

UTILIZATION OF SYNTHETIC PHILLIPSITE AS A MEANS FOR DECREASING THE CONCENTRATION OF AMMONIUM IONS IN WASTE WATERS

FRANTIŠEK KOVANDA, DAVID KOLOUŠEK*, VLASTIMIL SEIDL*, EVA PROCHÁZKOVÁ*,
JOLANA OBŠASNÍKOVÁ*

Research Institute of Crop Production, Prague

*Institute of Chemical Technology, Technická 5, 166 28 Prague

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The application of synthetic phillipsite prepared by hydrothermal alteration of power plant ashes to decreasing the concentration of ammonium ions in waste waters were followed. Final concentrations lower than 1 mg NH₄⁺/l were reached in batch arrangement. Sorption capacity of synthetic phillipsite was significantly higher than that of the natural Slovakian clinoptilolite.

INTRODUCTION

45 different zeolites were found and described in the nature but only 7 of them occur in deposits large enough to allow industrial exploitation: analcime, clinoptilolite, phillipsite, erionite, ferrierite, chabazite, and mordenite. The most important deposits of zeolites were found in the USA, Japan, Ukraina, and Georgia. On the territory of the Czech Republic, some zeolites were found as accessory minerals in volcanic rocks of the Central Bohemian Highlands and of the Doupov Mts. but no exploitable deposits have been discovered. Slovakia has larger deposits of sedimentary clinoptilolite at Nižný Hrabovec and Bartošova Lehotka.

Ion-exchanging properties of zeolites depend strongly on the Si/Al ratio in their structure. The most mined clinoptilolites belong to the group of zeolites with a rather higher SiO₂ content which has its negative consequence in the rather lower values of their ion-exchanging capacity. Zeolites with a lower Si/Al ratio can be prepared from solid products of the combustion of coal, i. e. flying ashes, ashes or slags (Koloušek & al. [1]). This preparation – hydrothermal alteration – is based on the reaction of ashes with alkaline aqueous solutions under elevated temperatures and pressures. This alteration yields the zeolite phillipsite, a synthetic form of a zeolite with one of the highest ion-exchanging capacities found among natural zeolites.

Many authors have studied possibilities of the separation of the ammonium ion from drinking water and from waste waters by zeolites (e. g. Hagivara & Uchida [2], Colella & Aiello [3], Ciambelli & al. [4], Dzhunko [5]). It is the aim of this study to compare sorption properties of natural clinoptilolite and of synthetic phillipsite with respect to their capabilities of binding NH₄⁺ ions.

EXPERIMENTAL

Sorption capacities of samples of synthetic phillipsite were determined in the following way. Hydrothermally altered ashes from the power station in Dětmarovice were used as a basic material for all measurements. The solid product of the alteration was dried at 105°C. The concentrations of sodium and potassium ions in aqueous eluates obtained from such preparates (1 part of synthetic zeolite per 10 parts of distilled water) were rather high and so were their pH values. After the products of alteration had been

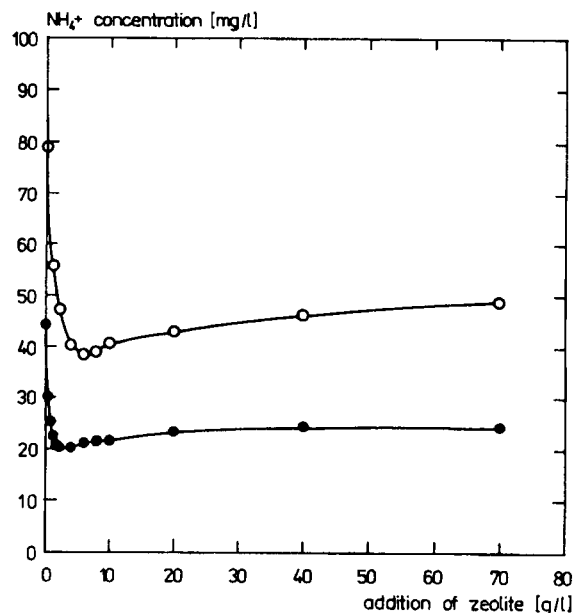


Fig. 1. Dependence of the decrease of the concentration of ammonium ions on the amount of synthetic phillipsite as synthesized added to the solution.

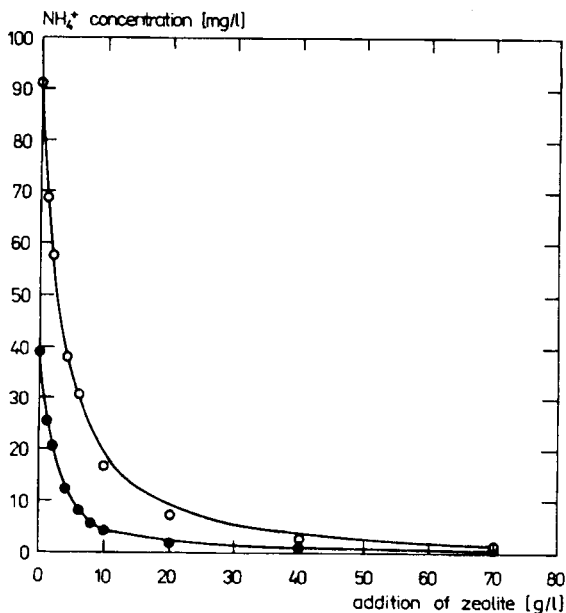


Fig. 2. Dependence of the decrease of the concentration of ammonium ions on the amount of neutralized and washed synthetic phillipsite added to the solution.

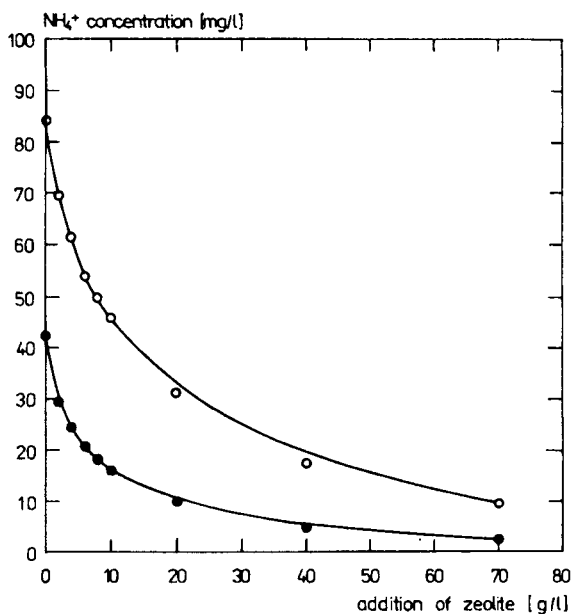


Fig. 3. Dependence of the decrease of the concentration of ammonium ions on the amount of natural clinoptilolite (Nižný Hrabovec) added to the solution.

washed with diluted hydrochloric acid and with distilled water, the pH value of the eluates dropped to pH=5.5 and their K^+ and Na^+ contents decreased from 230 to 30 mg K^+ /l and from 1100 to 120 mg Na^+ /l. Some measurements were also done with natural clinoptilolite from the deposit at Nižný

Hrabovec in Slovakia ground to the grain size of 30–100 μm and dried at 105°C.

Measurements were done in aqueous solutions of ammonium chloride containing approx. 40 and 80 mg NH_4^+ /l resp. The weighed amount of zeolite was shaken with 250 ml of the NH_4Cl solution for 60 minutes. The suspension was filtered afterwards and the concentration of the NH_4^+ ion in the filtrate was determined by NH_4^+ ion-selective electrode. Results of these measurements are plotted in figs. 1–3.

Further experiments were done to verify the effect of the addition of small amounts of zeolite to already partially purified solutions. 4g of zeolite were added to 2000 ml of the NH_4Cl solution containing 80 mg NH_4^+ /l. The suspension was stirred for 15 minutes and filtered. The NH_4^+ concentration in the filtrate was determined, a further portion of the zeolite was added to the filtrate, and the whole process was repeated. The obtained results are plotted in fig. 4.

RESULTS AND DISCUSSION

It is evident from figs. 1–3 that a sizable decrease of the concentration of ammonium ions in an aqueous NH_4Cl solution can be achieved by addition of a zeolite. Changes in the concentration of NH_4^+ ions in the solution obtained in dependence on the amount

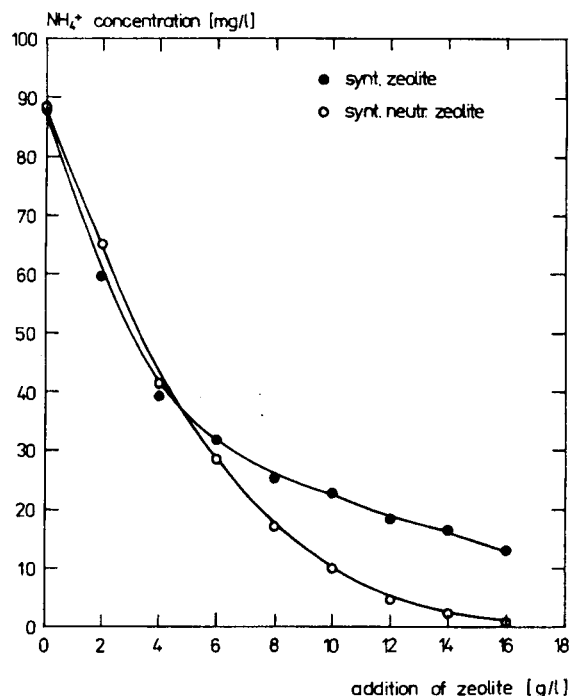


Fig. 4. Decrease of the concentration of ammonium ions in the solution at the stepwise addition synthetic phillipsite (additions of 2 g of phillipsite per 1l of the solution).

of the added zeolite indicate that phillipsite prepared by hydrothermal alteration of power plant ashes is a very effective sorbent of ammonium ions (2 g of the zeolite added to 1 l of the solution decreased its content of ammonium ions to approx. 1/2 of the original value) but a further enhancement of the amount of zeolite present in the solution did not lead to any further decrease of the NH_4^+ concentration in the solution (see fig. 1.). This phenomenon is apparently caused by the presence of sodium and potassium ions migrating to the solution from the remainders of altering solutions occluded on unwashed products of hydrothermal alteration. The K^+ and Na^+ ions also take part in ion-exchanging reactions and affect consequently the sorption of NH_4^+ ions. As a result, the sorption efficiency of the preparate is decreased. This assumption was confirmed by results of experiments done with synthetic zeolite neutralized previously by diluted hydrochloric acid and washed with distilled water (see fig. 2). Neutralized and washed synthetic phillipsite displays very good sorption properties towards the NH_4^+ ions (an addition of 70 g of phillipsite to 1 l of the NH_4Cl solution led to the decrease of the original 80 mg NH_4^+ /l to 1 mg NH_4 /l and of the original 40 mg NH_4^+ /l to 0.3 mg NH_4^+ /l resp.) The in this way treated synthetic zeolite displays better sorption properties towards the ammonium ions than the natural clinoptilolite which led to a decrease of the concentration of NH_4^+ ions from 80 to 9.6 mg/l and from 40 to 2.3 mg/l resp. under the same experimental conditions (see fig. 3.).

The degree of utilization of the sorption capacity of the zeolite decreases gradually with increasing ratio zeolite/ NH_4Cl solution because physico-chemical equilibrium is being established in the system. Sorption measurements with the 80 mg NH_4^+ /l solution and neutralized and washed synthetic phillipsite showed that 18.7 mg NH_4^+ were sorbed per 1 g of the zeolite when 1.2 g of phillipsite were added to 1l of the solution whereas 1.3 g NH_4^+ were sorbed per 1 g the zeolite when 70 g of phillipsite were added to 1l of the solution. Ion exchanges took place very quickly in case of the synthetic zeolite so that NH_4^+ concentrations established in the solution within 60 minutes after the first contact with the zeolite could be considered practically equilibrated. An experiment following concentration changes in a NH_4Cl solution in contact with synthetic phillipsite for 6 hrs showed that the NH_4^+ concentration decreased quickly at the beginning but remained constant after 1 hr. The amount of ammonium ions sorbed by the zeolite was calculated from the mass of the zeolite, the volume of liquid phase and the NH_4^+ concentration determined in the solution. These experimental data were then used to the evaluation of constants in an equation of the Langmuir type that describes the equilibrium distribution

of ammonium ions between the zeolite and the liquid phase:

$$q_{\text{NH}_4} = \frac{0.6624 c_{\text{NH}_4}}{1 + 0.0221 c_{\text{NH}_4}} \quad (1)$$

where q_{NH_4} [mg] is the amount of NH_4^+ ions sorbed per 1 g of zeolite and c_{NH_4} [mg/l] is the equilibrium concentration of NH_4^+ ions in the solution. The constants in equation (1) were computed from experimental data obtained for neutralized and washed synthetic phillipsite at 20°C and the range of concentrations $c_{\text{NH}_4} = 0.3\text{--}70$ mg NH_4^+ /l. The dependence expressed by the equation (1) and the respective experimental data are plotted in fig. 6.

The above facts indicated that it is possible to decrease substantially the concentration of ammonium ions in the solution by addition of large amounts of synthetic zeolite but for the price that its sorption capacity will be used up from a small part only. This is why a possibility of a stepwise reduction of the concentration of ammonium ions by repeated small additions (2 g/l) of the zeolite was verified. The solution was filtered before each further addition of the zeolite so that the previously added one was removed from the system. The experiment was realized in a stirred vessel containing 2 l the NH_4^+ solution; the starting concentration of NH_4^+ was 90 mg/l. The zeolite was added 8 times, the total amount was 32 g. i. e. 16 g/l. Fig. 4. shows that the concentration of NH_4^+ ions in

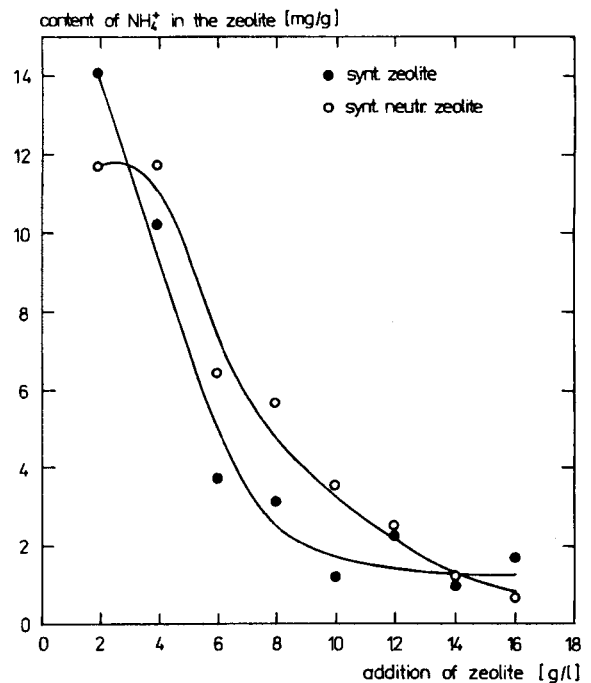


Fig. 5. Amounts of NH_4^+ ions sorbed at the stepwise addition of synthetic phillipsite (additions of 2 g phillipsite per 1l of the solution).

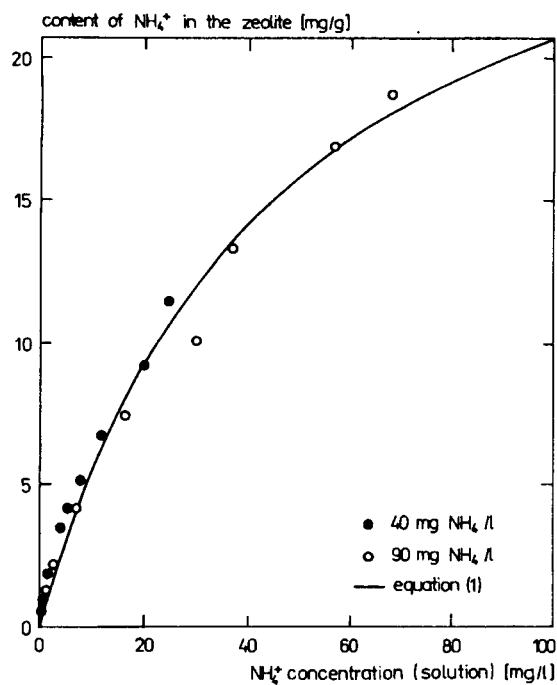


Fig. 6. Equilibrium distribution of NH_4^+ ions between the liquid phase and the zeolite (synthetic phillipsite neutralized with diluted hydrochloric acid and washed with distilled water). Experimental data were obtained at starting concentrations of 40 and 90 mg NH_4^+ /l resp., the amount of the added zeolite was changed in the range of 1.2–70 g per 1l of the solution at 20° C.

the solution could be decreased to the final approx. 14 mg/l by the addition of synthetic phillipsite as synthesized whereas the neutralized and washed one led to the final concentration of 1 mg NH_4^+ /l. This limit was reached at a one-step addition by an amount of zeolite (70 g/l) exceeding several times the amount corresponding to its full sorption capacity. The degree of utilization of the full sorption capacity of the zeolite decreased rapidly with increasing amount of the added zeolite even in the case of the stepwise addition, probably because of the equilibrium state being established (see fig. 5.).

CONCLUSIONS

It was verified that zeolites synthesized by hydrothermal alteration of power plant ashes can be used to the removal of ammonium ions from waste waters. Because of the relatively low concentrations of ammonium ions in these waters, it is necessary, however, to reduced the concentration of sodium and potassium ions present in water soluble forms in the solid alteration product which might compete with the ammonium ions at the sorption. It was found that the sorption capacity of the this way synthesized phillipsite towards the NH_4^+ ions is significantly higher than that of the natural clinoptilolite

currently used to these purposes. The degree of utilization of the sorption capacity of the synthetic zeolite decreases with its increasing addition and it is, therefore, necessary to find a suitable technology of the sorption process for its eventual industrial application. This study dealt with the method of stepwise addition of the zeolite to the purified solution with the result that the same decrease of the concentration of ammonium ions was achieved with a several times smaller total amount of zeolite than in the case of a single-step addition.

SUMMARY

The application of synthetic phillipsite prepared by hydrothermal alteration of power plant ashes to the removal of NH_4^+ ions from drinking and waste waters were studied and optimized. Experimental data were obtained from experiments with aqueous solutions of ammonium chloride containing approx. 40 and 80 mg NH_4^+ /l resp. All experiments were realized in batch arrangement. The as synthesized phillipsite contained remainders of reaction solutions that released relatively large amounts of sodium and potassium ions into the NH_4Cl solution. These ions affected adversely the amount of sorbed NH_4^+ ions and reduced the sorption efficiency of the prepate. This is why the synthesized phillipsite had to be neutralized with diluted hydrochloric acid and washed with distilled water. This operation reduced conspicuously the content of water eluable sodium and potassium ions in the zeolite and the pH value of the eluate. The this way treated synthetic phillipsite turned out an effective sorbent. Its addition to the above NH_4Cl solutions decreased their final NH_4^+ contents to values lower than 1 mg/l. Its ion-exchanging sorption was described by an equation of the Langmuir type and the respective constants were computed. A method of stepwise addition of the zeolite to the solution was suggested and verified for a fuller utilization of its sorption capacity; the zeolite was added to the solution in repeated small portions and each previous portion was filtered away before the next one was added. In this way, the same decrease of the concentration of ammonium was achieved with a several times lower total amount of the zeolite than in the case of a single-step addition. Comparative experiments with natural clinoptilolite from Nižný Hrabovec in Slovakia showed that the neutralized and washed synthetic phillipsite was an approximately 2.5 times more effective sorbent of ammonium ions than the natural clinoptilolite.

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MOŽNOSTI VYUŽITÍ SYNTETICKÉHO PHILLIPSITU PRO SNÍŽENÍ KONCENTRACE AMONNÝCH IONTŮ V ODPADNÍCH VODÁCH

FRANIŠEK KOVANDA, DAVID KOLOUŠEK*, VLASTIMIL SEIDL*, EVA PROCHÁZKOVÁ*, JOLANA OBŠASŇIKOVÁ*

Výzkumný ústav rostlinné výroby Praha

** Vysoká škola chemicko-technologická, 166 28 Praha 6*

Byly sledovány a optimalizovány možnosti použití syntetického phillipsitu vyrobeného hydrotermální alterací elektrárenského popílku k separaci iontů NH_4^+ z vodárenských a odpadních vod. Experimentální data byla získána ve vodných roztocích chloridu amonného o počáteční koncentraci přibližně 40 a 80 mg NH_4^+ /l. Všechny pokusy byly provedeny ve vsádkovém uspořádání. Po přidání vzorku syntetického phillipsitu do vody se uvolňovalo poměrně značné množství sodných a draselných iontů, které rezultují ze zbytků matečných louhů po syntéze. Ionty Na^+ a K^+ vnesené takto do roztoku nepříznivě ovlivňovaly množství sorbovaných amonných iontů a snižovaly tak účinnost preparátu. Proto byl vzorek syntetického phillipsitu promyt roztokem HCl a destilovanou vodou, čímž se výrazně snížil obsah vodou uvolnitelných sodných a draselných iontů a rovněž poklesla hodnota pH vodného výluhu. Takto upravený syntetický phillipsit se projevil jako účinný sorbent. Po jeho přidání do roztoku o uvedených počátečních koncentracích amonných

iontů bylo dosaženo výsledných koncentrací nižších, než 1mg NH_4^+ /l. Na základě experimentálních dat byla výměnná sorpce amonných iontů popsána rovnicí Langmuirova typu. Aby bylo dosaženo lepšího využití sorpční kapacity použitého zeolitu, byl zeolit do roztoku přidáván postupně ve více dávkách, přičemž před každým přidáním zeolitu byla odfiltrována předchozí dávka. Tímto způsobem bylo dosaženo stejného snížení koncentrace amonných iontů s několikanásobně menším celkovým množstvím použitého zeolitu. Byly provedeny rovněž srovnávací experimenty s přírodním klinoptilolitem těženým v lokalitě Nižný Hrabovec. Syntetický phillipsit promytý HCl a destilovanou vodou se projevil jako přibližně 2.5× účinnější sorbent amonných iontů než přírodní klinoptilolit.

Obr. 1. Závislost snížení koncentrace amonných iontů na množství zeolitu přidaného do roztoku pro syntetický phillipsit.

Obr. 2. Závislost snížení koncentrace amonných iontů na množství zeolitu přidaného do roztoku pro syntetický phillipsit neutralizovaný HCl a promytý destilovanou vodou.

Obr. 3. Závislost snížení koncentrace amonných iontů na množství zeolitu přidaného do roztoku pro přírodní klinoptilolit (Nižný Hrabovec).

Obr. 4. Závislost snížení koncentrace amonných iontů v roztoku při postupném přidávání syntetického phillipsitu (přidávky činily 2g zeolitu/l roztoku).

Obr. 5. Množství iontů NH_4^+ sorbovaných zeolitem při postupném přidávání syntetického phillipsitu do roztoku (přidávky činily 2g zeolitu/l roztoku).

Obr. 6. Rovnovážné rozdělení iontů NH_4^+ mezi kapalnou fází a zeolitem (syntetický phillipsit neutralizovaný HCl a promytý destilovanou vodou). Experimentální data byla získána při počátečních koncentracích 40 a 90 mg NH_4^+ /l, hmotnost přidaného zeolitu se měnila v rozmezí 1.2 až 70 g/l roztoku, teplota měření 20° C.