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Adsorption and Sequential Extraction of Copper in Technosols Prepared from Unconsolidated Mining Wastes Rich in Limestone, Bentonite, and Organic Matter

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Abstract: In this work the adsorption and immobilization of copper ions of four different Technosols constructed with wastes were tested. These soils were made from mixtures of limestone wastes, organic matter, sand, and bentonite. The methods used were “batch” and columns experiments, where the soils were in contact with a Copper (Cu) rich solution for 24 h and afterwards for 24-weeks. Total concentration of adsorbed Cu, sequential extraction in the Technosols and Cu concentration in the leachates were evaluated. The results showed that the Technosols have high efficiency to rapidly immobilize Cu ions, and the percentage of adsorption varied between 87 and 99% in the batch experiment after 24 h. The sequential extraction showed that the materials used in the construction of technosols demonstrated high affinity for the metal, especially the carbonates and organic matter, which adsorbed 14–16% and 10–16% respectively of total Cu added via solution. However, most of the adsorbed Cu was found in the residual fraction (50–64%), which represented the less labile form of Cu. These results demonstrate that in addition to adsorb great part of the Cu added via solution, the Technosols immobilize Cu in a highly stable form, representing a great option for the reclamation of contaminated-Cu areas. However, the decrease in pH with time (24 weeks) showed a strong influence on the adsorption of Cu in Technosols, influencing the amount of leached copper. We therefore recommend the design of Technosols with limestone wastes, bentonite, and organic matter with periodical control of pH for fast and efficient retention of Cu.

Keywords: soil contamination; ecological engineering; mining; clay; sustainability



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1. Introduction

Technosols are soils of anthropogenic origin comprising a new group of soils from the World Reference Base for Soil Resources—FAO, which combine “soils whose properties and pedogenesis are dominated by their technical origin and include among others, soils derived from wastes originated by human activities” [1]. These soils can be man-made or spontaneously developed from the mixture of several sort of wastes, tailings and residues, and can neutralize negative environmental impacts generated by human activities, such as metal contamination, while properly destining tailings and wastes, which represents great issues in mining sites around the world [2–7].

These soils can be designed to solve specific problems, such as mining areas with acid drainage or excess of metals in soil and/or water [8,9] and may; through biogeochemical interactions; minimize or eliminate the toxic effects of metals/acidity [6,10,11], while promote the recycling of essential nutrients and stabilization of organic matter, favoring the

recovery of the affected ecosystems and the development new agricultural areas [12–16]. Usually they have high ability to retain trace elements; however, its composition should be carefully studied, since they can also be sources of contamination depending on the materials used, jeopardizing the environmental quality of surround ecosystems [10,17].

Tailings and wastes from copper mines often have high levels of metals, especially Cu. This metal is known to form stable complexes with carbonates, iron oxides, clay minerals and organic matter [18,19]. Thus, using such materials to design Technosols can be a good option for remediation of copper by neutralizing its toxic effects, making it unavailable for uptake and thus decreasing the risks of contamination to the food chain [20,21].

Among the soil constituents, the organic matter has recognized affinity with Cu, by forming very stable organometallic complexes and decreasing copper mobility [22,23].

Another material that has great potential to immobilize copper in soil is the bentonite, which is a clay mineral of the montmorillonite group. The montmorillonite has excellent adsorption properties and possesses adsorption sites available within its interlayer space as well as on the outer surface and edges. Montmorillonite has a 2:1-layer structure, composed of two tetrahedral sheets of silicon ions surrounding a sandwiched octahedral sheet of aluminum ions [24–26]. Given its high cation exchange capacity—CEC, bentonite is widely used to study the adsorption of metals [27], and considering its relative low cost, this clay mineral has great potential to be used in the composition of Technosols.

Carbonates have also recognized affinity with Cu, and the addition of this material into soil tends to reduce the metal mobility. There are two main mechanisms in which carbonates can reduce the mobility of Cu in soils. The first is the increase in pH, which decreases the mobility of Cu due to the increase of negative charges on soil colloids. The other is the high capacity of Cu sorption, which usually is retained by precipitation [13,18,20,21].

Thus, the aim of this study was to construct four types of Technosols with different types and proportion of mining wastes and residues, to evaluate the ability of these soils to adsorb and immobilize Cu. For this, column and a batch experiments were conducted. The total concentration of adsorbed and leached Cu was analyzed in the column experiment, and a sequential extraction was performed in the Technosol mixtures after the batch experiment.

2. Material and Methods

2.1. Composition of Technosols

Four Technosols were prepared with three different types of wastes (limestone wastes, organic compost, and bentonite). We used waste rock from dolomitic limestone mining from the region of Saltinho/SP, Brazil. The limestone occurs in layers intercalated with black shales from the Irati Formation, beneath a layer of gray siltstones from the Corumbataí Formation [28]. The mine waste thus comprised of fragments of black shales siltstones, which had no economic interest.

The organic compost used was prepared from trees pruning, crop residues, parks maintenance residues and manure. Usually, they are used later by the city of Piracicaba (Brazil) itself to fertilize green areas. However, due to the large volume generated, much of the compost is not used and is discarded in landfills. These organic materials were selected, since they have high affinity and high capacity to retain copper [29,30], in addition to improving soil quality.

The used bentonite was a residue from a mine at Pernambuco state (Brazil), and it was rich in Fe^{3+} and interlayer cations such as Na^+ , K^+ and Ca^{2+} , and was selected due to its high cation exchange capacity (CEC), which would increase the sorption capacity for Cu^{2+} [31]. Considering the high expansion capacity of bentonite, sand was added to the mixture in bentonite: sand ratio of 1:4 to facilitate aeration and drainage of the solution.

The components were oven dried at 45 °C, sieved to <2 mm and then mixed. The proportions by volume of the mixtures that formed the Technosols is in the Table 1.

Table 1. Material (wastes) and its proportions used to form the Technosols.

Wastes	Technosol A	Technosol B	Technosol C	Technosol D
		%		
Limestone waste rock	33.3	50.0	25.0	25.0
Organic Compost	33.3	25.0	50.0	25.0
Bentonite + Sand (4:1)	33.3	25.0	25.0	50.0

2.2. “Batch” Experiment

After mixing and homogenization of Technosols, 2 g of each soil was placed in polyethylene centrifuge tubes and added 30 mL of a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, containing known concentration of 500 mg Cu/L. The pH was adjusted to 4.2 to render Cu soluble, according to calculations using the software Visual MINTEQ [32]. The tubes were shaken on a rolling table at 180 rpm for 24 h. The material was centrifuged at 3000 rpm for 15 min and filtered. The supernatant was collected, acidified, and refrigerated ($\leq 6^\circ\text{C}$) until analysis.

After filtering, 1 g of residual soil was collected for sequential extraction analysis. The sequential extraction used an adapted methodology described in Perlatti et al. [18], allowing differentiation into 7 fractions:

- F1—Exchangeable Cu—extracted with 8 mL of MgCl_2 1 M, at pH 7.0, with shaking for 1 h at room temperature. In this and the following steps, the extract was centrifuged at 3000 rpm for 15 min and filtered;
- F2—Cu associated with carbonates—extracted with 30 mL of a solution of 1 M NaOAc at pH 5.0, with 5 h of shaking at room temperature;
- F3—Cu associated with organic matter—extracted with 10 mL of 6% NaOCl, at pH 8.0, and shaking for 6 h at 25°C . This procedure was repeated three times;
- F4—Cu associated with amorphous iron oxides—extracted with 30 mL of oxalic acid 0.2 M + ammonium oxalate 0.2 M, at pH 3, with shaking for 2 h in the dark;
- F5—Cu associated with crystalline iron oxides—extracted with a solution of 0.25 M sodium citrate + 0.11 M sodium bicarbonate + sodium dithionite (3 g), shaking for 30 min at 75°C ;
- F6—Cu associated with sulfides—extracted with 4 M HNO_3 in a water bath for 16 h at 80°C , with occasional shaking;
- F7—Residual—calculated by subtracting the total amount of Cu added via solution (500 ppm) by the values obtained in the previous 6 fractions + Cu content obtained in the supernatant.

Between each extraction step, the residual soil was washed with ± 20 mL of ultrapure water, stirred manually, and centrifuged at 3000 rpm for 15 min. All samples were analyzed in triplicate. The sequential extraction of all Technosols before the Cu solution addition was also performed in triplicate, to obtain the original values of Cu in the mixtures. These amounts were deducted when calculating the Cu concentration adsorbed by Technosols.

2.3. Column Experiment

The leaching column experiment was prepared with transparent polypropylene medical burettes (100 mL) connected through a silicon tube to an empty PVC infusion bag at the top, and with another silicon tube to a 100 mL plastic bottle at the bottom. The bag was used to add a copper solution and the bottle to collect the leachates. The burette was filled with 80 mL of each Technosols (in triplicate). The opening of the bottle was sealed with plastic film to avoid external contamination and internally lined with a geotextile blanket, with grammage < 2 mm, to avoid the loss of solid material.

A solution containing 1000 mg Cu/L was prepared with reagent grade of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to artificially pollute the Technosols. The pH was also adjusted to 4.2 to avoid Cu precipitation from the solution [32]. A volume of 80 mL of this solution was added to each infusion bag every 5 days, for 24 times. Slowly the solution dripped in the top of the burette with Technosols percolating along all the material until it was collected and stored.

The leachates were collected in the bottles weekly, transferred to tubes, acidified, and refrigerated (≤ 6 °C) until analyses.

2.4. Analytical Procedures

The copper concentration in the solution of each fraction of the Technosols in the “batch” experiment, as well as in the leachates in the column experiment were determined by atomic absorption spectrometry, AAS (AANALYST 400, PerkinElmer, Waltham, MA, USA). The pH was also measured in the leachates with a pH-meter by potentiometry with glass electrode.

2.5. Statistical Analysis

Differences between Technosols and leachates ($n = 3$) were established by one-way ANOVA followed by a Tukey test, or Kruskal–Wallis One Way Analysis of Variance on Ranks for non-normally distributed data with the Minitab statistical package, version 16.2.4 (Minitab Inc, State College, PA, USA). Pearson’s correlation coefficient was used to evaluate the relationships between pH values and leached Cu concentrations.

3. Results and Discussion

3.1. Total Concentration of Cu in Technosols in the Batch Experiment

The results show that the Technosols demonstrated great capacity to adsorb copper (Figure 1). Considering the 500 mg Cu/L added via CuSO_4 solution, the Technosol A adsorbed 473.07 mg Cu/L, representing 95% of total Cu added. The Technosol B accumulate 488.93 mg Cu/L (98%), Technosol C 495.95 mg Cu/L (99%) and Technosol D 433.77 mg Cu/L (87%).

The Technosols A, B and C showed significant ($p < 0.05$) higher amounts of Cu adsorbed. However, even the Technosol D, which has adsorbed the smaller amounts of Cu, presented great result, having removed more than 433 mg Cu/L from solution.

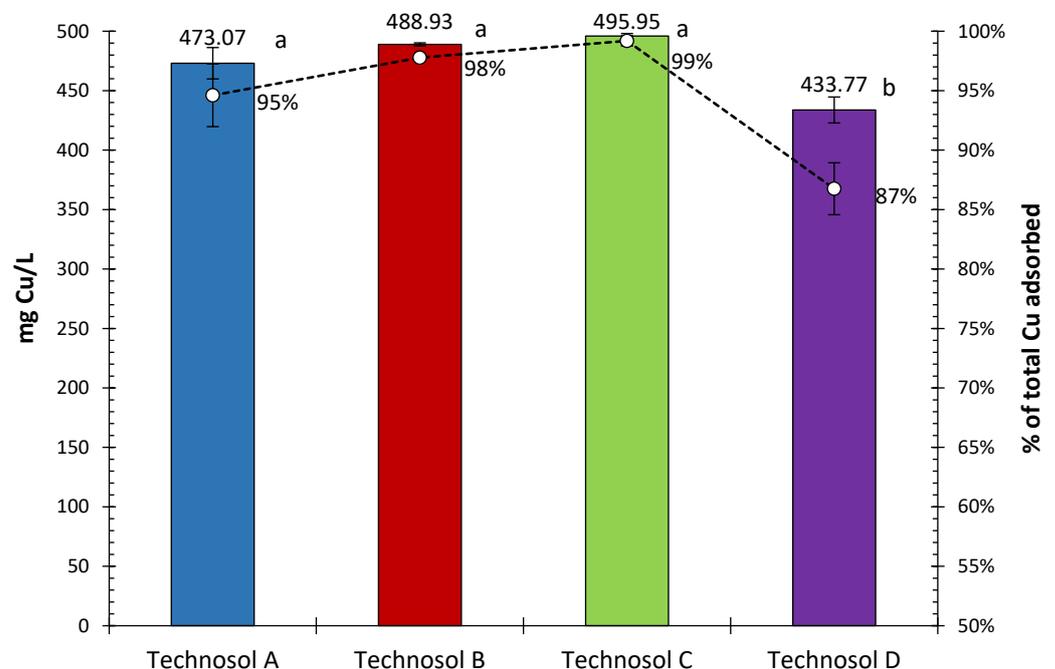


Figure 1. Mean concentration (bars) and percentage (dashed line) of total copper adsorbed by Technosols in the batch experiment. Values indicated by same letters in columns do not differ according to the Tukey test ($p < 0.05$) between Technosols ($n = 3$).

Although the adsorption capacity of Cu ions by the Technosols tested was already expected, due to the high affinity of materials used in their composition, the speed at which most of the Cu was adsorbed was astonishing. Tahervand & Jalali [33] in a similar

study evaluated the sorption and desorption of Cu in a soil where bentonite and calcite were added. These authors describe the greater retention capacity of soils amended with bentonite and calcite, in relation to natural soils, and attribute such behavior to the pH of the solution, in addition to the available area for the cations exchange of these minerals. Considering that bentonite is a highly expansive clay, with a great capacity to retain cations in its inter-layers, a large adsorption of Cu^{2+} ions in these Technosols was to be expected.

Minkina et al. [34] also evaluated the Cu sorption in Chernozem soils, using Langmuir isotherms. These authors also demonstrate a positive correlation between the amount of Cu^{2+} adsorbed and the size of soil particles, that is, clays such as bentonite have a high capacity to adsorb the metal. On the other hand, the same authors demonstrate, through analysis of the near-edge X-ray absorption fine structure, that despite adsorbing a smaller amount than clays, organic matter showed a greater binding force than clays, through the formation of octahedral inner-sphere chelate complexes.

The results demonstrate that the materials used in the construction of the Technosols tested in the batch experiment, have high capacity to adsorb Cu ions quickly and stably, emerging as excellent materials to be used in the elaboration of Technosols for reclamation of areas contaminated with copper. In this sense, the sequential extractions were used to identify which components used in the preparation of Technosols were the most efficient in adsorbing the metal.

3.2. Sequential Extraction

Regarding the distribution of copper in different fractions of the Technosols, the results show that the materials used in the preparation of the soil, revealed good affinity and high capacity for adsorbing Cu ions added via solution (Figure 2).

The concentration of Cu that was not adsorbed by the soils (which remained in solution) ranged from 0.74% to 13.25%. The proportion of Cu in the exchangeable fraction (F1) represent a small fraction of the total Cu in the Technosols, ranging from 0.43% to 9.40%. That is the most labile fraction of Cu, theoretically representing the fraction readily available in solution for uptake by plants and other organisms. The fraction F2 which represents the Cu sorbed or precipitated by carbonates represented between 14.18% and 16.66%, while the proportion of Cu associated to organic fraction (F3) ranged from 10.31% to 15.80% (Figure 2). These results are in line with expectations, since, in different proportions, limestone waste and organic matter formed the main components in the elaboration of Technosols (Table 1).

The concentrations of Cu adsorbed by oxides and sulphides were relatively low. These results were expected since the Technosols did not have these elements in its composition. However, it was observed that most of the Cu adsorbed by the Technosols lies in the residual fraction (F7), which represents the least labile form of Cu. The metal associated with this fraction is unlikely to be bioavailable to plants and other organisms, by process that occur naturally.

In this study, the Technosol B composed with 50% of carbonates, showed the lowest proportion of Cu in the exchangeable fraction (F1), probably by the increase in soil pH and formation of precipitates. In fact, carbonates may immobilize copper by precipitation, and thought increasing soil pH, decreasing its bioavailability by increasing the negative charge of the soil colloids [33,35].

The soil organic matter is perhaps one of the constituents with greater affinity for Cu [30]. The interaction between Cu and organic matter, often forming organometallic complexes of high stability, through strong covalent chemical bonds, which immobilizes the metal making it unavailable to plants and other organisms [34,36]. In fact, the Technosol C, which has a 50% of organic compound in its composition, presented the highest proportion of Cu associated with this fraction (F3).

Generally, metals associated with residual fraction (F7) are found in covalent chemical bonds forming inner sphere links, associated with silicates and/or at crystalline structure of minerals [37]. It could also be found in highly stable organometallic compounds, and

desorption in this case, will only occur through strong weathering or extreme environmental changes.

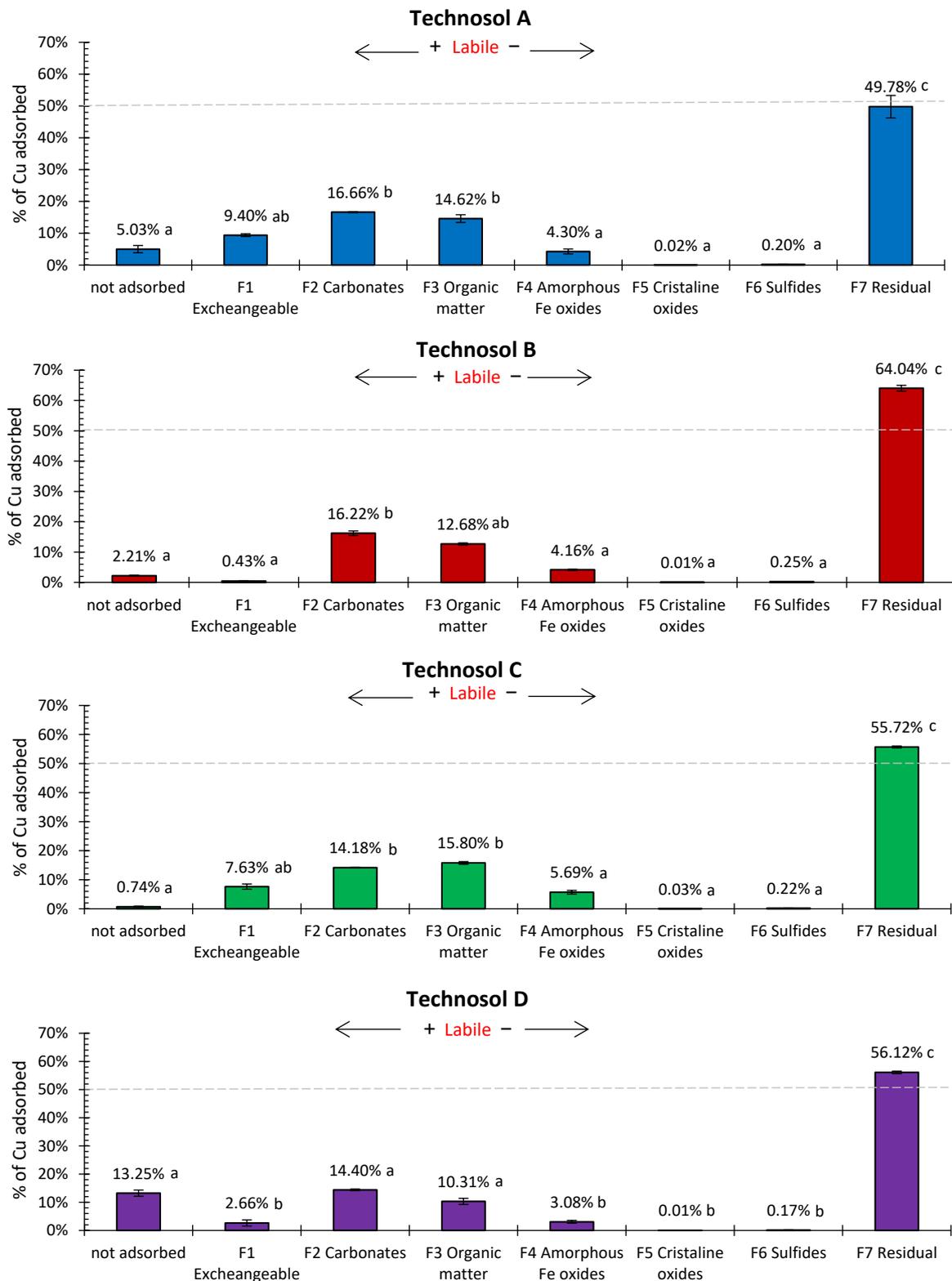


Figure 2. Percentage of copper adsorbed in each Technosol geochemical fraction. The bars from left to right represent from the most labile to the least labile forms of copper. Values indicated by same letters in columns do not differ according to the Tukey test ($p < 0.05$) between Technosols ($n = 3$).

A plausible explanation is that the bentonite may have formed covalent bonds with Cu in its inner structure, preventing desorption of Cu by reagents used in the sequential extraction. Qunaibit et al. [38] suggest that the strong link between Cu and bentonite occurs because the Cu^{2+} ions are strongly adsorbed mainly by layered silicate surface. Ferhat et al. [39] also demonstrate the high affinity between Cu ions and bentonite, suggesting the same geochemical mechanism. Thus, besides the ability to adsorb almost all of Cu in solution, the Technosols evaluated, were able to immobilize the metal in a way almost irreversible under natural conditions.

Individually, each component used has specific geochemical absorption mechanisms, i.e., bentonite has a large specific area for adsorption and cations exchange, the organic matter has the ability to form organo-metallic complexes of high stability, and carbonates, in addition to having the ability to adsorb and precipitate Cu, act in an important way by raising the pH, which controls the mobility of Cu in the soil solution, as discussed above.

Our results demonstrate that bentonite was the component with the highest Cu retention capacity, and in fact, it is recognized as an adsorbent of several potentially toxic elements, such as metals and organic contaminants [40] and could even be used individually for treatment in specific cases of copper contamination, either in soil or water.

However, the concept of creating and using Technosols goes beyond just immobilizing and/or inactivating contaminants. These soils must be elaborated by several components, which allow them to undergo pedogenetic evolution over time, becoming healthy soils [13] where, in addition to minimizing the impacts of contaminants, they develop the capacity to provide ecosystem services [41] such as plant growth [5,26,42,43], soil micro/macrofauna restoration [14,44], carbon sequestration and stabilization [16,45], among other environmental benefits that would not be achieved using each component separately.

3.3. Column Experiment

At the beginning of column experiment the amount of copper leached was practically negligible, and this situation persisted for approximately 14 weeks. During this period, the highest concentration of leached was observed in Technosol A, with 4.39 mg Cu/L. After this period, a gradual and significant increase ($p < 0.05$) in the Cu concentration in the leachates was observed until the end of the experiment (Figure 3).

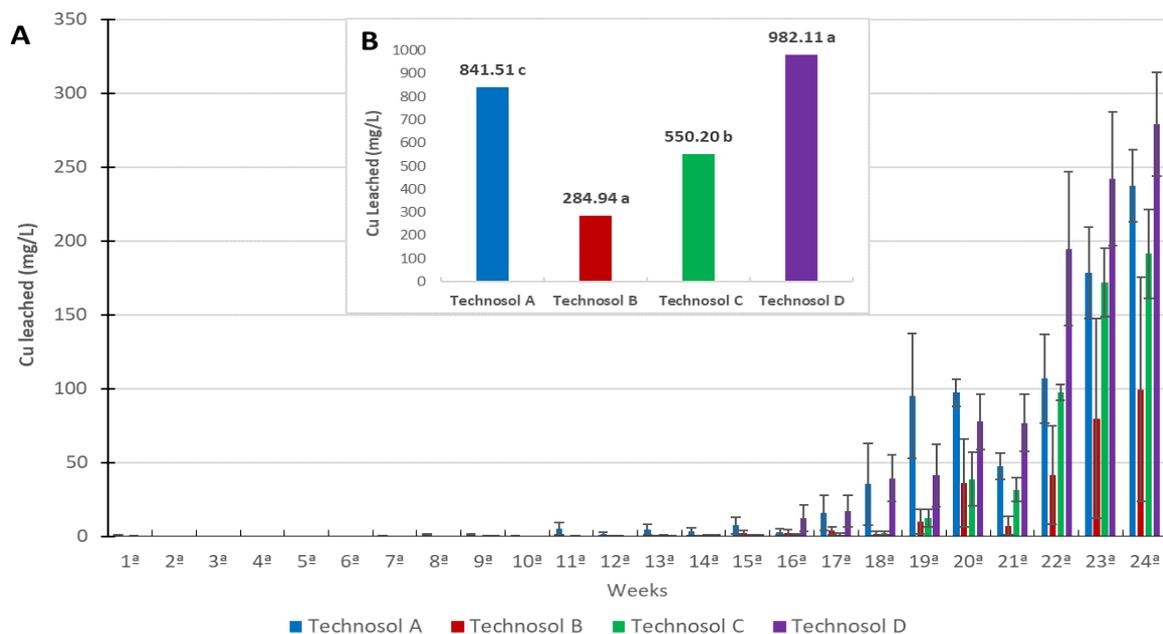


Figure 3. (A) Copper leached during the 24-weeks period of experiment. (B) Total Cu leached after 24-weeks. Values indicated by same letters in columns do not differ according to the Tukey test ($p < 0.05$).

At the end of 24 weeks, significant differences were observed in the concentration of copper leached. Technosol B has showed the greatest efficiency in retaining Cu, leaching only 284.94 mg Cu/L, while Technosols A and D were less efficient, leaching 841.51 and 982.11 mg Cu/L respectively. In Technosol D, practically all Cu added was leached in the period. It is clear, therefore, that initially, as observed in the batch experiment, copper is mostly adsorbed in the fraction associated with carbonates, organic matter and in the residual fraction. However, over time, geochemical interactions, most likely related to the dissolution of carbonates and organic matter, influence the transition from the more stable forms of Cu in the soil to the non-adsorbed or exchangeable fraction.

Also, the copper retained in the residual fraction, most likely associated with bentonite, underwent movement due to the decrease in pH. This desorption mechanism of metals and of macro and micronutrients in clays, in view of the pH decrease, is well described in the literature [33,46]. In this case, the exchange of cations adsorbed by clay minerals (bentonite) occurs, in exchange for anions that are then transferred to the soil solution, and can either be absorbed by plants, or be leached. The data that corroborates our observation are the pH values obtained in the leachates (Figure 4).

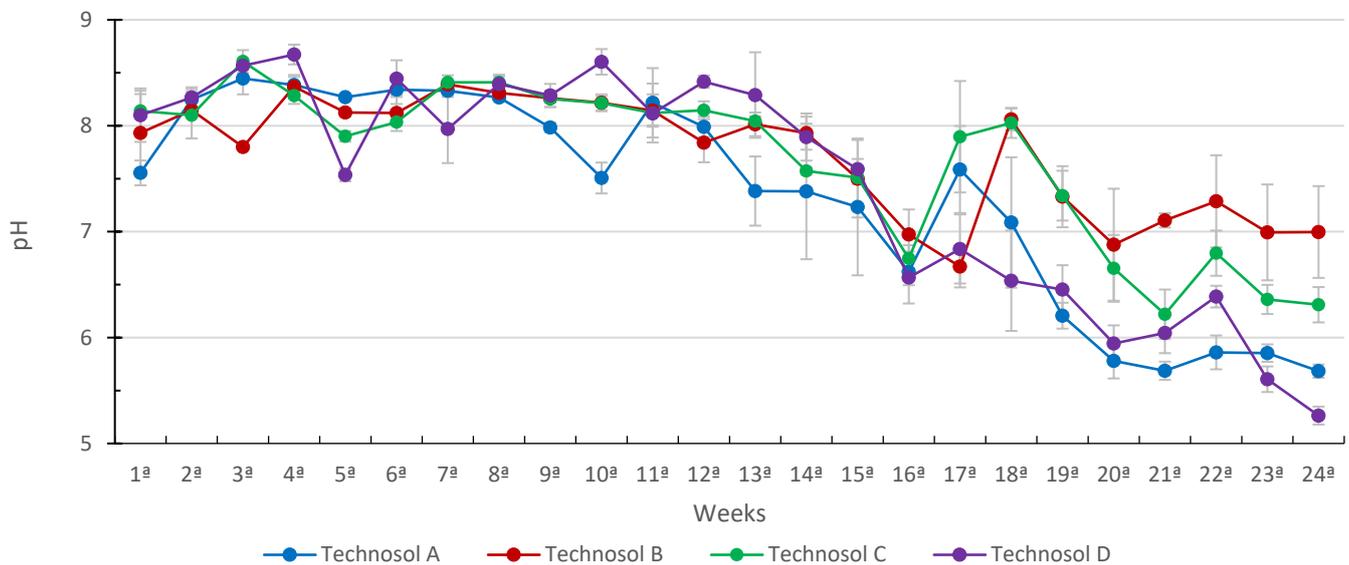


Figure 4. pH changes in leachates along the 24-week experiment indicating that the buffering capacity of carbonates decreases with time. Values indicated by same letters in columns do not differ according to the Tukey test ($p < 0.05$).

At the beginning of the experiment, the addition of limestone mining wastes raised the pH of the leachates, as well as the Technosols, to the range of 8.0. Considering that the copper sulphate solution added to the Technosols had a pH of 4.2, it is clear that these soils had a great capacity to raise the pH, coprecipitating a good part of the copper, and preventing its mobility through the soil solution. However, the dissolution of carbonates present in the limestone and even (water) soluble organic matter may occur with time due to and the addition and action of water and oxygen in addition to a forced pH decrease by the contaminating solution, [47,48]. This could lead to the release of Cu sorbed in these soil components (F2 and F3) to the F1 (exchangeable) fraction. Thus, there was probably a mobilization of Cu to the exchange and soluble phases facilitating its leaching.

Furthermore, the continuous addition of Cu over time leads to saturation of the binding sites of clay minerals and organic matter reducing the capacity to retain the metal.

Considering the parameters observed in this study, the pH seems to have had a great influence on the desorption of Cu initially retained by Technosols. Figure 5 shows the evolution in the concentration of leached Cu with the pH values obtained in the solutions. A significant correlation (R) was observed between the decrease in pH and the increase in

the concentration of Cu leached in the solution in Technosols A and D. In Technosols B and C, despite not demonstrating such a prominent correlation, the same tendency was also observed, represented by dashed lines in the graphs. These correlations between pH decrease and Cu leaching are also demonstrated by Ramirez-Pérez et al. [49].

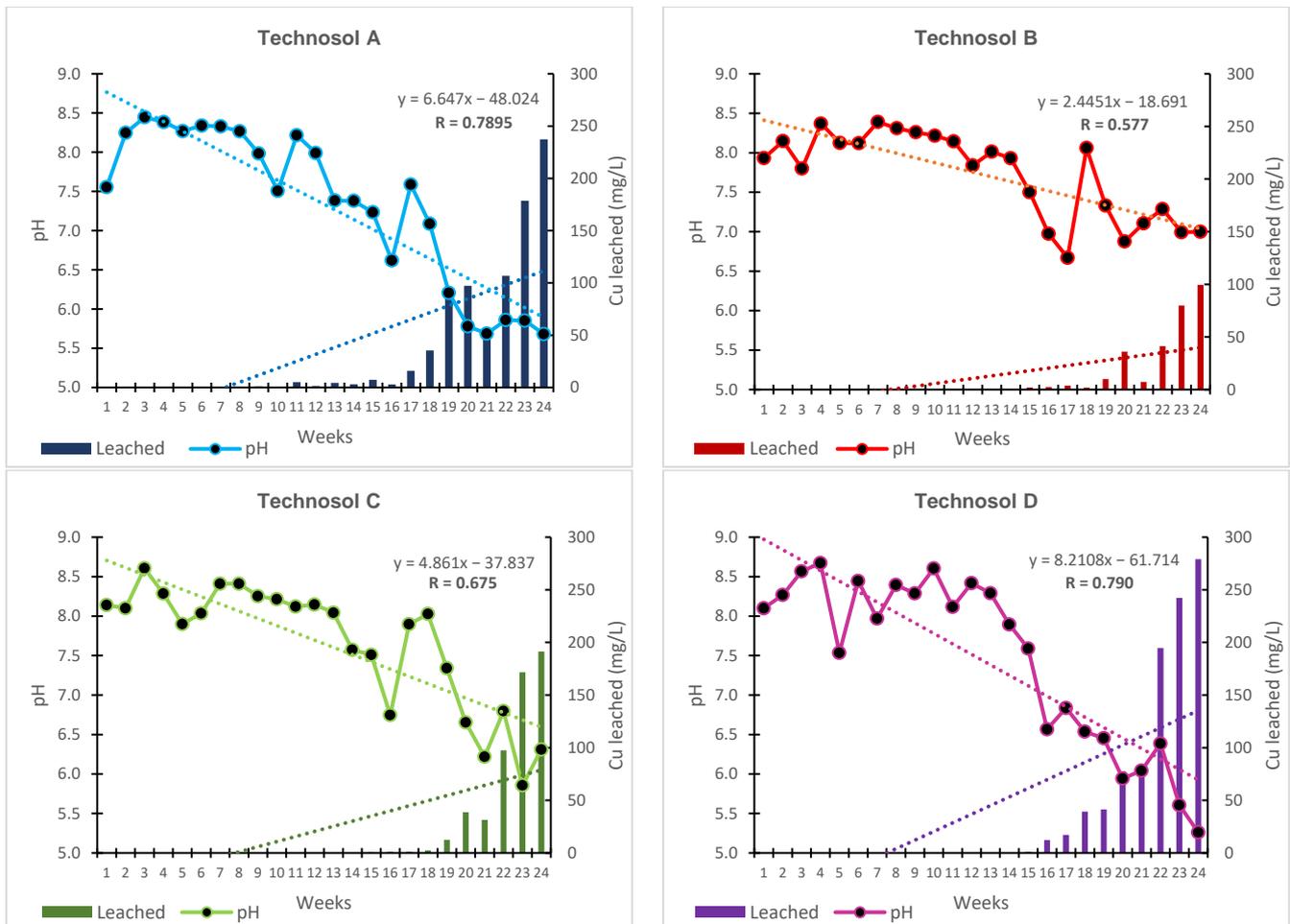


Figure 5. Pearson correlation (R) between pH and Cu leached (mg Cu/L) from Technosols, showing a positive correlation between pH decrease and the increase of copper leached from Technosols. The dashed lines demonstrate the correlation tendency.

4. Conclusions

The Technosols under study showed efficient adsorption of Cu ions. In the batch experiment most of the Cu was adsorbed in the fraction F7, which represents least labile form. Considering the total amounts of Cu adsorbed, the Technosols A, B and C were significantly ($p < 0.05$) more efficient in the initial adsorption of copper. However, even the Technosol D, which showed the lowest capacity to adsorb Cu, produced a satisfactory result, since it removed more than 85% of the Cu in solution. Considering the efficiency in immobilizing Cu, and that the F7 fraction is where the Cu are found in its less mobile form, it can be concluded that the efficiency scale of the evaluated Technosols was $B > C = D > A$.

Regarding the column experiment, the decrease in the pH of the solution caused an accentuated desorption of copper in the evaluated Technosols, demonstrated by the significant correlation between these two factors ($\text{pH} \times \text{Cu}$). Therefore, despite the efficient and rapid adsorption of Cu ions by the Technosols tested, the monitoring and maintenance of the pH at values above 7 must be constant. Further studies, to evaluate the sorption and desorption behavior of each material used individually, as well as possible dissolution of

carbonates or organic matter, may show which are the main mechanisms regulating these processes.

The designed Technosols proved to be an efficient and low-cost alternative for stabilization of Cu ions and for the reuse of mining wastes and organic residues that would otherwise be discarded, meeting the concepts of circular economy and Nature-based solutions. Furthermore, this environmental technology, which seeks to mimic nature, can be used in several mining sites and tackle some of the biggest challenges for companies around the world toward a sustainable mining: the management and disposal of waste rocks, tailings, among other residues, soil and water reclamation and sustainable mine closure and rehabilitation.

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Conflicts of Interest: The authors declare no conflict of interest.

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