Research article

Cadmium immobilization in river sediment using stabilized nanoscale zero-valent iron with enhanced transport by polysaccharide coating

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A R T I C L E   I N F O

A B S T R A C T

Proper management of metal-contaminated sediment plays a key role in sediment recovery and reuse. This study synthesized two kinds of stabilized nanoscale zero-valent iron (nZVI) with starch (S-nZVI) and carboxymethyl cellulose (C-nZVI) for the *in situ* immobilization of Cd(II) in river sediment and investigated their transport in porous media. Experimental data showed that when the sediment sample was treated with C-nZVI for 56 days at a dosage ranging from 5 to 10 mg/g-sediment as Fe^0, the TCLP (toxicity characteristic leaching procedure) leachability of Cd(II) in the sediment decreased by 93.75–96.43%, and the PBET (physiologically-based extraction test) bioaccessibility of Cd(II) decreased by 22.79–71.32%. Additionally, the acid soluble fraction of Cd(II) was partially transformed to a residual fraction, resulting in a 32.4–33.1% decrease of acid soluble Cd(II) and a 125.4–205.6% increase of the residual-Cd(II) fraction. Surface complexation with iron oxyhydroxide minerals might be the main mechanism of Cd(II) immobilization in sediment. Column experiments indicate that starch or carboxymethyl cellulose (CMC) could extend the travel distance of nZVI, but inherent site physical and chemical heterogeneities still posed challenges for nanoparticle transport. Over all, this study verifies the effectiveness of stabilized nZVI for Cd(II) immobilization in sediment and discusses the potential immobilization mechanism.

1. Introduction

River sediment is a basic composition in aquatic ecosystems due to its role as the nutrient source for organisms. Unfortunately, the sediment from rivers or lakes situated near industrial areas, especially mining areas, is being highly polluted with heavy metals (Wang et al., 2014). Cadmium (Cd) is a widespread heavy metal in sediment and is more mobile and soluble than many other metals; thus, this metal can cause direct toxicity for organisms, even at low concentrations (Liu et al., 2009). Like most other metals, the mobility and bioavailability of Cd(II) in soil and sediment are determined by its chemical speciation instead of its total concentration, and the main objective of many *in situ* remediation technologies is to transform the toxic fraction into an insoluble substance or into a less toxic species (Gil-Díaz et al., 2014a; Huang et al., 2008).

Over the years, iron-based nanoscale particles (such as Fe-Mn, FeS, Fe_3O_4, Fe^0 nanoparticles) have been widely applied for the removal of heavy metals, including Cd(II), Pb(II), Zn(II), Se(IV) and Cr(VI) from water, due to their strong adsorption or reducing abilities (Arshadi et al., 2014; Boparai et al., 2013; Huang et al., 2015; Ling et al., 2015; Xu et al., 2012). Subsequently, the immobilization of heavy metals in soil and groundwater using iron-based nanoscale particles has also recently attracted attention (Cheng et al., 2016; Gil-Díaz et al., 2014a; Su et al., 2016; Xie et al., 2015). However, the use of nanoscale zero-valent iron (nZVI) for the *in situ* immobilization of Cd(II) in soil or sediment has been rare. On the other hand, the transport behaviour of nZVI is directly related to whether nZVI can reach the contaminated subsurface zones and capture the target contaminants, so an investigation of the transport of nZVI in sediment is also needed. Due to the nanosize particles and large specific surface areas of nZVI, it is probable that

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nZVI aggregates easily, making nZVI undeliverable to the contaminated subsurface zones and, thus, unusable for *in situ* applications. To avoid rapid agglomeration, our group has developed various stabilizing strategies by using sodium alginate and sodium dodecyl sulfate as stabilizers (Huang et al., 2015, 2016). In addition, types of conventional polysaccharide stabilizer, starch (He and Zhao, 2005) and CMC (Ambika et al., 2016) are also popular due to their well stabilized performance, nontoxicity and biodegradation. Hydroxylated macromolecules in starch and CMC, which contain size-confined nanoscale pools of inter- and intramolecular origins, can promote the nucleation and crystallization of nZVI (He and Zhao, 2005). In addition, the molecules act as multidentate ligands, forming strong coordination bonds with nZVI to overcome the van der Waals or magnetic forces of attraction between nZVI (Ambika et al., 2016). Therefore, the use of starch or CMC could change the size and dispersibility of nZVI and significantly improve its transport in porous media (He and Zhao, 2007).

As reported by previous researcher (Boparai et al., 2013; Zhang et al., 2014), nZVI can not reduce the heavy metal ions (Cd^{2+}) to zero valent metals (Cd^0) because the standard potentials of cadmium and zero-valent iron are nearly identical:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad E^0 = -0.41 \text{ V} \tag{1}$$

$$Cd \rightarrow Cd^{2+} + 2e^- \quad E^0 = -0.40 \text{ V} \tag{2}$$

While Calderon et al. reported that nZVI could form the iron oxyhydroxide minerals (amorphous Fe(II)/(III) (hydr)oxide, i.e., α-, β-, γ-FeOOH) layer during nanoparticle synthesis and ageing (Calderon and Fullana, 2015). In addition, the relative stability of Cd(II) adsorption complexes on the FeOOH has been confirmed by Randall et al. (1999). Thus, adsorption or surface complex formation on the formed iron oxyhydroxide layer may be the most likely mechanism of Cd(II) immobilization.

In the present study, the effectiveness of starch- and CMC-stabilized nZVI for Cd(II) immobilization in sediment and nanoparticle transport in porous media were investigated. The main objectives were (a) to prepare and characterize the desired stabilized nZVI using water-soluble starch or CMC as a stabilizer; (b) to investigate the effects of the stabilizers, particle dosage and treatment time on the TCLP (toxicity characteristic leaching procedure) leachability/PBET (physiologically-based extraction test) bioaccessibility of Cd(II) and Cd(II) speciation; (c) to examine the nanoparticle transport in ideal and heterogeneous media; and (d) to analyse the potential mechanism of Cd(II) immobilization using stabilized nZVI. The research might be particularly significant to engineers, practitioners and sediment-repair company managers because these results could lead decision-makers to use nano-technologies, which are novel in environmental management, into practice. Additionally, the application of nZVI in metal-contaminated sediment provides a new direction for sediment recovery and reuse.

2. Materials and methods

2.1. Materials

All the chemicals were analytical grade or higher. Water-soluble starch and CMC were purchased from the Tianjin Damao Chemical Agent Factory (Tianjin, China). Other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. All solutions and suspensions were prepared with ultrapure deionized (DI) water (18.25 Ω, Milli-Q Millipore).

River sediment samples from the shallowest 25 cm were collected from the Xiang River in Hunan, China. Before use, the sediment samples were air-dried for one month and passed through a 2-mm sieve. The key sediment physicochemical characteristics are included in Table 1. The Cd(II) concentration in the sediment (22.50 mg/kg) was more than 18 times that of the sediment quality guidelines for metals (Cd(II): 1.2 mg/kg) (Burton, 2002). According to the potential ecological risk index (RI) (Hakanson, 1980), the potential risk of Cd(II) was 2045, which was much higher than those of Pb (48) or Cr (7) (Table S1). According to the European Community Bureau of Reference (BCR) sequential extraction procedure (Wan et al., 2016), the mobility and bioavailability of the three metals were calculated and compared, and they followed the sequence of Cd > Pb > Cr (Fig. S1).

2.2. Synthesis and characterization of stabilized nZVI

Stabilized nZVI was synthesized using the modified method described by He et al. (He and Zhao, 2005). Before use, DI water and stabilizer solution were purged with purified N_2 for 30 min to remove the dissolved oxygen. The preparation was carried out in a 250 mL three-necked round bottom flask attached to a nitrogen line. Traditionally, a 25 mL $FeSO_4 \cdot 7H_2O$ stock solution was added to a 100 mL stabilizer solution and was left to stir for 30 min to form starch- or CMC-Fe^{2+}. Then, the Fe^{2+} ions were reduced to Fe^0 by adding stoichiometric amounts of sodium borohydride solution dropwise into the mixture. When all of the sodium borohydride solution was added, the mixture was stirred for another 30 min. The whole period was kept at inert conditions to ensure the efficient use of the reducing agent BH^{4-}. The concentrations of the $FeSO_4 \cdot 7H_2O$ solution used in this study were 14.9 and 29.8 g/L. Accordingly, the stabilizer concentrations were either ~0.2% (w/w) for 0.5 g/L Fe^0 or ~0.4% (w/w) for a 1.0 g/L Fe^0 suspension. Bare-nZVI (B-nZVI) was also prepared via a similar method but in the absence of starch or CMC. Three kinds of nZVI suspensions were used for batch and column experiments after their synthesis.

Newly synthesized nanoparticles were dried in a vacuum drying oven (DZF-6020, Shanghai) at 80 °C for 8 h and were then ground into a fine powder in a nitrogen atmosphere. The nanoparticles were stored in brown bottles filled with nitrogen gas before their characterization. The hydrodynamic diameters of the nanoparticles were determined via dynamic light scattering (DLS) using NaNoZS (Malvern, UK). Scanning electron microscope (SEM) images of nZVI were taken by a JSM-6700F (JEOL, Japan). Fourier transform infrared spectrometry (FTIR) (Nicolet, USA) was performed at a spectral range varying from 4000 to 400 cm^{-1}. The x-ray diffraction (XRD) patterns of the nanoparticles were observed using a Philips-X'Pert Pro MPD (Netherlands) with a high-power Cu-Ka radioactive source ($\lambda = 0.154$ nm) at 40 kV/40 mA.

2.3. Sediment treatment with stabilized nZVI

The sediment samples were amended by mixing 0.5 g of stored

Table 1
Physicochemical characteristics of the river sediment used in this study.

Parameter	pH	CEC (cmol/kg)	TOC (%)	OM (%)	Cd (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Sand (%)	Silt (%)	Clay (%)
Sediment	7.6	21.6	3.49	6.02	22.50	159.80	221.77	65	32	3