INFLUENCE OF NATURAL ZEOLITE - CLINOPTILOLITE ON POTASSIUM AND NITRATE RETENTION IN DIFFERENT SOIL TYPES

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ABSTRACT

As-received and iron(III)-modified natural zeolites were used for studying of potassium and nitrate retention in different soil types (sandy, silty loam and silty clay) under laboratory conditions by using column systems. The concentration of K^+ and NO_3–N in the leachates was monitored during seven days. The results showed that the retention of K^+ and NO_3-N mainly depends on the soil type. The addition of zeolite has the highest impact on the K^+ retention in the acidic sandy soil. For all studied soil types, the leaching kinetics of K^+ follows the Avrami kinetics model with the parameter $n < 1$ indicating a high initial rate, which decreases with time.

Keywords: clinoptilolite, nitrate, potassium, retention, soil.

INTRODUCTION

Natural zeolites are aluminosilicate minerals with versatile applications including use as soil supplements due to their molecular sieving, ion-exchange and adsorption properties. Generally, addition of zeolites to soil can improve the soil fertility but prevent degradation of groundwater body due to retarding the nutrients leaching through the soil[1–3]. Taking this into account, the aim of this study was to examine the influence of a Serbian zeolitic tuff on the leaching process of potassium and nitrate from different soil types.

EXPERIMENTAL

Zeolite samples: The zeolitic tuff containing about 73 wt.% of clinoptilolite was obtained from Zlatokop mine (Vranjska Banja, Serbia). In this study, as-received (NZ) and its iron-modified form (FeZ) were used with particle size in the range of 0.063-0.2 mm. FeZ was prepared in accord with the previously published procedure[4].

Soil samples: The soil samples were collected from Norway (NW, 59°41'09" N and 10°46'37" E), Bosnia and Herzegovina (BH, 44°07'53" N and 18°06'27" E) and Serbia (SRB, 44°40'24" N and 19°39'25" E). The soil samples were classified as sandy (NW), silty loam (SRB) and silty clay soil (BH). The sandy soil and silty loam soil were acidic (pH = 5.1 and pH = 5.7, respectively) whereas the silty clay was slightly alkaline (pH = 7.5). NW and SRB soils were poor in organic matter content (OM = 1.3 and 4.3 wt.%, respectively), plant available K amounts (10 mg kg^{-1} and 115 mg kg^{-1}, respectively) and total nitrogen content (N_{TOT} = 0.01 and 0.16 wt.%) compared to BH soil (OM = 11.5 wt.%, plant available K amounts = 286 mg kg^{-1}, N_{TOT} = 0.47 wt.%).

Leaching experiments: Leaching experiments were performed at room temperature using 30 cm long plexiglas columns with inner diameter of 24 mm (Fig. 1). The columns were organized in eight systems shown in Table 1 with three replications of each.

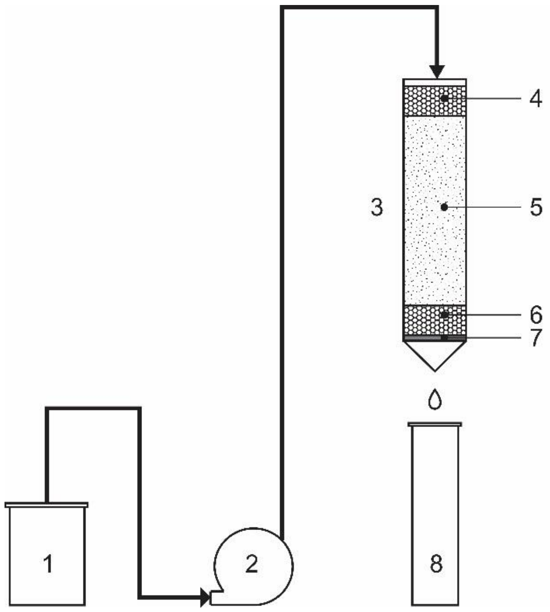

Figure 1. The experimental setup: 1. water tank; 2. peristaltic pump; 3. plexiglas column; 4. PVC balls; 5. soil or soil/NZ/FeZ, or KNO_3 mixture; 6. PVC balls; 7. PVC filter; 8. sample collector.

Table 1. Column systems used in the experiment.

System	Component		
I*	Soil	–	–
II	Soil	KNO_3	–
III	Soil	–	NZ, 1 wt.%
IV	Soil	KNO_3	NZ, 1 wt.%
V	Soil	–	FeZ, 0.5 wt.%
VI	Soil	KNO_3	FeZ, 0.5 wt.%
VII	Soil	–	FeZ, 1 wt.%
VIII	Soil	KNO_3	FeZ, 1 wt.%

*Control system

The amount of added KNO_3 corresponded to 10 mg N (100 g soil)$^{-1}$ and 28 mg K (100 g soil)$^{-1}$ which amounts to 200 kg N and 550 kg K ha^{-1} soil while the amounts of NZ (0.5 wt. %) and FeZ (0.5 and 1 wt.%) corresponded to about 10 and 20 t zeolite ha^{-1}, respectively. Columns were filled with soil or with previously homogenized mixture of soil and amendments (NZ/FeZ, or KNO_3) up to a 20 cm height. A PVC filter covered with PVC balls (about 2 cm in height) was placed at the bottom of each column. The top of filled column was also covered with PVC balls. After filling the columns, they were saturated and then irrigated with distilled water, at a flow rate of 1.3 ml h^{-1} during 7 days. The concentration of potassium and nitrate in the collected leachates was measured by a Corning 405 flame photometer and flow injection analysis (FIAstar 5000), respectively. All obtained results were analyzed by different kinetic models.

RESULTS AND DISCUSSION

Potassium leaching: The results of K leaching experiments indicated a high mobility of K from sandy NW soil due to a low content of clays (Fig. 2). However, addition of both NZ and FeZ improve the K retention, which is evident in the control system as well as in the systems containing KNO_3. The better efficiency obtained by addition of FeZ could be attributed to the Fe_2O_3 particles at the surface of the clinoptilolite phase and consequently a better adsorption ability of FeZ towards K. For all studied systems, K leaching from silty loam (SRB) and silty clay (BH) soils was lower than from NW soil (results not shown). The better K retention capacity of these soils could be attributed to the higher content of clays, which are of different origin than the NW soil. A slightly visible but statistically significant reduction effect was also obtained after addition of NZ and FeZ to SRB and BH soils. Finally, the presented results clearly show that the K leaching depends on the soil type.

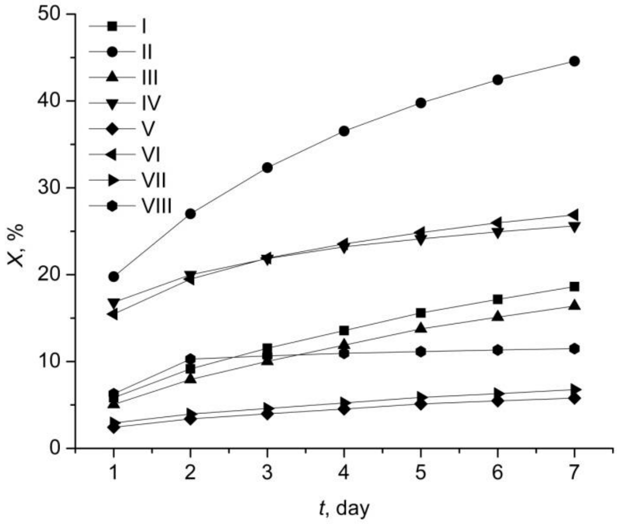

Figure 2. Percentage of the leached potassium (*X*) over time from NW sandy soil.

Several kinetic models (zero-order, first-order, second-order, parabolic diffusion, Elovich and Avrami model) were applied in order to describe the K leaching kinetics. The obtained results agree well with the Avrami model ($R^2 \sim 1$). Also, the values of Avrami constant n indicate that the initial rate of K leaching is high and decreases with time ($n < 1$).

Nitrate leaching: Irrespective of the soil types or treatments, the highest NO_3-N amount was leached out during the first day (about 90 %) because of a high amount of irrigation water and high nitrate solubility. Addition of zeolites (NZ or FeZ) to sandy NW soil has no positive effect on the retention of NO_3-N (not shown). In contrast, a positive effect of the zeolite addition in the control and systems with KNO_3 was observed for the SRB and BH soils (Fig. 3). Taking into account the fact that both parent (NZ) and modified zeolite (FeZ) decrease the leaching of NO_3-N from SRB and BH soils, it could be concluded that the presence of zeolite in the soil has not only an adsorption role but affects also the physical and hydraulic properties of the soil leading to preservation of NO_3-N[5]. The retention of NO_3-N was higher in the silty loam (SRB) soil which was acidic than in the alkaline silty clay (BH) soil. This can be explained by a competition between hydroxide and nitrate ions for the adsorption sites at the zeolite surface.

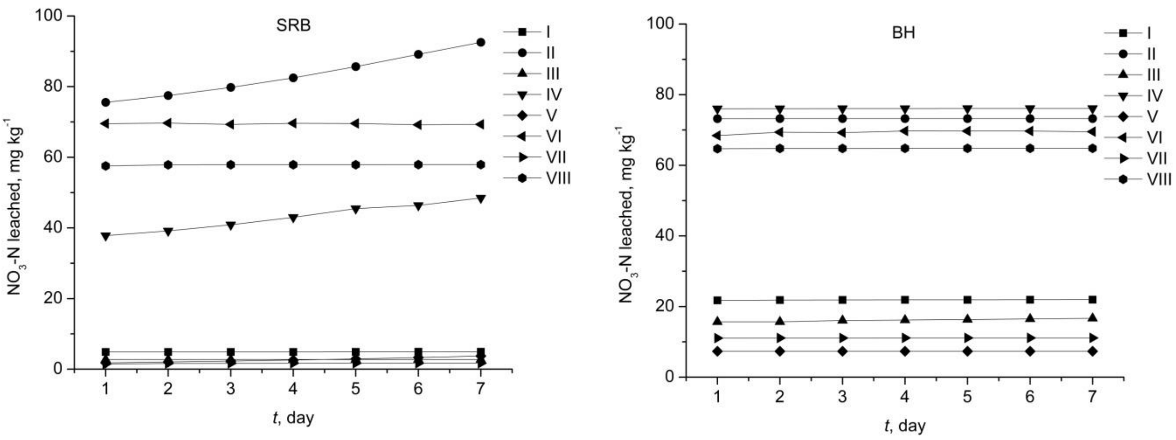

Figure 3. Amount of the leached NO_3-N over time from silty loam (SRB) and silty clay (BH) soils.

CONCLUSION

The presented results show that the addition of zeolites to the different types of soil had a retention effect towards potassium ions in the following order: silty loam < silty clay << sandy soil. A retention effect toward nitrate ions was obtained only for the silty loam and silty clay soils. Both NZ and FeZ showed a better retention effect for nitrate in the acidic silty loam than in the alkaline silty clay soil. Taking all into account, this study suggests that the addition of natural zeolites to the soil can be a beneficial option for reduction of the mobility of potassium and nitrate and for prevention of their leaching from soil.

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REFERENCES

[1] N. Colombani, M. Mastrocicco, D. Di Giuseppe, B. Faccini, M. Coltorti, *CATENA* **2015**, *127*, 64–71.
[2] A. Moirou, A. Xenidis, L. Paspaliaris, *Soil Sediment Contam.* **2001**, *10*, 251–267.
[3] R. Malekian, J. Abedi-Koupai, S. S. Eslamian, *J. Hazard. Mater.* **2011**, *185*, 970–976.
[4] J. Pavlović, J. Milenković, N. Rajić, *J. Serbian Chem. Soc.* **2014**, *79*, 1309–1322.
[5] M. Moradzadeh, H. Moazed, G. Sayyad, M. Khaledian, *Acta Ecol. Sin.* **2014**, *34*, 342–350.