



## Removal of hexavalent chromium from aqueous solutions by a novel biochar supported nanoscale iron sulfide composite



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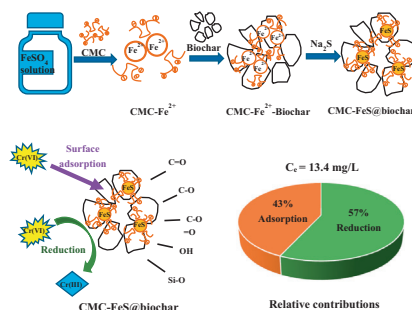
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### HIGHLIGHTS

- CMC-FeS@BC was synthesized combining the advantages of biochar, CMC, and FeS.
- 57% of Cr(VI) removal was due to reduction and 43% was ascribed to sorption.
- External mass transfer model adequately represents Cr(VI) sorption kinetics.
- Isotherm data of Cr(VI) were simulated adequately by Redlich-Peterson model.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A novel biochar supported nanoscale iron sulfide (FeS) composite (CMC-FeS@biochar) combining the advantages of biochar, carboxymethyl cellulose (CMC), and FeS was synthesized and tested for Cr(VI) removal efficiency and mechanisms. FeS particles were effectively soldered onto the surface of biochar through —OH, C=C, O=C—O, C—O, and Si—O functional groups. The composite at a mass ratio of FeS: CMC: biochar = 1:1:1 displayed an enhanced Cr(VI) adsorption capacity of 130.5 mg/g at pH 5.5 compared to 38.6 mg/g for FeS and 25.4 mg/g for biochar. Surface sorption and reduction were the dominant removal mechanisms. At the equilibrium Cr(VI) concentration of 13.4 mg/L, 57% of Cr(VI) removal was attributed to reduction and 43% was ascribed to surface sorption. The adsorption kinetic data were adequately simulated with pseudo second-order kinetic model and mass transfer model, suggesting that sorption kinetics were the combination of chemisorption and external mass transfer. The Redlich-Peterson model fitted better than the Langmuir and Freundlich models in simulating the adsorption isotherm data, again suggesting a hybrid chemical reaction-sorption process. The Dubinin–Radushkevich isotherm model resulted in an adsorption energy of 10.0 kJ/mol, implying a chemisorption between Cr(VI) and CMC-FeS@biochar. The present study demonstrated the promise of CMC-FeS@biochar composite as a low-cost, “green”, and effective sorbent for removal of Cr(VI) in the environment.

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## 1. Introduction

Chromium (Cr), a commonly occurring heavy metal in surface water and groundwater, is often derived from a variety of industrial processes such as metallurgy, chromate manufacturing, textile dyeing, tanneries, wood preservation, and metal electroplating [1,2]. It can pose a high risk to ecosystem and public health due to its carcinogenicity, persistence, and bioaccumulation [3]. In general, Cr is present as trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) in the natural environment [4]. Compared to Cr(III), which is less toxic and usually found in the form of precipitates (i.e.,  $\text{Cr}(\text{OH})_3$  and  $\text{Cr}_2\text{O}_3$ ), Cr(VI) is hyper-toxic and occurs as soluble and mobile oxyanions ( $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$ , and  $\text{Cr}_2\text{O}_7^{2-}$ ) [5]. Cr(VI) has been identified as a top priority hazardous pollutant by the United States Environmental Protection Agency (USEPA). In China, Cr(VI) is regulated with a mandatory discharge limit of 0.05 mg/L in surface water [6,7] and 0.5 mg/L in wastewater [8]. The USEPA formulates a maximum contaminant level (MCL) of 0.1 mg/L for total Cr in drinking water [9]. Typical Cr(VI) concentrations in Cr(VI)-contaminated water and wastewater are in the range of 30–200 mg/L [5,10]. Thus, it is of great importance to develop practically reactive materials which can adsorb and reduce Cr(VI) to Cr(III) to minimize the toxicity of Cr(VI).

Iron sulfide (FeS) is an efficient, economical, and environmentally friendly reducing agent. It can provide a source of Fe(II) and S(-II) species to facilitate Cr(VI) reduction. Lu et al. examined the effectiveness of natural clinopyrrhotite (FeS minerals) for reduction of Cr(VI) (9.9 mg/L) at pH 1.1–12.1, and showed that clinopyrrhotite removed greater than 90% of the Cr(VI) within 40 min at a dosage of 60 g/L and a pH < 5.0 [5].

Compared to bulk particles or natural minerals, nanoscale FeS particles show much higher reactivity due to the smaller particle size, and thus larger specific surface area. However, fine sized FeS particles are unstable and can agglomerate rapidly in aqueous solutions, which may limit the removal efficiency and present challenges to their environmental applications [11]. Gong et al. employed carboxymethyl cellulose (CMC) as a stabilizer and successfully prepared CMC-stabilized FeS nanoparticles with an enhanced mercury uptake of ~2800 mg/g (a 20% increase compared to non-stabilized FeS) [12]. Recent studies also indicated that the introduction of porous materials such as biochar [1,13,14], carbon microspheres [15], and natural silica sand [16–19] can effectively prevent the aggregation of particles and enhance their physical stability and removal efficiency.

Biochar is a stable solid, rich in carbon, porous with large surface area, and thus has been widely used as a mechanical support to disperse nanoparticles to facilitate their environmental application [13,20,21]. Our recent work [22] indicated that, compared to biochar, biochar-supported graphene composites showed larger surface area and pore volume, more functional groups, better thermal stability, and higher sorption capacities for phenanthrene and mercury. Yan et al. developed a new biochar-supported ZVI (nZVI@biochar) and investigated its application for aqueous trichloroethylene (TCE) removal. 99.4% of the TCE was degraded via nZVI@biochar compared to 56.5% by nZVI. The enhanced degradation efficiency was due to the larger specific surface area and abundant oxygen-containing functional groups originating from the backbone of biochar [14]. Biochar can be produced from biological solid wastes (e.g., agricultural residues, animal manure, and sludge) and is much cheaper than activated carbon. In addition, biochar itself can reduce Cr(VI) to Cr(III) by redox reactions of surface functional groups [23]. Using biochar to support nanoscale FeS for environmental application is efficient and economically beneficial. However, to our knowledge, no studies have been reported about the preparation of biochar-supported CMC-stabilized FeS nanoparticles (CMC-FeS@biochar), and no detailed investigation

into the effectiveness of Cr(VI) removal by CMC-FeS@biochar has been reported.

The overall goal of this study was to develop a novel CMC-FeS@biochar composite combining the advantages of biochar, CMC, and FeS and investigate its effectiveness for removal of aqueous Cr(VI). The specific objectives were to: (1) prepare and characterize CMC-FeS@biochar with various FeS:CMC:biochar mass ratios, and elucidate the interactions between FeS, CMC, and biochar; (2) determine the effects of FeS:CMC:biochar mass ratio, CMC-FeS@biochar dosage, pH, contact time, and initial Cr(VI) concentrations on the Cr(VI) removal effectiveness; and (3) acquire further insights into the underlying Cr(VI) removal mechanisms by CMC-FeS@biochar.

## 2. Materials and methods

### 2.1. Chemicals

All chemicals used in the present study were of analytical grade. Sodium sulfide nonahydrate ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ), iron sulfate heptahydrate ( $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ), and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) were purchased from Fengchuan Chemical Technology (Tianjin, China). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were obtained from Tianjin Chemical Reagent Technology (Tianjin, China). CMC (MW = 90 000 in the sodium form; degree of substitute = 0.7) was purchased from Anpel Laboratory Technology (Shanghai, China). Wheat straw obtained from Shandong province, China, was air-dried for 7 days, milled into particles of ~2 mm, and used as the feedstock biomass for biochar production.

### 2.2. Preparation of CMC-FeS@biochar composite

Biochar was prepared following an approach developed in our previous study [24], which is detailed in the Supporting Information (SI Section 1). The resultant biochar was stored in glass vials for the preparation of CMC-FeS@biochar composite.

CMC-FeS@biochar was prepared following a revised method by Zhou et al. [13] and Gong et al. [12] (SI Fig. S1). First, 1.75 g of  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$  ( $6.31 \times 10^{-3}$  mol  $\text{FeSO}_4$ ) was dissolved in 1000 mL deionized water and purged with purified  $\text{N}_2$  (>99%) for 1 h to remove dissolved oxygen. Then, 55 mL of CMC solution (1%, w/w) was added to the above solution under  $\text{N}_2$  purging to form  $\text{Fe}^{2+}$ -CMC complexes. Subsequently, 550 mg of biochar (particle size = 0.5–1 mm) was introduced into the mixture. With strong magnetic stirring, FeS particles were deposited on the surface of biochar by dropwise addition of 45 mL  $\text{Na}_2\text{S}$  solution (1.51 g  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , i.e.,  $6.31 \times 10^{-3}$  mol  $\text{Na}_2\text{S}$ ), and the mixture was stirred for another 30 min under  $\text{N}_2$  purging. The resultant suspension contained 500 mg/L FeS, 500 mg/L CMC, and 500 mg/L biochar (i.e., a FeS:CMC:biochar mass ratio of 1:1:1). To ensure complete reaction and full growth of the FeS, the suspension was sealed and aged for 24 h. The mixture was then freeze-dried, washed with  $\text{N}_2$ -purged deionized water to remove  $\text{Na}_2\text{SO}_4$ , and freeze-dried again for subsequent uses.

Five types of CMC-FeS@biochar composite were prepared by varying the FeS:CMC:biochar mass ratios, namely, 5:5:1, 3:3:1, 1:1:1, 1:1:3, and 1:1:5. For comparison, FeS, plain biochar, and CMC-FeS, which represented a FeS:CMC:biochar mass ratio of 1:0:0, 0:0:1, and 1:1:0, respectively, were also prepared under otherwise identical conditions.

### 2.3. Characterization of CMC-FeS@biochar

The amount of FeS coated on the biochar was quantified following a revised method by Yang et al. [25]. In brief, 0.1 g of

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