

EVALUATION OF AMMONIUM EXCHANGE CAPACITY FOR AGRICULTURAL SOILS TREATED WITH ZEOLITES

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Abstract

Natural zeolites are crystalline hydrated aluminosilicates formed by the deposition of volcanic ash in lakes with salted water. They are characterized by their ability to lose and gain water reversibly and to exchange some of the constituents without changing their structure. These properties recommend them as useful additives for agricultural soils as buffer matrix for the process of nutrients translocation.

Present study aims to evaluate the ammonium exchange capacity (AEC) of treated and untreated soils with natural zeolites as an indicator of quality soil improvement. The zeolites used in this study (with a content of approx. 60% clinoptilolite) were purchased from Cemacom, the exploiting company of volcanic tuff from Zalau, Salaj County. The soil samples were collected at various time intervals during one year. Furthermore, we collected soil samples from unprotected and protected (greenhouses) sources where soil had different degree of organic fertilization in order to obtain information on the effect of zeolites addition on AEC.

Keywords: *natural zeolites, soil, ammonium exchange capacity, fertilization*

1. Introduction

The growing demand for food increases the efforts to expand crop and animal production. Therefore, more attention is being paid to use different materials as soil amendments and / or as dietary supplements in farms.

Soils commonly used for agricultural purposes are generally in one of these situations: either they possess a low fertility or they became unfertile because of continuous elimination of the nutrients (without a good control and corresponding measures of appeared deficiencies). Also related to reduced soil fertility, the problem of low efficiency in using raw materials such as fertilizers or water may be considered. [1-3].

Recently, the group of zeolites minerals has emerged as having considerable potential in a wide variety of agricultural processes. The unique ion-exchange, dehydration-rehydration, and adsorption properties of zeolites recommend them as a possible solution for improving the quality of agricultural soils.

Zeolite is a natural super porous mineral (part of a group of hydrated alumino silicates). It carries a negative charge balanced by freely moving cations with positive charges. This provides an ideal trap for positive cations like ammonium and potassium, which are then released when demanded by plants.

Zeolites are ones of the best cation-exchangers, their capacity to exchange cations being 2-3 times higher than other materials and they are generally accepted to be safely embedded in soils. Zeolites are potential adsorbents due to the capacity of their porous microstructure to adsorb molecules at a low environmental pressure. Zeolites cation exchange capacity varies in rather wide ranges, due to several reasons: different nature of their cage structure, structural natural defects, adsorbed ions and their corresponding minerals. [4].

Among natural zeolites, clinoptilolite is the most present in soils and sediments as it

is the most commonly used in agricultural practices, to mention soil amendments and promoting of nitrogen retention as the most spread. [5].

Zeolites have a very open framework with a network of pores giving it a large surface area for trapping and exchanging valuable nutrients. The pore structure of zeolites is characterized by cages approximately 12Å in diameter, which are interlinked through channels about 8Å in diameter, composed of rings of 12 linked tetrahedrons [6]. The pores are interconnected and form long wide channels of varying sizes depending on the mineral. These channels allow the easy movement of the resident ions and molecules into and out of the structure. Zeolites have large vacant spaces or cages within and resemble honeycomb or cage like structures. The presence of aluminium results in a negative charge, which is balanced by positively charged cations. All these characteristics made them the subject of studies that look for their capacity to improve soils used in agriculture.

2. Experimental

2.1. Materials and equipment

The zeolites used in this study were purchased from Cemacom, the exploiting company of volcanic tuff from Zalau, Salaj County. The main component of the natural zeolite is clinoptilolite, $(\text{Na}, \text{K}, \text{Ca})_{2,3}\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$.

Soil samples were collected from vegetable garden in November before treating the soil and in April, June and September in order to catch possible season changes of soil matrix. Soil samples were collected from different places from the garden taking soil at 10 cm depth from the surface. All reactive were analytical grade and were purchased from Merck Millipore. Redistilled water (with conductivity below $0.10 \mu\text{S} \cdot \text{cm}^{-1}$ at 25 °C) was used for preparing all stock solutions.

2.2. Soil samples characterization

Samples of soils and natural zeolites combined in different ratios were used. Redistilled water was added to mixtures containing soil, zeolites and soil mixed with zeolites. The samples were held in laboratory conditions for 24 hours. Then we filtered and washed the content of the vessels using three portions of 50 mL redistilled water. Conductivity and pH of filtrates were measured with inoLAB Multi 9430 meter using IDS SenTix 980 pH-sensor (WTW). UV-VIS spectra and absorbance measurements were recorded using Thermo - Evolution 260 BIO spectrophotometer.

The precipitate was held 24 h, 48 h and 72 h at room temperature in laboratory conditions aiming to evaluate moisture content changes in order to appreciate water quantity absorbed by the solid matrix. Zeolites could catch water molecules in their 3D structure, thus releasing water molecules slower than untreated soil samples. Moisture content measurements were made using the HS153 / Mettler Toledo thermobalance.

2.3. Elemental analysis of soils by WDXRF technique

Elemental analysis of treated and untreated soils was performed by using a wavelength dispersive X-ray fluorescence spectrometer Rigaku Supermini 200 (system equipped with 3 position crystal changer: LiF (200) for heavy elements (Ti-U), PET and RX 25 for light elements (O-Mg and Al-Sc); Detection limit: 1ppm - 10ppb; Precision <0.1-0.5%).

Analyzed soil samples were dried (oven, 48 h, 105°C), grounded together with boric acid (10%) and pressed to obtain pellets of 30 mm diameter. Obtained sample pellets were analysed in air atmosphere by WDXRF technique.

2.4. Ammonium exchange capacity experimental setup

The second group of experiments was set to establish the ammonium exchange capacity of soil treated with zeolites by comparison with one of the untreated soil.

The study has two stages as presented in figure 1.

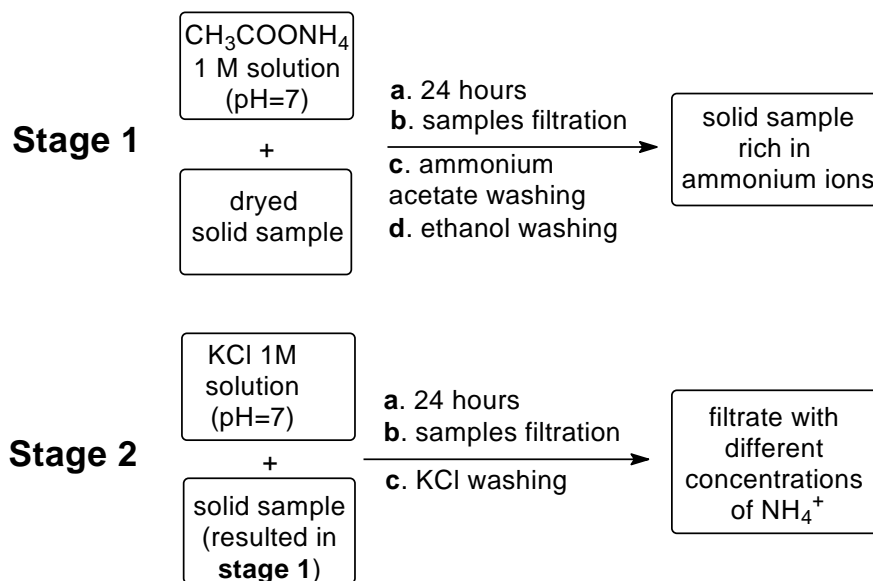


Fig.1 – Ammonium exchange capacity experimental procedure

2.5. Determination of ammonium content

Ammonium content determination in solutions resulted in stage II of the ion-exchange capacity experiment was performed according to standard method ISO 7150-1/2011.

Measurement principle was spectrometric determination, at 650 nm, of the coloured compound resulted from ammonium ion's reaction with salicylat and hypochlorite ions in the presence of sodium nitrozopentacianoferate (III). Calibration curve was realized by diluting standard stock solution of ammonium chloride 1 mg/L. Cuvette with 10 mm optical path were used.

Calibration procedure covered the following steps: each of the 10 (??) volumetric flasks of 50 ml received the corresponding volume of stock solution of NH₄Cl 1 mg/L, then 4 ml ± 0.05 of colouring reagent was added and thoroughly mixing for omogenization; after this, 4 ml ± 0.05 ml sodium dicloroisocianurat was added, and mixed to omogenize. Finally all volumetric flasks were brought to mark with redistilled water, mixed to omogenize and kept at 20°C ± 1°C for 60 minutes. A blank sample was prepared simultaneously by replacing stock solution with redistilled water. A significant remark is that after reagents addition, sample pH should be around 12.6; in this method, extreme acidity or alcalinity may attract deviations.

3. Results and discussion

3.1. Soil and zeolite samples characterization

In our procedure we decided to compare results obtained on untreated soil samples collected at the end of an agricultural season with soil samples collected in the next agricultural year after zeolites treatment. Zeolite was added according to general recommendations of supplying companies: 1 tone / hectare agricultural land.

Soil sampling was also performed in the months of April and June, so that correlations with factors as climate changes (during seasons - spring, summer, autumn, winter), variation of culture type (plants generally consume elements in different proportions, according to type of plant organism contained and to stage of vegetation) as well as elemental composition of soil.

Taking into consideration zeolites' properties as ion-exchangers, conductivity and pH measurements were performed in order to correlate measured values with concentration of added zeolites. In this set of measurements we made samples that contained soil as blank, zeolites only and soil with zeolites and redistilled water was added up to 500 g. Concentrations

of zeolites added to samples were 0.5%, 2% and 5% calculated relativ to 500 g mixture as presented in table 1 and table 2.

Tabel 1 - Conductivity measurements for soil samples with different content of zeolites:

Soil type	Soil	Soil + Zeolite 0,5%	Soil + Zeolite 2%	Soil + Zeolite 5%	Zeolite 0,5%	Zeolite 2%	Zeolite 5%
Conductivity (mS/cm)	127.6±1.8	138.1±1.5	197.7±2.7	232±2.1	9.2±0.8	16.9±0.9	30.5±0.8

Table 1 shows conductivities measured in samples containing soils treated and untreated with zeolites. Zeolite concentration was calculated by reporting to the mass of the mixture. One notice that adding a small quantity of zeolite (0.5 %) does not significantly influence conductivity of the solution. However, if zeolite concentration increases one observes an important change of mixture conductivity, once the comparison between samples with and without zeolite addition is made.

Tabel 2 - pH measurements for soil samples with different content of zeolites:

Soil type	Soil	Soil + Zeolite 0.5%	Soil + Zeolite 2%	Soil + Zeolite 5%	Zeolite 0.5%	Zeolite 2%	Zeolite 5%
pH	8.05±0.30	7.99±0.27	8.02±0.37	7.99±0.42	7.58±0.39	7.49±0.40	7.45±0.35

Table 2 shows pH values that remain constant after zeolite addition in soil, for all the three cases (concentration of zeolite in the mixture of 0.5 %, 2 % and 5 % respectively. Natural zeolites generally have the capacity to decrease soils pH [7]. However, given the bufferig capacity of soils, if small quantities of zeolite are added, soil mixture pH does not significantly change.

At the same time, soil samples that contained zeolites (0.5%, 2% and 5%) were washed with redistilled water and preserved in laboratory conditions in order to prepare them for moisture content determination. Determination of moisture content for blank soil sample and zeolite / soil mixtures was done using thermobalance at 24, 48 and 72 hours after washing procedure was done. Measurements of moisture content did not present significant variations. Although the concentration of zeolite added to mixture was much higher than the recommended amount for soil improvement according to zeolite traders, results indicate that addition of zeolites to soils did not improve their capacity to preserve water.

All collected soil samples that were treated with zeolites were analyzed by X-ray spectrometry (WDXRF) to obtain elemental composition of the mixture.

Figures 2 a), 2 b) and 2 c) show percentage of each element present in soil before and after zeolite addition. Fractions of each of the elements Al, P, S, K, Ca, Fe, Mg, Ti and Mn in the mixture do not change with zeolite addition, regardless the moment of the sampling moment.

Figure 2 c) shows variation of microelements percentage of soil samples collected from the garden. Chromium and Zinc show a decrease of their concentrations with exposure / contact time. This decrease in elements' concentration may be assigned with their involvement in fiziological processes of plants. [8]

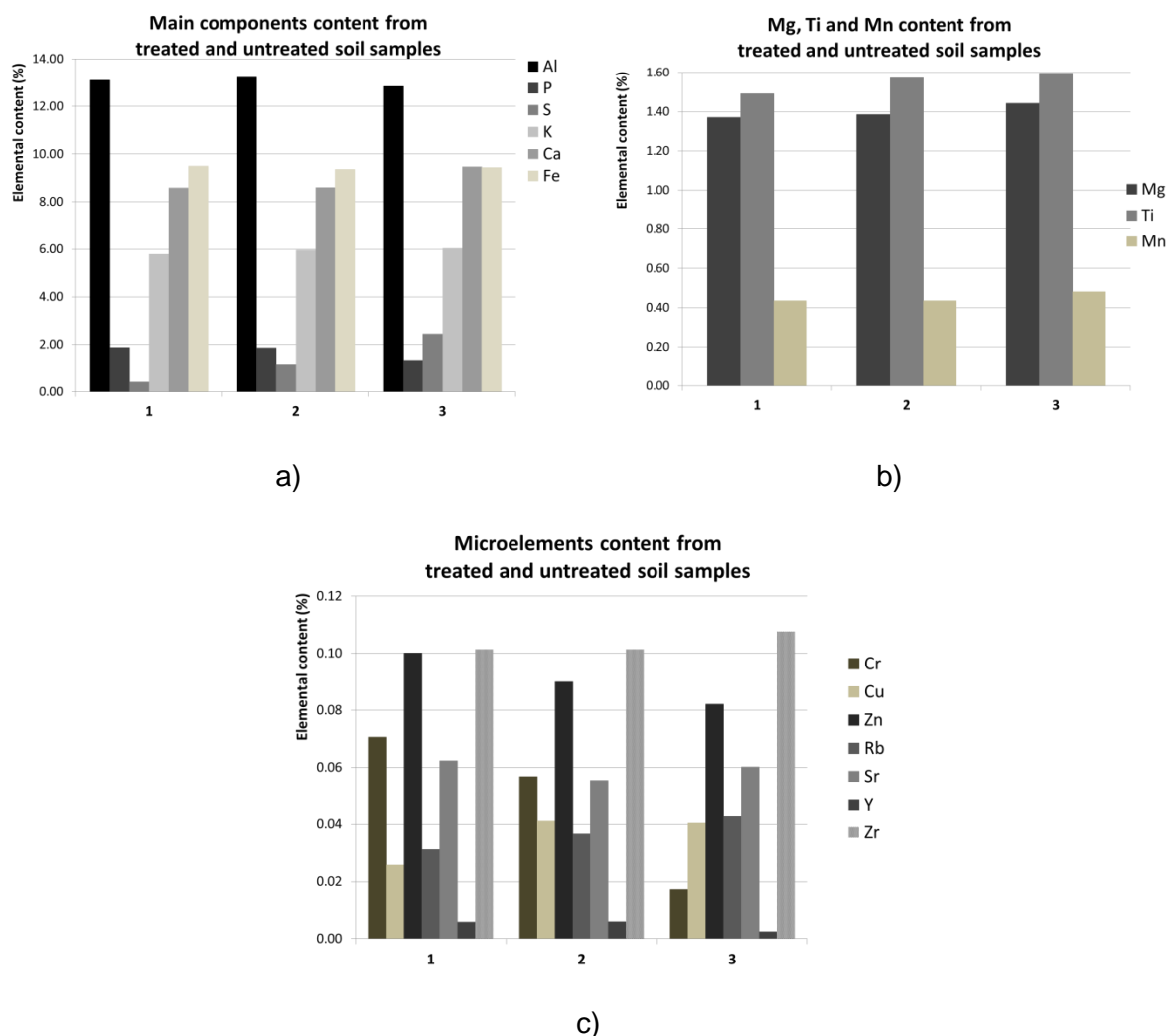


Fig.2 – Percentage content of soil elements (mass %): **1** – initial samples without zeolite (november 2015), **2** –treated soil (april 2015), **3** –treated soil (june 2015)

3.2. Characterization of ammonium exchange capacity of treated and untreated soil

Soils are complex matrixes whose composition and pH vary in time and space being influenced by various environmental conditions. According to this behaviour, ion exchange capacity is a key parameter in fertilization practices. Setting an efficient procedure of certain soil fertilization is taking into consideration its ion exchange capacity as an important and very useful parameter. For instance, soils with a low ion exchange capacity will record a faster water leaching of nutrients beyond the root zone of plants. This characteristic makes autumn fertilization useless, these type of soils being more suitable for spring fertilization [9].

Ammonium is one of the most important cations having important roles in plant growth and development. In this respect, ammonium is one of the nitrogen assimilation forms, together with NO_3^- .

The second group of experiments was set to establish variations of the ammonium exchange capacity of soil treated with zeolites compared to untreated soil. Samples were collected from a vegetable garden during one agricultural year, in all the seasons.

Tabel 3 – Ammonium content (mg/L) of final solutions resulted from ammonium exchange procedure presented in figure 1:

Month	November 2015	April 2016	June 2016	September 2016
Untreated soil	0.7448±0.0224	0.8575±0.0186	0.7084±0.0123	0.6900±0.0261
Soil mixed with zeolite		0.6946±0.0249	0.4686±0.0243	0.6027±0.0269

Tabel 3 shows ammonium concentration in solutions resulted from stage 2 of the ion exchange procedure determinations, for ammonium ion. Ammonium concentrations were determined according to the method described by ISO 7150-1/2011 standard. Concentration values were then converted in ion-exchange capacity of ammonium cation, and expressed in neq/100g soil.

Tabel 4 – Ammonium exchange capacity (nEq NH₄⁺/100 g soil) for soil samples:

Month	November 2015	April 2016	June 2016	September 2016
Untreated soil	5.517±0.165	6.351±0.137	5.247±0.091	5.111±0.193
Soil mixed with zeolite		5.145±0.184	3.471±0.180	4.464±0.199

From these experimental data, we noticed that ion exchange capacity for ammonium cation recorded differences in time (during an agricultural season), for soil samples collected from 10 cm depth.

Also, for all the soil samples collected during an entire agricultural season, it was found that zeolite addition in soils generates a decrease of their ion-exchange capacity for ammonium cation. According to values presented in table 4, the highest variations were recorded in months of April and June.

Taking into consideration the working procedure followed in present study, ion exchange capacity of soils for ammonium cation may be explained by the existence of a competitive NH₄⁺ vs. K⁺ ion exchange process at the level of the solid matrix studied.

4. Conclusions

Our experimental procedure was set to characterize ammonium exchange capacity of untreated soil samples collected at the end of an agricultural season before fertilization for the next year cultures with soil samples collected in the next agricultural year after zeolites treatment. WDXRF results showed no significant changes in mass ratio of main cations from the soil matrix, wether or not zeolite was present in soil samples .

Although the addition of zeolites was thaught to improve the capacity of solid matrix to retain water, this property of tested soil did not change, wether it was added zeolite or not.

However, the addition of zeolite to soil has some effect on solid matrix because conductivity measurements indicate that addition of zeolites to soil increases the conductivity of aqueous solution resulted from washing the solid samples. The resulted value of conductivity for the mixture soil and zeolite is higher than the sum of conductivity for the soil and zeolite separately

$$-\lambda_{(\text{soil} + \text{zeolite})} > (\lambda_{(\text{soil})} + \lambda_{(\text{zeolite})}).$$

Ion exchange capacity for ammonium cation recorded differences in time (during an agricultural season), for soil samples collected from 10 cm depth from different points of the garden with treated and untreated soil.

Zeolite addition in soils generates a decrease of their ion-exchange capacity for ammonium cation; the highest variations were recorded in months of April and June.

Ion exchange capacity of soils for ammonium cation may be explained by the existence of a competitive NH_4^+ vs. K^+ ion exchange process at the level of the solid matrix studied.

Acknowledgements

This study was carried as authors' contribution to a joint research activity involving Joint Institute for Nuclear Research (JINR), Dubna, Russia and Valahia University of Targoviste (UVT), Romania, funded under Protocol no. 4319-4-2014/2016.

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