



Remediation of hexavalent chromium contaminated soil by stabilized nanoscale zero-valent iron prepared from steel pickling waste liquor



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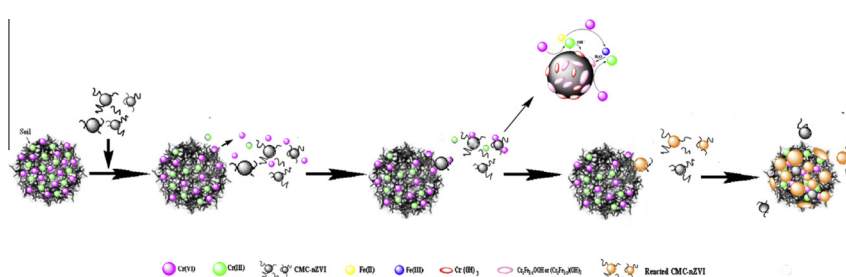
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HIGHLIGHTS

- Steel pickling waste liquor is used as iron precursor to prepare nZVI.
- Removal capacity of soil-bound Cr(VI) by CMC-nZVI is studied.
- The removal mechanism of Cr(VI) in contaminated soil by CMC-nZVI is proposed.
- Feasibility of CMC-nZVI in Cr(VI)-contaminated soil remediation is tested by TCLP.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal of Cr(VI) from contaminated soil using sodium carboxymethyl cellulose (CMC)-stabilized nanoscale zero-valent iron prepared from steel pickling waste liquor was systematically investigated. Laboratory batch experiments indicated that 0.09 g L⁻¹ of Fe⁰ nanoparticles at a soil to solution ratio of 1 g: 10 mL completely reduced the aqueous-bound Cr(VI), which contributed about 46% of the pre-sorbed Cr(VI) in the soil (Cr(VI) = 102 mg kg⁻¹). Furthermore, the addition of Fe⁰ nanoparticles only removed a portion of the soil-bound Cr(VI). When the soil was treated with 0.3 g L⁻¹ of Fe⁰ nanoparticles for 72 h, 80% of the loaded Cr(VI) was reduced to Cr(III), which resulted in a residual Cr(VI) concentration of 20 mg kg⁻¹. Based on the studies of elemental distributions and XPS analysis, it is proposed that reduction and immobilization may be equally important removal mechanisms for Cr(VI) by CMC-nZVI. Following the treatment by CMC-nZVI, the TCLP leachability of the Cr(VI) and Cr_{total} was significantly reduced by 100% and 82%, respectively. This study sheds new light on the remediation of Cr(VI)-contaminated soil by CMC-nZVI.

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1. Introduction

Soil contamination by chromium is a leading concern in China [1–3], where officials have classified it as the first major heavy metal to be controlled from 2010 to 2015 [4]. In natural soil,

chromium often exists in two highly stable oxidation states, trivalent (Cr(III)) and hexavalent (Cr(VI)) [5]. Compared with the relatively immobile Cr(III), Cr(VI) species is much more soluble and mobile. Of greater concern is that Cr(VI) is 100 times more toxic than Cr(III), and it has been added to the Class A Human Carcinogens list by the US Environmental Protection Agency (US EPA) [6]. Given its toxicity, efforts have been made to remove Cr(VI), including chemical reduction (e.g. calcium polysulfide [7,8], ferrous iron [9]), electrokinetic remediation [10,11], bioremediation [12,13] and phytoremediation [14]. Recently, the use of nanoscale

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zero-valent iron (nZVI) as a reactive media for in situ subsurface environment remediation of Cr(VI) has been extensively investigated [15,16].

Researchers have demonstrated that nZVI can serve as an effective agent for in situ remediation of chromium in solid waste [17–20]. To prevent aggregation and facilitate the transport of nZVI in field conditions, nZVI has also been modified with several types of organic coatings, such as starch [21], polyvinylpyrrolidone (PVP) [22] and sodium carboxymethyl cellulose (CMC) [23]. However, these kinds of iron-based materials prepared with traditional methodologies, consume a lot of chemical reagents such as ferrous sulphate and ferrous chloride, which results in high production costs and limits further engineering applications. To reduce the cost, steel pickling waste liquor discharged from the steel industry was used in this study to prepare the stabilized nZVI. The economic benefits of this method have been demonstrated in our previous studies [24,25].

To facilitate the in situ remediation of Cr(VI)-contaminated soil, extensive efforts have been made to optimize the influencing factors, including the dosage, pH, etc. [21,26]. To date, however, researchers have mainly focused their attention on the removal of aqueous-bound Cr(VI) rather than soil-bound Cr(VI), which may be absorbed by plants and subsequently spreads into the human food chain. Moreover, the mechanisms for the removal of Cr(VI) from contaminated soil proposed by different researchers are often contradictory. Cao and Zhang reported that Cr(VI) was primarily reduced to Cr(III) by nZVI and then precipitated as hydroxides on the soil surface, although they had insufficient evidence for that assumption [17]. Chrysochoou and Johnston suggested that sorption and co-precipitation may be the mechanisms for the removal of Cr(VI) by nZVI [18]. In light of these conflicting results, it is essential to clarify the ambiguities concerning the removal mechanisms for Cr(VI)-contaminated soil systems before they are widely applied. Finally, the nanoparticles used in this study were prepared from steel pickling waste liquor, which has been listed in the China Dangerous Wastes Catalogue [27]. To verify the feasibility of this material in the remediation of contaminated soil, TCLP was performed to determine the mobility of the Cr in the treated soil.

Therefore, the specific objectives were to (1) investigate the effects of different parameters on the removal of aqueous-bound Cr(VI) by CMC-stabilized nZVI (CMC-nZVI); (2) test the maximal removal capacity of soil-bound Cr(VI); (3) propose the possible removal mechanism of Cr(VI) in soil; (4) explore the leachability of chromium in the soil after remediation using TCLP.

2. Experimental

2.1. Materials and chemicals

Sodium borohydride (NaBH_4 , >98%), sodium carboxymethyl cellulose (CMC), ethanol (99.7%) and potassium dichromate were purchased from Tianjin Damao Chemical Agent Factory (Tianjin, China). 1,5-diphenylcarbohydrazide was obtained from Tianjin Regent Chemical Co. Ltd. (Tianjin, China). All chemicals used in this study were of analytical grade or higher. Pickling waste liquor was reclaimed from the Jinlai steel plant in Guangzhou. Some of the physical and chemical properties are as described previously [25]. Before use, the liquor was diluted by 10 times to obtain a Fe concentration of 12.2 mg L^{-1} .

2.2. Soil sample preparation

The soil sample was collected from the Higher Education Mega Center in Guangzhou, China. Before use, the raw soil was sieved

with a 0.25 mm standard sieve and then stored in a dryer for future use. Tests revealed that the soil sample was free from chromium and its physico-chemical characteristics are shown in Table 1.

Cr(VI)-spiked soil samples were prepared using the following procedure: 10 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution at the desired concentration was mixed with 10 g of air-dried soil and stirred until the mixture was air dried to a constant weight. Then, the soil samples were analyzed to determine the loaded Cr(VI) concentration. The error between repeated preparations was less than 5%. To identify the homogeneity of Cr(VI) in the soil, Cr(VI) contents in a series of soil samples which increased manifold in weight were detected. Results showed that Cr(VI) concentration was proportional to the amount of soil samples, which indicated the well dispersity of Cr(VI) in the soil.

The spiked soil samples with varying pH levels were prepared by the same procedure except adjusting the pH of $\text{K}_2\text{Cr}_2\text{O}_7$ solution by 1 M HCl or 5 M NaOH. The final pH values and Cr(VI) leachability of these spiked soil samples in 0.1% (w w^{-1}) CMC solution were measured (Table 2).

2.3. Preparation of CMC-stabilized nZVI

The CMC-nZVI was prepared by sodium borohydride reduction method using steel pickling waste liquor. In a typical synthesis, 120 mg CMC was dissolved in deionised (DI) water with purging by purified N_2 for 15 min and 3 mL of diluted waste liquor was accurately pipetted. The mixture was then vigorously stirred for 15 min under anaerobic conditions. Subsequently, CMC-stabilized nZVI was formed by drop-wise addition of 4.5 g L^{-1} sodium borohydride solution to the above solution with continuous stirring. To fully disperse the suspended nZVI, the suspension was then sonicated for 2 min before use. Brunauer–Emmett–Teller (BET) result showed that the sizes of these nanoparticles ranged from 10 to 100 nm with a surface area of $40 \pm 2 \text{ m}^2 \text{ g}^{-1}$. For comparison, non-stabilized nZVI (i.e. bare nZVI) was prepared following the same procedure but without CMC. The concentration of CMC used in this study was 0.1% (w w^{-1}).

2.4. Experimental procedures

The removal of Cr(VI) leached from the spiked soil (i.e. aqueous-bound Cr(VI)) was tested under different experimental conditions, including stabilizer, CMC-nZVI dosages, initial Cr(VI) concentrations and soil pH. Batch experiments were conducted to remediate the contaminated soil with a set of 10 mL centrifuge tubes, each of which was added with 1 g of Cr(VI)-spiked soil and 5 mL of CMC-nZVI. The mixtures were placed on an end-to-end rotator at 30 rpm to react for 24 h and then centrifuged at 4200 rpm for 10 min. The supernatant was filtered with 0.22 μm hydrophilic membranes and the Cr(VI) or Cr_{total} was then analyzed. Control tests were carried out under identical conditions, except that a 0.1% (w w^{-1}) CMC solution was used instead of a CMC-nZVI solution. The removal efficiency was calculated by Eq. (1):

$$\text{Cr removal efficiency (\%)} = \left(1 - \frac{C}{C_0}\right) \times 100\% \quad (1)$$

Table 1
Physical and chemical properties of the soil sample.

Property	Value	Method
pH	6.21	1:5 Soil/water slurry
Fe	13 g kg^{-1}	Acid digestion
Cr	ND.	Acid digestion
Cation exchange capacity	$16.1 \text{ cmol}_c \text{ kg}^{-1}$	Sodium saturation at pH 8.2 [35]
Organic matter	22.5 g kg^{-1}	Tinsley method [42]

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