

Research article

Synthesis of zeolite-supported microscale zero-valent iron for the removal of Cr⁶⁺ and Cd²⁺ from aqueous solution



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ABSTRACT

Zeolite-supported microscale zero-valent iron (Z-mZVI) was synthesized and used to remove heavy metal cation (Cd²⁺) and anion (Cr⁶⁺) from aqueous solution. Transmission electron microscope (TEM) confirmed that mZVI (100–200 nm) has been successfully loaded and efficiently dispersed on zeolite. Atomic absorption Spectroscopy (AAS) revealed the amount of stabilized mZVI was about 1.3 wt.%. The synthesized Z-mZVI has much higher reduction ability and adsorption capacity for Cr⁶⁺ and Cd²⁺ compared to bare nanoscale zero-valent iron (nZVI) and zeolite. Above 77% Cr⁶⁺ and 99% Cd²⁺ were removed by Z-mZVI, while only 45% Cr⁶⁺ and 9% Cd²⁺ were removed by the same amount iron of nZVI, and 1% Cr⁶⁺ and 39% Cd²⁺ were removed by zeolite alone with an initial concentration of 20 mg/L Cr⁶⁺ and 200 mg/L Cd²⁺. The removal of Cr⁶⁺ by Z-mZVI follows the pseudo first-order kinetics model, and X-ray photoelectron spectroscopy (XPS) analysis confirmed that Cr⁶⁺ was reduced to Cr³⁺ and immobilized on the surface of Z-mZVI. The removal mechanisms for Cr⁶⁺ include reduction, adsorption of Cr³⁺ hydroxides and/or mixed Fe³⁺/Cr³⁺ (oxy)hydroxides. The pseudo-second-order kinetic model indicated that chemical sorption might be rate-limiting in the sorption of Cd²⁺ by Z-mZVI. This synthesized Z-mZVI has shown the potential as an efficient and promising reactive material for removing various heavy metals from wastewater or polluted groundwater.

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1. Introduction

Heavy metals pollution is one of the most serious environmental problems due to their toxicity (Xi et al., 2010), carcinogenicity (Hashim et al., 2011) and persistency (Hua et al., 2012) especially in water system. For instance, Cr⁶⁺ is one of the most toxic contaminants which has been considered to be the priority pollutant in China (He et al., 2013), and Cd²⁺ contaminated paddy land has caused serious rice contamination in China (Bian et al., 2014) and Japan (Makino et al., 2007). Both of Cr⁶⁺ and Cd²⁺ could be released into the environment from a number of different industrial activities, including iron ore mining, alloy smelting, electroplating, tanning, pigments and other anthropogenic sources (Fu et al., 2013; Gutiérrez-Segura et al., 2012).

Using of adsorption materials has been thought to be an effective and economic way for the removal of heavy metals from

wastewater and groundwater (Xi et al., 2010; Simantiraki and Gidarakos., 2015). Zero-valent iron (ZVI) filled permeable reactive barriers (PRBs) have been used to remove heavy metals from water, but ZVI filled PRBs usually have low reactivity in wastewater treatment for low surface area and rapid loss of permeability due to mineral precipitation (Kim et al., 2013; Lee et al., 2009), especially for the remediation of high concentrations of pollutants. Alternatively, nanoscale zero-valent iron (nZVI) with higher specific surface area has been developed rapidly for the removal of various heavy metals from water (Zhang, 2003; Li et al., 2012; Fu et al., 2013). However, nZVI tends to aggregate rapidly in water, which would reduce its adsorption capacity significantly (Obiri-Nyarko et al., 2014). In order to prevent the aggregation of nZVI, clay minerals were used to support nZVI, such as kaolin (Zhang et al., 2011) and bentonite (Shi et al., 2011; Chen et al., 2011; Li et al., 2012). The supported nZVI has been successfully used to remove chlorinated organic compounds and heavy metals, and it has shown faster reaction rate and adsorption capacity. However, Clay materials tended to absorb water in the interlayer sites, the swelling factor should be taken into account since they may cause

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hydraulic conductivity drop when they are used in PRBs (Babel and Kurniawan, 2003).

As a kind of low-cost and easily obtaining aluminosilicate mineral, zeolite has high ion exchange capacity due to its particular three-dimensional frameworks of silica tetrahedron, which has been widely used in PRBs for the removal of cation contaminants from groundwater (Kocaoba et al., 2007). Moreover, zeolite was shown to have high selectivity for certain heavy metal ions such as Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} (Han et al., 2009). In addition, zeolite has rigid structure and do not swell in water compare to other clay minerals (Babel and Kurniawan, 2003). The abundant micro- and nano-porous of zeolite could also provide spaces for the mineral precipitation while polluted water flowing through (Wu et al., 2008). Zeolite supported nZVI may combine the adsorption ability of zeolite and the reduction ability of nZVI, and the composite also have synergetic effects due to the better dispersion of nZVI on zeolite.

In previous studies, zeolite supported ZVI/nZVI was synthesized and had shown good removal ability for Pb^{2+} (Kim et al., 2013), NO_3^- (Lee et al., 2007), and Cr^{6+}/Cd^{2+} mixture (Lee et al., 2006) from water, but the synergic effects of zeolite supported ZVI/nZVI compare with zeolite and nZVI have never been tested. Moreover, the mechanism and the form changes of pollutants during the reaction need to be further studied. In this study, improved method of synthesizing zeolite-supported microscale zero-valent iron (Z-mZVI) was performed and the produced Z-mZVI was used to remove heavy metal cation (Cd^{2+}) and anion (Cr^{6+}). The performance of Z-mZVI was compared with unmodified zeolite and unsupported nZVI produced by the same procedure to verify the superior adsorption and reduction abilities for contaminates. A variety of characterization methods and kinetic models were also used to investigate the reaction mechanism. To the best of our knowledge, this is the first study testing the synergetic effects of Z-mZVI for the removal of heavy metals from water.

2. Materials and methods

2.1. Materials

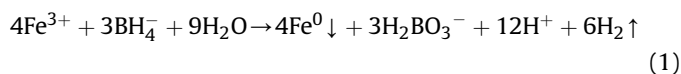
Zeolite was purchased from Shenyang Xingye Mining Co. Ltd (China), which was sieved and the particles between 80 and 100 mesh were collected for further use. X-ray diffraction analysis showed that this material was mainly clinoptilolite. The cation exchange capacity (CEC) is 130–150 meq/100 g. Zeolite was firstly soaked in 1 mol/L HCl for 24 h, and then washed to neutral pH by deionized water, lastly dried at 45 °C before use.

$FeCl_3 \cdot 6H_2O$, $K_2Cr_2O_7$, $Cd(NO_3)_2$, NaOH and $NaBH_4$ of analytical reagent grade were purchased from Guangfu Chemicals Co. Ltd (Tianjing, China). The stock solutions containing different concentration of Cr^{6+} or Cd^{2+} were prepared by dissolving $K_2Cr_2O_7$ or $Cd(NO_3)_2$ in deionized water.

2.2. Synthesis of nZVI and Z-mZVI

The nZVI was synthesized using the liquid-phase reduction method by borohydride as previously reported (Zhang, 2003; Chen et al., 2011). Briefly, 2.73 g of $FeCl_3 \cdot 6H_2O$ (0.1 M) was dissolved in 100 mL deionized water, and then $NaBH_4$ (1.5 M) with 0.1 wt.% NaOH solution was added drop wise into $FeCl_3$ solution and stirred constantly for 20 min. To ensure that Fe^{3+} in the mixture was reduced to Fe^0 completely, the amount of $NaBH_4$ solution was added excessive than the theoretical amount according to Eq. (1). To prevent the nZVI from oxidizing, the black solids were quickly rinsed three times with oxygen-free deionized water and froze immediately and dried in a vacuum freeze dryer (–50 °C) for 24 h.

Lastly, the dried nZVI powders were picked out by magnet rod and stored in a vacuum desiccator prior to use.



The detailed preparation method of Z-mZVI was as following: (1) Zeolite and $FeCl_3$ solution (10 mM) were added in a capped bottle with a mass ration of 1:40 and placed on a rotary shaker for 22 h (175 rpm, 25 °C). The $FeCl_3$ concentration and reaction time were determined by preliminary adsorption experiments (Fig. S1 and Fig. S2 in supporting information), and Fe^{3+} can reach saturate adsorption on zeolite on this weight ratio and reaction time. (2) Fe^{3+} saturated zeolite was washed five times with deionized water to remove residual $FeCl_3$ on surface, and was added into a fresh prepared 1.5 M $NaBH_4$ with 0.1 wt.% NaOH solution with a mass ration of 1:5 ($Fe^{3+}: BH_4^-$), the mixture was stirred 20 min to reduce the adsorbed Fe^{3+} to Fe^0 . The light yellow zeolite would change to black in this process. (3) After the reaction was completed, the composite was quickly rinsed three times with oxygen-free deionized water and froze immediately and dried in a vacuum freeze dryer (–50 °C) for 24 h, lastly stored in a vacuum desiccator prior to use.

2.3. Z-mZVI characterization

A JEOL JEM-2100 Transmission electron microscope (TEM, Japan) was used to investigate the micro-structure of zeolite before and after ZVI loaded. The samples for TEM were dispersed in acetone and then dropped on carbon coated films and dried at room temperature.

A Hitachi S-4800 scanning electron microscope with integrated energy dispersive X-ray system (SEM-EDX, Japan) was used for morphological studies. Images of samples were recorded at different magnifications at an operating voltage of 20–30 kV.

The element composition of Z-mZVI within a depth of 3 nm was measured by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, USA). Component analyses were undertaken using the Jandel Peak fit software package (Jandel Scientific).

Total Fe element contents of samples were analyzed by Atomic absorption spectroscopy (AAS, PerkinElmer AAS-100, USA) after dissolved in a mixed pure HNO_3 (7 mL) and HCl (3 mL) with microwave digestion.

2.4. Removal of Cr^{6+} and Cd^{2+} from aqueous solutions

To compare the removal efficiency of Cr^{6+} and Cd^{2+} in aqueous solution, the experiments were carried out using zeolite (1 g), nZVI (0.013 g), and Z-mZVI (1 g) added to 100 mL Cr^{6+} or Cd^{2+} solution, and the latter two materials had the same mass of iron. The experiments were performed in flasks under open (aerobic) laboratory conditions at room temperature (25 ± 3 °C). The initial concentration of Cr^{6+} and Cd^{2+} are 20 mg/L and 200 mg/L respectively. The reaction solutions were stirred at 175 rpm and periodically sampled.

In the kinetic experiments, Z-mZVI (1 g) was added to a 100 ml Cr^{6+} or Cd^{2+} solution in a three-necked bottle and placed on a rotating shaker (175 rpm, 25 °C). The Cr^{6+} or Cd^{2+} solutions of different concentrations were made before experiments. The pH and ORP were observed by a pH and ORP multi-parameter meter during the reaction.

All the experiments were carried out in duplicate, and the samples were filtered immediately using a membrane filter of 0.45 μ m pore size prior to measure the concentration of Cr^{6+} and Cd^{2+} .

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