SORPTION ABILITY OF SOIL IMPROVERS BASED ON SAPROPEL AND BIOCHAR TO MINERAL FERTILIZER NUTRIENTS

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Abstract: The aim of this study was to determine the ability of soil improvers based on sapropel and biochar to adsorb macronutrients of mineral fertilizer. The composition of soil improvers varied in the volume ratio of sapropel and biochar. Sequential three-stage irrigation of various mixtures of sand and soil improvers after the application of mineral fertilizer was carried out using the column system. The content of mineral nitrogen, phosphorus and potassium in the filtrate and the initial mixtures was analyzed. The data on the dynamics of leaching out of ammonium and nitrate nitrogen from different mixtures (sand + soil amendment + mineral fertilizer) indicated that the most intensive leaching of NO₃⁻N and NH₄⁺-N occurred after the first irrigation. Increasing of sapropel content in the composition of soil improvers was correlated with the resistance to leaching out of mineral nitrogen from mixtures after irrigation. The ability of soil improvers to fix phosphorus increased in mixtures with the highest input of sapropel. Intensive leaching of potassium from soil improvers under irrigation was observed. Soil improvers with content of 90% of sapropel and 10% of biochar in case of its application into the sand in ratio 4:1 had the best sorption characteristic.

1. Introduction
The requirements of environmental safety and economic efficiency of agricultural technologies require attentive attitude toward plant nutrition elements. International Code of Conduct for the Sustainable Use and Management of Fertilizers that was endorsed by member countries of Food and Agriculture Organization of the United Nations declares the importance of minimizing the nutrient losses from fertilizers, both in terms of improving the efficiency of fertilizer use and in terms of preventing environmental pollution and human health hazards.

Production of slow-release fertilizer capable of sustained release of nutrients into the soil is of great importance. The use of such fertilizer can reduce the level of pollution by biogenic elements of ground- and surface water in areas with intensive agriculture [1, 2]. One of the known ways to ensure the effect of the slow-release fertilizer is to use a carrier of nutrients (substrates) [3]. The capillary-
porous structure and the presence of functional groups of different nature make sapropels and biochar a promising raw material for getting such carriers.

The interest in using sapropel as soil improvers is due to unique ion-exchange, sorption properties and natural origin [4]. Sapropel is characterized as a multicomponent biogenic system, in the organic part of which cellulose, lignin and humic acids prevail. The specific surface area of solid organic sapropel reaches 150-190 m²/g [5]. A study of the pore structure of sapropel showed that sapropel are macroporous substrates [6]. In the article by Platonova & Adeeva [7] it was proposed the obtaining of a sorbent based on sapropel, by modifying the carbide mineral part of the sapropel with humic acids.

Biochar is produced by the thermal decomposition of biomass at 350–700°C under oxygen-limiting conditions [8]. Biochar is known to improve chemical, physical, and biological properties of soil contributing to reduced soil density, higher soil organic carbon and moisture and reduced leaching of plant nutrients [9]. There is numerous data in the literature on the ability of biochar to absorb various ions from solution by complexation, as well as due to electrostatic and capillary forces [10]. Biochar due to high porosity and high surface area can be used as a sorbent of organic and inorganic contaminants. The ability of biochar-amended soils to adsorb of per- and polyfluoroalkyl substances [11], oxyfluorfen [12], waste hydrocarbons [13], heavy metals [14, 15], herbicides [16] and 137Cs [17] was reported.

The study of sorption properties of various natural materials will contribute to the theoretical and experimental substantiation for production of environmentally friendly soil improvers of increased efficiency. Therefore, the aim of the study was to determine the sorption ability of soil improvers based on sapropel and biochar towards mineral forms of nitrogen, phosphorus and potassium.

2. Materials and Methods

Research of the sorption ability of different soil improvers (SI) towards macronutrients of mineral fertilizers was performed under laboratory experiment using column system [18]. Model experiment was carried out according to the following scheme: 1. Sand (control); 2. Sand 80 % + 20 % SI-1 + NPK; 3. Sand 60 % + 40 % SI-1 + NPK; 4. Sand 80 % + 20 % SI-2 + NPK; 5. Sand 60 % + 40 % SI-2 + NPK; 6. Sand 80 % + 20 % SI-3 + NPK; 7. Sand 60 % + 40 % SI-3 + NPK.

The composition of soil improvers (in volume percent) is as follows: 1) SI-1 = 70% sapropel + 30% biochar; 2) SI-2 = 80% sapropel + 20% biochar; 3) SI-3 = 90% sapropel + 10% biochar. One ton of wet sapropel contains 4.2 kg of total nitrogen, 0.2 kg of total phosphorus (10% is in available form), 0.2 kg of total potassium (10% is in exchangeable form); pH value is 5.4. The volumetric weight of the sapropel is 622 kg/m³. One ton of biochar contains 4.4 kg of nitrogen, 2.9 kg of phosphorus (9% is in available form) and 3.9 kg of potassium (51% is in exchangeable form). Biochar has a high pH value - 9.3. The volumetric weight of biochar is 364 kg/m³. Sand had mineral nitrogen content 81 mg/kg, phosphorus 179 mg/kg and potassium 353 mg/kg. One gram of water-soluble mineral fertilizer with an NPK ratio of 20:10:10 was added to each mixture.

According to the scheme of the experiment 250 dm³ of mixtures were placed in glass tubes with a diameter of 4 cm and a height of 50 cm and moistened to the lowest moisture capacity (20 %). Then, a three stage irrigation of the mixtures with distilled water of 400 ml was carried out for three days at a temperature of 22°C. Repetition of the experiment was three times.

Samples of mixtures and filtrates were analyzed according to the following indicators: ammonia nitrogen (NH₄–N) on FOSS Tecator AN 5232 and nitrate nitrogen (NO₃–N) on FOSS Tecator AN 5226, phosphorus and potassium by ICP-OES after pressure digestion. Statistical processing of research results (analysis of variance) was carried out using Statistica software.

3. Results and Discussion

The sorption ability of soil improvers in relation to the mineral forms of nitrogen, phosphorus and potassium was established (Table 1). The distribution of mineral nitrogen (NO₃–N + NH₄–N) between the filtrate and the initial mixtures after irrigation, indicated that SI-3 had the highest sorption capacity in relation to mineral forms of nitrogen, in which sapropel content was the highest. The high content
of sapropel (90%) in the soil improvers created the most favorable conditions for the sorption of mineral nitrogen from chemical fertilizer under irrigation. It should be noted that an increase of soil improvers: sand ratio has no significant effect on the fixation of mineral nitrogen in the mixture.

In studies [16, 19] it was established that the intensity of nutrients adsorption by biochar directly depends on the degree of saturation of a solution, and the maximum adsorption of an element by biochar is observed at the lowest concentration of an element in a solution. An increase in the percentage of biochar in the composition of soil improvers led to a higher content of macronutrients in the filtrate, which could be explained by the additional supply of macronutrients to the filtrate from biochar after irrigation. These findings are comparable with studies [20].

| Variant | Mineral nitrogen content | Phosphorus content | Potassium content |
|---------|-------------------------|--------------------|------------------|
|         | 1 [Mg/kg] | 2 [Mg/L] | 1 [Mg/kg] | 2 [Mg/L] | 1 [Mg/kg] | 2 [Mg/L] |
| Sand (control) | 19±2.2 | 342±8.1 | 205±7.2 | 35.2±1.1 | 355±11.2 | 162±4.4 |
| Sand 80 % + 20 % SI-1 + NPK | 854±38 | 470±12 | 305±8 | 1.6±0.02 | 485±12 | 505±11 |
| Sand 60 % + 40 % SI-1 + NPK | 1360±29 | 556±19 | 178±4 | 1.4±0.03 | 271±9 | 633±18 |
| Sand 80 % + 20 % SI-2 + NPK | 825±32 | 466±18 | 292±12 | 3.4±0.03 | 416±13 | 335±11 |
| Sand 60 % + 40 % SI-2 + NPK | 1168±52 | 490±22 | 284±13 | 4.0±0.04 | 387±13 | 481±15 |
| Sand 80 % + 20 % SI-3 + NPK | 1030±24 | 287±6 | 346±10 | 1.5±0.02 | 488±14 | 160±7 |
| Sand 60 % + 40 % SI-3 + NPK | 1196±49 | 480±20 | 239±8 | 1.1±0.04 | 334±7 | 264±6 |

Note: 1 - content in mixtures after application of mineral fertilizers and irrigation; 2 - content in filtrate after irrigation of mixtures with mineral fertilizers.

The ability of the soil improvers to fix phosphates depends on the content of various ions, on the composition of clay and organic fractions, and strongly on pH value. SI-3 (90% sapropel + 10% biochar) in case of application into sand in 4:1 ratio had the greatest effect on increasing the sorption properties of the mixture. The process of transition of phosphates to non-digestible forms occurs quickly in mixtures with low pH value and the medium content of mobile forms of iron [21]. An increase in the sorption of phosphorus occurs due to a decrease pH value of the mixture with an increasing percentage of sapropel in its composition.

Intensive leaching of potassium from the soil improvers themselves based on sapropels and biochar was observed due to their physicochemical properties. Potassium is fixed as a non-exchangeable K entering the crystal lattice of minerals. Under certain conditions, organic compounds glue together ground minerals and pack potassium in the crystal lattice. The high content of exchangeable potassium in the filtrates after irrigation of sand+soil improvers mixtures compared to sand, is primarily due to the presence of biochar, since it contains more exchangeable potassium than sapropel.

The data on the content of mineral forms of nitrogen in the filtrates after three irrigations of the studied mixtures of sand and soil improvers indicated that the most intensive leaching of NO₃⁻N and NH₄⁺-N occurred after the first irrigation (Table 2).

With an increase in soil improvers: sand ratio more intensive leaching of ammonium and nitrate nitrogen after irrigation was observed, which was connected with a higher initial content of these compounds in mixtures compared to sand. The lowest leaching of both ammonium and nitrate nitrogen during the first irrigation was recorded for a mixture of sand 80% + 20% SI-3. NO₃⁻N and
NH$_4$–N leaching from this mixture was by 20% and 40% lower compared with the control (sand without soil impropver), respectively.

Table 2. Dynamics of leaching out of ammonium and nitrate nitrogen from mixtures of sand and soil improvers

| Variant                  | 1 Filtrate | 2 Filtrate | 3 Filtrate |
|--------------------------|------------|------------|------------|
|                          | NO$_3$–N   | NO$_3$–N   | NO$_3$–N   |
| Sand (control)           | 166.2±8.2  | 158.7±7.2  | 1.4±0.3    |
| Sand 80 % + 20 % SI-1 + NPK | 176.7±6.1  | 131.8±4.2  | 20.7±0.5   |
| Sand 60 % + 40 % SI-1 + NPK | 202.3±7.4  | 208.7±8.4  | 28±1.0     |
| Sand 80 % + 20 % SI-2 + NPK | 189.8±4.8  | 92.4±4.6   | 74±1.5     |
| Sand 60 % + 40 % SI-2 + NPK | 168.3±4.6  | 129.6±6.7  | 94.1±3.5   |
| Sand 80 % + 20 % SI-3 + NPK | 131±5.6    | 97.2±4.7   | 22.6±0.3   |
| Sand 60 % + 40 % SI-3 + NPK | 238.1±11.0 | 146.8±5.7  | 28.5±0.5   |

The intensive leaching of phosphorus and potassium during the first irrigation of mixtures of sand and soil improvers was determined (Table 3). The use of soil improvers prevented the intensive leaching of phosphorus. The binding of water-soluble phosphorus with an absorbing complex of sapropel and biochar was observed as a result of converting it into sparingly soluble compounds under the influence of iron and calcium.

Table 3. Dynamics of leaching out of phosphorus and potassium from mixtures of sand and soil improvers

| Variant                  | 1 Filtrate | 2 Filtrate | 3 Filtrate |
|--------------------------|------------|------------|------------|
|                          | Phosphorus | Potassium  | Phosphorus | Potassium  | Phosphorus | Potassium  |
| Sand (control)           | 25.5±0.5   | 140.1±6.2  | 6.2±0.1    | 14.1±0.4   | 3.5±0.02   | 7.7±0.15   |
| Sand 80% + 20% SI-1 + NPK | 0.8±0.1    | 308.8±12.4 | 0.5±0.3    | 144.8±3.5  | 0.3±0.03   | 51.8±1.5   |
| Sand 60% + 40% SI-1 + NPK | 0.7±0.2    | 399.4±15.2 | 0.4±0.3    | 167.2±4.5  | 0.3±0.03   | 66.0±3.0   |
| Sand 80% + 20% SI-2 + NPK | 1.6±0.2    | 171.5±7.3  | 0.8±0.1    | 124.3±3.5  | 1.0±0.01   | 38.8±1.5   |
| Sand 60% + 40% SI-2 + NPK | 1.5±0.2    | 317.2±6.6  | 0.9±0.1    | 116.6±3.0  | 0.6±0.02   | 46.8±1.5   |
| Sand 80% + 20% SI-3 + NPK | 0.7±0.3    | 116.5±4.7  | 0.4±0.3    | 32.3±0.9   | 0.4±0.03   | 11.3±0.9   |
| Sand 60% + 40% SI-3 + NPK | 0.5±0.2    | 159.9±7.7  | 0.3±0.1    | 79.9±2.0   | 0.3±0.03   | 24.1±0.5   |

Statistically significant increase in potassium content in all filtrates after irrigation compared to the control was revealed. It indicated a significant mobility of potassium compounds in soil improvers. The high potassium content in the second and third filtrates of the mixtures compared to the control explained by leaching of the element from biochar.
An analysis of the content of macronutrients in studied mixtures after a three-stage irrigation indicated that the use of soil improvers based on sapropel and biochar decrease leaching of nitrogen and phosphorus from mineral fertilizers (Fig. 1). Regarding potassium, the studied soil improvers did not demonstrate sorption properties. That is because most of the potassium is in the liquid phase and it could be easily leached out.

4. Conclusions
Minimizing the loss of nutrients from the soil is of great importance to meet the agroecological and economic requirements of sustainable agriculture. Data on the content of macronutrients in different mixtures of sand and soil improvers based on sapropel and biochar with addition of mineral fertilizer after three-stage irrigation indicated that the highest sorption of mineral nitrogen, phosphorus and potassium of mineral fertilizers was in the mixture of sand and soil improvers in volume ratio of 4:1. It was found that application soil improvers 3 (90% sapropel + 10% biochar) promoted to fixing of ammonium and nitrate nitrogen and phosphorus of the mineral fertilizer in sand. After irrigation more than 75% of nitrogen, 99% of phosphorus and 75% of potassium applied with mineral fertilizer, remained in the mixture (sand 80% + 20% soil improver 3). The most intensive leaching of macronutrients from studied mixtures was observed during the first irrigation. Leaching of potassium of mineral fertilizers from all studied mixtures was observed compared with the control (sand), which determined the relevance of further studies on the development of potassium sorbents.

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