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Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions

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Abstract

The scope of this study is ammonium-ion uptake from synthetic aqueous solutions onto raw and pretreated forms of the natural zeolite Transcarpathian clinoptilolite under dynamic conditions. Hydrogen ions displaced exchangeable cations on the clinoptilolite in distilled water (sodium ions) and hydrochloric acid (sodium, potassium, and calcium ions) and destroyed the zeolite framework structure in the last case. Ammonium uptake onto the zeolite occurs by exchange with Na^+, Ca^{2+}, and K^+ ions. Although Na^+ ions were observed to be more easily exchanged for both hydrogen and ammonium ions, the role of Ca^{2+} ions increased with zeolite saturation by NH_4^+ ions. The maximum sorption capacity of the clinoptilolite toward NH_4^+ ions, estimated under dynamic conditions, is significantly higher than that measured under static conditions; proximity of the values of a distribution coefficient and a retardation factor for different conditions (215–265 dm^3/kg and 979–1107, respectively) allows us to use these parameters to model ammonium uptake onto the clinoptilolite. Slowing down or interruption in filtration resulted in the improvement of ammonium sorption properties of the zeolite. The ammonium removal improves with use of the finer fractions of the clinoptilolite up to 0.35 mm. A recycling study results confirmed the importance of external diffusion for ammonium sorption by the clinoptilolite. Preliminary treatment of the sorbent confirmed the predominant importance of the ion-exchange mechanism. The advantage of prior NaCl treatment of the clinoptilolite in improvement of ammonium removal over the other techniques was shown.
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1. Introduction

Mineral nitrogen forms, widespread pollutants of natural waters, often enter the hydrosphere in ammonium forms that may be relatively easier to extract from water than the nitrate forms. Among various methods available for ammonium removal from waters and wastes, ion exchange looks like most attractive when effective, low-cost materials are used as exchangers [1]. Zeolites are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water and by alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites (being cheap materials, easily available in large quantities in many parts of the world) show special importance in water and gas purification, adsorption and catalysis, and agriculture and aquaculture [2]. Zeolites also have the advantage over other filter materials

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of significant permeability and so are widely used for water purification by filtration.

Large-scale cation-exchange processes using natural zeolites were first developed by Ames [3] and Mercer et al. [4], who demonstrated the effectiveness of clinoptilolite for extracting ammonium from municipal and agricultural waste stream. The various aspects of removal from aqueous solutions by clinoptilolite have been investigated by many researchers [5–17]. Clinoptilolite, being a natural zeolite with the representative unit-cell formula $(Na_3K_3)(Al_6Si_{30}O_{72})\cdot24H_2O$, channel dimensions 3.9×5.4 Å, and cation exchange capacity 2.16 meq/g, seems to be the most attractive material for ammonium removal from drinking water and wastewater due to its ammonium-ion selectivity and good performance in ammonium sorption under low temperature [1,2]. Ammonium ions are removed from aqueous solutions by zeolites via exchange with cations or by adsorption in pores of aluminosilicate systems. Ion exchange prevails when concentration of ammonium is equal or lower than the concentration of exchangeable cations of the zeolite, and adsorption begins to predominate with increased ammonium content [6]. Ammonium adsorption occurs by the ion exchange of ammonium ions with sodium, potassium, magnesium, and calcium ions at cation-exchange sites of zeolites [17].

The ammonium cation-exchange capacity varies depending on the presence of other cations in the aqueous phase and initial ammonium concentrations [3,8,9,12,15]. Due to high selectivity of zeolites toward potassium ions, potassium is the main competitor for ammonium in removal from aqueous solutions by clinoptilolite [2]. The following selectivity order of ammonium ions over other cations on the clinoptilolite was given in [17]: $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$. Alkaline and alkaline-earth metal cations presented in aqueous solutions resulted in a significant decrease of the cation exchange capacity of clinoptilolite to ammonium ions [9]. Amounts of NH_4^+ sorbed by clinoptilolite increase with increasing initial concentration in aqueous solution and NH_4^+ adsorption and desorption by zeolite are particle-diffusion-controlled processes [13,14]. pH level is one of the important factors in cation-exchange purification of water, only ionized forms of ammonium can be removed by the cation-exchange process. Hence, for optimum operation, the pH level of the aqueous solution must be at or below 7 [1,15].

Cation-exchange capacity of clinoptilolite tends to increase with increasing relative content of alkaline metal cations and it is independent at alkaline earth cation content. The exchange effectiveness is influenced significantly by the chemical and physical pretreatment techniques and loading or regeneration of the zeolite. Sodium chloride solution treatment seems to be the best method of clinoptilolite preparation and regeneration [7,9,15]. Although the effectiveness of ammonium removal increases with decreased zeolite particle size [1,15], close agreement of the diffusion coefficient values for the different particle sizes was reported in [13].

Ammonium removal by passing a synthetic solution of 20 mg/dm^3 of ammonium ions through Bigadiç clinoptilolite (Turkey)-packed columns was studied recently by Demir and co-workers [15]. The authors established that a decrease of the superficial velocity resulted in an increase of the amount of ammonium sorbed. The studied interval of flow rates was from 25 up to 75 bed volumes per hour (nearly 10–31 cm^3/min or 3.5–10.5 m/h) using the clinoptilolite fraction sizes of 0.125–1.0 and 1.0–2.0 mm).

Ershov et al. [9] analyzed the use of Transcarpathian clinoptilolite (fraction size 1.0–3.0 mm) to extract ammonium ions from Kyiv sewage. Good results were obtained in filtration of wastewaters pretreated physically and biologically with 5–25 mg/dm^3 of NH_4^+ ions through a clinoptilolite-packed column at a flow rate of 6 m/h. Thermal regeneration at 250–300 °C improved the cation exchange capacity of the clinoptilolite, which was evaluated as equal to 0.61 meq/g toward NH_4^+ ions under dynamic conditions. Adsorption of heavy metals on Transcarpathian clinoptilolite under dynamic conditions was studied in [18–20].

We have previously investigated ammonium sorption from synthetic aqueous solutions by the natural zeolite Transcarpathian clinoptilolite under static conditions, as well as some physical properties of the sorbent. The maximum sorption capacity of the clinoptilolite toward ammonium ions was evaluated as 0.64 meq/g. The sorption effectiveness decreased somewhat with the rise in fraction size and improved insignificantly with the rise in the temperature of the zeolite by drying prior to experiment from 20 up to 110 °C [21].

The aim of the present work is to study the features of ammonium-ion sorption from synthetic aqueous solutions by raw and preliminarily treated forms of the natural zeolite Transcarpathian clinoptilolite under dynamic conditions and to estimate the optimal operating conditions of the process.

2. Materials and methods

2.1. Samples

Clinoptilolite rock from the Sokyrnytsya deposit (the Transcarpathian region, Ukraine) containing 70–75% clinoptilolite was used in this study. In its oxide form the formula of the Transcarpathian clinoptilolite is as follows (in %): SiO_2 66.7, Al_2O_3 12.3, Fe_2O_3 1.05, CaO 2.10, MgO 1.07, K_2O 2.96, Na_2O 2.06. Quartz, calcite, biotite, muscovite, chlorite, and montmorillonite are the main mineral admixtures. The exchangeable complex of Transcarpathian clinoptilolite is presented mainly by K^+, Na^+, Ca^+, and Mg^+ ions [20,22]. The clinoptilolite samples were ground in a metal mortar and divided into the fractions (in mm), 0.125–0.35, 0.35–0.5, 0.51–0.7, 0.71–1.0, 1.0–1.4, and 1.4–2.0 by mechanical sieves. Each fraction was washed with distilled water to remove turbidity and was dried at room temperature (air-drying). One part of the fraction 0.71–1.0 mm was dried at a temperature of 110 °C for 2.5 h to get rid of part of the

adsorbed water and the other part of the same fraction was dried at the temperature of 300 °C for 2.5 h to get rid all of the adsorbed water. Then the cliniptilolite samples were put into a desiccator.

The chemical treatment of the zeolite consisted of addition of 0.25 dm³ of 2 M solutions of HCl and NaCl to the samples of clinoptilolite fraction 0.71–1.0 mm (15 g). After 24 h the solid phases were separated from the solutions and from the Cl⁻ ions and dried at room temperature. An adsorption experiment in distilled water was carried out using the same routine. Concentrations of Na^+, K^+, Ca^{2+}, and Al^{3+} ions and of Fe_{total} were analyzed in the aqueous phase.

2.2. Tests of physical properties

The natural filtration flow rates of different fractions of the air-dried clinoptilolite were measured using the main arrangement with the hydraulic gradient being set equal to unity. The total porosity was evaluated using the saturation method by measurement of the water volume necessary to saturate all pores of the clinoptilolite sample and calculated by the formula

$$n = V_w / V_0, \tag{1}$$

where n is the total porosity, defined by the saturation method, expressed in parts of unity; V_w is the water volume necessary for saturation of the air-dried clinoptilolite (cm³); and V_0 is the volume of air-dried clinoptilolite (cm³).

2.3. Study of basic parameters for porous structure

The structural parameters of the raw clinoptilolite were determined by low-temperature (77.7 K) nitrogen adsorption/desorption. The adsorption data, obtained via an ASAP 2010, Version 2.00 instrument (Micrometrics, Norcross, GA, USA), allowed the specific surface area (S_{BET}), total porous volume (V_p), micropore volume (V_{mic}), meso- and macropore volume ($V_{mes+mac}$), and average pore diameter (D_p) to be calculated. Samples were outgassed overnight at a temperature of 200 °C under vacuum (1×10^{-3} Torr).

Surface area of pores occupied by exchangeable cations of the raw clinoptilolite was evaluated using the chemical composition of the raw zeolite and by ammonium ion sorbed under static and dynamic conditions assuming monolayer adsorption.

2.4. Sorption studies

For measurement of the adsorption kinetics under dynamic conditions, an arrangement of four glass columns was employed. The bed height and volume of the columns were equal to 8 cm and 14 cm³, respectively. The columns were filled with different fractions of the zeolite preliminarily weighed by turns. A peristaltic pump REGLO (Ismatec, Glattbrugg, Switzerland) was employed to feed ammonium solutions to the zeolite-filled columns.

During the first stage of the study the ammonium solutions of 10, 50, and 100 mg/dm³ were filtrated through the columns by upflow at three different real velocities of 1.8, 6, and 9 cm³/min. The ammonium concentration of the samples collected from the column exit was monitored. The clinoptilolite fraction of 0.125–0.35 mm was studied with addition of the fraction of 0.35–0.5 mm as an overhead cover to prevent suffusion. The solutions were filtered through the columns until ammonium breakthrough larger than 2 mg/dm³ $N–NH_4^+$ was achieved. An ammonium solution of 100 mg/dm³ was run through the clinoptilolite fraction of 0.5–0.71 mm at three different velocities until an ammonium breakthrough of 100 mg/dm³ was achieved. The initial solution of 100 mg/dm³ was also run through the columns filled by the zeolite fractions of 1.4–2.0, 1.0–1.4, 0.71–1.0, and 0.5–0.71 mm at a real velocity of 9 cm³/min until an ammonium breakthrough of 100 mg/dm³ was achieved. In such cases, as well as in the case of filtration velocity of 1.8 cm³/min and ammonium concentration of 10 mg/dm³, the experiment was periodically stopped for nighttime. Concentrations of exchangeable cations were analyzed periodically in the effluents.

During the second stage of the study, 2.5 dm³ of the ammonium solution of 50 mg/dm³ was circulated through the column filled by a clinoptilolite fraction of 0.71–1.0 mm at a real velocity of 9 cm³/min. The $N–NH_4^+$ concentration of the samples collected from the column exit was determined. The solution samples of ammonium concentration more than 2 mg/dm³ were allowed to circulate through the same sorbent column again.

During the third stage of the experiment, ammonium sorption by the thermally and chemically modified clinoptilolite was studied. In this case the ammonium solution of 50 mg/dm³ was run at a real velocity of 6 cm³/min through the experimental columns filled by the clinoptilolite (fraction 0.71–1.0 mm) dried at temperatures of 110 and 300 °C and modified with HCl and NaCl solutions.

2.5. Chemical analysis

The ammonium concentration of the aqueous phase was determined by the standard Nesslerization method using the UniCam Helios α spectrophotometer (Cambridge, UK) equipped with a glass cuvette with an optical wawelength of 1 cm. Concentrations of aluminum and iron in the aqueous phase were analyzed using the Merck SQ 118 photometer (Darmstadt, Germany) equipped with a glass cuvette with optical wawelengths of 5 and 2 cm, respectively. Sodium, potassium, and calcium contents were determined by flame emission spectrometry using a Perkin–Elmer AA800 atomic absorption spectrometer. All chemicals of analytical grade used in this study were obtained from POCh, Gliwice, Poland.

2.6. Calculation of sorption parameters

The amount of ammonium sorbed from aqueous solution in a certain filtration time was determined by the formula

$$q_t = m_s/m = \big((C_0 - C_t)Qt\big)/m, \qquad (2)$$

where q_t is the amount of ammonium ions sorbed in a certain time expressed in mg/g sorbent; m_s is the mass of ammonium sorbed (mg); m is the adsorbent mass (g); C_0 is the initial concentration of NH_4^+ ions expressed in mg/dm^3; C_t is the concentration of NH_4^+ ions in the solution after filtration through the clinoptilolite column for this time (mg/dm^3); Q is the real flow rate of ammonium solution (dm^3/min); and t is the time of filtration (min).

The aggregate amount of ammonium ions sorbed for the total filtration time expressed in mass of ammonium sorbed (m_a, mg) and mass of ammonium sorbed per gram of the sorbent (q mg/g) was calculated by summing up the timed amounts.

The sorption effectiveness was evaluated by the formula

$$E = 100m_a/m_0 = 100m_a/(QtC_0), \qquad (3)$$

where E is the sorption effectiveness expressed in %; m_a is the mass of ammonium ions sorbed for the total filtration time expressed in mg; and m_0 is the mass of ammonium in the aqueous solution run through the zeolite-filled column (mg), with all the other symbols having been explained already.

A retardation factor of ammonium-ion front movement in filtration through the sorbent was calculated by the equation [23]

$$F_d = 1 + (\gamma/n)K_d, \qquad (4)$$

where F_d is the retardation factor of ammonium-ion front movement (equal to half of the initial concentration) through the sorbent; γ is the specific gravity of the sorbent expressed in kg/dm^3; n is the total porosity of the sorbent expressed in parts of unity; K_d is the distribution coefficient, dm^3/kg ($K_d = q_e/C_e$); q_e is the equilibrium amount of ammonium ions sorbed by the sorbent, g/kg; and C_e is the equilibrium concentration of NH_4^+ ions in solution, g/dm^3.

3. Results and discussion

Low-temperature nitrogen adsorption on Sokyrnytsya clinoptilolite (Fig. 1) is expressed by IV-type isotherm (BDDT) classification with a hysteresis loop of B-type [24] or by H3-type by IUPAC classification [25]. This type of isotherm testifies to the mesoporous structure of the clinoptilolite. The sharp rise of the isotherm under the lowest relative pressures ($p/p_0 = 10^{-6}–10^{-4}$) may be caused by the presence of free micropores in the clinoptilolite sample. A low nitrogen adsorption shown at the isotherm is conditioned by porous space occupation by exchangeable cations and water molecules partially.
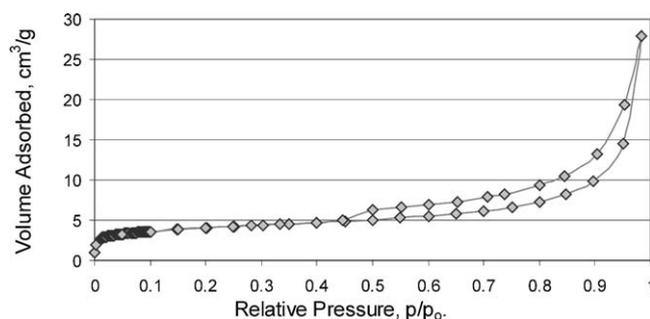

Fig. 1. Nitrogen adsorption/desorption isotherms for raw clinoptilolite.

Table 1
Basic parameters of clinoptilolite porous structures

S_{BET} (m^2/g)	V_p (cm^3/g)	$V_{mes+mac}$ (cm^3/g)	V_{mic} (cm^3/g)[a]	D_p (Å)
13.17	0.0432	0.0392	0.00396	131.83

[a] Calculated as difference between V_p and $V_{mes+mac}$.

Table 2
Surface area and volume of pores occupied by exchangeable cations by chemical composition of the Sokyrnytsya clinoptilolite and by ammonium ions sorbed

Parameters	K$^+$	Na$^+$	Ca^{2+}	Mg^{2+}	NH$_4^+$	
					Static	Dynamic
Surface area (m^2/g)	22.15	13.08	14.18	5.2	32.55	78.08
Porous volume (cm^3/g)	0.00407	0.0017	0.0019	0.0005	0.0071	0.017
Contents in the zeolite (meq/g)	0.61	0.64	0.75	0.53	0.64	1.54

The differential curves of nitrogen adsorption (BJH method) show polymodal distribution of pore sizes in the mesoporous section. There are maxima of pore volume corresponding to diameter intervals 19.4, 32.7, 48.3, 64.2, and 110–250 Å. Micropore volume values calculated by the method of Hovarth–Kovazoe and by a difference in V_p and $V_{mes+mac}$ are enough close to one another. By the Hovarth–Kovazoe method, V_{mic} of the raw samples is 0.0048 cm^3/g. Data listed in Table 1 illustrate the basic parameters of clinoptilolite porous structures [26].

Notice that the nitrogen adsorption isotherm reflects only the part of the zeolite porous volume not occupied by exchangeable cations and water molecules. Parameters of the clinoptilolite porous space occupied by exchangeable cations and by sorbed ammonium ions are demonstrated in Table 2. Hence the main exchangeable cations occupy a surface area of 54.61 m^2/g with a total pore volume of 0.0126 cm^3/g in raw clinoptilolite.

Data listed in Table 3 demonstrate that there is no simple direct connection between the fraction size and the values of the natural filtration flow rate and the total porosity of the air-dried clinoptilolite. At the same time the natural filtration flow rate decreases suddenly at transmission from

Table 3
Values of the natural filtration flow rate and the total porosity of the bare clinoptilolite depending on the fraction size

Fraction size (mm)	Natural filtration flow rate (cm^3/min)	Total porosity (%)
1.4–2.0	21	0.5
1.0–1.4	15	0.55
0.71–1.0	19	0.57
0.5–0.71	2.4	0.57
0.35–0.5	1.3	0.56
0.125–0.35	0.7	0.52

Table 4
Concentration of dissolved cations, iron, and alumina from the clinoptilolite in distilled water and hydrochloric acid

Components	HCl		H_2O	
	(mg/g)	(meq/g)	(mg/g)	(meq/g)
Al^{3+}	9.67		–	–
Fe	0.35		–	–
Na^+	11.32	0.49	6.79	0.11
K^+	5.36	0.14	–	–
Ca^{2+}	5.00	0.25	–	–

fractions of 0.71–1.0 to 0.5–0.71 mm, which has no adequate reflection in porosity change. One bed volume of ammonium solution was near 8 cm^3 for all fraction samples.

The concentrations of dissolved cations, iron, and alumina from the clinoptilolite in hydrochloric acid and distilled water are demonstrated in Table 4. Although only Na^+ ions were removed from the zeolite, probably by exchange with H^+ ions in distilled water, all three analyzed cations were replaced by H^+ ions in hydrochloric acid in the following order: $Na^+ > Ca^{2+} > K^+$. The results indicate that the clinoptilolite aluminosilicate structure is destroyed by hydrochloric acid.

Fig. 2 illustrates a general reverse connection between the amount of ammonium ions sorbed by the zeolite and ammonium solution flow rates. But in the saturation experiment (up to achieving the maximum sorption capacity), an inversion of this connection was observed beginning from some moment. The clinoptilolite (fraction 0.5–0.71 mm) was saturated by ammonium ions from the 100 mg/dm³ N–NH₄ solution passed with flow rates of 9, 6, and 1.8 cm^3/min for 28.5, 23.5, and 31.5 h that corresponds to filtration of 1924, 1058, and 425 bed volumes of the solution. By this, after passage of 425 bed volumes, the ammonium sorbed amount was increased mostly at the flow rate of 9 cm^3/min.

The observed proximity of the breakthrough curves is caused by a higher concentration gradient and by rapid removal of exchange products at flow rate increase compensating for the advantage of zeolite-solution contact duration at lower flow rates.

Although the saturation time was independent of the fraction sizes, ammonium sorption effectiveness of the clinoptilolite samples increased with decreasing fraction size (Fig. 3) as well as with flow rate value.
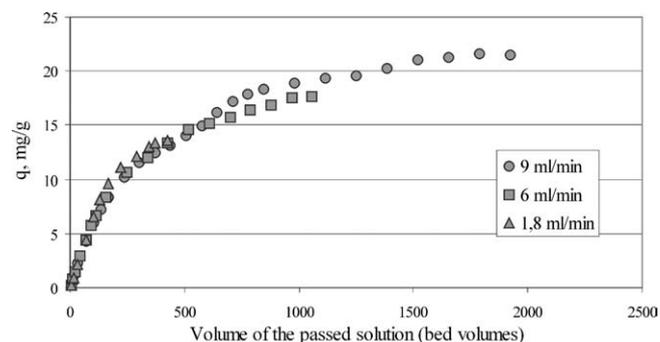

Fig. 2. Influence of the flow rate on the breakthrough curve of ammonium ion sorption by clinoptilolite (05–0.71 mm) at N–NH₄ initial concentration 100 mg/dm³.
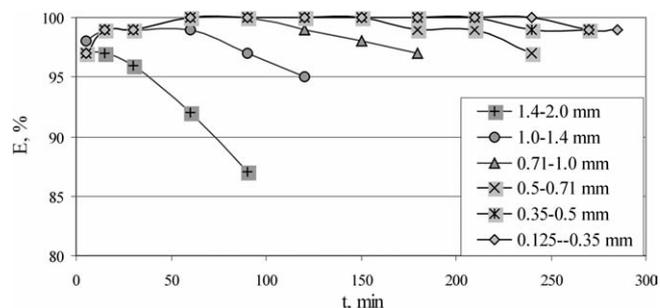

Fig. 3. Influence of the clinoptilolite fraction size on the sorption effectiveness of ammonium removal at 50 mg/dm³/N–NH₄ initial concentration at flow rate 6 cm^3/min.
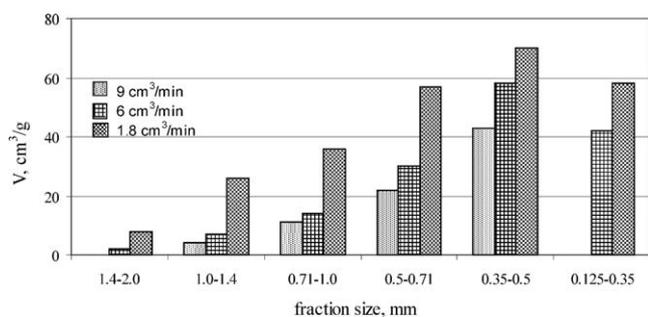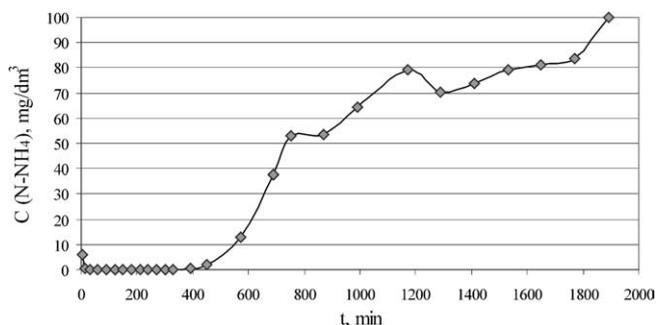
At the same time the maximum sorption capacity of clinoptilolite toward ammonium increased with decreasing fraction size and as the flow rate increased. For all values of maximum sorption capacity the distribution coefficients are close, as determined for the dynamic and static conditions. Results shown in Table 5 demonstrate that the dynamic ion-exchange capacity is higher than the static capacity. This is conditioned by higher concentration gradients and by constant removal of exchange products under dynamic conditions. Taking into account the clinoptilolite specific gravity [21], we evaluated the retardation factor of ammonium-ion front movement depending on the fraction size and the flow rate of the solution (Table 5). The proximity of the values of the distribution coefficients and the retardation factors for different conditions at an initial ammonium concentration of 100 mg/dm³ makes it possible to use these parameters for modeling of ammonium sorption by the clinoptilolite under dynamic conditions for chosen filtration parameters. For example, it may be used for calculation of the lifetime of permeable barriers for ammonium-polluted water purification.

It has been established that the use of a clinoptilolite fraction finer than 0.35 mm is ineffective for ammonium removal under dynamic conditions because of suffusion in the zeolite column. Generally the optimal results in ammonium solution up to the maximum admissible concentration (2 mg/dm³) were obtained at the lowest filtration rate through the clinoptilolite fraction 0.35–0.5 mm (Fig. 4).
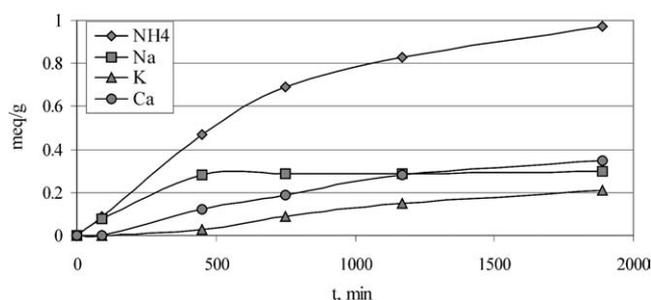
Table 5
Ammonium sorption parameters of the clinoptilolite under static and dynamic conditions at the initial ammonium concentration of 100 mg/dm^3

Sorption conditions		Maximum sorption capacity (mg/g)	Sorption effectiveness (%)	Distribution coefficient (dm^3/kg)	Retardation factor
Fraction size (mm)	Flow rate (cm^3/min)				
Static conditions					
0.16–0.315	–	6.8	69	219	1003
Dynamic conditions					
1.4–2.0	9	18.51	15	215	1024
1.0–1.4	9	19.24	16	226	979
0.71–1.0	9	20.37	16	240	1003
0.5–0.71	9	21.52	17	256	1070
0.5–0.71	6	17.61	25	235	982
0.5–0.71	1.8	13.56	49	265	1107

Fig. 4. Solution volume (V, cm^3/g) purified to 2 mg/dm^3 of ammonium ions per gram of the sorbent (at initial concentration 100 mg/dm^3).

Fig. 6. Dynamics of ammonium sorbed and cations desorbed amounts at the clinoptilolite column test (fraction 0.5–0.71 mm, 100 mg/dm^3 N–NH$_4$ initial concentration at flow rate 1.8 cm^3/min).

Fig. 5. Dynamics of the ammonium concentration at the zeolite column exit (fraction 0.5–0.71 mm, 100 mg/dm^3 N–NH$_4$ initial concentration at flow rate 1.8 cm^3/min).

Ammonium sorption by the clinoptilolite under dynamic conditions reached maxima as well as minima of ammonium concentration in the zeolite column exit after some time from the process beginning (Fig. 3). Then the sorption effectiveness was at the same level during a certain period depending on the filtration parameters and decreased after some time. This effect became more evident with decreasing fraction size, initial ammonium concentration, and flow rate value. For example, the maximum solution volume passed before reaching 100% sorption effectiveness was 135 bed volumes at 10 mg/dm^3 N–NH$_4$ initial concentration for flow rate 1.8 cm^3/min.

Breaks of 12 h in the sorption process led to stabilization or even to decrease in the ammonium concentration in the column exit solutions. The results, pictured in Fig. 5, demonstrate a clear decrease of the exit concentrations corresponding to the night breaks after 750 and 1170 min of the process. These phenomena, observed for all initial concentrations and flow rates, may be conditioned by ordering of NH$_4^+$ ions sorbed on sorption centers and by effects of particle diffusion as well as by changes of clinoptilolite exchangeable cations taking part in ammonium removal from aqueous solution. In the last case sharp increases in ammonium sorption may be noted also during the nonstop filtration. Amounts of ammonium sorbed by the zeolite as well as of desorbed cations analyzed at the time periods of 90, 450, 750, and 1170 min corresponding to the sharp changes in ammonium exit contents are shown in Fig. 6.

One can notice that during the first 90 min of the process when N–NH$_4$ concentration in the effluent decreased from 5 to 0 mg/dm^3, ammonium ions were removed from the solution by exchange with Na$^+$-ions only. After 90 min, contents of three replaced cations increased continually in the order Na$^+$ > Ca^{2+} > K$^+$ until 1170 min, when Ca^{2+} > Na$^+$ > K$^+$ was substituted. The night interruption after 300 min has no reflection in Figs. 5 and 6 and the sharp change of the exit ammonium concentration was not connected with the nature of the exchangeable cations. Beginning from 450 min, the amount of sodium ions replaced was stable up to full saturation of the clinoptilolite. Hence sodium was observed to be more easily exchanged than other
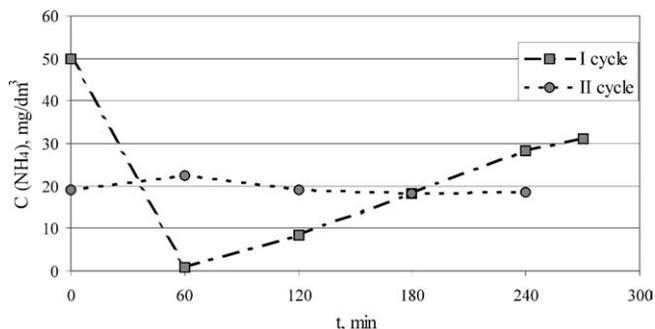
Fig. 7. Dynamics of the ammonium concentration at the zeolite column exit at the recycling study.
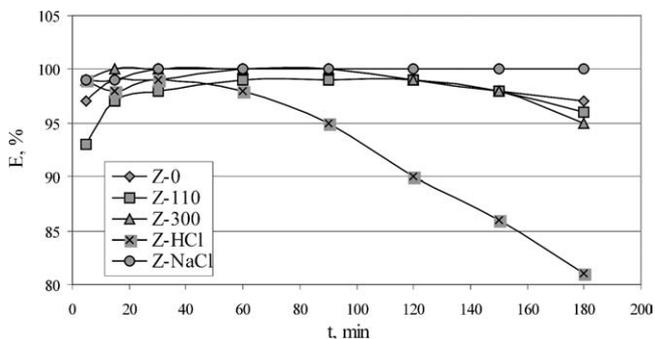

Fig. 8. The sorption effectiveness of ammonium removal at 50 mg/dm^3 N–NH$_4$ initial concentration and flow rate 6 cm^3/min of the zeolite treated chemically, by temperature.

cations in the zeolite and to be the most important in water purification up to the first milligrams per liter of N–NH$_4$.

During the recycling study the first exit solution, analyzed an hour after the process beginning, was purified to 0.96 mg/dm^3. The rest of the solution, 1.95 dm^3, with a sum ammonium concentration of 18.98 mg/dm^3 was allowed to circulate through the same sorbent column for cycle II. Notice that during cycle I the total ammonium amount sorbed by the clinoptilolite was equal to 6.36 mg/g, that is significantly lower than the maximum sorption capacity of the clinoptilolite evaluated under the same conditions as 20.37 mg/g. But the results shown in Fig. 7 demonstrate that during cycle II ammonium ions were desorbed from the clinoptilolite with an exit ammonium concentration of 21.28 mg/dm^3.

Process stopping long before the maximum sorption capacity of the sorbent was reached emphasizes the importance of concentration gradient and the external diffusion for ammonium sorption by the clinoptilolite.

In contrast to the chemical preparation, the heat treatment of the clinoptilolite samples at temperatures of 110 and 300 °C has no influence on clinoptilolite ability for ammonium removal (Fig. 8, clinoptilolite: Z-O—nonmodified; Z-110 and Z-300—dried at temperatures 110 and 300 °C; Z-HCl and Z-NaCl—modified by 2 M HCl and NaCl solutions), which corresponds to the results for static conditions [21].

The significant decrease of the ammonium sorption effectiveness of the acid-treated clinoptilolite, together with the removal of nearly 16% aluminum from the clinoptilolite during the acid treatment, estimated in this study may confirm the predominant importance of the ion-exchange mechanism of ammonium removal from the aqueous solution in comparison with the sieve effects. It is known that the zeolite ion-exchange ability is conditioned mainly by silicon substitution for aluminum in the crystalline framework with formation of noncompensated negative charges and that the zeolite may lose the aluminum with structure conservation [1]. Therefore aluminum removal from the clinoptololite has to result in decrease of the ion-exchange ability of the sorbent. The highest NH$_4^+$-ion uptake effectiveness was reached using the clinoptilolite sample modified by sodium chloride (Fig. 8). Apparently, thanks to the high concentration gradient, the majority of zeolite exchangeable cations are substituted for sodium ions bound weakly in the structures of the clinoptilolite, which improved the ammonium removal effectiveness.

4. Conclusions

Maximum sorption capacity of the Transcarpathian clinoptilolite toward ammonium evaluated under dynamic conditions varies in the interval 13.56–21.52 mg/g, being significantly higher than determined under static conditions.

The values of the sorption distribution coefficient and of the retardation factor of ammonium-ion front movement were calculated as equal to 215–265 dm^3/kg and 979–1107, respectively, for different clinoptilolite fractions and the flow rate of the solution. The proximity of the values of the corresponding results for different conditions at a certain initial ammonium concentration makes it possible to use these parameters in modeling ammonium sorption by the clinoptilolite.

Slowing of the filtration velocity of the initial solution, as well as 12-h breaks in the sorption process, resulted in improvement of ammonium sorption properties of the natural zeolite, which is probably connected with ordering of the ammonium sorbed on sorption centers and with effects of particle diffusion. The order of NH$_4^+$-ion exchange selectivity for cations on the zeolite is Na$^+$ > Ca^{2+} > K$^+$ with replacement of sodium by calcium close to ammonium saturation of the zeolite.

The ammonium sorption effectiveness increases with use of the finer fractions of the clinoptilolite, but utilization of the fraction finer than 0.35 mm is needless for the dynamic conditions because of suffusion phenomena.

The relatively lower sorption effectiveness at the beginning of the filtration experiment with its following increase was observed. This effect became more evident with the decrease of the fraction size, the initial ammonium concentration, and, the flow rate value.

In contrast to the heat preparation of the clinoptilolite that not influencing the ability for ammonium removal, acid treatment accompanied by destruction of the zeolite framework led to a decrease in sorption ability. Because of weak binding of Na^+ ions in the structure of the Transcarpathian clinoptilolite, NaCl treatment of the zeolite resulted in ammonium uptake improvement.

Recycling study results confirmed the importance of external diffusion for ammonium sorption by the clinoptilolite. Preliminary treatment of the sorbent confirmed the predominant importance of the ion-exchange mechanism in the process.

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