MIRJANA STOJANOVIĆ[1], MARIJA MIHAJLOVIĆ[1], ZORICA LOPIČIĆ[1], MARIJA PETROVIĆ[1], JELENA MILOJKOVIĆ[1], ČASLAV LAČNJEVAC[2], DRAGAN RADULOVIĆ[1]

Review paper
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Raw phosphate composite as a natural fertilizer and soil remediation amendment

Our investigation is focused on the design of novel multifunctional material based on the synergistic conjunction of raw phosphate, zeolites modified with ammonium ions and waste biomass, in support to increase phospho-mobilization in various soil types and wider pH range. The results of the vegetation experiment in semi-controlled conditions with maize on soil type distric cambisol indicates that the addition of modified zeolite and ash pit cherries to the rock phosphate favors the growth of the culture and its yield. Released phosphate ions have a dual role as donor of nutrients, and soil remediation amendment through phosphate-induced stabilization of heavy metals. The field vegetation experiment with maize on soil type leached chernozem showed that NH_4^+-zeolite/raw phosphate composite has multifunctional properties applicable in sustainable agriculture.

***Key words**: modified zeolite, phosphate rock, ash pit cherries, nature mineral fertilizers, soil remediation amendment*

INTRODUCTION

Application of the rock phosphate (RP) in agriculture has a significant impact on increasing crop yields, but with limited use on acid soils [1,2]. In very acidic soils (pH below 4.5), effects of RP are identical with the used water-soluble industrial phosphorus fertilizers [3]. The dissolution of the RP in soils depend on the availability of H^+, humidity, Ca^{2+} and P removal from the solution. Cation exchange capacity of acidic soils are low, the concentration of Ca^{2+} in the soil solution around the particles increases rapidly, delaying RP dissolution [4]. Unlike a highly soluble superphosphate, RP has the ability of controlled release of phosphorus, as a result of a specific chemical reactions in the soil. As phosphate is taken up by plants or by soil fixation, the chemical reaction releases more phosphate and ammonium in the attempt to reestablish equilibrium.

Zeolites, as aluminosilicate porous minerals, with high cation-exchange capacity, that can help control the release of plant nutrients in agricultural systems and can contribute to the increase of rock phosphate solubility [5]. When saturated with monovalent nutrient cations, such as NH_4^+, zeolites additionally enhance increase dissolution of RP [6]. The mechanism proposed for solubilisation of RP is exchange-induced dissolution in wich plant uptake of $NH4^+$ liberates exchange sites which are occupied by Ca^{2+}, lowering the soil solution Ca^{2+} concentration and inducing further dissolution of RP. Simultaneously, the zeolite takes up Ca^{2+} from the phosphate rock, thereby releasing both, phosphate and ammonium ions, according to equation:

$$RP + NH_4^+\text{-zeolite} \leftrightarrow Ca\text{-zeolite} + NH_4^+ + H_2PO_4^- \quad (1)$$

The tribochemical activation of RP -NH_4-clinoptilolite mixtures facilitates the transitions of hardly assimilated by plants P_2O_5 forms into readily accessible ones. Procedure leads to deformation and rupture of Si-O-Si and Si-O-Al bonds and decreasing of ion-exchange capacity in the clinoptilolite sample and defectiveness and isomorphism in the apatite structure which caused to increased reactivity, especially in the case of apatite domination [7].

It is proved that zeolite modified with ammonium ions has a higher capacity than natural zeolite to protect *Hieracium aurantium* and *Rumex acetosella* growing on tailing ponds, by reducing the quantity of the accumulated heavy metal ions (Pb, Zn, Cu, Fe) [8]. *Hieracium aurantium* and *Rumex acetosella* adopt a smaller quantity of metal ions in roots and leaves in the presence of zeolite modified with ammonium ions than in the presence of natural zeolite. In terms of reducing the uptake of ions of heavy metals, only the zeolite modified with ammonium has a significant protective effect on *Hieracium aurantium*, while both natural zeolite and modified zeolite demonstrate a significant role for *Rumex acetosella*, as revealed by statistical tests [8].

Agricultural waste materials have proved to be highly efficient, low cost and renewable source of biomass that can be exploited for heavy metal remediation and nutrient holder, which leads to increase of their life cycle and also solve their

Author's address: [1]Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia, [2]Faculty of Agriculture, University of Belgrade, Serbia

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disposal problem [9, 10]. On the other hand, research indicates that natural apatite from Lisina can be used for in situ phosphate-induced immobilization of heavy metals, Pb anad Cd, in polluted soils, as inexpensive remediation amendments [11,12]. Phosphate amendment is less effective for Cu and Zn immobilization [13]. This is explained by the fact that Pb was immobilized by P via formation of an insoluble pyromorphite mineral in the surface and subsurface of the soil, which is not the case with Zn or Cu.

Researches of this study has been led in three directions: (i) Investigated the basic parameters of zeolite modification with ammonium ions, to be most economically in the respective raw materials needed to produce an effective supplement for ecological fertilizer and soils remediation amendments, (ii) The efficiency of natural fertilizer was further investigated through the vegetation experiments with maize in semi-controlled conditions. (iii) The efficiency of natural fertilizer as soil remediation amendment through phosphate-induced stabilization of heavy metals, as an acceptor.

This paper presents the results of preliminary investigations that were employed domestic RP, apatite from Lisina deposit, in combination with NH_4-zeolite and waste biomass – ash pit cherries (APC), in order to improve RP dissolution and maize yield. New cost-effective natural fertilizer with required characteristics could enhance soil fertility and quality with the aim of safer food production.

MATERIAL AND METHODS

(i) Zeolites originating from deposit Baia Mare, Romania (K-zeolite type) was used for this study. Chemical composition of starting zeolitic tuff was determined by atomic absorption spectrophotometry (AAS) using the Perkin Elmer AAS "703". The natural K -zeolite tuff contained: 63.60% SiO_2, 11.81% Al_2O_3, 1.74% Fe_2O_3, 7.35% CaO, 0.69% MgO, 0.17% TiO_2, 0.4% Na_2O, 4.40% K_2O and loss of ignition was 9.81%. Modification of zeolite with different initial concentrations of ammonium sulfate (AS) (1 M $(NH4)_2SO_4$) 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 rounds per min. 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".

(ii) The fertilizer, concentrate of RP, used in these experiments was made by flotation method of apatite, from ore deposit „Lisina" Bosilegrad, containing 32-35% P_2O_5. The complete mineral characterization from this deposit can be found elsewhere [14]. RP was grounded to about 80μm size particles. With a wet milling and wet classification process was excluded fraction of < 37 μm, which were used in the experiments.

Waste biomass material, cherry stones, were obtained from "Vino Župa" Company from Aleksandrovac, where they have been disposed as by-products from the Juice Factory. After receiving, the pit samples were separated from soft fruit residues, washed and dried at room temperature. Later, they were manually crushed and separated from kernels, which were discharged. For further analyses only ash of hard stone part (burnt at 1000ºC), was used. Chemical composition of starting ash pit cherries was determined by atomic absorption spectrophotometry (AAS) using the Perkin Elmer AAS "703". The amounts of P after sample preparation were mesaured by analysis of the supernantant by colorimetry. The ash pit cherries contained about: K 8.5%, Na 0.3%, Ca 11.8%, Mg 2.46%, Fe 2.12%, Mn 0.053%, Al 2.1% P_2O_5 8.94% Pb 0.011%, Ni 0.007%, Cd <0,01%, Zn 0.014%, Cu 0.016%, SO_3 1.05% and loss of ignition at 600 °C and 1000 °C were 3.89 % and 11.31% respectively.

Vegetation experiment in semi-controlled conditions was set up with a hybrid ZP 434 on soil type distric cambisol Table 1. Four different growing media placed in the 4 different pots: (RP)/soil, (RP+zeolite)/soil and (RP+NH_4-zeolite)/soil and (RP+NH_4-zeolite+ ash pit cherries (APC))/soil, were tested. In each experimental variants were entered 20g of fertilizer per 100 kg of soil. Based on the literature data it was decided that the fertilizer contains initial ratio the zeolite and the RP of 5:1 [2] and NH_4-zeolite/RP/APC of 5:1:1. Plants were collected with three to five leaves and dried. Maize yield was determined via total increase of dry matter content (m) and its heights (h). The amounts of P after sample preparation were mesaured by analysis of the supernantant by colorimetry.

Table 1 - Chemical properties of experimental soil

Horizon	Depth (cm)	pH		EC (μS)	Humus (%)	CEC (meq/100g)
		H_2O	KCl			
Ah	0-30	5.55	4.50	71.12	2.12	16.2

(iii) The effectiveness of natural mineral fertilizers on physiological and morphological and nutritional properties of of corn were conducted at the experimental field "Radmilovac", owned by the Faculty of Agriculture – Zemun. Zemun. Hybrid FAO560 planted on leached chernozem soil type

The field experiment was set up and carried out during the 2012. on a plot size of 15m x 60m, which included ten basic plot size 12m x 7.5m., or unit of 90 m^2, with nine rows of corn. Each plot, except the control and treated with different variant model of manure. Each variant is composed of different combinations of modified zeolite grain size <100 μm, natural and concentrated apatite grain size <63 um and ash pit cherries grain size <0.9 mm, as donors of potassium (12.08% K_2O), compared 5:1, in two doses. Dose 1 is the input of 25 kg fertilize, dose 2 is the input of 40 kg fertilizer unit area of 90 m^2 (Table 2). Fertilizer efficiency was evaluated by measuring the content of nutritive elements and heavy metal (Pb, Zn,Cd and Cu) in soils and plant roots.

Table 2 - Nutrition treatments in vegetation experiments with maize

Nutrition treatments	nutrition variant
control	without treatment
AZA 1	20 kg of modified zeolite, 4 kg of natural apatite, (Dose 1)
AZA 2	20 kg of modified zeolite, 4 kg of natural apatite, (Dose 2)
AZAK 1	20 kg of modified zeolite, 4 kg of apatite concentrate, (Dose 1)
AZAK 2	20 kg of modified zeolite, 4 kg of apatite concentrate, (Dose 2)
PEP	20 kg modif. Zeolite, a natural apatite 4 kg, 4 kg ash pit cherries, (Dose 1)
PEPK	20 kg modif. Zeolite, a natural apatite 4 kg, 4 kg ash pit cherries, (Dose 2)

In order to enable more comprehensive comparison between examined samples, particularly the effects of different fertilization treatments, standard score (SS), assigning equal weight to all assays applied, has been introduced. Analyses of variance (ANOVA) have been applied to show relations between applied assays. Descriptive statistical analyses for all the obtained results were expressed as the mean ± standard deviation (SD). Furthermore, the evaluations of one-way analysis of variance (ANOVA) of the obtained results were performed using StatSoft Statistica 10.0® software. Collected data were subjected to one-way ANOVA for the comparison of means and significant differences are calculated according to Turkey's HSD test at $P < 0.05$ level. Data were reported as means ± standard deviations. To get a more complex observation of the ranking of contents of the elements in the soil and maize roots, standard scores (SS) were evaluated using statistical approach by integrating the measured values generated from various fertilization treatments. In order to compare various characterristics of complex soil and root samples after different fertilization treatments using multiple measurements, samples were ranked based on the ratio of mean value and standard deviation of the measurement used. As the scale of the data from various samples were different, the data in each data set should be transformed into standard scores (SS), dimensionless quantity derived by subtracting the mean from the raw data divided by the standard deviation. The standard scores of a sample for different measurements when averaged give a single unit less value termed as SS, which was a specific combination of data from different measuring methods with no unit limitation and no variance among methods.

RESULTS AND DISCUSSION

(i) After modification of zeolite with different initial concentrations of AS, ion-exchangeable cation concentration in the residual solution was investigated and results shows a gradual increase in concentrations of Ca, Mg and Na with increasing of initial concentrations of modifier [15]. The content of K in the solution increases rapidly at 1:5 ratios, after which it decreases. At the same ratio, gradual decrease of Mg displacement was observed (Figure 1).

Analysis showed that the ratio at 1:10 for ion-exchange is generally the best, although it's not complete (Fig.1). It is fully substituted only Na, while other exchangeable cations are partially residual in the zeolite [15]. Considering the conclusions of the previously published experiments, where mixtures with NH4-zeolites [2, 16-18] as effective sources of nitrogen and other nutrients as well as the promoters of RP dissolution have been used, herein proposed basic parameters of zeolite modification should be viable for plants. In addition, exchangeable Ca^{+2} and K^+ remained in zeolite are readily available for plant uptake [15].

(ii) The results of the experiment in semi-controlled conditions with maize, as test culture, indicate that the addition of natural zeolite to RP favors the growth of the culture and its yield (Table 3). The yield in the mass of maize was increased for an additional 85%, in the treatment with (RP+Z) fertilizer and for 92% in the treatment with (RP+ NH_4^+-Z), in comparison with the RP treatment. The yield in the mass of maize was increased for 90%, in the treatment with (RP+ NH_4^+-Z+APC), in comparison with the RP treatment.

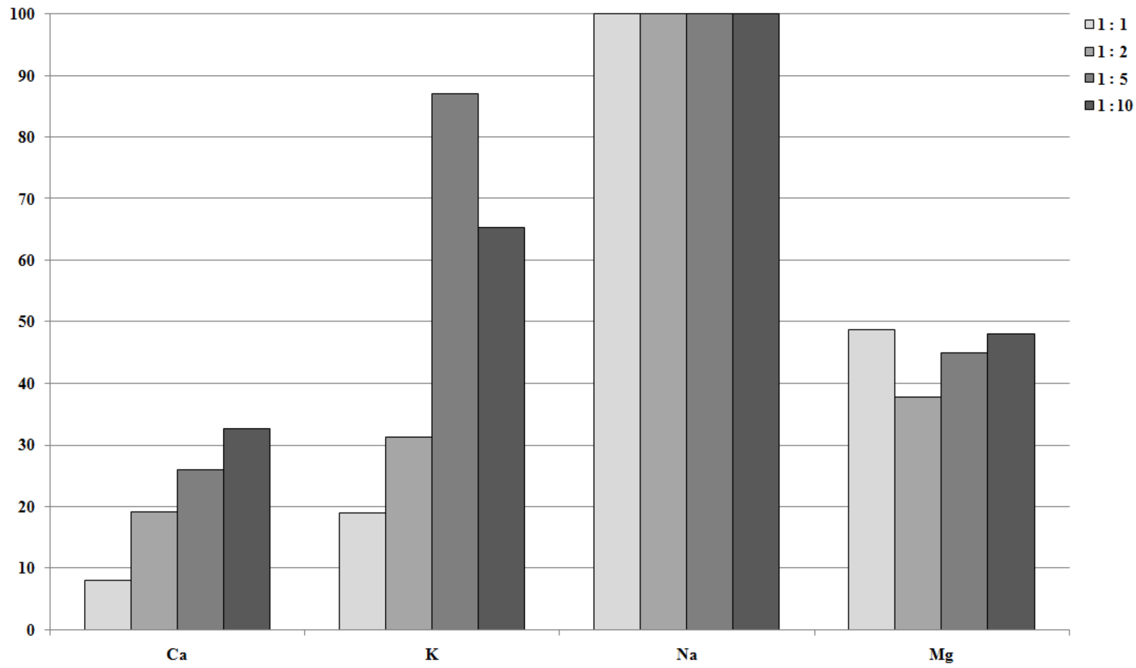

Figure 1 - The percentage of exchanged cations after modification of natural K-zeolite with different ratios of AS [15]

The obtained values of K^+ content in all three samples of maize showed higher amounts of this nutrient in plants treated with zeolite enriched fertilizer. The highest Ca^{+2} content of 1.66 % was found in sample with (RP + Z) treatment. The expected decrease in content of Ca^{+2} was observed in the sample treated with fertilizer which has the least of this element (0.73%). Surely the most significant parameter of the applied fertilizer treatments was P content in the prepared plant samples. At the treatment with the addition zeolite to the RP, content of P was increased from 0,181% to 0.198%. As expected, the highest P content of 0.287%, was detected in the sample of maize treated with the (RP + NH_4^+-Z +APC) fertilizer.

Table 3 - The results of semi-contoled vegetation experiment with maize

Treatment	h (%) [a]	m (%)[b]	K (%)	Ca (%)	P (%)
RP [c]	100	100	1,62	0,77	0,181
RP+Z [c]	143	185	2,08	1,66	0,198
RP+ NH_4^+- Z	148	192	2,37	0,73	0,263
RP+NH_4^+-Z+APC	152	190	2.89	1.05	0.278

[a] The percentage of increase in heigh of the maize, compared to the RP treatment

[b] The percentage of increase of maize yield, compared to the RP treatment

[c] Mihajlovic et al 2012 [19].

(iii) Analyzing of the soil samples and maize roots, ANOVA and the subsequent post-hoc Tukey's HSD test were evaluated for comparison of element concentration under different fertilization treatments (Table 4, 5). Statistically significant differences for quantity of elements were found in almost all samples. Standard scores (SS) for the evaluations of the content of different elements under different methods of fertilization have been calculated for the soil (Table 4.) and maize roots (Table 5.) samples. It can be seen from the results that different fertilization treatments strongly influence the final score result. Final score of control soil samples demonstrated generally better SS results. Best scores of maize roots have been obtained for samples of AZA2 (0.380) and AZAK1 (0.341) fertilization treatments. Obtained SS scores are in good correlation with the phosphorus content in the roots of maize. With regard to the element mobility, all the applied treatments contributed to the increased uptake of nutrients P, Zn, Cu and K by the maize. Peter et all [8], have concluded that NH_4-zeolite reduce the uptake of heavy metal ions in the roots and leaves of *Hieracium aurantium* and *Rumex acetosella*. This is in agreement with the obtained results for Pb in maize roots (Table 5). The highest content of Fe and Pb was noticed in the control samples of maize roots. This can be explained by the rhizosphere effect, consists in the local acidification of the environment due to the adsorption of the heavy metal ions on the cell walls by replacing the protons from -COOH, -OH, -SH, and -NH_2 groups with heavy metal ions [8].

This paper also presents the results of preliminary investigation of the impact of ash pit cherries on the solubility of RP in real conditions. Thanks to H^+ present in the ash structure, APC contribute to the increasing of the quantity of phosphorus in the maize roots, compared to the control, but not to the same extent as AZAK treatments. Phases of the vegetation test are shown in Figure 2.

Table 4 - The mean concentration of elements ±SD found in soil following different fertilization treatments

	Ca	Mg	Fe	Na	K
Kontrola	3,4867±0,0153^{b}	0,8333±0,0153^{ab}	4,0867±0,0153^{d}	1,1067±0,0115^{b}	2,1133±0,0153^{d}
AZA1	3,5000±0,0600^{b}	0,8000±0,0100^{a}	3,8033±0,0153^{a}	1,0300±0,0100^{a}	1,8100±0,0100^{ab}
AZA2	3,7500±0,0500^{c}	0,7967±0,0153^{a}	3,3833±0,0153^{f}	0,9900±0,0100^{a}	1,7800±0,0100^{ac}
AZAK1	3,2667±0,0351^{a}	0,8033±0,0153^{a}	4,0000±0,0200^{c}	1,0267±0,0252^{a}	1,8400±0,0100^{b}
AZAK2	4,3333±0,1528^{e}	0,8800±0,0100^{c}	4,0300±0,0608^{cd}	1,0000±0,0173^{a}	1,7433±0,0375^{c}
PEP	3,2533±0,0153^{a}	0,8000±0,0200^{a}	3,8967±0,0153^{b}	0,9900±0,0100^{a}	1,8300±0,0100^{ab}
PEPK	3,2400±0,0200^{a}	0,8533±0,0153^{bc}	3,1867±0,0153^{e}	1,0367±0,0153^{a}	1,8167±0,0153^{ab}

Table 4 - Continue

	Cu	Pb	Cd	Zn	P	SS
Kontrola	0,0039±0,0001^{e}	0,0031±0,0001^{a}	0,0003±0,0000^{a}	0,0082±0,0001^{c}	0,0096±0,0002^{e}	**0,986**
AZA1	0,0032±0,0002^{bcd}	0,0030±0,0002^{a}	0,0003±0,0000^{a}	0,0076±0,0002^{a}	0,0041±0,0001^{a}	-0,251
AZA2	0,0031±0,0001^{abc}	0,0029±0,0001^{a}	0,0005±0,0000^{a}	0,0073±0,0001^{ab}	0,0032±0,0003^{b}	-0,575
AZAK1	0,0030±0,0002^{ab}	0,0025±0,0001^{b}	0,0015±0,0020^{a}	0,0076±0,0001^{a}	0,0039±0,0002^{a}	-0,116
AZAK2	0,0028±0,0001^{a}	0,0045±0,0001^{d}	0,0003±0,0000^{a}	0,0071±0,0001^{b}	0,0039±0,0001^{a}	0,150
PEP	0,0035±0,0001^{de}	0,0030±0,0001^{a}	0,0002±0,0002^{a}	0,0074±0,0002^{ab}	0,0054±0,0001^{c}	-0,329
PEPK	0,0028±0,0003^{a}	0,0035±0,0002^{c}	0,0011±0,0014^{a}	0,0073±0,0002^{ab}	0,0081±0,0002^{d}	-0,128

$^{a-f}$Different letter within the same row indicate significant differences p<0.05 level (according to post-hoc Tukey's HSD test)

Table 5 - The mean concentration of elements ±SD found in maize roots following different fertilization treatments

	Ca	Mg	Fe	Na	K
Kontrola	4,6600±0,0200^{bc}	0,8667±0,0208^{ab}	3,0367±0,0208^{ab}	0,0447±0,0029^{a}	0,8800±0,0100^{a}
AZA1	4,4667±0,0289^{a}	0,8667±0,0115^{ab}	3,0600±0,0520^{a}	0,0447±0,0006^{a}	0,7600±0,0173^{a}
AZA2	6,0100±0,0100^{e}	0,8633±0,0058^{ab}	3,0333±0,0577^{ab}	0,1593±0,2352^{a}	0,8300±0,0000^{a}
AZAK1	5,6733±0,0231^{d}	0,8733±0,0231^{ab}	2,7933±0,0058^{bc}	0,0580±0,0035^{a}	0,9267±0,0058^{a}
AZAK2	4,5267±0,0643^{ab}	0,8700±0,0265^{ab}	3,0200±0,0265^{ab}	0,0500±0,0020^{a}	0,8267±0,0306^{a}
PEP	6,8067±0,1007^{f}	0,8233±0,0208^{a}	2,5967±0,1704^{c}	0,0560±0,0026^{a}	0,6767±0,5000^{a}
PEPK	5,7400±0,0557^{d}	0,9167±0,0153^{bc}	3,2133±0,0808^{a}	0,0560±0,0040^{a}	0,7067±0,0306^{a}

Table 5 - Continue

	Cu	Pb	Cd	Zn	P	SS
Kontrola	0,0034±0,0002^{a}	0,0078±0,0002^{d}	0,0004±0,0000^{a}	0,0098±0,0001^{a}	0,2933±0,0153^{b}	-0,309
AZA1	0,0063±0,0000^{d}	0,0049±0,0001^{ab}	0,0011±0,0014^{a}	0,0083±0,0003^{a}	0,5233±0,0321a	-0,121
AZA2	0,0049±0,0000^{bc}	0,0048±0,0000^{ab}	0,0014±0,0019^{a}	0,0110±0,0000^{a}	0,5560±0,0000^{ac}	**0,380**
AZAK1	0,0054±0,0001^{c}	0,0051±0,0002^{b}	0,0007±0,0000^{a}	0,1027±0,0023^{b}	0,6667±0,1155^{c}	**0,341**
AZAK2	0,0065±0,0001^{d}	0,0045±0,0001^{a}	0,0006±0,0000^{a}	0,0095±0,0001^{a}	0,5933±0,0058^{ac}	-0,128
PEP	0,0045±0,0002^{b}	0,0075±0,0003^{d}	0,0007±0,0001^{a}	0,0087±0,0067^{a}	0,3200±0,0361^{b}	-0,416
PEPK	0,0036±0,0004^{a}	0,0067±0,0002^{c}	0,0005±0,0000^{a}	0,0083±0,0064^{a}	0,3467±0,0153^{b}	-0,137

$^{a-f}$ Different letter within the same row indicate significant differences p<0.05 level (according to post-hoc Tukey's HSD test

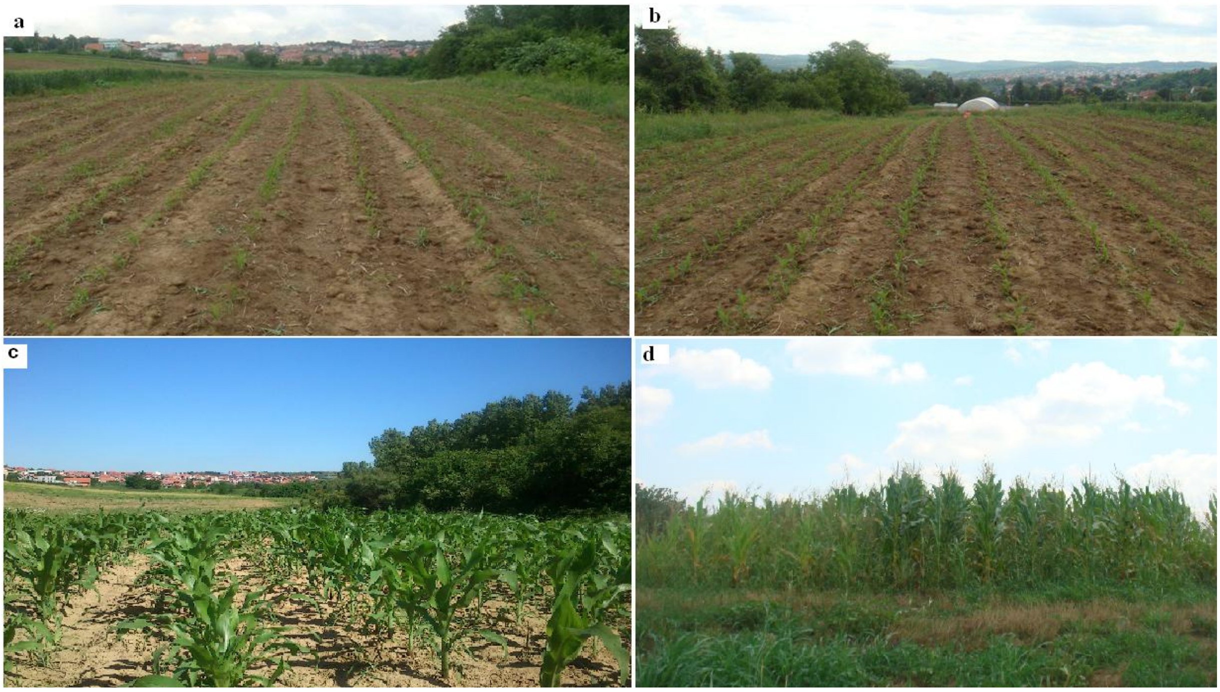

Figure 2 - Phases of the vegetation test: (a, b) corn germination stage (c) in the half maturity (g) full maturity plants

CONCLUSION

Presented results of the verification process parameters to obtain natural fertilizer based on natural phosphate, NH_4-zeolite and ash pit cherries through the vegetation tests in real and semi- controlled conditions with maize indicate the contribution of used treatments on maize yield. Presence of NH_4^+-zeolite and APC additionally facilitates release of P from RP in soil and thus affects the increase in maize yield. The results from field experiment indicate a chemical immobilization of heavy metals, so that NH_4^+-zeolite/RP composite material has a multi-functional effect as an “eco friendly” fertilizer and as a soil amendment for in situ remediation of heavy metals.

New cost-effective natural RP composite demonstrated characteristics which were potentially competitive the widely used chemical fertilizers. In addition, their implementation could improve soil fertility and the concept of safe food production. Utilisation of phosphorus mineral resource in Bosilegrad -“Lisina” creates economic revitalization and development of the chemical industry with competitive products at an international level.

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IZVOD

KOMPIZITI NA BAZI SIROVOG FOSFATA KAO PRIRODNA DJUBRIVA I REMEDIJACIONI AGENSI

Naša istraživanja su bila usmerena ka dizajniranju novog multifunkcionalnog materijala na bazi sinergističkog dejstva sirovog fosfata i modifikovanog zeolita amonijum jonima i otpadne biomase, u cilju povećanja fosfo-mobilizacije u različitim tipovima zemljišta i širokom opsegu pH vrednosti Efikasnost je ispitana na vegetacionom ogledu sa biljkama kukuruza u polukontrolisanim uslovima , na tipu zemljišta, distrični kambisol. Rezultati ukazuju da dodavanje modifikovanog zeolita i pepela koštica višnji, prirodnom fosfatu, doprinosi rastu, razvoju i povečanju prinosa ispitivane kulture. Otpušteni fosfatni joni imali su dvostruku ulogu kao donor hranljivih materija i remedijacioni agens mehanizmom fosfatno -indukovane stabilizacije teških metala. Rezultati ukazuju da kompozit NH_4^+ - zeolit/prirodni fosfat ima multifunkcionalna svojstva pogodna za u održivoj poljoprivredi.

Ključne reči: *modifikovan zeolite, sirovi fosfat, pepeo koštica višnji, prirodna djubriva, remedijacioni agens*

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