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Editors:
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COPPER SORPTION CAPACITY OF THE SOIL TREATED WITH UNCONVENTIONAL ALKALIZING AGENTS

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ABSTRACT – The influence of unconventional alkaline additives (ground seashells and bauxite residue) on the copper (Cu) sorption and retention capacity of acidic soil was investigated. The soil collected near the mining and metallurgical complex in Bor (Serbia) was treated with different doses of additives, and the Cu sorption and desorption were assessed in batch conditions. The waste-derived materials proved to be efficient and sustainable alternatives to conventional alkalizers, increasing the maximum sorption capacity for Cu in correspondence with the soil pH increase. Nevertheless, added Cu was largely mobilized by weak acid extraction, demonstrating the importance of maintaining optimal soil pH for Cu leaching prevention.

Keywords: Soil Management, Seashell Waste, Red Mud, Copper Sorption Capacity.

INTRODUCTION

Copper mining and metallurgy are important activities that cause significant damage to the environment and biota through the emission of waste gases and the inadequate disposal of waste enriched with metals [1]. The deposition of metals in soil is a long-term process that leads to the accumulation, but also to the transport and biotoxicity of their mobile and bioavailable chemical forms. In addition to heavy metals with no known biological significance, essential metals such as copper (Cu) can be found in the surrounding soils in concentrations with high toxic potential [2]. The quality of soil is further compromised by acidification from acid precipitation and leaching, which causes nutrient imbalance, reduced microbial community activity, and reduced soil's natural ability to retain heavy metals to which they are continuously exposed [3]. Agricultural land located close to industrial plants is a significant element of risk due to the bioaccumulation of elements in the food chain.

Treating soil with alkaline additives is one of the leading methods for improving pH to bring it into the optimal range, reducing the mobility and availability of toxic metals and mitigating environmental risks [4]. Due to the incentive policy of the circular economy, many alkaline waste materials and by-products are currently being considered for possible application in the soil to achieve multiple benefits [5,6].

As a producer of copper and precious metals with a tradition of more than a hundred years, the mining and metallurgical complex in Bor causes the greatest heavy

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metal pollution in Serbia, especially high concentrations of Cu in the surrounding soils and plant species [7].

In this study, the Cu sorption properties of acid soil sampled near the complex and soil samples treated with unconventional additives were investigated in batch sorption and desorption experiments. The objective was to determine and compare the influence of two waste materials (ground seashells and bauxite residue) and their dosage on the sorption and retention of Cu in the soil.

EXPERIMENTAL

The control soil (S) from Slatina village (Serbia) and the samples of soils treated with different doses of grounded seashell waste (SW: 0.15%, 0.3%, 2%, and 5%) and red mud (RM: 0.3%, 2%, and 5%) were prepared as previously described [8]. The sorption of Cu was examined by equilibrating the soil samples and $\text{Cu}(\text{NO}_3)_2$ solutions with increasing Cu concentrations (10^{-4} – $5 \cdot 10^{-3}$ mol/L). Working solutions were prepared in a background electrolyte (NaNO_3) with a concentration of 10^{-2} mol/L, and their initial pH was adjusted to 5.0. Suspensions with a soil/liquid ratio of 1g/10mL were agitated on an overhead laboratory shaker (10 rpm) at room temperature ($21 \pm 1^\circ\text{C}$) for 48 h to attain equilibrium. After phase separation by centrifugation and filtration, residual Cu concentrations and the concentrations of displaced Ca ions were measured (Inductively Coupled Plasma Optical Emission Spectroscopy, ICP-OES, Perkin Elmer Avio 200). The equilibrium solution pH values were measured by a WTW InoLab pH meter.

The dry solid residues from sorption experiments were exposed to the extraction with 0.11 mol/L acetic acid. The solid/solution ratio was 1g/40mL, and the extraction was performed during 16 h of agitation at room temperature to isolate the most mobile metal fraction (F1) of the sequential extraction scheme recommended by the European Community Bureau of Reference (BCR) [9]. The extracted Cu concentrations were measured in filtrates by ICP-OES.

RESULTS AND DISCUSSION

The pH of SW and RM samples (9.30 and 10.0, respectively) was markedly higher than the soil pH (4.93) [8]. Accordingly, the addition of SW and RM led to the soil pH increase and influenced other essential soil properties. The descriptive statistics of soil properties are presented in Table 1.

Table 1 Descriptive statistics of soil properties (n=8) [8]

Variable	Unit	Mean	Minimum	Maximum	StDev
pH	/	6.44	4.93	7.65	1.05
CaCO_3	%	1.181	0.000	6.090	2.159
Cation exchange capacity (CEC)	cmol _c /kg	11.82	11.40	12.20	0.34
N	%	0.171	0.164	0.177	0.005
C	%	1.669	1.460	2.280	0.273
Available P	mg P_2O_5 /100g	6.21	2.88	15.60	4.04
Available K	mg K_2O /100g	42.46	41.10	43.40	0.70
Electrical conductivity (EC)	dS/m	0.724	0.378	1.214	0.324

The sorption of Cu by tested soil samples is given in the form of isotherms (Figure 1) representing the relationships between equilibrium Cu concentrations in the liquid (C_e , mmol/L) and solid (Q_e , mmol/g) phase. The linear relationships almost parallel to the y-axis, obtained for soil samples SW2, SW5, and RM5, reflect their high affinity for Cu in the entire investigated concentration range, while the isotherms characteristic for samples S, RM0.3, RM2, SW0.15, and SW0.3 exhibit an "L" type shape, indicating gradual saturation of the soil. Compared to the control soil, all treatments stimulated increased Cu sorption. Experimentally obtained maximum sorption capacities ($Q_{max,sor}$) ranged from 0.040 mmol/g (control soil, S) to 0.053 mmol/g (SW2 and SW5) and followed the order: SW2=SW5>RM5>RM2>SW0.3>SW0.15>RM0.3>S.

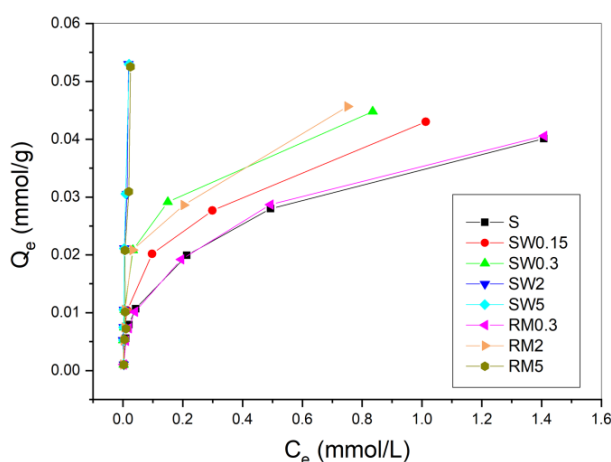


Figure 1 Cu sorption isotherms on the control and treated soil samples

As shown in Figure 2a, the pH values of the Cu solutions in equilibrium with treated soil samples were commonly higher compared to the control soil. The pH was influenced by both the type and quantity of additive so that the lowest values were obtained for the lowest doses of both additives, while at the same dose, higher values were obtained using SW compared to RM. Furthermore, with the increased amounts of Cu ions sorbed, the pH decreased in all investigated systems demonstrating that the specific Cu sorption takes place on protonated surface groups accompanied by the release of H^+ ions.

Figure 2b further discloses the linear relationships between the amounts of Cu ions sorbed and Ca ions released into the solution. After adding SW, the amount of displaced Ca is higher compared to the control soil and increases with the increase in the dose of SW, which is a consequence of its high calcium carbonate content (95.8%) [8]. On the other hand, even though the RM's high alkalinity and complex oxide composition [8] resulted in increased Cu sorption with the increase in RM dose, the amount of released Ca decreased and turned out to be lower compared to the amount displaced from the untreated soil. The results overall indicate different contributions of Cu-binding mechanisms, such as specific Cu sorption, ion exchange, and, possibly, precipitation, in soils treated with SW and RM.

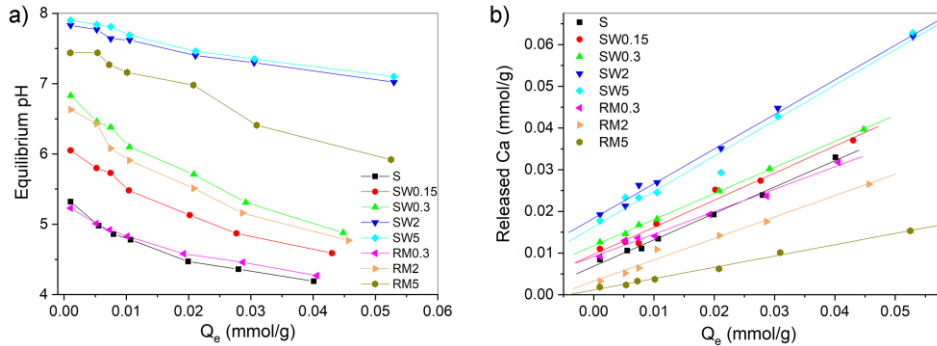


Figure 2 Relationships between the sorbed amounts of Cu and a) final pH values, b) displaced amounts of Ca

The isotherm sorption data (Figure 1) were fitted with the Freundlich linear equation:

$$\log Q_e = \log K_F + 1/n \log C_e \tag{1}$$

The calculated empirical constants K_F ((mmol/g)/(mmol/L)^{1/n}) and $1/n$, related to the capacity and affinity of the sorbent, are given in Table 2.

Table 2 Cu sorption parameters by soil samples calculated using the Freundlich model

Soil sample	K_F	$1/n$	R^2
S	0.036	0.393	1.00
SW0.15	0.044	0.351	0.99
SW0.3	0.053	0.323	0.98
SW2	0.233	0.471	0.82
SW5	1.828	0.872	0.96
RM0.3	0.037	0.414	1.00
RM2	0.055	0.362	0.96
RM5	1.803	0.892	0.88

Considering the coefficients of determination (R^2), good fitting with the Freundlich model ($0.96 < R^2 < 1.00$) was obtained for all Cu sorption isotherms except for samples SW2 and RM5 where more significant deviations ($R^2 = 0.82$ and 0.88 , respectively) result from almost complete Cu sorption in the entire tested range of concentrations. The K_F values increased with the application of SW and RM and reached the highest values when 5% of additives were applied.

Linear correlation analysis (Table 3) was used to examine the dependency of the Cu sorption parameters on essential properties of the soil, and the statistical importance of the correlation coefficients (r) was evaluated by calculating the Pearson correlation coefficients (p). The $Q_{max,sor}$ was significantly and positively correlated with soil pH, EC, and the Freundlich constant K_F . The pH values >6 specifically promote the increase in pH-dependent surface charge on Fe, Al, and Mn oxides, as well as the metal chelation

by organic matter, and metal-hydroxide precipitation, thus, stimulating several mechanisms of Cu binding [10].

Table 3 Coefficients of correlation (r) between Cu sorption/desorption parameters and soil properties

	CaCO ₃	CEC	N	C	Available P	Available K	pH	EC	$Q_{max,sor}$	K_F
$Q_{max,sor}$	0.649	-0.040	0.124	0.589	0.486	0.454	0.980**	0.932**		
K_F	0.568	0.108	-0.464	0.482	0.653	0.419	0.712*	0.710*	0.728*	
$Q_{max,des}$	0.569	-0.085	-0.213	0.455	0.576	0.128	0.813*	0.838**	0.856**	0.849**

Statistically significant at confidence levels of *95% ($p < 0.05$) and **99% ($p < 0.01$).

The relationships between the Cu quantities sorbed by the control and treated soil samples and the quantities extracted within the BCR1 fraction are displayed in Figure 3. In contrast to the Cu distribution pattern characteristic for the original soil [8], added Cu ions were present mainly in the weak acid soluble fraction.

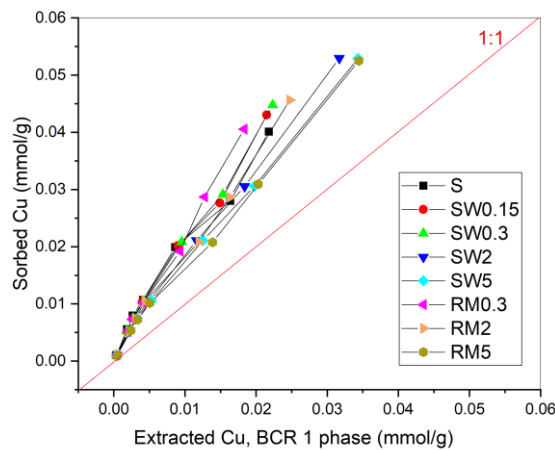


Figure 3 Relationships between sorbed and extracted Cu amounts

The experimentally obtained maximum desorbed quantities ($Q_{max,des}$) were significantly and positively correlated with soil pH and with the Cu sorption parameters $Q_{max,sor}$ and K_F (Table 3). These results confirm the association of recently added Cu with soil inorganic and organic constituents by cation exchange and specific sorption mechanism. Therefore, increasing migration risk through runoff and leaching arises under lower pH conditions.

CONCLUSION

The treatments with variable doses of SW and RM altered the Cu sorption and retention in the soil under the leading influence of soil pH. From both environmental and economic points of view, soil treatment with SW should be a more practical option due to the higher purity of the material and smaller doses for achieving the positive effects on soil pH and Cu sorption capacity. The soil amended with investigated

alternative alkalizers can prevent Cu migration; nevertheless, the long-term retention performance should be ensured by preventing re-acidification of the soil. Continuous monitoring of soil conditions is thus required for the assessment of risks and the necessity of periodic repetition of the treatment.

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