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# Removal of ammonia from waste air streams with clinoptilolite tuff in its natural and treated forms

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**Abstract** Natural and impregnated clinoptilolite tuffs were studied to assess their potential to remove ammonia from air and, in a subsequent application, to use the spent adsorbent as a fertilizer. $H_2SO_4$, $H_3PO_4$ and $HNO_3$, as agents containing important plant nutrients compatible with soil, were selected for impregnation to enhance sorption capacity of the natural clinoptilolite tuffs for ammonia removal. Sorbents were characterized using $N_2$ adsorption isotherms at 77 K, X-ray analysis and high pressure mercury porosimetry. Ammonia breakthrough curves on fixed beds of sorbent were determined using appropriate $NH_3$ and $H_2O$ input concentrations, flow rates and temperatures similar to the conditions in animal breeding farms. Impregnated clinoptilolite tuffs showed adsorption capacities comparable to SSP-4, an activated carbon that is commercially used for $NH_3$ removal. Impregnations with $H_2SO_4$ and $HNO_3$ are particularly important, since such modified adsorbents exhibit relatively high breakthrough capacities, thus rendering them potentially useful for practical applications in controlling ammonia emissions. The main contribution to the sorption capacity enhancement on impregnated clinoptilolite tuff samples seems to be due to the chemical reaction of ammonia with acids remaining in the macro- and mesopores.

**Keywords** Clinoptilolite tuffs · Ammonia · Adsorption · Impregnation

## Introduction

Ammonia is a frequent air pollutant in the atmosphere. The worldwide emissions of ammonia have been estimated annually at 25 to 35 mil t. Only 1 to 2 mil t/year originates from natural sources (Bottger et al., 2001). The bulk of ammonia emitted to the atmosphere results from anthropogenic activities (Kapahi and Gross, 1995).

The most significant source of ammonia pollution, among anthropogenic sources, originates from agricultural production. In addition, ammonia is also an odour nuisance in the proximity of animal breeding farms (Paul, 1998). On the other hand, ammonium nitrate is one of the most widely used fertilisers in agriculture. Therefore, there is a lasting interest to search for ways how to utilize ammonia from animal breeding in crop farming. A feasible way to remove ammonia from air can be carried out by employing a sorption process. Relevant agrochemical tests can provid evidence

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**Table 1** Clinoptilolite tuff composition based on chemical analysis

| Compound | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Mass % | 75.62 | 0.33 | 14.35 | 1.42 | 0.03 | 0.71 | 3.48 | 0.24 | 3.51 | 0.30 |

related to a slow release of important nutrients from impregnated clinoptilolite saturated by ammonia into the soil. Considering a low price of natural clinoptilolite, the impregnated clinoptilolite looks as a promising material for non-waste technology of ammonia removal in breeding farms (Melenová et al., 2002a, b).

Industrial adsorbents that are used to remove ammonia from waste gas streams are designed for adsorption-desorption cycles involving sorbent regeneration (Sattler, 1988). The expenses related to these technologies are relatively high with respect to both capital and operating costs. For that reason they are not considered economical to use for the above applications in agriculture.

This study proposes a simple, non-waste technology for ammonia removal using natural clinoptilolite tuff. Tuffs of many localities have a content of clinoptilolite higher than 60% by mass (Satokawa and Itabashi, 1997). The structure of the clinoptilolite tuffs was determined and their sorption and ion exchange properties were extensively evaluated in a number of earlier studies (Townsend and Loizidou, 1984; Tomazović et al., 1996; Hlavay et al., 1983; Roque-Malherbe et al., 1984).

In comparison with today's widely used activated carbon (Sattler, 1988) the price of natural clinoptilolite tuff for ammonia removal is approximately 35 times lower. The sorption capacities of natural clinoptilolite tuffs from many localities such as Nižní Hrabovec, Slovakia (Melenová et al., 2002a, b; Ciahotný et al., 2001, 2002) or Tokay Mountain, Hungary (Hlavay et al., 1983) are usually very low (Melenová et al., 2002a, b; Hlavay et al., 1983; Ciahotný et al., 2001; Ciahotný et al., 2002; Armbruster, 2001). A conceivable way to increase sorption capacity of the clinoptilolite tuff for $NH_3$ lies in its impregnation with selected inorganic acids such as $H_2SO_4$, $HNO_3$, and $H_3PO_4$, since phosphorus and nitrogen from these acids additionally provide important plant nutrients. One of the major objectives of this paper is to examine the applicability of the adsorbent loaded with ammonia as a fertilizer with a controlled release of nutrients to soil (Melenová et al., 2002b). This concept looks promising, because of the following reasons: (i) a treatment of clinoptilolite tuff with acids is generally accepted method to increase a secondary porosity of the clinoptilolite particles, thus increasing the accessibility to micropores of the material (Kubínyiová et al., 1992), (ii) a non treated clinoptilolite is used as a soil conditioner (Kubínyiová et al., 1992), (iii) no thermal activation will be necessary prior to its use, thus lowering operating cost.

## Materials and methods

### Natural clinoptilolite tuff

Clinoptilolite tuff used in this study originates from a large deposit ( about 7 mil ton) in Slovakia, close to the Nižný Hrabovec settlement (Melenová et al., 2002a, b). The thickness of this deposit is estimated to be about 100 m, and exploitation is mostly carried out close to the surface, i.e., 0.5–1 m. The content of the clinoptilolite in the mineral rock is between 65% and 85% by mass. The current price of the crushed and screened mineral (with a particle size of 2 mm) is between 100 and 130 € per tonne. The chemical analysis of the clinoptilolite tuff is compiled in Table 1.

XRD analysis of our untreated samples showed the presence of cristobalite crystals $\approx 10\%$ , in addition to the clinoptilolite phase ($\cong 70\%$). Trace amounts of other phases, such as muscovite and illite were also identified.

### Clinoptilolite modification

To increase the adsorption capacity of clinoptilolite tuffs for ammonia removal, the treatment (impregnation) of the adsorbent by selected inorganic acids was carried out according to the following procedure: 80 grams of clinoptilolite tuffs with grain size 1.2–2.5 mm was immersed in 125 ml of 20%, 30% and 40% by mass of inorganic acids in a water solution. The selected acids were $H_2SO_4$, $H_3PO_4$ and $HNO_3$. After a contact time of 10 minutes, the volume above the slurry was evacuated for 10 minutes by a vacuum pump. All the procedures were performed at ambient temperature. The impregnated clinoptilolite was filtered and dried in a vacuum oven at 135°C for 2 h. Content of Al, Si, K, Ca and Fe cations in the acid extracts were analysed using atomic absorption spectroscopy.

In order to determine the effect of acids on the clinoptilolite framework structure by X-ray analysis, the impregnated material was in certain cases additionally washed by distilled water just before the drying.

Adsorption capacities of natural and impregnated clinoptilolite samples were compared to activated carbon SS4-P (Chemivron Carbon), which is a commercial material used for ammonia removal.

## Characterization of adsorbents

Ion exchange capacity (IEC) of clinoptilolite tuff was measured with respect to exchange capacity of $NH_4^+$ ions by contacting 1 g clinoptilolite tuff of the grain size <0.3 mm with 250 ml solution $NH_4CH_3COO$ at 90°C (5 hours). After filtration and washing, the sample was transferred into a distillation flask, and 100 ml of distilled water was added to the sample. Ammonia was released from the sample by boiling, while continuously adding 50 ml of 2M NaOH solution, and was subsequently introduced into 0.1 M $H_2SO_4$ solution. $NH_4^+$ ions were then determined using an ammonia selective electrode. The IEC of natural clinoptilolite tuff with respect to $NH_4^+$ was then estimated at 1.275 mmol/g based on mass of natural clinoptilolite tuff containing 9.1% by mass of water. Assuming that an upper limit for adsorption capacity of non-treated natural clinoptilolite tuff corresponds to IEC, one can then estimate upper limit of sorption capacity of natural clinoptilolite tuff for $NH_3 \approx 21.7$ mg/g based on mass of natural clinoptilolite tuff.

Textural characteristics of natural and impregnated clinoptilolite tuffs were obtained mainly from $N_2$ adsorption isotherms at 77 K using the Coulter Analyser (SA 3100+). The samples were out-gassed at 100°C for 120 min before analysis. Low temperature for the activation was used to avoid decomposition of acids in the clinoptilolite tuff porous system. Natural clinoptilolite tuff was additionally activated at 250°C for 120 min and 240 min, respectively, to determine the differences due to different ways of activation.

The pore size distribution of the original material was determined by mercury porosimetry using the Micromeritics PoreSizer 9320. In the low pressure region (0.003 to 0.15 MPa) the pore radii between 4 and 200 $\mu$m were obtained, as well as the bulk density of the samples. In the high pressure region between 0.15 and 200 MPa the pore size distribution for the range of the radii region between 3 nm and 4000 nm was also determined.

The relative content of clinoptilolite phase in the natural sample was determined by XRD powder analysis using XRD-analyser Bruker (Cu lamp ($\lambda = 1.5418$ Å), 40 kV, 30 mA, step 0.02°, speed 1°/min).

## Ammonia adsorption

Adsorption of ammonia was carried out in a flow system using a fixed bed of adsorbent. The experimental conditions simulated the conditions of animals breeding farms. The natural clinoptilolite tuff was not heated prior to the breakthrough measurements, and there was no other treatment of impregnated samples, except for what was described in the "Clinoptilolite modification" section. The experimental conditions were as follows: (i) ammonia concentration in the air, (ii) air humidity (corresponding to the humidity in lab, e.g., 45%), (iii) temperature of sorption (20°C, 35°C and 50°C). Water content of the natural clinoptilolite tuffwas estimated after heating the sample for 2 hours at 250°C. The mass loss of sample due to the activation was about 8%. "

The flow apparatus used to study ammonia adsorption from a simulated gas stream is shown in Fig. 1. It consists of: (i) source of air stream with a required ammonia content, (ii) thermostated sorption beds and (iii) IR analyzer Horiba VIA 510 to monitor effluent ammonia concentrations.

The simulated gas mixture was prepared by mixing the ambient air and pure ammonia taken from cylinder. The air was delivered using a membrane pump (supply 2.3 m$^3$/hrs). The ammonia containing cylinder was placed on a digital balance to monitor the amount of supplied ammonia. After mixing of gases, the mixture was fed to the set of glass adsorbers (12.5 cm and 15 cm in length and 22 mm in diameter) connected in parallel. The flow rates though sorption beds were measured by a dry gas flow meter.

In all experiments the concentration of ammonia was in the range of 50 to 400 mg/m$^3$. The equilibrium sorption and breakthrough capacities were calculated from mass balance using breakthrough curves.

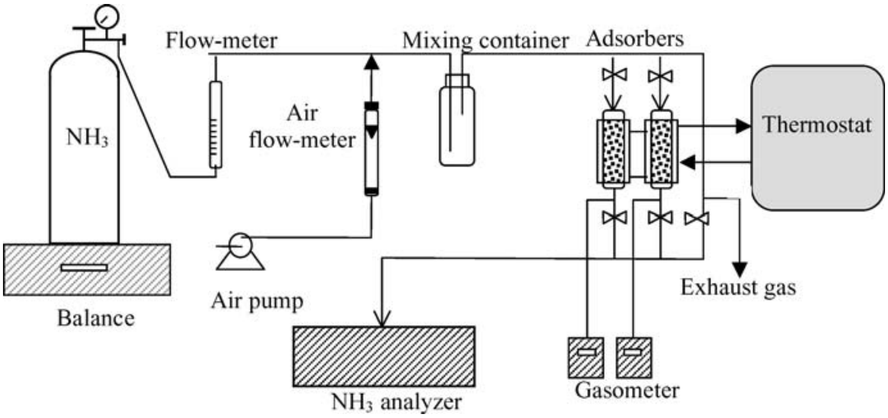

**Fig. 1** Schematic of experimental setup

## Results and discussion

### The effect of acid treatment on clinoptilolite tuff

Treatment of the clinoptilolite tuff with mineral acids and the subsequent washing with distilled water caused a significant removal of cations from the material. The degree of cation removal was more affected by nature of the acid than its concentration. The extent of cation removal upon treatment with acids and subsequent washing is shown in Table 2.

Negligible decrease of silica content (<0.1% by mass) in the impregnated material, together with XRD powder analysis, indicates that the effect of impregnation on the clinoptilolite crystallinity was not significant. X-ray patterns are exemplified in Fig. 2 for the case of clinoptilolite tuff impregnated with 40% $H_3PO_4$. It can bee seen that XRD spectra of natural clinoptilolite tuff (1), clinoptilolite tuff impregnated with 40% $H_3PO_4$ (3) and then washed with distilled water (2) are practically identical.

**Table 2** Mass percentage of extracted species from the clinoptilolite tuff treated with inorganic acids (30% by mass in a water solution)

| | Portion of extracted species | | | | |
|---|---|---|---|---|---|
| Acid | Si | Al | K | Ca | Fe |
| $H_2SO_4$ | <0.1% | 22.1% | 56.2% | 0.4% | 11.1% |
| $H_3PO_4$ | <0.1% | 6.8% | 11.3% | 30.6% | 3.8% |
| $HNO_3$ | <0.1% | 16.5% | 60.1% | 37.1% | 1.4% |

### Textural properties of the natural and impregnated clinoptilolites

Textural properties of the natural and impregnated clinoptilolites were characterized by high pressure mercury porosimetry and $N_2$ adsorption isotherms.

The pore size distributions obtained from the high pressure mercury porosimetry measurements in the form of incremental volume $\Delta V$ ($cm^3 \cdot g^{-1}$) vs. pore radius $r$ (nm) are summarized in Fig. 3. The corresponding textural parameters of the adsorbents are summarized in Table 3. It can be seen from Fig. 3 that pore size distributions exhibit two clearly distinguished maxima that are strongly affected by treatment with acids. Their positions are at $r = 0.0078$ $\mu$m and $r = 0.0209$ $\mu$m. The position of maxima is essentially independent with respect to the nature of the acid. It can also be seen (cf. Table 3) that the natural clinoptilolite tuff has a specific mesopore volume ($V_{\text{meso}}$) of 0.048 $cm^3 \cdot g^{-1}$, and the specific macropore volume ($V_{\text{macro}}$, $2r > 50$ nm) of 0.120 $cm^3 \cdot g^{-1}$. The treatment with

**Table 3** Textural properties from mercury porosimetry

| Sample | $V_{\text{meso}}$ ($cm^3/g$) | $V_{\text{macro}}$ ($cm^3/g$) | $V_{\text{total}}$ ($cm^3/g$) | S ($m^2/g$) |
|---|---|---|---|---|
| Natural clinoptilolite | 0.0475 | 0.1201 | 0.1676 | 26.797 |
| Impregnated with $H_2SO_4$ | 0.0457 | 0.0535 | 0.0992 | 12.035 |
| Impregnated with $H_3PO_4$ | 0.03728 | 0.02702 | 0.0643 | 7.392 |
| Impregnated with $HNO_3$ | 0.07794 | 0.10096 | 0.1789 | 23.557 |

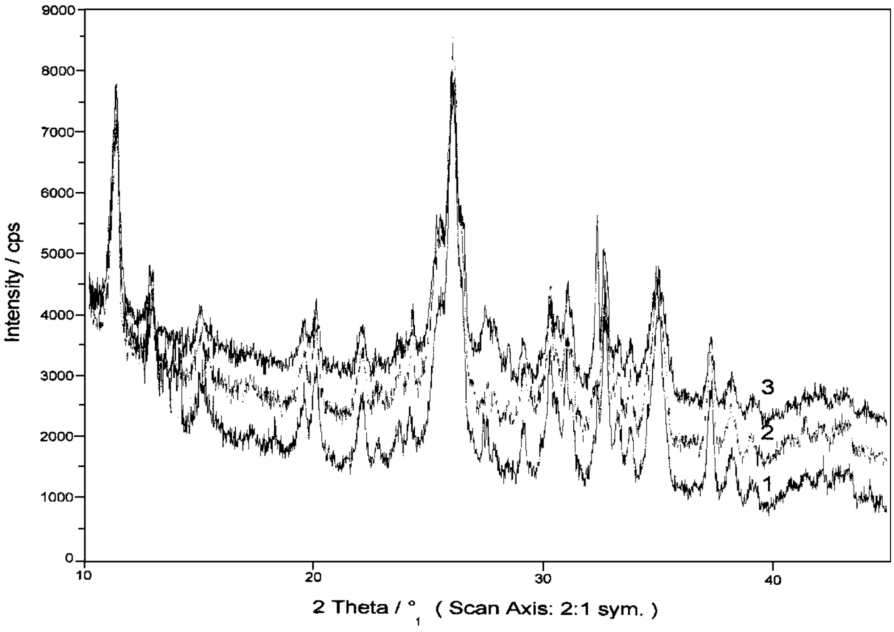

**Fig. 2** Difractograms of natural clinoptilolite tuff (1), clinoptilolite tuff pre-treated with 40% $H_3PO_4$ after leaching in distilled water (2), clinoptilolite tuff pre-treated with 40% $H_3PO_4$ (3)

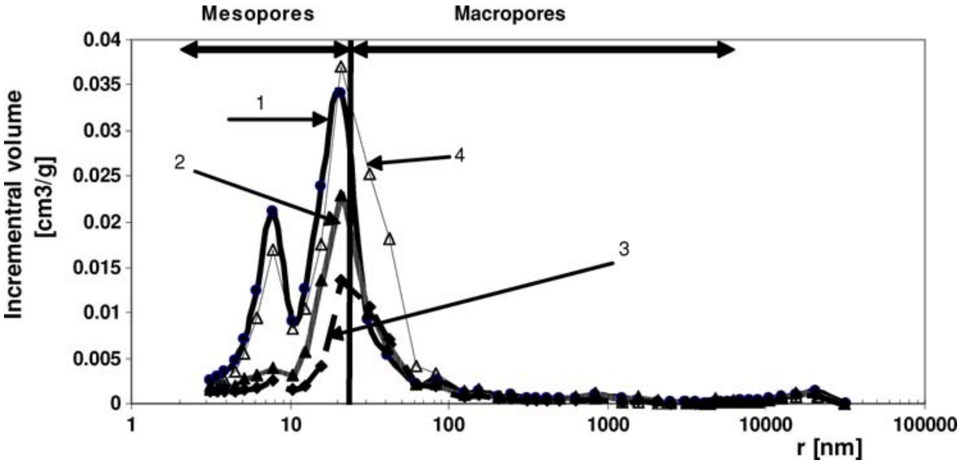

**Fig. 3** Pore size distribution of natural and impregnated clinoptilolite samples, 1-natural clinoptilolite, 2-clinoptilolite impregnated with 30% $H_2SO_4$, 3-clinoptilolite impregnated with 30% $H_3PO_4$, 4-clinoptilolite impregnated with 30% $HNO_3$

$HNO_3$ instigates a slight increase of total pore volume $V_{\mathrm{total}}(V_{\mathrm{meso}} + V_{\mathrm{macro}})$ by about 7%. This increase is largely due to the mesopore volume increase from $V_{meso} = 0.048$ cm$^3$·g$^{-1}$ to $V_{\mathrm{meso}} = 0.078$ cm$^3$·g$^{-1}$. Furthermore, it is obvious from the same table, that there is a maximum decrease of $V_{\mathrm{total}}$ for clinoptilolite impregnated with phosphoric acid, and a smaller decrease for the sample impregnated with sulphiric acid. These changes are related to the decrease of both volumes, i.e., $V_{\mathrm{meso}}$ and $V_{\mathrm{macro}}$. It can also be assumed that the major part of ammonia is trapped on the surface of the mesopores and macropores due to the reaction with acids as will be further explained.

Figure 4 illustrates the $N_2$ adsorption isotherms of clinoptilolite transformed into *t-plots* according to Harkins-Jura standard isotherm. From a slope of the linear part of the $t$-plot and an intercept of the $V$ axis, the surface of mesopores $S_{t\text{-meso}}$ and micropore volume $V_{t\text{-micro}}$, were evaluated, respectively. Table 4 summarizes these results.

Table 5 shows ammonia adsorption capacities of the samples. It follows from the experimental results that

**Table 4** Textural properties of clinoptilolite samples obtained from $N_2$ adsorption isotherms

| Sample | $V_1^{\mathrm{t-micro}}$ ($cm^3/g$) | $S_2^{\mathrm{t-meso}}$ ($m^2/g$) |
|---|---|---|
| Natural clinoptilolite | 0.009 | 22.59 |
| Impregnated with 30% $H_2SO_4$ | 0.0011 | 2.68 |
| Impregnated with 30% $H_3PO_4$ | 0.0021 | 6.22 |
| Impregnated with 30% $HNO_3$ | 0.0039 | 10.59 |

[1] Volume of micropores accessible for $N_2$ at 77 K (from $t$-plot).

[2] Surface of mesopores (from $t$-plot).

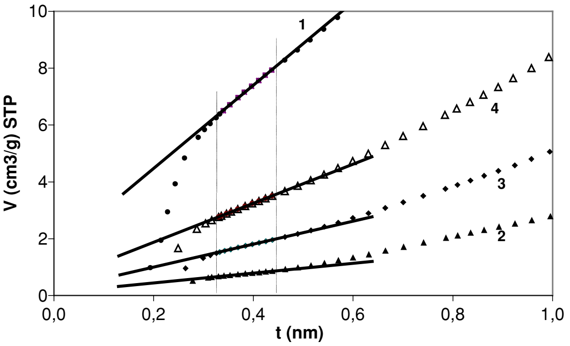

**Fig. 4** Adsorption isotherms of $N_2$ at 77 K transformed into t-plot according Harkins-Jura standard isotherm, 1-natural clinoptilolite, 2-clinoptilolite impregnated with 30% $H_2SO_4$, 3-clinoptilolite impregnated with 30% $H_3PO_4$, 4-clinoptilolite impregnated with 30% $HNO_3$

a correlation exists between portion of the mesopore surface ($S_{t\text{-meso}}$) and micropore volume $V_{t\text{-micro}}$ occupied by acid molecules (see Tables 3 and 4) and adsorbed ammonia. The lower ($S_{t\text{-meso}}$)/$V_{t\text{-micro}}$ values—the larger space blocked with acid and finally the larger absorption space for ammonia. An increase in the space occupied by acid ($S_{t\text{-meso}}$) as well as $V_{t\text{-micro}}$ enhance reaction with ammonia molecules, thus a larger adsorption capacity of the sample is obtained. We conclude that a considerable increase in clinoptilolite tuff capacity for ammonia adsorption is due to an adsorption mechanism accompanied by chemical reaction of ammonia with the acid leading to the formation of ammonia salt. All samples after impregnation and consequently followed by their leaching in the distillated water showed $NH_3$ adsorption capacities very close to that of the natural clinoptilolite tuff, see Table 5. Together with the X-ray experiments it is obvious that the acid treatment at room temperature did not affect the clinoptilolite structure. Table 5 also shows breakthrough capacities of natural clinoptilolite as well as samples impregnated with 20% acids. It is obvious from these results that the materials impregnated with

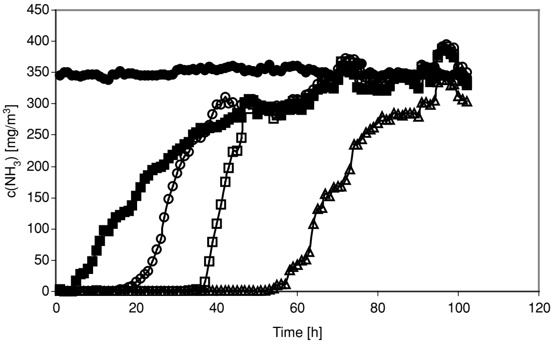

**Fig. 5** Ammonia breakthrough curves on natural and modified clinoptilolite tuff with 20% acids: ● inlet $NH_3$ concentration was kept at 350 mg/m$^3$, ■ natural clinoptilolite tuff, ○ clinoptilolite tuff modified with $H_3PO_4$, □ clinoptilolite tuff modified with $HNO_3$, △ clinoptilolite tuff modified with $H_2SO_4$. T = 25˚C, flow rate 60 dm$^3$/h, relative humidity 45%, bed length 15 cm

**Table 5** Total sorption capacity of $NH_3$ on natural and impregnated clinoptilolites with 20% and 30% acids

| Sample | $NH_3$adsorption capacity[1] (mg/g) | $NH_3$breakthrough capacity[1] (mg/g) | $NH_3$ adsorption capacity[2] (mg/g) |
|---|---|---|---|
| Natural clinoptilolite | 12.2 | 2.2 | 10.8 |
| Impregnated with $H_2SO_4$ | 31.5 | 26.0 | 21.6 |
| Impregnated with $H_3PO_4$ | 16.8 | 8.8 | 20.0 |
| Impregnated with $HNO_3$ | 20.3 | 18.2 | 19.1 |
| After leaching of the sample impregnated with $H_3PO_4$) | 10.4 | | |

[1] at 25˚C, inlet $NH_3$concentration 350 mg/m$^3$, total flow 60 dm$^3$/h, air humidity 45%, bed length 15 cm, 20% acids.

[2] at 20˚C, inlet $NH_3$ concentration 360 mg/m$^3$, total flow 200 dm$^3$/h, air humidity 45%, bed length 15 cm, 30% acids.

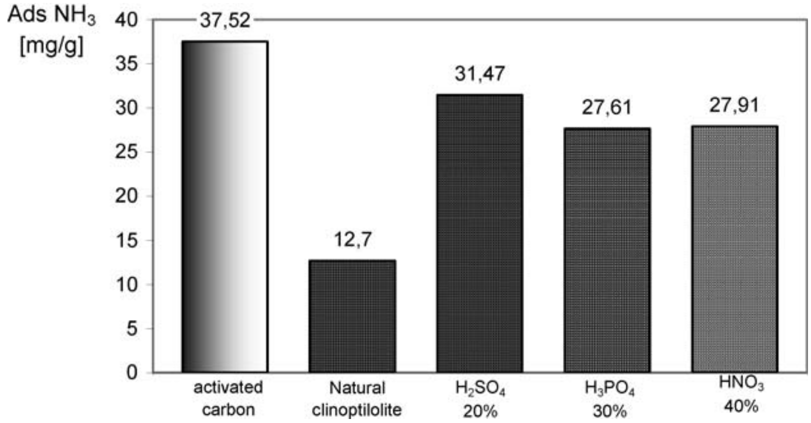

**Fig. 6** Adsorption capacities of ammonia on impregnated and natural clinoptilolite samples and activated carbon. Conditions of adsorption: inlet $NH_3$ concentration 333 mg/m$^3$, total flow 50 dm$^3$/h, $T = 20^\circ$C, humidity of gas mixture 45%

$H_2SO_4$ and $HNO_3$ are good candidates for the practical applications in removing ammonia from waste air streams. The results also reveal interesting information that an increase in acid concentration, e.g., from 20 to 30%, does not improve the adsorption capacity (in fact, an increase in the acid concentration decreases adsorption capacity, with the exception of $H_3PO_4$ impregnated sample).

Figure 5 shows ammonia breakthrough curves of clinoptilolite tuff in its natural form, as well as the samples impregnated with inorganic acids. Ammonia adsorption and breakthrough capacities (second and third column of Table 5) were obtained by appropriate integration of these curves.

Impregnation of clinoptilolite tuff with inorganic acids increased its adsorption capacity with respect to $NH_3$ nearly by factor 2–3. This increace is caused due to the chemical reaction of ammonia with acid remaining in the pores of clinoptilolite tuff. Figure 6 compares selected adsorption capacities of impregnated clinoptilolite tuffs with natural clinoptilolite tuff and activated carbon.

## Conclusions

Experimental results indicate that the impregnation of natural clinoptilolite tuff with inorganic acids leads to an increase of adsorption capacity for ammonia by factor 2–3. This improvement renders the new material comparable with widely used activated carbon. Its low price and the fact that the ammonia removal process proceeds without prior temperature activation can make this material economically attractive. In particular, clinoptilolite adsorbents impregnated with 20% $H_2SO_4$ or $HNO_3$ seem to be good candidates for removing ammonia from waste air streams using packed adsorption columns due to their relatively high breakthrough capacities. Further increase of acid concentrations beyond 20% does not generally improve the removal efficiency.

The main contribution to the sorption capacity enhancement appears to be due to the chemical reaction of ammonia in the mesopores impregnated with acids.

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