the natural zeolites as received differed from the information provided by the suppliers (Table 2 and 3). The Si/Al ratio of the aluminosilicates was lower for

Table 3. Chemical composition as analysed by X-ray fluorescence spectroscopy and particle size d80 of the eight natural zeolites

Sample code	Particle size d80 (µm)	Si/Al	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	FeO	MgO
1	1180	5.3	71.6	11.9	2.66	4.75	0.27	2.29	0.77
2	1950								
3	980	4.5	69.8	13.7	3.45	2.64	0.51	1.71	1.62
4	1150	5.2	71.5	12.1	1.44	4.24	3.77	1.35	0.81
5	1250								
6	910								
7	1350	3.2	60.4	16.6	0.53	1.15	8.38	2.98	0.82
9	1850	4.9	71.6	12.9	1.94	1.94	3.45	0.99	0.74
11	1100								
12	1340	5.3	71.8	12	2.86	4.34	0.47	2.3	0.74
14	2550	5.0	71.6	12.6	3.57	2.64	0.39	1.22	1.03
15	1500	5.0	73	12.8	2.96	3.04	0.36	1.26	0.001

the samples as received compared to suppliers information (Table 3), indicating a smaller net charge and amount of counterions. The natural zeolites made up between 83 and 95% of the mineral composition as analysed by MLA, including minor amounts of erionite (sample 7 with 8.8%) and mordenite (sample 3, 11, and 14 with up to 13.3%) (Table 4). Furthermore, the samples contained mica clay minerals (1.2–14.1%), feldspars (0.2–6.5%) and quartz (up to 9%) (Table 4).

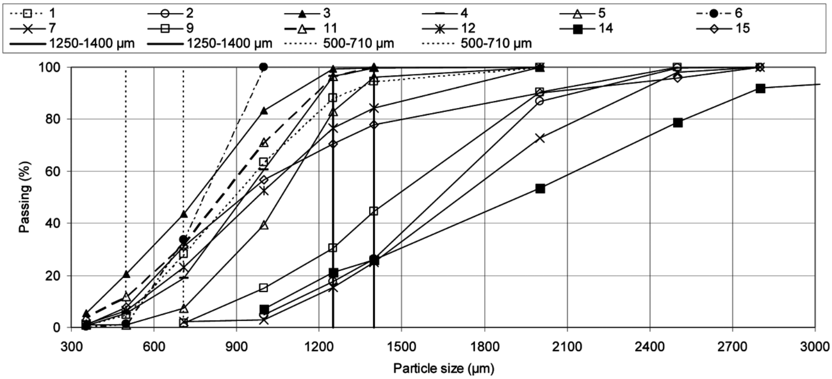

Figure 1. Particle size distribution of zeolites. Vertical dashed and solid lines indicate the particle fraction 500–710 µm used in continuous tests and 1250–1400 µm used in batch tests, respectively.

Table 4. Modal mineralogical composition of natural zeolites analysed by mineral liberation analysis

	Sample code							
Mineral	1	3	6	7	11	12	14	15
Chabazite (Na_2,K_2,Ca,Mg) $(Al_2Si_4O_{12})*6H_2O)$				83.1				
Clinoptilolite $(Na,K,Ca)_6$ $(Si,Al)_{36}O_{72}*20H_2O$	88.5	71.1	91.5	3.3	81.2	82.6	83.6	92.6
Erionite $(K_2,Ca,Na_2)_2$ $Al_4Si_{14}O_{36}*15H_2O$				8.8				
Mordenite (Ca,Na_2,K_2) $Al_2Si_{10}O_{24}*7H_2O$		12.7			13.3		6.5	
Quartz	1.4	2.3	0.8		1.6	2.2	2.3	1.4
Feldspars	0.7	2.7	0.4	0.2	2.5	0.6	2.7	1.3
Clinopyroxene			0.1					
Hornblende	0.1	0.1	0.1					
Fe-silicate	0.1	0.1		0.5		0.1	0.3	
Mica-clay minerals	8.8	10	5.6	3.5	1.2	14	4.3	
Calcite		0.1	0.9			0.1		
Gypsum			0	0.2				
Fluorite	0.1							
Ilmenite		0.1	0					
Goethite	0.1		0.1	0.1				0.01
Talc			0.2					
Plagioclase								4.4
Muscovite								0.2
Unclassified	0.1	0.3	0.2	0.2	0.1	0.3	0.1	0.1
Total (%)	100	100	100	100	100	100	100	100

Batch Adsorption Tests

The effect of particle size on the ion exchange kinetics was tested with different particle size fractions of the same zeolites (sample 4, 5, 6). The kinetics of ammonium adsorption was greatly affected by particle size, especially during the first 60 min (Fig. 2). Initial ammonium removal was rapid within the first 15 min and the adsorption rate declined after 2 hours (Fig. 2). An increase of potassium concentration and pH negatively affected the ammonium adsorption (Fig. 3). The effect was more

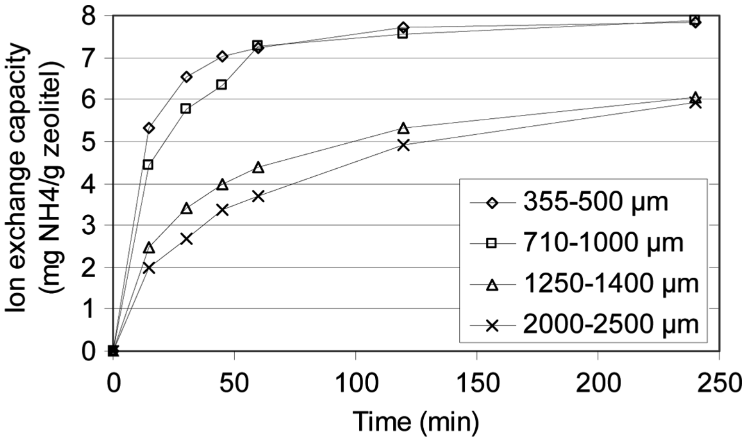

Figure 2. Positive effect of decreasing particle size on sorption kinetics. Zeolite 4, 5 and 6, initial ammonium concentration 50 mg/l.

pronounced at low ammonium concentration, which is of importance for the removal of ammonium from dilute aqeous solutions. The highest measured Q_e value was 32.4 mg/g at 500 mg NH_4^+/l for the chabazite sample 7. In tests with clinoptilolites (500 mg NH_4^+/l, 10 mg K^+/l, pH 7.5) the highest measured Q_e value was 22.8 mg/g with sample 4. The Freundlich adsorption isotherm was applied to determine the adsorption parameters (Eq. 1), since it gave a comparable or better fit than linear (3) and Langmuir adsorption isotherms (3,40). The tested materials can be ranked based on the Freundlich capacity factor K_f as follows: $1 > 7 > 4 > 2 > 15 > 14 > 3 > 12 > 9$.

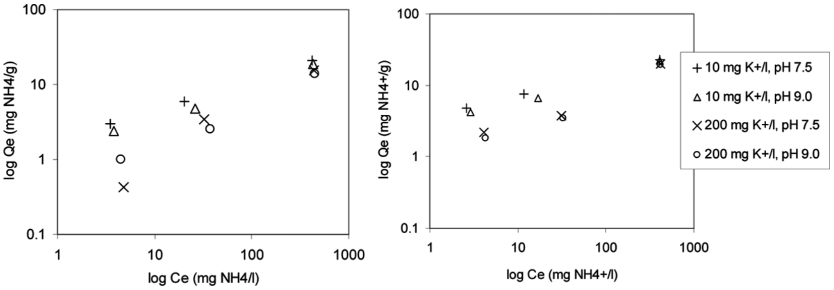

Figure 3. Left sample 1, right sample 4, 5, 6. Negative effect of increasing potassium concentration and pH on Freundlich adsorption isotherms of zeolites (1250–1400 µm, initially 50 mg NH_4^+/l) at 295 K.

The Freundlich parameter 1/n indicates the strength of the adsorption bond. The intensity factor decreased in following order: $4 > 7 > 2 > 14 > 1 > 12 > 3 > 9 > 15$

$$Q_e = K_f C_e^{1/n} \quad \text{or} \quad \log Q_e = \log K_f 1/n \log C_e \tag{1}$$

where Q_e is the mass of adsorbate per unit mass of adsorbent (mg/g)

with C_e equilibrium concentration of adsorbate in solution after adsorption (mg/l)

1/n is the Freundlich parameter called intensity or heterogeneity factor and

K_f is the Freundlich capacity factor

Studies have claimed none (1,26,40), positive (27–29) or negative (25) effects of temperature on adsorption on ammonium onto zeolites in the range of 277 to 343 K. In this study, the ammonium adsorption capacity decreased with temperature (279 and 295 K). The free energy ΔG^0 was calculated based on following formula (Eq. (2)–(4)) (25). The free energy ΔG^0 values ranged from −3.6 to 7.9 and from −2.3 to 8.5 kJ/mol at 279 and 295 K, respectively.

$$\ln K_c = \ln(C_e/C_s) \tag{2}$$

where C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/l)

C_s is the mass of adsorbate adsorbed per liter of solution at equilibrium (mg/l)

$$\ln K_c = (\Delta S^0/R) - (\Delta H^0/RT) \tag{3}$$

where ΔS^0 is catropy, ΔH^0 is enthalpy and R the ideal gas constant

$$\Delta G^0 = -RT \ \ln \ K_c \tag{4}$$

Continuous Adsorption Tests

In the column tests, chabacite (sample 7) proved again to be superior to all other samples (Fig. 4). The calculated exchange capacity of the sample material 7 was 46 mg NH_4^+/g sample material during the column tests over 107 days and almost 6700 bed volumes (Table 5). The column containing sample 7 retained NH_4^+ over the first 80 days, whereas other zeolites like 1, 12, and 14 released NH_4^+ after the first 20 days (Fig. 4). The best clinoptiolite was sample 11, which contained 94.5% zeolites and only 5.5% inert material. The natural zeolites were rapidly regenerated by an alkaline sodium chloride solution (Fig. 6).

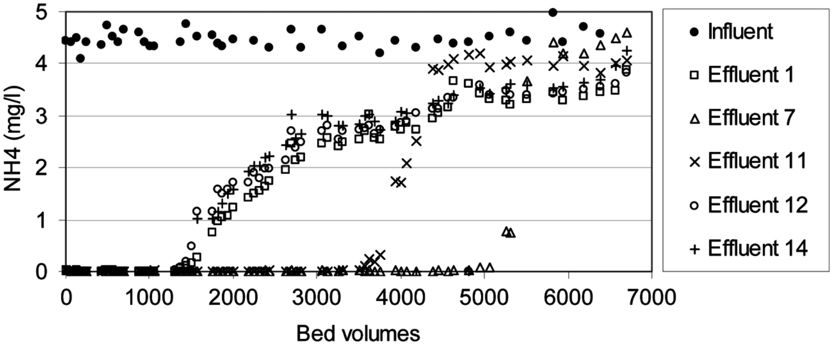

Figure 4. Ammonium concentration in influent and effluent (sample code) of the continuous adsorption columns.

Table 5. Determined ammonium adsorption capacity of natural zeolites in continuous tests. Adsorption capacities were corrected based on mineralogical results (see Table 4)

Initial NH_4^+ concentration in aqueous solution	Adsorption capacity	Normalized adsorption capacity[a]	Theoretical ammonium exchange capacity[b]	Normalized adsorption capacity/ Theoretical ammonium exchange capacity	References (Sample code)
mg NH_4^+-N/l	mg NH_4^+/g sample	mg NH_4^+/g zeolite	mg NH_4^+/g zeolite	%	
4.5	14.8	16.7	36.7	46	This study (1)
4.5	46.0	48.3	66.5	73	This study (7)
4.5	23.6	25.0	39.4	63	This study (11)
4.5	16.3	19.7	34.2	58	This study (12)
4.5	14.1	15.7	37.5	42	This study (14)
17	4.05				[36]
27	4.07				[36]
45	4.47				[36]
34.3	1.78				[37]
16	2				[38]
6	10.2				[20]
5	1.08				[22]
5	7.74				[34]
7.7	16.9				[41]

[a] normalized to zeolites content in samples as based on Table 4.

[b] calculated based on Tables 1 and 4.

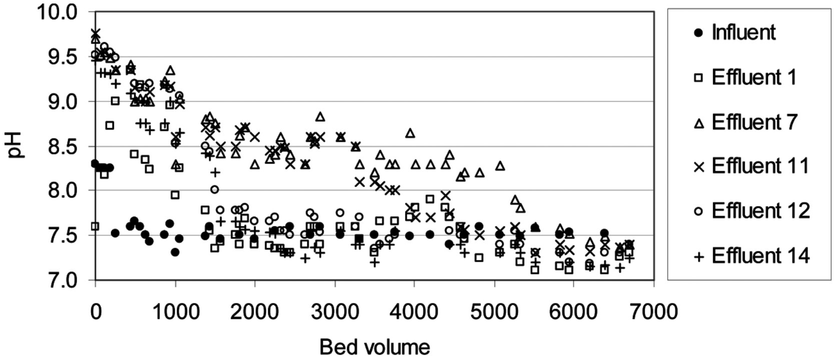

Figure 5. The pH of the influent (about 7.5) and effluent (sample code) of the continuous adsorption columns.

DISCUSSION

This is the first report on comparative studies of commercially available natural zeolite products. The wide particle size distribution of the commercially available natural zeolite products as received indicates that they require further classification prior to application in water treatment processes (Fig. 1). A decrease of particle size positively affected the ammonium adsorption, expressed on a weight/weight basis, by increase of the surface area as earlier reported (19,23) (Fig. 2). Nguyen and Tanner (21) showed that the efficiency of ammonium removal from

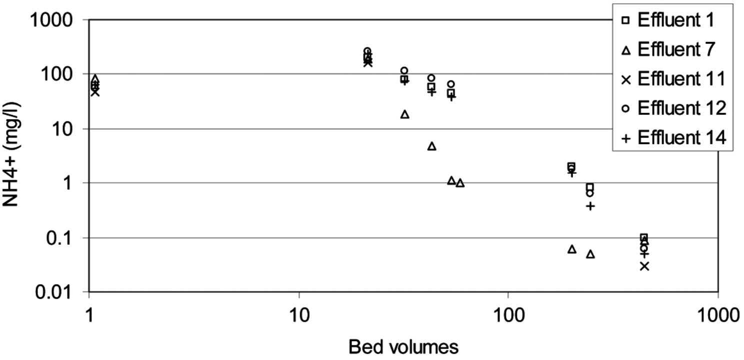

Figure 6. Concentrations of ammonium in the effluent (sample code) of columns during continuous regeneration of zeolites with 29.2 g/l NaCl of pH 9.3 at 1.5 l/h each column. Final pH of the effluent 1, 7, 11, 12, and 14 was 7.2, 6.7, 8.8, 8.8, and 8.7, respectively.

aqueous solutions depends mostly on the type of zeolite used and to a lesser extent on particle size and contact time. The mineralogical analysis of the natural zeolite samples as-received showed that four out of eight samples contained only one zeolite mineral whereas the other four samples contained a mixture of zeolite minerals (Table 4). The main minerals were chabazite in sample 7 and clinoptiolite in samples 1, 3, 6, 11, 12, 13, 14, and 15. The Si/Al ratio is not a straightforward parameter for predicting adsorption capacity, since for example the chabazite sample had only a Si/Al value of 3.2, but showed the highest ammonium adsorption capacity is all tests. The comparison of ammonium sorption capacities of clinoptiolite in batch tests shows that the determined capacities in this study are well in the range of other reports (Fig. 7). Further, the comparison indicates a shortage of studies on ammonium adsorption on clinoptiolite minerals at low ammonium concentration (Fig. 7). In the batch tests, sample 14 from Turkey showed a Q_e value of 20.8 mg/g, while Sariglu (22) measured a Q_e value of 25.9 mg/g for a clinoptilolite sample from Turkey, initially 885 mg NH_4^+/l. As for as the Freundlich isotherm is concerned, the strength of the adsorption bond as indicated by the Freundlich parameters 1/n was similar to other studies (Table 6). The results show that the adsorption bond becomes weaker if the potassium concentration and the pH are increased. The Freundlich capacity factor K_f was up to 7.78 higher than earlier reported (Table 6). However,

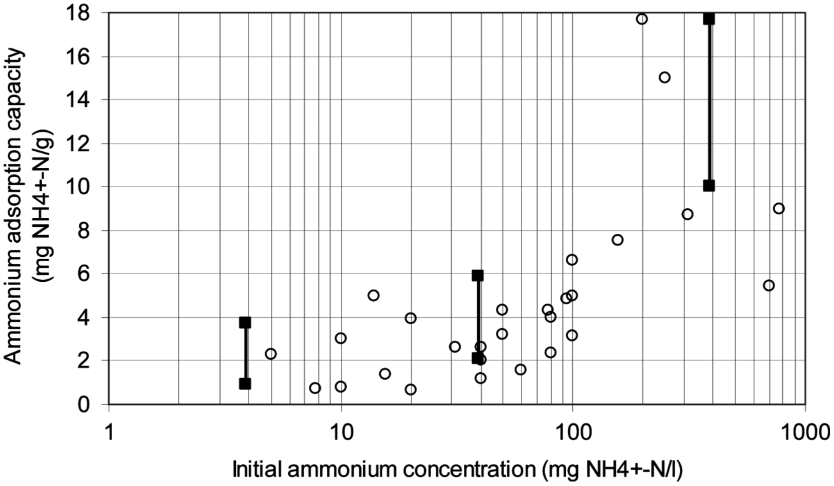

Figure 7. Comparison of sorption capacities of clinoptiolite in batch adsorption tests in this work (vertical bars) and other studies (o) [21, 22, 23, 29, 30, 31, 32, 33, 34, 35, 40].

the correlation between the Freundlich capacity factor K_f of the batch tests and adsorption capacity in continuous tests is minor.

The measured free energy ΔG^0 values varied over a wider range than ΔG^0 values from -0.6 to 0.1 kJ/mol as determined at 298 and 328 K by Karadag et al. (25). Increase in temperature negatively affected the ammonium adsorption capacity in this study and in the tests by Karadag et al. (25). The result indicates that the ammonium adsorption is exothermic; however the effect is rather small and requires more studies especially at low temperatures.

In continuous adsorption tests a diluted aqueous solution of ammonium was used (Fig. 4). The achieved ammonium sorption level of up to 23.6 mg NH_4^+/g of the sample 11 (81% clinoptiolite and 13% mordenite, Table 5) compares well to a capacity of 17.6 mg NH_4^+/g for a sample of 70–75% pure clinoptiolite of same the particle size, but slightly higher flow rate of 6 ml/min (19). However, the initial ammonium concentration in the continuous test was 129 mg NH_4^+/l (19), whereas in this study the feed concentration was ten times lower, i.e. 4.5 mg NH_4^+/l. Wang et al., measured high ammonium adsorption capacities in flow tests with Na-mordenite and low ammonium content in the feed (10 mg NH_4^+/l) and a temperature of 333 K (41). The ion-exchange level was 79% and ammonium adsorption was more strongly affected by the competing ions Ca^{2+} and Mg^{2+} than K^+ and Na^+ (41). Based on the mineralogical results calculated theoretical ammonium exchange capacity was with 34.2 to 39.4 48.3 mg NH_4^+/g zeolite

Table 6. Freundlich model parameters obtained in other studies

K^+ mg/l	pH	Temp. K	Freundlich capacity factor K_f	Freundlich parameter 1/n	Reference
10	7.5	295	1.47^a	0.56^a	This study
nm	nm	nm	0.37	0.72	[40]
nm	nm	nm	0.61	0.54	[31]
nm	nm	nm	2.51	0.24	[23]
nm	nm	293	2.23	0.38	[22]
0	5.5–6.5	285	1.81	0.26	[35]
nm	6.0	nm	1.36	0.28	[34]
0	nm	298	0.61	0.52	[25]
		313	0.44	0.55	
		328	0.40	0.50	

nm: not mentioned.

^{a}average.

similar for all clinoptiolite samples (1,1,12,14). The total amount of the ammonium adsorbed was for all studied zeolite samples less than the theoretically expected amount, i.e. 42 to 73% (Table 5). A comparison of the calculated ratio of observed vs. theoretical adsorption capacity for sample 1 vs. 12, and 11 vs. 14, indicates that the achieved adsorption capacity depends on parameters other than zeolite type alone (see Table 4 and 5). Also the Si/Al ratio can not explain the differences in the measured adsorption capacities (see Table 3 and 5). In this study, the ion-exchange level was highest at 73% for sample 7 (Table 5). The ion-exchange was calculated on a basis of mg NH_4^+/g pure zeolite, i.e. the normalized exchange capacity was 48.3 mg NH_4^+/g zeolite, while the theoretical exchange capacity is 66.5 mg NH_4^+/g zeolite (Table 5). However, in the chabazite column the initial effluent pH of 9.8 decreased much more slowly compared to the other four columns (Fig. 5). Therefore, some of the ammonium might have escaped from the system as ammonia gas, which would result in an overestimation of the exchange capacity. Verkerk and van der Graaf (20) studied earlier a chabazite from the same deposit as sample material 7 and achieved only up to 10.2 mg NH_4^+/g since 75% of adsorption capacity was used by the competing cations such as K^+, Ca^{2+}, Na^+, and Mg^{2+} and only 25% by ammonium. Sarioglu (22) reported for a sample of clinoptiolite and modernite a 60% breakthrough concentration of initial concentration already after 80 bed volumes exchanged (5 mg NH_4^+-N/l, pH 7.5, 0.5 ml/min), while in this study breakthrough occurred only after about 1400 bed volumes exchanged (10.3 mg NH_4^+-N/l, pH 7.5, 5 ml/min) (Fig. 4). Regeneration of zeolites is achieved at pH 10 or higher due to conversion of NH_4^+ to NH_3. The sampling could have been more frequent in the beginning of the regeneration since the ammonium concentration might have peaked within the first 10 exchanged bed volumes as also reported for regeneration of column filled with sample material 7 (20). Other reports also indicate that the peak of ammonium concentration in spent regeneration solution peaks before 5 bed volumes are eluted and rapidly decreases afterwards (2,34,22). This is beneficial for short regeneration cycles. The final pH of the spent regeneration solution was after 444 bed volumes exchanged nevertheless not the same as the pH of the regeneration solution which is contrary to the results of Du et al. (34) and would affect the potential biological treatment of the regeneration brine (39).

CONCLUSIONS

Ammonium adsorption onto natural zeolite depends mainly on the zeolite mineral type. The chabazite containing zeolite was superior to clinoptiolite for the removal of low concentrations of ammonium from water. In the batch tests, the ammonium adsorption capacity decreased with increasing particle size, pH, temperature, and potassium ion concentration. In continuous operations, short regeneration cycles with all natural zeolites can be achieved.

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