Science of the Total Environment 596–597 (2017) 266–273

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Facile modification of nanoscale zero-valent iron with high stability for Cr(VI) remediation

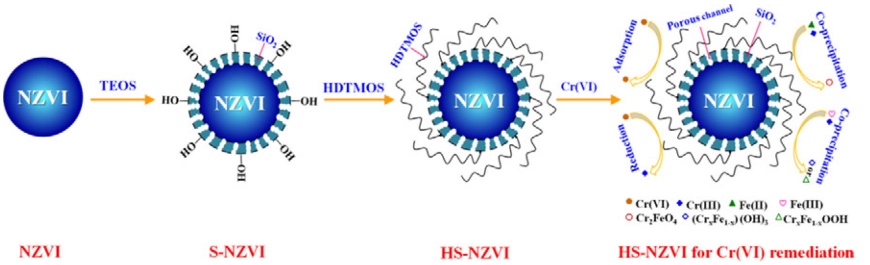
Ziling Peng, Chunmei Xiong, Wei Wang *, Fatang Tan, Yang Xu, Xinyun Wang *, Xueliang Qiao

State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan, 430074, Hubei, PR China

HIGHLIGHTS

- NZVI was modified using tetraethyl orthosilicate and hexadecyltrimethoxysilane.
- HS-NZVI showed high removal ability towards Cr(VI) in water.
- HS-NZVI exhibited higher stability and reusability than pure NZVI and S-NZVI.
- HS-NZVI has excellent magnetic properties to facilitate separation and recycling.
- The mechanism for Cr(VI) removal was adsorption, reduction and co-precipitation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 February 2017
Received in revised form 14 April 2017
Accepted 16 April 2017
Available online 21 April 2017

Edited by: J. Gan

Keywords:
Nanoscale zero-valent iron
Modification
Stability
Cr(VI) remediation

ABSTRACT

In this study, a highly stable nanoscale zero-valent iron composite (HS-NZVI) was obtained via modifying nanoscale zero-valent iron (NZVI) with tetraethyl orthosilicate (TEOS) and hexadecyltrimethoxysilane (HDTMOS), and used for Cr(VI) remediation in aqueous solution. The obtained HS-NZVI remained stable in water without being oxidized for over 12 h. After four consecutive runs, the Cr(VI) removal efficiency of HS-NZVI maintained a value of more than 82%. Moreover, the Cr(VI) removal capacity per unit weight of NZVI in HS-NZVI reached 292.8 mg/g within 60 min at the initial Cr(VI) concentration of 120 mg/L at pH 5. The Cr(VI) removal efficiency of HS-NZVI increased with decreasing solution pH, and the experimental data for Cr(VI) removal by HS-NZVI were well-described by the pseudo-first-order reaction model. Additionally, scanning electron microscope (SEM) images, X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) measurements of the product after reaction revealed that the mechanism of Cr(VI) remediation by HS-NZVI mainly involved adsorption, reduction and co-precipitation. Considering the advantages of easy preparation, excellent stability and reusability, and high Cr(VI) removal capacity as well as the magnetic recovery property, HS-NZVI is expected to have notably promising applications for the remediation of Cr(VI) contaminated sites.

1. Introduction

Chromium pollution commonly caused by electroplating, mining, leather manufacturing, dyeing and other industrial processes has brought great harm to human health and ecosystems (Wang et al., 2015; Zhu et al., 2016; Melak et al., 2016; Lv et al., 2012). Cr(VI) mainly exists as anions (CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$) in solution, and its solubility and mobility are higher than that of Cr(III) (Ai et al., 2008; Habibul et al., 2016). Furthermore, the toxicity of Cr(VI) is 100 times higher than that of Cr(III) (Lv et al., 2011). Therefore, the study of Cr(VI) remediation in solution is of vital significance. Many methods such as chemical reduction, electrolytic reduction, membrane filtration, evaporation

---

* Corresponding authors.
E-mail addresses: weiwang@hust.edu.cn (W. Wang), wangxy_hust@hust.edu.cn (X. Wang).

http://dx.doi.org/10.1016/j.scitotenv.2017.04.121
0048-9697/

and adsorption have been developed to treat chromium-containing wastewater (Zhao et al., 2015; Doke and Yadav, 2014; Sun et al., 2011a; Qiu et al., 2014). Among them, adsorption and chemical reduction have been proven to be efficient for Cr(VI) remediation due to their low cost, simple operating processes, remarkable removal efficiencies and lack of secondary pollution (Fu et al., 2015; Qiu et al., 2015).

As an effective adsorbent and reducing agent, nanoscale zero-valent iron (NZVI) has attracted great attention due to its small particle size, high surface activity, strong reducing potential, magnetic recovery property and environmental friendliness (Sun et al., 2006). It has been widely applied in the removal of microorganisms (Zhan et al., 2015; Chaithawiwat et al., 2016), organic pollutants (Jin et al., 2016; Peng et al., 2017) and heavy metal ions (Zhou et al., 2015; Li et al., 2016). However, NZVI easily aggregates and is prone to be oxidized in air and water, leading to low reactivity in applications (Shi et al., 2011). Therefore, improving the dispersity and stability of NZVI is one of the key points to settle the problem of its practical application. Recently, various strategies have been developed to prevent NZVI from aggregating and oxidizing (Dai et al., 2016; Yang et al., 2011). A number of supporting or cladding materials such as sepiolite (Fu et al., 2015), bentonite (Shi et al., 2011), chitosan (Gupta et al., 2012), carbon fibers (Huang et al., 2014), silica (Petala et al., 2013; Li et al., 2012a) and sulfide (Su et al., 2015), have been reported to improve the dispersity and stability of NZVI. These materials can prevent NZVI from aggregating, and show slightly higher stability than NZVI alone. However, it is difficult to preserve the reusability of NZVI over repeated cycles, because the dispersed NZVI is still susceptible to oxidation. Promisingly, some long-chain organics and macromolecules were used to prepare stable and efficient NZVI for environmental remediation (Kim et al., 2017; Mines et al., 2016). However, the reusability of these NZVI-based materials was not studied in their work. Toli et al. (2016) incorporated NZVI in cationic resin beads for Cr(VI) remediation, and this composite could be regenerated by re-loading new NZVI for reuse. However, the multi-step regeneration process was tedious and costly, restraining its practical application. Hence, great efforts are needed to solve the problem of the stability and reusability of the NZVI-based materials.

In this work, nanoscale zero-valent iron was modified with tetraethyl orthosilicate (TEOS) and hexadecyltrimethoxysilane (HDTMOS), to create a highly stable nanoscale zero-valent iron composite (HS-NZVI) (Fig. 1). Here, the hydrolysis of TEOS could produce porous SiO_2 covering NZVI particles, playing the role of a dispersive agent. Further, the *Si*-OH group on the SiO_2 surface could facilitate the graft of HDTMOS, exerting a protective effect to inhibit oxidation by oxygen. Thus, the synergistic effect of TEOS and HDTMOS would reduce the aggregation of NZVI and prevent the oxidation of NZVI. The structure, morphology, stability and reusability of HS-NZVI, and the Cr(VI) removal capacity by HS-NZVI in aqueous solution were systematically studied. Additionally, the mechanism of Cr(VI) removal by HS-NZVI was investigated in detail.

2. Materials and methods

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. HDTMOS was purchased from Aladdin Chemistry Reagent Chemistry Co., Ltd. Potassium dichromate ($K_2Cr_2O_7$) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. 1.5-Diphenylcarbazide was obtained from Chengdu Kelong Chemical Reagent Co., Ltd. Potassium borohydride (KBH_4), tetraethyl orthosilicate (TEOS), sodium hydroxide (NaOH), nitric acid (HNO_3), n-hexane and ethanol were acquired from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were of analytical grade and used without purification.

2.2. Synthesis of HS-NZVI nanocomposite

The preparation procedure of TEOS-modified NZVI (S-NZVI) was similar to the previous work (Li et al., 2012b). In a typical synthesis, 0.145 g of $FeCl_3 \cdot 6H_2O$ was put into a three-necked flask and dissolved in a mixture of 10 mL of water and 20 mL of ethanol to obtain a clear solution. Next, 0.1 mL of TEOS was added in one shot. After purging with high-purity argon for 30 min, an excess of KBH_4 solution was slowly dropped into the mixture at room temperature (~25 °C). After completion of the dropwise addition, the mixture was continuously stirred for another 2 h to form S-NZVI. The resulting product was separated by a magnet and washed with distilled water and ethanol several times to remove any residue.

The prepared S-NZVI was transferred into a 100 mL conical flask. 20 mL of n-hexane and 0.05 mL of HDTMOS were added in succession, and then the suspension was placed in a shaker with a speed of 150 rpm at room temperature (~25 °C). After continuous shaking for 12 h, HS-NZVI was obtained. For comparison, NZVI, SiO_2 and HDTMOS-modified SiO_2 (H-SiO_2) were synthesized according to similar procedures.

2.3. Characterizations

X-ray diffraction (XRD) patterns of samples were recorded on a Philips X′ Pert Pro X-ray powder diffractometer. Fourier transform infrared (FTIR) spectra were collected using a Bruker VERTEX 70 spectrometer in the wavenumber range of 4000–400 cm^{-1}. Thermogravimetric analyses (TGA) were conducted on a Netzsch STA449F3 analyzer from 30 °C to 800 °C with a heating rate of 10 °C/min under a N_2 atmosphere. Morphologies and elemental compositions were characterized using a Tecnai G220 transmission electron microscope (FEM) and Nova Nano450 scanning electron microscope (SEM) equipped with an Oxford X-Max 50 energy-dispersive X-ray (EDX) analyzer. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Kratos Axis Ultra DLD-600 W spectrometer with a monochromatic Al K_a X-ray source (1486.6 eV). Brunauer-Emmett-Teller (BET) surface area

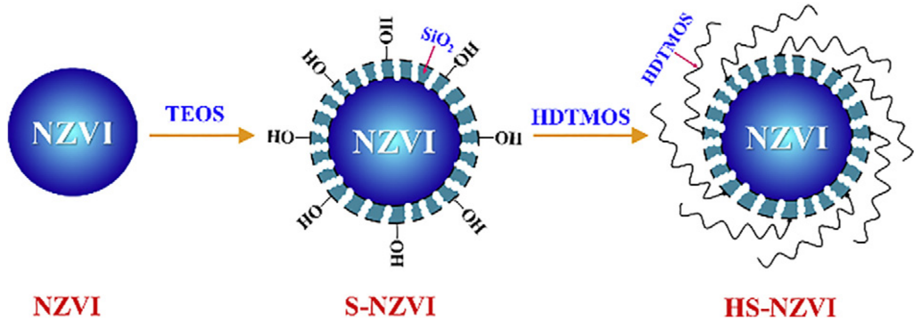


Fig. 1. Schematic diagram for the modification of NZVI with TEOS and HDTMOS.