



# Stabilisation of nanoscale zero-valent iron with biochar for enhanced transport and in-situ remediation of hexavalent chromium in soil<sup>☆</sup>



Huijie Su<sup>a, b</sup>, Zhanqiang Fang<sup>a, b, \*</sup>, Pokeung Eric Tsang<sup>b, c</sup>, Jianzhang Fang<sup>a, b</sup>, Dongye Zhao<sup>d</sup>

<sup>a</sup> School of Chemistry and Environment, South China Normal University, Guangzhou, Guangdong 510006, China

<sup>b</sup> Guangdong Technology Research Center for Ecological Management and Remediation of Water System, Guangzhou, Guangdong 510006, China

<sup>c</sup> Department of Science and Environmental Studies, Hong Kong Institute of Education, 00852, Hong Kong, China

<sup>d</sup> Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL 36849, USA

## ARTICLE INFO

### Article history:

Received 23 January 2016

Received in revised form

25 March 2016

Accepted 29 March 2016

### Keywords:

Cr(VI)-contaminated soil

nZVI@BC

Stability

Mobility

Phytotoxicity

## ABSTRACT

In this study, a biochar-supported nanoscale zero-valent iron (nZVI@BC) material was used for in situ remediation of hexavalent chromium-contaminated soil. Sedimentation tests and column experiments were used to compare the stability and mobility of nZVI@BC and bare-nZVI. The immobilisation efficiency of chromium, toxic effect of chromium and the content of iron were assessed through leaching tests and pot experiments. Sedimentation tests and transport experiments indicated that nZVI@BC with nZVI to BC mass ratio of 1:1 exhibited better stability and mobility than that of bare-nZVI. The immobilisation efficiency of Cr(VI) and Cr<sub>Total</sub> was 100% and 92.9%, respectively, when the soil was treated with 8 g/kg of nZVI@BC for 15 days. Moreover, such remediation effectively reduced the leachability of Fe caused by bare-nZVI. In addition, pot experiments showed that such remediation reduced the phytotoxicity of Cr and the leachable Fe and was favourable for plant growth.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Chromium contamination in the soil has received great attention in recent years. Cr(VI) is released into soil by various industrial activities, such as chromate manufacturing, electroplating, leather tanning and wood preservation (Reyhanitabar et al., 2012), and agricultural activities, such as sludge and sewage irrigation (Su and Fang, 2015). According to bulletins on the nationwide investigation of soil pollution conditions in 2014, chromium pollution in China exceeded the standard rate in the national soil sampling points by 1.1% (EPD and MLR, 2014). Cr(VI) in the soil not only affects crop yields and quality, but can also enter the human body through the food chain and cause various diseases. Consequently, remediation technologies for Cr(VI)-contaminated soil are urgently needed.

At present, in situ remediation of Cr(VI)-contaminated soil by nanoscale zero-valent iron (nZVI) appears to be one of the most promising technologies. Du et al. (2012) reported that 6% nZVI

could achieve a nearly complete Cr(VI) reduction in chromium ore processing residue (Cr(VI) = 15.9 mg/kg) under water content higher than 27%. Singh et al. (2012) revealed that the remediation rate of Cr(VI) in the soil (Cr(VI) = 43.3 mg/kg) was 99% using 5 g/L of nZVI after 40 days of in-situ remediation. Although nZVI has been widely used in the remediation of Cr(VI)-contaminated soil in recent years, nZVI prepared using traditional methods tends to agglomerate, making it undeliverable to the soil, and thus, unusable in the in-situ applications (He and Zhao, 2005; Xu and Zhao, 2007). Moreover, iron amendments may cause soil structure problems such as aggregate cementation and the high leachable Fe concentrations, which negatively affect capacity of the soil for reuse and plant regeneration (Kumpiene et al., 2008; Sneath et al., 2013). One solution is to attach nZVI to a support material which prevents the iron from agglomeration and presents a higher surface area of iron, such as calcium alginate beads (Singh et al., 2011), resin (Park et al., 2009) and silica fume (Li et al., 2011a). However, a good support also should be cheap, safe and able to reduce negative affects caused by bare-nZVI treatment.

Biochar (BC), which is generated by the pyrolysis of carbon-rich biomass in low oxygen conditions (Gaunt and Lehmann, 2008), is chosen as an ideal support for several reasons (Choppala et al.,

<sup>☆</sup> This paper has been recommended for acceptance by B. Nowack.

\* Corresponding author. School of Chemistry and Environment, South China Normal University, Guangzhou, Guangdong 510006, China.

E-mail addresses: [sunmoon124@163.com](mailto:sunmoon124@163.com), [zhqfang@scnu.edu.cn](mailto:zhqfang@scnu.edu.cn) (Z. Fang).

2013; Ying et al., 2014; Yang and Fang, 2014). First, BC is non-toxic, cheap and easy to obtain. Second, BC is rich in organic content, which can improve soil fertility. Third, because of its porous structure and large specific surface area, BC can disperse and stabilise engineered nanoparticles to further enhance their stability and mobility. Furthermore, BC has a high ion exchange capacity and an increased number of oxygen-containing functional groups on its micropore surface, which is useful for reducing metal leachability and bioavailability. Recent studies have used compounds or mixtures of BC and iron-based materials to remediate pollutants. Biochar and iron filing amendments were used for the remediation of arsenic and phenanthrene co-contaminated spoil by Sneath et al. (2013). Zhou et al. (2014) studied the effects of biochar-supported zerovalent on various contaminants from aqueous solutions. Yan et al. (2015) used biochar supported nZVI composite as persulfate activator to remove trichloroethylene. However, few studies have been reported on biochar-supported nZVI in remediation of Cr(VI)-contaminated soil till now.

The objectives of this study were to (1) prepare nZVI@BC, (2) compare the stability and mobility of nZVI@BC with that of bare-nZVI, (3) explore the immobilisation and bioaccessibility potential of Cr in nZVI@BC treated soil and (4) evaluate whether such remediation may restore soil quality for planting.

## 2. Materials and methods

### 2.1. Materials

All chemicals used in the study were of analytical grade. The cabbage mustard seeds were purchased from the Vegetable Research Institute at the Guangdong Academy of Agriculture Sciences (Guangzhou, China). The BC was produced by the pyrolysis of bagasse for 2 h at a temperature of 600 °C under oxygen-limited conditions (Dong et al., 2011; Ding et al., 2014). To prepare the nZVI@BC, the BC (0.42 g) was firstly dissolved in a 100 mL 0.075 mol/L FeSO<sub>4</sub>·7H<sub>2</sub>O solution. The mixture was then stirred for 60 min under anaerobic conditions to form a homogenous solution. The nZVI@BC particles were synthesised by the drop-wise addition of 50 mL 0.3 mol/L NaBH<sub>4</sub> to the homogenous solution with continuous stirring. The composited particles that formed were settled and separated from the liquid phase. Then, the particles were respectively washed with ethanol and acetone for several times and finally vacuum dried at 60 °C. The prepared product was nZVI@BC with nZVI to BC mass ratio of 1:1. For comparison, bare-nZVI was prepared following the same procedure but without BC. nZVI@BC with nZVI to BC mass ratio of 1:0.5 and 1:2 were also synthesised by varying the mass of BC in above process, respectively. Brunauer-emmett-teller (BET) result showed that the specific surface area of BC, bare-nZVI and nZVI@BC (nZVI to BC mass ratio of 1:1) was 353 m<sup>2</sup>/g, 35 m<sup>2</sup>/g and 71 m<sup>2</sup>/g, respectively. The specific surface area of nZVI@BC was higher compared to the surface area of bare-nZVI (2-fold). In addition, the materials were characterised by a Scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR) analysis.

### 2.2. Sedimentation tests

To compare the colloidal stability of three kinds of nZVI@BC with bare-nZVI, the sedimentation rates of the suspensions were determined at the same time (Liang et al., 2014). Three kinds of nZVI@BC and bare-nZVI suspensions (with consistent iron content) were prepared and sonicated for 5 min, while the absorbance was held at 508 nm with a UV-Vis spectrophotometer, respectively.

### 2.3. Column experiments

To evaluate the mobility of bare-nZVI and nZVI@BC, their transport behaviour were examined in water-saturated silica sands that were packed in a vertical glass column (Jiemvarangkul et al., 2011; Liang et al., 2014). The sand was rinsed with deionised water for 3 times before use. Organic impurities were removed by soaking the rinsed sand in hydrogen peroxide (5%) for 3 h, rinsing the sand again with deionised water and then soaking it in hydrochloric acid (12 mol/L) overnight. Finally, the sand was thoroughly rinsed with deionised water and air-dried. The column was 1.5 cm in diameter and 10.0 cm in length, and was fitted with a nylon sieve (80 mesh) at the bottom to prevent loss of sand. 10 pore volumes (PVs) of deionised water was initially pumped through the column to ensure uniform packing and a steady state flow (6 mL/min). Next, 100 mL of nZVI@BC suspension was introduced into the column at the same state flow. To prevent sedimentation of nZVI@BC, the suspension containing nZVI@BC was continuously sonicated prior to injection at room temperature. After above suspension was entire pumped through the column, the deionised water was used to elute the materials in the column. The effluent was collected at selected time intervals, then was digested with 1 mol HCl for 2 h. The total iron concentration in the outflow was determined by a UV/Vis spectrophotometer at a wavelength of 580 nm (Wang et al., 2011). For comparison, the transport behaviour of bare-nZVI was examined following the same procedure. And bare-nZVI suspension was the same amount of iron with nZVI@BC suspension.

### 2.4. In-situ remediation of Cr(VI)-contaminated soil

The Cr-free soil samples were collected from the Higher Education Mega Center in Guangzhou, China. To prepare Cr(VI)-spiked soil samples, 1 L of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution at the desired concentration was mixed with 1 kg of air-dried soil (soil-to-solution ratio of 1:1) and stirred until the mixture was air dried to a constant weight (Wang et al., 2014a). The concentrations of the resulting Cr<sub>total</sub> and Cr(VI) were 800 mg/kg and 320 mg/kg, respectively. Untreated soil samples consisted of: the Cr-free soil (S0), Cr(VI)-contaminated soil (S1). To examine the effect of nZVI, BC and nZVI@BC on Cr(VI) reduction, the Cr(VI)-contaminated soil samples were mixed with 4 g/kg nZVI, 4 g/kg BC and 8 g/kg nZVI@BC and incubated at 60% water holding capacity for 15 days, respectively. All of the treatments were performed in triplicate. Treatment soil samples consisted of: 4 g/kg nZVI-treated soil (S2), 4 g/kg BC-treated soil (S3), 8 g/kg nZVI@BC-treated soil (S4). The Cr(VI)-contaminated soil samples incubated for 15 days with remediation materials were used for in vitro toxicity tests or pot experiments.

### 2.5. Chemical stability of Cr in soil after remediation

The effectiveness of the nZVI@BC for Cr immobilisation was estimated by comparing the leachability and bioaccessibility of Cr in the soil before and after remediation. The leachability was determined following the toxicity characteristic leaching procedure (TCLP, US EPA, 1990). In the TCLP tests, air-dried soil samples were extracted with the TCLP fluid (so-called fluid No.1) for 18 h at a solid-to-solution ratio of 1 g–20 mL on a rotating shaker at room temperature (21 ± 1 °C).

The immobilisation efficiency was calculated using Eq. (1):

$$\text{Cr immobilisation efficiency (\%)} = (1 - C_i/C_0) \times 100\% \quad (1)$$

where  $C_i$  and  $C_0$  are the Cr(VI) or Cr<sub>total</sub> concentration (mg/L) in the supernatant of the treated soil and untreated soil, respectively.

Download English Version:

<https://daneshyari.com/en/article/6315197>

Download Persian Version:

<https://daneshyari.com/article/6315197>

[Daneshyari.com](https://daneshyari.com)