Chromium removal using resin supported nanoscale zero-valent iron

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ABSTRACT

Resin supported nanoscale zero-valent iron (R-nZVI) was synthesized by the borohydride reduction method. Batch experiments were conducted to evaluate the factors affecting Cr(VI) removal. It was found that nZVI loads, resin dose, pH value and initial concentration of Cr(VI) were all important factors. Scanning electron microscopy showed that the nZVI particles in R-nZVI became sphere after reacting with Cr(VI). This phenomenon was attributed to the co-precipitation of Cr(III) and Fe(III) on the surface of resin. X-ray diffraction pattern confirmed that Fe^0 diminished after the reaction. At optimum conditions, the Cr(VI) removal efficiency was 84.4% when the initial concentration of Cr(VI) was 20.0 mg/L. Regeneration of R-nZVI and resin was possible. R-nZVI can also remove Cr(III) efficiently. However, the removal mechanisms of Cr(VI) (anion) and Cr(III) (cation) are different. The former is chemical reduction, while the latter is ion exchange at pH below 6.3 and precipitation at pH above 6.3. This study demonstrates that R-nZVI has the potential to become an effective agent for treating wastewater containing Cr(VI) and Cr(III).

1. Introduction

Heavy metal pollution is one of the most serious environmental problems today. Hexavalent and trivalent chromium (Cr(VI) and Cr(III)) are released into the environment from a number of different industrial activities, including iron and steel manufacturing, tanning, chromium plating, and other anthropogenic sources (Maine et al., 2004). Cr(VI) is one of the most toxic and carcinogenic water contaminants and is considered to be one of priority pollutants in China (He et al., 2013). Cr(III) is less toxic and could be a nutrient for humans at low concentrations, however, the uptake of higher dosages of Cr(III) may cause harmful health effects and long-term exposure to Cr(III) can cause allergic skin reactions and cancer (Vilar et al., 2012).

The removal of chromium is mainly focused on Cr(VI) since Cr(VI) is more toxic than Cr(III). A number of treatment processes are employed to remove Cr(VI) from wastewater, including chemical reduction (Lai and Lo, 2008; Singh et al., 2011a), adsorption (Park and Tavlarides, 2008; Cao et al., 2012), bioremediation (Hasin et al., 2010; Panda et al., 2011), and electrocoagulation (Zongo et al., 2009). Among these methods, chemical reduction by zero-valent iron (ZVI) is the most efficient and simplest method. Nanoscale

zero-valent iron (nZVI) has been used for the reduction of wastewater containing Cr(VI) (Hoch et al., 2008; Fang et al., 2011), due to its higher reactivity than ZVI. However, engineering applications of nZVI have produced new problems, such as the toxic substance or nZVI release into the environment (Shu et al., 2010). Hence, supporting materials such as bentonite (Shi et al., 2011), kaolinite (Zhang et al., 2011) and chitosan (Liu et al., 2010) have been used to immobilize nZVI. The use of nZVI supported on ion exchange resin has been employed to treat dye or nitrate wastewater (HeeSu et al., 2009; Shu et al., 2010); however, nZVI supported on resin to remove heavy metals has not been studied.

Ion exchange resins have been efficiently utilized for the removal of heavy metal from wastewater (Xing et al., 2007; Kołodyńska, 2011; Tao et al., 2011). However, one kind of ion exchange resins can only remove cation or anion heavy metals. In our study, we found that resin supported nZVI can remove both cation and anion heavy metal. D001 was selected as the model of cation exchange resin because of its abundant porous structure, excellent chemical stability, and mechanical strength (Chen et al., 2011). Considering the toxicity of Cr(VI) is much greater than that of Cr(III), we mainly investigated the removal of Cr(VI). The purposes of this study were to: (1) synthesize and characterize R-nZVI; (2) examine the feasibility of the removal of anion and cation heavy metals, using Cr(VI) and Cr(III) as a model; (3) evaluate the factors affecting Cr(VI) removal (such as initial nZVI loads, resin dose, initial Cr(VI) concentration and pH value); and (4) investigate the recycle times of R-nZVI or resin.

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2. Materials and methods

2.1. Materials

All chemical reagents, including $K_2Cr_2O_7$, $FeSO_4 \cdot 7H_2O$, H_2SO_4 and NaOH were of analytical reagent grade. Distilled water (DI water) was used in all preparations. $NaBH_4$ (99.5%) was purchased from Tianjin Beilian Fine Chemicals Development Co., Ltd. A stock solution containing Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ in DI water. A series of solutions used during the experiment were prepared by diluting the stock to the desired concentration. A stock solution containing Cr(III) was prepared by dissolving $Cr(NO_3)_3$ in DI water.

A macroporous, polystyrene-based strongly acidic cation-exchange resin containing sulfonic groups, D001, was purchased from Hebei Resin Industrial Co., Ltd., China. Its physical properties were as follows: shape, bead; size, 0.32–1.25 mm; exchange capacity, 4.50 mmol/g; true density, 1.25–1.28 g/mL; water content, 45–55%. The fresh resins were placed in 10% NaCl solution over 20 h and then washed with DI water before use.

2.2. Synthesis of R-nZVI

The synthesis of R-nZVI was performed by the borohydride reduction method. 20 g of resin was weighed in a 500 ml wide-mouth bottle. The resin was mixed with 100 ml $FeSO_4$ solutions of 0.119, 0.145, 0.175 or 0.183 M, to obtain different nZVI loads per g resin. The mixture was agitated for 60 min to absorb ferrous ion in the resin. Then the resin was washed with DI water three times to remove residual $FeSO_4$ solution. Ferrous concentration in the resin was calculated by initial ferrous concentration to deduct the residual ferrous concentration from the supernatant drawn and the ferrous ion was analyzed by a flame atomic absorbance spectrometer (AAS, Z-2000, Hitachi, Japan). 0.5 M $NaBH_4$ was added dropwise, and the mixture was stirred continuously on a magnetic stirrer until no significant H_2 production was observed (approximately 30 min). The ferrous ion was reduced to nZVI according to the following reaction:

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \uparrow \qquad (1)$$
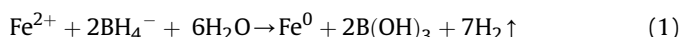
The solid materials were recovered from filtering the suspension, rinsed with DI water, and stored in a water–ethanol solution for use or dried under vacuum.

2.3. Batch experiments

The batch experiments for the reduction of Cr(VI) were performed in flasks at room temperature. R-nZVI particles were added to the flasks containing 0.2 L $Cr_2O_7^{2-}$ aqueous solution. The reaction solution was stirred at 150 rpm. The solutions were periodically sampled, and filtered immediately using a membrane filter of 0.45 μm poresize. The effects of nZVI loadings, resin amount, pH, and initial Cr(VI) concentration on Cr(VI) removal were evaluated. The initial Cr(VI) concentrations were 20.0–40.0 mg/L. The solutions of 0.5 M H_2SO_4 or NaOH were used to adjust the water pH. During the reaction the pH was not controlled.

The potential to reuse the used R-nZVI was also evaluated. After R-nZVI reacted with the Cr(VI) solution for 60 min, centrifugation was performed for 10 min to obtain solid–liquid separation. The supernatant was carefully decanted and the used R-nZVI was washed with DI water three times. The obtained used R-nZVI was then reused again to remove Cr(VI) for four times under identical conditions of R-nZVI treating Cr(VI). The regeneration of the used resin was also investigated. The used resin was reloaded with nZVI

according to the method of the synthesis of R-nZVI and then used to remove Cr(VI).

2.4. Analytical methods

Cr(VI) concentration was determined with 1,5-diphenylcarbazide at 540 nm, using a UV–visible spectrophotometer (UV-3101PC, Japan). The concentration of total chromium, Cr(III) and total iron in solution was determined using AAS. pH value was measured using a PHS-25C pH meter (Shanghai, China). The morphology of the metal particles was observed under a scanning electron microscope (SEM S-3400N, Hitachi Co., Japan), using an operating voltage of 15.0 kV. X-ray diffraction (XRD) of R-nZVI was performed before and after reacting with Cr(VI), using an X-ray power diffractometer (XD-2, Purkinje General Instrument Co., Ltd., Beijing, China) that employed Cu Kα radiation. The accelerating voltage and applied current were 36 kV and 20 mA, respectively.
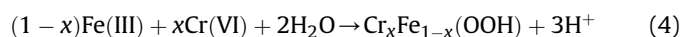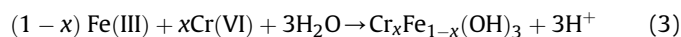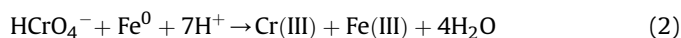
3. Results and discussion

3.1. Characterization of R-nZVI

Fig. 1 shows the SEM images of the (a) original resin, (b) R-nZVI, (c) R-nZVI before reaction and (d) after reaction. The necklace-like aggregates of nZVI particles supported on the resin were observed. This type of aggregation was attributed to the magnetic interactions between the primary iron particles. After reacting with Cr(VI), most nZVI particles became sphere (Fig. 1(d)). This phenomenon was attributed to the co-precipitation of Cr(III) and Fe(III) on the surface of resin.

The XRD patterns of R-nZVI after reacting with Cr(VI) (Fig. 2(c)) were compared with those before reaction (Fig. 2(b)) and initial resin (Fig. 2(a)). According to the JCPDS file, two major peaks in Fig. 2(b) were identified as Fe^0 (PDF #: 06-0696, $2\theta = 44.9$ and 82.6). It is obvious that the characteristic peak of Fe^0 weakened after reaction (Fig. 2(c)), indicating that the amount of nZVI dose in the resin had diminished. The resin supported nZVI had a different structure compared to unsupported resin, indicating that the nZVI may be located on the surface of the resin. The XRD results implied that nZVI was composed of very small crystals. The chromium peaks could hardly be observed, indicating that the amount of chromium in the resin was very small.

3.2. Cr(VI) removal by R-nZVI

It has been proposed that Cr(VI) was reduced to Cr(III), and nZVI was primarily oxidized to Fe(III). The reaction mechanism of Cr(VI) is seen in Fig. 3(b)–(c). $HCrO_4^-$ is the dominant form of Cr(VI) at pH 1.0–6.0 (Mohan and Pittman, 2006) and it can enter the vicinity of resin or can be adsorbed on the resin. It will react with nZVI, generating Cr(III) and Fe(III) (Eq. (2)). The generated Cr(III) and Fe(III) can co-precipitate and form $Cr_xFe_{1-x}(OH)_3$ (or $Cr_xFe_{1-x}(OOH)$) precipitates (Eqs. (3) and (4)) (Hou et al., 2008; Singh et al., 2011b). With the formation of $Cr_xFe_{1-x}(OH)_3$ precipitates on the resin, the Cr(VI) removal decreases for the resistance the electron transfer on the iron surface and redox reactions also slow or stop.

$$HCrO_4^- + Fe^0 + 7H^+ \rightarrow Cr(III) + Fe(III) + 4H_2O \qquad (2)$$

$$(1-x)Fe(III) + xCr(VI) + 3H_2O \rightarrow Cr_xFe_{1-x}(OH)_3 + 3H^+ \qquad (3)$$

$$(1-x)Fe(III) + xCr(VI) + 2H_2O \rightarrow Cr_xFe_{1-x}(OOH) + 3H^+ \qquad (4)$$