The efficacy of chitosan-modified biochar in reducing heavy metal mobility

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ABSTRACT

Presently, the global concern for soil health stems from its direct impact on food safety. The extensive application of agrochemicals contributes significantly to the issue of soil pollution. The commonly identified pollutants in agricultural areas encompass heavy metals such as Pb, Cd, Cu, Zn, and various others. These toxic metals become entrenched in contaminated land and subsequently infiltrate plants, eventually accumulating in different plant tissues. This progression leads to the production of food that lacks the essential qualities for consumption. While soil enhancement agents like biochar and chitosan are widely acknowledged for their potential in bolstering soil health, their usage remains limited and often isolated. The granule coating technology offers a viable solution to address soil-related predicaments. The amalgamation of biochar and chitosan into granular structures, termed chitosan-coated biochar technology, represents an innovative approach to soil amendment, operating in a multifaceted manner. This research formulated sustainable soil amendment materials using the fabrication of biosan using granulation technology, followed by an extensive assessment of soil attributes and subsequent analyses. The amassed data were subjected to ANOVA at significance levels of 5% and 1%, followed by the BNT test in cases of significant variation. Specific parameters underwent descriptive analysis, which, which results showed that 100-mesh biochar, coated with a 20 grams/liter dose of chitosan, yielded a notably robust durability value of 81.83%. These results were not significantly different from the utilization of 60-mesh biochar alongside a chitosan dosage of 15 grams/liter. The 100-mesh biochar treatment exhibited the longest dispersion time at 182.50 minutes, while chitosan treatment recorded a dispersion time of 104.15 minutes. The use of biochar coated with humate emerged as a promising source of carbon and silica, boasting a carbon content ranging between 45.50% to 53.31% and Si content ranging from 15% to 22%. This formulation demonstrated efficacy in diminishing the concentrations of heavy metals, specifically Cu by 37.78% and Pb by 39.65%.

Keywords: modified biochar, durability, dispersion time, soil water capacity, soil heavy metal.

INTRODUCTION

Biochar plays a pivotal role in sustainable agriculture by significantly enhancing soil quality. As a soil amendment, biochar not only enriches soil fertility, but also improves water retention and nutrient availability, fostering vigorous plant growth. Its integration into soil systems leads to healthier soils and increased biodiversity, which in turn benefits the broader environment. Additionally, biochar excels in remediating contaminated

sites due to its extensive surface area and porous nature, allowing it to effectively adsorb and retain pollutants. This reduces the mobility and bioavailability of contaminants in soil and water, thereby helping to mitigate the environmental risks associated with hazardous substances.

The interplay between soil, heavy metals, and biochar is critical in addressing soil contamination and promoting sustainable agricultural practices. Heavy metals, such as cadmium, lead, and mercury can accumulate in soils due to industrial

activities, posing severe risks to plant and human health. Biochar, a carbon-rich material derived from the pyrolysis of organic biomass, has gained attention for its potential to immobilize heavy metals in contaminated soils. The application of biochar can alter soil pH, increase cation exchange capacity, and promote the formation of stable metal complexes, thereby reducing the mobility and bioavailability of heavy metals like lead, cadmium, and zinc. Research also has shown that biochar can effectively immobilize heavy metals in the soil through adsorption and complexation processes, thereby reducing their bioavailability and toxicity to plants (Ahmad et al., 2014).

Biochar, produced through the pyrolysis of organic materials like wood and crop residues, has shown great promise in reducing the availability of heavy metals in contaminated soils. Its highly porous structure and large surface area, combined with functional groups, such as hydroxyl, carboxyl, and phenolic groups, enable it to adsorb and immobilize heavy metals effectively. Studies have demonstrated that biochar amendments can significantly decrease the uptake of heavy metals by plants, thus mitigating their entry into the food chain. Additionally, the ability of biochar to persist in the soil for extended periods ensures long-term stabilization of heavy metals, making it a sustainable strategy for soil remediation.

Das et al. (2015) demonstrated that the behavior of biochar varied based on factors like pyrolysis temperature, feedstock type, and duration. The characteristics of biochar, such as its strong absorption capacity and anti-microbial properties (Das et al., 2016), make it potentially suitable for various applications. Additionally, the microstructure of biochar particles also influences their absorption capabilities (Choi et al., 2012). Biosorption is an effective and efficient treatment method in removing heavy metals due to its natural renewability and low production costs, as it allows for the recovery of contaminants either through biomass incineration or desorption (Martins et al., 2019). To enhance the capacity of biochar for heavy metal fixation and promote its practical application in environmental remediation, various modification methods, including acid-base modification, nano-material composites, and others, have been explored globally (Ahmad et al., 2014; Liu et al., 2020; Lehmann and Joseph, 2015; Inyang et al., 2016).

Currently, the most commonly used biochar modification techniques include physical, chemical, and biological modifications (Rajapaksha et al., 2016). Generally, the physical method is more suitable for real-world applications due to its ease of operation on a large scale. Chemical modification can alter the surface properties of biochar to suit specific applications, though it may require the use of potentially polluting or costly chemicals. Biological modification can also be applied on a large scale, but it typically requires a longer contact time to effectively change the structures and surface properties of the biochar (Xu et al., 2017; Tan et al., 2020).

The effectiveness of biochar in heavy metal immobilization varies depending on the feedstock used, pyrolysis conditions, and it can be enhanced through various methods, including coating techniques. Coatings with such materials as clay minerals, metal oxides, and organic compounds can alter the surface properties of biochar, improving its adsorption capacity and stability. For instance, coating biochar with iron oxide can create additional binding sites for heavy metals, thus enhancing its ability to immobilize metals like lead and cadmium. Similarly, the biochar coated with chitosan, a natural biopolymer, can increase its affinity for negatively charged metal species through electrostatic interactions. These modified biochars exhibit improved performance in heavy metal immobilization due to the synergistic effects of the coating materials, which enhance the physicochemical properties and functionality of the biochar, thereby reducing the bioavailability and environmental risk of heavy metals in polluted soils.

The chitosan-modified biochar composite has gained significant attention in recent years due to its potential applications in environmental remediation, particularly in the removal of heavy metal ions from contaminated soil (Bak et al., 2022). This composite combines the advantages of biochar and chitosan, enhancing its surface functional groups, adsorption sites, and stability, making it a promising material for soil decontamination (GAo et al., 2022). The inclusion of chitosan in the biochar matrix increases adsorption capacity, as seen in the results for the adsorption of various metal ions such as Pb (II), Cd (II), and Zn (II) (Basem et. al., 2024). The ability of the composite to remove heavy metal ions is attributed to the presence of amino and hydroxyl groups in chitosan, which facilitate the sorption of these ions. Additionally, the chitosan-modified biochar has been shown to be effective in removing other pollutants like dyes, and phosphates.

Biochar exhibited improved performance after modification with chitosan, which introduced additional functional groups ($-NH_2$ and $-OH$) that enhanced electrostatic interactions as well as complexation between methyl orange (MO) and chitosan-modified biochar (CSBC); thus increase the maximum capacity adsorption of CSBC for the MO dye (Loc et al, 2022).

Overall, the research on modified biochar with chitosan illustrates a promising approach to enhance the functionality and applications of biochar, addressing both environmental and agricultural challenges with sustainable solutions. The main challenge in using modified biochar chitosan for soil remediation is the lack of comprehensive knowledge regarding its long-term effectiveness and environmental interactions. Challenges include optimizing the modification process to ensure uniformity and stability of the biochar-chitosan composite. It is necessary to assess the efficacy of this composite in different soil types, pH levels, and environmental conditions. Moreover, there is a lack of complete understanding regarding the processes involved in the adsorption of heavy metals and the long-term stability of these metals within the soil. This uncertainty gives rise to the concerns about the possibility of metal leaching and the availability of these metals to living organisms. To effectively and sustainably employ modified biochar chitosan in soil remediation, it is crucial to conduct extensive investigations on how it interacts with soil components. Additionally, standardized application methods need to be developed. This will help address the gaps in knowledge and ensure its successful implementation (Ren et al., 2020; Zhu et al., 2021).

MATERIAL AND METHODS

Sample preparation

Modified chitosan-coated biochar was employed by a two-step process involving the preparation of biochar followed by chitosan coating. First, biochar was produced by pyrolyzing biomass feedstock, such as agricultural waste or wood, at high temperatures (typically 600–700 °C) in an oxygen-limited environment. This process yields a porous, carbon-rich material. The biochar that passed the 40, 60, and 100 mesh was then mixed and blended with starch in an amount of 20 grams as a binding agent to facilitate the

granule formation. This mixture was then subjected to pan granulation resulting in uniform particles. The granulation process continued for 10 minutes until granules formed, with an average diameter of 2 to 5 mm. Next, chitosan powder, a biopolymer derived from chitin, i.e. 10, 15 g, and 20 g was dissolved gradually in a 1% acetic acid solution by stirring it until fully dissolved, and then the solution was filtered and ready to use.

The biochar was then mixed and coated with the chitosan solution, ensuring even coverage through mechanical agitation. Following this, the coated biochar dried at moderate temperatures, typically between 60 to 80 °C. The drying procedure persisted until the moisture content of the granules materialized within the range of 9% to 12%. This drying step removes excess solvent and secures a strong bond between the chitosan and the biochar surface. This modification enhances the surface properties of biochar, increasing its ability to adsorb various pollutants, including heavy metals and organic contaminants (Qiu et al., 2019; Tan et al., 2020). To study the long-term stability and viability of biochar as a soil amendment, it is essential to test the strength of biochar to ensure its durability and performance in various applications. There are three parameters that need to be measured, i.e. (1) Durability test; (2) Water absorbance ability; and (3) Dispersion time.

Durability test

The durability and persistence of biochar will impact heavy metal mobility. The major objective of the durability test of chitosan coated biochar was to objectively assess the physical characteristics of the chitosan-coated biochar granules. The durability of the granules was determined by mechanical durability test, i.e. abrasion resistance test. The durability test will determine the mechanical quality of the granules. This was accomplished by quantifying the proportion of the granules that remained intact, using a physical testing device in the shape of a shaker. This process involved placing 500 grams of chitosan coated biochar granules into a shaker or rotated in a drum with abrasive materials and shaking it for a period of 10 minutes. Biochar granules are tumbled or rotated in a drum with abrasive materials. The amount of material lost due to abrasion over time is measured. Following this the shaker was deactivated, and the intact granules of chitosan coated biochar were measured in weight.

$$\% \ Durability \ = \frac{m_o}{m_i} \cdot 100\% \qquad (1)$$

where: m_o – entire granule weight (g), m_i – initial weight of granule (g).

Water absorbance ability

The water absorption test was conducted to assess the capacity of the granules to absorb water when soaked. The water absorption test using the gravimetric method. For this test, 5 grams of chitosan-coated biochar granules were immersed in water for 1 hour, to ensure the entire surface was submerged. Then, the unbroken granules were taken out and removed from the water, and the remaining solution was collected and dried in an oven, cooled in a desiccator for about 5 minutes, and then weighed. The water absorption capacity of the granules is calculated using the following equation.

$$Water \ Absorbance \ (\%) = \frac{m_a - m_b}{m_a} \cdot 100\% \ (2)$$

where: m_a – wet granule weight (g), m_b – dry granule weight (g).

Dispersion time

The dispersion time was evaluated by adding 5 grams of chitosan-coated biochar granules to a beaker filled with 100 ml of water. The time required for the granules to break down was then observed and recorded. A longer disintegration time suggested improved physical properties of the granules, according to the findings from the referenced study (Utari et al, 2015).

Research experiment

The experiment involved 5 kg of soil and two treatment factors. The first factor was the biochar particle size (B), with three levels: B1 at 40 mesh, B2 at 60 mesh, and B3 at 100 mesh. The second factor was the chitosan concentration (C) used as a coating material, with three levels: C1 at 10 g/L, C2 at 15 g/L, and 20 g/L. The experiment was replicated three times, resulting in 24 experimental pots. The treated soil was maintained at field capacity, and each pot was covered with plastic. The pots were then placed in a screen house for 4 weeks, with the incubation period lasting 1 month. The purpose of the experiment was to evaluate the effectiveness of the chitosan-coated biochar in mobilizing heavy metals. Soil samples were collected at the start and end of the experiment to measure the available heavy metal content. The copper (Cu) and lead (Pb) levels were analyzed to determine the reduction in heavy metal percentages due to the addition of biochar-coated chitosan. Additionally, the characteristics of chitosan-coated biochar were examined using scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS).

RESULTS AND DISCUSSION

Effect of particle size of biochar and coating thickness on the durability

The durability of biochar is influenced by several important factors, including particle size, surface area, chemical composition, and environmental conditions to which it is exposed. An essential factor influencing the durability of biochar is its particle size; smaller particles often have larger surface areas, which can enhance their reactivity, but also make them more susceptible to degradation. The elemental composition of biochar, which includes its carbon content and the presence of stable aromatic compounds, plays a vital role in determining its capacity to resist microbial breakdown and chemical weathering. Moreover, environmental factors, such as temperature, moisture content, and the presence of microorganisms can either accelerate or decelerate the degrading process. Recent research has indicated that the biochar with more aromaticity and more stable carbon structures has improved durability, particularly in soil and environmental conditions (Liu et al., 2021; Wang et al., 2022). Moreover, the application of coatings on biochar, leading to the formation of a protective barrier against environmental factors, has been shown to enhance its durability, hence improving its ability to withstand prolonged usage (Zhao et al., 2023). The results suggest that by optimizing the manufacturing procedures and post-production treatments of biochar, its resistance to degradation can be significantly improved, thereby enhancing its effectiveness in environmental and agricultural applications.

The effect of biochar granulation size and the thickness of the chitosan coating on the treatment results can be observed in the table. The treatments with smaller biochar granule sizes and thinner chitosan coatings, such as B1K1 (69.40 ± 2.33) and B1K2 (71.10 ± 1.26), show relatively lower average values and are grouped under "b," indicating less effectiveness compared to other

treatments. As the granulation size increases or the chitosan coating thickens, the performance improves, as seen in B1K3 (77.62 ± 2.66) and B2K1 (78.22 ± 2.21), both labeled "d." However, B2K2 (75.74 ± 4.04), B3K1 (76.57 ± 3.62), and B3K3 (75.02 ± 2.91), grouped as "c," suggest that further increases in granulation size or coating thickness reach a threshold where performance plateaus or even slightly decreases. Interestingly, B2K3 (63.95 ± 2.34), the lowest result labeled "a," indicates that too large a granule size or too thick a coating can reduce effectiveness. Meanwhile, B3K2 (79.78 ± 3.08), labeled "e," demonstrates that optimal granulation and coating thickness can lead to the highest performance. These findings suggest that both granulation size and coating thickness significantly impact performance, with an optimal range for maximizing the desired outcome.

The results from the analysis of the assortment of particle sizes and chitosan concentration on durability are provided in Table 1.

The effect of biochar granulation size and chitosan coating thickness on various treatment results can be understood by analyzing the interaction between these two factors. On the basis of the data provided, it is evident that the treatments with different biochar particle sizes and chitosan coating thicknesses showed significant variation in performance. For instance, treatments B1K3, B2K1, and B3K2, which involved larger biochar granulation sizes and thicker chitosan coatings, resulted in higher average values (77.62, 78.22, and 79.78, respectively). This suggests that larger

Table 1. Effect of particle size and chitosan dosage on durability treatment

Treatment	Average	
B1K1	69.40 ± 2.33	b
B1K2	71.10 ± 1.26	b
B1K3	77.62 ± 2.66	d
B2K1	78.22 ± 2.21	d
B2K2	75.74 ± 4.04	c
B2K3	63.95 ± 2.34	a
B3K1	76.57 ± 3.62	c
B3K2	79.78 ± 3.08	e
B3K3	75.02 ± 2.91	c

Note: numbers followed by the same letter in the same column are not significantly different. Particle size of biochar (B), B1=40 mesh, B2=60 mesh, B3=100 mesh. Chitosan concentration (C), K1=10 g/l, K2=15 g/l, K3=20 g/l water.

granulation sizes paired with thicker coatings enhance performance, potentially due to improved structural integrity and nutrient release mechanisms provided by the biochar-chitosan matrix.

Conversely, treatments like B2K3, with smaller granulation sizes and thinner coatings, showed lower average values (63.95), indicating that reduced particle size and thinner coatings may limit the efficacy of nutrient delivery and water retention, leading to less desirable results. The use of biochar in larger particle forms improves the surface area for absorption and retention, while thicker chitosan coatings provide better protection and slow release of nutrients, as shown in studies on role of biochar in coating and nutrient delivery systems. This observation aligns with recent research showing that both biochar particle size and the thickness of coatings can influence physical properties like nutrient retention, structural stability, and overall performance in agricultural applications.

Durability and water sorption are critical factors in evaluating the long-term performance of materials, particularly in the environments exposed to moisture. Durability refers to a ability of a material to withstand physical, chemical, and environmental stresses over time without significant degradation. In contrast, water sorption measures how much moisture a material absorbs when exposed to humid or wet conditions. A high degree of water sorption can compromise the structural integrity of materials by causing swelling, deformation, or weakening of the material bonds, thereby reducing durability. The materials that exhibit low water sorption tend to have higher durability, as they resist moisture-induced damage such as cracking, erosion, or microbial growth. Conversely, the materials with high water sorption often show signs of wear, such as dimensional changes, loss of mechanical strength, or even failure over time. Testing for both durability and water sorption is therefore essential in the applications where materials are expected to face constant or intermittent exposure to moisture, such as in construction, packaging, or biomedical devices. Understanding the balance between durability and water sorption helps in selecting the right materials for specific environments, ensuring that performance is maintained over the intended lifespan of the material.

The increase in biochar durability across treatments suggests that higher granulation sizes improve mechanical stability, likely due to enhanced

surface area and better water retention capacity. The ability of biochar to increase durability over time can be attributed to its porous structure and high stability, which helps improve the resistance of a material to environmental degradation. These findings are in line with recent studies, which indicate that larger biochar particles improve mechanical strength in composite systems (Zhang et al., 2023). Chitosan exhibits high durability in earlier treatments, peaking at treatment 2, but it declines in treatment 3. This drop may be due to an overly thick chitosan coating, which can reduce flexibility and make the material more brittle, causing it to degrade faster. Research shows that while chitosan coatings are highly effective in moderate thicknesses, excessive thickness can compromise the properties of the material by making it less resistant to external stress (Yu et al., 2021) (Figure 1).

Studies have shown that biochar granulation size can greatly influence the durability and effectiveness of coated materials. For example, the research on biochar-coated seeds has demonstrated that the optimal granulation size provides a balance between mechanical strength and nutrient release. Similarly, the coatings with chitosan have been widely studied for their biocompatibility and mechanical properties, but excessive coating thicknesses often lead to reduced effectiveness due to the brittleness introduced by over-application. The trends seen in the graph mirror these findings, suggesting that while both biochar and chitosan improve durability, there are clear thresholds for optimal performance. This analysis highlights the importance of finding the right balance in biochar granule size and chitosan coating thickness to maximize material durability.

Water absorbance ability test

The water absorption ability of biochar is crucial for several reasons, particularly in agricultural and environmental applications: (1) The porous structure of biochar allows it to absorb and retain significant amounts of water, which can be gradually released into the soil. This improves water availability for plants, especially in arid or drought-prone regions. Studies have demonstrated that biochar-amended soils can hold more water, enhancing plant growth and reducing the need for irrigation. The water absorption of biochar also aids in retaining nutrients within the soil. The water absorption capacity of biochar makes it a valuable tool for enhancing agricultural productivity, improving soil health, and mitigating the impacts of drought, which is why its use has gained significant attention in sustainable agriculture practices (Figure 2).

Biochar shows a relatively stable pattern, starting at 56.96% (B1), peaking at 58.38% (B2), and slightly declining to 56.98% (B3). On the other hand, chitosan begins with a similar value to biochar at 57% (C 1), then drops to 55.44% (C2), before significantly increasing to 59.88% (C3).

The water sorption capacity of biochar shows a slight improvement from C1 to C2, but declines marginally in C3. This slight fluctuation can be attributed to the inherent porous structure of biochar, which typically allows it to absorb and retain moisture effectively. Research has shown that
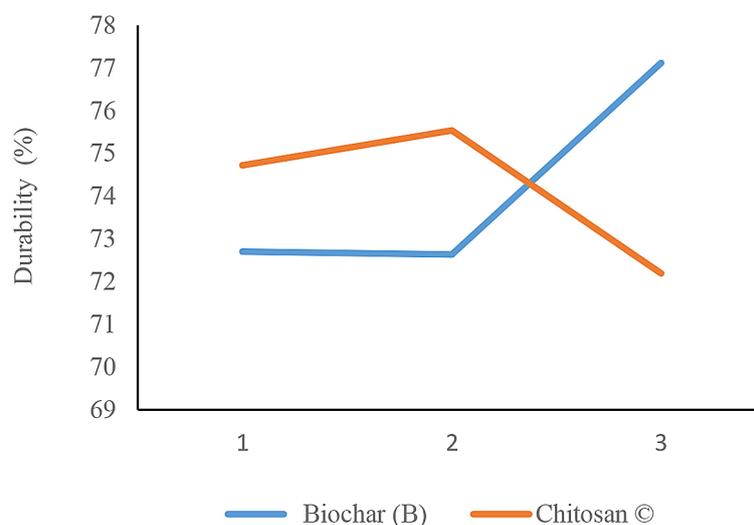

Figure 1. The effect of size of biochar and chitosan concentration on durability of biochar
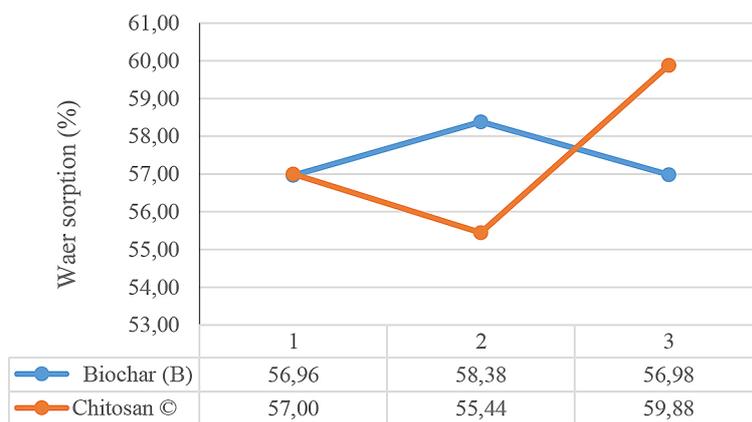
Figure 2. The effect of size of biochar and chitosan concentration on durability of biochar

the water retention properties of biochar depend heavily on its particle size and surface area, where larger granules tend to improve water sorption (Yu et al., 2021). The stability of biochar water sorption across treatments is consistent with the findings that the hydrophilic properties of biochar enable it to retain moisture at moderate levels. In contrast to biochar, the water sorption of chitosan decreases between C1 and C2, but dramatically increases in C 3. This surge in C3 suggests that thicker chitosan coatings may enhance its capacity to absorb water, although its performance in earlier treatments shows a decline. The water sorption of chitosan is likely influenced by its coating thickness, where thinner coatings (as in C 2) reduce water retention. Previous studies have shown that the ability to absorb water exhibited by chitosan is highly dependent on its thickness and the application method.

These trends are in line with existing research. Studies suggest that the moderate increase in water sorption characterizing biochar can be linked to its high surface area and porous structure, which allows it to store moisture efficiently (Zhang et al., 2023). On the other hand, the fluctuating water sorption of chitosan is more sensitive to its coating thickness. Thin layers may not provide enough surface area to absorb water, while thicker layers, as seen in chitosan with, improve water retention by creating a larger surface area for absorption. Biochar demonstrates stable water sorption capabilities across the treatments, while chitosan shows a significant dependency on its coating thickness, improving water absorption as the thickness increases (Table 2).

B2K3 (64.10) and B1K3 (59.94) exhibit the highest water absorption values. This suggests that under these specific conditions (likely related to larger biochar granulation size or thicker chitosan coatings), the materials demonstrate superior water retention abilities. This can be linked to either the increased porosity of biochar or more effective water holding capacity of the chitosan coating. In contrast, B1K2 (53.77) has the lowest water absorption capacity. This lower value could be indicative of an insufficient biochar granulation size or a chitosan coating that is too thin, reducing its ability to hold water effectively. Thin coatings or smaller granule sizes may lead to less surface area available for water retention. Several treatments, including B1K1 (57.18), B2K1 (55.60), B2K2 (55.46), B3K1 (58.22), B3K2 (57.11), and B3K3 (55.61), fall within a middle range of water absorption values. These treatments likely represent more balanced conditions, where both biochar granulation size and chitosan coating thickness are optimized for moderate water retention.

Table 2. Effect of particle size and chitosan dosage on water sorption ability

Treatment	Average	
B1K1	57.18 ± 6.93	b
B1K2	53.77 ± 8.87	b
B1K3	59.94 ± 7.50	d
B2K1	55.60 ± 9.07	d
B2K2	55.46 ± 10.10	c
B2K3	64.10 ± 6.45	a
B3K1	58.22 ± 10.38	c
B3K2	57.11 ± 8.28	e
B3K3	55.61± 7.38	c

Note: numbers followed by the same letter in the same column are not significantly different. Particle size of biochar (B), B1=40 mesh, B2=60 mesh, B3=100 mesh. Chitosan concentration (C), K1=10 g/l, K2=15 g/l, K3=20 g/l water.

This pattern of results aligns with studies that suggest that both biochar particle size and chitosan coating thickness are crucial in determining water retention capacity. Research has shown that the biochar with larger granule sizes tends to have higher porosity, which improves water sorption by increasing the available surface area for water absorption (Zhang et al., 2024 ;Yu et al., 2021). Similarly, chitosan, when applied in optimal thicknesses, can enhance water retention, but excessively thick coatings may lead to a drop in performance due to brittleness and cracking (Yu et al., 2021).

Dispersion time

Dispersion time refers to the amount of time it takes for a material to disperse or spread evenly in a liquid. The dispersion time of biochar granules can vary widely depending on the specific application and conditions. It depends on: (1) Particle size: Smaller granules tend to disperse more quickly than larger ones; 2) surface properties: the surface characteristics of the biochar, such as hydrophobicity or hydrophilicity, can affect its dispersion rate; (3) water quality: the properties of the water, such as pH, temperature, and salinity, can influence dispersion, and (4) stirring conditions: The speed and intensity of stirring can affect the dispersion process. Figure 3 shows that the dispersion time of biochar increases significantly for all treatments. This indicates that biochar becomes more difficult to disperse as time progresses.

The dispersion properties of biochar and chitosan can be crucial in various applications, such as water treatment, agriculture, and food processing. Understanding their dispersion behavior can help optimize their use in these fields. If the dispersion properties of biochar or chitosan are not suitable for a particular application, modifications can be made to improve them. For example, surface treatments or chemical modifications can alter the hydrophobicity or particle size of these materials.

Table 3 presents averages and standard deviations for various treatments, labeled from B1K1 to B3K3. Each value reflects a specific property (possibly water absorption or another material property related to biochar and chitosan), with accompanying significance levels indicated by letters (a, b, c, etc.). The data shows a clear trend of increasing values from the B1 treatments to the B3 treatments, which suggests that the treatments in the B3 group likely involve conditions (such as larger biochar granulation or thicker chitosan coating) that enhance the performance of the material.

B1K1 (30.56 ± 6.29, "a") has the lowest average, suggesting that this treatment produced the least effective results. The B1K2 (48.51 ± 14.92, "b") and B1K3 (48.17 ± 11.83, "b") are statistically similar but perform better than B1K1. These values likely represent smaller biochar particles or thinner chitosan coatings, which limit their performance in terms of the measured property. The highest values are seen in the B3 group, with B3K3 achieving the maximum value (154.45 ± 41.57, "i"), followed by B3K2 (122.70 ± 28.81, "h") and B3K1 (95.97 ± 14.52, "g"). This dramatic increase in performance likely results from the optimal biochar granulation size and chitosan coating thickness, suggesting that these conditions are the most favorable for the studied parameter. Research suggests that the size of biochar particles significantly impacts properties such as
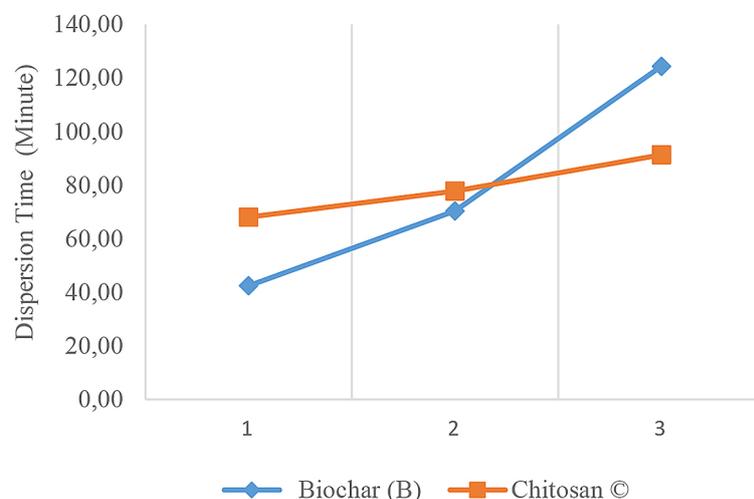

Figure 3. The effect of size of biochar and chitosan concentration on dispersion time of biochar

Table 3. Effect of particle size and chitosan dosage on water sorption ability

Treatment	Average	
B1K1	30.56 ± 6.29	a
B1K2	48.51 ± 14.92	b
B1K3	48.17 ± 11.83	b
B2K1	77.59 ± 11.76	f
B2K2	62.22 ± 18.35	c
B2K3	71.24 ± 15.16	e
B3K1	95.97 ± 14.52	g
B3K2	122.70 ± 28.81	h
B3K3	154.45 ± 41.57	1

Note: numbers followed by the same letter in the same column are not significantly different. Particle size of biochar (B), B1=40 mesh, B2=60 mesh, B3=100 mesh. Chitosan concentration (C), K1=10 g/l, K2=15 g/l, K3=20 g/l water.

water retention, sorption capacity, and durability. Larger biochar granules provide more surface area for water absorption and retention, as well as improved structural integrity in composite materials. For instance, studies by Liang et al. (2021) found that increasing biochar particle size improved its water holding capacity, aligning with the trends seen in the B3 treatments in this table.

Chitosan is widely studied for its coating properties, particularly in enhancing water retention, material strength, and biodegradability. Thicker chitosan coatings can provide better structural integrity and moisture barriers. However, excessively thick coatings can sometimes lead to a loss of flexibility and even brittleness. The research by Zhou et al. (2020) also showed that moderate increases in chitosan coating thickness on biochar resulted in higher water absorption and durability, which corresponds to the performance improvements seen in the B3 treatments in this table.

Characterization of the chitosan-coated biochar

The process of characterizing the chitosan-coated biochar involved the utilization of Scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS). This technique was employed to assess the surface attributes and elemental composition of the subject material under examination. The outcomes of image and spectrum analysis conducted for each treatment are visually displayed in Figure 4. The outcomes presented in Figure 5, derived from SEM analysis, reveal that when utilizing a 20 µm particle size,
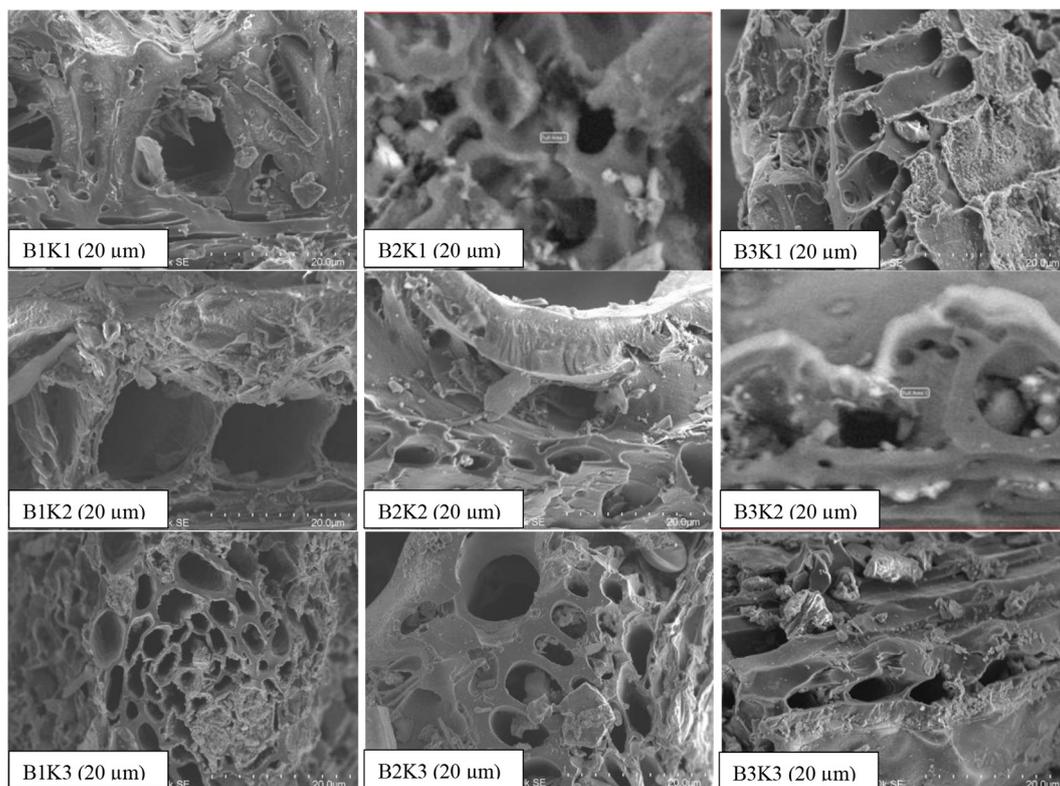

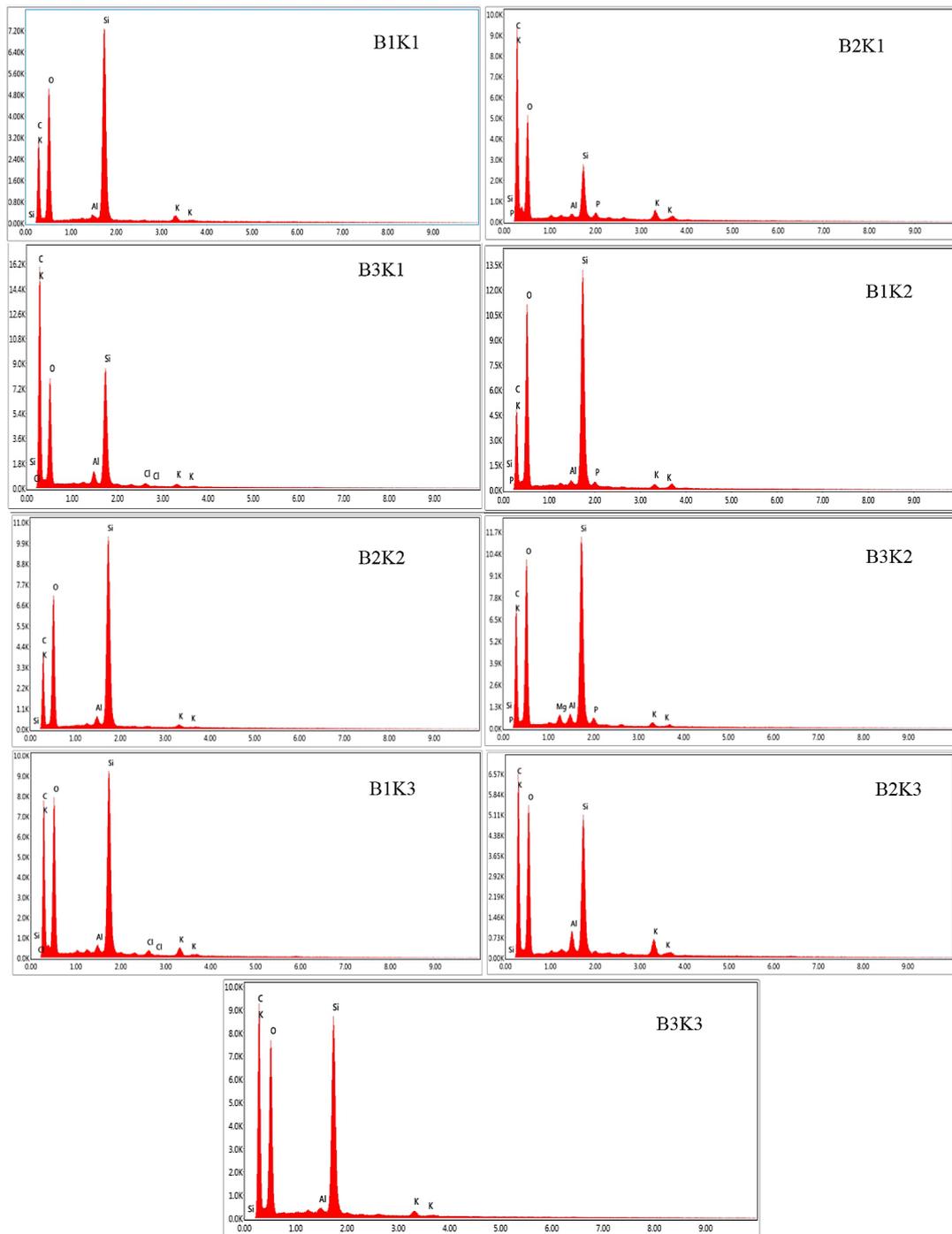**Figure 4.** The results of SEM-EDX on chitosan-coated biochar

Figure 5. The EDS spectrum of chitosan-coated biochar

the application of chitosan treatment results in visibly expanded pore size distribution. A discernible trend emerges wherein smaller mesh sizes correspond to reduced pore dimensions. Additionally, the incorporation of elevated chitosan dosages holds the potential to yield smaller pore sizes. This observation highlights the proficient adsorption attributes of biochar, with the chitosan coating playing a significant role. The introduction of chitosan coating contributes to the filling of larger

pore spaces within the biochar, thereby leading to the formation of smaller pores (Basem, 2024).

Chitosan was chosen because of its amine- and hydroxyl-rich functional groups, which offer divalent metal ions strong coordination sites. However, comparison with other biopolymers (such as alginate, starch, or xanthan gum) is still a crucial avenue for further optimization research.

This study indicated that as the dose of chitosan increased, the size of the pore spaces decreased

in comparison to a lower chitosan dose. This illustrates the potential of biochar, enriched with chitosan, to effectively occupy and reduce pore spaces. For instance, straw biochar treated with Fe exhibited an absorption capacity of 35.43 mg g^{-1}, whereas untreated biochar managed to absorb only approximately 15.44 mg g^{-1} (Mahapatra et al., 2021).

The SEM-EDX analysis depicted in Figure 5 indicates that the pore spaces are poised to serve as habitats for microbes, facilitating the nutrient release process. Specifically, the incorporation of biochar can intricately impact the nutrient cycle of soil by retaining and absorbing nutrients, enhancing their bioavailability, and mitigating leaching concerns (Schmidt et al., 2021). Notably, in both acidic and alkaline soils, it can dramatically elevate the release of K, P, and Mg by a factor of approximately 40-50, with even higher rates observed in alkaline soils (Shi et al., 2019). Furthermore, a separate study (Shu et al., 2023) demonstrated that the introduction of biochar led to an increase in the overall quantity of heavy metals present in the soil. However, a significant proportion—ranging from 43% to 97%—of these heavy metals in the amended soil remained confined within the less bioavailable residual fraction. This outcome highlights the potential of biochar and chitosan supplementation in curbing the accumulation of heavy metals. Consequently, the application of chitosan-coated biochar holds promise as a means to effectively regulate and enhance soil quality (Gonzaga et al., 2019).

The outcomes derived from the EDS spectra analysis, as depicted in Figure 5, illustrate discernible peaks corresponding to the elements Si, C, O, P, Al, Mg, and K. Among these, the most prominent peaks pertain to Si and are evident in Figure 5 as K1B1. K2B1. and K3B1. Additionally, the presence

of elements O, C, and K is consistently detected across nearly all treatments. The preeminent element O is notably abundant, encompassing a range of 30% to 44%. Analogously, elements C and K follow similar patterns within this range. For a comprehensive understanding of the elemental composition of each sample, please refer to Table 4.

The findings presented in the table above reveal the prevalence of several key elements, including C, O, Al, Si, and K, each exhibiting varying concentrations. Conversely, elements such as P, Cl, and Mg are either undetected or absent. The low concentrations of Mg, Cl, and P in comparison to SEM–EDS detection limits, as well as partial volatilization and redistribution during high-temperature pyrolysis, may be the cause of their absence or non-detection in some samples. Additionally, the loss of certain elements during the high-temperature combustion process, when some elements may have undergone deterioration, could be the reason for their absence.

The highest recorded C concentration reached 53.31%, closely resembling findings from a prior study (Beillouin et al., 2023) which reported an average C content of 65%. Divergent outcomes were observed in investigations conducted by other researchers analyzing activated carbon sourced from coconut shell material; here, a significantly higher C content of 82.92% was achieved (Budi et al., 2012). This variance can be attributed to the dissimilarity in fundamental materials employed. Specifically, our study utilized rice husk biochar as the base material subjected to pyrolysis. The implications of applying biochar and similar organic amendments extend to the enhancement of soil health with enduring effects. This, in turn, has the potential to yield favorable outcomes for crop production (Hamzah, Priyadarshini, and Astuti, 2022).

Table 4. The element composition of EDS analysis outcome of chitosan-coated biochar

Treatment	Element (%)							
	C	O	Al	Si	K	P	Cl	Mg
B1 K1	35.19	39.87	0.95	22.47	1.52	-	-	-
B2 K1	49.37	39.75	0.71	6.6	2.72	0.84	-	-
B3 K1	53.31	32.89	1.48	11.24	0.57	-	0.52	-
B1 K2	31.81	44.37	0.8	21.61	0.88	0.53	-	-
B2 K2	34.20	40.41	1.51	23.3	0.85	-	-	-
B3 K2	38.08	40.24	1.1	17.68	0.91	0.87	-	1.12
B1 K3	42.09	38.68	0.94	15.89	1.62	-	0.77	-
B2 K3	43.49	38.57	2.39	12.37	3.17	-	-	-
B3 K3	45.50	38.19	0.73	14.71	0.88	-	-	-

Heavy metal content reduction

The outcomes derived from the soil analysis demonstrate the efficacy of chitosan-coated biochar in mitigating the presence of heavy metals, specifically Pb and Cd, as depicted in Figure 6. Notably, the utilization of chitosan-coated biochar proves to be notably effective in regulating the concentrations of Cu and Pb heavy metals. Heavy metals, characterized by their intrinsic resistance to degradation, pose a significant challenge. However, the employment of biochar coated with humate showcases a promising approach to diminish the concentrations of Cu and Pb heavy metals.

The figure illustrates the changes in copper (Cu) and lead (Pb) concentrations before and after treatment, together with their respective percentage reductions. Prior to treatment, the Cu and Pb concentrations were 89.71 and 55.82 mg kg^{-1}, respectively. Following treatment, Cu decreased to 33.89 mg kg^{-1}, while Pb declined to 10.23 mg kg^{-1}, corresponding to removal efficiencies of 62.22% for Cu and 81.67% for Pb. This decline is attributed to the potential of chitosan-coated biochar to disrupt the ionic bonds sourced from organic acids. Notably, biochar emerges as a promising soil amendment material with regulatory capabilities for soil enhancement (Hamzah et al., 2021).

The markedly higher reduction observed for Pb indicates a stronger immobilization mechanism compared to Cu. This behavior is consistent with the higher affinity of Pb for negatively charged surfaces and oxygen-containing functional groups commonly present on chitosan-modified biochar, resulting in enhanced surface complexation and stabilization (Beesley et al., 2011; Uchimiya et al., 2011; Zhang et al., 2022). In contrast, Cu tends to exhibit greater mobility due to its stronger hydration shell and competitive complexation in soil solution, which can limit its sorption efficiency (Park et al., 2011).

The effective reduction of both metals confirms the potential of chitosan-coated biochar as a soil amendment for heavy metal remediation (Ahmad et al., 2014; Liu et al., 2023). Nevertheless, this study focused exclusively on rice husk-derived biochar, and the influence of alternative biomass feedstocks was not evaluated. Considering that the physicochemical features of biochar and its ability for metal immobilization differ based on biomass type, it is imperative that future studies conduct comparative assessments utilizing the biochars generated from alternative feedstocks, such as woody or manure-based materials. Given that the physicochemical properties and metal immobilization capacity of biochar vary with feedstock type, future studies should compare the biochars derived from woody or manure-based materials to optimize remediation performance (Ahmad et al., 2014). These findings are consistent with previous reports on nano-biochar and chitosan-based amendments demonstrating enhanced heavy metal stabilization in contaminated soils (Taraqqi et al., 2021; Liu et al., 2023).

Prior research (Taraqqi et al., 2021) has demonstrated the pollution-controlling capabilities of nano biochar. In this context, the current study utilized nano-biochar of varied sizes, aligning with the aforementioned research. This principle extends to chitosan as well, as indicated by (Tripathi
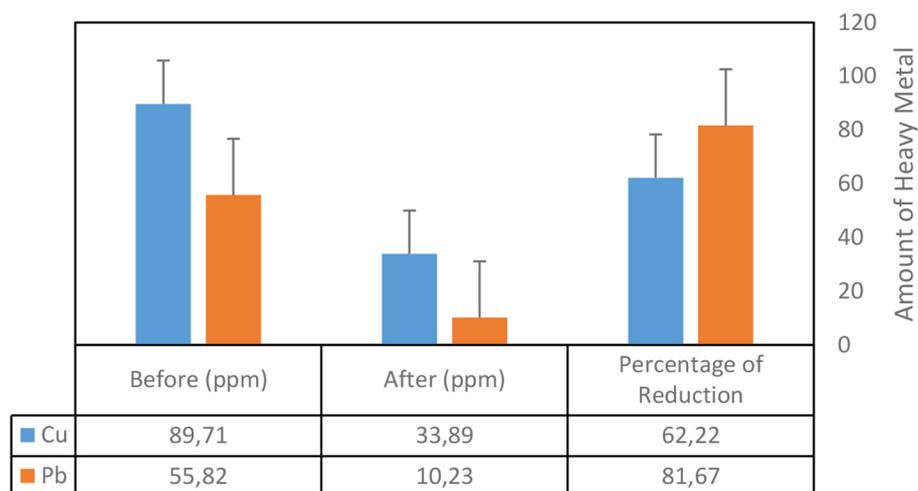
	Before (ppm)	After (ppm)	Percentage of Reduction
■ Cu	89,71	33,89	62,22
■ Pb	55,82	10,23	81,67

Figure 6. The reduction of Cu and Pb heavy metals

et al., 2017), where the combination of chitosan and mono-calcium phosphate successfully curtails the bioavailability of Zn. Likewise, Sealin, an agent applied in remediating the soil contaminated with As, Pb, and P, achieved reductions of 17.00%, 1.80%, and 31.00% respectively. It is important to note that the depicted figures remain higher than those attained in the present study.

CONCLUSIONS

The utilization of 100-mesh-sized biochar coated with a dose of 15 grams per liter of chitosan exhibits a high durability value (79.78 with dispersal times of 122.70 minutes.

SEM-EDX analysis results indicate that the use of the chitosan-coated biochar holds potential as a source of carbon and silica due to its content ranging between 45.50% to 53.31% for carbon and 15% to 22% for silica.

The application of the chitosan-coated biochar is capable of reducing Cu and Pb by 37.78% and 39.65%, respectively.

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