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Effective mitigation of Cadmium contamination in soil through Sawdust Biochar application

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Abstract

Cadmium (Cd) contamination in soil is a serious environmental concern, and this study examines the effectiveness of sawdust biochar in reducing Cd contamination over three months. The study explores different sawdust biochar application rates and their effects on the amount of extractable Cd in the soil. According to the study, sawdust biochar has a high potential for addressing Cd pollution. Importantly, over the duration of the investigation, extractable Cd concentrations gradually decreased as a result of the use of biochar. In particular, compared to lesser application rates of 2.5% and 1.25%, the highest biochar application rate (5%) resulted in a significant reduction in cumulative leachable Cd content. Additionally, compared to the control group, all biochar-amended soils showed considerably decreased cumulative leachable Cd levels. The leachate study demonstrated the time-dependent efficiency of biochar in lowering Cd concentrations, with Cd concentration declining from 14 mg/L in August 2023 to a meager 0.004 mg/L in October 2023. Diffusion within the porous structure of biochar was determined to be the main process underlying heavy metal adsorption. However, the observed decrease in the effectiveness of heavy metal removal with biochar may be explained by surface oxidation, which creates a greater number of accessible adsorption sites. Furthermore, the soil's capacity to absorb Cd^{2+} was greatly improved by the raised pH brought on by biochar application, further enhancing Cd removal. The study also showed the importance of pyrolysis temperature on biochar characteristics, with higher temperatures greatly improving Cd adsorption capability. This study's findings highlighted the significant potential of sawdust biochar as a powerful technique for reducing soil Cd pollution. These results highlighted the potential of biochar for Cd remediation and crucial role that pyrolysis temperature plays in determining biochar's characteristics and adsorption capacity.

Keywords: *Biochar, cadmium, contamination, pyrolysis temperature, sawdust*

Introduction

The demand for affordable solutions to satisfy environmental remediation and restoration needs has increased dramatically on a global scale. Stabilizing potentially dangerous materials in polluted soil requires practical, affordable solutions with strong adsorption properties. In a low-oxygen environment, biomass sources such as wood, crop residues, and manure are pyrolyzed to produce biochar (BC), a substance rich in carbon (Chi *et al.*, 2021). It acts as a beneficial soil additive, enhancing soil fertility, productivity, and cleaning locations with metal contamination. Additionally, according to Zwolak *et al.* (2019), biochar is essential for carbon sequestration and lowering greenhouse gas emissions. The pyrolysis conditions, such as temperature and feedstock type, have an impact on the physicochemical characteristics of biochar,

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which has a major impact on their impact on soil processes, functions, and microbial communities (Ding *et al.,* 2017).

Large amounts of sawdust, a small particulate substance produced by the sawmill and wood processing industries, can be difficult to dispose of and has little economic use. Therefore, it is crucial to turn these inexpensive waste materials into usable and profitable products. According to research done in 2016 by Najam & Andrabi (2016), Populus alba sawdust has proven to have the ability to successfully remove Cd^{2+} ions from aqueous soil solutions. The creation of biochar from waste materials has the potential to enhance the environment as well as bring about significant economic gains.

This study revealed the possibility of making biochar from wood sawdust and characterizing the final material based on its adsorption ability. It aims to accomplish the following goals:

- To assess the efficiency of sawdust biochar as a remediation method for reducing cadmium (Cd) contamination in soil over a three-month period.

- To find out how various biochar application rates affect the amount of extractable Cd in soil.

- To evaluate how the pyrolysis temperature affects the characteristics of sawdust biochar and how that affects the soil's ability to bind Cd.

This study intends to contribute to the creation of sustainable and affordable methods for soil remediation and environmental improvement by addressing these goals.

Materials and Methods

Soil samples were taken from the Kaliodai River in Sri Lanka's eastern region, namely between the coordinates of 7°17'51.12" N latitude and 81°50'54.12" E longitude. Altogether, 100 Soil samples were collected in a zigzag pattern from 0 to 20 cm depth. The study was conducted using the Factorial Completely Randomized Design (CRD) with four replications. After inducing Cd contamination in the soil by adding 6 mg of $CdCl_2$ to 1 kilogram of dry soil, the final contaminated soil sample showed a total Cd content of 3.7 mg kg^{-1} after 60 days of culture.

Figure 1: Soil sample preparation

Wood sawdust from a Pandiruppu, Batticaloa, Sri Lanka sawmill was employed as the feedstock for the synthesis of biochar. To reduce the moisture content, the biomass was first dried at 105°C for 24 hours and then sieved to a size of 0.85mm. Then, using pyrolysis, biochar was created in a muffle furnace for constant residence durations of 2 hours, 1 hour, and 30 minutes at 450°C, 550°C, and 650°C. The resulting biochar was named B-450, B-550, and B-650, with sawdust completely combusting at 650°C to generate ashes. The pH of the biochar was then measured in a 1% (w/v) biochar/deionized water suspension using a pH meter and the method described by Thomas (1996) with a 1:20 (biochar: water) suspension ratio.

Figure 2: Sawdust biochar preparation

Leaching columns were built from polyvinyl chloride tubes cut to the proper size and secured to a wood table with 32 holes. The bottoms of the tubes were coated with three layers of muslin cloth to prevent soil particles from moving, and funnels were positioned to help collect leachate. These columns were labeled and sorted randomly based on the treatment, replication, and temperature. Before each column was filled with 750 g of soil, biochar produced at concentrations of 0%, 1.25%, 2.5%, and 5% was mixed with the soil to maintain constant soil bulk density. The columns were placed vertically on a hardwood table and allowed to develop for two months. At monthly intervals, 200 ml of distilled water was introduced into each leaching column, and the resulting leachates were collected and treated with a 65% HNO_3 solution to acidify them. The concentrations of Cd in these leachates were subsequently determined using Atomic Absorption Spectrophotometry (AAS). This leaching and analysis process was repeated twice over three months (August 1^{st} and October 1^{st}, 2023), with regular monitoring of Cd content in the leachates.

Table I: Treatment used in the experiment

Treatment	Biochar (w/w) %
T1	Control (without biochar)
T2	Soil + 1.25% biochar recommendation
T3	Soil + 2.5% biochar recommendation
T4	Soil + 5% biochar recommendation

SPSS version 22 was used to analyze the data collected. The significant difference (LSD) test was used to analyze variance among treatments, temperatures, and their interaction effects at $p < 0.05$. Two-way ANOVA was used to determine the effect of treatments, temperature on Cd level.

Results and Discussion

Table II: Properties of Wood Sawdust Biochar in Carbonization

Feedstock	Carbonization Characteristics of Sawdust				
	Duration(hour)	**Initial feedstock weight (kg)**	**Biochar weight (kg)**	**Efficiency per weight (%)**	**Temperature (^{0}C)**
Sawdust					
	2	3.8	0.35	9.3	450
	1	5	0.35	7	550

The carbonization properties of wood sawdust biochar are shown in Table II. During the carbonization process, two different variables—duration (in hours) and temperature (in degrees Celsius) were taken into account. The starting feedstock weight was 3.8 kg, and the first set of conditions (2 hours at 450°C) produced a yield of 0.35 kg of biochar, or an efficiency of 9.3%. The starting feedstock weight was 5 kg in the second set of circumstances (1 hour at 550°C), and a yield of 0.35 kg of biochar was produced with an efficiency of 7%. These numbers offer information on the effectiveness and yield of making biochar from wood sawdust under various carbonization configurations.

Table III: The mean Cd content level in leachate for August and October 2023

Treatment	Cd content (mg/L) (Mean ± SE)	
	August	**October**
T1 (0%)	60.88 ± 8.118[a]	0.03 ± 0.002[a]
T2 (1.25%)	27.25± 8.118[b]	0.008 ± 0.002[b]
T3 (2.5%)	28.38 ± 8.118[b]	0.010 ± 0.002[b]
T4 (5%)	14.00 ± 8.118[b]	0.004 ± 0.002[b]
Treatment (P)	0.000	0.000
Temperature (P)	0.402	0.009
Interaction (P)	0.805	0.751

The values are means of four replicates ± standard error. The means with the same letters are not significantly different from each other at 0.05 level based on Tukey Post Hoc test (Source: Data Analysis SPSS Output)

Table III displays the levels of extractable Cd from soil contaminated with varying rates of biochar over a three-month period. The study demonstrates that treatment affects Cd content in the months of August and October 2023 after incubation, while temperature and the combination of temperature and treatment had no impact on Cd levels. Importantly, the amount of extractable cadmium gradually reduces three months after adding biochar to contaminated soil. The cumulative leachable Cd concentration in the soil treated with 5% biochar (T4) was significantly lower than the 2.5% and 1.25% rates. However, all of the biochar-treated soil displayed noticeably lower cumulative leachable Cd levels than the control group. The leachate had a Cd level of 14 mg/L in August, but with the same 5% biochar level (T4) in October, this value substantially dropped to 0.004 mg/L. This drop in Cd concentration was gradually observed with the usage of biochar.

The concentration of leachable Cd leachate generally decreased noticeably as biochar application rates rose. The leachate's cadmium concentration decreased consistently at all levels due to the increased biochar application amounts. This pattern is consistent with the observations made by Arthur et al. (2015), who discovered that adding EFB biochar to mine tailing-contaminated soil reduced the amount of leachable heavy metals in the leachate. Due to the increased CEC that occurs when biochar is added to the soil, this result is anticipated. According to Kavitha et al. (2018), the addition of biochar causes a series of subsequent consequences, including increased porosity, the development of active surface sites, greater contact between cadmium and biochar, changes in redox potential, and increased cadmium removal effectiveness. Additionally, larger application rates of biochar had a more noticeable effect on the pH and cation exchange capacity (CEC) of the soil than lower application rates.

Diffusion within the biochar's pores is the main mechanism for heavy metal adsorption in soil using biochar. However, Fahmi *et al*. (2018) pointed out that surface oxidation, which increases the accessible sites for heavy metal adsorption, can be responsible for the observed reduction in heavy metal removal with biochar. According to Park *et al*. (2019), the adsorption of Cd onto biochar specifically begins with rapid surface boundary layer adsorption and subsequently progresses through intraparticle diffusion. According to Qian *et al.* (2016), dissolved phosphorus has the capacity to co-precipitate with Cd, and oxygen-containing functional groups present in biochar-derived compounds may be able to cause a decrease in hexavalent chromium. In addition, an increase in pH led to less H^+ ion competition for Cd^{2+} adsorption inside the soil, which improved the soil's ability to adsorb Cd^{2+}. According to the study by Zhu *et al.* (2020), the increase in pH also boosted the hydrolysis of Cd^{2+} ions, making them more susceptible to adsorption by both charcoal and soil. Park *et al.* (2019) reported a similar pattern, noting that at pH 5, a lower hydrogen ion concentration is linked with an enhanced ability for cadmium adsorption. This correlation was attributed to the negative charge carried by functional groups like carboxyl and hydroxyl, which facilitate cadmium adsorption. This study reveals that the most practical solution for the specific case of soil contaminated with Cd, where Cd is 3.7 mg/kg, is to apply 6.7 t/ha of sawdust biochar to reduce the Cd contamination.

Effect of different biochar temperatures on Cd adsorption

Comparison of Cd Leachate Concentrations in Soil Amended with B-450 and B-550 Biochar

In the study, Cd levels in leachate from contaminated soil treated with biochar produced at various pyrolysis temperatures (450, 550 ^{o} C) were examined.

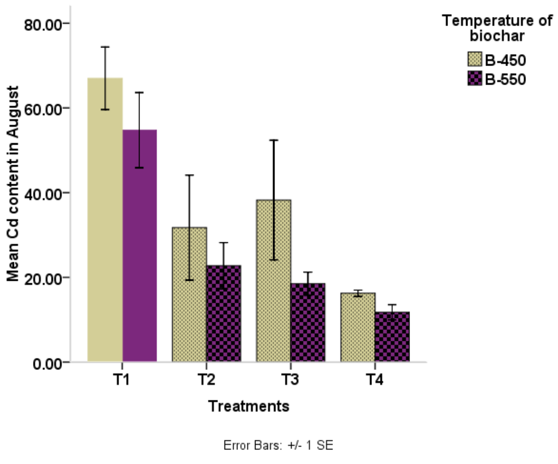

Figure 3: The mean Cd content level in leachate for August 2023

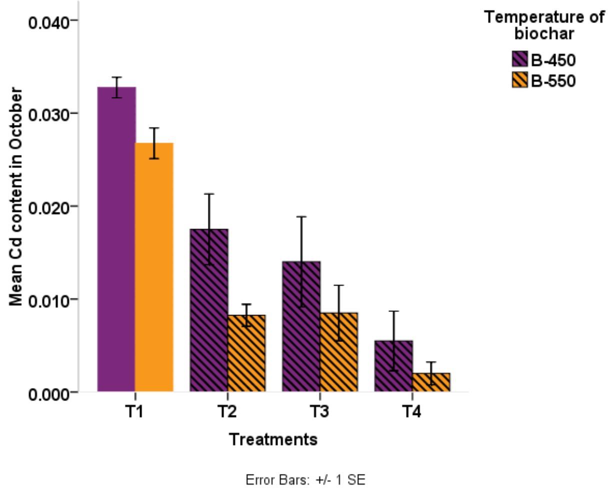

Figure 4: The mean Cd content level in leachate for October 2023

Figure 3 and 4 show that B-550 demonstrated more cadmium absorption than B-450 in August and October 2023. Despite no discernible influence from temperature, B-550 showed greater cadmium absorption than B-450 in August and October, 2023, suggesting that additional factors or mechanisms may be affecting cadmium absorption.

However, other characteristics of the biochar produced at higher temperatures (B-550) may be contributing to its enhanced cadmium absorption compared to biochar produced at lower temperatures (B-450). This is because the temperature itself may not have a significant direct impact on cadmium absorption in this particular context. This is because biochar made at higher temperatures has a larger surface area and a higher pH, which can yield more CEC. The increased CEC of biochar improves the soil particles' capacity to adsorb heavy metals (Papageorgiou *et al.*, 2021). As a result, B-550 showed a stronger ability than B-450 to lower the cadmium levels in soil leachate.

$Cd_3(PO_4)_2$ and CdO make up the majority of the poplar sawdust biochar (PB-600 °C) following the adsorption procedure. This observation demonstrates the effective removal of Cd^{2+} from the soil as Cd^{2+} underwent precipitation with the mineral components at the elevated temperature of PB-600 °C, as reported by Cheng *et al.* (2021). Wang *et al.* (2021) claim that greater pyrolysis temperatures result in the production of additional heavy metal ion binding sites. According to Li *et al.* (2022), the biochar's surface area grows and the number of tiny pores increases as the pyrolysis temperature rises, potentially boosting the adsorption of heavy metals. According to Park *et al.* (2019), the specific surface area, the quantity of functional groups like C=C, and the exchangeable cation capacity all increase when the pyrolysis temperature rises to 600°C. A greater specific surface area is good for biochar's ability to absorb heavy metals. As the pyrolysis temperature increased, however, the average pore width in the biochar showed a discernable trend, demonstrating that the production of micropore structures became more noticeable in biochar generated at higher temperatures, as demonstrated by Xian *et al.* (2018). The rapid volatilization of organic components during the pyrolysis process at 300 °C led to the creation of wide pores on the surfaces of (*Pleurotus* *ostreatus* substrate) PC300 and (*Shiitake* substrate biochar) SC300 biochar. Biochar PC500 and SC500, on the other hand, showed a greater surface area, perhaps as a result of a layered structure. However, as a thin and smooth lamellar structure developed at higher pyrolysis temperatures (PC700 and SC700), the average number of pores dropped, according to a study by Xian *et al.* (2018).

According to Wang *et al.* (2021), the biochar's sulfur concentration grows as the temperature rises, and the existence of sulfur-containing functional groups is connected to the binding of Cd. Additionally, the H/C atomic ratios suggest that aromatic sheets or clusters form at high temperatures, which may facilitate interactions between the biochar and heavy metals as electron donors and acceptors (Wang *et al.*, 2021). According to the examination of the adsorption mechanism, the attraction to sulfur-containing functional groups and electron-rich C=C bonds is most likely what drives the removal of Cd (II) (Wang *et al.*, 2021). According to Wang *et al.* (2021), greater pyrolysis temperatures cause increased graphitization carbon and reduced functional groups, which significantly improve Cd adsorption. Their study highlights the substantial influence of pyrolysis temperature on biochar properties and adsorption behaviour, with BC900 demonstrating improved Cd(II) adsorption capabilities due to metal ion coordination, delocalized electrons, and an abundance of chemisorption sites.

Conclusion

The study investigated the impact of different rates of sawdust biochar application on the extractable Cd content in sandy loam soil over three-month period. It was found that treatment had a significant effect on Cd levels in the months of August and October 2023. Importantly, over the course of three months, the amount of extractable cadmium gradually decreased, with the highest rate of biochar application (5%) by showing the most significant reduction. Overall, higher biochar application rates led to a consistent decrease in cadmium concentration in the leachate, a phenomenon attributed to various factors including enhanced porosity, surface sites, contact between cadmium and biochar, changes in redox potential, and improved cadmium removal efficiency. Higher biochar application rates also had a more pronounced impact on soil pH and cation exchange capacity (CEC). The mechanism for heavy metal adsorption in soil using biochar primarily involves diffusion within the biochar's pores, although surface oxidation can increase available sites for adsorption. Moreover, increased pH resulted in enhanced Cd^{2+} adsorption capacity in the soil. In the specific case of Cd-contaminated soil with a Cd content of 3.7 mg/kg, the study recommends 6.7 t/ha of sawdust biochar application to mitigate Cd contamination effectively. Additionally, biochar produced at higher temperatures demonstrated greater cadmium absorption capacity, attributed to its higher surface area and pH, which enhances cation exchange capacity (CEC). The research emphasized that higher pyrolysis temperatures result in increased graphitization carbon content, decreased functional groups, and improved Cd adsorption capacity. These findings underscore the significant influence of pyrolysis temperature on biochar properties and its potential for Cd remediation. Additional research and tests would be required to precisely ascertain which elements or processes are in charge of the variations in cadmium absorption between these two different pyrolysis temperatures in the biochar.

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