

Research Article

Characteristics and Applications of Sewage Sludge Biochar Modified by Ferrous Sulfate for Remediating Cr(VI)-Contaminated Soils

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Background. Soil contamination by hexavalent chromium is becoming a main environmental concern in China. This study developed a sewage sludge biochar modified by FeSO_4 (CHBC) as a new reductant for Cr(VI)-contaminated soil. The effectiveness of CHBC-stabilized Cr(VI)-contaminated soil was investigated. **Methods.** Typical industrial Cr(VI)-contaminated soil in China was chosen as the medium. The total and Cr(VI) contents of the contaminated soil were 1014.6 and 973.5 mg/kg, respectively. The effectiveness of the Cr(VI)-contaminated soil stabilized by CHBC was investigated by the leaching test (US EPA method 1312), the simplified bioaccessibility extraction test (US EPA 2007 protocol and British Geological Survey), alkaline digestion (US EPA method 3060A), sequential extraction (BCR sequential extraction procedure), X-ray diffraction, and the risk assessment code test. **Results.** Results show that CHBC substantially reduced the leachability and Cr(VI) content of the contaminated soil. The leachability and content of Cr(VI) were lower than the thresholds of the Environmental Quality Standards of Soil in China for civil reuse and the China Environmental Quality Standards of surface water for civil use when the soil was stabilized with 10% dosage of CHBC. **Conclusion.** CHBC is highly efficient in stabilizing Cr(VI) and can effectively reduce the leachability and bioavailability of Cr in contaminated soil and thus feasible for stabilizing Cr(VI)-contaminated soil and shows potential for application in the field.

1. Introduction

Chromium (Cr) is a common soil contaminant, and nearly 1.1% of China's land is contaminated by Cr according to Chinese officials [1–3]. Cr often exists in soil in two main redox states: Cr(III) and Cr(VI). Cr(III) is a nutrient for plant growth, while Cr(VI) is highly toxic and has been added to Class A human carcinogens [4]. Given its carcinogenic and toxic properties, efforts have been exerted in removing Cr(VI) from contaminated soil. Chemical reduction has been widely used for removing Cr(VI) from soil due to its speed and effectiveness [5]. Ferric salts (nano-zero valent iron, bivalent iron, and ferrous sulfate) and sulfides (calcium polysulfide and sodium thiosulfate) are promising reagents that have been used in large amounts of Cr-contaminated soil for many years. However, ferric salts and

sulfides have adverse effects due to the acidity or high-sulfur content they impart to the soil [6, 7]. Thus, green, environmentally friendly reducing agents must be urgently developed as substitutes for ferric salts and sulfides. The use of biochar as a reducing agent to remove Cr(VI) has been extensively investigated [8–15]. Dong et al. [8] successfully applied the biochar from sugar beet tailings to reduce Cr(VI) in aqueous solutions and obtained favorable results. Agrafti et al. [9] used the biochar from sewage sludge treated with Cr(VI)-contaminated water and observed its high capacity to adsorb Cr(VI) (64.1 mg/g). Ma et al. [10] discovered that biochar is a useful adsorbent for removing Cr(VI) from aqueous solutions. Shen et al. [11] reported that the biochar from coconut coir has a high capacity to reduce Cr(VI) (124 mg/g). Zhou et al. [12] used biochar and acidified manure treated with Cr(VI)-contaminated soil and

observed their high capacity to adsorb Cr(VI) (34.1 mg/g). Xia et al. [13] found that biochar is a promising material for remediated Cr(VI)-contaminated soils and wastewater, displaying factors that affect the removal efficiency of Cr(VI), including pH, temperature, initial concentration, reaction time, biochar characteristics, and coexisting contaminants. Li et al. [14] compared the biochars from maize stalk and peanut shell for reduced Cr(VI) in soils. Their results show that the maximum Cr(VI) reduction capacities of maize stalk and peanut shell were 238 and 231 mg/kg, respectively. Pei et al. [15] applied the biochar from vinegar-residue-supported nanoscale zero-valent iron to remediate Cr(VI) contaminated soil and found that it could achieve Cr(VI) and Cr immobilization efficiencies of 100% and 91.83% at 10% dosage, respectively.

According to previous studies, the biochars derived from sewage sludge, sugar beet tailings, and rice husk have great potential for remediating Cr(VI) contamination. However, considerably high reduction capacities must be achieved to accelerate the application of biochars in Cr(VI)-contaminated water and soil. Modification by using iron salts is a promising method of improving the reduction capacities. Zero valent iron modification offers effective absorptivity and reducing capacity [16, 17]. However, zero valent iron is characterized by high costs, difficult production, and difficult storage. Ferrous sulfate (FeSO_4), which is relatively inexpensive and highly effective for remediating Cr(VI)-contaminated soil, can substitute for zero valent iron. China is the largest producer of sewage sludge, generating more than 80 million metric tons every year [18]. A small proportion of sewage sludge is used in the agriculture sector and burned, while the rest ends up in landfills or is discarded, causing environmental problems [19]. A prior work showed that the biochar from sewage sludge has effective absorptivity, high reducing capacity, and various chemical functional groups [20]. The modified biochar derived from sewage sludge has great potential for Cr(VI)-contaminated soil remediation. However, no peer-reviewed literature has methodically investigated the stability of the sewage sludge biochar modified by FeSO_4 in Cr(VI)-contaminated soil.

This study developed a sewage sludge biochar modified by FeSO_4 (CHBC) as a new reductant for Cr(VI)-contaminated soil. The effectiveness of the CHBC-stabilized Cr(VI)-contaminated soil was investigated by the leaching test (SPLP), the simplified bioaccessibility extraction test (SBET), alkaline digestion, sequential extraction, X-ray diffraction (XRD), and the risk assessment code (RAC). This study can provide a new reductant for stabilized Cr(VI)-contaminated soil and is relatively valuable for sewage sludge resource reuse.

2. Materials and Methods

2.1. Cr(VI)-Contaminated Soil. Cr(VI)-contaminated soil was collected from a Cr-contaminated site in the Qingdao Red Star Chemical Group, Qingdao City, Shandong Province, China (Figure 1). The Cr(VI)-contaminated soil was sieved (2-mm mesh) and homogenized to obtain a composite sample. Table 1 presents the physicochemical properties of the soil.

2.2. Sewage Sludge Biochar Modified by Ferrous Sulfate. The sewage sludge collected from the Qingdao Tuandao cape wastewater treatment plant was air dried and then sieved through a 0.15 mm mesh. We manufactured a sewage sludge biochar by modifying the approach of Su et al. [21]. Briefly, the pretreated sewage sludge was pyrolyzed in an oxygen-free furnace at 400°C for 2 h. After cooling, the biochar particles were ground and then sieved through a 0.075 mm screen. The sewage sludge biochar was then soaked in a FeSO_4 solution of 2 M for 1 h in an oxygen-free condition. Then, the solids were finally vacuum-dried at 60°C . This sewage-sludge-biochar-supported FeSO_4 was identified as "CHBC." The sewage sludge and CHBC are presented in Figure 2. The physicochemical properties of the sewage sludge and CHBC are presented in Table 2.

2.3. Sample Preparation. CHBC was added to the Cr(VI)-contaminated soil at reductant-to-dry soil ratios of 0%, 1%, 3%, 5%, and 10%. The experimental design for the stability study is presented in Table 3. CHBC- and Cr(VI)-contaminated soils were mixed using a Spar mixer. Deionized water was then added to the mixture until the water content reached 30%. The mixture was withdrawn from sealed plastic bottles after 28 days of incubation at room temperature to allow the CHBC- and Cr(VI)-contaminated soils to react adequately. Figure 3 presents the CHBC-stabilized Cr(VI)-contaminated soil.

2.4. Chemicals. The FeSO_4 heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), concentrated sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), magnesium chloride (MgCl_2), diphenylcarbazide ($\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$), acetic acid (CH_3COOH), hydrochloric acid amide ($\text{NH}_2\text{OH} \cdot \text{HCl}$), hydrogen peroxide (H_2O_2), ammonium acetate ($\text{CH}_3\text{COONH}_4$), hydrofluoric acid (HF), and perchloric acid (HClO_4) used as ACS-certified reagents in this study were purchased from Sinopharm Chemical Reagent Co Ltd., China.

3. Test Methods

The heavy metal contents of the contaminated soil, sewage sludge, and magnetic biochar were determined by EPA Method 3050B (soil acid digestion) [22]. Briefly, 1 g of representative soil was dried at 110°C and placed in a glass test tube with a reflux system. After adding 10 mL of concentrated HCl, the sample was heated to 95°C and kept in agitation for 15 min. The glass test tube was cooled to 25°C , and 15 mL of HNO_3 was then added to the solution. The mixture's temperature was then maintained at 95°C for 2 h and subsequently cooled down to 25°C . After the addition of 2 mL of H_2O and 10 mL of H_2O_2 , the solution was heated to 95°C for 2 h. The leachate was filtrated through a polycarbonate filter with an effective pore size of $0.45 \mu\text{m}$. The Cr and Cr(VI) concentrations in the filtrate were measured using inductively coupled plasma mass spectrometry (ICP-MS) and colorimetric analyses, respectively.



FIGURE 1: Picture of chromium contaminated site.

TABLE 1: Physicochemical properties of Cr(VI) contaminated soil.

Index	Water content (%)	Organic content (%)	pH	Total Cr	Cr(VI)
Value	27.26	1.75	9.80	1014.6 mg/kg	973.5 mg/kg

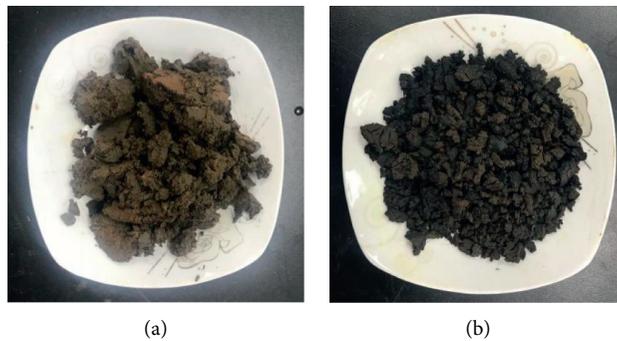


FIGURE 2: Picture of sewage sludge and CHBC. (a) Sewage sludge. (b) CHBC.

The leachability of Cr(VI) and Cr was determined by a synthetic precipitation leaching procedure (i.e., US EPA method 1312) [23]. Briefly, 10 g of the sample was mixed with 200 mL of SPLP extraction fluid and tumbled for 18 h at 30 ± 2 rpm. The leachate was filtrated through a polycarbonate filter with an effective pore size of $0.45 \mu\text{m}$. The Cr concentration in the filtrate was measured using ICP-MS.

The Cr(VI) content was determined by an alkaline digestion method (i.e., US EPA method 3060A) [24]. The Cr(VI) concentration in the leachate was measured by colorimetric analysis (i.e., the US EPA method 7196A) [25]. Briefly, 5 g of representative soil was digested in a phosphate-

buffered alkaline digestion solution ($0.28 \text{ M Na}_2\text{CO}_3/0.5 \text{ M NaOH}$) at 90°C – 95°C for approximately 60–65 min. Then, 100 mg of Mg^{2+} in the form of magnesium chloride was also added to the digestion solution to suppress the oxidation of Cr(III). The digested solution was cooled to room temperature. The leachate was filtrated through a polycarbonate filter with an effective pore size of $0.45 \mu\text{m}$. The concentration of Cr(VI) in the filtrate was measured using colorimetric analysis.

The bioaccessibility of Cr(VI) and Cr was determined by the US EPA protocol [26] and the British Geological Survey [27]. Briefly, 5 g of sample was mixed with 500 mL

TABLE 2: Physicochemical properties of sewage sludge and CHBC.

Items	Sewage sludge	CHBC
Water content (%)	78.65	—
Organic content (%)	81.34	—
pH	6.31	7.96
Total N (%)	2.72	1.14
Total P (%)	1.81	2.18
BET specific surface area (m ² /g)	—	24.73
Cu (mg/kg)	75.63	75.12
Zn (mg/kg)	56.27	54.32
Pb (mg/kg)	81.32	78.71
Cr (mg/kg)	67.85	68.46
Ni (mg/kg)	73.64	72.17
Cd (mg/kg)	2.32	2.56
Hg (mg/kg)	0.12	0.11
As (mg/kg)	0.78	0.64

TABLE 3: Experimental design for the stability study.

Test no.	Cr(VI)-contaminated soil (kg)	CHBC dosage (kg)	CHBC dosage (%)
1	5	0	0
2	5	0.05	1
3	5	0.15	3
4	5	0.25	5
5	5	0.5	10



FIGURE 3: Picture of Cr(VI)-contaminated soil stabilized by CHBC.

of SBET extraction fluid and tumbled for 2 h at 30 ± 2 rpm at 37°C . The leachate was filtrated through a polycarbonate filter with an effective pore size of $0.45 \mu\text{m}$. The Cr and Cr(VI) concentrations in the filtrate were measured using ICP-MS and colorimetric analysis, respectively.

The species distribution of Cr was measured by the BCR sequential extraction procedure [28]. The sequential extraction procedure consisted of four steps, namely, the exchangeable, reducible, oxidizable, and residue fractions. Briefly, 2 g of the sample was tested using the sequential extraction procedure. The exchangeable fraction was

determined through the extraction with 80 mL of 0.11 M HOAc for 16 h at 30 ± 2 rpm at room temperature. The reducible fraction was determined through the extraction with 80 mL of 0.5M $\text{NH}_2\text{OH.HCL}$ and 0.05M HNO_3 for 16 h at 30 ± 2 rpm at room temperature. The oxidizable fraction was determined through the extraction with 20 mL of 8.8 M H_2O_2 and 100 mL of 1 M NH_4OAc with a pH of 2.0 for 16 h at 30 ± 2 rpm at room temperature. The residual fraction was determined after digestion with 60 mL of mixed acid (20 mL of each of HNO_3 , HClO_4 , and HF) for 3 h.

The sequential extraction procedure is presented in Table 4. The risk assessment of Cr was measured by the RAC [29]:

$$\text{RAC}(\%) = \left(\frac{\sum_{n=1}^1 F_n}{\sum_{n=1}^4 F_n} \right) \times 100, \quad (1)$$

where F_n is the concentration of Cr in the nth fraction. The RAC criteria are presented in Table 5.

A Youke 722N spectrophotometer was used at the 540 nm optical path to determine the Cr(VI) concentrations in the leachate. Turbidity blanks were incorporated into the analysis procedure. The Cr(VI) solution was used in K_2CrO_4 form to calibrate the spectrophotometer. Blank and spike recoveries were conducted to check the accuracy of the method.

Agilent 7700 ICP-MS was used to determine the Cr concentrations in the leachate. For quality control purposes, the Cr ICP standard was used to calibrate the ICP-MS, and quality control blank and spikes were measured for every 10 samples per batch.

TABLE 4: Sequential extraction procedure.

Step	Extraction procedure	Chemical phases
1	Extracted by 0.11 mol/L of HOAc at a liquid to solid (L/S) ratio of 40	Exchangeable fraction
2	Extracted by 0.5 mol/L of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (adjusted to $\text{pH} = 1.5$ with HNO_3) at a liquid to solid (L/S) ratio of 40	Reducible fraction
3	Extracted by 8.8 mol/l of H_2O_2 at a liquid to solid (L/S) ratio of 10, and then extracted by 1 mol/l of NH_4OAc (adjusted to $\text{pH} = 2.0$ with HNO_3) at a liquid to solid (L/S) ratio of 50	Oxidizable fraction
4	HNO_3 -HF- HClO_4 digestion	Residual fraction

TABLE 5: RAC criteria.

Grade	Exchangeable fraction content	Risk
I	<1	No risk
II	1–10	Low risk
III	11–30	Medium risk
IV	30–50	High risk
V	50	Very risk

4. Results and Discussion

4.1. Cr(VI) Content of Stabilized Soils. Cr(VI) content is a key parameter for ensuring the reuse environmental security of stabilized soil. The Ministry of Ecology and Environment of China recommends risk screening and intervention values of 3.0 and 30 mg/kg, respectively, for the Cr(VI) content in first-category development lands. The risk screening and intervention values of second-category development lands are 5.7 and 78 mg/kg, respectively. According to the “Soil Environment Quality Risk Control Standard for Soil Contamination of Development Land” (GB36600-2018) [30], residential, medical and health, and education lands belong to first-category development lands and industrial, transportation, and green belong to second-category development lands. Figure 4 shows that the Cr(VI) content changed substantially for all stabilized soils and decreased considerably at increased CHBC dosage. When the CHBC dosage increased from 0% to 10%, the Cr(VI) content decreased from 970.1 mg/kg to 1.2 mg/kg. Figure 4 shows that the Cr(VI) content in CHBC-stabilized soil with 3% dosage was below the risk screening value of second-category development lands (5.7 mg/kg) and the risk screening value of first-category development lands (3.0 mg/kg) was achieved with a CHBC dosage of 5% [30]. Zhang et al. studied the Cr(VI) content of a contaminated soil stabilized by FeSO_4 and CaS_5 . The Cr(VI) content of the stabilized soil decreased from 168 to 94 mg/kg to 21 and 4.2 mg/kg when the reductant dosage increased from 1% to 5%, respectively [31]. These results indicate that CHBC is more advantageous than FeSO_4 and CaS_5 in stabilized Cr(VI) soil. CHBC has a higher reduction capability than FeSO_4 and CaS_5 and could substantially reduce the Cr(VI) content of contaminated soil.

4.2. Leachability of Cr and Cr(VI) of Stabilized Soils.

Figure 5 shows the leachability of the Cr and Cr(VI) of stabilized soils with different CHBC dosages. The Cr(VI) and Cr concentrations decreased with the increase in CHBC dosage. When the CHBC dosage increased from 0% to 10%, Cr(VI) and the total Cr decreased from 38.6 and 40.1 mg/L to 0.024 and 0.07 mg/L, respectively. Figure 5 shows that the Cr(VI) and Cr concentrations of stabilized soils satisfy the Standards for Hazardous Waste regulatory limits in China (5 and 15 mg/L, respectively) at respective CHBC dosages of 1% and 3%; the values were also within the Standard for Pollution Control on the landfill site of the municipal solid waste regulatory limit in China (1.5 mg/L for Cr(VI) and 4.5 mg/L for Cr) [32, 33]. The Cr(VI) concentrations of stabilized soils were lower than the China Environmental Quality Standards of surface water for the agriculture and civil use regulatory limits (0.1 and 0.05 mg/L) at respective CHBC dosages of 5% and 10% [34]. This phenomenon occurred because Cr(VI) was reduced to Cr(III) by FeSO_4 , whereas Cr(III) formed the $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ precipitate and complexations or complexed with functional groups [11]. Dong et al. [8] and Chen et al. [18] observed that many active functional groups (C-H, C=O, C-O, OH, and COOH) appeared on the biochar surface when organic solid wastes were modified by ferric chloride and pyrolyzed in an oxygen-free furnace. These functional groups with high specific surface areas, strong reducibility, and high concentration of radicals could result in Cr(III) coprecipitation or complexation with functional groups [35]. These results demonstrate that CHBC could notably reduce the leachability of Cr and Cr(VI) and can be applied in Cr(VI)-contaminated soil remediation.

4.3. Bioaccessibility of Cr and Cr(VI) of Stabilized Soils.

Figure 6 shows the bioaccessibility of Cr- and Cr(VI)-stabilized soils with different CHBC dosages. The Cr(VI) and Cr concentrations in the SBET test decreased with the increase in CHBC dosage. When the CHBC dosage increased from 0% to 10%, Cr(VI) and the total Cr decreased from 9.7 and 10.1 mg/L to 0.03 and 0.08 mg/L, respectively. These findings suggest that the bioaccessibility risk of Cr decreased with the increasing CHBC dosage. The leachant used in the bioaccessibility test was a strong acid solution (with pH of 1.5); thus, the Cr in CHBC-stabilized soils has high erosion-resisting characteristics in a strong acid environment. This result agrees with the findings of Wang et al. [36] and Jobby et al. [37].

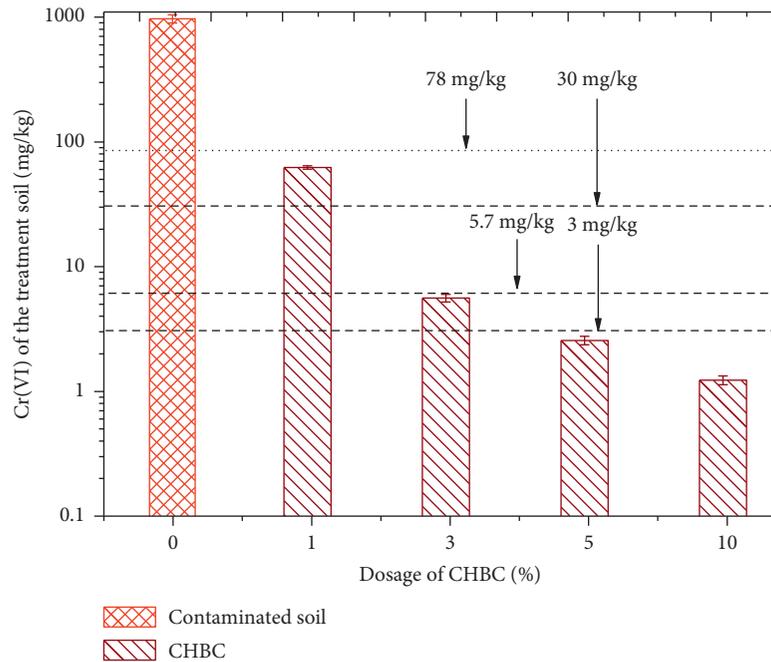


FIGURE 4: Effect of CHBC dosage on Cr(VI) content of stabilized soils.

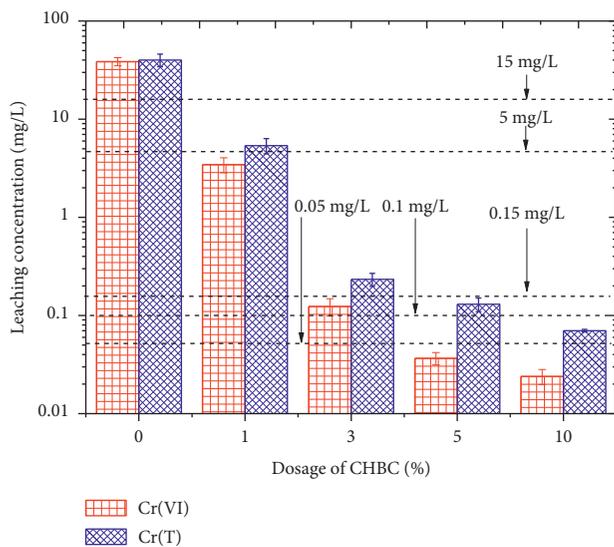


FIGURE 5: Effect of CHBC dosage on leachability of Cr and Cr(VI) of stabilized soils.

4.4. Speciation Distribution of Cr and Cr(VI) in Stabilized Soils. Figure 7 shows the speciation distribution of the Cr of stabilized soils with different CHBC dosages. Most of the Cr in the contaminated soil was in exchangeable fraction (86.27%). However, the reducible (7.73%), oxidizable (5.62%), and residue fractions (0.38%) were minimal. The Cr speciation in stabilized soils changed substantially, and the exchangeable fraction was converted to reducible, oxidizable, and residue fractions with CHBC addition. The exchangeable, reducible, oxidizable, and residue fractions decreased to 6.656%, 17.41%, 74.34%, and 1.443%,

respectively, when the CHBC dosage was increased to 5%. This phenomenon occurred because Cr(VI) was reduced to Cr(III) by FeSO_4 , and Cr(III) formed the $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ precipitate and complexation or complexed with functional groups [18, 35]. Figure 7 also displays the considerable decrease in reducible fraction from 17.41% to 5.47%; the oxidizable and residue fractions increased from 74.34% to 89.53% and from 1.43% to 3.91%, respectively, when the CHBC dosage was increased from 5% to 10%. The decrease in reducible fraction can also be attributed to the active functional groups (C-H, C=O, C-O, and OH). The FeSO_4 levels increased with CHBC addition and caused the increased formation of Cr-organic complex and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ precipitation. These results agree with the findings of Zhou et al. [12] and Agrafioti et al. [16]. Gabarrón et al. [38] and Zimmerman and Weindorf [39] observed that species distribution determines the leachability of heavy metals in stabilized soil. Zhang et al. [40] showed that the availability and mobility of heavy metals in soil are related to the content of exchangeable forms. These results demonstrate that CHBC substantially increases the chemical stability of Cr in stabilized soil. This alteration in the Cr speciation of CHBC-stabilized soil accounts for the reduced leachability and bioaccessibility of Cr.

4.5. Risk Assessment of Cr in Stabilized Soils. RAC, which considers the mobility fraction of metals, is used to identify the risk of heavy metals in contaminated soils. Figure 8 shows the effect of CHBC dosage on the RAC of stabilized soils. The RAC decreased with the increase in CHBC dosage. When the CHBC dosage increased from 0% to 10%, the RAC decreased from 97.6 to 0.91. This result suggests that the risk decreased from very-risky to no-risk condition. Figure 8

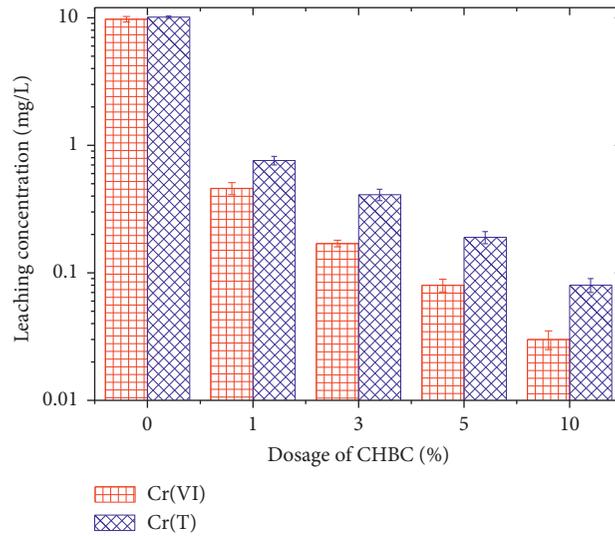


FIGURE 6: Effect of CHBC dosage on bioaccessibility of Cr and Cr(VI) of stabilized soils.

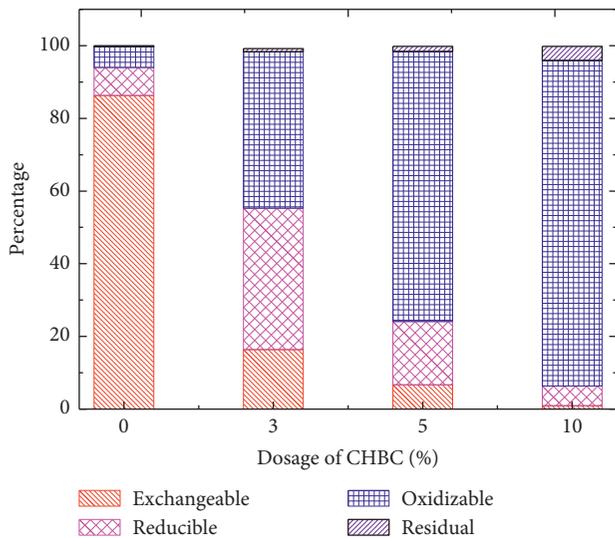
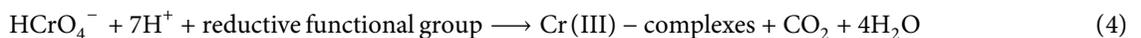
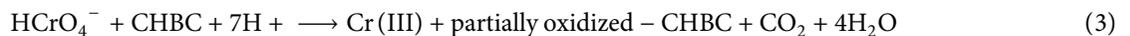


FIGURE 7: Effect of CHBC dosage on speciation distribution of Cr of stabilized soils.

shows that the RAC of the stabilized soils with 10% CHBC dosage indicates no risk. Giridharan et al. [41] and Sundaray et al. [42] noted that heavy metals in high-risk and very-high-risk categories are potentially bioavailable and may easily enter the food chain. Heavy metals in medium-risk

categories of stabilized soil could be controlled by utilizing subgrade fill materials. Heavy metals in no-risk and low-risk categories are safe for the environment. The results of the risk assessment of stabilized soils agree with the Cr(VI) content findings on CHBC-stabilized soils. This phenomenon indicates that CHBC is a high-efficiency reducing agent in the remediation of Cr(VI)-contaminated soils.

4.6. Probable Immobilization Mechanism of Cr. Figure 9 displays the XRD results of Cr(VI)-contaminated and CHBC-stabilized soils. The contaminated soil showed the same distribution of peak position before and after stabilization with CHBC. Illite, quartz, albite, and montmorillonite were identified as the major phases in Cr(VI)-contaminated and CHBC-stabilized soils. This result precludes the formation of new crystal lattices in CHBC-stabilized soil. The changes in the leachability, bioaccessibility, and speciation distribution of Cr in the contaminated soil before and after stabilization with CHBC can be attributed to the following reasons. (1) Cr(VI) was reduced to Cr(III) by active functional groups (C-H, C=O, C-O, and OH) and FeSO₄. (2) Cr(III) formed (Cr_xFe_{1-x}(OH)₃ precipitates and complexed with carbonyl and carboxyl groups. The coupled redox reactions between Cr(VI) and CHBC are expressed in the following equations:



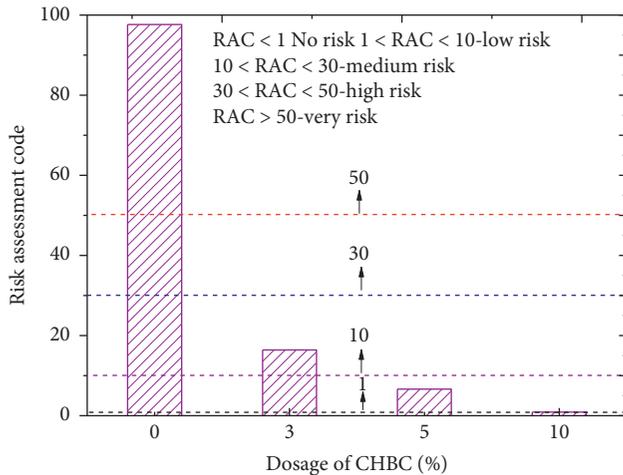


FIGURE 8: Effect of CHBC dosage on risk assessment of stabilized soils.

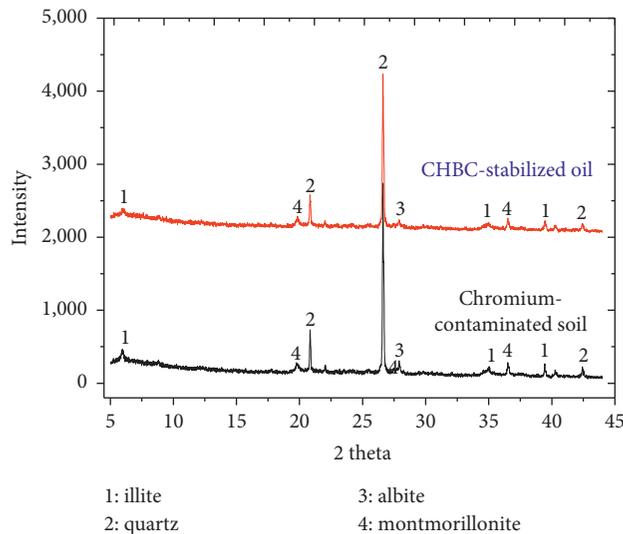


FIGURE 9: The XRD patterns of the Cr(VI)-contaminated soil and CHBC stabilized soil.

Kostarelos et al. [43] suggested that Cr(VI) is reduced to Cr(III) by FeSO_4 and forms Cr(III)-Fe(III) hydroxide precipitates ($\text{Cr}(\text{OH})_3$ and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$). Reyhanitabar et al. [44] and Tytlak et al. [45] observed that the sewage sludge biochar favors the Cr(VI) reduction into the less mobile Cr(III), which is the main mechanism for Cr(VI) stabilization in soil. Lu et al. [46] suggested that Cr(III) could form surface complexation with the free carboxyl and hydroxyl functional groups of CHBC. Chen et al. [47] reported that Cr(VI) and Cr(III) could form inner-sphere complexation and coprecipitation with the functional groups (-R-O-, -COO-, and -O-mineral oxides) of sewage sludge biochar. Costa et al. [35] noted that carboxyl (R-COOH) and alcoholic or phenolic hydroxyl groups (R-OH) are generally accepted as the main groups contributing to the coordination between Cr(III) and sorbent surfaces. Han et al. [48] suggested that the Cr(VI) removal mechanism of biochar is

the electrostatic attraction on protonated -OH on the $\gamma\text{-Fe}_2\text{O}_3$ surface, and it could be stabilized in an acid solution. Miretzky et al. [49] and Tsang et al. [50] consider the Cr(VI) reduction by reductive functional groups (such as C=C and -COO) irreversible, whereas Cr(III) sorption is reversible in alkaline solutions. This result agrees with that of Oluwatuyi et al. [4, 51]. Thus, the leachability, bioaccessibility, and toxicity of Cr(VI) and Cr changed in the CHBC-stabilized soil.

5. Conclusions

This study developed CHBC as a new reductant for Cr(VI)-contaminated soil. The effectiveness of CHBC-stabilized Cr(VI)-contaminated soil was investigated by SPLP, SBET, alkaline digestion, sequential extraction, XRD, and RAC. The following conclusions were drawn:

- (1) CHBC has high efficiency in stabilizing Cr(VI). This material can effectively reduce the leachability and bioavailability of Cr in contaminated soil. The Cr(VI) content in CHBC-stabilized soil at 3% dosage is below the risk screening value of second-category development lands (5.7 mg/kg). The risk screening value of first-category development lands (3.0 mg/kg) was achieved with the CHBC dosage of 5%. At CHBC dosages of 1% and 3%, the Cr(VI) and Cr concentrations of stabilized soils meet the Standards for Hazardous Waste regulatory limit in China (5 and 15 mg/L, respectively); the values for the Standard for Pollution Control on the Landfill Site of Municipal Solid Waste regulatory limit in China were also met (1.5 mg/L for Cr(VI) and 4.5 mg/L for Cr). The Cr(VI) and Cr concentrations of the stabilized soils were lower than the China Environmental Quality Standards of surface water for the agriculture and civil use regulatory limit (0.1 and 0.05 mg/L, respectively) when the CHBC dosages were 5% and 10%.
- (2) CHBC substantially reduced the environmental risk of Cr in the stabilized soil. The risk of Cr in the stabilized soil decreased from very risky to no risk, and the exchangeable fraction of Cr was mainly converted to oxidizable fraction when the CHBC dosage was increased from 0% to 10%. The changes in leachability, bioaccessibility, and risk of Cr(VI) and Cr in stabilized soil were attributed to the reaction between CHBC and Cr(VI) and Cr. Cr(VI) was reduced to Cr(III) by FeSO_4 , whereas Cr(III) formed the $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ precipitate and complexations or complexed with the functional groups of CHBC.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

Yuan-Yuan Li and Ting-Ting Zhang are regarded as the co-first authors.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Contributions

Yuan-Yuan Li and Ting-Ting Zhang contributed to the work equally.

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