

## **IN SEARCH FOR ADEQUATE NH<sub>4</sub> - CLINOPTILOITE FERTILIZER SUPPLEMENT: PARAMETER OPTIMIZATION**

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### **ABSTRACT**

This study investigates the basic parameters of K- and Ca-clinoptilolite modification with ammonium ions, to be most economically in the respective raw materials needed to produce an effective ecological fertilizer. A uniform quantity of zeolites was loaded with different initial concentrations of ammonium ions, in order to determine their quotient which provides the best defining consumption of the necessary components in the production. The point of zero charge, mineral composition and CEC of used zeolites were determined. Cation exchange mechanism at various quantities of modifier was investigated. The obtained results indicate that successful zeolite modification with ammonium ions requires a smaller quantity of modifier than the one commonly used.

Keywords: sustainable agriculture, zeolite, modification, fertilizer supplement

### **INTRODUCTION**

Clinoptilolite is the most widely used zeolite mineral which exists in rock formation worldwide [1]. Zeolites possess rigid three-dimensional structure composed of interconnected exchange sites network, in the form of tunnels and cages, which enables them to retain large quantities of water while maintaining the original structure. The high cation-exchange capacity (CEC) arises from the substitution of aluminum ions with silicon ions in a segment of the tetrahedral units that make up the zeolite crystal. Due to their high CEC, water retention properties and rigid structure, zeolites are valuable widely-used multi-purpose soil amendments. Exchanging sites on natural zeolites are site dependent and predominantly occupied by four major cations, potassium, calcium, sodium and magnesium. A small amount of trace elements may also be present. Due to above referred characteristic, zeolites can help control the release of plant nutrients in agricultural systems [2]. In zeoponics, natural zeolites have their ion-exchange sites loads with selected nutrient cations such as ammonium ion or potassium. Charged zeolites interact in the plant rhizosphere to provide nutrients in a slow-release manner through a combination of chemical dissolution and ion-exchange reaction. Saturated with monovalent ammonium ion, zeolites increase the solubility of rock phosphate (RP) [3]. The mechanism proposed for dissolution of RP is ion-exchange process in which plant uptake of ammonium ion liberates exchange sites which are occupied by calcium ion, lowering its concentration the soil solution and inducing further dissolution of RP [4]. The data from the literature show that modification of zeolite with ammonium ions exercised most commonly by treating natural zeolite with ammonium salts in large excess in order to perform the entire amendment of exchangeable cations [5, 6].

This paper presents the results of experiment that investigated the basic parameters of zeolite modification with ammonium ions, to be most economically as the respective raw materials needed to produce an effective supplement for ecological fertilizer. Two various types of zeolites (K- and Ca- clinoptilolite) were used. The point of zero charge, mineral composition and CEC of used zeolites were specified.

## **EXPERIMENTAL**

Zeolites originating from deposit Baia Mare, Romania (K-zeolite) and Igros, Kopaonik, Serbia (Ca-zeolite), were used for this study. Chemical composition of starting zeolitic tuff was determined by atomic absorption spectrophotometer (AAS) using the Perkin Elmer AAS "703". The natural K-zeolite tuff contained: 63.60% SiO<sub>2</sub>, 11.81% Al<sub>2</sub>O<sub>3</sub>, 1.74% Fe<sub>2</sub>O<sub>3</sub>, 7.35% CaO, 0.69% MgO, 0.17% TiO<sub>2</sub>, 0.4% Na<sub>2</sub>O, 4.40% K<sub>2</sub>O and loss of ignition was 9.81%. The natural Ca-zeolite tuff contained: 65.89% SiO<sub>2</sub>, 12.86% Al<sub>2</sub>O<sub>3</sub>, 2.06% Fe<sub>2</sub>O<sub>3</sub>, 4.90% CaO, 0.95% MgO, 0.17% TiO<sub>2</sub>, 0.97% Na<sub>2</sub>O, 1.14% K<sub>2</sub>O and loss of ignition was 11.26%. Zeolite samples were milled and sieved to separate fraction ranging from 0.5 to 1 mm by means of mechanical sieves. This fraction was washed with distilled water and dried at 105°C for 24 h to remove any adsorbed water. Finally, the zeolite samples were stored in desiccators before performing the chemical activation in NH<sub>4</sub>-form. The XRD method was used to determine the phase composition. The XRD patterns were obtained on a Philips PW 1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angle range from 4 to 65°, counting for 0.5 s (qualitative identification) at every 0.02° step. The divergence and receiving slits were fixed 1 and 0.1, respectively. All the XRD measurements were performed at room temperature in a stationary sample holder. The CEC value of the zeolite was determined using a standard procedure that is applicable to both calcareous and non-calcareous soils (EPA Method No. 9081, September 1986.).

Modification of zeolites with different initial concentrations of ammonium sulfate (AS) (1 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) was performed at four ratios of natural zeolite and modifier (1:1, 1:2, 1:5 and 1:10). 20 g of each zeolite was modified with 75 ml of 0.2 M AS (1:1 ratio), 0.4 M AS (1:2 ratio) and 1M AS (1:5 ratio) and 150 ml 1M AS for 1:10 ratio. The above ratios are the stoichiometric ratios between the cation exchange capacity of natural zeolite and ammonium ions from AS required for complete ion exchange. Samples were shaken on rotary shaker for 24 hours at 220 rpm. After draining, the resulting solutions were examined on the contents of Ca, K, Na, and Mg. The concentration of the exchanged cations has been measured using the "Perkin Elmer AAS "703".

## **RESULTS AND DISCUSSION**

The X-ray powder diffraction analyses confirm that the major mineralogical component in all three samples is clinoptilolite (>75%). The K-zeolite predominantly contains zeolite minerals from the group heulandites - clinoptilolite (HEU) and feldspars, and smaller amounts of quartz and mica. In feldspar are dominant plagioclases in relation to the K-feldspars. The contents of gypsum and apatite are negligible. A fraction of volcanic glass is a significant and degree of crystallinity is very low. The Ca-zeolite predominantly contain zeolite minerals from the group heulandites - clinoptilolite (HEU) and feldspars, and smaller amounts of quartz. The contents of carbonates, gypsum and apatite are negligible. A fraction of volcanic glass is a significant and degree of crystallinity is very low (Figure 1 a,b). In order to determine potential difference in the cation exchange mechanism depending on the nature of the zeolite, the point of zero charge as an important parameter of the ionic affinity of the zeolite was determined. The points of zero charge (pH<sub>pzc</sub>) of K-zeolite and Ca-zeolite type were 7.1 and 7.7, respectively. CEC determined for K-zeolite was 158.2 meq/100g of which Ca holds 92 meq, K 51.5 meq, Na 8.85 meq and Mg 5.54 meq/100g of zeolites. CEC of Ca-zeolite was 153.5 meq/100g of which Ca holds 98.8, K 20.7, Na 11.1 and Mg 22.92 meq/100g of zeolites.

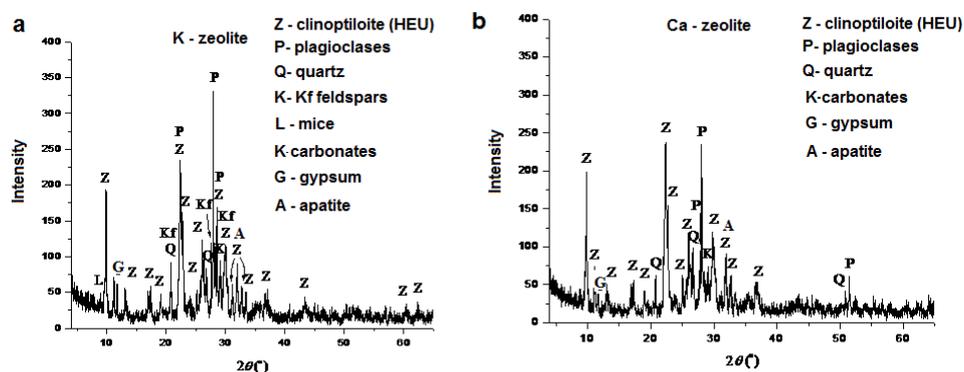


Figure 1. Diffractograms of the natural K - zeolite (a) and Ca - zeolite (b)

After modification of both zeolite types, with different initial concentrations of AS, ion-exchangeable cation concentration in the residual solution was investigated. Table 1 shows a gradual increase in concentrations of Ca, Mg and Na with increasing of initial concentrations of modifier, in both cases. In the K-zeolite, content of K in the solution increases rapidly at 1:5 ratio, after which it decreases. In the Ca-zeolite an increase of K was significant at 1:10 ratio modification. At the same ratio in Ca-zeolite, gradual decrease of Mg displacement was observed.

Table 1. Concentrations of ion-exchangeable cations in the solution subject to the amount of modifier, after 24h for both zeolite types

	K-zeolite				Ca - zeolite			
mg/kg	1:1	1:2	1:5	1:10	1:1	1:2	1:5	1:10
Ca	440	860	1273	1425	470	525	810	2000
K	1170	1700	4670	3776	84.5	391	449	610
Na	560	727	817	491	604	870	1154	1675
Mg	91	82,5	70.6	69	462	700	694	282.5

pH values of the solution in all four cases of modification ranged from 7.1 to 7.6 (data not shown) for both types of zeolites or around the point of zero charge of zeolites. At this pH, zeolite particle's surface is uncharged implying that the adsorption of ammonium ions on the zeolite takes place through ion-exchange mechanism [7]. Also, at water pH 7, competition of hydrogen ions with ammonium ions for adsorption/exchanging sites onto zeolite particles is reduced. This overcomes the necessity of pH manipulation for maximizing the adsorption, which in turns makes the treatment more cost-effective.

Analysis showed that the ratio at 1:10 for ion-exchange is generally the best, although it's not complete (Figure 2). It is fully substituted only Na, while other exchangeable cations are partially residual in the zeolite. Ion exchange of Na and K is very high, while about half of Ca and Mg altered. For K-zeolite modification at 1:5 ratios was also very effective. Generally, modification of K-zeolite at lower concentrations favors amendment of monovalent cations, while in the Ca-zeolite, favors exchange of Mg. Exchange of Ca gradually increases with increasing concentration of modifier, in both zeolite types.

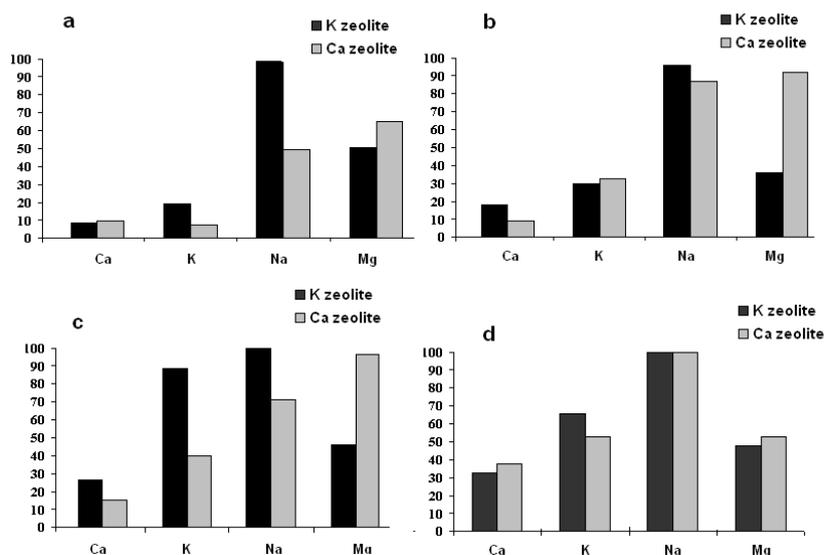


Fig.2. The percentage of exchanged cations after modification of natural zeolite with different ratios of AS (a) 1 : 1, (b) 1 : 2, (c) 1 : 5, (d) 1 : 10.

## CONCLUSION

This study demonstrated effective modification of natural zeolite, at lower quantities of modifier than usual, to produce an amendment to ecological fertilizer. Judging from plant grow experiments which used mixture of  $\text{NH}_4$ -exchangers, as effective sources of N and RP, the proposed basic parameters of zeolite modification should work for plants. In addition, exchangeable Ca and K remained in zeolite is readily available for plant uptake. Thus, the system has the potential to supply all of the major plant nutrients. Plant growth experiments that are currently underway in our laboratory demonstrate that 1:10 ratio of zeolite to AS is reasonable choice in order to obtain appropriate zeoponic mixture. Data on efficiency of modified zeolite at 1:10 ratio in  $\text{NH}_4$ -zeolite/RP exchange-induced dissolution system will soon be available.

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