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Structural and fertilizer properties of potassium doped natural zeolite

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Abstract

In this study the structure, morphology and fertilizer capacity of potassium doped natural zeolite is investigated. The surface characterization of potassium doped natural zeolites has been investigated by X-ray diffraction (XRD), scanning electron microscope (SEM)/ EDX analysis. The potassium doped zeolitic materials were tested for potential application as fertilizer in growing of wheat (*Triticum aestivum* L) and oat (*Avena Sativa*).

Keywords: natural zeolite, potassium, fertilizer, wheat (*Triticum aestivum* L), oat (*Avena Sativa*).

1. Introduction

Zeolites are a group of minerals, highly crystalline hydrated aluminosilicates that, when dehydrated, develop a porous structure with minimum pore diameters of between 3 to 10 Å. The structural frame is made up of Si-O (SiO_4^{4-}) and Al-O (AlO_4^{5-}) tetrahedrons, which bond together sharing vertices and forming square and hexagonal structures [1].

Natural zeolites attract a lot of attention in many applications due to their low cost, abundant deposits and selectivity for a large number of cations [2,3]. In this context, natural clinoptilolite, which is formed in abundance, is one of the most appreciated due to its nonpoisonous nature and great accessibility.

The unique physical and chemical properties of natural zeolites, based on their ion exchange, catalytic and molecular sieve properties, make them useful for many agricultural and horticultural applications and also for other environmental uses [4].

In literature there are many published research works relative to the application of zeolites to soil remediation, however, the most of them concern laboratory experiments (mainly pots, batch and column experiments) or small scale applications [5].

Zeolites added to fertilizers help to retain nutrients and, therefore, improving the long term soil quality by enhancing its absorption ability. It concerns the most important plant nutrients such as potassium (K), and also calcium, magnesium and microelements. Zeolite can retain these nutrients in the root zone to be used by plants when required. Consequently this leads to the more efficient use of K fertilizer by reducing their rates for the same yield, by prolonging their activity or finally by producing higher yields [6].

This work aimed to the preparation, characterization of natural zeolite doped with potassium. The structure and the morphology of natural zeolite doped with potassium was characterized through X-ray diffraction and SEM/EDX analysis.

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The materials were tested as fertilizer for the wheat (*Triticum aestivum L)* and oat (*Avena Sativa*) grown in laboratory conditions.

2. Material and methods

Natural zeolite with high clinoptilolite content was supplied by Cemacon Company, Romania. The mass composition of clinoptilolite zeolitic mineral was: 62.20% SiO_2, 11.65% Al_2O_3, 1.30% Fe_2O_3, 3.74% CaO, 0.67% MgO, 3.30% K_2O, 0.72% Na_2O, 0.28% TiO_2.

For a more efficient ion exchange, the natural zeolite was modified as sodium form (Z-Na); the preparation of the chemically modified zeolite presumes two stages, a acid form using HCl (2M) and a sodium form using $NaNO_3$ (2M).

The achievement of the fertilizer is made by mixing the sodium form of zeolitic tuff, grain size 315-500 µm and 0.8-1.2 mm , with 2M KCl solution, for 8 hours at room temperature and then washed and dried at 100°C for 12 hours.

The degree of emergence is percentage evaluated based on the formula:

$$\text{Raised plants} = \frac{\text{Number of raised plants}}{\text{Number of seeds sown}} \times 100\ [\%]$$

Table 1.

Type	Zeolite (g/vessel)	Zeolite-K
W_0	0	315-500 µm
W_1	2	
W_2	5	
W_3	10	
W_4	15	
W_5	2	0.8-1.2 mm
W_6	5	
W_7	10	
W_8	15	

Table 2.

Type	Zeolite (g/vessel)	Zeolite-K
O_0	0	315-500 µm
O_1	2	
O_2	5	
O_3	10	
O_4	15	
O_5	2	0.8-1.2 mm
O_6	5	
O_7	10	
O_8	15	

The mixed K-zeolite complex fertilizer was introduced by different weight in vessels with soil and 30 grains of wheat (*Triticum aestivum L)* and oat (*Avena Sativa*) were sown in every vessel. The establishments of experimental variants are presented below:

The content of exchangeable ions from soil and plants solution was established by laboratory analysis which proposed the using of atomic absorption spectroscopy *(*AAS*)* SPECTRAA 110-Varian. This method is very sensitive and it is used to determined a lot of elements.

3. Results and Discussion

3.1. The materials characterization. The crystallinity of the prepared samples was measured by X-Ray diffraction (XRD) using PANalytical X'PertPRO MPD Difractometer with Cu tube. A scanning electron microscopy (SEM) using Inspect S PANalytical model coupled with the energy dispersive X-ray analysis detector (EDX) was used to characterize the external surfaces of the materials, using catalyst powder supported on carbon tape.

3.1.1. XRD analysis The XRD patterns of natural zeolites are illustrated in figure 1 The presented results revealed that the natural zeolite used is mostly clinoptilolite (2 theta: 10º; 22.5º; 30º). The presence of other crystalline compounds, e.g., mordenite, quartz and illite is also revealed [3].

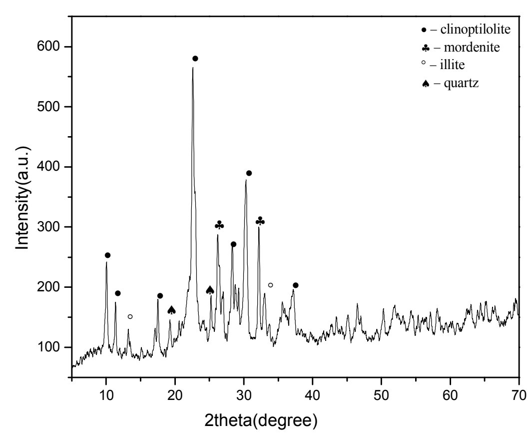
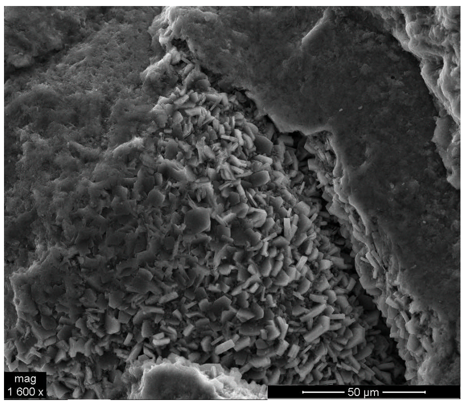
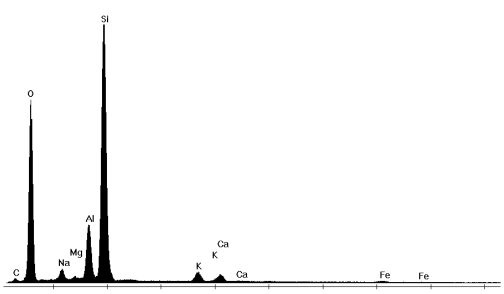


Figure 1. XRD pattern of ZN-K

3.1.2. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) results. According to the literature data the crystals of these materials have characteristic monoclinic symmetry of blades and laths, some of which are similar to the coffin shape of megascopic heulandite that occurs in vugs in basalts [7,8]. EDX spectra (figure 2b) provided a semiquantitative elemental analysis of the surface indicating that Si/Al ratio is about 4-5 and the presence of potassium in natural zeolite network.



(a)



(b)

Figure 2. SEM and EDX images for ZN-K

3.2. Fertilizer capacity of potassium doped zeolit. Using potassium doped zeolite as fertilizer show that for the wheat crop, the number of the fiber is much bigger versus the oat crop. In table 3 are presented the number of fiber in percentage for each seeds. Also with the increasing the zeolite amount the number of the fiber is increasing, and the efficiency of zeolite with lower size (315-500 μm) is better than the zeolite with bigger size (0.8-1.2 mm).

Table 3. Number of raised plants

No.	Raised wheat %	Raised oat %
0	12	10
1	25	15
2	50	25
3	83	51
4	90	75
5	30	13
6	73.33	18
7	80	40
8	93.33	55

To determine the Na and K amount from the plants was obtained a solution thus the plants was cuted from the soil level, and the green mass was weighed. The plants were thermally treated at 105°C for 2 hours, and after that was again weighed. The plants calcinations was made in owen at 550°C, for 5 minutes when was obtained a gray ash, these was also weighed and the analysis was made by preparing a HCl concentrated solution. The Na and K content from the solution was determined using atomic absorption spectroscopy *(*AAS*)* SPECTRAA 110-Varian

Table 4. The humidity gradient of the oat plants function of zeolitic tuff amount

Type	*Humidity %*	*Content of organic substance %*
O_0	13.46	10.63
O_1	12.5	83.33
O_2	14.29	85.71
O_3	21.42	72.72
O_4	25.64	68.96
O_5	18.75	44.73
O_6	22.22	80.76
O_7	22.66	75.86
O_8	40.62	78.57

Table 5. The humidity gradient of the wheat plants function of zeolitic tuff amount

Type	*Humidity %*	*Content of organic substance %*
W_0	25.74	12.80
W_1	35.68	19.00
W_2	45.69	29.39
W_3	59.66	53.24
W_4	79.05	69.02
W_5	33.19	14.77
W_6	39.19	31.28
W_7	49.82	45.90
W_8	63.03	58.64

The experimental research was made to establish the correlation between the different amount of zeolitic tuff and the retained capacity of water in plants. The experimental data are presented below. The experimental values are different function of the experimental dose used in experiment.

Transfer factors. The transfer factor show the metal quantity which pass from soil to root tissue, where it accumulate and become available to move to another parts of plant tissue. The value of transfer factor is function of the bioavailable metal quantity from soil and the plant affinity for one or more accessed metals.

The transfer factors (TF) of Na and K, from soils to vegetables were calculated as follows:

$$(TF = Q_R/Q_S),$$

Where:
Qr = metal concentration in plant tissue
Qs = metal concentration in soil
The concentrations are in mg/kg, dry substances

In figure 3 is present the transfer factor of the plants concerning the metal quantity cumulated in root vs. metal concentration from soil of different experimental types.

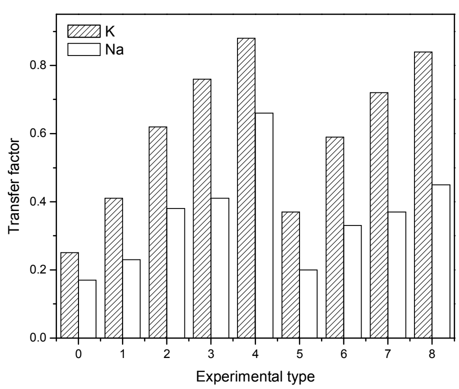


Figure 3. Transfer factor from soil

Figure 3 shows that the transfer factor is modified when is added the volcanic tuff, the zeolitic fertilizer determine the major effects of Na and K access in plants roots.

4. Conclusion

This study was based on the assumption that natural zeolites (clinoptilolite) are used like fertilizers for K releaser and successfully used in growing the wheat and oat . The experimental results showed that the K doped natural zeolite at 315-500 µm is suitable for a proper grown of the wheat and oat crop, and the number of fibers were increased with the increasing of the zeolite amount.

These exploratory experiments show the feasibility of this simple synthesis method of zeolite fertilizer for K releaser in growing the wheat and oat . The results are part of on-going investigations in our laboratory aimed at developing the zeolite based fertilizer.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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