Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1025848

57 (2016) 8289–8301
April

Ammonium adsorption from synthetic and real mining wastewaters by eight-clay based adsorbents

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Received 2 June 2014; Accepted 15 February 2015

The main purpose of this study was to examine commercial clay-based adsorbents without modifications for ammonium adsorption and compare their ability to reduce the amount of ammonium from a liquid phase. For the first time, to our knowledge, bentonite, chabazite, clinoptilolite, and phillipsite were tested for ammonium adsorption in the same study. The comparison of the materials was conducted in both simulated and real wastewaters to obtain reliable information about their performance in real conditions. It was found that all the adsorbents possessed ammonium removal capacity, but the amount reduced depended on the pH and other cations present in the examined liquid. Experimental isotherms were compared with the Langmuir, Freundlich, and Sips isotherms. Among these three isotherm models, the best fit was found with the Sips model in all of the cases. It was also observed that zeolite from Sigma–Aldrich had the best maximum ammonium adsorption capacity of the examined adsorbents. All in all, in different conditions, the zeolite and the two chabazites were the best ones to adsorb ammonium.

Keywords: Ammonium; Adsorption; Clay minerals; Zeolite; Isotherms; Mining wastewater; Kinetics; Competition

1. Introduction

The ammonium ion is among the inorganic pollutants in aquatic ecosystems. The ion enables growth of the vegetation and this can lead to a loss of oxygen in lakes and rivers among other things. Therefore, it is an important task to reduce ammonium leakage to aquatic systems.

Traditionally, wastewater treatment consists of chemical and/or biological processes. Nitrogen species are typically removed by biological treatments, where nitrification and denitrification processes take place. By nitrification, ammonium ion is first transformed into nitrite and then into nitrate. This process demands aerobic conditions and the presence of suitable bacteria. Activated sludge process utilizes nitrification–denitrification processes and due to its biological nature there are certain factors, which have an impact on treatment efficiency. These include oxygen level, temperature, pH, the growth of the bacteria, and possible toxins in wastewater [1]. On the other hand, ammonium can also be removed by adsorption (including ion-exchange). This method is not dependent on the biological factors in contrast to denitrification and

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nitrification processes. The used material, adsorbent, also has the potential to be regenerated and reused. This might also reduce the amount of waste coming from the wastewater purification.

There has been a lot of research on different adsorbents for ammonium removal [2–10]. Studied adsorbents were natural zeolites such as clinoptilolites and chabazites, which have shown a good potential for ammonium adsorption. Zeolites are crystalline-hydrated aluminosilicates that have cavities and pores in their structure. They have exchangeable cations on their surface, and therefore can be used for the removal of cationic species from contaminated waters. Clinoptilolite, chabazite, and phillipsite belong to the group of zeolite and each has a slightly different composition [11]. Another potential clay mineral for ammonium removal is bentonite with a crystalline structure and several practical applications as well. On its surface, bentonite also has easily exchangeable cations due to the negative nature of the clay. Therefore, bentonite can be used for ion exchange in a similar way than zeolites. However, properties of bentonite include considerable swelling, which is disadvantageous in adsorption processes [12]. Generally, removal of ammonium by clay minerals can be presented as a cation-exchange reaction as follows:

$$\text{S-Me}^{n+} + n\text{NH}_4^+ \rightarrow \text{S} - n\text{NH}_4^+ + \text{Me}^{n+} \qquad (1)$$

where S is a clay mineral and Me^{n+} an exchangeable cation on its structure [13].

In this study, eight commercial clay-based adsorbents were compared for the ammonium removal. There has been a lot of research done on ammonium adsorption, but to our knowledge, this may at least be one of the first studies to include the comparison of bentonite, chabazite, clinoptilolite, and phillipsite for ammonium adsorption. The comparison of the materials in the same study makes the evaluation of the performances of different materials more reliable. To do this, the study must also include testing of the materials in real wastewaters. It is most likely that competition in the form of other cations exists in wastewaters and it is a necessity to find out how well the studied adsorbents can reduce ammonium despite the competition. Therefore, experiments in this study were done with synthetic ammonium solutions also containing K^+, Mg^{2+}, and Ca^{2+} ions and with real mining wastewaters spiked with ammonium. The effect of pH was also tested. Furthermore, one of the goals was to use non-modified adsorbents, because modifications in larger scale may create extra costs. The regeneration and reuse of the adsorbents was not studied in this case, but there are some earlier studies showing the potential accordingly [2,14,15].

2. Materials and methods

2.1. Materials

Zeolite (Z) and bentonite (B) were obtained from Sigma–Aldrich Finland and clinoptilolite (C) and phillipsite (P) from OTTO Industries Poland. St. Cloud$^{\text{TM}}$ provided samples of two different types of chabazite (CHA and CHAMIX) and clinoptilolite (ZS and ZK). More detailed information about the adsorbents mentioned can be seen in Table 1.

For the purpose of doing adsorption tests with synthetic solutions, different amounts of NH_4Cl (Merck KGaA, >99.8%) were diluted in ultraclear water. Solutions with other cations were made of KCl (Merck KGaA, ≥99.5%), $Cl_2Mg\cdot 6H_2O$ (Sigma–Aldrich, 99.0–102.0%), and $CaCl_2\cdot 2H_2O$ (Riedel-de Haen min. 99%). All the chemicals were used without further purification.

2.2. Methods

High-performance liquid chromatography (HPLC) was used to analyze the amount of ammonium and other cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}). The columns used were Shodex IC YS-50 and IC YS-G. In these columns, methanosulfonic acid (Sigma–Aldrich, ≥99.5%) ($4\,\text{mmol}\,\text{L}^{-1}$) was used as the eluent. Some of the ammonium concentrations were analyzed using spectrophotometric analysis (method ISO 7150:1984) in another laboratory. The used equipment was Aquakem 250 from Thermo Scientific.

The adsorption experiments were conducted at room temperature (21–23°C) and the solid-to-solution ratio was $2\,\text{mg}\,\text{mL}^{-1}$ unless otherwise stated. The adsorption tests were carried out in a shaker for 20–24 h to ensure the establishment of the adsorption equilibrium. Diluted HCl and NaOH were used to adjust the pH to the desired value. The isotherm and kinetic experiments were conducted at pH 6. This pH value was selected for the ease of operation.

Fourier transform infrared spectroscopy (FTIR) was used to analyze the adsorbents both before and after adsorption. Samples were dried to remove humidity at 80°C overnight before the measurements.

2.3. Calculations

The adsorption capacity q_e was calculated with the Eq. (2), where C_o ($\text{mmol}\,\text{L}^{-1}$) is the initial concentration

Table 1
The studied adsorbents

	Named	Origin	Composition	Source/Other information
Nanoclay, hydrophilic Bentonite	B	Sigma–Aldrich	$H_2Al_2O_6Si$	Material safety data sheet, Sigma–Aldrich
Clinoptilolite	C	OTTO industries, Poland	–	The content of clinoptilolite 81–74% (XRD, Phillips X′pert APD diffractometer)
Zeolite	Z	Sigma–Aldrich	SiO_2, Al_2O_3, metallic oxides	Material safety data sheet, Sigma–Aldrich
Phillipsite	P	OTTO industries, Poland	–	Material composition: phillipsite 27%, chabazite 27%, plagioclase 15%, and other impurities (XRD, Phillips X′pert APD diffractometer)
Anhydrous sodium aluminosilicate, natural Herschelite-sodium chabazite	CHA	St. cloud	Two major: SiO_2, Al_2O_3 (Si/Al = 3, 2)	Product data sheet (ZS500), st. cloud
Hydrous calcium sodium aluminosilicate, natural Herschelite-calcium/sodium chabazite	CHAMIX	St. cloud	Two major: SiO_2, Al_2O_3 (Si/Al = 3,7)	Product data sheet (ZC500), st. cloud
Hydrous sodium aluminosilicate, natural clinoptilolite	ZS	St. cloud	Two major: SiO_2, Al_2O_3 (Si/Al = 5,1)	Product data sheet (ZS403H), st. cloud
Potassium aluminosilicate, natural Winston clinoptilolite	ZK	St. cloud	Two major: SiO_2, Al_2O_3 (Si/Al = 4,8)	Product data sheet (SCM ZK406), st. cloud

of the adsorbate, C_e (mmol L^{-1}) the equilibrium concentration of the adsorbate, V(L) the volume of the used solution and m_{ads} (g) the mass of the adsorbent [16]. With this Eq. (2), it is possible to calculate the amount of the adsorbate on the adsorbent surface (mmol g^{-1}) in an equilibrium state.

$$q_e = \frac{(C_o - C_e)V}{m_{ads}} \tag{2}$$

The removal percentage was determined with the following Eq. (3).

$$\text{removal}(\%) = \frac{(C_o - C_e)}{C_o} \times 100\% \tag{3}$$

Kinetic models were applied in order to investigate rates of the adsorption reaction. The used models were non-linear pseudo-first-order (PS1) (4) and pseudo-second-order (PS2) (5) models which are as follows:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{4}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{5}$$

where q_t and q_e (mmol g^{-1}) represent the amount of ammonium adsorbed at time t (min) and at equilibrium, respectively, and k_1 (1 h^{-1}) and k_2 (g mmol h^{-1}) are the kinetic rate constants.

The results from the isotherm experiments were modeled with the Langmuir, Freundlich, and Sips isotherms. These models are most often used to explain the isotherm phenomena. Langmuir (6) represents adsorption, which takes place evenly on only one layer of the adsorbent. q_e (mmol g^{-1}) is the adsorption capacity and q_{max} (mmol g^{-1}) is the maximum adsorption capacity. C_e is the concentration of the adsorbate at equilibrium and K_L (L $mmol^{-1}$) the Langmuir constant, which depicts the nature of the bond between the adsorbate and the surface [16].

$$q_e = \frac{q_{max} K_L C_e}{(1 + K_L C_e)} \tag{6}$$

Unlike Langmuir, Freundlich (7) represents heterogeneous adsorption, where adsorption can take place on more than just one layer of the adsorbent. K_f and n_f are Freundlich's constants [16].

$$q_e = K_f C_e^{\frac{1}{n_f}} \tag{7}$$

The Sips isotherm (8) was modified from the Langmuir and Freundlich isotherms. The Sips isotherm reduces to the Langmuir isotherm when $n_S = 1$. n_S being something else though, the Sips isotherm corresponds better to the Freundlich isotherm. K_S (L/mmol) and n_S are Sips's constants [16].

$$q_e = \frac{q_{\max}(KSCe)^{nS}}{1 + (K_S Ce)^{nS}} \tag{8}$$

Non-linear fitting was conducted using Excel Solver option by minimizing the sum of the squares of the errors (ERRSQ) function across the time/concentration range studied.

3. Results and discussion

3.1. Characterization of the adsorbents

3.1.1. FTIR results

Two FTIR measurements were conducted for each adsorbent and the samples were taken before (as reference) and after adsorption tests. The results showed no difference between the two samples, and therefore, only the spectra of reference samples are presented. There were notable similarities between clinoptilolites: C, ZK, and ZS; although, C was not totally pure clinoptilolite (see Fig. 1(a) and Table 1). Furthermore, remarkable similarities between CHA and CHAMIX were observed (see Fig. 1(b)). The rest of the results (P, B, and Z) are presented in Fig. 1(c). These adsorbents, although quite similar, did not have as much resemblance to any of the adsorbents like the earlier mentioned ones. Fig. 1(d) collects together FTIR results of all the adsorbents studied (4,000–600 cm^{-1}).

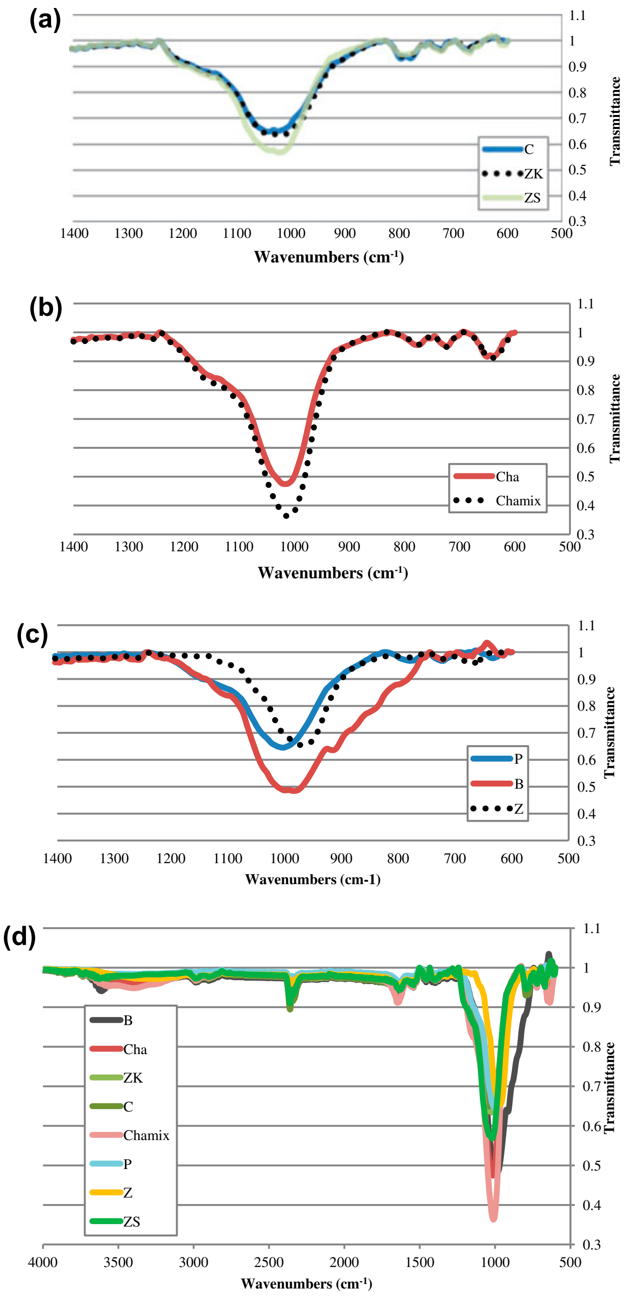


Fig. 1. Results from FTIR measurements of (a) clinoptilolites: C, ZS, and ZK, (b) chabazites: CHA and CHAMIX, (c) phillipsite, bentonite, and zeolite, and (d) all adsorbents studied from 4,000 to 600 cm^{-1}.

In all the adsorbents, there were wide peaks at around 1,000 cm^{-1}. It is possible that it is caused by Si–O–Si asymmetric stretch. Bentonite had a peak around 3,650 cm^{-1} and peaks around 1,630 cm^{-1} can be caused by the presence of water. Smaller peaks at around 800 cm^{-1} could be Si–O–Si symmetric stretches [17]. In one study, it was noted that synthetic zeolite had a peak at 726 cm^{-1} which was explained to be symmetric stretching vibrations of Si–O–Si [18]. This may also be the case with all of the adsorbents in the current study. Same study [18] assigned a peak at 670 cm^{-1} to be symmetric stretching vibrations of Si–O–Al. Z, ZS, ZK, and C also had peaks around that mentioned wavenumber.

3.2. Adsorption studies

3.2.1. The effect of pH

The effect of the pH value on the ammonium adsorption was analyzed at pH 4, 6, 8, and 10. The initial ammonium concentration was 3 mmol L^{-1}. The results can be seen in Fig. 2. It can be generalized that the two chabazites and zeolite had the best capacities at every pH value tested. For all the adsorbents studied, the results show that at pH 10 adsorption performances decreased significantly. In earlier studies, this has been attributed to the partial dissolution of zeolite and conversion of NH_4^+ into NH_3 [19]. Furthermore, the difference between capacities at pH 4, 6, and 8 was found to be quite insignificant and pH 6 was used in all the further experiments.

3.2.2. Adsorption kinetics

The kinetic experiments were conducted with B, Z, and C using initial ammonium ion concentration of 0.5 mmol L^{-1} and the solid-to-solution ratio 4 mg/mL. Lower initial concentration was used in order to see better the features in the kinetic curves and higher dose was used to keep the solid/solution ratio approximately constant during the sampling. The pH of the solution was adjusted to 6. The first results are from 5 min of adsorption and the last ones from 24 h of adsorption (in the figures, the timescale is from 0 to 6 h for better seeing the initial stage of adsorption). According to the results, it seems that the adsorption process was fast and the adsorbed amount of ammonium stayed approximately the same during the whole time span with bentonite and zeolite. In these cases, the capacities were approximately 0.08 mmol g^{-1}. Clinoptilolites capacity, on the other hand, reached the equilibrium stage approximately after 2.5 h adsorption (see Fig. 3(a)). This indicates that pore diffusion has some influence on the adsorption process [20].

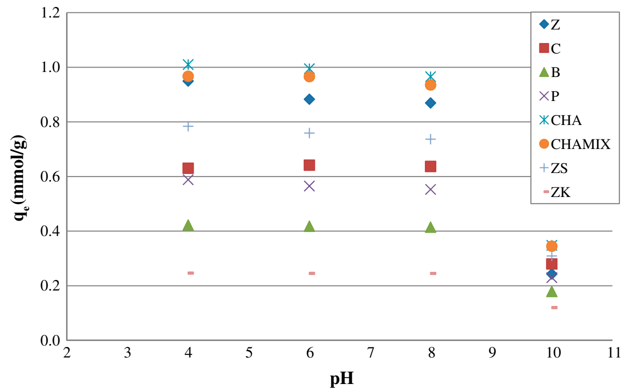


Fig. 2. The effect of pH on the NH_4^+ adsorption.

Kinetic experiments were also conducted with CHA, CHAMIX, and ZK. The initial ammonium concentration was increased to 1 mmol L^{-1} and pH was adjusted to 6. The solid-to-solution ratio was 4 mg_{ads} to 1 mL_{sol}. Because of the large amount of sodium in the solution, most probably due to ion exchange, the results from CHA and CHAMIX cannot be displayed

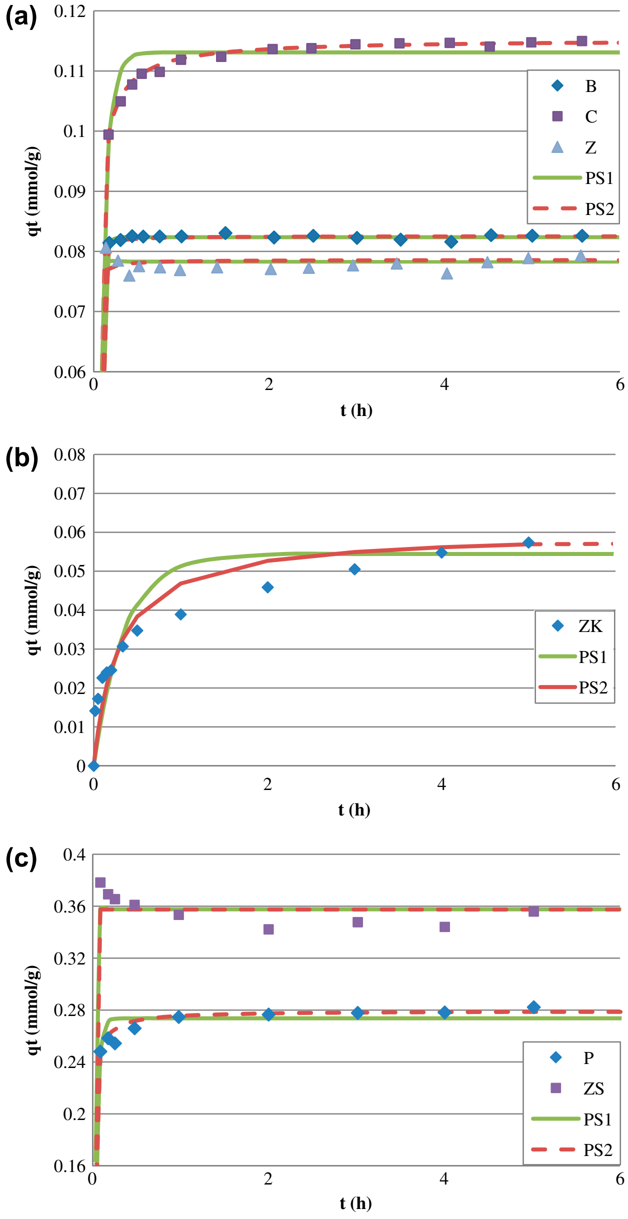


Fig. 3. The kinetic experiments with (a) bentonite, clinoptilolite, and zeolite, (b) ZK, and (c) phillipsite and ZS (pH 6).

quantitatively (sodium peak interfered the ammonium peak, see Table 4). Instead, chromatograms from the experiments can be approximately interpreted. The results from the CHA and CHAMIX experiments showed that the adsorption process took place rapidly and that the first results from 1 min time showed already great reduction in the initial ammonium concentration. Similar trend was also seen in the samples taken later. According to this, only a few minutes of adsorption seem to reduce the ammonium amount to a level that is approximately achievable with CHA and CHAMIX. This mentioned time did not seem to be a critical factor. On the other hand, the adsorption equilibrium was not achievable within 23 h with ZK (Fig. 3(b)). Unlike with CHA and CHAMIX, there were only a few milligrams of sodium in the solution after adsorption with ZK and, as already noticed in this study, ZK did not remove ammonium as effectively. This clearly slower kinetic behavior of ZK could arise from (1) exchanging cations other than sodium (in this case, potassium and calcium (see Table 4)), (2) pore clogging, (3) internal precipitation of hydroxides, or (4) narrow pore structure inhibiting "two way traffic" of exchanging ions [21].

Lastly, for P and ZS, it took approximately one hour for both of the adsorbents to nearly reach the equilibrium (Fig. 3(c)). In the case of ZS, however, some of the instantly adsorbed ammonium was desorbed within two hours indicating a cation-exchange reaction to the reverse direction. Indeed, it was observed that potassium was at first released into the solution, but after 3 min, part of it was adsorbed again presumably causing release of ammonium.

Fig. 3 also shows the PS1 and PS2 model fittings to the obtained kinetic data. Generally, it can be concluded that PS2 model gave better fitting results than PS1. Especially, most of the q_e values predicted by the PS2 model were closer to the experimental ones compared to those predicted by the PS1 model (Table 2). This indicates that chemical reaction was governing the ammonium adsorption process on the surfaces of most of the studied clay materials. Highest reaction rates were obtained for ZS, B, and Z. However, as stated earlier, some ammonium was desorbed from the surface of ZS after very fast initial adsorption. Rather poor fit of both of the models was obtained for ZK and a shape of the kinetic curve seen in Fig. 3(b) suggests that the diffusion played a significant role in the adsorption of ammonium by ZK. Interestingly, all the studied clinoptilolites (C, ZS, and ZK) showed rather different kinetic behavior most likely arising from their different surface structure including surface area and porosity.

3.2.3. Adsorption isotherms

The isotherm experiments were conducted with every adsorbent at pH 6. The initial ammonium concentration varied from 0.1 to 20 mmol L^{-1}. Results of the isotherm studies are presented in Fig. 4 and Table 3. The highest experimental adsorption capacity was obtained for zeolite (Z) followed by the two chabazites CHA and CHAMIX. In the case of clinoptilolites ZS had the highest capacity followed by C and ZK. Notable differences between ZS and ZK were again noticed, just like it was observed with the kinetic studies.

Table 2
Kinetic parameters for ammonium adsorption by studied adsorbents

PS1					
	$q_{e,\,exp}$ (mmol g^{-1})	q_e (mmol g^{-1})	k_1 (1 h^{-1})	r^2	SD
B	0.082	0.082	23.7	1.000	0.0191
C	0.116	0.113	11.5	0.991	0.0263
P	0.288	0.274	25.2	0.987	0.0804
Z	0.081	0.078	35.6	0.991	0.0182
ZS	0.359	0.358	171.9	0.990	0.0106
ZK	0.075	0.054	2.8	0.797	0.0205
PS2					
	$q_{e,\,exp}$ (mmol g^{-1})	q_e (mmol g^{-1})	k_2 (g mmol h^{-1})	r^2	SD
B	0.082	0.083	4,369	0.999	0.0191
C	0.116	0.115	301	1.000	0.0263
P	0.288	0.279	260	0.996	0.0804
Z	0.081	0.079	4,059	0.991	0.0182
ZS	0.359	0.357	584,825	0.990	0.0105
ZK	0.075	0.060	59	0.879	0.0204

Leyva-Ramos et al. [22] compared the ability of clinoptilolite and chabazite to reduce the ammonium amount and they discovered chabazite to be the best one of the two types of zeolite. They explained the difference with the smaller Si/Al ratio that chabazite had compared to clinoptilolite. In this study, the two chabazites, CHA and CHAMIX, also had smaller Si/Al ratios than the two clinoptilolites, ZK and ZS, (see Table 1) and the chabazites were found to be better ammonium reducers than ZK and ZS.

Obtained equilibrium data were modeled using three different isotherm models. The values of correlation coefficient presented in Table 3 and apparent fits in Fig. 4 indicate that, in all of the cases, the Sips isotherm described the experimental data better than the Langmuir or Freundlich isotherms. Although the Langmuir model gave $q_{\max}$ values closer to the experimental ones, it could not explain the shape of the equilibrium curves. No clear plateaus were obtained indicating the higher real maximum adsorption capacities, which were indeed predicted by the Sips model. This indicates that adsorption process had mainly a heterogeneous nature.

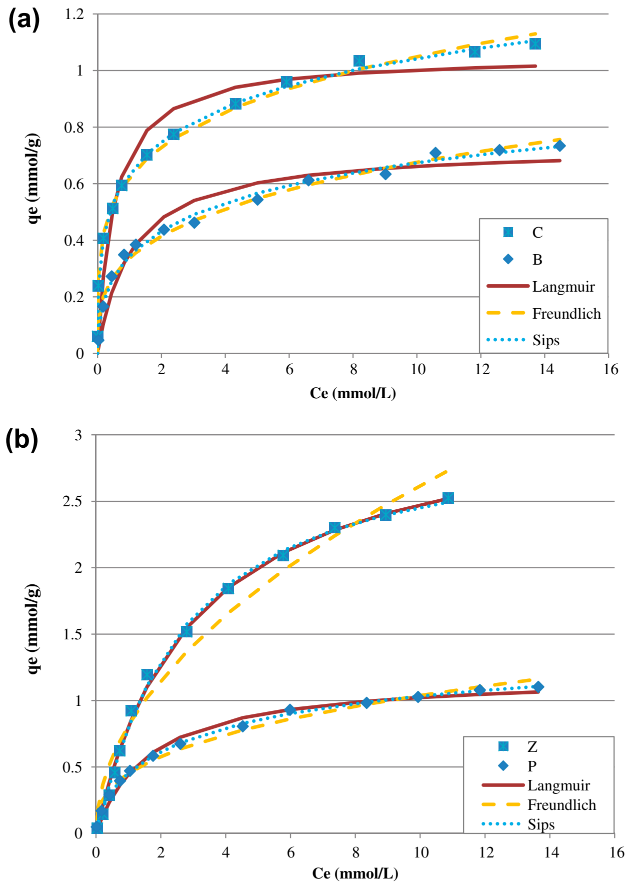


Fig. 4. The adsorption isotherm of (a) bentonite and clinoptilolite, (b) phillipsite and zeolite, (c) chabazites: CHA and CHAMIX and (d) clinoptilolites: ZS and ZK (pH 6).

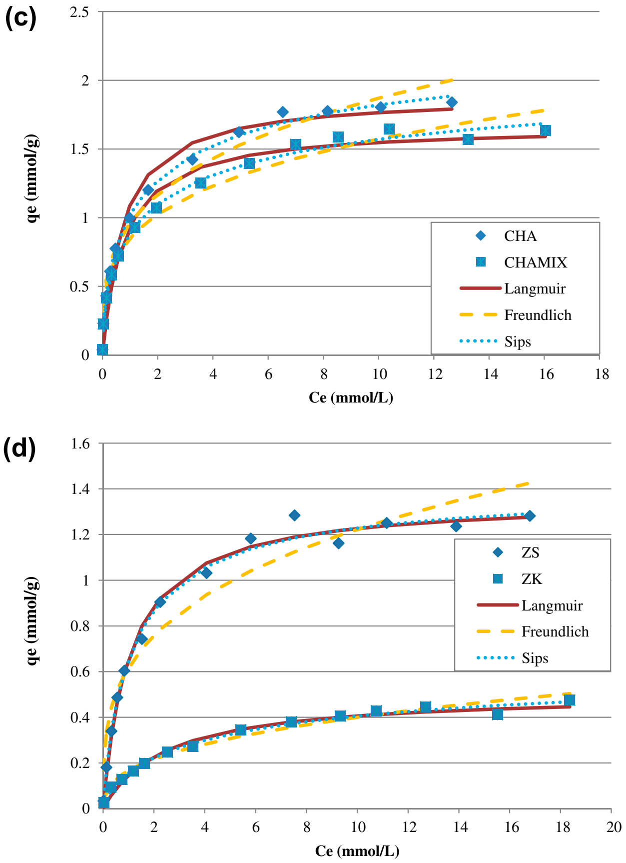


Fig. 4. (*Continued*).

Some studies suggest that the Langmuir model fitted better than the Freundlich model when clinoptilolite was used as adsorbent [3,23]. In this study, it was found that Z, ZK, and ZS were best described by the Sips model, but the Langmuir also gave nearly as good a fit. C was the only one of the clinoptilolites, of which adsorption properties could have been explained also by the Freundlich model. Lei et al. [24] found that Redlich–Peterson and Sips being three parameters equations gave better fittings than two parameter models, such as Freundlich and Langmuir. Comba et al. [25] studied ammonium adsorption onto zeolite, in which main component was chabazite, and found that the Freundlich model fits the experimental data pretty well. In this study, the two chabazites could be modeled well only with the Sips isotherm. This was also the case with bentonite, although the Freundlich isotherm gave nearly as good a fit. On the other hand, Buragohain et al. [4] found that the

Langmuir model gave better fit than the Freundlich for bentonite.

To further verify that ion-exchange takes place during the uptake of ammonium, Table 4 shows the amount of released cations from the studied adsorbents for selected ammonium concentrations. Mostly, ammonium removal occurred via sodium exchange and in the case of P and ZK potassium and calcium were playing the most important role. However, at higher ammonium concentrations potassium and calcium ions were also released into the solution from C, Chamix, and ZS. This indicates that sodium was the most easily exchangeable ion followed by potassium and calcium when the concentration of ammonium was high enough and the structure contained these other exchangeable cations. This observation is also supported by the previous literature [21].

3.2.4. The effect of K^+, Mg^{2+}, and Ca^{2+} ions

Other cations can affect negatively on the ammonium adsorption. For this reason, the effect of K^+, Mg^{2+}, and Ca^{2+} ions were examined in four different solutions. The concentration of each cation was initially 3 mmol L^{-1}. pH was not adjusted. The first solution consisted only of ammonium ions (pH 5.9). The second one consisted of ammonium and potassium ions (pH 5.5), the third one ammonium and magnesium ions (pH 5.6), and the last one ammonium and calcium ions (pH 5.9).

As shown in Fig. 5, the adsorption capacity of ammonium was influenced by another cation in all the cases. The adsorption capacity dropped approximately from one-third to a half of the original capacity when there were potassium ions present. A part from the two chabazites and bentonite magnesium ions did

Table 3
Isotherm parameters for ammonium adsorption by studied adsorbents

Langmuir

	$q_{\max,\ \exp}$ (mmol g^{-1})	$q_{\max}$ (mmol g^{-1})	K_L (L $mmol^{-1}$)	r^2	SD
B	0.73	0.73	0.932	0.951	0.220
C	1.11	1.05	1.921	0.927	0.352
P	1.11	1.20	0.589	0.988	0.362
Z	2.52	3.22	0.331	0.997	0.884
Cha	1.83	1.90	1.359	0.980	0.652
Chamix	1.62	1.67	1.276	0.972	0.570
ZS	1.29	1.36	0.938	0.991	0.434
ZK	0.50	0.51	0.405	0.982	0.145

Freundlich

	K_f	$1/n_f$	r^2	SD
B	0.337	0.302	0.984	0.211
C	0.624	0.227	0.994	0.335
P	0.45	0.363	0.986	0.347
Z	0.811	0.509	0.970	0.866
Cha	0.963	0.288	0.974	0.626
Chamix	0.854	0.265	0.971	0.544
ZS	0.618	0.296	0.936	0.412
ZK	0.167	0.378	0.971	0.142

Sips

	$q_{\max,\ \exp}$ (mmol g^{-1})	$q_{\max}$ (mmol g^{-1})	K_S (L $mmol^{-1}$)	n_S	r^2	SD
B	0.73	1.33	0.105	0.469	0.991	0.213
C	1.11	2.34	0.052	0.334	0.996	0.336
P	1.11	1.62	0.236	0.655	0.999	0.354
Z	2.52	3.01	0.388	1.089	0.997	0.888
Cha	1.83	2.46	0.569	0.599	0.997	0.637
Chamix	1.62	2.24	0.475	0.551	0.994	0.554
ZS	1.29	1.41	0.847	0.892	0.992	0.431
ZK	0.50	0.65	0.203	0.716	0.989	0.144

Table 4
The amount of ammonium adsorbed and other cations released at different initial ammonium concentrations

		Adsorbed (mmol)		Released (mmol)		
Initial NH_4^+ conc. (mmol L^{-1})	Material	NH_4^+	Na	K	Ca	Total
1	B	0.006	0.011	0.000	0.000	0.011
	C	0.008	0.007	0.000	0.000	0.007
	P	0.006	0.001	0.003	0.002	0.006
	Z	0.006	0.014	0.000	0.000	0.014
	Cha	0.009	0.019	0.000	0.000	0.019
	Chamix	0.009	0.013	0.000	0.000	0.013
	ZS	0.007	0.012	0.001	0.000	0.013
	ZK	0.003	0.001	0.002	0.001	0.004
3	B	0.009	0.013	0.000	0.000	0.013
	C	0.015	0.010	0.001	0.001	0.012
	P	0.012	0.002	0.006	0.003	0.010
	Z	0.019	0.027	0.000	0.000	0.027
	Cha	0.020	0.029	0.000	0.000	0.029
	Chamix	0.018	0.020	0.000	0.000	0.020
	ZS	0.015	0.015	0.003	0.001	0.019
	ZK	0.005	0.001	0.002	0.002	0.005
6	B	0.011	0.014	0.000	0.001	0.015
	C	0.018	0.010	0.002	0.002	0.014
	P	0.016	0.001	0.007	0.004	0.013
	Z	0.033	0.043	0.000	0.000	0.043
	Cha	0.028	0.034	0.001	0.000	0.035
	Chamix	0.025	0.023	0.001	0.001	0.024
	ZS	0.020	0.017	0.005	0.002	0.023
	ZK	0.007	0.001	0.002	0.003	0.006
10	B	0.011	0.014	0.000	0.002	0.016
	C	0.019	0.013	0.003	0.003	0.019
	P	0.018	0.002	0.009	0.005	0.016
	Z	0.043	0.054	0.000	0.000	0.054
	Cha	0.036	0.038	0.001	0.001	0.040
	Chamix	0.031	0.025	0.001	0.002	0.027
	ZS	0.026	0.018	0.007	0.003	0.028
	ZK	0.008	0.001	0.002	0.003	0.006

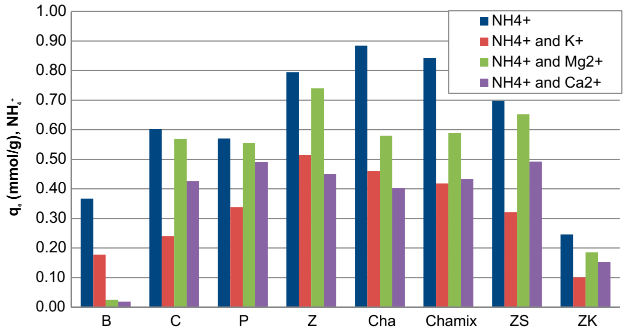


Fig. 5. The adsorption capacities of NH_4^+ without and with competition.

not have a great effect on the ammonium removal. With CHA and CHAMIX, the capacity dropped approximately to one-third of the original when magnesium was added in the solution. In the case of bentonite, both magnesium and calcium ions influenced dramatically on its ability to remove ammonium. With other adsorbents calcium ions had greater effect than magnesium on the ammonium adsorption. All in all, with potassium ions and magnesium ions present, the best adsorbent was found to be zeolite and with calcium ions ZS and P had the highest capacities. The effect of the other cations on the ammonium adsorption capacity from the most influenceable ion to the least is presented in Table 5. According to the results, potassium ion is the major competitor when using C, P, CHAMIX, ZS, and ZK as

Table 5
The effect of K^+, Mg^{2+}, and Ca^{2+} ions from greatest to smallest on the ammonium adsorption capacity according to the results

Adsorbent	The order of the effect
B	$Ca^{2+} > Mg^{2+} > K^+$
C	$K^+ > Ca^{2+} > Mg^{2+}$
P	$K^+ > Ca^{2+} > Mg^{2+}$
Z	$Ca^{2+} > K^+ > Mg^{2+}$
CHA	$Ca^{2+} > K^+ > Mg^{2+}$
CHAMIX	$K^+ > Ca^{2+} > Mg^{2+}$
ZS	$K^+ > Ca^{2+} > Mg^{2+}$
ZK	$K^+ > Ca^{2+} > Mg^{2+}$

the adsorbents while calcium ion is the biggest competitor when B, Z, and CHA are concerned.

The ammonium adsorption on zeolites is dependent on the channels of the materials and the cation occupied sites found in those channels. Different cations, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, found in the material have different effects and, for example, Ca^{2+} ions can block channels and adsorption sites, and therefore inhibit the adsorption of other ions [26]. Due to these framework properties and the other cations in the used solutions, it is possible that the adsorption of ammonium, at least in some extent, has been blocked.

Wang et al. [27] studied natural clinoptilolite for its ability to reduce ammonium ions from solutions, which consisted another ion also (Ca^{2+}, Mg^{2+}, or K^+). They discovered that potassium ion has the biggest negative impact and magnesium ion has the smallest effect of the three ions. This was also the case in a study of Wang et al. [28] and the present study as seen for natural clinoptilolites C, ZS, and ZK in Fig. 5 and Table 5.

Langwaldt [2] studied the effect of potassium on the adsorption capacity of ammonium. He compared eight natural zeolites and found that compared to the samples of clinoptilolite, chabazite had the best ability to adsorb ammonium when potassium was present. The used chabazite had the same chemical composition as CHAMIX. In this study, zeolite from Sigma (Z) had the best ability to remove ammonium in the presence of potassium and the two chabazites were found to be the second best ones.

Taneva [6] studied NaCl-treated clinoptilotite from Bulgaria for the removal of ammonium. The ammonium removal was studied with and without the presence of calcium ions. It was found that the presence of calcium had a negative effect on the ammonium adsorption. The use of clinoptilolite for ammonium removal from calcium-rich waters was therefore questioned. The same negative effect was also discovered in this current study. All the three natural clinoptilolites (C, ZS, and ZK) studied also had smaller ammonium adsorption capacities when calcium was present. Though, it must be concluded that in all the cases, other studied cations had a negative effect on the adsorption of ammonium.

In another case, sodium and potassium ions were found to be the most significant competitors of ammonium adsorption onto microwave-treated clinoptilolite [24]. In the present study, sodium was not one of the examined cations because it was observed that the initial amount of sodium increased after adsorption. This was interpreted as a result of the ion-exchange when the amount of sodium varied depending on the adsorbents themselves. Therefore, sodium was not considered for competition experiments.

In general, it can be concluded based on the literature and the obtained results that different cations have different kind of effects on the uptake of ammonium and also a type of material plays an important role. The reasons are not usually analyzed in detail and, for example, ion size and charge are suggested to be involved. Some reported results suggest that Ca^{2+} and Mg^{2+} affect mostly on the ion-exchange occurring in the side pockets of clay minerals and K^+ and Na^+ on the ion-exchange occurring in the main channels [28]. Therefore, in this study, binding of ammonium by bentonite seemed to occur mainly in the side pockets, which was highly affected by Ca^{2+} and Mg^{2+}, and clinoptilolite, philipsite, ZS, ZK, and Chamix sorbed ammonium through the main channels affected mostly by K^+.

For the studied adsorbents, the adsorption capacities of potassium, magnesium and calcium was also determined (see Fig. 6). Results shown are from the same experiments. It was found that Z, CHA, and CHAMIX had the greatest adsorption capacities of potassium among the examined adsorbents. Furthermore, zeolite clearly had the largest adsorption capacities of magnesium and calcium.

3.2.5. Results from the spiked real wastewaters

The eight adsorbents were tested also with real mining wastewater from Yara Siilinjärvi. The wastewater sample was collected after the chemical purification plant where $Ca(OH)_2$ is added to the water to reduce the amount of phosphorus. The collection place is situated near the lake where the treated wastewaters run to. The composition of the wastewater was as follows: pH: 11.2, NH_4^+: $0.56\ \mathrm{mmol\,L^{-1}}$, K^+: $0.83\ \mathrm{mmol\,L^{-1}}$,

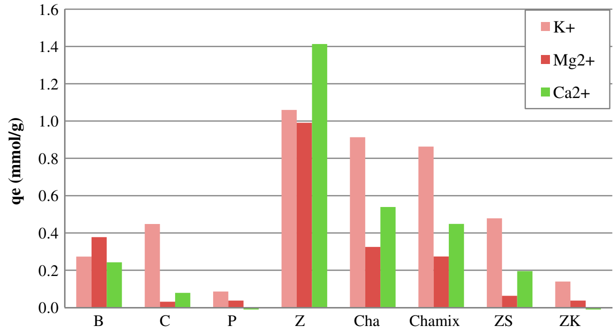


Fig. 6. The adsorption capacities of potassium, magnesium, and calcium ions.

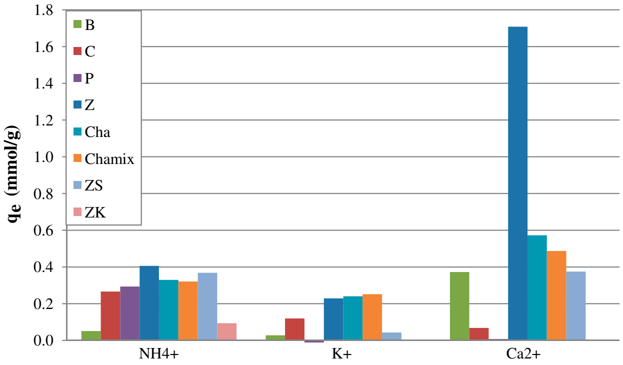
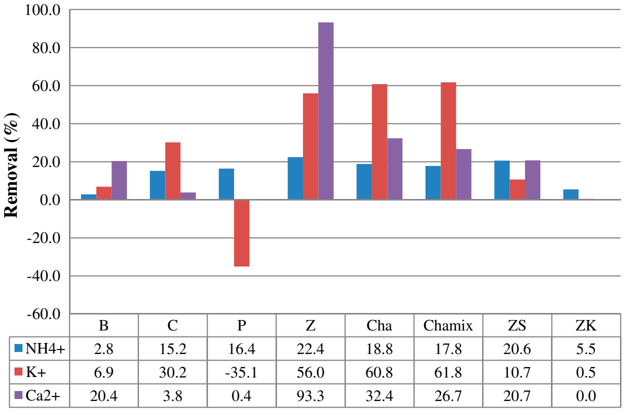


Fig. 7. The adsorption capacities of ammonium, potassium, and calcium from spiked mining wastewaters.



	B	C	P	Z	Cha	Chamix	ZS	ZK
NH4+	2.8	15.2	16.4	22.4	18.8	17.8	20.6	5.5
K+	6.9	30.2	-35.1	56.0	60.8	61.8	10.7	0.5
Ca2+	20.4	3.8	0.4	93.3	32.4	26.7	20.7	0.0

Fig. 8. The removal of ammonium, potassium, and calcium from spiked mining wastewaters.

Mg^{2+}: 0.015 mmol L^{-1}, Ca^{2+}: 3.61 mmol L^{-1}, SO_4^{2-}: 2.8 mmol L^{-1}, F^-: 0.6 mmol L^{-1}, and COD: 7.9 mg L^{-1}. In order to get more reliable results, the water sample was spiked with NH_4Cl to increase the ammonium content up to 3.6 mmol L^{-1}. After adding ammonium, pH of the wastewater dropped from the original value of 11.2–9.5.

The results from the adsorption tests are shown in Figs. 7 and 8. According to the results, ammonium was removed almost equally well by zeolite, two chabazites and ZS, while bentonite and ZK had the poorest adsorption efficiencies for ammonium. These results are consistent with the studies done in simulated ammonium solutions both with and without the competing ions (see Table 3 and Fig. 5). In the case of other ions, zeolite removed nearly all of the calcium present in the wastewater and clinoptilolote, phillipsite, and ZK showed low affinities towards calcium, which is also evident from Fig. 6. Thus, the behavior of the adsorbents was quite well predicted also in the simulated solutions.

From Fig. 8, it is also obvious that some potassium was released from phillipsite during the adsorption experiments, which was not surprising because phillipsite can be used as a fertilizer for potassium release [29]. The most efficient potassium adsorbents from the real wastewater sample were zeolite and two chabazites as also observed in Fig. 6.

Earlier, Turkish clinoptilolite has been studied for its ability to reduce ammonium concentrations from landfill wastewaters [15]. It was observed that the other cations present in the simulated wastewaters inhibited ammonium removal, which is consistent with the present study. However, high ammonium adsorption capacities were obtained in column experiments even if the real wastewaters were used. This and the results of the present study indicate a potential to use the studied clay materials in practical applications.

4. Conclusions

In this study, eight different clay-based adsorbents were tested for the ammonium removal from both simulated and real wastewaters. The effects of pH, contact time, ammonium concentration, and presence of competing cations were tested. The removal of ammonium was almost independent on the pH at the range of 4–8, while at pH 10 its removal was clearly inhibited. For most of the clay materials, adsorption kinetics were fast and the PS2 model described the kinetic data rather well. The Sips isotherm model fitted best to the experimental equilibrium data in all of the cases indicating heterogeneous adsorption phenomena. Amongst the competing cations tested, potassium had the most significant reducing effect on the ammonium adsorption. Zeolite from Sigma–Aldrich and the two chabazites from St. Cloud were found to be the best materials for ammonium removal among the tested adsorbents. Especially, these adsorbents could remove ammonium although adsorbing other cations as well from both simulated and real wastewater samples. On the whole, the obtained results are promising for the practical applications' point of view.

Acknowledgments

The authors gratefully acknowledge the European Regional Development Fund for the financial support. Elisa Ahonen, Sakari Modig, and others are acknowledged for their contribution in performing experiments in laboratory. Evgenia Iakovleva is thanked for her help in HPLC analysis.

List of symbols

q_e (mmol g^{-1}) — equilibrium adsorption capacity
C_o (mmol L^{-1}) — initial concentration of adsorbate
V (L) — volume of the used solution
m_{ads} (g) — mass of adsorbent
q_t (mmol g^{-1}) — amount of adsobate adsorbed at time t (min)
k_1 (L h^{-1}) — pseudo-first-order rate constant
k_2 (g mmol h^{-1}) — pseudo-second-order rate constant
q_{max} (mmol g^{-1}) — maximum adsorption capacity
C_e (mmol L^{-1}) — concentration of the adsorbate at equilibrium
K_L (L mmol^{-1}) — Langmuir constant
K_f — Freundlich's constant
n_f — Freundlich's constant
K_S (L mmol^{-1}) — Sips's constant
n_S — Sips's constant

References

[1] Metcalf and Eddy, Wastewater Engineering, Treatment and Reuse, fourth ed., The McGraw-Hill Companies, New York, NY, 2003, p. 1819.
[2] J. Langwaldt, Ammonium removal from water by eight natural zeolites: A comparative study, Sep. Sci. Technol. 43 (2008) 2166–2182.
[3] D. Kucic, M. Markic, F. Briski, Ammonium adsorption on natural zeolite (clinoptilolite): Adsorption isotherms and kinetics modeling, Holist. Approach Environ. 2 (2012) 145–158.
[4] P. Buragohain, S. Shekharan, N. Saiyouri, A study on the adsorption of ammonium in bentonite and kaolinite, Int. J. Chem. Environ. Biol. Sci. 1 (2013) 157–160.
[5] A. Mazeikiene, M. Valentukeviciene, M. Rimeika, A.B. Matuzevicius, Removal of nitrates and ammonium ions from water using natural sorbent zeolite (clinoptilolite), J. Environ. Eng. Landsc. 16 (2008) 38–44.
[6] N. Taneva, Removal of ammonium and phosphates from aqueous solutions by activated and modified Bulgarian clinoptilolite, J. Chem. Eng. Mater. Sci. 3 (2012) 79–85.
[7] M. Wang, L. Liao, X. Zhang, Z. Li, Z. Xia, W. Cao, Adsorption of low-concentration ammonium onto vermiculite from Hebei province, China, Clays Clay Miner. 59 (2011) 459–465.
[8] S. Balci, Nature of ammonium ion adsorption by sepiolite: Analysis of equilibrium data with several isotherms, Wat. Res. 38 (2004) 1129–1138.
[9] M. Bernal, J.M. Lopez-Real, Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials, Bioresour. Technol. 43 (1993) 27–33.
[10] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chem. Eng. J. 156 (2010) 11–24.
[11] F.A.Mumpton, La roca magica: Uses of natural zeolites in agriculture and industry. Proc. Nat. Acad. Sci. 96 (1999) 3463–3470. Colloquium paper.
[12] S.D.J. Inglethorpe, D.J. Morgan, D.E. Highley, A.J. Bloodworth, Industrial Minerals Laboratory Manual, Bentonite, British Geological Survey, Technical report WG/93/20, Mineralogy and Petrology Series 1993.
[13] L. Lin, Z. Lei, L. Wang, X. Liu, Y. Zhang, C. Wan, D.-J. Lee, J.H. Tay, Adsorption mechanisms of high-levels of ammonium onto natural and NaCl-modified zeolites, Sep. Purif. Technol. 103 (2013) 15–20.
[14] A. Malovanyy, H. Sakalova, Y. Yatchyshyn, E. Plaza, M. Malovanyy, Concentration of ammonium from municipal wastewater using ion exchange process, Desalination 329 (2013) 93–102.
[15] D. Karadag, S. Tok, E. Akgul, M. Turan, M. Ozturk, A. Demir, Ammonium removal from sanitary landfill leachate using natural Gördes clinoptilolite, J. Hazard. Mater. 153 (2008) 60–66.
[16] E. Repo, J.K. Warchol, T.A. Kurniawan, M.E. Sillanpää, Adsorption of Co(II) and Ni(II) by EDTA- and/or DTPA-modified chitosan: Kinetic and equilibrium modeling, Chem. Eng. J. 161 (2010) 73–82.
[17] B. Smith, Infrared Spectral Interpretation, A Systematic Approach, CRC Press LLC, 1999, 265 p ISBN 0-8493-2463-7.
[18] W. Mozgawa, M. Krol, K. Barczyk, FT-IR studies of zeolites from different structural groups, CHEMIK 2011(65) (2011) 667–674.
[19] H. Huang, X. Xiao, B. Yan, L. Yang, Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent, J. Hazard. Mater. 175 (2010) 247–252.
[20] S. Komarowski, Q. Yu, Ammonium ion removal from wastewater using Australian natural zeolite: Batch equilibrium and kinetic studies, Environ. Technol. 18 (1997) 1085–1097.
[21] V.J. Inglezakis, C.D. Papadeas, M.D. Loizidou, H.P. Grigoropoulou, Effects of pretreatment on physical and ion exchange properties of natural clinoptilolite, Environ. Technol. 22 (2001) 75–82.
[22] R. Leyva-Ramos, J.E. Monsivais-Rocha, A. Aragon-Piña, M.S. Berber-Mendoza, R.M. Guerrero-Coronado, P. Alonso-Davila, J. Mendoza-Barron, Removal of ammonium from aqueous solution by ion exchange on natural and modified chabazite, J. Environ. Manage. 91 (2010) 2662–2668.

[23] T.C. Jorgensen, L.R. Weatherley, Ammonia removal from wastewater by ion exchange in the presence of organic contaminants, Water Res. 37 (2003) 1723–1728.

[24] L. Lei, X. Li, X. Zhang, Ammonium removal from aqueous solutions using microwave-treated natural Chinese zeolite, Sep. Purif. Technol. 58 (2008) 359–366.

[25] S. Comba, M. Martin, D. Marchisio, R. Sethi, E. Barberis, Reduction of nitrate and ammonium adsorption using microscale iron particles and zeolite, Water Air Soil Pollut. 223 (2012) 1079–1089.

[26] M. Sakizci, B.E. Alver, E. Yörükoğullari, Influence of the exchangeable cations on SO_2 adsorption capacities of clinoptilolite-rich natural zeolite, Adsorption 17 (2011) 739–745.

[27] Y.-F. Wang, F. Lin, W.-Q. Pang, Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite, J. Hazard. Mater. 142 (2007) 160–164.

[28] Y. Wang, Y. Kmiya, T. Okuhara, Removal of low-concentration ammonia in water by ion-exchange using Na-mordenite, Water Res. 41 (2007) 269–276.

[29] J.S. Notario del Pino, I.J. Arteaga Padrón, M.M. González Martin, J.E. Garcia Hernández, Phosphorus and potassium release from phillipsite-based slow-release fertilizers, J. Control. Release, 34 (1995) 25–29.