

Article

Fixation Effect of Modified Bamboo Charcoal on Typical Heavy Metals in Sediment

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Abstract: In this study, we studied the influence of the dosage of modified bamboo charcoal (KAM-500-400-3) on the fixation effect of single Cu(II)-contaminated and mixed Cu(II)–Cd(II)-contaminated sediment. The results showed that it could effectively fix the heavy metals in both sediment types. In the single Cu(II)-contaminated sediment, when the amount of added KAM500-400-3 was greater than or equal to 5%, the Cu(II) content in the overlying and pore water was substantially reduced, and the form of heavy metal Cu(II) in the sediment changed from the acid-extractable state to a relatively stable, reducible, oxidizable, and residual state, its bioavailability markedly reduced, and the toxic leaching amount of heavy metal TCLP in the sediment also gradually reduced. In the sediment polluted by Cu(II)–Cd(II), the Cu(II) and Cd(II) could not be detected in the overlying or pore water when the addition amount was greater than or equal to 2.5%. The contents of Cu(II) and Cd(II) in the acid-extractable state considerably decreased and they transformed into other forms with low bioavailability, in which the content of Cd(II) in the oxidizable state was so low that it was lower than the detection limit. The TCLP toxicity of the leached amount of Cd(II) also gradually decreased. This showed that adding KAM500-400-3 to sediment helps with inhibiting the release of heavy metals from contaminated sediment into water bodies, so KAM500-400-3 is a material that can effectively adsorb and fix heavy metals Cu(II) and Cd(II) in sediment.

Keywords: modified bamboo charcoal; heavy metal fixation; sediment; Cu; Cd



Citation: Wang, Y.; Li, H.; Lin, S. Fixation Effect of Modified Bamboo Charcoal on Typical Heavy Metals in Sediment. *Water* **2023**, *15*, 1230. <https://doi.org/10.3390/w15061230>

Academic Editor: Catherine N. Mulligan

Received: 11 February 2023

Revised: 13 March 2023

Accepted: 15 March 2023

Published: 21 March 2023



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1. Introduction

With the continuous improvement in people's daily lives and in industry production levels, the heavy metal pollution of water and sediment is worsening. Additionally, the sources of heavy metals are wide-ranging, from industrial production industries such as the machinery processing, steel, and nonferrous metal smelting industries. The emissions from automobile exhausts, the disposal of batteries, and the abuse of agricultural fertilizers are also causing serious heavy metal pollution of river-bottom mud [1,2].

The composition of surface river and lake sediments is complex, mainly including clay, sediment, organic matter, and various mineral bodies [3,4]. Heavy metals in sediment mainly originate from polluted water bodies, and a series of transformation and migration processes such as adsorption–desorption, precipitation–dissolution, complexation–decomplexation, ion exchange, and redox occur between the sediment and the water body [5].

Because of their slow mobility and long residence time, heavy metals in the sediment are not degraded easily by microorganisms [6], and if they are not treated in time, they will become a “new source of pollution”, polluting the water body twice, poisoning the plants and animals in the water, and then further endangering human life and health through transmission via the food chain [7]. The problem of how to treat heavy metals in river sediments and water bodies has become a pressing one [8].

Long-term exposure to heavy metal ions can cause serious harm to the human body, e.g., the activity of enzymes, the nervous system, and some organs with detoxification

functions will be affected [9]. The use of water contaminated with heavy metals can cause direct harm to the human body; for example, in the 1950s and 1960s, Japanese production mines exceeded the Cd(II) standard in nearby waters, causing some nearby residents to suffer from “bone pain”, leading to osteochondrosis and general pain. Furthermore, the accidental release of chemicals containing Hg(II) in Taiwan has contaminated the soil in several locations, and the consumption of crops grown on these soils can cause the heavy metal Hg(II) in the human body to exceed the limit. When people consume Hg(II)-poisoned fish, they will suffer from neurological toxicity, impaired sensation at the ends of their limbs, and narrowed vision [10]. The problem of how to deal with heavy metals in river sediments and water bodies has become pressing [8].

Adsorption is the most commonly used method for treating heavy metals in water bodies and sediments, with the main advantages of being renewable, low cost, creating no “secondary pollution”, and being suitable for treating various concentrations of wastewater.

Biochar is a carbon-rich product obtained by charring biomass, and it has been widely studied for its advantages of low cost and a wide range of sources. With its large porosity as well as specific surface area and the presence of many functional groups on its surface, it is an efficient and low-cost adsorbent and is often widely used to remove heavy metal pollutants from water [11]. Singh et al. conducted batch experiments on Cu(II), Cr(VI), Cd(II), and Pb(II) to investigate the effects of contact time, adsorbent dose, pH, and charring temperature on the adsorption of heavy metals. The experimental results showed that the adsorption capacity was positively correlated with the adsorption time in the first 20 min, but gradually tended to reach equilibrium after 20 min. The adsorbent dose and pyrolysis temperature were positively correlated with the removal effect of biochar for heavy metals, and the maximum removal efficiency of biochar could reach 99.86% at pH = 4 [12]. Park et al. investigated the adsorption of heavy metals on sesame straw charcoal (SSB) and compared its adsorption of single and multiple metals. They found that SSB had superior adsorption effects on heavy metals, and the adsorption capacities of SSB for single heavy metals were, in descending order, Pb(II) > Cu(II) > Cr(VI) > Zn(II) > Cd(II), and for polymetals were, in descending order, Pb(II) > Cd(II) > Cr(VI) > Cu(II). The adsorption capacity for polymetallics was much greater than for monometallics [13].

Although biochar has a certain adsorption effect on heavy metals, the adsorption capacity is relatively limited, and in order to improve the utilization of biochar, it should be further modified to effectively enhance its remediation function [14]. This investigation mainly studied the influence of the dosage of the best effect modified bamboo charcoal (KAM-500-400-3) on the fixation effect of single Cu (II)-contaminated sediment and mixed Cu (II)–Cd (II)-contaminated sediment. KAM500-400-3 refers to the strongest adsorption capacity of heavy metals Cu (II) and Cd (II) in all modified bamboo charcoal under the conditions of activation and modification of KOH: the alkali–carbon ratio is 3:1, and the activation temperature is 400 °C. Therefore, it was selected for the study of adsorption characteristics. The sediment used was taken from Xuanwu Lake in Nanjing (where the content of Cu (II) is about 50 mg/kg). In this experiment, appropriate amounts of Cu (II) and Cd (II) were added to the original sediment, respectively, to simulate the single Cu (II) pollution and the mixed Cu (II)–Cd (II) pollution of the sediment, in which the concentration of Cu (II) in the single Cu (II) pollution sediment is about 100 mg/kg, the concentration of Cu (II) in the mixed Cu (II)–Cd (II) pollution sediment is about 50 mg/kg, and the concentration of Cd (II) is about 6 mg/g.

2. Materials and Methods

2.1. Main Experimental Apparatus and Materials

The selected biomass material in this experiment is *Phyllostachys pubescens*, which is from a bamboo forest in Jurong, Jiangsu Province. The Supplementary Material lists the experimental instruments, instrument specifications, and applications required for this experiment. It also lists the reagents, specifications, and purity required for this experiment. The water used in this experiment is ultrapure water (the resistivity is 18.25 MQ·cm) [15].

2.2. Preparation Method of Bamboo Charcoal

Moso bamboo, retrieved from a bamboo forest in Jurong, was washed with tap water and deionized water and then allowed to dry naturally. The moso bamboo was dried in a constant-temperature drying oven at 80 °C after being cut into small pieces with a chainsaw [12]. The dried bamboo pieces were cut into strips with branch shears, ground to a powder, and passed through a 100-mesh sieve to obtain 100-mesh bamboo powder in a self-sealing bag. A quartz tube was filled with 100 g of 100-mesh bamboo powder and placed in a tube furnace [16]. The conditions of KOH activation modification were a 3:1 alkali-to-carbon ratio and 400 °C activation. KAM500-400-3 had the strongest adsorption capacity for heavy metals Cu(II) and Cd(II) among all modified bamboo charcoals, so it was selected for the adsorption characteristics study [17].

2.3. Collection and Treatment Method of Sediment

The sediment used in the experiment was selected from the sediment on the banks of Xuanwu Lake in Nanjing (in which the content of Cu (II) is about 50 mg/kg). The sediment samples were collected from the sediment layer of 0–20 cm. After the impurities were removed, the sediment was evenly spread on the plastic film cloth for natural air-drying. After the air drying was completed, it was broken into small pieces, then ground again with a stone mortar to make it pass through a 100-mesh sieve, and placed it into a sealed bag at 4 °C for use [18].

The experimental method for simulating 100 mg/kg of single Cu (II)-contaminated sediment is as follows: since the content of Cu (II) in the original sediment is about 50 mg/kg, use an electronic balance to weigh 900 g of sediment into a bucket, and transfer 900 mL of 50 mg/L CuSO₄ solution into the bucket to ensure that the water content of the sediment is 50%.

The experimental method for simulating mixed Cu(II)–Cd(II)-contaminated sediment is as follows: the content of Cu(II) in the original sediment is about 50 mg/kg, and 5.4 mg of Cd (II) is added to it, that is, 6 mg/kg of Cd(II) is added. A total of 900 g of sediment is weighed with an electronic balance and transferred into a bucket, and 540 mL of 10 mg/L of CdSO₄ solution is added to the bucket, ensuring that the water content of the sediment is 50%.

Mix the sediment sample and the heavy metal solution with a wooden stick, leave it standing for one month, and pre-culture it in a constant-temperature incubator at 25 °C. After the completion of cultivation, the sediment should be developed for 100 days and placed into a self-sealing bag and stored at 4 °C for use [19].

2.4. Sediment Cultivation Experiment

First, 40 g of dried sediment was placed in a 100 mL screw-top bottle, 60 mL of deionized water was added into the bottle, the cap was tightened, and it was left to stand for 24 h. Then, 0% (blank sample), 1% (0.4 g), 2.5% (1 g), 5% (2 g), and 10% (4 g) of the dry weight of the bottom mud was added to the Cu (II)-contaminated bottom mud bottle (three duplicate samples for each condition). The best effect modified bamboo charcoal (3 duplicate samples for each condition) with the dry weight of 0% (blank sample), 1% (0.4 g), 2.5% (1 g), 5% (2 g) of the sediment, respectively, was added into the mixed polluted sediment bottles of Cu (II) and Cd (II). They were shaken up and then placed in an artificial climate box at the temperature of 25 °C and cultivated in the dark.

2.5. Determination of Heavy Metal Concentration in Overlying Water and Pore Water

After 100 days of cultivation of the biochar-treated sediment, the overlying water was taken out and filtered with a 0.22 µm filter head, and then the concentration of heavy metals Cu (II) and Cd (II) in the overlying water was measured with an atomic absorption spectrophotometer. After the overlying water was removed, the appropriate bottom mud was taken from the screw-top bottle and moved into a 100 mL centrifuge tube. It was centrifuged at a speed of 4000 r/min for 15 min. The supernatant of the centrifuge tube

was taken and filtered in the same way to determine the concentration of heavy metals Cu (II) and Cd (II) in the pore water of the bottom mud. The remaining part of the bottom mud in the centrifuge tube was put into a freeze-dryer for freeze-drying for 48 h. After crushing and grinding, it was sieved for 100 days and stored in a sealed bag at 4 °C for subsequent analysis and standby.

2.6. Determination of Total Heavy Metals in Sediment

In this experiment, the above sediment solids were digested using the three-acid digestion method to determine the concentration of heavy metals Cu (II) and Cd (II). First, an electronic balance was used to weigh 0.1 g of the bottom mud in a polytetrafluoroethylene crucible and it was moistened with a little water. Then, 5 mL of nitric acid (HNO₃) was added and it was digested at 150 °C for 15 min, then 4 mL of hydrofluoric acid (HF) was added under the condition of maintaining 150 °C, it continued to be digest at a low temperature for 20 min, then the temperature of the electric heating plate was adjusted to 240 °C and 1 mL of perchloric acid (HClO₄) was added. After the white smoke had finished, the polytetrafluoroethylene crucible was removed from the electric heating and it was cooled slightly, then 5 mL nitric acid (HNO₃)–hydrochloric acid (HCl) mixed acid (volume ratio: 20:1, dilute it with water) was added it was heated to 120 °C on the electric heating plate, and extracted for 1 min. Finally, the digested liquid was transferred into a 100 mL polytetrafluoroethylene volumetric flask, it was diluted with water to the scale, and shaken evenly.

2.7. Determination of Different Forms of Heavy Metals in Sediment through BCR Extraction Method

According to the BCR extraction method, the different forms of heavy metals in soil and sediment can be divided into weakly extractable, reducible, oxidizable, and residual. The BCR method includes the determination of acid-extractable heavy metal (ACI) content, determination of reducible heavy metal (FEM) content, determination of oxidizable heavy metal (ORG) content, and determination of residual heavy metal (RES) content. The operation steps of BCR, such as sample collection, storage and treatment, dissolution equipment operation procedures, reagent preparation, and related calculation methods, can be found in the methods in the Supplementary Material.

2.8. Determination of TCLP Leaching Toxicity Risk of Heavy Metals in Sediment

The TCLP (toxicity characteristic leaching procedure) toxicity characteristic leaching method is a standard method for testing the mobility of organic or inorganic pollutants in liquid, solid, or multiphase waste, and is adopted by the United States Environmental Protection Agency (USEPA). The State Environmental Protection Administration of China has also incorporated this method into the national standard.

TCLP extraction equipment can be roughly divided into two categories: non-volatile and volatile substances. After the waste is extracted through the TCLP program, the extracted liquid is then analyzed using an atomic absorption spectrometer (AA), series gas chromatograph (GC), liquid chromatograph (HPLC), or ion chromatograph (IC) to determine the concentration of inorganic or organic pollutants in the dissolved liquid, and it is determined whether the analyzed waste is general waste or toxic waste.

The operation steps of TCLP, such as sample collection, storage and treatment, dissolution equipment operation procedures, reagent preparation, and related calculation methods, can be found in the methods in the Supplementary Material.

3. Results

3.1. Morphological Analysis

The surface morphologies of bamboo charcoal, as well as modified bamboo charcoal, are shown in Figure 1. Figure 1 shows the surface morphologies of unmodified BC500 and KAM500-400-3-modified charcoal, respectively. As can be seen from Figure 1, the

surface of unmodified BC500 is smoother, and the char is mainly tubular in shape with a relatively intact structure. The surface of KAM500-400-3 after KOH activation showed a lot of collapse and unevenness; its structure was far from that of BC500, and large pores were clearly visible in the cross section.

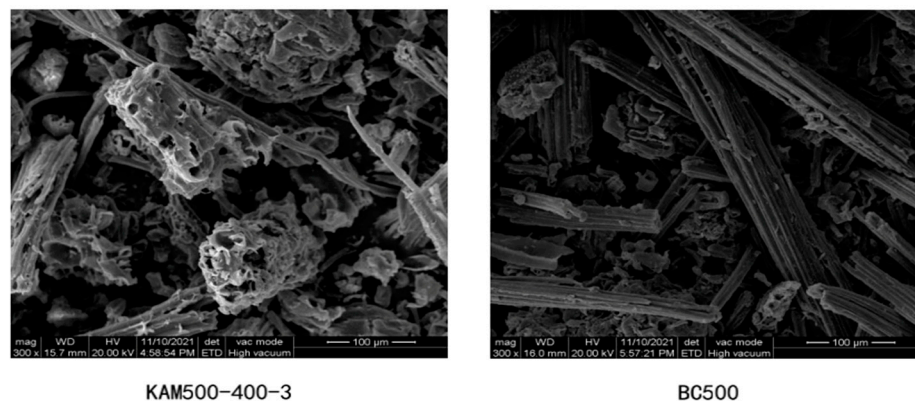


Figure 1. SEM images of bamboo charcoal and modified bamboo charcoal.

3.2. Concentration of Heavy Metals in Pore Water and Overlying Water

3.2.1. Concentration of Heavy Metals in Overlying Water and Pore Water Polluted by Single Cu(II)

The effect of KAM-500-400-3 addition on the concentration of Cu(II) in the water overlying single Cu(II)-contaminated sediment is shown in Figure 2. The figure shows that when the added amount of KAM500-400-3 was 1% and 2.5% of the sediment mass, the Cu(II) content in the overlying water was not significantly different from that of the sediment without the addition of KAM500-400-3. When the addition amount was 5% and 10% of the sediment mass, the Cu(II) content in the overlying water was 12.18% and 24.36% lower than that of the sediment without KAM500-400-3, respectively. We found that when the amount of carbon added was low, the impact on the Cu(II) content in the overlying water was weak. When the amount of carbon added gradually increased, the Cu(II) content in the overlying water decreased. KAM500-400-3 showed a strong fixation effect on the Cu(II) in the sediment. After a certain amount of carbon is added, the heavy metal Cu(II) in the sediment can be prevented from further polluting a water body [20–24].

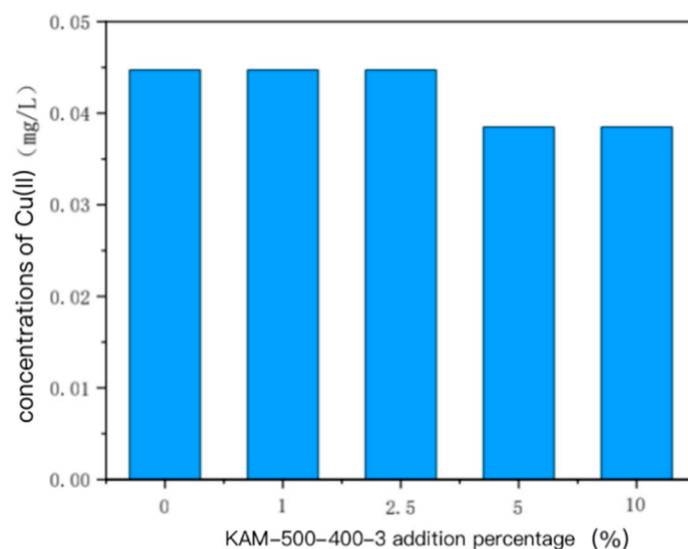


Figure 2. Effect of KAM-500-400-3 addition percentage on the concentrations of Cu(II) in the overlying water of single Cu(II)-contaminated sediment.

The effect of the amount of KAM-500-400-3 on the Cu(II) concentration in the pore water of single Cu(II)-contaminated sediment is shown in Figure 3, and its pattern was similar to that in the overlying water. When the added amount of KAM500-400-3 was 1% and 2.5% of the sediment mass, we found no obvious change in the Cu(II) concentration compared with that in the sediment without KAM500-400-3. When the amount we added was further increased to 5% and 10%, the corresponding concentration of Cu(II) in the pore water gradually decreased. When we added a small amount of KAM500-400-3, the effect on Cu(II) in the pore water was also weak. When the amount of KAM500-400-3 that we added was greater than or equal to 5% of the sediment mass, the Cu(II) concentration in the pore water of the sediment was lower than that when the added amount of KAM500-400-3 was low, which further proved that KAM500-400-3 has a certain fixing effect on the heavy metal Cu(II) in sediment [25–27].

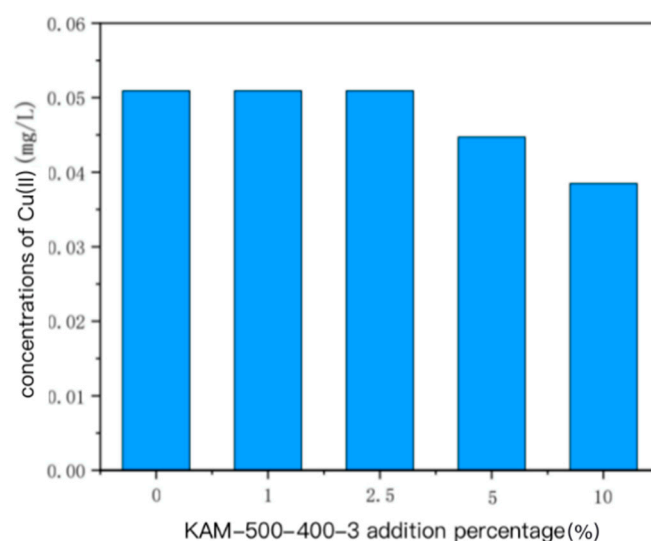


Figure 3. Effect of KAM-500-400-3 addition percentage on the concentrations of Cu(II) in the pore water of single Cu(II)-contaminated sediment.

3.2.2. Concentration of Heavy Metals in Overlying Water and Pore Water of Cu(II)–Cd(II) Mixed Polluted Sediment

The experimental results showed that Cd(II) was not detected in the overlying or pore water of mixed Cu(II)–Cd(II)-contaminated sediment. This may have been because the content of Cd(II) was too low, so the degree of pollution of the overlying and pore water was low [28,29]. The effect of the amount of KAM-500-400-3 added on the concentration of Cu(II) in the overlying water of mixed Cu(II)–Cd(II)-contaminated sediment is shown in Table 1. When the added amount of KAM500-400-3 was 0% (blank control) and 1% of the sediment quality, the corresponding Cu(II) concentrations in the overlying water were 0.01 and 0.01 mg/L, respectively. When the added amount was further increased to 2.5% and 5%, the Cu(II) concentration in the overlying water was lower than the detection limit and could not be measured. The pattern of the change in the concentration of the overlying water for the sediment contaminated with a mixture of Cu(II)–Cd(II) with the addition of KAM-500-400-3 was similar to that for the sediment contaminated with single Cu(II); that is, when the amount of added carbon was low, the impact on Cu(II) in the overlying water was weak. When the amount added was gradually increased, the concentration of Cu(II) in the overlying water decreased. We found that KAM500-400-3 had a notable fixation effect on the Cu(II) in the sediment polluted with Cu(II)–Cd(II). After a certain amount of input, it can inhibit the Cu(II) in the sediment from further polluting water bodies [12,16,30].

Table 1. Effect of KAM-500-400-3 addition percentage on Cu(II) concentrations in overlying water and pore water of Cu(II)–Cd(II) mixed contaminated sediment.

	KAM-500-400-3 Addition Percentage (%)			
	0	1	2.5	5
Cu(II) concentrations in overlying water	0.01	0.01	—	—
Cu(II) in pore water	0.01	0.01	—	—

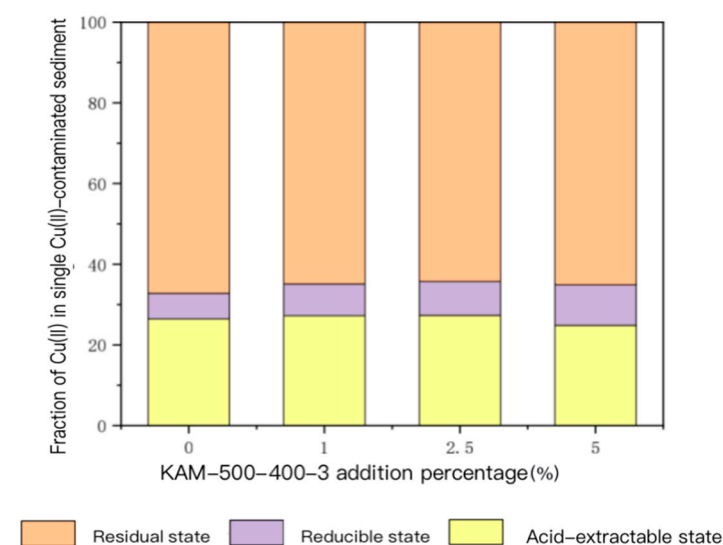
The effect of the added amount of KAM-500-400-3 on the concentration of Cu(II) in the pore water of Cu(II)–Cd(II)-contaminated sediment was also similar to that observed for single Cu(II)-contaminated sediment. As shown in Table 1, when the added amount of KAM500-400-3 was 0% (blank control) and 1% of the sediment mass, the corresponding Cu(II) concentration in the overlying water was 0.01 and 0.01 mg/L, respectively. When the added amount of KAM500-400-3 was further increased to 2.5% and 5%, Cu(II) could not be detected. When a small amount of KAM500-400-3 was added, it polluted the Cu(II)–Cd(II) mixture [13]. The influence of Cu(II) on the sediment pore water was also weak. When the amount of KAM500-400-3 added was greater than or equal to 2.5% of the sediment mass, the Cu(II) concentration in the sediment pore water was substantially lower than that when the added amount was lower, which further proved that KAM500-400-3 has a certain fixation effect on Cu(II) in sediment contaminated by Cu(II)–Cd(II) [31,32].

3.3. Fixation Effect of Heavy Metals

3.3.1. Fixation Effect of Heavy Metals in Single Cu(II)-Contaminated Sediment

(1) Analysis of speciation changes of heavy metal Cu(II) in sediment

According to the BCR extraction method, the forms of heavy metals in sediment can be divided into acid-extractable, reducible, oxidizable, and residue states according to the biological availability from the most to the least. In general, heavy metals with high bioavailability cause more harm to the environment due to their strong migration ability and toxicity, so heavy metals with low bioavailability are relatively stable [33–36]. The morphology of Cu(II) in single Cu(II)-contaminated sediment continuously extracted through BCR with different amounts of KAM500-400-3 is shown in Figure 4.

**Figure 4.** Fraction of Cu(II) in single Cu(II)-contaminated sediment determined through BCR sequential extraction under different addition percentages of KAM500-400-3.

According to the experimental results, the acid in the sediment without adding KAM500-400-3 could be extracted, reduced, and oxidized. The proportion of residual

Cu(II) in the total Cu(II) was 20.48%, 8.17%, 20.36%, and 50.99%, respectively. When the content of KAM500-400-3 was 1% of the sediment mass, the proportions of extractable, reducible, oxidizable, and residual Cu(II) in the sediment to the total Cu(II) were 20.52%, 8.00%, 21.45%, and 50.03%, respectively [37]. When the content of KAM500-400-3 was 2.5% of the sediment mass, the proportions of extractable, reducible, oxidizable, and residual Cu(II) in the sediment mass to the total Cu(II) were 15.60%, 8.60%, 24.32%, and 51.48%, respectively. When the content of KAM500-400-3 was 5% of the sediment mass, the proportions of extractable, reducible, oxidizable, and residual Cu(II) in the sediment to the total Cu(n) were 10.32%, 10.41%, 25.29%, and 53.98%, respectively. When the content of KAM500-400-3 was 10%, the corresponding acid-extractable Cu(n) accounted for 6.99% of the total Cu(n), reducible Cu(II) accounted for 11.96% of the total Cu(II), oxidizable Cu(II) accounted for 26.28% of the total Cu(II), and residual Cu(II) accounted for 54.76% of the total Cu(II) [38,39]. The experimental results showed that with the increasing addition of KAM500-400-3, the proportion of Cu(n) in the acid-extractable state with the highest bioavailability to the total Cu(n) continually decreased, while the proportions of relatively stable reducible, oxidizable, and residual Cu(II) content to the total Cu(n) gradually increased. We found that KAM500-400-3 could effectively fix the heavy metal Cu(II) in passivated sediment and gradually transform it from the acid-extractable form, which is highly bioavailable, to the reducible, oxidizable, residual, and other forms, which have low bioavailability [40–42].

(2) TCLP leaching toxicity risk analysis of heavy metal Cu(II) in sediment

The TCLP-extractable concentration of Cu(II) in single Cu(II)-contaminated sediment with different amounts of KAM500-400-3 is shown in Figure 4. According to the experimental results, when the dosage of KAM500-400-3 was 0% (blank control), 1%, 2.5%, 5%, and 10%, the concentration of Cu(II) in the sediment extractable through TCLP was 2.34, 2.26, 1.81, 1.72, and 1.43 mg/kg, respectively [43]. When the dosage of KAM500-400-3 was 1%, 2.5%, 5%, and 10%, the concentration of Cu(II) extractable through TCLP was 3.42%, 22.65%, 26.50%, and 38.89% lower than that of the sediment without KAM500-400-3, respectively. The results showed that the TCLP toxic leaching concentration of Cu(II) in the sediment gradually decreased with the increase in the amount of KAM500-400-3 applied, which showed that the addition of KAM500-400-3 could inhibit this heavy metal in the sediment from entering the water body and could effectively fix the heavy metal Cu(II) in the sediment, thus reducing its leaching toxicity risk [44].

3.3.2. Fixation Effect of Heavy Metals in Mixed Polluted Sediment of Cu(II)–Cd(II)

(1) Analysis of speciation changes in Cu(II) and Cd(II) in sediment

The morphological changes in Cu(II) in the sediment polluted with Cu(II)–Cd(II) under different amounts of KAM500-400-3 addition are shown in Figure 5. According to the experimental results, the proportions of extractable, reducible, oxidizable, and residual Cu(II) in the sediment without adding KAM500-400-3 to the total Cu(II) were 11.42%, 2.95%, 14.82%, and 70.81%, respectively. When the added amount of KAM500-400-3 was 1% of the sediment mass, the proportions of extractable, reducible, oxidizable, and residual Cu(II) in the sediment to the total Cu(II) were 12.09%, 3.76%, 16.09%, and 68.07%, respectively. When the content of KAM500-400-3 was 2.5% of the sediment mass, the proportions of extractable, reducible, oxidizable, and residual Cu(II) in the sediment to the total Cu(II) were 10.62%, 3.75%, 16.95%, and 68.68%, respectively. When the added amount of KAM500-400-3 was 5% of the sediment mass, the proportions of acid-extractable, reducible, oxidizable, and residual Cu(II) in the sediment to the total Cu(II) were 6.56%, 4.31%, 17.82%, and 71.31%, respectively [29].

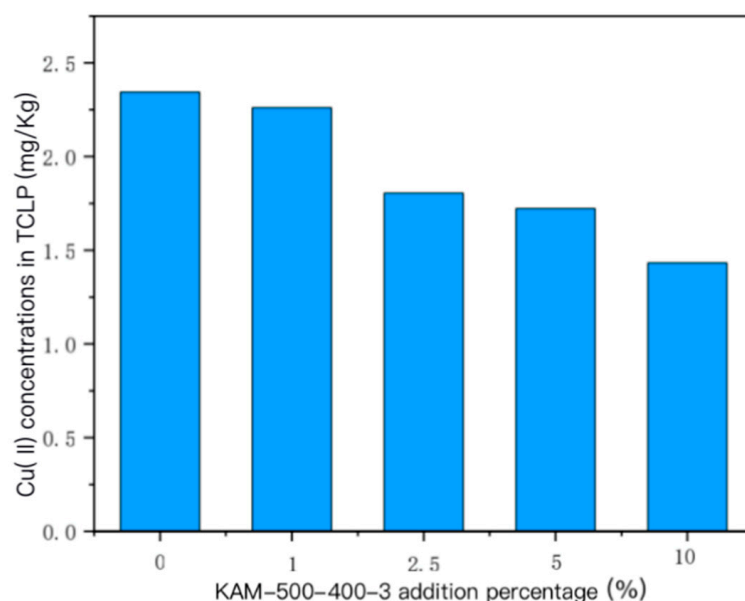


Figure 5. Cu(II) concentrations in TCLP leachates of single Cu(II)-contaminated sediment under different addition percentages of KAM500-400-3.

The form of Cd(II) in the sediment polluted with Cu(II)–Cd(II) was continuously extracted through BCR with different amounts of KAM500-400-3, as shown in Figure 6. The experimental results showed that the proportions of extractable, reducible, and residual Cd(II) in the sediment without adding KAM500-400-3 to the total Cd(II) were 26.46%, 6.34%, and 67.20%, respectively; at 1%, the proportions were 27.23%, 7.89%, and 64.88%, respectively; at 2.5%, the proportions were 27.32%, 8.39%, and 64.29%, respectively; at 5%, the proportions were 24.85%, 10.04%, and 65.14%, respectively [45].

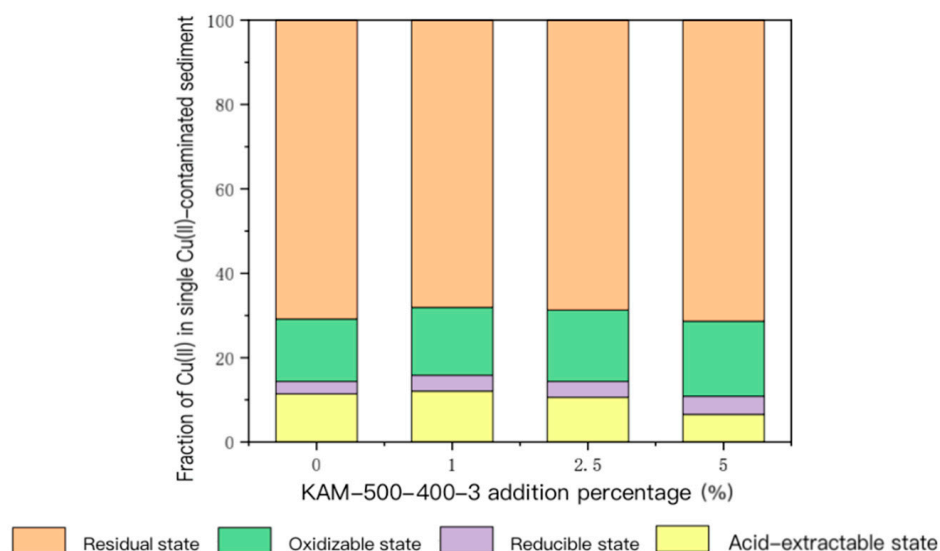


Figure 6. Fraction of Cu(II) in Cu(II)–Cd(II) mixed contaminated sediment determined through BCR sequential extraction under different addition percentages of KAM500-400-3.

The experimental results showed that the main form of Cu(II) in the sediment contaminated by Cu(II)–Cd(II) was residual. With the increase in the amount of KAM500-400-3 applied, the change in residual Cu(II) content was not remarkable. The content of acid-extractable Cu(II) decreased and its proportion of the total amount of Cu(II) gradually decreased, and the content and proportion of reducible and oxidizable Cu(II) gradually

increased with increasing KAM500-400-3 addition. In the sediment contaminated by Cu(II)–Cd(II), the content of Cd(II) in the oxidizable state was lower than the detection limit. To summarize, KAM500-400-3 can reduce the bioavailability of the heavy metals Cu(II) and Cd(II) in mixed Cu(II)–Cd(II)-contaminated sediment and convert them into more stable forms. Therefore, KAM500-400-3 is an effective material that can be used to fix Cu(II)–Cd(II)-contaminated sediment [46].

(2) TCLP leaching toxicity risk analysis of heavy metals Cu(II) and Cd(II) in sediment

The TCLP-extractable concentration of Cu(II) in the sediment polluted by Cu(II)–Cd(II) under different amounts of KAM500-400-3 addition is shown in Figure 7, and the TCLP-extractable concentration of Cd(II) is shown in Figure 8. Figure 9 shows Cd(II) concentrations in TCLP leachates of Cu(II)–Cd(II) mixed contaminated sediment under different addition percentages of KAM500-400-3. The figures show that when the addition of KAM500-400-3 was 0% (blank control), 1%, 2.5%, and 5%, the concentration of Cu(II) extractable through TCLP in the sediment was 0.55, 0.51, 0.47, and 0.43 mg/kg, respectively, and the concentration of Cd(II) extractable through TCLP in the sediment was 1.21, 1.06, 0.80, and 0.52 mg/kg, respectively. When the amount of added KAM500-400-3 was 1%, the concentration of Cu(II) extractable through TCLP was 7.27% lower than that of the sediment without KAM500-400-3, and the concentration of Cd(II) extractable through TCLP was 12.40% lower than that of the sediment without KAM500-400-3 [47]. When the addition amount was 2.5%, the concentrations of Cu(II) and Cd(II) extractable through TCLP were 14.55% and 33.88% lower than that of the sediment without KAM500-400-3, respectively. When the added amount was 5%, the concentrations of Cu(II) and Cd(II) extractable through TCLP were 21.82% and 57.02% lower than that of the sediment without KAM500-400-3, respectively. The results show that the increase in KAM500-400-3 addition enhanced its adsorption capacity for the heavy metals Cu(II) and Cd(II), reduced the leaching concentration of Cu(II) and Cd(II) TCLP in the polluted sediment, effectively fixed the heavy metals in the sediment, and reduced its leaching toxicity risk [17,18].

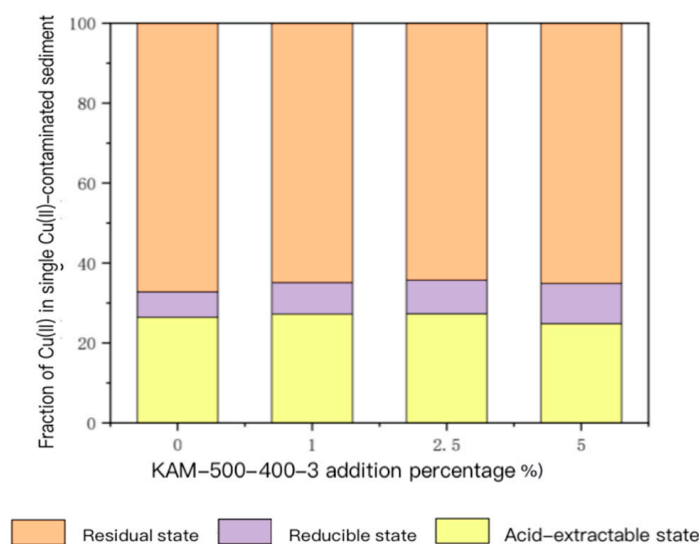


Figure 7. Fraction of Cd(II) in Cu(II)–Cd(II) mixed contaminated sediment determined through BCR sequential extraction under different addition percentages of KAM500-400-3.

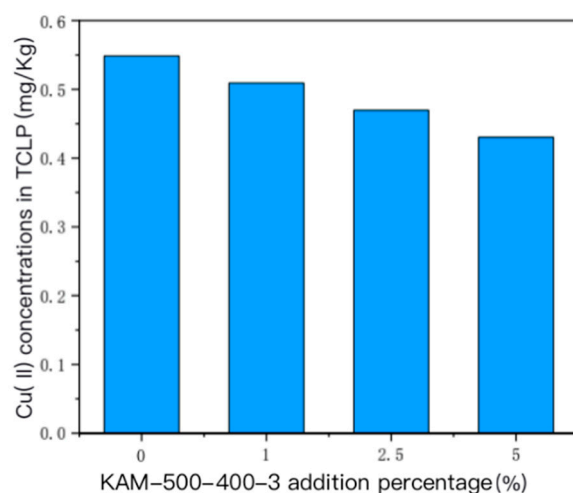


Figure 8. Cu(II) concentrations in TCLP leachates of Cu(II)–Cd(II) mixed contaminated sediment under different addition percentages of KAM500-400-3(%).

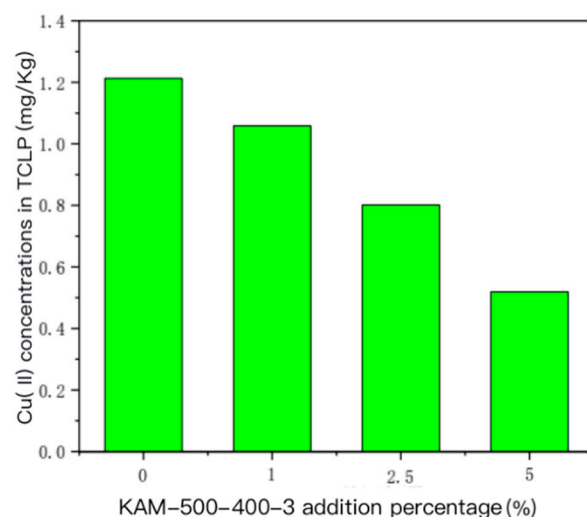


Figure 9. Cd(II) concentrations in TCLP leachates of Cu(II)–Cd(II) mixed contaminated sediment under different addition percentages of KAM500-400-3.

4. Discussion

We studied the fixation effect of KAM500-400-3 on sediment polluted with single Cu(II) and mixed Cu(II)–Cd(II), and explored the effect of KAM500-400-3 addition on the overlying water, pore water, heavy metal forms in sediment, and TCLP toxic leaching risk for the two kinds of sediment. Our specific experimental conclusions are as follows:

- (1) With the increase in KAM500-400-3 addition, the concentrations of Cu(II) in the overlying and pore water in the single Cu(II)-contaminated sediment and the mixed Cu(II)–Cd(II)-contaminated sediment were similar; that is, when a small amount was added, the impact on Cu(II) in the overlying and pore water was weak. When the addition amount gradually increased, the concentration of Cu(II) in the overlying water and pore water decreased. The Cd(II) content in the overlying and pore water of Cu(II)–Cd(II)-contaminated sediment was lower than the detection limit, so it could not be detected [19,47].
- (2) For the sediment polluted by single Cu(II), with the gradual increase in KAM500-400-3 addition, the content of acid-extractable Cu(II), which is highly bioavailable, gradually decreased, and its proportion in the total Cu(II) also continually decreased. The content and proportion of Cu(II) in the reducible, oxidizable, and residual states

gradually increased. For sediment contaminated by Cu(II)–Cd(II), the main form of Cu(II) in the sediment was residual. With the increase in the KAM500-400-3 addition amount, the change in residual Cu(II) was not remarkable. The proportion of acid-extractable Cu(II) in the total amount of Cu(II) substantially reduced, and the proportions of reducible and oxidizable Cu(II) gradually increased. The form of Cd(II) in the sediment was also dominated by that in the residual state, and the pattern of the changes in the various forms of Cd(II) was also similar to that of Cu(II); that is, with the increase in the amount of added KAM500-400-3, the change in the residual state of Cd(II) was not remarkable, the proportion of the acid-extractable state of Cd(II) in the total amount of Cd(II) gradually decreased, the proportion of the reducible state of Cd(II) gradually increased, and the content of the oxidizable state of Cd(II) was lower than the detection limit and could not be detected [48].

- (3) For the sediment polluted by single Cu(II), the concentration of the TCLP-extractable solution of Cu(II) in the sediment gradually decreased with the increase in the amount of added KAM500-400-3. For the sediment polluted by Cu(II)–Cd(II), the increase in the added amount of KAM500-400-3 reduced the extractable concentrations of Cu(II) and Cd(II) TCLP, thus effectively fixing the heavy metals in the sediment and reducing their leaching risk.

To summarize, KAM500-400-3 has a strong fixation effect for single Cu(II)-contaminated sediment and mixed Cu(II)–Cd(II)-contaminated sediment. It can transform the heavy metals Cu(II)/Cd(II) into a relatively stable form to a certain extent, reduce their bioavailability, and inhibit the toxic leaching of heavy metal TCLP in the sediment, thus further inhibiting the heavy metal pollution of water. Therefore, KAM500-400-3 is a material that can effectively fix the Cu(II) and Cd(II) in sediment.

5. Conclusions

The adsorption method is the most commonly used method to treat heavy metals in water at present. It has the advantages of being renewable, low cost, no “secondary pollution”, and being suitable for treating wastewater of various concentrations. Biochar adsorbents have been widely used to treat heavy metals in wastewater because of their environmental friendliness, low cost, and easy availability. Although biochar can adsorb heavy metals to some extent, its adsorption capacity is relatively limited. In order to improve the utilization rate of biochar, it is necessary to modify biochar to enhance its repair function effectively.

In the future, we can explore new biomass carbonization materials and the rational use of renewable waste resources in order to find a more suitable adsorbent. At the same time, the modified biochar materials will be further applied to the treatment of heavy metals in water and soil in a reasonable way. It is also worth noting that in the future, it is possible to consider the preparation of selective adsorbent materials through optimized modification, which can be more effectively applied to the treatment of water and soil pollution in mixed systems in actual production and life. In addition, in the context of green environmental protection, we should pay more attention to the repeated recycling of waste biomass to ensure good treatment effects without causing secondary pollution to the environment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15061230/s1>, Table S1: Experimental instruments. Table S2: Experimental reagents.

Author Contributions: Conceptualization, S.L. and H.L.; methodology, H.L. and Y.W.; validation, Y.W., H.L. and S.L.; formal analysis, Y.W.; resources, Y.W.; writing—original draft preparation, Y.W.; writing—review and editing, Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

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