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## TO WHAT EXTENT DO SOFT MECHANICAL ACTIVATION AND PROCESS PARAMETERS INCREASE THE EFFICIENCY OF DIFFERENT ZEOLITE/PHOSPHATE ROCK FERTILIZER MIXTURES?

### Article Highlights

- Effect of mechanical activation on different exchange-fertilizer mixtures was investigated
- Substantially increased P content than that of the similar non-activated mixtures was observed
- Influence of different process parameters was explored using multivariate statistics
- The results confirmed a high fertilization potential of the selected mechanically activated substrates

### Abstract

*In order to obtain effective mineral fertilizer, different mixtures of phosphate rock (PR) with natural clinoptilolite (Cp) and NH<sub>4</sub><sup>+</sup> saturated clinoptilolite (NH<sub>4</sub>-Cp) were subjected to soft mechanical activation. Mean concentrations of P released from mechanically activated (MA) substrates, MACp/PR and MANH<sub>4</sub>-Cp/PR, ranged between 2.81–3.19 mg L<sup>-1</sup> and 2.02–7.74 mg L<sup>-1</sup>, respectively. These are 10 to 15 times higher P concentrations than those released from the corresponding non-activated mixtures. Solution Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> concentrations varied according to the composition of the mixtures and the contact time between the two minerals within their optimal values required for plant growth. The obtained results suggest that the efficiency of the NH<sub>4</sub>-Cp/PR mixtures can be significantly increased by the proposed mechanical activation. Influence of process parameters on the observed concentrations of nutrients was shown using multivariate statistics. The highest fertilization potential demonstrated MANH<sub>4</sub>-Cp/PR mixture with the largest NH<sub>4</sub>-Cp share and the longest proposed mixing time.*

*Keywords: exchange-fertilizer mixtures, phosphate rock, clinoptilolite, mechanical activation, multivariate analysis.*

Correct use of fertilizers and natural resources contributes to environmental sustainability. Inorganic fertilizers account for about 80% of all phosphate applications, of which more than 99% originate from the phosphate rock (PR) [1]. Traditional technologies for production of high soluble mineral fertilizers from natural PR include acid treatments causing environmental contamination and eutrophication [2]. To avoid

these issues, it is necessary to find new methods to obtain soluble fertilizers with less negative impact on the environment. The direct application of PR seems to be one of the effective strategies with lower energy usage and production costs. However, the low solubility, therefore the low attainability of nutrients for the plant growth, is the main disadvantage of the PR direct utilization [3,4]. One of the proposed approaches, in aim to increase dissolution of PR, is the application of combined zeolite/PR mixtures. The addition of natural zeolites to the PR, usually clinoptilolite (Cp), improves the PRs agrochemical effect [5,6]. The high cation-exchange capacity, soil texture enrichment and water-retention ability are main features of zeolites,

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which determine their successful agricultural applications [7-11]. Characteristics of fertilizer mixtures could be further enhanced through modification of natural zeolites with nutrient elements such as  $\text{NH}_4^+$  [12-14]. Thus, the zeolites, beside the increase of the PR solubility can become a source of N,  $\text{Ca}^{2+}$  and  $\text{K}^+$  required for plant growth [6,14].

Another approach for increasing PR solubility is its mechanical activation that produces physical and chemical changes in close surface regions where mechanical energy leads to contact between the solids [15,16]. The extensive knowledge of solid-state mechanochemistry has been expanded with the observations of the influence of high pressure and shear on the rate of chemical solid-state reactions [16]. However, some authors note that the particle size reduction due to mechanical activation affects the PRs reactivity to a greater extent than the resulting deformations of its crystal structure [17]. Subsequently, it has been found that the efficiency of exchange-fertilizer mixtures may be further enhanced by their mechanical activation [18-22]. To what extent this procedure increases the efficiency of different zeolite/PR mixtures, so that its inclusion into the production process could be considered rational, was the subject of our survey. Therefore, the influence of soft mechanical activation on improvement of the PR dissolution in the presence of two types of clinoptilolites, natural (Cp) and partially  $\text{NH}_4^+$  saturated ( $\text{NH}_4\text{-Cp}$ ) was studied. The changes in mineralogical structure, and concentrations of plant available nutrients released from both MACp/PR and MANH<sub>4</sub>-Cp/PR mixtures, were investigated and compared with that of the corresponding non-activated mixtures. Differences in concentrations of the released nutrients and their dependencies on the process parameters between various MA-substrates were analyzed using multivariate statistical methods.

## EXPERIMENTAL

### Characterization of materials

Natural phosphate ore, PR, from deposit Lisina, near Bosilegrad in Serbia with average content of 9%  $\text{P}_2\text{O}_5$  and zeolite tuff (with >75% of clinoptilolite (Cp)) from deposit Baia Mare, Romania, were used for the preparation of the mixtures. Selected characteristics of the Cp and PR samples are presented elsewhere [6]. To obtain the  $\text{NH}_4$ -exchanged Cp, a partial saturation of the Cp with  $\text{NH}_4^+$  at 1:7.5 ratios was performed, according to the procedure described by Mihajlović *et al.* [23].

Powder X-ray diffraction (XRD) was used to determine the phase composition of the Cp/PR and  $\text{NH}_4\text{-Cp/PR}$  mixtures before and after mechanical activation. 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  $2\theta$  Bragg angle range from 5 to  $60^\circ$ , counting for 2 s (qualitative identification) at every  $0.02^\circ$  step. The divergence and receiving slits were fixed at 1 and 0.1 units, respectively. The XRD measurements were performed at room temperature in a stationary sample holder.

### Experimental procedure

Both groups of mixtures (Cp/PR and  $\text{NH}_4\text{-Cp/PR}$ ), in three replicates, were assembled in three ratios of Cp and the PR; 5:1 10:1 and 15:1. Each mixture originally contained 4 g of PR and the corresponding share of zeolite (20, 40 and 60 g, respectively). The mechanical activation of the mixtures was carried out in a vibrating ring-mill (KHD, Humboldt Wedag, AG). To avoid sticking, the period of mechanical activation was of 30 s per sample at room temperature. After mechanical activation, mixtures were placed in 300 ml volumetric flasks. Then, in each volumetric flask was added 200 ml of distilled water and mixtures were shaken on a rotary shaker for 24, 48 and 72 h at 220 rpm. In the resulting solutions, after draining, the concentrations of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  were determined using a Perkin Elmer AAS 703 atomic absorption spectrometer. The concentration of P from the solution was determined by colorimetry [24] using a Spekol 1300 UV-Vis spectrophotometer.

### Exploratory data analysis

Descriptive statistical analyses of the results were expressed as the mean  $\pm$  standard deviation (*SD*). Analysis of variance (ANOVA) and the following posthoc Tukey's HSD were performed to determine whether there are any significant differences between the average values of the released nutrients between the groups.

### Multivariate statistical analysis

Principal component analysis (PCA) as a multivariate analytical method was used to display the data in a multidimensional space, where the variables determine the axes [25]. These axes are projected into a few principal components (PCs), which are linear combinations of the original variables and define the maximum variation within the data. The first principal component (PC1) accounts for the largest

variance in the data set. The following principal components account for the maximum of the remaining variance in the data set. Each PC is characterized by 2-D scores plot maps, which shows a data overview and similarities or dissimilarities within the data. In this study PCA was employed to establish: *i*) the differences between nutrients release from the pure PR and mechanically activated substrates (MACp/PR and MANH<sub>4</sub>-Cp/PR mixtures) by calculating score plots and *ii*) the influence of process parameters (zeolite/PR ratio and the mixing time) on the content of nutrients (P, Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup>) in the solutions of both MA-mixtures by calculating correlation loading plots. All PCA calculations were carried out by PLS ToolBox, (Eigenvectors Inc., v. 7.9), for Matlab 7.12.0 (R2011a) and The Unscrambler (version 9.7, CAMO Process AS, Oslo, Norway). PCA was applied by using a 0.95 confidence level for Q and T2 Hotelling limits for outliers and a singular value decomposition algorithm (SVD). All data were auto scaled prior to any PCA analysis.

## RESULTS AND DISCUSSION

### Mineral characterization

The mineralogical compositions of Cp/PR and NH<sub>4</sub>-Cp/PR substrates (with highest zeolite share,

15:1) before and after mechanical treatment are shown in Figure 1. All mixtures irrespective of the composition were of similar mineralogical structure (for which XRD patterns for mixtures at 5:1 and 10:1 Cp/PR ratio are omitted) and contained Heu-type zeolite, quartz, plagioclase, muscovite, and apatite. The crystallinity degree of minerals between non-activated and MA samples remained unchanged. Also, systematic shifting of diffraction maximums of the dominant mineral in the mixture, Cp, was rather negligible. Crystallite size for Heu-type zeolite measured at (020) and (200) diffraction maximums were: Cp/PR for  $\langle D \rangle = 212 \text{ \AA}$ , MACp/PR for  $\langle D \rangle = 283 \text{ \AA}$ , NH<sub>4</sub>-Cp/PR for  $\langle D \rangle = 207 \text{ \AA}$  and MANH<sub>4</sub>-Cp/PR for  $\langle D \rangle = 227 \text{ \AA}$ . The observed differences were due to the presence of larger quantities of quartz and plagioclases in the Cp/PR and NH<sub>4</sub>Cp/PR, in relation to the corresponding MA-mixtures, respectively (Figure 1a and b).

### The influence of mechanical activation on nutrient release from the Cp/PR fertilizer mixtures

Solution P and Ca<sup>2+</sup> concentrations released from the MA-mixtures were compared with the concentration of the same elements leached from corresponding non-activated mixtures [6], subject to their composition and mixing time (Figure 2).

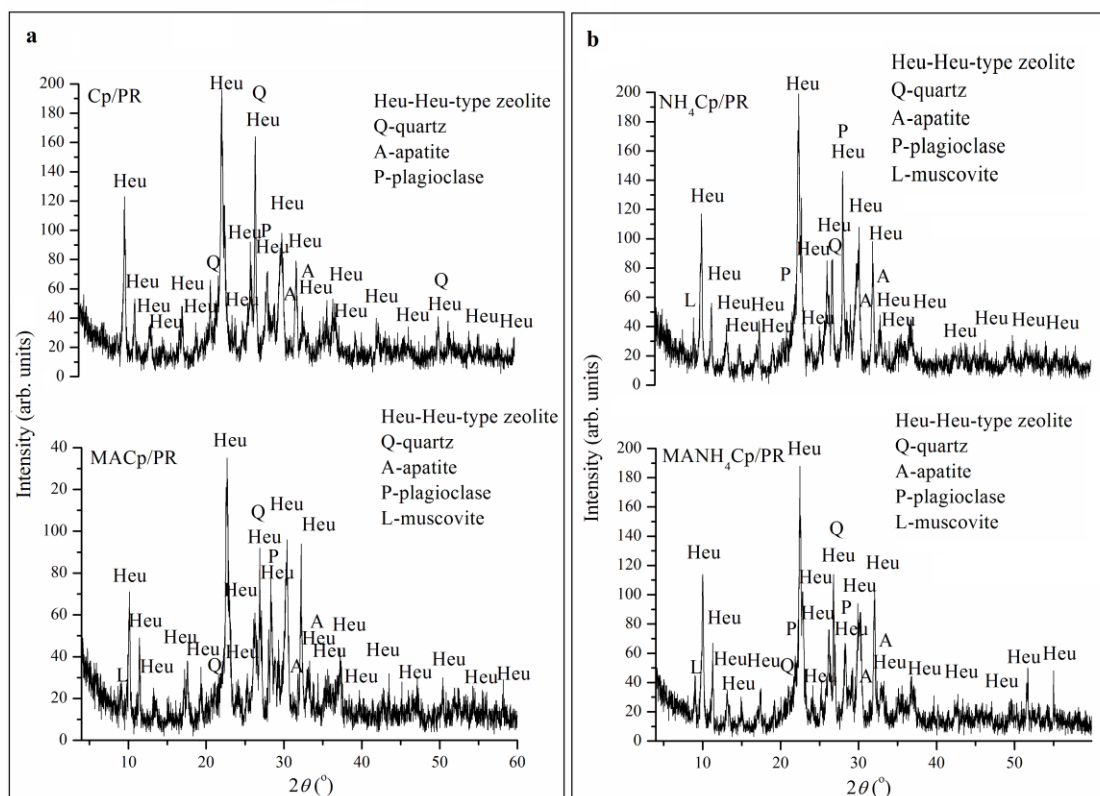


Figure 1. Diffractograms of Cp/PR and MACp/PR mixtures (a) and NH<sub>4</sub>-Cp/PR and MANH<sub>4</sub>-Cp/PR mixtures (b).

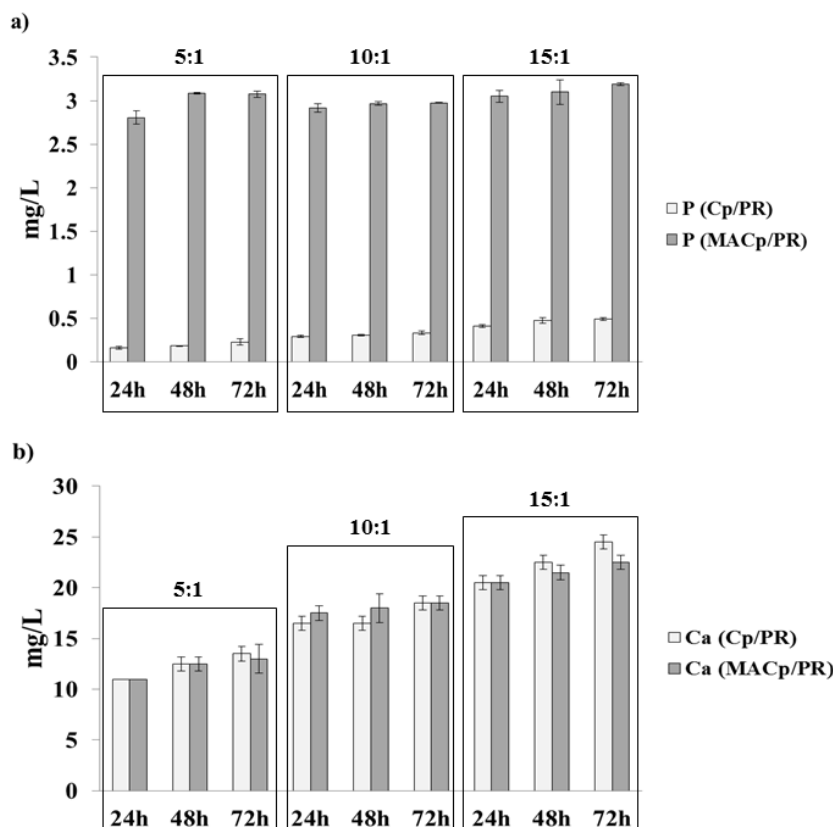


Figure 2. Mean solution P (a) and Ca<sup>2+</sup> (b) concentrations  $\pm$  SD of the Cp/PR [6] and MACp/PR mixtures.

The concentrations of P released from the MACp/PR mixtures ranged between 2.81 and 3.19 mg L<sup>-1</sup> (Figure 2a). This is on average fifteen times higher P concentration than those released from the corresponding non-activated mixtures (0.15 to 0.26 mg L<sup>-1</sup>) [6]. The observed increase in P concentrations due to soft mechanical activation of the mixtures was in accordance with the expected upward trend for P found in the literature [21]. Solution Ca<sup>2+</sup> concentrations gradually increased with the increase of the MACp/PR ratio and the mixing time and were between 11 and 22.5 mg L<sup>-1</sup>. However, Cp/PR and MACp/PR substrates had similar solution Ca<sup>2+</sup> concentration implying that mechanical activation did not affect the changes in solution Ca (Figure 2b).

Solution K<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> concentrations released from the MACp/PR and the comparable Cp/PR mixtures [6] are shown in Figure 3. The increase in MACp/PR ratio and contact time caused a slight increase of K<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> concentrations in the solution. Solution K<sup>+</sup> and Na<sup>+</sup> concentrations of the MACp/PR mixtures were between 5.66-7.99 mg L<sup>-1</sup> and 11.7-17.15 mg L<sup>-1</sup>, respectively. This is on average 30% lower than that of the corresponding non-activated mixtures. Petkova *et al.* [20] previously reported that tribochemical activation of the Cp/PR leads to decrease of the Cp ion-exchange ability whereas at the same time dissolution of the PR has been increased [20]. Solution Mg<sup>2+</sup> concentration of the activated mixtures ranged between 0.83-1.65 mg

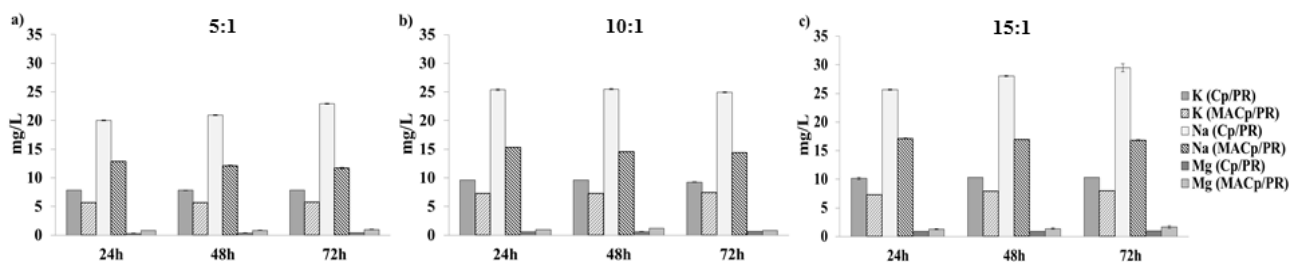


Figure 3. Mean solution K<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> concentrations  $\pm$  SD of the Cp/PR [6] and MACp/PR mixtures at a) 5:1, b) 10:1 and c) 15:1 zeolite/PR ratio.

L<sup>-1</sup> or around twofold higher in relation to the corresponding Cp/PR mixtures (Figure 3).

#### The influence of mechanical activation on nutrient release from the NH<sub>4</sub>-Cp/PR fertilizer mixtures

Solution P and Ca<sup>2+</sup> concentrations of the MANH<sub>4</sub>-Cp/PR mixtures were compared with the content of same nutrients leached from corresponding non-activated mixtures [6], subject to their composition and the mixing time (Figure 4).

The mean concentrations of P released from the MANH<sub>4</sub>-Cp/PR mixtures were between 2.02 and 7.74 mg L<sup>-1</sup>, which is ten times higher than those released from the corresponding non-activated mixtures (0.36–0.82 mg L<sup>-1</sup>) [6]. Similarly, 10–15 times higher extraction of P to the acid media from the MA-phosphorite has been reported previously [21]. Figure 4a shows that in addition to mechanical activation, an increase of the content of partially saturated NH<sub>4</sub>-zeolite in the mixture and duration of contact between the two minerals significantly contributes the solubility of the PR.

Solution Ca<sup>2+</sup> concentrations released from the MANH<sub>4</sub>-Cp/PR mixtures varied between 445 and 510.5 mg L<sup>-1</sup>. The differences between dissolved Ca from the NH<sub>4</sub>-Cp/PR and MANH<sub>4</sub>-Cp/PR were most evident at 5:1 zeolite/PR ratio (Figure 4b). At higher zeolite/PR ratios, the content of Ca in the solutions

was in favor of the non-activated mixtures. Furthermore, the Ca<sup>2+</sup> concentration slightly decreased with the increase of mixing time and Cp/PR ratio, similar to the non-activated mixtures previously reported by Mihajlovic *et al.* [6]. These results support the conclusions from the literature that the released Ca<sup>2+</sup> from the PR, compelled by cation exchange with NH<sub>4</sub><sup>+</sup>, was partially withdrawn by the zeolite before equilibrium [20,26].

Solution K<sup>+</sup> and Na<sup>+</sup> concentrations of the MANH<sub>4</sub>-Cp/PR mixtures ranged from 40 to 59.4 mg L<sup>-1</sup> and from 7.14 to 15.45 mg L<sup>-1</sup>, respectively (Figure 5). The content of both elements in the solution slightly increased with the Cp/PR ratio increase, but ranged around similar values in relation to the mixing time. Nevertheless, in comparison to the non-activated mixtures, the K<sup>+</sup> and Na<sup>+</sup> concentrations in MA-fertilizers with saturated zeolite were increased by 30 and 50%, respectively. This supports the utilization of soft mechanical activation, aiming to increase the leaching of K from the tested fertilizer mixtures. Solution Mg<sup>2+</sup> concentrations in the MANH<sub>4</sub>-Cp/PR substrates proportionally increased with increasing of zeolite share in the mixtures and the mixing time, and ranged between 20 and 54.5 mg L<sup>-1</sup>, very much alike to that of the corresponding non-activated mixtures [6].

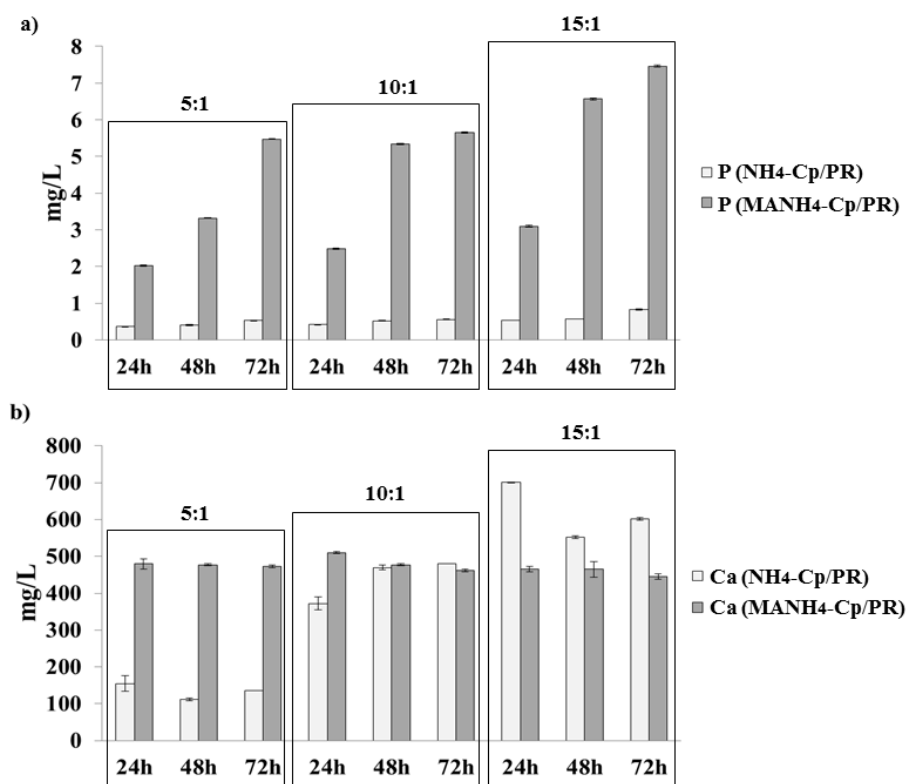


Figure 4. Mean solution P (a) and Ca<sup>2+</sup> (b) concentrations  $\pm$  SD of the NH<sub>4</sub>-Cp/PR [6] and MANH<sub>4</sub>-Cp/PR mixtures.

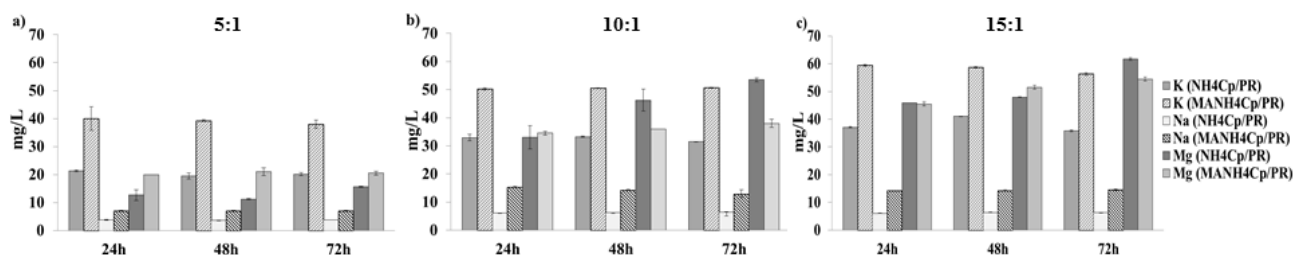


Figure 5. Mean solution  $K^+$ ,  $Na^+$  and  $Mg^{2+}$  concentrations  $\pm$  SD of the  $NH_4$ -Cp/PR [6] and  $MANH_4$ -Cp/PR mixtures at a) 5:1, b) 10:1 and c) 15:1 zeolite/PR ratio.

## ANOVA

One-way ANOVA was applied to compare the means between the concentrations of nutrients released from the MACp/PR and the  $MANH_4$ -Cp/PR mixtures of different composition at various mixing times (Tables 1 and 2). Statistical differences were determined at the  $p < 0.05$  level, 95% confidence limit, according to Tukey's HSD test.

Calculated one-way Fisher's statistic critical value was  $F_{crit} = 5.14$  and Tukey's HSD post hoc critical value was 4.34 for each element in both group of mixtures. These values numerically define the levels of significant differences in nutrient content, released from the various mixtures according to their composition and mixing time. If the obtained statistical value,  $F$  and/or Tukey HSD value (between labeled groups) for each element is larger than its critical value, the differences in concentrations of the released nutrient from the compared groups of mixtures are significant at 0.05 levels.

Conversely to solution P concentrations, the differences between solution  $Ca^{2+}$ ,  $K^+$ ,  $Mg^{2+}$  and  $Na^+$  concentrations released from the MACp/PR sub-

strates, were found to be significant in relation to the composition of the mixtures (Table 1). Regarding the calculated Tukey HSD values from Table 1, the concentrations of  $K^+$  released from the MACp/PR mixture at 5:1 ratio and  $Mg^{2+}$  released from the MACp/PR mixture at 15:1 ratio, were found to be significantly different in comparison to the other two groups. The effect of mixing time did not affect the occurrence of significant differences between solution concentrations of the elements within the groups (Table 1).

Significant differences in relation to the mixture composition were also found for  $K^+$  and  $Mg^{2+}$  released from MA-substrates with saturated Cp, while the concentrations of  $Na^+$  released from the mixtures with lowest  $NH_4^+$ -Cp share were significantly different in comparison to the other two groups. Differences in composition of the mixtures did not significantly affect solution  $Ca^{2+}$  and P concentration, while the effect of mixing time in the  $MANH_4$ -Cp/PR mixtures was significant at the  $p < 0.05$  level only for P (Table 2).

Table 1. ANOVA of the MACp/PR mixtures;  $F$  - one way Fisher's statistic test;  $p$ -value - function of the observed sample results; HSD - Tukey's post hoc test

Parameter	P ratio	Ca ratio	K ratio	Na ratio	Mg ratio	Parameter	P time	Ca time	K time	Na time	Mg time
$F$	2.07	85.75	76.14	84.97	8.57	$F$	1.94	0.09	0.06	0.09	0.22
$p$ -Value	0.21	$3.86 \times 10^{-5}$	$5.45 \times 10^{-5}$	$3.97 \times 10^{-5}$	0.02	$p$ -Value	0.22	0.91	0.94	0.92	0.81
$HSD_{[15:1-10:1]}$	-	6.87	3.25	8.55	4.45	$HSD_{[72h-48h]}$	-	-	-	-	-
$HSD_{[15:1-5:1]}$	-	18.33	16.47	18.42	5.53	$HSD_{[72h-24h]}$	-	-	-	-	-
$HSD_{[10:1-5:1]}$	-	11.46	13.23	9.87	1.09	$HSD_{[48h-24h]}$	-	-	-	-	-

Table 2. ANOVA of the  $MANH_4$ -Cp/PR mixtures;  $F$  - one way Fisher's statistic test;  $p$ -value - function of the observed sample results; HSD - Tukey's post hoc test

Parameter	P ratio	Ca ratio	K ratio	Na ratio	Mg ratio	Parameter	P time	Ca time	K time	Na time	Mg time
$F$	0.88	2.03	222.12	99.67	83.27	$F$	7.53	1.82	0.02	0.02	0.06
$p$ -Value	0.46	0.21	$2.37 \times 10^{-6}$	$2.49 \times 10^{-5}$	$4.2 \times 10^{-5}$	$p$ -Value	0.02	0.24	0.98	0.98	0.94
$HSD_{[15:1-10:1]}$	-	-	11.904	0.32	8.72	$HSD_{[72h-48h]}$	1.64	-	-	-	-
$HSD_{[15:1-5:1]}$	-	-	29.62	17.45	18.25	$HSD_{[72h-24h]}$	5.36	-	-	-	-
$HSD_{[10:1-5:1]}$	-	-	17.71	17.13	9.53	$HSD_{[48h-24h]}$	3.72	-	-	-	-

### Principal component analysis

PCA was performed in order to explore the main variation patterns between the data for pure PR, MACp/PR and MANH<sub>4</sub>-Cp/PR mixtures in relation to the different process parameters (Figure 6). The PCA score plot with samples labeled in accordance to the zeolite/PR ratio is presented in Figure 6a and the PCA score plot with samples labeled in accordance to mixing time is presented in Figure 6b. PCA resulted in a two-component model, which explains 93.27% of total variance. The first principal component, PC 1, accounted for 70.67% and the second one, PC 2, for 22.60% of the overall data variance. The addition of more PCs did not change the classification of the samples. Taking into account PC1 and PC2 score values, pure PR samples are grouped in the lower-left part of the PCA score plot, MACp/PR samples in the upper-left and MANH<sub>4</sub>-Cp/PR are separated in the right part of the PCA score plots.

The zeolite share in the fertilizer mixtures caused greater clustering of different MACp/PR samples, visible along positive PC2 axis. However, the overall impact of the substrate composition is more evident in the case of the MANH<sub>4</sub>-Cp/PR mixtures with obvious greater separation of the samples along the first component.

Also, the highest zeolite share has the strongest influence on solution cation concentrations (Figure 6a).

The different mixing times better affected the separation of the MANH<sub>4</sub>-Cp/PR mixtures than of the MACp/PR and the PR alone which is visible along PC1 axis (Figure 6b). Furthermore, the influence of mixing time increases as the zeolite/PR ratio increases, implying that the strongest effect of mixing time is observed for the substrates with 15:1 zeolite/PR ratio. Contrary to this, the influence of the mixing time has a very weak effect on the MACp/PR substrates. This indicates that changes in process parameters had a greater impact on the release of nutrients from the MANH<sub>4</sub>-Cp/PR mixtures.

To obtain a better overview of the effects of zeolite/PR ratio in the mixtures and mixing time on solution cation concentrations, two additional principal component analyses were performed on the subsets of data: for MACp/PR and for MANH<sub>4</sub>-Cp/PR samples using correlation loading plots (Figure 6c and 6d).

From the correlation loading plot calculated for MACp/PR substrates, it can be observed that the highest zeolite/PR ratio exhibits the strongest influence on solution P, Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> concentrations. The P content in the solution correlates the best with MACp/PR ratio of 15:1.

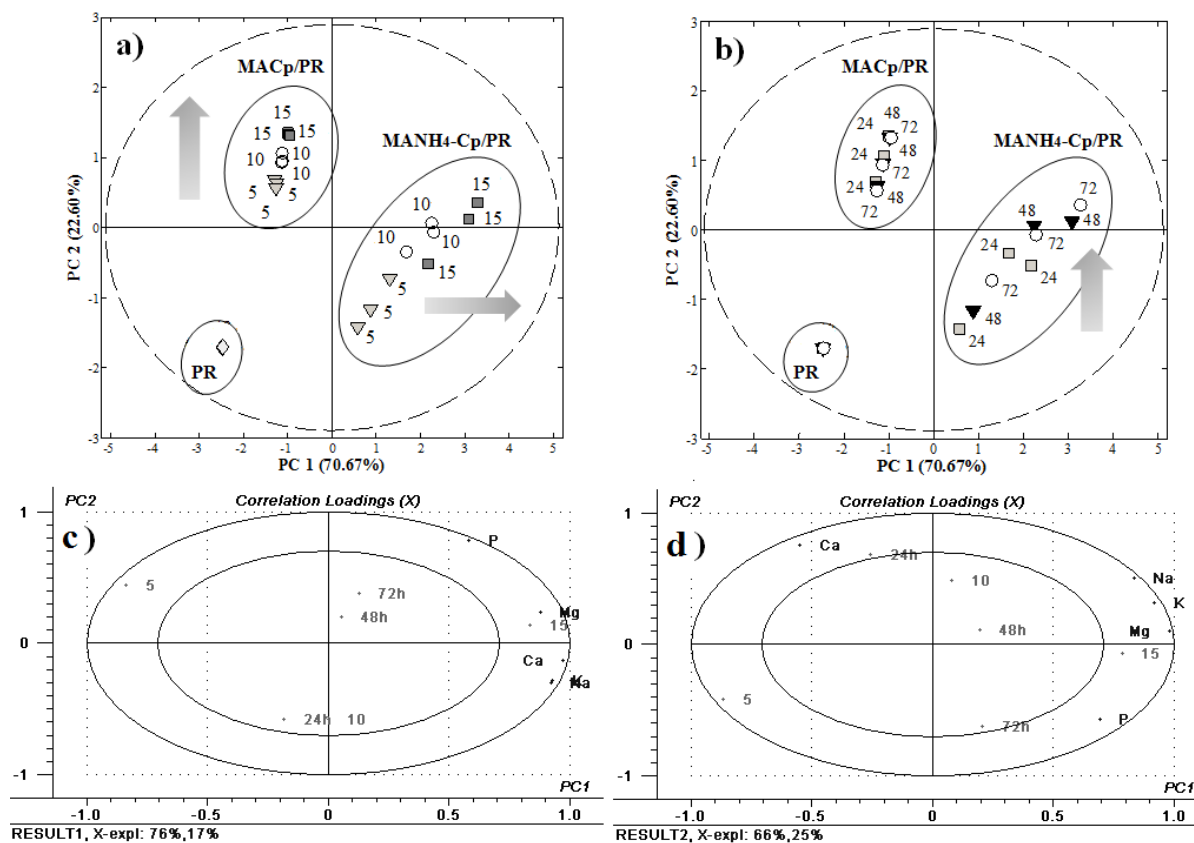


Figure 4. Mean solution P (a) and Ca<sup>2+</sup> (b) concentrations ± SD of the NH<sub>4</sub>-Cp/PR [6] and MANH<sub>4</sub>-Cp/PR mixtures.

The correlation loading plot calculated for MANH<sub>4</sub>-Cp/PR substrates shows that the highest zeolite/PR ratio exhibits the strongest influence on solution P, K<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> concentrations, while the Ca content was in best correlation with the lowest zeolite share in the mixture and the shortest mixing time. Also, Ca is highly negatively correlated with P. The best correlation between solutions P concentration, was found for 72 h mixing time and MANH<sub>4</sub>-Cp/PR ratio of 15:1.

## CONCLUSION

The obtained results showed that the use of soft mechanical activation of tested fertilizer mixtures followed by inducted particle size reduction, although did not produce significant structural changes in minerals, notably intensified the passage of nutrients to the liquid media, especially P. Solution P concentrations of both MA substrates were up to fifteen times higher than that of the corresponding non-activated mixtures, while the release of K<sup>+</sup> from the MANH<sub>4</sub>-Cp/PR mixtures was increased by a third. Furthermore, all concentrations of the nutrients released from the MANH<sub>4</sub>-Cp/PR substrates were within their optimal values necessary for plant growth [27,28]. Solution Ca<sup>2+</sup> concentrations were between 445 and 510.5 mg L<sup>-1</sup>, which suggests that the use of the MANH<sub>4</sub>-Cp/PR mixtures may resolve a potential deficiency of the Ca<sup>2+</sup> in the solution, very common for substrates of similar composition [6].

PCA revealed that the highest NH<sub>4</sub>-zeolite share in the mixture had the most positive impact on the PR dissolution. A growth of fertilization potential with time, particularly of the MANH<sub>4</sub>-Cp/PR mixtures, was observed. This supports the use of the selected MANH<sub>4</sub>-Cp/PR mixture as a slow-release fertilizer, very favorable for plants since fertilization can be performed less frequently, which, besides the efficiency, increases the cost-effectiveness of its utilization.

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NAUČNI RAD

## U KOJOJ MERI BLAGA MEHANIČKA AKTIVACIJA I PROCESNI PARAMETRI POVEĆAVAJU EFIKASNOST RAZLIČITIH ZEOLIT/RUDA FOSFORA SMEŠA PRIRODNIH ĐUBRIVA?

*U cilju dobijanja efikasnog mineralnog đubriva, različite smeše rude fosfora (PR) sa prirodnim klinoptilolitom (Cp) i NH<sub>4</sub><sup>+</sup>-klinoptilolitom (NH<sub>4</sub>-Cp) podvrgnute su blagoj mehaničkoj aktivaciji. Srednje koncentracije P otpuštene iz mehanički aktiviranih (MA) smeša, MACp /PR i MANH<sub>4</sub>-Cp/PR, varirale su u rasponu od 2,81-3,19 mg L<sup>-1</sup> i 2,02-7,74 mg L<sup>-1</sup>, redom. Ovo su 10 do 15 puta veće koncentracije P od onih otpuštenih iz odgovarajućih neaktiviranih smeša. Koncentracije Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> i Mg<sup>2+</sup> u rastvorima smeša varirale su u zavisnosti od sastava smeše i vremena kontakta dva minerala, a u okviru njihovih optimalnih vrednosti potrebnih za rast i razvoj biljaka. Dobijeni rezultati pokazuju da se efikasnost NH<sub>4</sub>-Cp/PR smeše može značajno povećati predloženim postupkom mehaničke aktivacije. Uticaj procesnih parametara na sadržaj posmatranih nutrijenata prikazan je upotrebom multivarijantne statističke analize. Najveći potencijal đubrenja pokazala je MANH<sub>4</sub>-Cp/PR smeša sa najvećim udelom zeolita i najdužim predloženim vremenom mešanja.*

*Ključne reči: smeše đubriva, ruda fosfora, klinoptilolit, mehanička aktivacija, multivarijantna analiza.*