Stabilization of chromium ore processing residue (COPR) with nanoscale iron particles

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Abstract

Laboratory batch experiments were conducted on heavily contaminated groundwater and chromium ore processing residue (COPR) samples to determine the rate and extent of hexavalent chromium [Cr(VI)] reduction and immobilization by nanoscale iron particles. Laboratory synthesized nanoscale iron particles (<100 nm, specific surface area 35 m^2/g) were used for this work. Groundwater ([Cr(VI)] = 42.83 ± 0.52 mg/L, pH 11.0 ± 0.5) and COPR samples ([Cr(VI)] = 3280 ± 90 mg/kg) were collected from an industrial site in New Jersey. Cr(VI) in the water and COPR samples was quickly reduced and precipitated out of the aqueous solution. The surface area normalized reaction rate constant of Cr(VI) reduction by nanoscale iron particles was 0.157 ± 0.018 mg m^{-2} min^{-1}, about 25 times greater than that by iron powders (100 mesh). One gram of nanoparticles can reduce 84.4–109.3 mg Cr(VI) in the groundwater and 69.3–72.7 mg Cr(VI) in the COPR. This reduction capacity is 50–70 times greater than that of iron powders under the same experimental conditions.

1. Introduction

Chromium is a vital industrial material for which there is no ready substitute. It is estimated that U.S. has a chromium stockpile over 5 million metric tons [1]. Chromium contamination of soil, sediment, and water has been found from mineral extraction, electroplating, steel and alloy production, leather tanning, pigment and chemical manufacturing, etc. [2–6]. In the United States, chromium is the second most common inorganic groundwater contaminant, after lead [7]. Chromium has been classified as a potential carcinogen [8], and has high and acute toxicity to humans, animals, plants, and microorganisms. Consequently, chromium contaminant in groundwater, chromium ore processing residue (COPR), and sediment represents a significant environmental and public health concern [9]. The U.S. EPA maximum contaminant level (MCL) for total chromium in water is 0.1 mg/L [10].
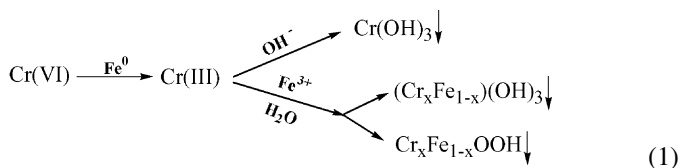
Chromium in natural waters exists primarily in +3 and +6 valence states [11]. Hexavalent chromium (Cr(VI)), such as chromate [CrO$_4$$^{2-}$, HCrO$_4$$^-$] is highly soluble reactive and mobile in aquatic systems. On the other hand, trivalent chromium [Cr(III)] is relatively stable and has low solubility (<10^{-5} M) in aqueous solutions over a wide pH value range (4–12) [11]. Stable ionic forms of Cr(III) in aqueous systems include Cr(OH)$^{2+}$ and Cr(OH)$_2$$^+$ [11].

Remediation of chromium-contaminated soil and groundwater has largely followed the pathway of reduction and precipitation/immobilization. For example, biologically induced Cr(VI) reduction and remediation has been frequently reported [12–16]. Bacterial genera, such as *Schewanello*, *Pseudomonas*, *Bacillus*, *Enterobacter*, and others have been shown to reduce and precipitate Cr(VI) [13–16]. Dissolved organic compounds, such as oxalate and citrate are capable of slowly reducing of Cr(VI), and the rate is accelerated in presence of TiO$_2$, FeOOH, or Al$_2$O$_3$ [17–20]. Ferrous iron (Fe(II)) is also capable of reducing Cr(VI) to Cr(III) [21–24]. The reduced chromium can precipitate in the form of (Cr$_x$Fe$_{1-x}$)(OH)$_3$ (x < 1) by reacting with Fe(III) produced from the oxidation of Fe(II) [23]. Consequently, in situ Fe(II) barriers for Cr(VI) remediation have been proposed accordingly [24]. It was also reported that Cr(VI) may be removed from aqueous solution by forming a precipitate directly with Fe(III) [25].

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Zero valent iron (ZVI) is increasingly being utilized for in situ application to remediate soil and groundwater containing metals, such as Cr, Pb, U, Mo, Hg, V, and other metal ions [26–40]. Compared to biological methods and Fe(II), reduction of Cr(VI) to Cr(III) by ZVI is relatively rapid and complete. Eq. (1) depicts the mechanisms of reduction and immobilization of Cr(VI) by ZVI.

$$\text{Cr(VI)} \xrightarrow{\text{Fe}^0} \text{Cr(III)} \begin{array}{c} \xrightarrow{\text{OH}^-} \text{Cr(OH)}_3\downarrow \\ \xrightarrow{\text{Fe}^{3+}} (\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3\downarrow \\ \xrightarrow{\text{H}_2\text{O}} \text{Cr}_x\text{Fe}_{1-x}\text{OOH}\downarrow \end{array} \tag{1}$$

In this work, we report the use of nanoscale iron particles for the treatment of chromium contaminated groundwater and soil. Previously, we have reported the use of nanoscale iron and palladium/iron bimetallic particles as remedial reagents for reductive dechlorination of various chlorinated hydrocarbons, such as chlorinated ethenes, aromatics, and polychlorinated biphenyls (PCBs) [34]. The nanoscale metallic particles have diameters of less than 100 nm. The average specific surface area of the nanoparticles is in the range of 10–40 m^2/g, which is significantly greater than that of conventional microscale iron powder (typically $\leq 1\,m^2/g$). The surface area normalized reactivity (k_{SA}) of the nanoscale Pd/Fe bimetallic particles for dechlorination of various chlorinated organic solvents is one to two orders of magnitude higher than that of conventional microscale iron particles [34,35]. The high activity of nanoscale Pd/Fe bimetallic particles can be attributed to the large surface area and the presence of catalytic palladium on the iron surface.

A conceptual model of reduction and immobilization of Cr(VI) by the nanoscale iron particles is illustrated in Fig. 1. Nanoscale iron particles reduce Cr(VI) primarily to Cr(III). Recent research suggests that the rates of reduction of Cr(VI) and Pb(II) in aqueous solution by supported zero-valent iron nanoparticles (Ferragels, 10–30 nm in diameter) were up to 30 times higher than that by iron powders (~40 mesh, Fisher) [39]. Cr(III) then precipitates as hydroxides on the soil surface. In addition, the adsorption of the nanoscale iron particles on the soil surface provides long-term reducing power and protects Cr(III) from re-oxidation and subsequent leaching back into the aqueous phase.

In this work, heavily contaminated water and COPR samples were used to determine the efficacy of the nanoiron technology f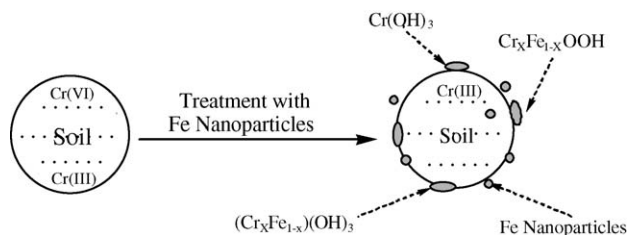or chromium treatment. Primary objectives of the laboratory studies described herein include: (1) evaluation of the effectiveness of the nanoscale iron particles for reduction and immobilization of Cr(VI) in groundwater and COPR; (2) determination of the stoichiometry and kinetics of Cr(VI) reduction; and (3) assessment of the stability of the reduced chromium.
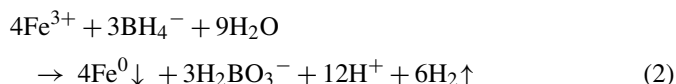
2. Materials and methods

2.1. Chemicals and materials

The following reagents were used in this work: ferric chloride anhydrous (ACS grade, Alfa Aesar), sodium borohydride (98%, Finnish Chemicals, Finland), hydrogen peroxide (ACS grade, Aldrich), iron (II) sulfate heptahydrate (ACS grade, Aldrich), potassium dichromate (99%, ACS grade, Aldrich).

2.2. Preparation of nanoscale iron particles

Synthesis of nanoscale iron particles was achieved by adding 1:1 volume ratio of sodium borohydride (0.25 M) into ferric chloride (0.045 M) solution [34,39]. Ferric iron was reduced by borohydride according to the following reaction:

$$4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O}$$
$$\rightarrow 4\text{Fe}^0\downarrow + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+ + 6\text{H}_2\uparrow \tag{2}$$

The suspension was mixed vigorously at room temperature ($22 \pm 1\,°C$). The resulted nanoscale particles were separated using laboratory vacuum filter and were washed with distilled water and ethanol. The metal particles formed from the above reaction have sizes generally less than 100 nm with an average diameter at 60 nm and an average specific surface area of 35 m^2/g. The specific surface area was measured with a Micromeritics ASAP 2100 surface area analyzer. A TEM image of the nanoparticle is shown in Fig. 2. In this work, only the nanoscale iron particles were used. No palladium or other noble metal was added as preliminary tests indicated little or no benefit from the addition of palladium.

Commercially available iron powders (Fisher, 100 mesh) were used in several tests as a benchmark material. The iron filing was pretreated with 0.1 N HCl solution for 5 min and washed

Fig. 1. Schematic of reduction and immobilization of Cr(VI) in COPR–water system with nanoscale iron particles.

Fig. 2. TEM image of laboratory synthesized iron particles. The scale bar in the figure is 100 nm.

with distilled water for three times to remove any residual iron oxide layer and chloride.

2.3. Methods of analysis

A UV–vis Spectrophotometer (Agilent 8453) was used for determination of the aqueous Cr(VI) concentrations. Experimental procedures specified in the USGS method I-1230-85 for wastewater (1.5-diphenylcarbohydrazide method) were followed. Distilled water was used as blank. The average value of Cr(III) was calculated from three identical sample analyses.

2.4. Water and COPR samples

Groundwater and COPR samples were collected from a heavily contaminated site located in eastern New Jersey, and the samples were not aerated. The site had been used as a chromium ore processing facility for many years. Large amounts of COPR remained at the site. COPR was typically treated with excessive amounts of lime to neutralize the acids used in the chromium extraction/leaching. The pH of the groundwater of the site was typically between 10 and 11. High chromium concentrations have been found both in COPR and groundwater at the site. The average Cr(VI) concentration in the aqueous phase was 42.83 ± 0.52 mg/L. The Cr(VI) concentration in the air-dried COPR was measured at 3280 ± 90 mg/kg in alkaline solutions (pH 11.0). Standard procedures for the alkaline extraction (SW 846, method 3060A) were followed. Total chromium in COPR was estimated by treating the COPR with excessive hydrogen peroxide (H_2O_2) at acidic pH (pH 3). Under such conditions, near complete Cr(III) oxidation to Cr(VI) was expected. Total chromium concentration in the COPR was thus determined to be 7730 ± 120 mg/kg.

2.5. Experimental setup

This section describes the experimental setups and objectives of four batch experiments.

(1) Removal efficiency: the objective of this test was to determine the optimal nanoparticle dose for complete reduction and precipitation of Cr(VI). Variable quantity of nanoscale iron particles (0–10 g/L) or microscale iron powder (Fisher, 100 mesh) was added into groundwater/COPR slurry (40 mL and 2 g COPR). The 100 mL batch bottles were agitated for 24 h using a wrist-action shaker (30 rpm). The initial solution pH was between 10 and 11. All samples were analyzed for residual Cr(VI) in the aqueous phase after 24 h of reaction time. Cr(VI) removal efficiency was then calculated accordingly.

(2) Removal rate: the purpose of this test was to determine the rate of Cr(VI) reduction and precipitation by the nanoscale iron particles and microscale iron powders. Eight parallel batch experiments were conducted with groundwater and nanoparticles (or microscale iron powders) at varied concentrations. Residual Cr(VI) in the aqueous phase was

analyzed at pre-determined time intervals. 1 mL up aliquot was removed for analysis of resident Cr(VI) concentration.

(3) Reductive capacity: in this experiment, the stoichiometry of Cr(VI) reduction was determined. A batch reactor was spiked repeatedly with Cr(VI) containing groundwater or groundwater/COPR slurry. The solution was continuously agitated until the reduction capacity of the nanoparticles or iron powders was exhausted. The reductive capacity of nanoparticles or microscale iron powders was then calculated from the change of Cr(VI) concentration and mass.

(4) Residue in solution: Fenton's reagent was used to re-oxidize any residual aqueous Cr(III) to Cr(VI) in the aqueous phase and to determine the total aqueous chromium. The total efficiency of reduction and immobilization is then determined from the difference of Cr(VI) concentrations before and after re-oxidization.

3. Results and discussion

3.1. Cr(VI) removal efficiency

The COPR samples were collected from a spoils of chromium ore processing residue at the site while the groundwater samples (pH 10–11) was obtained from a shallow monitoring well at the depth of approximately 6 m. Fig. 3 illustrates the Cr(VI) concentration as the function of reaction time for batch reactors with 10 g COPR and 40 mL groundwater. Nanoscale iron particles and microscale iron powders were used under identical experi-
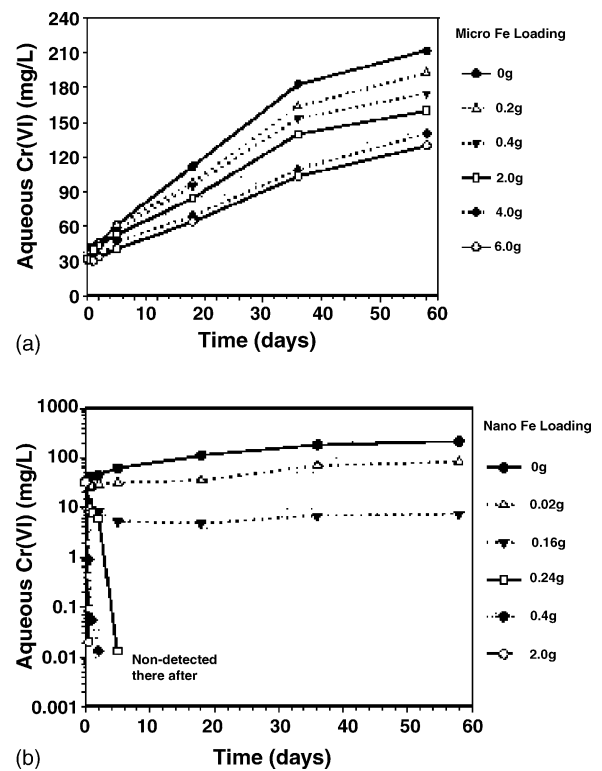

Fig. 3. Reduction and immobilization of Cr(VI) by (a) Fisher iron (100 mesh) and (b) nanoscale iron particles in groundwater/COPR slurries. Batch reactors contained 10 g COPR, 40 mL groundwater and varied amounts of iron.

mental conditions. Fig. 3a shows the results from the reactions with the microscale iron. When 10 g COPR was added to 40 mL groundwater, aqueous Cr(VI) concentration rose from 43 mg/L to 220 mg/L, suggesting substantial desorption and dissolution of Cr(VI) from the COPR matrix to aqueous solutions. However, adding the microscale iron only resulted in modest reduction of Cr(VI) concentration as shown in Fig. 3a. A slight reduction (~9% after 58 days) of Cr(VI) was observed in the batch bottle with 0.2 g microscale iron. A batch bottle with 6.0 g pretreated microscale iron (iron/COPR ratio = 0.6) had a Cr(VI) concentration of 120 mg/L after 58 days, representing a 45% reduction compared to the control reactor without iron. It is evident that the reduction capacity of the microscale iron is rather limited. To achieve complete Cr(VI) reduction, a substantial amount (>50%) of iron powder was needed.

Results with the nanoscale iron particles are shown in Fig. 3b. For example, with 0.24 g nano particles, the Cr(VI) concentration in the aqueous phase fell below the detection limit (<10 μg/L) within 6 days. The reduction efficiency of Cr(VI) in water was greater than 99.99%. A dose of only 0.16 g of the nanoparticle resulted in more than 90% aqueous Cr(VI) reduction. The equilibrium Cr(VI) concentration was maintained below 7.0 mg/L, well below the initial concentration in the aqueous phase of 43 mg/L and COPR–water equilibrium concentration of 220 mg/L. When the amount of nanoparticles was increased to 2.0 g, complete Cr(VI) reduction was achieved in less than 4 h. The remaining chromium concentration in water after treatment was below 10 μg/L.

A potential advantage of the nanoiron technology is the enhanced availability of the nanoiron particles to penetrate the microporous COPR matrix, and hereby increase the contact with Cr(VI). A portion of the air-dried COPR was pulverized to reduce the size to less than 2 mm. Results from batch tests with 2.0 g each of pulverized and original COPR (air-dried) are shown in Fig. 4. The data were measured after a 24-h reaction time. 0.8 g nanoiron particles essentially reduced all the aqueous
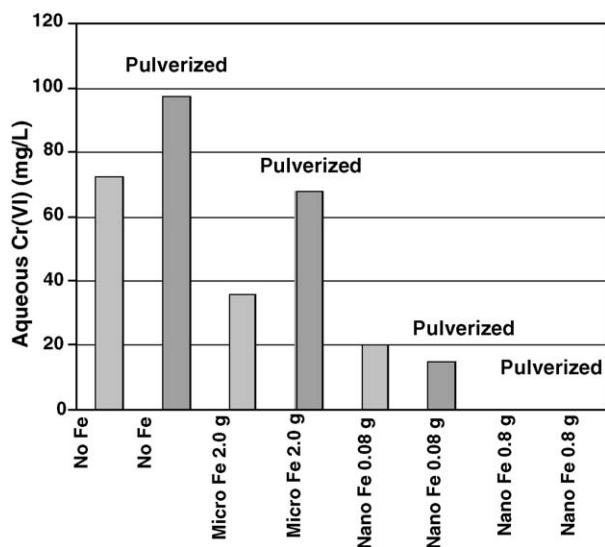
Cr(VI) (>99%). In comparison, 2.0 g microscale iron immobilized less than 33% Cr(VI). Note that with the microscale iron, higher Cr(VI) concentrations were observed with the pulverized COPR suggesting that the small grain size of the pulverized COPR likely increased the desorption and dissolution of Cr(VI). With the limited reduction capacity of the microscale iron, the aqueous Cr(VI) concentrations in the batch reactors with the pulverized COPR was therefore higher. No such difference was noticed with the nanoscale iron particles, indicating potentially a higher reaction capacity and rate.

3.2. Reductive capacity of Cr(VI) by nanoscale Fe and microscale Fe

Fig. 5 presents results from a batch reactor repeatedly spiked with the chromium containing groundwater. The reactor initially contained 40 mL groundwater (Cr(VI)) and 0.2 g nanoparticles. Every 2 h, the solution was centrifuged, and the upper aliquot was then analyzed for Cr(VI) concentration. Another 40 mL groundwater was added to the bottle and shaken for an additional 2 h before the liquid phase being analyzed. After six spikes, 11.7 mg Cr(VI) was reduced. Normalizing that to 1 g of nanoparticles yields a capacity of 57.5 mg Cr(VI)/gFe^0. From the stoichiometry of Cr(VI) reduction by Fe^0 (Eq. (1) and (3)), 1 mole Fe^0 can theoretically reduce 2/3 mole Cr(VI) to Cr(III) (assuming that Fe(0) is oxidized to Fe(II)), meaning the theoretical reduction capacity of Cr(VI) by zero-valent iron is 621.2 mg Cr(VI)/gFe^0. Reactions with water and other oxidants, such as dissolved oxygen will consume some iron. It is also likely that iron in the core of the nanoparticles remains unreacted. Thus, there was still some reducing capacity remaining in the batch reactor.

$$3Fe^0 + 2Cr^{6+} \rightarrow 3Fe^{2+} + 2Cr^{3+} \qquad (3)$$

Fig. 4. Residual Cr(VI) in the aqueous phase after 24 h. The batch reactors contained 40 mL groundwater and 2.0 g COPR.
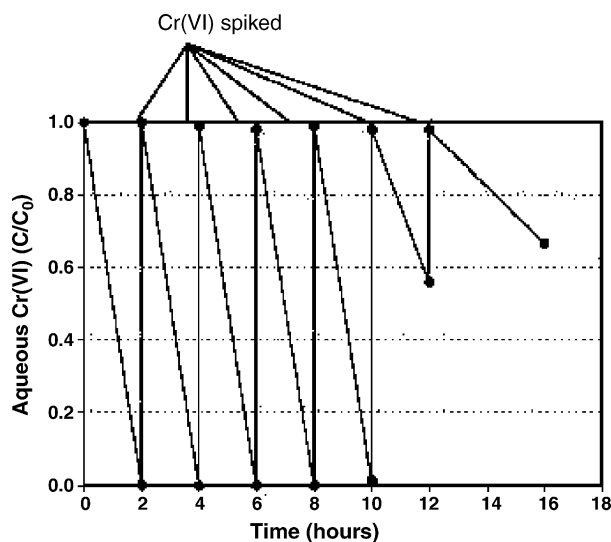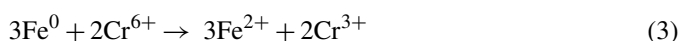

Fig. 5. Reduction of Cr(VI) by nanoparticles. Batch bottle containing 0.5 g iron particles were spiked repeatedly with the chromium-containing groundwater sample utill the reductive capacity is exhausted (initial Cr(VI) concentration 42.83 ± 0.52 mg/L, pH 11.0 ± 0.5).

Table 1
The reductive capacity of Cr(VI) by iron

	Type of Fe	mg Cr(VI)/g Fe^0
Groundwater	Micron Fe[a]	1–3
	Micron Fe	1.53–1.75
	Nano Fe	84.40–109.30
COPR (in distilled water)[b]	Micron Fe	1.26–1.33
	Nano Fe	64.16–67.67
COPR/groundwater[c]	Micron Fe	1.07–1.12
	Nano Fe	69.28–72.65

[a] Reported by Kjeldsen and Locht [41].
[b] 2 g (dried and pulverized) COPR in 40 mL distilled water.
[c] 2 g (dried and pulverized) COPR in 40 mL groundwater.

Fig. 6. Reduction kinetics of Cr(VI) in aqueous solutions. The batch reactors contained 40 mL groundwater (initial Cr(VI) concentration 42.83 ± 0.52 mg/L, pH 11.0 ± 0.5).

To further determine the reductive capacity of the nanoparticles, several more batch tests were conducted with varied doses of nanoparticles. The total Cr(VI) reduction was measured after 60 days and the reductive capacities were calculated accordingly. The results are summarized in Table 1.

The total capacity of the iron nanoparticle for the reduction of Cr(VI) in the groundwater or COPR samples is approximately about 50–70 times greater than that of the Aldrich microscale iron. We noted that the reductive capacity of the microscale iron (1.53–1.75 mg Cr(VI)/gFe) is close to the values (1–3 mg Cr(VI)/gFe) reported by Kjeldsen and Locht [41]. Table 1 also shows that the reductive capacity of the nanoparticle for Cr(VI) in COPR/water slurry was substantially (24–38%) less than that in groundwater.

The reductive capacities of the nanoscale iron particles for the treatment of hexavalent chromium may vary under different conditions. For example, tests of reduction of Cr(VI) by the nanoparticles in solutions with different pH showed that the reduction rate and capacity were slightly higher at low pH. More experiments are needed to determine the optimal environmental conditions, such as pH and alkalinity.

3.3. Reduction kinetics of Cr(VI)

It is generally accepted that the reductive reactions by zero valent iron are a surface-mediated process. The oxidant (e.g., chlorinated hydrocarbons or Cr(VI)) is adsorbed onto the surface of iron and subsequently reduced. The initial reaction can be treated as a pseudo first order reaction where the rate constant in normalized to the total surface area of iron. An example is given in Fig. 6. The surface area normalized reaction rate constant k was calculated to be 0.157 ± 0.018 mg Cr(VI)m^{-2} min^{-1} for the nanoparticles and 0.0063 mg Cr(VI)m^{-2} min^{-1} for the micro iron, respectively. In other words, the surface area normalized rate (K_{SA}) for the nanoparticles is about 25 times greater than that for the micro iron.

3.4. Residual Cr(VI) in solution

The above tests, as well as another recent report [39], show that nanoparticles can readily reduce Cr(VI) into Cr(III). An important unresolved question concerns the precipita-
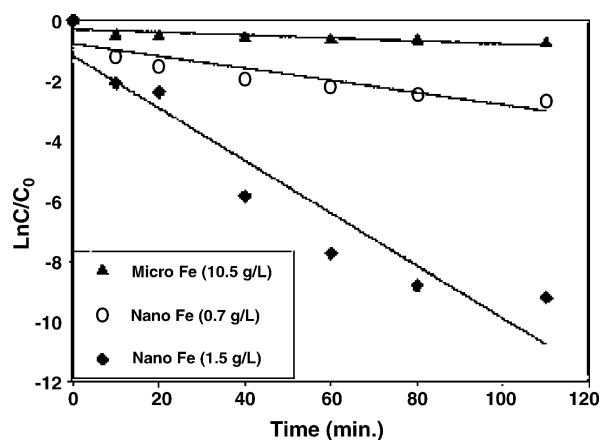
tion/immobilization efficiency of the reduced Cr(III). As described in the introduction section, the reduced Cr(III) may still remain in the solution phase in the various forms of hydroxide and/or hydroxyl species. To determine the distribution of chromium in the batch reactors, several batch experiments with COPR/groundwater slurries were conducted. Water samples were filtered through 0.2 μm PTFE membranes after various time intervals. The aliquots were then charged with an excessive dosage of Fenton's reagent to re-oxidize remaining Cr(III) to Cr(VI), if any Cr(III) remained in the aqueous phase. The change of Cr(VI) concentration in the aqueous aliquot was measured before and after the oxidation as illustrated in Fig. 7.

In the three tests shown in Fig. 7, the Cr(VI) concentration after re-oxidation was very close to that before re-oxidation. The difference was less than 5%. In other words, little chromium remained dissolved/suspended in the aqueous phase. Nearly, all the reduced Cr(III) precipitated out of the solution, either on the iron or the COPR particles. This further validates the immobilization efficiency of Cr(III) by the nanoparticles. A similar conducted over a period of 6 months showed little increase of the aqueous Cr(VI) concentration, confirming the stability of Cr(III) on the COPR particles.
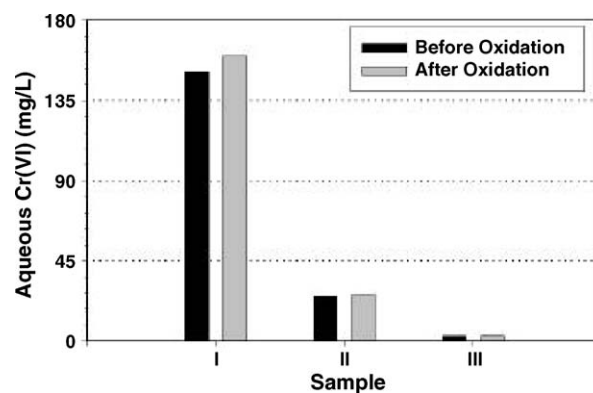

Fig. 7. Cr(VI) concentration in the aqueous phase before and after re-oxidation with Fenton's reagent. Samples I–III were taken at 0.3, 2.0, and 5.0 h, the batch test contained 2.0 g dried soil, 40 mL groundwater and 0.2 g nanoparticles.

4. Concluding remarks

Groundwater and COPR samples from an industrial site showed high levels of hexavalent chromium. Laboratory experiments were conducted to determine the rate and efficiency of Cr(VI) reduction and immobilization with nanoscale iron particles. Specific conclusions from the bench scale tests include:

1. Nanoparticles can reduce and immobilize Cr(VI) in both groundwater and COPR.
2. Under similar conditions, the reduction capacity of the nanoparticles is 50–70 times greater than that of iron powder.
3. The rate of reduction produced by the nanoparticles is approximately 25 times higher than the rate of reduction by microscale iron powder.
4. Reduced Cr(VI) can be effectively removed from the aqueous phase and remains stable in solid forms.

Results obtained from this study suggest that immobilization of hexavalent chromium from groundwater and COPR with the nanoscale particles is feasible. The high reactivity and diminutive size of the iron nanoparticles make them promising cargo for groundwater treatment, such as subsurface injection. Methods for field applications of the nanoparticle technology are available and have been tested under comparable environmental conditions [35]. While these preliminary results are indeed encouraging, additional work is required to better understand the underlying reaction mechanisms and speciation of precipitates and complexes formed at the nanoparticle and COPR, also additional tests are needed to determine the optimal environmental conditions for the Cr(VI) reduction and precipitation.

Acknowledgement

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