

Synthesis of Nanoscale Zerovalent Iron Particle and Its Application to Cr(VI) Removal from Aqueous Solutions

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Abstract: Zerovalent iron (ZVI) is one of the most commonly used metallic reducing agents for the treatment of toxic contaminants in wastewater. Traditional ZVIs are less effective than nanoscale ZVI (nZVI) due to prolonged reaction time. However, the reactivity can be significantly increased by reducing the size of ZVI particles to nanoscale. In this study, nZVI particles were synthesized under laboratory condition and their efficiency in removing hexavalent chromium (Cr(VI)) from aqueous solutions were compared with commercially available ZVI particles. The results showed that the synthesized nZVI particles (SnZVI) reduced >99% of Cr(VI) at the application rate of 0.2% (w/v), while commercial nZVI (CnZVI) particles resulted in 59.6% removal of Cr(VI) at the same application rate. Scanning electron micrographs (SEM) and energy dispersive spectra (EDS) of the nZVI particles revealed the formation of Fe-Cr hydroxide complex after reaction. Overall, the SnZVI particles can be used in treating chromium contaminated wastewater.

Key Words: Nanoscale zerovalent iron, Reduction, Hexavalent chromium, Wastewater, Redox reaction

Introduction

Iron has been extensively used as a wastewater

treatment that it acts as a coagulant, an adsorbent, or a redox catalyst. In solution, iron may exist as forms of ferrous (Fe^{2+}), ferric (Fe^{3+}), ferryl (Fe(IV)), ferrate (Fe(VI)), and elemental or zerovalent iron (Fe^0) (Waite *et al.*, 2002; Yang *et al.*, 2006). Zerovalent iron (ZVI) has been investigated as one of the commonly used metallic reducing agents for control of toxic contaminants in wastewater (Bigg and Judd, 1999). Use of ZVI as a chemical reduction treatment of wastewater is an alternative technique to conventional methods and is widely available with an advantage of low cost. Additionally, it has the excellent performance to decompose toxic contaminants (Bigg and Judd, 1999; Junyapoon, 2005).

Commercially available ZVIs, at present, indicate low reacting ability and need prolonged reaction time for effectively degrading toxicants (Wang and Zhang, 1997). However, the reacting ability of ZVI particles can be improved by reducing the size of iron particles to nanoscale that increasing the specific surface area (Fan *et al.*, 2008). Several methods have been attempted to synthesize nanoscale zerovalent iron (SnZVI) particles using a sonochemical method (Suslick *et al.*, 1991; de Caro *et al.*, 1996), an electrochemical method (Chen *et al.*, 2004), a gas phase reduction (Kanel *et al.*, 2005), and a liquid phase reduction (Wang and Zhang, 1997; Schrick *et al.*, 2004; Wang *et al.*, 2009). Until now, a borohydride liquid phase reduction method has been known as the most effective way (Wang *et al.*, 2009).

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Generally, chromium in the oxidation state of Cr(VI) is a toxic chemical contaminant to humans, animals and plants, while Cr(III) indicates less toxic (Zayed and Terry, 2003; He and Traina, 2005). For safety, the reduction of Cr(VI) is commonly recommended in order to reduce mobility and toxicity (Fendorf and Li, 1996). Zerovalent iron has a high redox potential to transfer Cr(VI) to Cr(III) in aqueous solutions (Lee *et al.*, 2003; Yang *et al.*, 2007). Numerous studies have been reported on the use of ZVIs for removing Cr(VI) in aqueous solutions (Fendorf and Li, 1996; Ponder *et al.*, 2000; Yang *et al.*, 2006; Yang *et al.*, 2007; Li *et al.*, 2008). The mechanism of Cr(VI) removal from aqueous solutions by nZVIs consists of the reduction, complexation, adsorption, precipitation or coprecipitation (Yang *et al.*, 2007). The objectives of this study were (1) to synthesize nZVI particles in laboratory using a borohydride reduction method, (2) to elucidate the efficiency of the SnZVI particles for removing Cr(VI) from aqueous solutions, and (3) to predict the mechanistic evidence of Cr(VI) reduction using SnZVI particles.

Materials and Methods

Materials

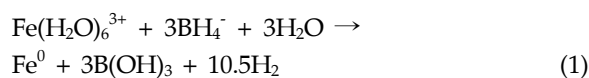
The ACS reagent grade chemicals and reagents were used in this study. Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium borohydride powder (NaBH_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sodium hydroxide (NaOH), sodium chloride (NaCl), anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$), acetone ($(\text{CH}_3)_2\text{CO}$), and hydrochloric acid (HCl) were obtained from Sigma-Aldrich Co. Commercial nanoscale zerovalent iron (nZVI) was purchased from the Xuzhou Hongwu Nanometer Material Co. (China), and Fe^0 powder was obtained from the Daejung Chemicals & Metals Co. (Korea). All reagents (e.g., deionized water, ethanol, and acetone) were degassed using an ultrasonic bath (JAC Ultrasonic 1505 Jinwoo Alex) and were purged with N_2 gas prior to use.

Morphological analysis of the ZVI particles was conducted using a scanning electron micrographs (SEM; HITACHI-S-4300) operated at 15 KeV. Energy dispersive spectra (EDS) was also applied to quantify iron content and adsorbed chromium in the iron particles. Standard 1,5-diphenylcarbazide colorimetric method (Bartlett and James, 1996) was employed to measure the Cr(VI) concentration using UV-spectrophotometry (UV-1800, SHIMADZU, Japan). The inductively

coupled plasma atomic emission spectrometer (ICP-AES, Perkin Elmer Optima 3100XL, Wellesley, MA) was also used to determine total Cr concentration in aqueous solutions.

Synthesis of nanoscale zerovalent iron particles

Nanoscale zerovalent iron particles were synthesized using a borohydride reduction method as described by Wang *et al.* (2009). The overall chemical reaction can be described below ((1); Wang *et al.*, 2009):



Briefly, 0.018 M ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was dissolved into 500 mL of 90% ethanol solution and 1.4 g sodium borohydride (NaBH_4) was dissolved into 50 mL of deionized water (previously purged with N_2 and containing <0.8 mg/L dissolved oxygen). Then, the NaBH_4 aqueous solution was dropped at a rate of 7-7.5 mL/min into the prepared FeCl_3 solution and stirred for 13 min at 500 rpm. The mixture was stirred for additional 5 min after the addition of NaBH_4 . After reaction, the ZVI particles were collected using a magnet. The supernatant was removed and then the precipitated iron particles were washed twice with anhydrous ethanol to ensure removal of salt produced as a by-product. The produced slurry was centrifuged at 2,000 rpm for 12 min after removing supernatant. The residue was washed with dilute HCl (0.001M) and ethanol/acetone (1:1 v/v) (Fan *et al.*, 2008). The iron particles were gathered again using a magnet. Finally, the SnZVI particles were washed with acetone and were subsequently dried under N_2 gas at 110°C for 6 h as described by Wang and Zhang (1997). The produced gray-black solid was broken up with a spatula to form a fine black powder (Ponder *et al.*, 2000).

Batch experiment

A batch experiment was conducted to evaluate the efficiency of SnZVI particles for removing Cr(VI) from aqueous solution. The Cr(VI) solution was prepared by dissolving appropriate amount of $\text{K}_2\text{Cr}_2\text{O}_7$ in N_2 purged deionized water at the initial concentration of 100 mg/L and the solution pH was adjusted to 3.0 to prevent oxidation of Fe(II) to Fe(III) during the test (Fendorf and Li, 1996). A constant ionic strength was also maintained using a 0.1 M NaCl electrolyte (Yang

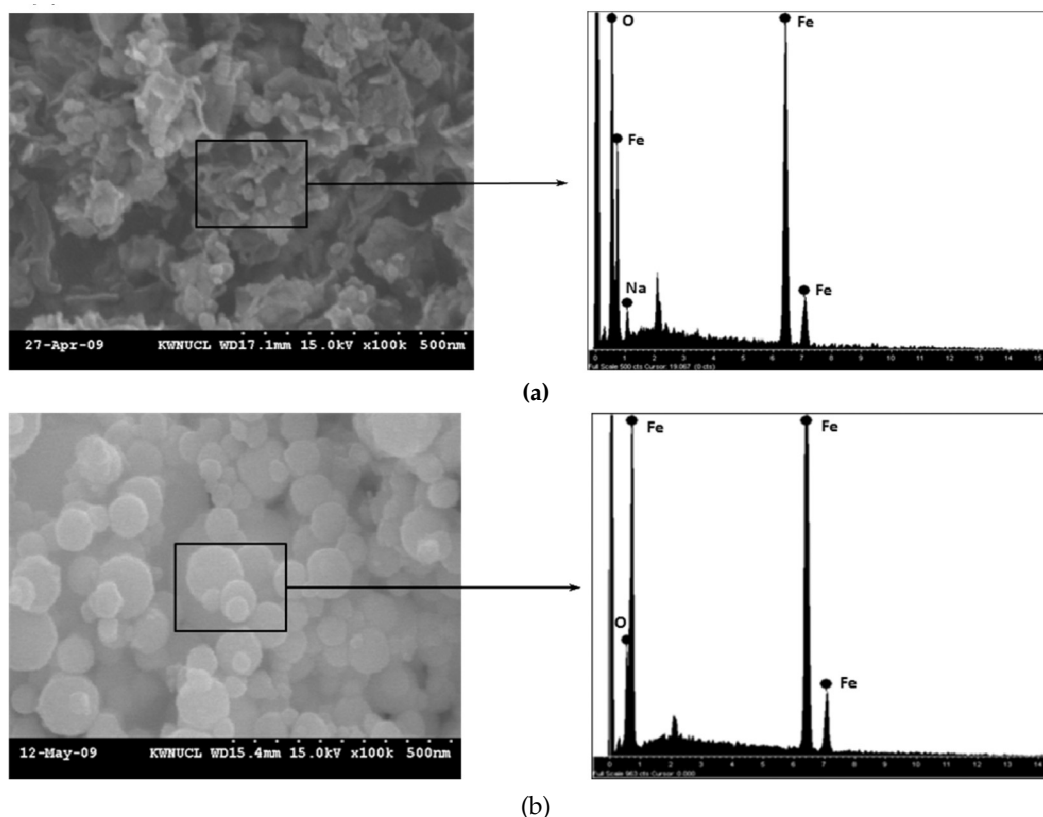


Fig. 1. Scanning electron micrographs with energy dispersive spectra of (a) synthesized nanoscale zerovalent iron and (b) commercial nanoscale zerovalent iron.

et al., 2006). Three zerovalent irons including SnZVI, CnZVI, and ZVI were applied to Cr(VI) solution. The application rates were eliminated to 0.05, 0.1, and 0.2% (w/v) for both SnZVI and CnZVI, whereas 1% (w/v) for ZVI. The solution was shaken at 150 rpm for 24 h at 25°C (Yang *et al.*, 2006). The supernatant from each treatment was analyzed for the concentrations of Cr(VI) and total Cr as described earlier. All experiments were performed with more than two replications.

Results

Surface structure analysis of SnZVI

Scanning electron micrographs of SnZVI and CnZVI with corresponding EDS were presented in Fig. 1. The SnZVI has a sharp and coarse surface, while CnZVI has a smooth and globular surface. The SnZVI particles were also interconnected with one another forming nanoclusters. Quantitative analysis for elemental composition using EDS indicated 76.06% Fe, 21.43% O, and 2.51% Na in SnZVI, and 94.31% Fe and 5.69% O in CnZVI. These morphological results found that

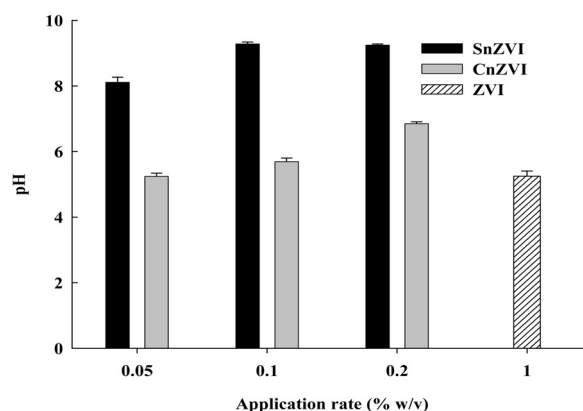


Fig. 2. Changes in aqueous solution pH treated with synthesized nanoscale zerovalent iron (SnZVI), commercial nanoscale zerovalent iron (CnZVI), and zerovalent iron (ZVI) particles. Reaction conditions were 100 mg/L Cr(VI) in 0.1 M NaCl and initial pH of 3.0 at 25°C.

Fe^0 was the primary component of SnZVI with surface layers of iron oxide.

Batch experiment

Tested three ZVIs increased the solution pH after reaction compared to the initial solution pH (Fig. 2).

At their maximum application rates, the SnZVI highly increased the solution pH up to 9.3 compared to CnZVI and ZVI which had the small increases to 6.9 and 5.3, respectively. All tested ZVI particles decreased the concentrations of Cr(VI) and total Cr in aqueous solutions (Fig. 3). Both SnZVI and CnZVI reduced the Cr(VI) concentration in aqueous solutions as the application rates increase. Especially, the SnZVI reduced the Cr(VI) concentration by >99% at the application rate of 0.2%. The applications of 0.2% CnZVI and 1% ZVI indicated the reductions in the Cr(VI) concentration by 59.6% and 35.8%, respectively. The concentrations of total Cr in the solutions were similar to those of Cr(VI) and the order of the efficacy in removing Cr was SnZVI > CnZVI > ZVI.

The SEM-EDS analysis of SnZVI and CnZVI reacted with Cr(VI) in aqueous solutions was shown in Fig. 4. The surfaces of both SnZVI and CnZVI became soft and smooth upon reaction with Cr(VI). The reductions in both material size and coverage were also observed. The EDS spectra of SnZVI and CnZVI indicated the presence of Cr on the reacted surfaces of iron particles. The higher Cr peak of SnZVI in the EDS spectrum revealed better efficiency of SnZVI in Cr removal in aqueous solution compared to CnZVI. Our findings were similar with a study of Yang *et al.* (2006) that reporting the morphological changes.

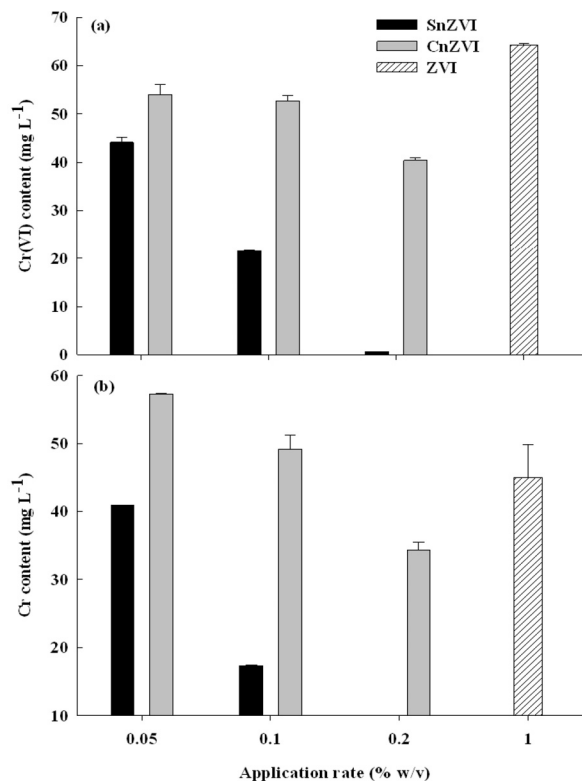


Fig. 3. Concentrations of (a) Cr(VI) and (b) total Cr in aqueous solution treated with synthesized nanoscale zerovalent iron (SnZVI), commercial nanoscale zerovalent iron (CnZVI), and zerovalent iron (ZVI) particles. Reaction conditions were 100 mg/L Cr(VI) in 0.1 M NaCl and initial pH of 3.0 at 25°C.

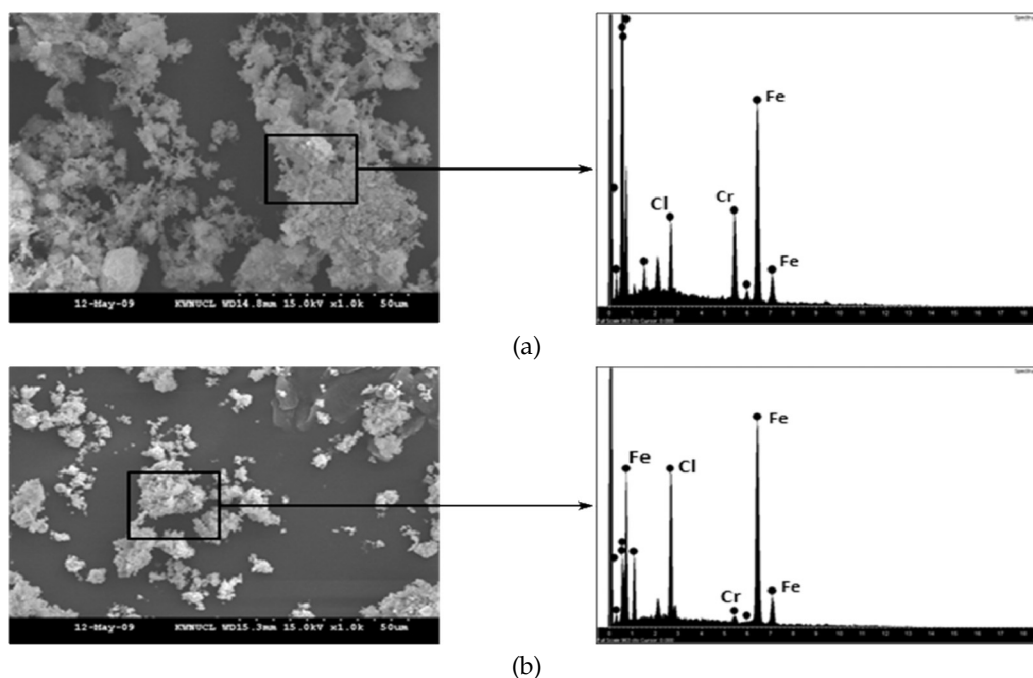
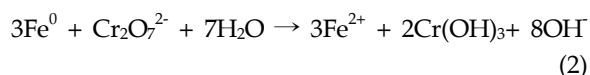


Fig. 4. Scanning electron micrographs with energy dispersive spectra of (a) synthesized nanoscale zerovalent iron (SnZVI) and (b) commercial nanoscale zerovalent iron (CnZVI) particles reacted with Cr(VI) in aqueous solution. Reaction conditions were 100 mg/L Cr(VI) in 0.1 M NaCl at pH 3.0, 25°C.

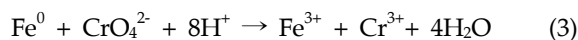
Table 1 represented the quantitative elemental composition of the reacted iron particles after reaction with Cr(VI) from the SEM-EDS analysis. The major elements in all tested ZVI particles were Fe and O. However, 10.93%, 6.76% and 2.36% of Cr were also presented in SnZVI, CnZVI, and ZVI particles, respectively. The higher concentration of Cr in SnZVI indicated its better adsorption capacity in comparison with CnZVI. The Fe contents in SnZVI and CnZVI reduced by 41% and 17%, respectively, after reaction with Cr(VI) in aqueous solutions.

Discussion

Morphological characterization of SnZVI illustrated the present of coarse nanoclusters as shown in Fig. 1 and indicated formation of particle aggregates. Due to magnetic properties of iron nanoparticles, they are willing to form aggregates (Fan *et al.*, 2008). In addition, the effectiveness of metal removal can be determined using applied SnZVI into aqueous solution of Cr(VI). Rise in the solution pH may be contributed to the release of OH⁻ ions due to redox reaction below (Li *et al.*, 2008):



Zerovaleant iron particles effectively remove Cr(VI) and total Cr in the aqueous solution. Because of the unstable ZVI (Fe⁰) state, it can be readily oxidized to Fe²⁺ and Fe³⁺ in aqueous solution resulting in reduction of Cr(VI) to insoluble Cr(III) (Lee *et al.*, 2003):



Our SEM-EDS results found that the presence of Cr, Fe, and O in the reacted SnZVI and CnZVI particles. Formation of iron complexes with Cr such as Fe-Cr oxyhydroxide showed the mechanistic evidence of Cr removal by ZVI particles. Yang *et al.* (2007) also reported the formation of Fe-Cr complexes in aqueous solutions by commercial ZVI, supported from SEM-EDS, XRD, and XPS analysis.

Higher efficiency of SnZVI compared to CnZVI and ZVI could be explained by the higher reduction of Cr(VI) to Cr(III) at high solution pH. This finding was confirmed by the EDS spectra showing a higher peak and Cr concentration at a 0.2% application rate of SnZVI to Cr(VI) aqueous solution (Fig. 4 and Table

Table 1. The elemental composition (%) of the reacted iron particles with Cr(IV) based on SEM-EDS analysis

Element	SnZVI [†]	CnZVI [‡]	ZVI [¶]
	0.2% (w/v)	0.2% (w/v)	1.0% (w/v)
Al	0.86	-	-
C	5.20	2.67	5.45
Cl	3.27	0.74	-
Cr	10.93	6.76	2.36
Fe	45.04	78.05	62.50
Na	-	-	10.85
O	34.70	11.78	18.84

[†]synthesized nanoscale zerovalent iron particles

[‡]commercial nanoscale zerovalent iron particles

[¶]zerovaleant iron particles

1). Silva *et al.* (2009) observed that higher pH values enhance total Cr removal from aqueous solution using bacterial biomass. Moreover, SEM images revealed that the surface of nZVI particles and the material size were reduced after reaction with Cr(VI). This finding may be resulted from the rapid oxidation of Fe⁰ to Fe³⁺ at high pH (Vance, 1994).

Conclusion

The nanoscale zerovalent iron particles were synthesized using a borohydride reduction method and were applied to the aqueous Cr(VI) solution to evaluate its removal efficiency. Multiple reactions were involved in the Cr removal using nZVI particles: 1) reduction of Cr(VI) to insoluble Cr(III) and 2) complexation of Fe-Cr oxyhydroxide. The SnZVI particles indicated the best performance in removing Cr in aqueous solution compared to the CnZVI particles or conventional iron powder. Additionally, solution pH is one of the most important factor to determine the effectiveness of SnZVI on Cr(VI) removal in aqueous solution. Future studies would be needed to elucidate the practical use of SnZVI particles in removing Cr and other heavy metals in wastewater.

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