

Enhancing Copper-Contaminated Soil Remediation Using Walnut and Sunflower Residues

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Abstract. Soil contamination with heavy metals, particularly copper (Cu), poses a significant challenge to environmental health and agricultural. This study evaluates the potential of organic amendments, including walnut shell biochar (produced at 700°C), sunflower husk biochar (produced at 500°C) and nutshell flour, to reduce Cu availability in contaminated soils. The amendments were applied at two concentrations (2.5% and 5%) to soils spiked with 2,000 mg/kg Cu. The untreated control soil exhibited the highest mean Cu availability (342.7 mg/kg), highlighting the severity of contamination. Upon treatment with 2.5% walnut shell biochar, Cu availability decreased significantly to 231.6 mg/kg, while 2.5% sunflower husk biochar, further reduced Cu availability significantly to 222.2 mg/kg. A more substantial reduction was achieved with 2.5% nutshell flour, which lowered Cu availability significantly to 181.4 mg/kg. At the higher application rate (5%), the amendments showed enhanced efficacy. Walnut shell biochar and sunflower husk biochar reduced Cu availability to 223.2 mg/kg and 190.7 mg/kg, respectively. Notably, 5% nutshell flour exhibited the highest immobilization potential, decreasing Cu availability significantly to 142.9 mg/kg. While in other hand study also investigates the effects of walnut shell biochar, sunflower husk biochar, and nutshell flour on the pH of Cu-contaminated soil (2,000 mg/kg Cu), The untreated control soil had a neutral pH of 7.52, while Cu contamination significantly reduced pH to 6.47, reflecting increased acidity. Application of 2.5% and 5% walnut shell biochar and 2.5% sunflower husk biochar significantly elevated the pH to 8.0, 8.21 and 7.96, respectively, achieving near-neutral or slightly alkaline conditions. Conversely, 2.5% nutshell flour resulted in a marginal pH increase to 6.59, indicating limited neutralizing potential.

Keywords. Cu contaminated soil, Biochar, Walnut and Sun Flower Residue.

1. Introduction

Soil contamination by heavy metals, particularly copper (Cu), has become a significant environmental concern due to its persistence, bioaccumulation, and toxic effects on ecosystems. The primary sources of Cu pollution are anthropogenic activities, including the excessive application of Cu-based fungicides and fertilizers in agriculture, industrial emissions, mining, and wastewater discharge [1,2]. Although Cu is an essential micronutrient for plants and microorganisms, elevated concentrations can disrupt soil microbial communities, reduce fertility, and hinder plant growth. Beyond its impact on agricultural productivity, Cu contamination also increases the risk of heavy metal transfer within food chains, leading to potential health hazards for humans and animals [3]. Consequently, the development of sustainable and environmentally friendly strategies to mitigate Cu contamination is essential. In recent years, biological adsorbents have emerged as an effective and efficient alternative for removing

heavy metals from contaminated environments. Biosorption, a process that employs low-cost biological materials to capture toxic heavy metals, offers several advantages over conventional remediation methods. These include the reusability of biomaterials, low operating costs, high metal selectivity, rapid processing times, and the absence of chemical sludge production [4]. The adsorption process involves the interaction between a solid surface (adsorbent) and dissolved metal ions (adsorbate), resulting in the accumulation of heavy metals onto the adsorbent material.

A wide range of agricultural byproducts can serve as effective adsorbents due to their high adsorption capacity, selectivity, thermal and chemical stability, and low solubility in water. Examples of such materials include rice husks, coconut shells, walnut and almond shells, peanut shells, tea leaves, fruit peels, sugarcane bagasse, sawdust, tree bark, neem leaves, and biochar. These natural materials not only provide a cost-effective solution for heavy metal removal but also contribute to waste management and environmental sustainability [5,6]. Traditional remediation techniques, such as soil washing, chemical stabilization, and phytoremediation, often present challenges in terms of cost, efficiency, and potential environmental risks [7,8]. Therefore, investigating sustainable, cost-effective approaches for mitigating Cu contamination remains a crucial focus in environmental management and agricultural sustainability.

The application of organic amendments, particularly plant-based residues, has gained significant attention as an effective strategy for immobilizing heavy metals in contaminated soils while enhancing overall soil quality. Recent research has highlighted the potential of bio-based materials, such as walnut and sunflower residues, in stabilizing heavy metals through mechanisms like sorption, complexation, and pH modification [9,10]. Specific research has shown that biochars derived from different raw materials vary in their ability to sorb and transform heavy metals like Zn in soil [11]. However, some studies have suggested that certain heavy metals adsorbed onto biochar can undergo desorption, potentially impacting their long-term stabilization [10]. Given that biochar properties depend on feedstock type and pyrolysis conditions, optimizing production methods is crucial to maximize its effectiveness in remediating contaminated soils [12]. For example, peanut shell biochar has been tested for its effectiveness in immobilizing Pb and Zn in contaminated soils [11]. This study presents a novel comparative evaluation of three distinct organic amendments—walnut shell biochar, sunflower husk biochar and nutshell flour—for their effectiveness in immobilizing copper (Cu) in highly contaminated soils (2,000 mg/kg Cu). While biochars have been widely studied, this work uniquely highlights the underexplored potential of nutshell flour, particularly at higher application rates, as a superior agent for Cu immobilization. Additionally, the study provides new insights into the pH-modulating effects of each amendment under identical contamination conditions.

2. Material and Methods

This study employed a controlled model experiment to assess copper contamination stabilization in Fluvisol.

2.1. Soil Sampling and Analysis

Soil samples were collected from the upper 20 cm layer of an undisturbed site, distant from pollution sources. Before the experiment, soil samples were dried, ground to <1 mm, and cleared of plant debris and large fragments. Physicochemical analysis revealed a soil pH of 7.3, with 48.1% physical clay (<0.01 mm), 28.6% silt (<0.001 mm), 3.7% organic carbon, and 0.1% carbonates. The cation exchange capacity (CEC) was measured at 36 cmol (+) kg⁻¹ [13]. Portions of 100 g soil were placed in plastic containers and thoroughly mixed with an aqueous copper acetate solution 2,000 mg/kg. After a two-week incubation period, % biochar was added—equivalent to 200 kg per 100 m² (or 20 t/ha for the top 20 cm of soil). Moisture was maintained at 60% of total capacity, and contaminated soil was incubated at room temperature under natural light. Biosorbent production followed a three-stage pyrolysis process, optimizing meso- and micropore distribution and surface area.

2.2. Experimental Setup

We accomplished model experiments to study the efficiency of the recultivation of the contaminated soil based on biosorbent. For this purpose, Soil – 100g. Options with soil contamination and the use of biochars (from sunflower husks and nut shells), as well as powdered nut shells in raw form - in two

repetitions. Total - 2.4 kg of soil for the experiment. we sampled the upper humus horizon (0–20 cm) of the clay loamy Fluvisol in the Kamenka district (Rostov region). The pollutant was represented by Cu (300 mg/kg per pure element). Before starting

- Common chernozem (Haplic Chernozem) unpolluted (background) represented by C.
- Chernozem (background) +2000 mg/kg Cu (CuCH₃COO)₂) represented by (T1).
- Chernozem (background) +2000 mg/kg Cu +2.5% biochar from nut shell represented by (T2).
- Chernozem (background) +2000 mg/kg Cu +2.5% biochar from sunflower husk (T3).
- Chernozem (background) +2000 mg/kg Cu +2.5% nut shell flour (T4).
- Chernozem (background) +2000 mg/kg Cu +5% biochar from nut shell (T5).
- Chernozem (background) +2000 mg/kg Cu +5% biochar from sunflower husk (T6).
- Chernozem (background) +2000 mg/kg Cu +5% nut shell raw (T7).

2.3. Biochar Production

The process of preparation biochar involved a 30 minute sample holding time, a final temperature of 700°C for walnut shell biochar, and 500°C for sunflower husk biochar a heating rate of 15°C per minute. The treatments were added in different concentration of %2.5 and %5 for walnut shell biochar (produced at 700°C), sunflower husk biochar (produced at 500°C) and nutshell flour.

2.4. Copper Determination

The Procedure for measuring the mass fractions of mobile metals: copper samples of soils was by flame atomic absorption spectrometry [3].

2.5. Statistical Analysis

Duncan's Multiple Range Test (DMRT) is a post-hoc statistical method used to compare the means of different treatment groups after a significant result has been found using analysis of variance (ANOVA). Based on the results, treatments with the same letter (e.g., "a", "b", "c", "d", etc.) in their mean values do not differ significantly, while those with different letters are significantly different at a given confidence level.

3. Results and Discussion

3.1. Cu Availability in Soil

As shown in Fig. (1), the uncontaminated control (C.) was significantly different ($p < 0.05$) from all other treatments, as indicated by its unique grouping ("e"). The contaminated control (T1) belonged to group "a," confirming that Cu contamination drastically increases its availability in the soil. The highest Cu availability (342.7 ppm) was observed in the soil contaminated with 2,000 mg/kg Cu without any amendments. The addition of 2.5% Walnut Shell Biochar (T2) reduced Cu availability to 231.6 ppm (group "b"), showing a significant reduction compared to the contaminated soil but not the most effective treatment. Similarly, 2.5% Sunflower Husk Biochar (T3) also fell into group "b," indicating a comparable effect to walnut shell biochar. In contrast, 2.5% Nutshells (Flour Form) belonged to group "c," showing a statistically significant improvement over treatments in group "b" and demonstrating superior Cu immobilization, reducing Cu availability to 181.4 ppm.

Increasing the walnut shell biochar concentration to 5% (Soil + Cu + 5% Walnut Shell Biochar) remained in group "b," suggesting that a higher biochar concentration did not significantly enhance Cu immobilization. However, 5% Sunflower Husk Biochar showed a significant improvement over the 2.5% treatment and belonged to group "c." The most effective treatment was 5% Nutshells (Flour Form), which belonged to group "d" and resulted in the lowest Cu availability among all Cu-treated soils, indicating the highest Cu immobilization efficiency. Bakshi et al [14] demonstrated that biochar application reduced Cu leaching loss from approximately 47% to 10% in Cu-spiked Alfisol and from 48% to 9% in Cu-spiked Spodosol. The study attributed this reduction to Cu retention on biochar surfaces through complexation, converting Cu from an available pool to more stable forms [15] found that biochar amendments decreased exchangeable Cu and increased Cu bound to organic matter and residual fractions in contaminated soils. This shift led to reduced Cu bioavailability and enhanced plant production, notably in *Solanum lycopersicum*, which exhibited up to 12 times more growth than

plants in non-amended soil [16] reported that biochar significantly reduced the concentration of Cu in sweet corn and soybean under Cu stress. The study suggested that biochar addition decreased soil acid-soluble Cu and increased residual Cu, thereby reducing Cu bioavailability and uptake by crops [17]. examined the effectiveness of biochars derived from soybean and pine feedstocks in immobilizing lead (Pb) and Cu in contaminated soils. The study confirmed that these biochars effectively reduced the mobility and bioavailability of these heavy metals.

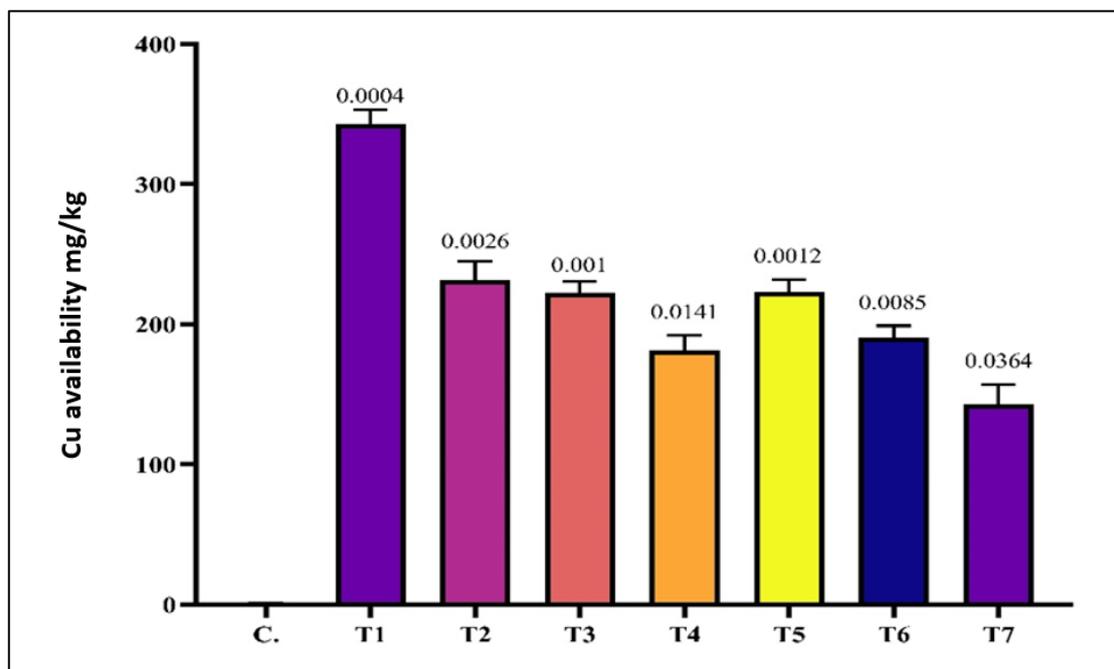


Figure 1. Effect of different treatment of amendments on Cu availability mg/kg.

3.2. PH level of the Soil

As shown in Fig. (2), the unpolluted control (C. column had a pH of 7.52, while the polluted control (T1, soil + 2,000 mg/kg Cu) experienced a significant decrease in pH to 6.47, indicating strong acidification due to copper contamination. Heavy metals such as copper (Cu) are known to lower soil pH by increasing hydrogen ion (H^+) concentration [18,19]. The addition of Walnut Shell Biochar at 2.5% and 5% increased soil pH to 8.0–8.215 (group "a"), significantly neutralizing the acidity compared to both control and Cu-only soil. Similarly, 2.5% Sunflower Husk Biochar raised the pH to 7.965 (group "a"), while 5% Sunflower Husk Biochar had a moderate effect, increasing pH to 7.635 (group "ab"). Biochar, being alkaline in nature, neutralizes soil acidity by releasing basic cations (Ca^{2+} , Mg^{2+} , K^+), which helps reduce copper toxicity [9,20].

In contrast, nutshell amendments had a limited effect on soil pH. The 2.5% nutshell treatment resulted in a pH of 6.595 (group "b"), and 5% nutshells further decreased pH to 6.37 (group "b"), showing no significant alkalizing effect compared to the control. This suggests that nutshells are less effective in neutralizing soil acidity than biochar [10,11,21]. These findings are consistent with previous studies that emphasize biochar's capacity to ameliorate soil pH and stabilize heavy metals, making it an effective soil amendment for contaminated environments.

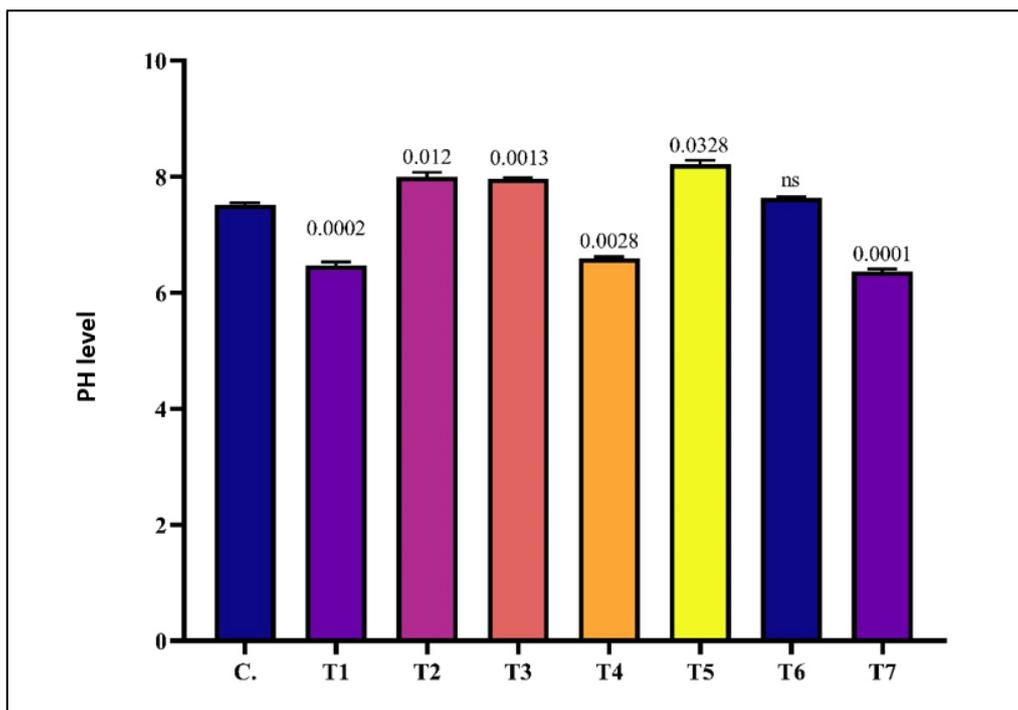


Figure 2. Effect of different treatment of amendments on PH level.

Conclusions

The reductions in Cu availability across all treatments are statistically significant compared to the control ($p < 0.05$), with effectiveness ranking as follows: nutshell flour > sunflower husk biochar > walnut shell biochar. The use of nutshell flour at higher concentrations proved to be the most effective strategy for Cu availability, suggesting its potential as a sustainable and low-cost amendment for remediating Cu-contaminated soils. At the 5% application rate, walnut shell biochar demonstrated the highest pH improvement, followed by sunflower husk biochar, both significantly neutralizing the acidic conditions. These findings provide critical insights into the role of biochar and organic residues in mitigating heavy metal contamination, emphasizing their application in sustainable soil management and environmental protection strategies.

Further research is recommended to evaluate the long-term stability and ecological impacts of these amendments in field conditions.

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