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## Removal of ammonium ions by selected natural and synthetic zeolites

### Introduction

Nitrogen is an essential and main nutrient for all forms of life. It constitutes a basic building block of plant and animal proteins. However, too much of nitrogen, can be toxic. The presence of excess nitrogen in the environment caused crucial distortions in the natural nutrient cycle between organisms and the soil, water, and atmosphere. Nitrogen in the form of nitrous oxide, nitric oxide, nitrate, nitrite or ammonia/ammonium is soluble in water, so it can be found in ground and drinking water (Rožič et al. 1998).

The extent of nitrogen contamination in water has raised due to the large quantities of industrial and domestic wastewater discharges to the environment. Increased its concentrations in domestic wastewaters are becoming significant among the pollutants. Nitrogen pollution in hydrosphere causes eutrophication of lakes and rivers all over the world. The ammonia and ammonium ions, which cause undesired odours and several diseases, are the most commonly encountered nitrogenous compounds in wastewaters (Balci 2004).

The term ammonia came from chemical-related use in approximately since 1799 and is derived from the name of the ancient Egyptian deity Ammon. In this context, ammonia means the gas emitted by camel dung and urine in the vicinity of temples honoring Ammon (Lewis 1993). Today, ammonia is understood as the result of the bacterial decomposition of organic matter containing nitrogen (O'Neill 1985). For instance, the degradation of the simple organic molecule urea ((NH<sub>2</sub>)<sub>2</sub>CO) in water:

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results in the formation of un-ionized ammonia ( $\text{NH}_3$ ) and carbon dioxide ( $\text{CO}_2$ ). At the same time, complex organic molecules present in industrial and municipal wastes, plants and animal matter also form  $\text{NH}_3$  when degraded. Therefore, in aqueous solution, ammonia exists in two forms as a function of pH, ion strength and temperature (Burgess et al. 2003):



In the same way ammonium is the inorganic ion form of nitrogen pollution occurring in municipal sewage, industrial wastewaters and agricultural wastes or decomposed from organic nitrogen compounds in those wastewater and wastes. Higher concentration of ammonium could cause a sharp decrease of dissolved oxygen and dissolved oxygen depletion and obvious toxicity on aquatic organisms in receiving water (Du et al. 2005; Wen et al. 2006). Ammonia, present in the aquatic environment, is toxic to all the vertebrates and cause convulsions, coma and death, probably, because elevated  $\text{NH}_4^+$  displaces  $\text{K}^+$  and depolarises neurons inducing cell death in the central nervous system (Gefeniené et al. 2006). Because of its toxicity to fish species, the complete removal of ammonium from wastewater is required. The most widely applied traditional processes of ammonia removal are air stripping, ion exchange and biological nitrification–denitrification.

The efficiency of the air stripping and biological nitrification–denitrification processes is significantly impaired by the low temperature in winter (Gefeniené et al. 2006; Du et al. 2005).

The removal of ammonia/ammonium ions from industrial wastewaters and municipal sewage is a problem of environmental and economic concern. The major sources of these impurities include: nitrogen fertilizers production, chemical fiber plants, aquaculture industry, agricultural run-off and others. Ammonium concentration depends on the source of the pollution. It varies from less than  $1 \text{ mg/dm}^3$  in agriculture industry to much higher (10-fold) in the wastewaters from chemical industry (Gefeniené et al. 2006).

Inorganic nitrogen species, which are 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 (Sprynskyy et al. 2005).

Today, many techniques for the removal of ammonia/ammonium ions are applied. A number of them, such as biological treatment, air stripping lead to the destruction of the ammonium species and also the recovery become impossible. Among various methods available for ammonium removal from waters and wastes, ion exchange seems to be most attractive and the easiest when effective, low-cost materials are used as exchangers (Sprynskyy et al. 2005) (for example sorption on solid substrate such as silicate clay minerals) (Balci 2004). So from a practical standpoint, ion exchange is one of the most promising techniques. Therefore they are often and detailed examined by different

authors using various sorbents (see Karadag et al. 2006; Wang et al. 2008; Ivanova et al. 2010 etc.).

For this purpose the zeolite seems to be the very promising material. They have high cation-exchange ability as well as molecular sieve properties. Especially natural zeolites, because they are very cheap materials, easily available in large quantities in many part of the world. By adsorption in their cavities zeolites are able to bind various substances – inorganic, organic, biologically active and others, which may in turn modify their physico-chemical properties (Mačala et al. 2009). So, they could be applied to water and gas purification, adsorption and catalysis, and agriculture and aquaculture. Zeolites also play an important role in over other filter materials of significant permeability and so are widely used for water purification by filtration (Sprynskyy et al. 2005).

Natural zeolites, especially clinoptilolites, show greater selectivity in relation to univalent ions. The order of selectivity for clinoptilolites is presented in the following sequence, described by Mercel and Ames (1976):  $Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}$  which perform that clinoptilolites are promising to removal of ammonium ions (Kaleta et al. 2007).

Ammonium ions are removed from aqueous solutions using zeolite by exchange with cations or by adsorption in pores of aluminosilicate groups. Ion exchange are dominant when concentration of ammonium is equal or lower than the concentration of exchangeable cations of the zeolite, and adsorption begins to predominate with increase of ammonium content (Jorgensen et al. 1976). Ammonium adsorption in case of zeolites consists in ion exchange of ammonium ions with sodium, potassium, magnesium, and calcium ions at cation-exchange sites of zeolites (Watanabe et al. 2003).

Therefore those researches describe usage possibilities of ammonium ions removal from water solutions with natural and synthetic zeolites applications.

## 1. Materials and methods

### 1.1. Materials

For investigations, four types of materials were used: two natural zeolites and two synthetic zeolites. Natural zeolites were represented by clinoptilolite rocks from Dylągówka deposit (Poland) (Fig. 1A) and Sokyrnytsya deposit (Ukraine) (Fig. 1B). Dylągówka zeolite has constituted clinoptilolite material which was a result of laboratory treatment of clinoptilolite-montmorillonite clay (Franus 2000). Ukrainian zeolite from Sokyrnytsya deposit was a commercial product with about 70–75% of clinoptilolite (Sprynskyy et al. 2005). The synthetic zeolites were represented by sodalite material (Fig. 1C) and Na-X (both of them were obtained in hydrothermal reaction of fly ash with NaOH) (Fig. 1D) (Derkowski et al. 2006).

## 1.2. Methods

The mineral composition for all samples was determined via X-ray diffraction (XRD) by means of Philips X'pert APD diffractometer with PW 3020 goniometer, Cu tube and graphite monochromator. The identification of phases was based on ICDD PDF-2 database and collection of patterns recommended by IZA (International Zeolite Association) (Treacy, Higgins 2001). Random preparations were made in a mortar taking 300 mg of a sample grinded to ca. < 20  $\mu\text{m}$  fraction.

Observations and analysis of chemical composition of the reaction products in micro-range were carried out using field emission scanning electron microscope (SEM) HITACHI S-4700 equipped with energy dispersive spectrometry (EDS) system VANTAGE NORAN.

Measurements of the surface area and pore volume were conducted by means the ASAP 2405 instrument (Micromeritics). Using programming provided by Micromeritics, the instrument performs physical adsorption and desorption of gases. All procedures are workable with nitrogen and helium, and for low surface areas also with krypton. Before analysis the samples were degassed at 350°C for 24h, until the pressure in the tubes stabilized at  $2 \cdot 10^{-3}$  mm Hg. In the course of analysis the sample is penetrated by pure nitrogen (99.999%) in order to obtain the required pressure  $P/P_0$  (an adequate number of points to calculate the isotherms). During the analysis the sample is immersed in a container filled with liquid nitrogen. Next, nitrogen dosage (adsorption) is continued until the atmospheric pressure is reached, which is followed by the reverse process (desorption) (Derkowski et al. 2007).

The cation exchange capacity (CEC) was determine using  $\text{NH}_4\text{Cl}$  method. The 0.5 g of sample was treated by 30 ml of 1M  $\text{NH}_4\text{Cl}$ . Next, over 8 hours, these solutions were mixed using magnetic stirrer and heated to the temperature of 60°C. After that the solutions was left for 24h in order to separate and decant solutions over precipitates. Those procedures were repeated 5 times. In obtained solutions, using AAS (Atomic Adsorption Spectrometer) instrument, the content of calcium, magnesium, sodium and potassium were measured. The sum of those elements contents was converted to CEC per 100g of sample (Natural... 1995). The experiment of cation exchange capacity was repeated for each sorbent after its thermal activation at temperature of 200°C in 24h period.

The sorption process of  $\text{NH}_4^+$  on tested materials was conducted via batch methods. This experiment was carried out as follow: 0.5 g of adsorbent sample was mixed with 50  $\text{cm}^3$   $\text{NH}_4\text{Cl}$  solutions, in which initial concentration of  $\text{NH}_4\text{Cl}$  ranging from 10 to 500  $\text{mg}/\text{dm}^3$  and next, such prepared sample were shaken out during 60 min and after that centrifuged during 10 min (at 3000 rpm).

After centrifugation the amount of  $\text{NH}_4^+$  was determine using Flow Injection Analyser FIAstar 5000 (FOSS).

The amount of adsorbed  $\text{NH}_4^+$  ions were calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (3)$$

where:

- $q_e$  – total amount of adsorbed  $\text{NH}_4^+$  ions [mg/g],
- $C_0$  – initial concentration of  $\text{NH}_4^+$  in the solution [mg/dm<sup>3</sup>],
- $C_e$  – equilibrium concentration of  $\text{NH}_4^+$  in the solution [mg/dm<sup>3</sup>],
- $V$  – volume of the analysed solution [dm<sup>3</sup>],
- $M$  – adsorbent mass [g].

The experiment of cation exchange capacity, the BET surface area, PSD and sorption was repeated for thermal activated sorbents at temperature of 200°C.

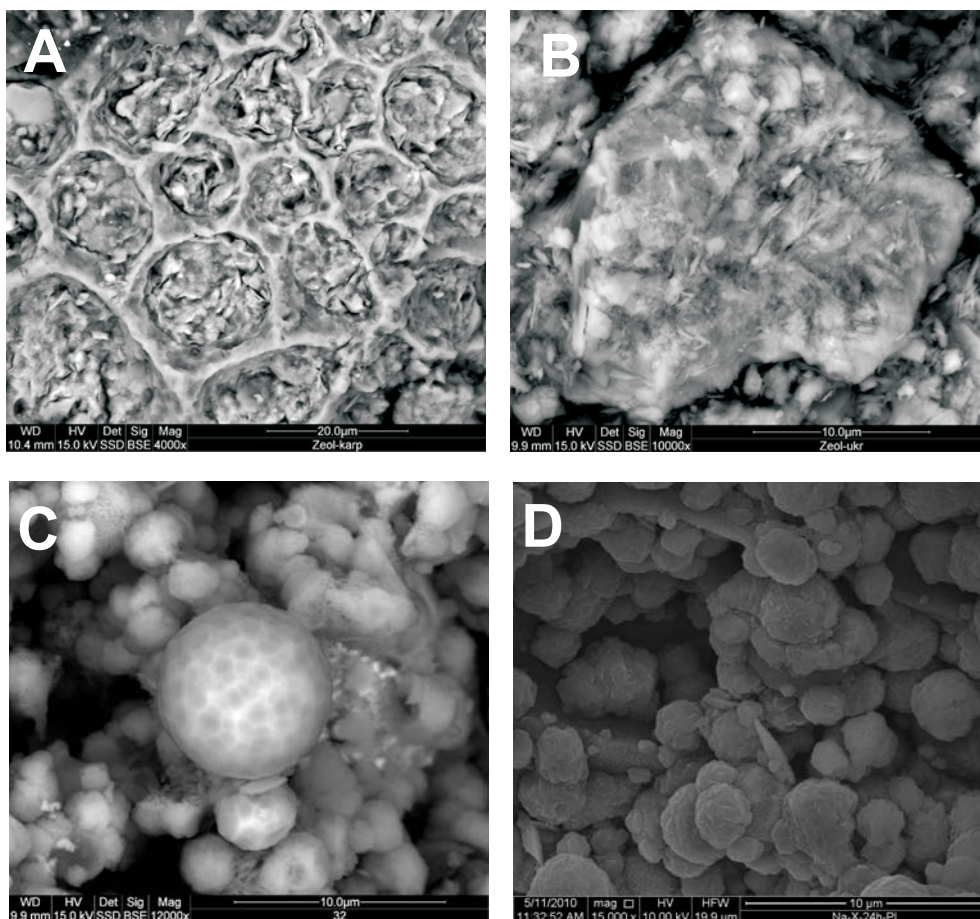


Fig. 1. SEM microphotographs of tested zeolite materials  
(A – Dylagówka zeolite, B – Sokyrnytsya zeolite, C – sodalite, D – Na-X)

Rys. 1. Mikrofotografie SEM badanych materiałów zeolitowych  
(A – zeolit z Dylagówki, B – zeolit z Sokyrnytsya, C – sodalit, D – Na-X)

## 2. Results

### 2.1. Mineralogical-chemical investigations

The mineralogical analysis of selected, untreated materials has concerned a determination of mineralogical composition by XRD, description of mineral grains morphology and determination of chemical composition in microareas (SEM-EDS).

In case of natural zeolites the XRD analysis has shown that the dominant mineral component in both cases is clinoptilolite. The Dylągówka zeolite has constituted the subjected to laboratory treatment a clinoptilolite-montmorillonite clay material (where the average content of clinoptilolite was about 25%). The clinoptilolite was separated from those materials by sedimentary method, where that mineral has constituted the filling of radiolarian frustules. Obtained in such way zeolitic material contained about 80% of pure clinoptilolite. The content of clinoptilolite in zeolitic material from Sokyrnytsya deposit was about 70–75% (Sprynskyy et al. 2005). Besides in both natural zeolites the small amount of CT opal, quartz and K-feldspars were observed. For Dylągówka zeolite additionally occurs montmorillonite coming from initial materials.

The morphological forms of those zeolites are different. Dylągówka zeolite forms elongated laminas about 5–25  $\mu\text{m}$  size and constituted a filling of radiolarian frustules (Fig. 1A). Sokyrnytsya zeolite formed aggregates about 20–30  $\mu\text{m}$  size with laminas-like habit (Fig. 1B).

Synthetic zeolites are represented by sodalite and Na-X. Both are obtained in synthesis of fly ash with NaOH at hydrothermal condition. Sodalite material mineral consisted mainly of sodalite occurring with small amount of mullite and quartz. Sodalite forms typical for themselves cubic-octahedrons (Fig. 1C) whose sizes reach up to 5  $\mu\text{m}$ .

Second synthetic zeolite constituted rich in Na-X (about 70% content) material. The remaining material is unreacted in synthesis process residuum (where the main component is mullite, small amount of aluminosilicate glass and quartz). The Na-X zeolite occurs in intergrowth laminas aggregates forming spherical forms or isometric crystals (Fig. 1D). The size of predominant grains is generally smaller than 5  $\mu\text{m}$ .

Natural zeolites (clinoptilolites) have similar chemical compositions. Their main oxide are  $\text{SiO}_2$  – 64.82% and  $\text{Al}_2\text{O}_3$  – 11.53% for Dylągówka zeolite,  $\text{SiO}_2$  – 65.59% and  $\text{Al}_2\text{O}_3$  – 10.98% for Sokyrnytsya zeolite, respectively. Exchangeable cations in both cases are mainly calcium, which content is CaO – 2.21% for Dylągówka and 3.10% for Sokyrnytsya, respectively. Sum of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  for Dylągówka zeolite is 1.47% and 1.80% for Sokyrnytsya zeolite.

Different chemical composition, in relation to natural zeolites, have synthetic zeolites. They have lower content of  $\text{SiO}_2$  35.45% for sodalite and 56.83% for Na-X and also much lower content of  $\text{Al}_2\text{O}_3$  30.56% for sodalite and 32.33% for Na-X, respectively. Exchangeable ions are represented by sodium which content are 23.47% for sodalite and 5.42% for Na-X, respectively.

## 2.2. Textural investigations

The textural analysis has shown that the largest BET surface area has synthetic zeolite Na-X (262 m<sup>2</sup>/g). Much lower values were observed for zeolite from Dylągówka – 14 m<sup>2</sup>/g, and zeolite from Sokyrnytsa – 24 m<sup>2</sup>/g and synthetic sodalite (34 m<sup>2</sup>/g). The PSD (pore size distribution) analyses for all zeolites have performed bimodal distribution of pores with predominant pores with diameter from 3 to 5 nm for synthetic zeolites and from 6 to 9 nm and from 15 to 18 nm for natural zeolites (Fig. 2).

## 2.3. CEC determination

The largest CEC has showed synthetic zeolite Na-X (257 mval/100g). Natural zeolite from Sokyrnytsa cation exchange capacity is 142 mval/100g. The lowest values of CEC have sodalite material 84 mval/100g and natural zeolite from Dylągówka 35 mval/100g. The thermal activation at 200°C temperature during 24 hours practically did not influence on CEC values which amount as follow: Na-X – 242 mval/100g, sodalite 87 mval/100g, zeolite from Sokyrnytsa 140 mval/100g, zeolite from Dylągówka 38 mval/100g.

## 2.4. Sorption experiments

The results of ammonium ions removal experiment on tested materials (before and after thermal activation at temperature 200°C) for different concentration ammonium chloride solutions (50–500 mg/dm<sup>3</sup>) are performed in the Fig. 3. Generally, the higher initial concentration of NH<sub>4</sub>Cl the higher amount of adsorbed ions from the solution using zeolitic minerals as sorbents. Fig. 3 has shown that thermal activation of tested materials did not influence on amount of adsorbed ammonium ions.

The maximal amount of ammonia ions were adsorbed by Sokyrnytsya zeolite (6.0 mgNH<sub>4</sub>/g) and Na-X (5.0 mgNH<sub>4</sub>/g) at concentration of NH<sub>4</sub>Cl solution 400mg/dm<sup>3</sup>. A lower sorption values revealed sodalite 4.5 mgNH<sub>4</sub>/dm<sup>3</sup> at initial concentration of solution 500mgNH<sub>4</sub>/dm<sup>3</sup>. The worst sorbent seems to be Dylągówka zeolite which adsorbed only 3.3 mgNH<sub>4</sub>Cl/dm<sup>3</sup> at initial concentration of solution 400 mg/dm<sup>3</sup>.

## 2.5. Ammonium exchange isotherms

The ion exchange of NH<sub>4</sub><sup>+</sup> on the tested materials was analyzed using Langmuir and Freundlich isotherm models. For linear form of Langmuir equation the following procedure was used:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (4)$$

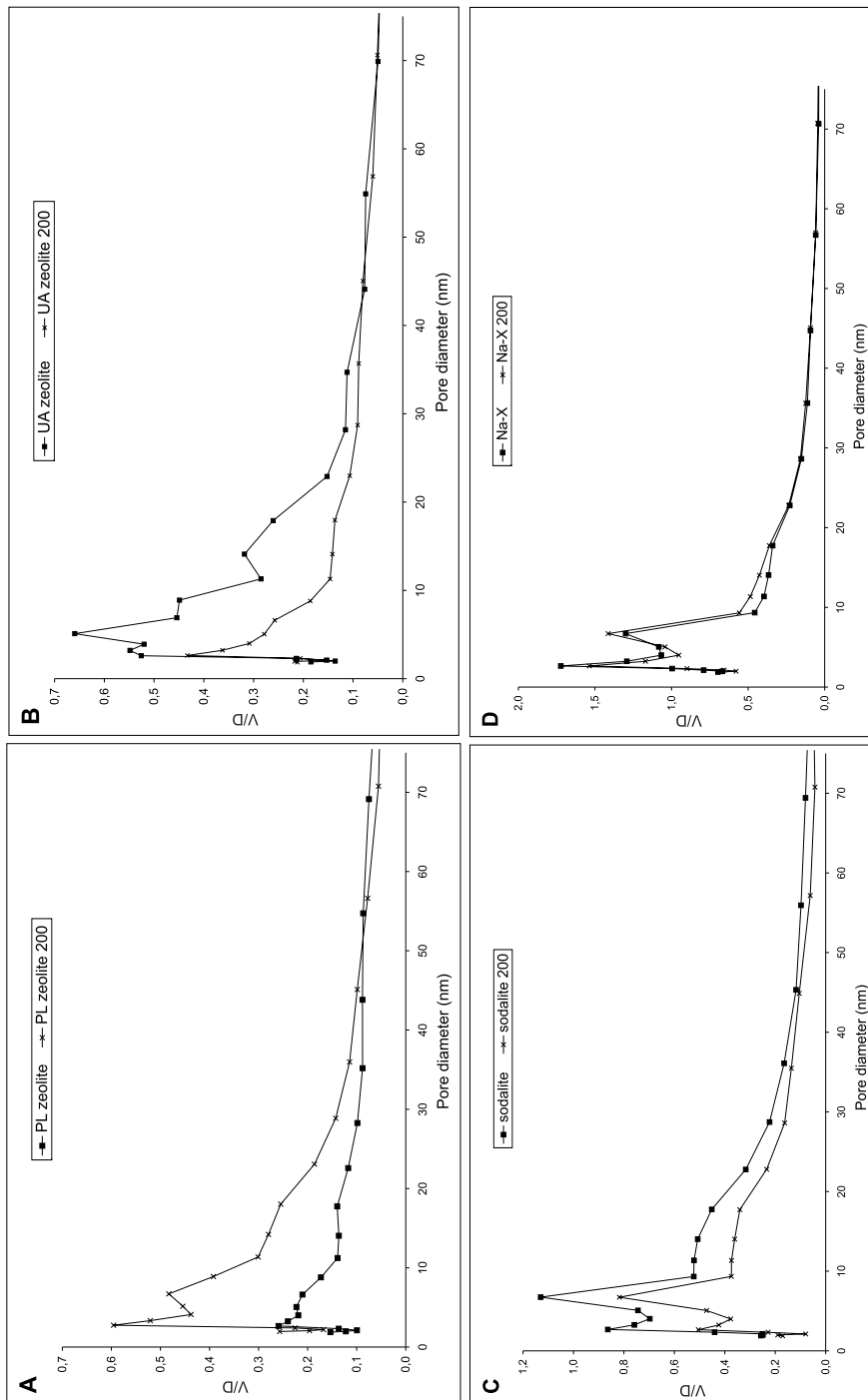


Fig. 2. Pore size distribution for tested zeolite materials (A – Dylągówka zeolite, B – Sokymytsya zeolite, C – sodalite, D – Na-X)

Rys. 2. Rozkład wielkości porów dla badanych materiałów zeolitowych (A – zeolit z Dylągówki, B – zeolit z Sokymytsya, C – sodalit, D – Na-X)



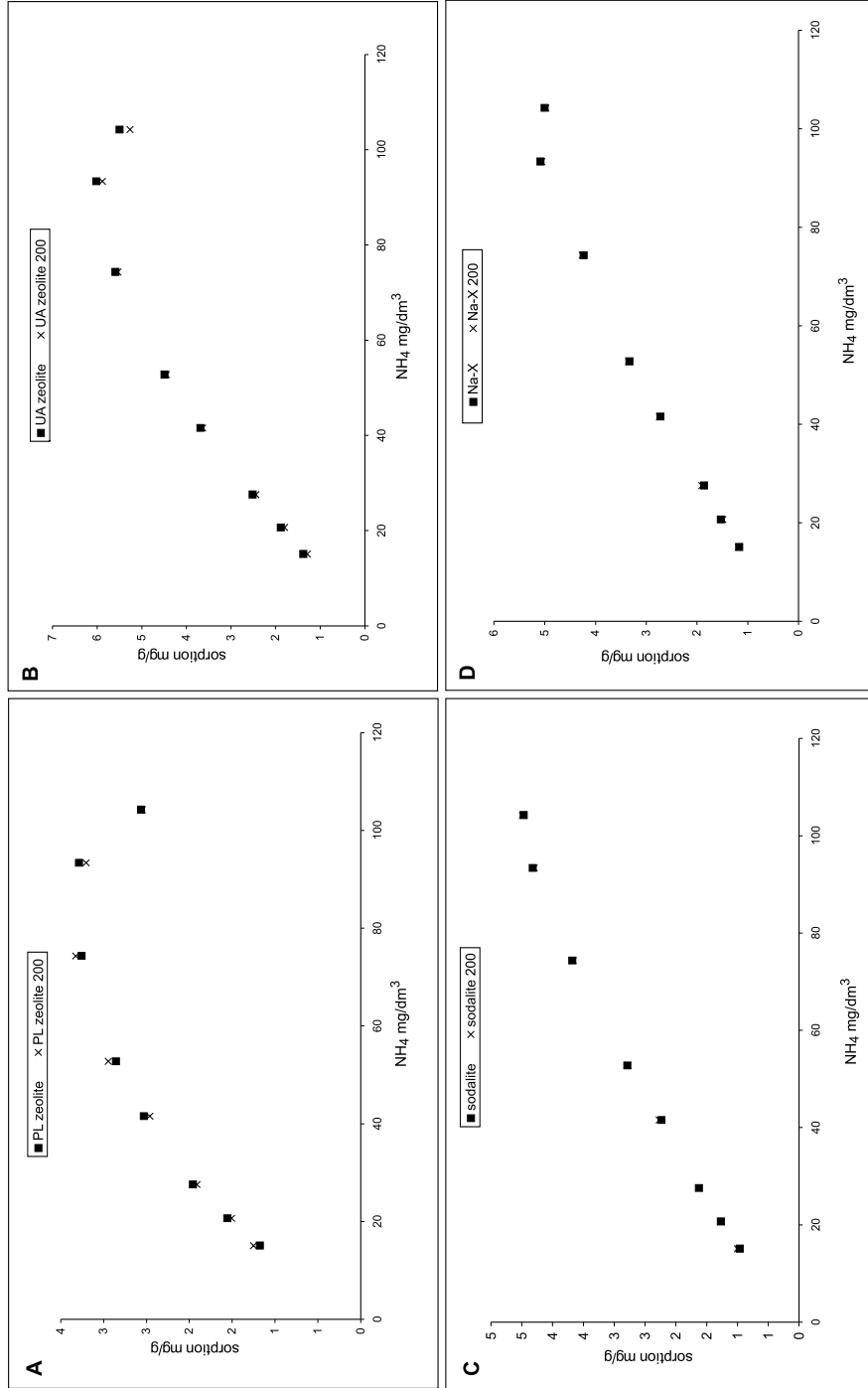


Fig. 3. Sorption curves of NH<sub>4</sub><sup>+</sup> for tested zeolitic materials (A – Dylągówka zeolite, B – Sokymytsya zeolite, C – sodalite, D – Na-X)

Rys. 3. Krzywe sorpcji NH<sub>4</sub><sup>+</sup> dla badanych materiałów zeolitowych (A – zeolit z Dylągówki, B – zeolit z Sokymytsya, C – sodalit, D – Na-X)

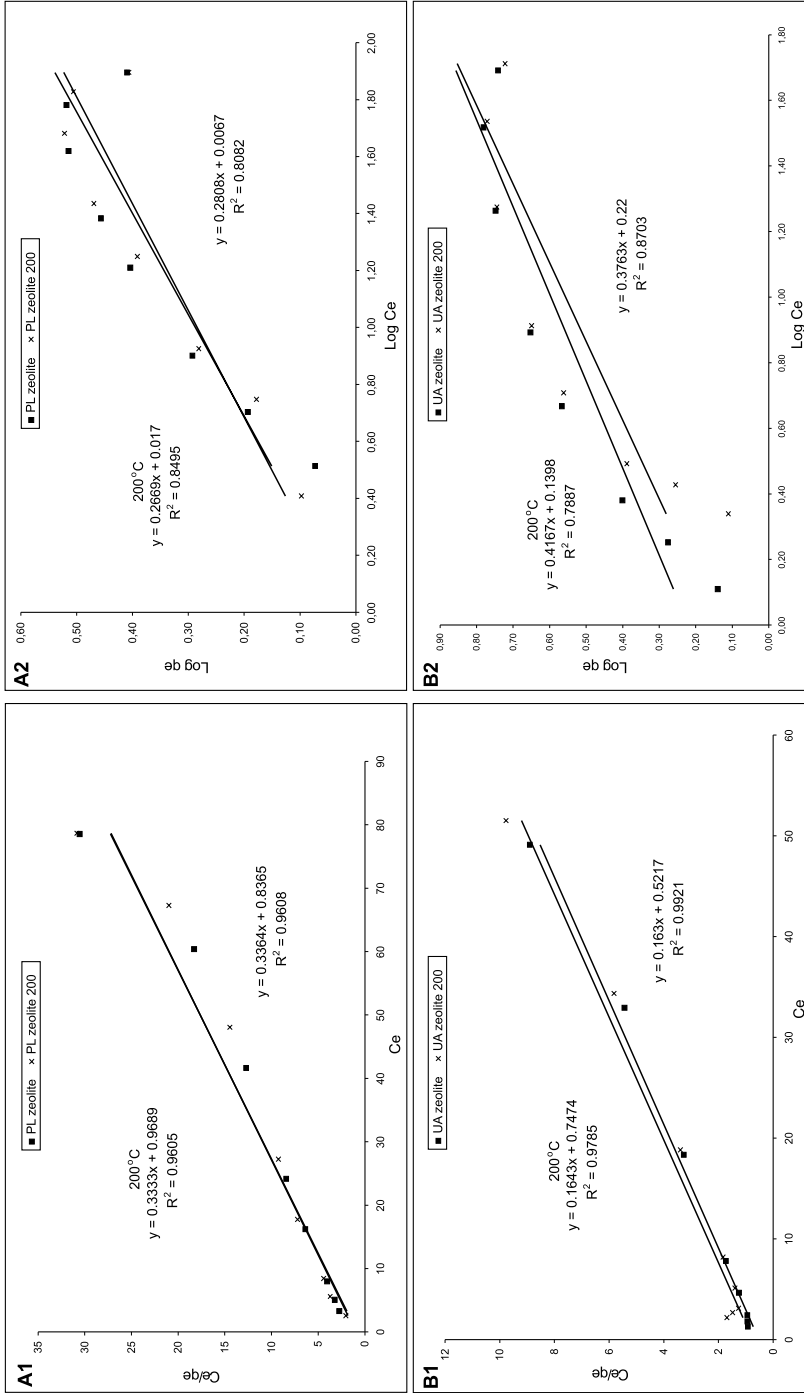


Fig. 4. Sorption isotherms of  $\text{NH}_4^+$  ions for tested zeolitic materials (Langmuir: A1 – Dylągówka zeolite, B1 – Sokyrnytsa zeolite; Freundlich: A2 – Dylągówka zeolite, B2 – Sokyrnytsa zeolite)

Rys. 4. Izotermny sorpcji jonów  $\text{NH}_4^+$  dla badanych surowców zeolitowych (Langmuira: A1 – zeolit z Dylągówki, B1 – zeolit z Sokyrnytsa; Freundlich: A2 – zeolit z Dylągówki, B2 – zeolit z Sokyrnytsa)

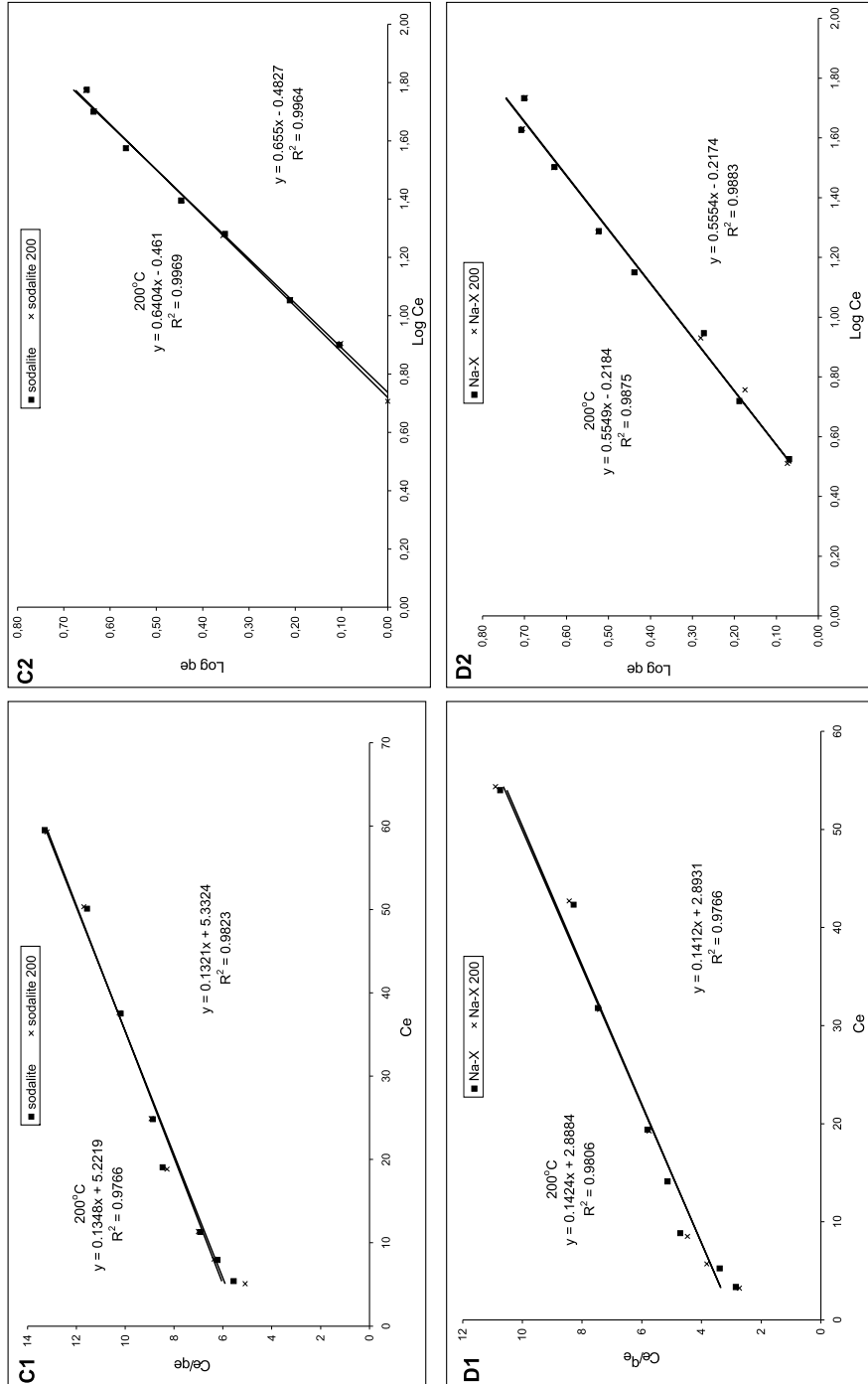


Fig. 5. Sorption isotherms of  $\text{NH}_4^+$  ions for tested zeolitic materials (Langmuir: C1 – sodalite, D1 – Na-X; Freundlich: C2 – sodalite, D2 – Na-X)

Rys. 5. Izotermny sorpcji jonów  $\text{NH}_4^+$  dla analizowanych surowców zeolitytowych (Langmuira: C1 – sodalit, D1 – Na-X; Freundlicha: C2 – sodalit, D2 – Na-X)

where:

- $q_e$  – equilibrium amount of  $\text{NH}_4^+$  exchanged by tested materials [mg/g],
- $C_e$  – is the equilibrium  $\text{NH}_4^+$  concentration in the solution [mg/dm<sup>3</sup>],
- $q_{\max}$  – is the maximum uptake of ammonia exchanged [mg/g],
- $K_L$  – is the Langmuir constant [dm<sup>3</sup>/mg].

For linear form of Freundlich equation the following procedure was used:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where

- $K_F$  – is Freundlich constant [dm<sup>3</sup>/g],
- 1/n – is the heterogeneity factor.

The result of linear plot of Langmuir and Freundlich isotherms for each sample before and after thermal treatment are presented in the Fig. 4 and 5.

Analyzing obtained for tested materials Langmuir and Freundlich isotherms the best fitting is for Langmuir model where  $R_2$  is satisfying and give a results ranging from 0.96–0.99 (Table 1). The thermal activation both for natural and synthetic zeolites did not influence on the change of sorption properties. In case of Langmuir model trend curves have almost the same equations.

Coefficients  $K_L$  and  $K_F$  in case of synthetic zeolite initial and activated are almost the same however in case of natural zeolite a small decrease for activated materials are observed

TABLE 1

Isotherm constants for ammonium exchange by tested zeolitic materials

TABELA 1

Stałe izoterm dla sorpcji jonów amonowych na badanych materiałach zeolitowych

Sample	Langmuir			Freundlich			
	$q_{\max}$	$K_L$	$R^2$	n	1/n	$K_F$	$R^2$
PL zeolite 25	2.9727	0.4022	0.9608	3.5613	0.2808	1.0155	0.8082
PL zeolite 200	3.0003	0.3440	0.9605	3.7467	0.2669	1.0399	0.8495
UA zeolite 25	6.1350	0.3124	0.9921	2.6546	0.3767	1.6596	0.8703
UA zeolite 200	6.0864	0.2198	0.9785	2.3998	0.4167	1.3797	0.7887
Sodalite 25	7.5700	0.0248	0.9823	1.5267	0.6550	0.3291	0.9964
Sodalite 200	7.4190	0.0258	0.9766	1.5615	0.6404	0.3459	0.9969
NaX25	7.0822	0.4880	0.9766	1.8005	0.5554	0.6062	0.9883
NaX200	7.0225	0.4930	0.9806	1.8021	0.5549	0.6048	0.9875

(what indicate on exothermic reactions for ammonium exchange by those materials). The values of  $1/n$  for all tested zeolites are smaller than 1 what indicate on favorable removal conditions (Karadag et al. 2006; Ivanova et al. 2010).

For Langmuir sorption isotherms also dimensionless constant separation factor  $R_L$  was calculated (Fig. 6A, B) using the following equation (Ho, McKay 1999):

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where:

$C_0$  – initial concentration of  $\text{NH}_4^+$  [ $\text{mg}/\text{dm}^3$ ].

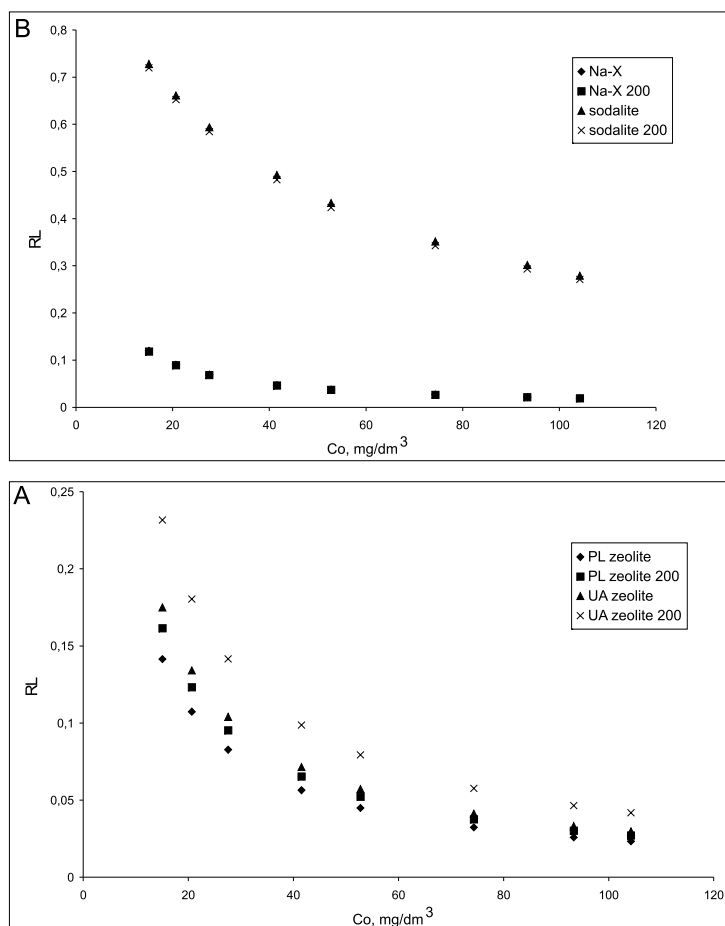


Fig. 6. Separation factor  $R_L$  of  $\text{NH}_4^+$  ions exchanged by tested zeolitic materials (A – natural zeolites, B – synthetic zeolites)

Rys. 6. Czynniki rozdzielania  $R_L$  jonów  $\text{NH}_4^+$  wymienianych przez analizowane materiały zeolitowe (A – zeolity naturalne, B – zeolity syntetyczne)

This dimensionless constant separation factor was calculated for each tested zeolites at usage of the different concentrations of solutions (Fig. 6A, B). For synthetic zeolites, both before and after thermal activation, those values ranging from 0.11 to 0.019 for Na-X and from 0.72 to 0.27 for sodalite. In case of natural zeolites (also before and after thermal activation) the values are as following: from 0.15 to 0.02 for Dylągówka zeolite and about from 0.2 to 0.3 for Sokyrytsya zeolite. Such result indicates that the exchange of  $\text{NH}_4^+$  by all zeolites is favorable (Karadag et al. 2006).

### Conclusion

The amount of removal ammonium ions from aqueous solutions increase in proportion to increase of initial concentration of  $\text{NH}_4^+$  in purified solution.

The thermal activation of tested materials did not influence onto the amount of removed ammonium ions from the solution. The sequence of the best sorbents is in the following order Sokyrytsya zeolite > Na-X > sodalite > Dylągówka zeolite. The lowest values of sorption properties obtained for Dylągówka zeolite could be result of unsuitable separation of clinoptilolite from clinoptilolite-montmorillonite clay.

The best sorbents of ammonia ions is natural zeolite (Sokyrytsya zeolite) in relation to zeolites obtained by hydrothermal transformation of fly ash (Na-X, sodalite). In spite of lower ion capacities and surface areas they have the highest selectivity with respect to ammonia ions (Wang et al. 2008).

The thermal activation not improve sorption properties and consequently the amount of adsorbed ammonium ions. This is probably caused by applying batch experiment instead of dynamic/flow tests. Experiment conducted in dynamic conditions carried out by Zheng et al. (2008) on untreated and thermal activated zeolite has shown improving sorption properties on tested zeolites.

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## USUWANIE JONÓW AMONOWYCH NA WYBRANYCH ZEOLITACH NATURALNYCH I SYNTETYCZNYCH

## Słowa kluczowe

Adsorpcja, klinoptilolit, Na-X, sodalit, jony amonowe

## Streszczenie

Celem pracy była analiza możliwości wykorzystania zeolitów naturalnych i syntetycznych do usuwania jonów amonowych z roztworów wodnych. Materiał badawczy stanowiły dwa zeolity naturalne i dwa syntetyczne. Materiały naturalne bogate były w klinoptilolit. Pochodziły ze złoża Dylągówka (Polska) i Sokyrnytsya (Ukraina). Syntetyczny materiał zeolityowy reprezentowany był przez zeolity otrzymane w wyniku reakcji hydrotermalnej NaOH z popiołem lotnym tj. sodalit i Na-X. Dla analizowanych materiałów dokonano charakterystyki mineralogiczno-chemicznej. W celu polepszenia właściwości sorpcyjnych przeprowadzono również aktywację termiczną w temperaturze 200°C przez 24 h. Dla materiałów wyjściowych i aktywowanych termicznie przeprowadzono badania teksturalne, oznaczono pojemność jonowymienną CEC oraz przeprowadzono badania sorpcji metodą statyczną. W tym celu wykorzystano laboratoryjnie przygotowane roztwory NH<sub>4</sub>Cl o różnym stężeniu (od 50 do 500 mg/dm<sup>3</sup>). Dominującym składnikiem w składzie mineralnym surowców naturalnych był klinoptilolit. Natomiast syntetyczne zeolity reprezentowane były przez sodalit z podrzędnym udziałem mullitu. Materiał zasobny w Na-X dodatkowo poza mulitem zawierał niewielkie ilości kwarcu. Badania wykazały, że najwyższą pojemnością jonowymienną CEC charakteryzuje się syntetyczny materiał Na-X (257 mval/100 g), natomiast najniższą wartość uzyskano dla zeolitu z Dylągówki 35 mval/100 g. Uzyskane wyniki sorpcji wykazały lepsze dopasowanie izoterm sorpcji Langmuira dla każdego z badanych materiałów. Najlepszym sorbentem względem jonów amonowych okazał się zeolit ze złoża Sokyrnytsya, najgorsze właściwości wykazał zeolit z Dylągówki. Aktywacja termiczna nie wpłynęła na poprawę właściwości sorpcyjnych badanych materiałów.

## REMOVAL OF AMMONIA IONS BY SELECTED NATURAL AND SYNTHETIC ZEOLITES

## Key words

Adsorption, clinoptilolite, Na-X, sodalite, ammonium ions

## Abstract

The main aim of this study was to analyze of the adsorption equilibrium of ammonia ions from artificial aqueous solutions by natural and synthetic zeolites. The tested material has constituted two natural and two synthetic zeolites. Rich in clinoptilolite natural zeolites come from Dylągówka deposit (Poland) and Sokyrnytsya deposit (Ukraine). Synthetic materials were represented by zeolites obtained during hydrothermal reaction of NaOH with fly ash e.i. sodalite and Na-X. For examined materials the mineralogical-chemical characteristic was carried out. Also the thermal activation at temperature 200°C during 24 h on tested materials was conducted in order to test an influence of temperature on sorption properties. For both type of materials (before and after thermal activation) the textural parameters, the cation exchange capacity (CEC) were determine and batch experiment were conducted. For sorption investigations the solutions of NH<sub>4</sub>Cl about different concentrations (form 50 to 500 mg/dm<sup>3</sup>) were used. The dominant component in mineralogical composition of natural zeolites was clinoptilolite. Synthetic zeolites were represented by sodalite with small amount of mullite. Rich in Na-X material apart form secondary amount of mullite contained quartz. Results have shown that the highest cation exchange capacity have Na-X (257 mval/100 g), the lowest value was obtained for zeolite from Dylągówka 35 mval/100 g. The obtained sorption data were fitted by Langmuir and Freundlich isotherms. The result has shown that the Langmuir model fits better with experimental data. The best sorbents of ammonia ions from aqueous solution turned out zeolite from Sokyrnytsya, the worst was Dylągówka zeolite. The thermal activation did not influence on tested materials sorption.