



J. Serb. Chem. Soc. 80 (9) 1203–1214 (2015) JSCS–4791 JSCS-info@shd.org.rs • www.shd.org.rs/JSCS UDC 546.171.1:541.183+549.67:537.872: 504.53–035.22 Original scientific paper

The use in grass production of clinoptilolite as an ammonia adsorbent and a nitrogen carrier

JELENA MILOVANOVIĆ¹, SUSANNE EICH-GREATOREX², TORE KROGSTAD², VESNA RAKIĆ³ and NEVENKA RAJIĆ^{4*}

¹Innovation Centre of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia, ²Faculty of Environmental Science and Technology, Norwegian University of Life Sciences, 1432 Aas, Norway, ³Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Zemun, Serbia and ⁴Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

(Received 17 March, revised 14 May, accepted 18 May 2015)

Abstract: Clinoptilolite-rich tuff (NZ) from the Zlatokop deposit (Vranjska Banja, Serbia) was studied as a nitrogen carrier for grass production. The mechanism of binding ammonium cations present in aqueous solutions by NZ was examined, as well as the possibility of adsorption of ammonia released in fresh cattle manure during its fermentation. The NH₄⁺ binding from solutions proceeded *via* an ion-exchange process that followed pseudo-second-order kinetics. Adsorption isotherms studied at 298–318 K followed the Freundlich isotherm equation. The NZ readily adsorbs ammonia liberated from manure and the addition of 10 wt. % of NZ to manure can preserve up to 90 % of ammonia. The potential benefit of this effect was examined in greenhouse pot experiments with Italian ryegrass (*Lolium multiflorum*, var. Macho) using three different types of soil (silty, clayey and sandy). The zeta potential measurements showed that the stability of their colloidal dispersions differed mutually and that the addition of NZ affected the stability and nitrogen cycling differently. All results indicated that NZ could be applied in grass production.

Keywords: zeolites; manure; Freundlich isotherm; soil; Italian ryegrass.

INTRODUCTION

Nitrogen is an essential nutrient for plant growth that has to be added to the soil to ensure the best growth and yield of crops. However, mineral nitrogen fertilizers have been implicated in various environmental issues. Ammonium and nitrate ions are readily lost from the soil by volatilization, leaching or surface run-off. As a result, different nitrogenous species are frequently present not only in agricultural wastewater, but also in groundwater. This may cause serious envi-

^{*}Corresponding author. E-mail: nena@tmf.bg.ac.rs doi: 10.2298/JSC150317042M

ronmental problems such as eutrophication of water bodies and deterioration of water sources, also with possible consequences for humans, in particular for the health of small children.¹

The removal of NH₄⁺ from water through adsorption using various available sorbents was studied by many authors.^{2–7} Natural zeolites as non-toxic, ecologically advantageous and affordable materials appear to be well suited for binding NH₄⁺ from aqueous media due to their ion exchange and adsorption properties.^{8–11} Moreover, the use of natural zeolites for agricultural purposes is becoming widespread because zeolites are particularly useful for controlling agricultural soil fertilization and for preventing or retarding leaching and for increasing yields.^{12–14}

Clinoptilolite is a very widespread zeolitic mineral in Serbia. The clinoptilolite-rich tuff from the deposit Zlatokop (Vranjska Banja, Serbia) contains more than 70 wt. % of clinoptilolite and was found to exhibit good adsorptive and ion-exchange properties.^{15–17} In the present study, the tuff was investigated as a sorbent for ammonium ions and ammonia, and subsequently the ammonium-enriched zeolite was evaluated as a fertilizer.

In particular, the present study examined: 1) the kinetics of binding of NH_4^+ from aqueous solution to NZ; 2) the efficiency of NZ in binding the NH₃ released from fresh cattle manure; 3) whether the addition of ammonium-loaded NZ (AM–NZ) influences the ζ -potential of the soil and accordingly the availability of NH₄⁺ for plants; 4) the effect of the use of NZ in herbage grass growth.

EXPERIMENTAL

Materials and methods

The zeolite material (NZ) was obtained from a large sedimentary Zlatokop deposit in Vranjska Banja. The particle size of the samples used was in the range of 0.063–0.1 mm. A detailed X-ray powder diffraction analysis based on quantitative Rietveld refinement showed that the NZ contained 72.6 % clinoptilolite, 14.6 % feldspar plagioclase and 12.8 % quartz.¹⁸

Chemical analysis of the clinoptilolite phase present in the NZ obtained by scanning electron microscopy and X-ray microanalysis (JEOL JSM-6610LV) gave the following composition expressed by corresponding oxides (wt. %): SiO₂, 65.63; Al₂O₃, 12.97; Fe₂O₃, 1.48; Na₂O, 0.95; K₂O, 1.33; CaO and MgO. 1.41. The loss on ignition at 1073 K, obtained by thermal analysis (TA Instruments, SDT, Q600), was 12.9 wt. %. Furthermore, the porosity of NZ measured by nitrogen adsorption at 77 K (Hiden Isochema HTP1-V Volumetric Analyzer) gave for the BET specific surface area (S_{BET}) and micropore volume (V_{mic}) 42 m² g⁻¹ and 0.0032 cm³ g⁻¹, respectively.

Prior to the experiments, the NZ was washed with deionised water and ethanol to remove soluble amorphous impurities, and then dried to a constant mass at 105 $^{\circ}$ C.

Adsorption/desorption studies in solution

The adsorption experiments were performed in the batch mode using NH_4Cl solutions of different (initial) strengths, *i.e.*, 5, 10, 25, 50 and 100 mg NH_4^+ dm⁻³. The study was realized by mixing 1 g of NZ with 100 cm³ of a solution of the chosen concentration. The suspension

was shaken in a thermostated water bath (Memmert WNB22) for a period from 30 min to 24 h. The solid, ammonia-loaded NZ (AM–NZ) was separated by filtration.

Three parameters were varied in the experiment: initial concentration of NH_4^+ in solution, temperature and contact time. Adsorption isotherms were determined at 298, 308 and 318 K.

The NH_4^+ desorption experiments were conducted at 298 K by treating AM–NZ (containing 1.1 mg NH_4^+ g⁻¹) with the KCl or NaCl solutions varying the salt concentration from 0.1 to 0.001 mol dm⁻³.

Adsorption study in manure

The capture of ammonia released during fermentation of fresh cattle manure (some of its chemical characteristics are given in Table I) was studied using a modified procedure described by Sharadqah and Al-Dwairi.¹⁹ Glass jars (volume 0.5 dm³) were filled with fresh cattle manure up to 2/3 their volume and tightly closed. Into four of the jars, a well homogenized mixture of the fresh cattle manure and NZ was added in different 100:*n* weight ratios (n = 5, 10, 15 or 20). The fifth jar without NZ served as the system control.

ΤA	٩B	L	E 1	I. (Ch	lem	ical	c	haracterist	ics	of	the	e 1	manure	used	in	the	expe	riments	(g	kg-1	1)
----	----	---	-----	------	----	-----	------	---	-------------	-----	----	-----	-----	--------	------	----	-----	------	---------	----	------	----

pН	Dry matter	Loss on ignition	Total C ^a	Total N ^a	NO ₃ -N ^b	NH ₄ -N ^b	Total P	Total K	
7.60	28.5	713.2	390.0	18.9	0.08	27.01	8.9	67	
an (Manager die die dae werden besteren die Geschanzungen								

^aMeasured in dried sample; ^bmeasured in fresh sample

In each jar, a porcelain crucible containing 10 cm^3 of $0.1 \text{ M } \text{H}_2\text{SO}_4$ was placed on a tripod. After 24 h, the crucibles were replaced by new ones containing fresh H_2SO_4 , and the solutions from the old ones were collected in a volumetric flask. The same process was repeated every day during 10 days, taking care that the jars were held open for the shortest possible time. The experiment was performed in triplicate.

Zeta potential measurements

Zeta (ζ) potentials of the soil samples and mixtures of the soil and AM–NZ suspended in water were measured. Prior to the measurements, a suspension of 5 g of the soil sample (or a homogenized mixture of 5 g of soil and 100 mg of AM–NZ) in 25 cm³ deionised water was homogenized by a standard procedure²⁰ for 30 min by horizontal orbital shaking (120 rpm). The suspensions were left to settle overnight, and then a part of the colloid fraction was taken for the measurement. All measurements were performed in triplicate and expressed as mean values of the ζ -potential ± standard deviation.

Pot experiments

A greenhouse pot experiment was conducted under controlled conditions (20 °C, 18 h per day) with three different soil types and the Italian ryegrass (*Lolium multiflorum*, var. Macho) as the test crop. The soil types included a loam, a silt and a sandy soil. The former two were passed through a 5-mm mesh filter prior to being filled into pots of 3 dm³ volume. Some chemical parameters of the soils are given in Table II.

The following treatments/fertilizers were used in the pots: a) control without any fertilizer, b) mineral fertilization with NH_4NO_3 , c) fresh cattle manure, d) fresh cattle manure with the addition of 10 wt. % NZ, and in the silt soil only experiment and e) AM–NZ (containing 1.1 mg NH_4^+ g⁻¹). All treatments were performed in triplicate. In all treatments, except in the control, the amounts of fertilizer corresponded to that typically used in grass production

in Southern Norway (a nitrogen dose at the start of the experiment being equivalent to 120 kg N ha⁻¹). The amount of manure was determined based on the NH_4^+ content in the wet sample and assuming that approximately 10 % of the organically bound N would be available over the experimental period, based on a previous mineralization study (results not shown).

P-AL^t Sand Silt Clay LOI^a Total C Total N K-AL Soil pН <u>g</u> kg⁻¹ mg kg⁻¹ Clay 450 380 170 61.0 5.2 23.1 2.1 58 195 10 Sand 940 30.0 30.0 13.0 5.1 2.8 0.1 16 20 930 50.0 37.0 6.5 14.5 1.0 49 200 Silt

TABLE II. Some properties of the soils used in the pot experiments

^aLoss on ignition; ^bammonium acetate lactate extractable

In addition, an amount phosphorus equivalent to 20 kg ha⁻¹ and an amount of potassium equivalent to approximately 100 kg ha⁻¹, as well as all other macro- and micronutrients in appropriate amounts, were added in the case of the mineral fertilizer treatment. After the first cut, in all treatments except the one without nutrients, an additional amount of mineral N, equivalent to 60 kg N ha⁻¹, was added. The pots were sown with 0.3 g of the seeds of Italian ryegrass. The moisture content in the soil was maintained at 60 % of the field capacity by irrigation with deionised water. The grass was cut three times after 5, 9 and 13 weeks of growth.

Analytical methods and instrumentation

The NH_4^+ concentration in the solutions was determined photometrically (Hach DR2800) using the Nessler reagent (Hach Method 8038). The cation concentrations of Na, K, Mg and Ca in solution ere determined by AAS using a Varian Spectra 55B instrument; at least five measurements were performed for each determination.

Fourier transformed infrared (FTIR) spectra of NZ and AM–NZ were recorded in the 4000–400 cm⁻¹ range on a Digilab-FTS-80 spectrophotometer, using the KBr pellet technique.

Measurements of the ζ -potential were performed by electrophoresis using the laser Doppler method and a SZ-100 (Horiba Co. Ltd.) instrument in which a cell containing carbon electrodes is employed as a sample holder. The ζ -potential was calculated using the peak values of the mobility distributions detected by the Doppler shift in light scattering – the electrophoretic mobility of the particles was automatically calculated and converted to the ζ -potential using the Smoluchowski equation.²¹

The particle size distribution of the soils was determined by the pipette method.²² Soil and manure samples were ignited overnight at 823 K in order to determine the loss on ignition. The pH of the soil samples was measured by suspending the soil in H₂O, with a soil to solution ratio of 1:2.5. The pH of the manure was measured directly in a wet sample. For both the soil and manure analyses, the total C content was determined in crushed samples by dry combustion²³ at 1323 K using a Leco CHN-1000 instrument (St. Joseph, MI, USA). The total N content was measured using the same instrument according to the Dumas method.²⁴ The ammonium and nitrate contents in the manure (NH₄-N, NO₃-N) were measured by flow injection analysis (FIA, Tecator FIAstar 5010 Analyzer, Hillerød, Denmark) after extracting a fresh sample with 2 mol dm⁻³ KCl. The plant-available P and K in the soil were estimated by extraction with an ammonium acetate lactate solution (0.1 M ammonium lactate and 0.4 mol dm⁻³ acetic acid, pH 3.75),²⁵ followed by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5300 DV, Waltham, MA, USA). The total P and K

Available on line at www.shd.org.rs/JSCS/

in the manure were determined on the same instrument after autoclave digestion in concentrated HNO_3 (0.25 g to 0.3 g sample in 5 cm³) and subsequent dilution to 50 cm³.

The effect of different treatments on the yield in the pot experiments was tested statistically by analysis of the variance (General linear model). The Student–Newman–Keuls test was performed to identify the different means. Results with p < 0.05 were considered significant. The statistical analysis was realized using SAS 9.3 software (SAS Institute Inc., Cary, NC, USA).

RESULTS AND DISCUSSION

Adsorption study

Adsorption capacity of the NZ increased with the initial NH₄⁺ solution concentration and slightly decreased with temperature. At 298 K, it varied from 0.37 mg NH₄⁺ g⁻¹ (for $c_0 = 5$ mg NH₄⁺ dm⁻³) to 6.45 mg NH₄⁺ g⁻¹ (for $c_0 = 100$ mg NH₄⁺ dm⁻³). A slight decrease in the adsorption capacity was found at 318 K: 0.32 mg NH₄⁺ g⁻¹ (for $c_0 = 5$ mg NH₄⁺ dm⁻³) and 6.10 mg NH₄⁺ g⁻¹ (for $c_0 =$ = 100 mg NH₄⁺ dm⁻³). The results showed that the adsorption of NH₄⁺ by NZ is an exothermic process, which agrees with the results obtained for a Turkish and clinoptilolite-rich tuff.²⁶

The Langmuir and Freundlich models were used to describe the equilibrium isotherm data. $^{\rm 27}$

The Langmuir model can be represented as:

$$q_{\rm e} = \frac{q_{\rm max} b_{\rm L} c_{\rm e}}{1 + b_{\rm L} c_{\rm e}} \tag{1}$$

where c_e is the equilibrium concentration of the solute (mg dm⁻³), q_e is the equilibrium concentration of the adsorbed solute (mg g⁻¹), while q_{max} (mg g⁻¹) and b_L (dm³ mg⁻¹) are Langmuir constants (q_{max} corresponding to the maximum achievable uptake by a system, and b_L is related to the affinity between the adsorbate and the adsorbent).

The Freundlich model can be represented as:

$$q_{\rm e} = K_{\rm F} c_{\rm e}^n \tag{2}$$

where $q_e \text{ (mg g}^{-1)}$ is the equilibrium solute uptake, $K_F \text{ (dm}^3 \text{ g}^{-1)}$ is the isotherm constant of the Freundlich model, $c_e \text{ (mg dm}^{-3)}$ is the equilibrium solution concentration, and *n* is the exponent of the Freundlich model. K_F and *n* are characteristics of the system and are indicators of the adsorbent capacity (or affinity for the solute) and adsorption intensity, respectively.

For the Langmuir isotherm analysis, the value of the separation factor (R_L) defined as:

$$R_{\rm L} = \frac{1}{1 + b_{\rm L} c_0} \tag{3}$$

is of special importance²⁸ and for the Freundlich isotherm the value of the exponent (1/n) is significant. In all the experiments, the values of R_L , which can be calculated using the b_L values from Table III, and the 1/n values prove, according to the literature,^{16,28} that the adsorption was a favourable process ($0 < R_L < 1$ and 1/n < 1, Table III), in accord with the fact that NZ readily adsorbs NH₄⁺ from aqueous solutions. As can be seen from Table III, the equilibrium adsorption data gave a better fit (higher values of R^2) for the Freundlich than for the Langmuir model.

TABLE III. Isotherm constants for the sorption of NH_4^+ from aqueous solution by NZ

Tomporatura V	Lang	muir isotherm	Freundlich isotherm				
Temperature, K	$q_{\rm max}^{a}$ / mg g ⁻¹	$b_{\rm L}^{\rm b}$ / dm ³ mg ⁻¹	R^2	$K_{\rm F}^{\ \rm c} / {\rm dm}^3 {\rm mg}^{-1}$	$1/n^{d}$	R^2	
298	8.8879	0.0794	0.9943	0.9507	0.5531	0.9663	
308	7.6329	0.1115	0.9836	1.2017	0.4663	0.9929	
318	9.7514	0.0554	0.9906	0.7724	0.6150	0.9963	
		1		1			

^aMaximal monolayer adsorption capacity; ^bLangmuir constant; ^cFreundlich constant; ^dFreundlich model exponent

The NH₄⁺ adsorption kinetics were studied at 298, 308 and 318 K for solutions with $c_0 = 5$, 10, 25, 50 and 100 mg NH₄⁺ dm⁻³. The experimental data were analyzed by the Lagergren pseudo-first-order model and by the pseudo-second-order kinetics model.²⁷ A linear dependence was obtained only for the pseudo-second-order model, indicating that the binding of NH₄⁺ by NZ occurs by the pseudo-second-order reaction mechanism described by the following equation:²⁵

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2 \left(q_\mathrm{e} - q_t\right)^2 \tag{4}$$

where $q_e \text{ (mg g}^{-1}\text{)}$ is the adsorption capacity at equilibrium and $k_2 \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$ is the rate constant of the pseudo-second-order adsorption. Integration between the limits t = 0 to t = t and q = 0 to $q = q_e$, gives the following expression:

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

The plot of $t/q_t vs. t$ is a straight line if the experimental data conform to this kinetic model, and the values of q_e and k_2 are obtained respectively from the slope and intercept of such a plot. As representative, the results obtained at different temperatures for the initial concentration $c_0 = 25$ mg NH₄⁺ dm⁻³ are shown in Fig. 1. The adsorption capacity at equilibrium (q_e) decreases with temperature whereas the rate constant changes irregularly with temperature. This was also observed for the other initial concentrations studied (data not presented). No acceptable explanation could be offered nor found in the literature for this phenomenon.



Fig. 1. Kinetic curves at different temperatures obtained by fitting the experimental data to the pseudo-second-order rate model ($c_0 = 25 \text{ mg NH}_4^+ \text{ dm}^{-3}$).

The FTIR spectrum of AM-NZ (not shown) confirmed the presence of NH_4^+ in the sample (vibration band at about 1400 cm⁻¹ attributed to NH_4^+ , which was not present in the spectrum of NZ), suggesting that the binding of NH₄⁺ from aqueous solution by NZ proceeds by an ion-exchange reaction. This was proved further by elemental AAS analysis of the liquid phase after the adsorption studies, i.e., after AM-NZ separation from the suspensions. The concentrations of Na⁺, K⁺, Ca²⁺ and Mg²⁺ determined in the filtrate entirely corresponded to the amount of NH_4^+ bound by the NZ.

In order to check whether the NH4⁺ in AM–NZ could be desorbed and thus become available as a nutrient in the soil, NH4⁺-desorption experiments were performed by treating AM-NZ with the NaCl or KCl solutions. The obtained results are given in Table IV. It is evident that the percentage of NH₄⁺ desorption depended on the initial Na⁺/K⁺ concentration, showing that the desorption was

also an ion-exchange process. It is interesting to note that desorption was more efficient in the KCl than in the NaCl solution. This could be explained by the fact that the radius of the NH_4^+ (151 pm) is very similar to that of the K⁺ (152 pm). Desorption in 0.1 M KCl was completed in 30 min.

TABLE IV. Percentage NH_4^+ desorbed at 298 K from AM–NZ into solutions of NaCl or KCl in dependence on the salt concentration

Concentration of NaCl/KCl mol dm ⁻³	Released NH ₄ ⁺ , %			
Concentration of NaCi/KCi, mol diff	in NaCl(aq)	in KCl(aq)		
0.100	64	100		
0.010	42	50		
0.005	24	42		
0.001	17	18		

It is well known that fresh cattle manure is rich in nitrogen, making it a good fertilizer. Nitrogen is present mainly in the organic matter, the content of which in the fresh manure being about 50 wt. %. However, during fermentation, manure looses significant amounts of nitrogen. Thus, the loss in four days may reach up to 90 % due to the extensive liberation of ammonia.²⁹ In order to mitigate this loss, investigations were performed to determine: a) whether the addition of NZ to fresh cattle manure could retain the liberated NH₃, and b) the optimal amount of NZ that has to be used for NH₃ capture.

Addition of the NZ to fresh manure conserved the NH₃ released during fermentation, and the percentage of the captured NH₃ ranged between 67 and 98 % depending on the applied amount of NZ (5–20 wt. %). Since about 90 % of NH₃ was captured on addition of 10 wt. % NZ in comparison to the control, this amount of NZ was chosen as the optimal amount for the pot experiments (*vide infra*).

ζ -potential values

The zeta potential is an important parameter for soil/zeolite suspensions in water since it could be interpreted as an indicator of the stability of the suspended colloidal dispersions with respect to particle aggregation.³⁰ For most soils, the ζ potential has a negative value because the ground surface is usually negatively charged. Moreover, the soil stability is a qualitative indicator of biological activity, energy flow and nutrient cycling. A dispersion is regarded as stable, when the ζ -potential is < -30 mV.³¹ The results of the ζ -potential measurements are listed in Table V. It is evident that the clayey soil showed the lowest value of ζ , which could be explained by the strong electronegativity of the clays present in the soil sample. The sandy soil also showed a very low ζ -potential, which could be attributed to the presence of organic matter in which carboxyl groups are ionized.³¹ The silty soil exhibited the highest ζ -potential, implying a lower sta-

bility. The addition of AM–NZ influenced the ζ -potential of all three types of soil but the changes were most pronounced for the clayey and sandy soils. The stability of clayey soil decreased on addition of AM–NZ in contrast to sandy soil in which the colloidal fraction became more stable.

Soil comple		System
Son sample —	Soil/water	Soil+AM-NZ/water
Clay	-45.0±0.7	$-38.0{\pm}0.8$
Silt	-23.6 ± 1.1	$-22.3{\pm}1.6$
Sand	-37.0 ± 0.9	-40.6 ± 0.7

TABLE V. The values of ζ -potentials, mV

Pot experiments

To obtain an insight into a possible use of NZ in grass production, pot experiments were performed with Italian ryegrass, *Lolium multiflorum*, var. Macho. Italian ryegrass was used because it is fast-growing and responds to high N fertilization by yielding an abundance of vegetative matter.

The results for the three cuts in the pot experiment are given in Fig. 2, expressed as tones of dry matter (DM) per hectare.





Figure 2 reveals similar overall yields for the mineral fertilizer, the manure and the manure+NZ treatments, with the exception of the sandy soil where con-

siderably less biomass was produced in the control than in the other two treatments. In general, there was little difference between the amounts of biomass harvested at different cuts for these three treatments. A slight but significant difference (statistics for the separate cuts are not shown) was found in the silt, with a somewhat lower biomass in the first cut in the manure+NZ treatment compared to mineral fertilizer and manure alone. However, this slower growth at the beginning was compensated for by a good yield in the second cut.

It seems that NZ added to the silt binds NH_4^+ strongly at least in the initial phase of the growing period. This could, at least partly, have been due to the relatively high pH value of the silty soil (6.5), at which value cations are strongly adsorbed and hence less available than in the clayey and sandy soils. This suggestion is in accordance with the zeta potential measurement, which showed that the stability of colloidal fractions of the silty soil is not influenced by the addition of zeolite.

The yields in the treatments without fertilizer are, as expected, much smaller than in the other treatments, especially in the sandy soil, which contained the smallest amount of nutrients. Even when the sandy soil was treated with the mineral fertilizer, the plants grew poorly – most likely due to the low original pH of the soil (*i.e.*, 5.1, Table II). Treatments including both manure and manure+NZ improved the growing conditions in the sandy soil, which was reflected in the much higher yields.

In the silty soil, the treatment with AM–NZ resulted in slightly higher overall yields than in the manure+NZ and the mineral fertilizer treatment but not compared to the manure alone. The may be explained by the fact that the AM– NZ was obtained by the ion-exchange reaction using a NH_4^+ -solution of welldefined strength as opposed to the NZ exposed to manure. In the latter case, less NH_4^+ was bound by NZ because the manure used possessed not only NH_4^+ present in the liquid phase, but also organically bound N. It should be stressed that the available N from manure cannot be determined accurately in comparison to the available N in AM–NZ. Accordingly, the resulting differences are likely to have caused the small differences in growth between the different treatments in the silty soil.

CONCLUSIONS

This study evaluated the adsorption ability of zeolitic tuff from the Zlatokop deposit towards NH_4^+ present in liquid medium and towards NH_3 liberated in manure, as well as its capability to be a nitrogen reservoir for plant growth.

The adsorption studies show that the process proceeded *via* an ion-exchange mechanism, which followed the pseudo-second-order kinetic model ($R^2 > 0.99$). The adsorption isotherms studied at 25–45 °C followed the Freundlich isotherm model.

Available on line at www.shd.org.rs/JSCS/

The addition of 10 wt. % of the tuff to fresh cattle manure conserved about 90 % of ammonia and preserved its nutritive value. Greenhouse pot experiments with Italian ryegrass suggested that the plants utilize the NH_4^+ bound by the tuff in a similar manner to the NH_4^+ in easily soluble mineral fertilizers. Further work will be directed towards exploitation of the tuff in odour control as well as towards its potential use in the reduction of the nitrogen oxide emission during manure application in agriculture. The results of such work could be expected to significantly contribute not only to a less odoriferous, but also to a healthier environment.

Acknowledgements. This research was supported by the Norwegian Programme in Higher Education, Research and Development HERD (Project "The use of natural zeolite (clinoptilolite) for the treatment of farm slurry and as a fertilizer carrier") and by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172018).

ИЗВОД

ПРИМЕНА КЛИНОПТИЛОЛИТА КАО АДСОРБЕНТА АМОНИЈАКА И НОСАЧА АЗОТА ЗА ПРИМЕНУ У УЗГОЈУ ТРАВЊАКА

ЈЕЛЕНА МИЛОВАНОВИЋ¹, SUSANNE EICH-GREATOREX², TORE KROGSTAD², BECHA РАКИЋ³ и НЕВЕНКА РАЈИЋ⁴

¹Иновациони ценшар Технолошко-мешалуршкої факулшеша,Универзишеш у Беоїраду, Карнеїијева 4, 11000 Беоїрад, ²Faculty of Environmental Science and Technology, Norwegian University of Life Sciences, 1432 Aas, Norway, ³Пољойривредни факулшеш, Универзишеш у Беоїраду, Немањина 6, 11080 Земун и ⁴Технолошко-мешалуршки факулшеш, Универзишеш у Беоїраду, Карнеїијева 4, 11000 Беоїрад

Зеолитски туф (NZ) са великим садржајем клиноптиолита из рудника Златокоп (Врањска Бања) испитиван је као носач азота за потребе гајења траве. Проучен је механизам и кинетика везивања амонијум-јона из водених раствора за NZ као и могућност везивања амонијака који настаје ферментацијом свежег стајњака. Везивање амонијумјона је реакција јонске измене која следи кинетику псеудо-другог реда. Адсорпционе изотерме испитане на 298–318 К следе Фројндлихову једначину. NZ лако везује амонијак који се ослобађа у стајњаку и додатак 10 мас. % NZ може да сачува 90 % амонијака. Потенцијална корист овог ефекта испитивана је праћењем раста Италијанског љуља (Italian ryegrass, *Lolium multiflorum*, var. Macho) у саксијама у стакленој башти применом три различите врсте земљишта (прашина, глина, песак). Мерењем цета потенцијала утврђено је да се стабилност колоидних дисперзија земљишта међусобно разликује и да додатак NZ утиче различито на стабилност, а тиме и на кружење азота у земљишту. На основу укупних резултата закључено је да се NZ може користити при узгоју травњака.

(Примљено 17. марта, ревидирано 14. маја, прихваћено 18. маја 2015)

REFERENCES

- 1. K. G. Cassman, A. Dobermann, D. T. Walters, AMBIO 31 (2002) 132
- 2. H. Liu, Y. Dong, H. Wang, Y. Liu, Desalination 263 (2010) 70
- 3. M. Khan, N. Yoshida, Bioresource Technol. 99 (2008) 575
- 4. P. Vassileva, P. Tzvetkova, R. Nickolov, Fuel 88 (2009) 387

- 5. P. Vassileva, D. Voikova, J. Hazard. Mater. 170 (2009) 948
- 6. T. C. Jogensen, L. R. Weatherley, Water. Res. 37 (2003) 1723
- 7. W. M. Rostron, D. Stuckey, A. A. Young, Water Res. 35 (2001) 1169
- M. Reháková, S. Cuvanová, M. Dyivák, J. Rimár, Z. Gaval'ová, Solid State Mater. Sci. 8 (2004) 397
- 9. P. J. Leggo, B. Ledésert, G. Christie, Sci. Total Environ. 363 (2006) 1
- S. Leung, S. Barringtin, Y. Wan, X. Zhao, B. El-Husseini, *Bioresource Technol.* 98 (2007) 3309
- 11. J. Venglovsky, N. Sasakova, M. Vargova, Z. Pacajova, I. Placha, M. Petrovsky, D. Harichova, *Bioresource Technol.* **96** (2005) 181
- A. C. de Campos Bernardi, P. P. Anchão Oliviera, M. B. de Melo Monte, F. Souza-Barros, *Micropor. Mesopor. Mater.* 167 (2013) 16
- 13. H. V. Der Stok, T. Sofyan, DE and WO2013119108 A1 (2013)
- 14. S. Belboom, A. Leonard, in *Plant Sciences Reviews*, D. Hemming, Ed., CABI, Wallingford, 2011, p. 52
- 15. Dj. Stojakovic, J. Milenkovic, N. Daneu, N. Rajic, Clay Clay Miner. 59 (2012) 277
- 16. Dj. Stojakovic, J. Hrenovic, M. Mazaj, N. Rajic, J. Hazard. Mater. 185 (2011) 408 17. N. Rajic, Dj. Stojakovic, M. Jovanovic, N. Z. Logar, M. Mazaj, V. Kaucic, Appl. Surf.
- *Sci.* **257** (2010) 1524
- Š. Cerjan Stefanović, N. Zabukovec Logar, K. Margeta, N. Novak Tušar, I. Arčon, K. Maver, J. Kovač, V. Kaučič, *Micropor. Mesopor. Mater.* 105 (2007) 251
- 19. S. I. Sharadqah, R. A. Al-Dwairi, Jordan J. Civ. Eng. 4 (2010) 378
- 20. M. W. I. Schmidt, C. Rumpel, I. Kogel-Knabner, Eur. J. Soil Sci. 50 (1999) 87
- 21. R. J. Hunter, Zeta Potential in Colloidal Science: Principles and Applications, Academic Press, London, 1981
- 22. P. Elonen, Acta Agralia Fenn. 122 (1971) 1
- D. W. Nelson, L. E. Sommers, in *Methods of Soil Analysis Part 2*, A. L. Page, R. H. Miller, D. R. Keeney, Eds., American Society of Agronomy Inc., Soil Science Society of America Inc., Madison, WI, 1982, pp. 539–579
- J. M. Bremner, C. S. Mulvaney, in *Methods of Soil Analysis Part 2*, A. L. Page, R. H, Miller, Eds., Vol. 9 of Agronomy Monograph, American Society of Agronomy, Madison, WI, 1982, pp. 595–624
- 25. H. Egnér, H. Riehm, W. R. Domingo, Lantbrukshögskolans Annaler 26 (1960) 199
- A. Mishra, J. H. Clark, G. A. Kraus, P. R. Seidl, A. Stankiewicz, Y. Kou, *Green Materials for Sustainable Water Remediation and Treatment*, The Royal Society of Chemistry, Cambridge, 2013, p. 93
- 27. S. Sen Gupta, K. G. Bhattacharyya, Adv. Colloid Interface Sci. 162 (2011) 39
- A. M. Yusof, L. K. Keat, Z. Ibrahim, Z. A. Majid, N. A. Nizam, J. Hazard. Mater. 174 (2010) 380
- 29. K. A. Rabai, O. H. Ahmed, S. Kasim, Afr. J. Biotechnol. 11 (2012) 12825
- 30. Y. Yukselen, A. Kaya, Water Air Soil Poll. 145 (2003) 155
- J. P. Mendez, F. P. Garcia, O. A. A. Sandoval, M. A. M. Marzo, Acta Montan. Slovaca 18 (2013) 17.

Available on line at www.shd.org.rs/JSCS/