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Immobilization of hexavalent chromium in contaminated soils using biochar supported nanoscale iron sulfide composite

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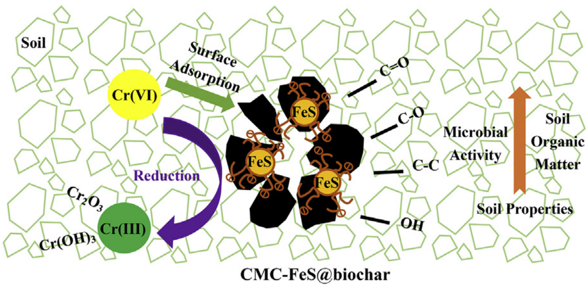
HIGHLIGHTS

- First study on CMC-FeS@biochar for enhanced Cr(VI) immobilization in soil.
- Surface sorption and reduction/precipitation are dominant immobilization mechanisms.
- The composite converts more accessible Cr into less accessible forms.
- The composite greatly reduces bioavailability of Cr(VI) to wheat and earthworms.
- The addition of the composite enhances soil organic matter and microbial activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar supported carboxymethyl cellulose (CMC)-stabilized nanoscale iron sulfide (FeS) composite (CMC-FeS@biochar) was prepared and tested for immobilization of hexavalent chromium Cr(VI) in soil. Results of UV–vis and transmission electron microscopy (TEM) showed that the backbone of biochar suppressed the aggregation of FeS, resulting in smaller particle size and more sorption sites than bare FeS. The composite at a dosage of 2.5 mg per gram soil displayed an enhanced Cr(VI) immobilization efficiency (a 94.7% reduction in the toxicity characteristic leaching procedure (TCLP) based leachability and a 95.6% reduction in the $CaCl_2$ extraction) compared to plain biochar and bare FeS. Sequential extraction procedure (SEP) and X-ray photoelectron spectroscopy (XPS) analysis suggested that CMC-FeS@biochar promoted the conversion of more accessible Cr (exchangeable and carbonate-bound fractions) into the less accessible forms (iron-manganese oxides-bound, organic material-bound, and residual fractions) to reduce the toxicity of Cr(VI) and that surface sorption and reduction were dominant mechanisms for Cr(VI) immobilization. CMC-FeS@biochar greatly reduced the bioavailability of Cr(VI) to wheat and earthworms (*Eisenia fetida*). Moreover, the application of CMC-FeS@biochar enhanced soil organic matter content and microbial activity. This work highlighted the potential of CMC-FeS@biochar

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composite as a low-cost, “green”, and effective amendment for immobilizing Cr(VI) in contaminated soils and improving soil properties.

1. Introduction

Chromium (Cr) is widely used in a variety of industrial applications, such as electroplating, metallurgy, leather tanning, wood preservation, and chromate manufacturing. The acidic industrial wastewater containing high content of Cr can lead to a widespread contamination of the surrounding soil (Ajmal et al., 1984; Koenig et al., 2016). A nationwide survey of soil pollution conducted in 2014 in China showed that chromium contents of the soil sampling points exceeded the standard rate by 1.1% (Faisal and Hasnain, 2005). Cr(VI) and Cr(III) are the two oxidation states of Cr in natural environment. Cr(III) is less toxic, easy to hydrolyze in aqueous solution ($Cr(OH)_3$, Cr_2O_3), and recognized as an essential trace element for human nutrition, while Cr(VI) is hyper-toxic and soluble in aqueous media over a wide pH range. Due to its carcinogenicity, persistence, and bioaccumulation, Cr contamination causes the accumulation of Cr in plants, enters the food chain via plants, and eventually presents potential threat to human health (Husson, 2013). Sivakumar and Subbhuraam (EPD and MLR, 2014) reported that Cr(VI) was lethal to earthworms at concentrations ranging from 225 to 257 mg kg^{-1} in soil. In China, chromium is regulated with a critical value of 1000 mg kg^{-1} for total Cr (Cr_{total}) and 30 mg kg^{-1} for Cr(VI) in soil of commercial use. Thus, it is important to reduce the potential toxicity of Cr(VI) in soil by converting Cr(VI) to insoluble Cr(III) precipitates, which can be immobilized in soil.

In situ remediation of Cr(VI)-contaminated soil by delivering reactive materials into input source zones has recently been considered as a promising technology (Fang et al., 2016; Mahdieh et al., 2016; Su et al., 2016). Su et al. (2016) reported that nano zero-valent iron@biochar (nZVI@biochar) composite reduced the toxicity characteristic leaching procedure (TCLP)-leachable Cr(VI) concentrations from Cr(VI) spiked soil (Cr(VI) content = 320 mg kg^{-1}) by 100% and decreased the physiological based extraction test (PBET)-based bioaccessibility of Cr(VI) by 100% when the soil was treated with 8 g kg^{-1} of nZVI@biochar for 15 d. Pot experiments showed that nZVI@biochar effectively reduced Cr contents in the leaves, stems, and roots of the cabbage mustard by 78.8%, 86.9%, and 83.4%, respectively. However, when applied to environmental remediation, ZVI may preferentially reduce nitrate and/or oxygen which may not be the targets, leading to a decrease in the immobilization efficiency (Henderson and Demond, 2011).

Iron sulfide (FeS) is effective for the reduction of Cr(VI) because it can provide a source of Fe(II) and S (-II) species. However, bare FeS particles tend to agglomerate rapidly, greatly diminishing their removal efficiency. The introduction of carboxymethyl cellulose (CMC) as a stabilizer and biochar as a Supporting Material can effectively prevent the aggregation of particles and enhance their physical stability and removal efficiency (Gong et al., 2014; Yan et al., 2014). Our previous work indicated that biochar supported nanoscale FeS (CMC-FeS@biochar) was effective in the removal of aqueous Cr(VI) (Lyu et al., 2017). The composite offered higher removal capacity and affinity toward Cr(VI) compared to bare FeS and plain biochar due to a synergistic effect induced by interaction between individual components. The Cr(VI) removal capacity (q_m = 150 mg g^{-1}) was much greater than the reported value of biochar-supported ZVI (10.6 mg g^{-1}). Moreover, the synthetic procedure of CMC-FeS@biochar is simple and environmentally friendly, and no costly chemicals are required. Yet, the feasibility of CMC-FeS@biochar for remediating Cr(VI)-contaminated soil has not been reported.

Biochar related materials are among the most commonly used adsorbents for the immobilization of heavy metals in soils due to their relatively high sorption capacities and friendly environmental compatibility. Cao et al. (2011) reported that biochar could decrease the leaching of Pb(II) in soils and reduce their uptake by earthworms. Significant increases in seed germination and growth have been reported in the soils amended with biochars (Zhou et al., 2013; Ahmad et al., 2014; Sun et al., 2014). However, the biological effects of the CMC-FeS@biochar composite to earthworms and plants are still unclear. Information about the fate and eco-toxicity of Cr species in CMC-FeS@biochar-remediated soil is urgently needed before field application.

The overall goal of this study was to determine the feasibility of CMC-FeS@biochar for immobilization of Cr(VI) in Cr-contaminated soils. The specific objectives were to (1) examine the effects of CMC-FeS@biochar dosage and equilibrium time on the effectiveness of Cr(VI) immobilization; (2) examine the change of Cr speciation in treated soil and explore the underlying Cr(VI) immobilization mechanisms; (3) evaluate the ecological uptake of Cr in earthworms in remediated soil; and (4) determine the effects of CMC-FeS@biochar on seeds germination, early growth, and the bioaccumulation of Cr.

2. Materials and methods

2.1. Materials

All chemicals used in the present study were of analytical grade. Sodium sulfide nonahydrate ($Na_2S\cdot 9H_2O$), iron sulfate heptahydrate ($FeSO_4\cdot 7H_2O$), and potassium dichromate ($K_2Cr_2O_7$) were purchased from Fengchuan Chemical Technology (Tianjin, China). CMC (in the sodium form, M.W. = 90 000, degree of substitute = 0.7, melting point = 274 °C, and density = 1.6 g cm^{-3}) were purchased from Anpel Laboratory Technology (Shanghai, China). Wheat (Shannong26) seeds were purchased from Zaozhuang Seed Company (Shandong, China). Earthworms (*Eisenia fetida*) were purchased from Jurong Wang Jun earthworm breeding base (Jiangsu, China). Wheat straw obtained from Shandong province, China was air-dried for 7 d and milled into powders of 2 mm as the feedstock biomass for biochar production.

2.2. Soil sample preparation and analysis

A Cr(VI)-free soil sample was obtained from Nankai University in Tianjin, China. Before use, the soil was washed three times with tap water to remove suspended colloids and water leachable compositions. The washed soil was then air-dried for 7 d, and sieved through a standard sieve of 2-mm opening. Cr_{total} content was determined per the US Environmental Protection Agency (EPA) method 3050B (1996) and Cr(VI) content was determined per the US EPA method 3050A (1996). The Cr_{total} content was 31.1 ± 2.9 mg kg^{-1} and no detectable Cr(VI) was found. To prepare