Mitigation of Chromium Contamination by Copper-ZVI Bimetallic Particles

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Abstract: Soil and water pollution by chromium is a major environmental concern. Although existence of chromium in the Cr^{3+} state is considered benign, its presence in the Cr^{6+} state poses an environmental concern. Hence, reduction of chromium(VI) to chromium(III) is considered as a satisfactory environmental solution to mitigate chromium contamination. The oxidation of a metal substrate can be enhanced by depositing a small amount of nobler metal on its surface. The present study thus examines the efficiency of chromium(VI) reduction upon deposition of copper (oxidation potential: -0.34 V) on the surface of zero-valent iron (ZVI) (oxidation potential: 0.04 V) particles. Batch experiments and pH and Eh measurements revealed that presence of copper loading on ZVI particles increases the efficiency of chromium(VI) reduction by 11–233% in relation to the uncoated ZVI particles owing to enhanced electron activity and release of hydroxyl ions that converted chromium(VI) to mixed Fe–Cr oxide. The chromium(VI) reduction was accomplished in periods ranging from 60 to 240 min in the batch experiments and obeyed the pseudo first- or second-order kinetics. **DOI: [10.1061/(ASCE)HZ.2153-5515.0000169](#).** © 2013 American Society of Civil Engineers.

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Introduction

Chromium generally occurs in the Cr^{6+} and Cr^{3+} oxidation states (Palmer and Puls 1994; Proctor et al. 1997; Gui et al. 2009). Water-insoluble chromium(III) compounds are not considered health hazards, whereas chromium(VI) ions are toxic in nature (Barceloux and Barceloux 1999; Jacobs and Testa 2005). Chromium(III) ions predominantly occur as Cr^{3+} at pH < 3.5, and increasing pH tends to hydrolyze the ions (Rai et al. 1987; Palmer and Puls 1994). The nontoxic nature of chromium(III) ions and their ease of hydrolysis in the pH range of 4.5–10 renders reduction of chromium(VI) to chromium(III) as a satisfactory environmental solution (Erdem et al. 2004).

A permeable reactive barrier composed of granular iron has been constructed to remediate hexavalent chromium—contaminated groundwater (Blowes et al. 1999). The oxidation of Fe^0 to Fe^{3+} ions facilitates reduction of chromium(VI) to chromium(III) state. Chromium(III) ions in turn precipitate as $Cr(OH)_3$ or coprecipitate as mixed Fe–Cr hydroxide (Eary and Rai 1988; Puls et al. 1999; Powell et al. 1995; Blowes et al. 1997). The precipitates formed by hydrolysis of chromium(III) and iron(III) ions tend to block pathways for electron transfer from interior of zero-valent iron (ZVI) particles, thereby affecting the efficiency of chromium(VI) removal (Alowitz and Scherer 2002; Melitas and Farrell 2002; Lo et al. 2006; Hu et al. 2010).

Depositing a small amount of nobler metal (Pd, Pt, Ag, Ni, and Cu) on the surface of ZVI particles was observed to accelerate the degeneration rate of nitrates and chlorinated organic compounds (Muftikian et al. 1995; Grittini et al. 1995; Cheng et al. 1997; Kim and Carraway 2000; Lin et al. 2004; Liou et al. 2005). Hu et al. (2010) observed that coating ZVI particles with copper enhanced the chromium(VI) removal efficiency of ZVI. According to Liou et al. (2005), when iron is coated with nobler metal, a relative potential difference drives the electron from iron particles; these electrons are accepted by adsorbed hydrogen ions to form adsorbed atomic hydrogen, and the hydrogen gas formed by combination of adsorbed hydrogen atoms contributes to the reduction process. Hu et al. (2010) observed that coating the ZVI (oxidation potential to Fe^{3+}:0.04 V) with copper (oxidation potential to Cu^{2+}: -0.34 V) resulted in threefold to ninefold higher chromium(VI) removal per unit mass of ZVI particles. The present paper extends the work of Hu et al. (2010) on chromium(VI) reduction by Cu–ZVI bimetallic particles by examining the kinetics of chromium(VI) reduction and the influence of variations in compositional parameters [solids:solution ratio, initial chromium(VI) concentration]. Further, the magnitude of copper deposition on the surface of ZVI particles is enhanced by performing the bimetallic particle preparation at an elevated temperature of 60°C.

Materials and Methods

Analytical reagent-grade $K_2Cr_2O_7$, $CuCl_2 \cdot 2H_2O$, and H_2SO_4 were used in the studies. Zero-valent iron (99.6%, electrolytic, and finer than #75 mesh) was obtained from J. T. Baker Chemicals (Mumbai, India). The specific gravity and surface area (determined by the BET method) of ZVI particles were determined to be 7.5 and 0.56 m^2/g, respectively.

The 10-, 30-, and 50-mg/L nonbuffered chromium(VI) ion solutions were prepared by suitable dilutions of 100-mg/L stock

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Table 1. Copper Consumed and Release of Fe Ions during Preparation of Bimetallic Particles

Mass of ZVI (g) in CuCl$_2$ solution	$Q_{Cu/Fe}$ (percentage)	Volume of CuCl$_2$ solution (mL)	Initial amount of copper present in Cu solution (mg)	Residual copper concentration (mg/mL)	Amount of Fe ions released in solution (mg)
0.5	1	2.5	5	0.002	4.25
	5	12.5	25	0.0024	20.43
	8	20	40	0.003	33
1	1	5	10	0.003	8.46
	5	25	50	0.003	45.9
	8	40	80	0.003	70.7
2	1	10	20	0.003	15.22
	5	50	100	0.003	90.1
	8	80	160	0.003	120.5

solution using N$_2$-purged ultrapure water (electrical conductivity = 0.055 μS/cm). To examine chromium(VI) reduction under alkalinity buffered groundwater conditions, 5-mg/L chromium(VI) solution buffered with 250-mg/L HCO$_3^-$ (bicarbonates) was prepared (pH = 7.9) on the basis of the concentration level reported by Ramesh et al. (2012) for chromium(VI)-contaminated groundwater in an industrial locality of Bangalore, India.

Preparation of Copper-Loaded ZVI Particles

A 2,000 mg/L Cu^{2+} solution was prepared by dissolution of copper chloride salt in N$_2$-purged ultrapure water. Known mass [0.5, 1, and 2 g (Table 1)] of acid-activated ZVI particles were agitated with definite volumes [2.5–80 mL (Table 1)] of 2,000-mg/L Cu^{2+} solution at 60°C for 15 min to achieve $Q_{Cu/Fe}$ ratios of 1, 5, and 8% on a dry mass basis, where $Q_{Cu/Fe}$ is defined as (Hu et al. 2010)

$$Q_{Cu/Fe} = mass_{Cu}/mass_{Fe} \times 100\% \qquad (1)$$

After equilibration, the suspensions were filtered, washed twice with N$_2$-purged ultrapure water, and dried in a vacuum desiccator for 24 h.

Batch Experiments

Batch experiments were performed by agitating 2 g of ZVI or 0.5, 1, or 2 g of Cu–ZVI bimetallic particles with 100 mL of nonbuffered chromium(VI) solutions (10, 30, or 50 mg/L) and buffered (with 250-mg/L HCO$_3^-$ ions) chromium(VI) solution (5 mg/L) using a wrist-action shaker at ambient temperature (27 $\pm$ 1°C). Care was taken to leave no headspace between the solution and the screw cap of the polytetrafluoroethylene bottle to prevent oxygen from entering the solution. Solutions were sampled at regular time intervals up to 360 min; the withdrawn samples were immediately subjected to pH and Eh measurements. After measurement of pH and Eh values, the samples were filtered through a 0.22-μm membrane and subjected to chemical analysis.

Analytical Methods

The total chromium (Cr^{6+} and Cr^{3+}), copper, and iron concentrations in the filtrates were determined by atomic absorption spectrometer. The chromium(VI) concentration in the filtrate was measured by the 1,5-diphenylcarbazide method using ultraviolet (UV) visible spectrophotometer (measuring wavelength = 540 nm). The chromium(III) concentration in the filtrate was obtained as chromium(III) = total chromium − chromium(VI).

Results and Discussion

Characterization of Copper-ZVI Specimens

Fig. 1 presents the X-ray diffraction (XRD) pattern of ZVI. Major peaks corresponding to Fe^0 (2θ = 44.7 and 82.4°), Fe$_2$O$_3$(s), and Fe$_3$O$_4$(s) (2θ = 35.5°) are identified. Oxides of iron form because of oxidation reactions occurring on the ZVI surface. The bimetallic particle preparation adopted in the present study differs from the procedure of Hu et al. (2010) in that ZVI in that study had been equilibrated with 1,000-mg/L copper chloride solution at room temperature. The higher equilibration temperature employed in the present study increased copper deposition, as evidenced by the marginal [0.3–0.005 mg/L (Table 1)] residual copper ion concentrations in the copper solution after equilibration. Comparatively, Hu et al. (2010) observed much higher residual copper concentrations of <10 mg/L, despite employing a less concentrated copper solution (1,000 mg/L). The increase in mass of Fe ions released in response to increase in $Q_{Cu/Fe}$ ratio (at given mass of ZVI particles) in Table 1 also implies enhanced reduction of copper ions and their subsequent deposition on the surface of ZVI particles.

Fig. 2(a) presents the XRD pattern of bimetal particles with $Q_{Cu/Fe}$ = 8%. Besides the Fe^0 and Fe oxides peaks (identified in Fig. 1), Cu^0 (2θ = 43.7°) reflection appears in the XRD pattern. Figs. 3(a and b) compare the scanning electron micrographs of ZVI particles before and after copper deposition (2 g of ZVI agitated with 80 mL of 2,000 mg/L Cu solution, $Q_{Cu/Fe}$ = 8%). The micrograph in Fig. 3(a) shows that ZVI occurs as discrete particles with smooth particle surfaces. The smooth surfaces of the ZVI particles appear eroded after copper deposition and exhibit growth of <2-μm-sized precipitates [Fig. 3(b)]. Comparison of XRD patterns in Figs. 1 and 2(a) indicate that the intensities of Fe$_2$O$_3$(s) and Fe$_3$O$_4$(s) (2θ = 35.5°) peaks appear stronger after copper deposition [Fig. 2(a)]. The precipitates on the ZVI particles in Fig. 3(b) are
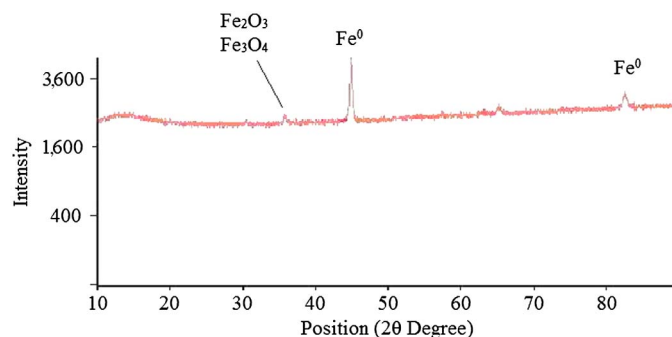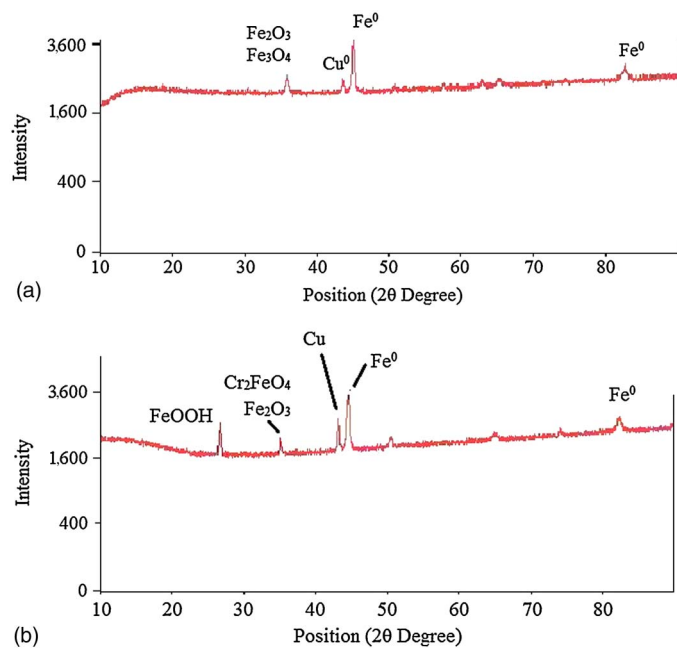

Fig. 1. XRD pattern of ZVI particles

Fig. 2. XRD patterns: (a) Cu–ZVI particles ($Q_{Cu/Fe} = 8\%$); (b) Cu–ZVI particles ($Q_{Cu/Fe} = 8\%$) exposed to 50-mg/L chromium(VI) solution

therefore attributed to additional growth of Fe oxides consequent to Fe^0 oxidation in the presence of copper.

Effect of Copper Loading on Chromium(IV) Reduction

Fig. 4 plots the mass of chromium(VI) reduced per gram of bimetallic particle as a function of time on agitating 0, 1, 5, and 8% copper-loaded ZVI particles with 10 mg/L nonbuffered chromium(VI) solution (solids:solution ratio = 2:100). Figs. 5 and 6 plot similar data for 30- and 50-mg/L chromium(VI) solutions (solids:solution ratio = 2:100). At a given chromium(VI) concentration (10–50 mg/L), the rate of chromium(VI) reduction rapidly increases up to certain period (60–240 min) and thereafter reaches equilibrium, the time needed to attain equilibrium being higher for the solution with higher initial chromium(VI) concentration. Interestingly, for a given chromium(VI) concentration (Figs. 4–6), the time required to attain equilibrium is independent of the $Q_{Cu/Fe}$ ratio, though the mass of chromium(VI) reduced increases with this ratio at a given time period. Similar data were generated for 0.5- and 1-g ZVI particles loaded with 0, 1, 5, and 8% copper and agitated with 10-, 30-, and 50-mg/L chromium(VI) solutions; for brevity, however, the plots are not presented in this paper.

Table 2 summarizes the percent increase in chromium(VI) reduction at equilibrium (agitation period = 360 min) upon copper loading with reference to unloaded ZVI particles. The data are presented for various solids:solution ratios (0.5–2 g/100 mL) that were exposed to 5-, 10-, 30-, and 50-mg/L chromium(VI) solutions. The percentage increase in chromium(VI) reduction is calculated as

$$[\text{milligrams of chromium(VI) reduced per gram of Cu-ZVI particle}]$$
$$- [\text{milligrams of chromium(VI) reduced per gram of ZVI particle}]$$
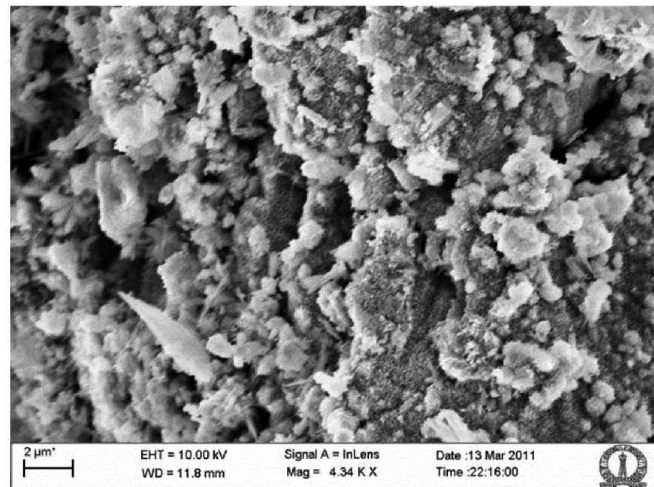$$\times 100\% \tag{2}$$

It is shown in Table 2 that for a given chromium(VI) concentration and a given solids:solution ratio, a greater magnitude of chromium(VI) reduction is facilitated by increase in copper loading
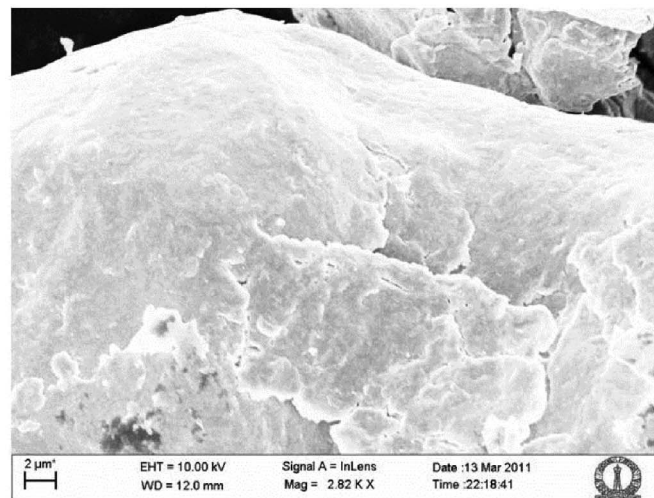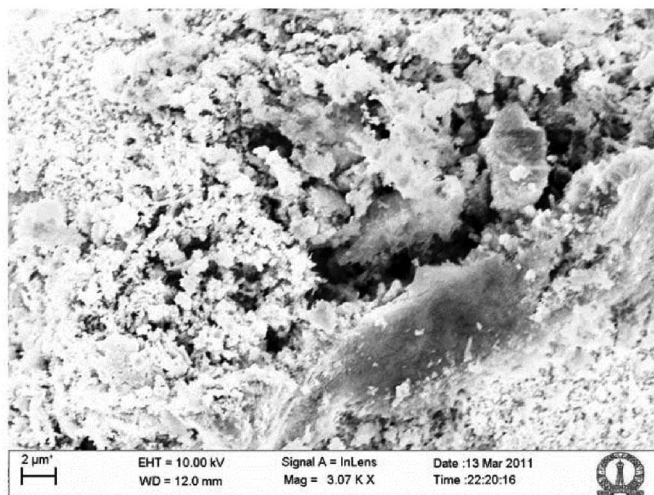
Fig. 3. Scanning electron micrographs: (a) ZVI particles; (b) Cu–ZVI particles ($Q_{Cu/Fe} = 8\%$); (c) Cu–ZVI particles ($Q_{Cu/Fe} = 8\%$) exposed to 50-mg/L chromium(VI) solution

on the ZVI particle surface. According to Bureau of Indian Standards (BIS) drinking water specification BIS 10500, the permissible limit for chromium(VI) ion concentration in drinking water is 0.05 mg/L (BIS 1991). This condition is attained only at solids:solution ratios of 2:100 ($Q_{Cu/Fe}$, 1, 5, and 8%) and 1:100
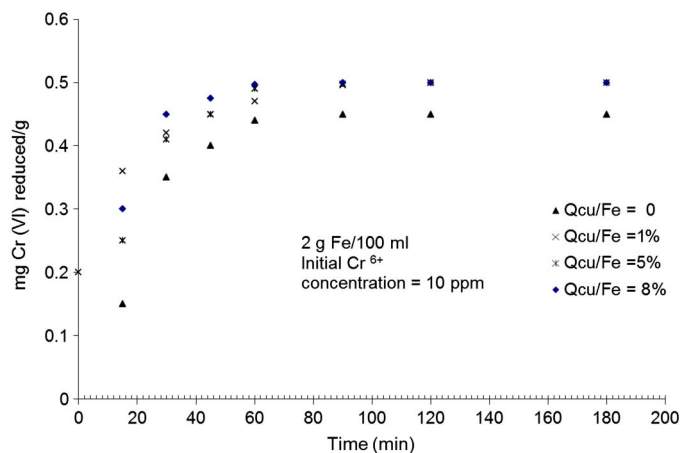
Fig. 4. Mass of chromium(VI) reduced as function of time [initial chromium(VI) concentration = 10 mg/L; solids:solution ratio = 2:100]
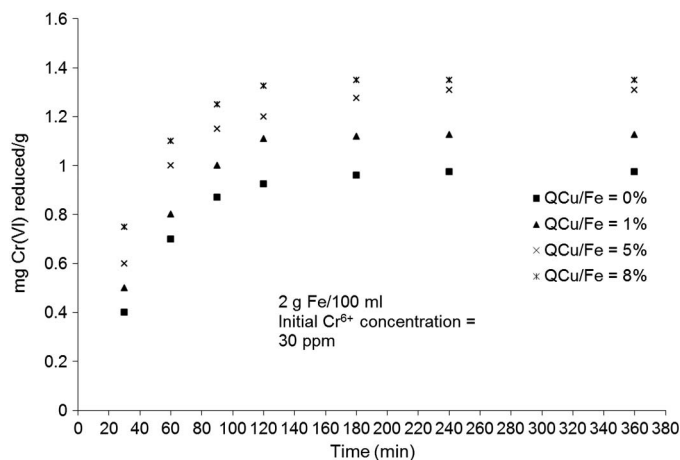

Fig. 5. Mass of chromium(VI) reduced as function of time [initial chromium(VI) concentration = 30 mg/L; solids:solution ratio = 2:100]
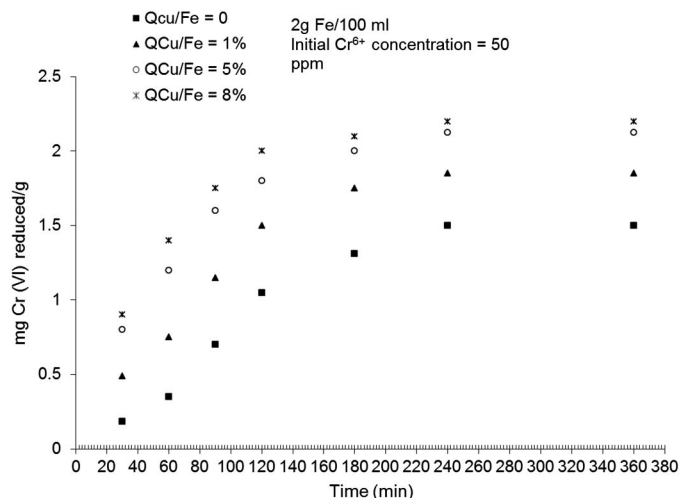

Fig. 6. Mass of chromium(VI) reduced as function of time [initial chromium(VI) concentration = 50 mg/L; solids:solution ratio = 2:100]

($Q_{Cu/Fe}$, 5 and 8%) on contact with 10-mg/L chromium(VI) solution for 360 min.

Table 2 also includes experimental results performed with buffered (with 250-mg/L bicarbonate) chromium(VI) solutions. The initial chromium(VI) (5 mg/L) and bicarbonate (250 mg/L) concentrations were guided by values reported for contaminated groundwater in an industrial locality in Bangalore, India, by Ramesh et al. (2012). These experiments were performed to simulate the groundwater chromium concentrations and to examine the influence of bicarbonate buffering on the pH of the treated solution (discussed subsequently). The permissible limit for chromium(VI) ion concentration in drinking water (0.05 mg/L) is attained at solids:solution ratios of 2:100 and 1:100 ($Q_{Cu/Fe}$, 1, 5, and 8%) on contact with 5-mg/L chromium(VI) solution for 360 min.

Previously, Qian et al. (2008) had observed that chromium(VI) reduction by iron powder follows pseudo first-order kinetics, and that the rate of chromium(VI) reduction increased with Fe^0 addition and temperature. The kinetic parameters for pseudo first-order kinetics are derived by using a simple Lagergren equation (Ho and McKay 1999):

$$\ln(q_e - q_T) = \ln(q_e - k_1 T) \tag{3}$$

where q_e and q_T = mass of chromium(VI) reduced per gram of bimetallic particle at equilibrium (q_e) and time T (q_T); and k_1 = pseudo first-order rate constant (Gupta and Bhattacharya 2005). Fig. 7 presents the pseudo first-order kinetic plots for chromium(VI) reduction from a 50-mg/L solution (solids:solution ratio = 2:100) by copper-loaded ZVI particles ($Q_{Cu/Fe}$ = 1, 5, and 8%). All three plots exhibit high correlation coefficients (R^2 values = 0.97–0.99). Besides strong correlation coefficients, obeying pseudo first-order kinetics requires that the experimental $\ln q_e$ values agree with the graphical intercepts ($\ln q_e$) of the $\ln(q_e - q_T)$ versus T plots. Examination of the data indicates that the graphical (intercept of plot in Fig. 7) $\ln q_e$ agrees with the experimental values at copper loadings of 5 and 8% but deviates at copper loading of 1%. The graphical $\ln q_e$ values at 1, 5, and 8% loading correspond to 0.61, 0.75, and 0.79, respectively, whereas the experimental $\ln q_e$ values at similar copper loadings correspond to 1.07, 0.81, and 0.79, respectively.

When chromium(VI) reduction does not follow pseudo first-order kinetics, pseudo second-order kinetics may be assumed (Gupta and Bhattacharya 2005; Ho et al. 2001):

$$T/q_T = 1/h + (1/q_e) \cdot T \tag{4}$$

where $h = k_2 q_e^2$; and k_2 = pseudo second-order rate constant. Fig. 8 presents the pseudo second-order rate plot for chromium(VI) reduction (initial solution concentration = 50 mg/L) by copper-loaded ZVI particles ($Q_{Cu/Fe}$ = 1%, and solids:solution ratio = 2:100). A linear form of the plot results (R^2 = 0.95); the graphical q_e value (1/slope) of 2.56 is in excess of the experimental value (1.85).

Variations in pH and Eh

Tables 3 and 4 present the changes in pH and Eh (redox potential) experienced by ZVI and copper-loaded ZVI particles on equilibration with nonbuffered and buffered (with 250-mg/L bicarbonate) chromium(VI) solutions for 360 min. An increase in pH and a decrease in Eh are noted at all solids:solution ratios, implying enhanced electron activity and release of hydroxyl ions from net corrosion reaction of the type (Powell et al. 1995)

$$Fe^0 + CrO_4^{2-} + 4H_2O \leftarrow \rightarrow Fe(OH)_3 + Cr(OH)_3 + 2OH^- \tag{5}$$
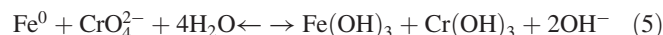
Further, at a given solids:solution ratio and initial chromium concentration, an increase in copper loading promotes lower Eh and higher pH, implying a stronger corrosion reaction. Copper does

Table 2. Percent Increase in Chromium(VI) Reduction from Copper Loading of ZVI Particles

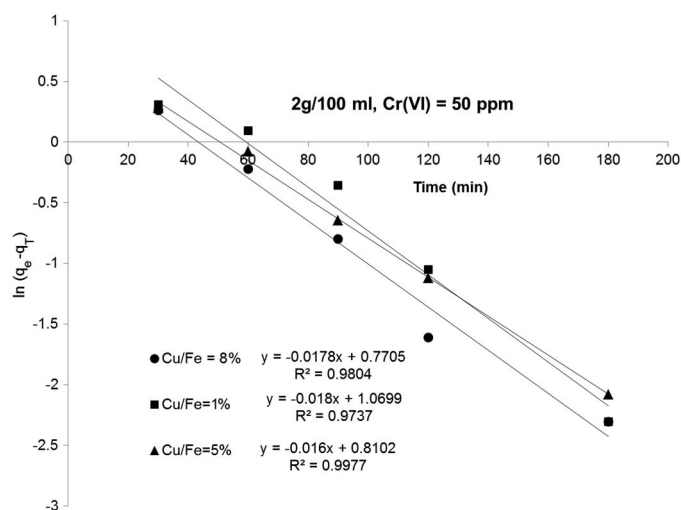| Initial Cr (mg/L)	$Q_{Cu/Fe}$ (percentage)	2 g/100 mL		1 g/100 mL		0.5 g/100 mL	
		Percentage increase in chromium(VI) reduction	Residual chromium(VI) concentration (mg/L)	Percentage increase in chromium(VI) reduction	Residual chromium(VI) concentration, (mg/L)	Percentage increase in chromium(VI) reduction	Residual chromium(VI) concentration (mg/L)
				Nonbuffered chromium(VI) solutions			
50	1	23	13	50	20	167	30
	5	42	7.5	75	15	233	25
	8	47	6	80	14	233	23.8
30	1	15	7.5	39	10	75	16
	5	34	3.8	53	8	100	14
	8	38	3	60	7	106	13.5
10	1	11	0.004	29	1	25	5
	5	11	0.004	42	0.04	70	3.2
	8	11	0.004	43	0.02	75	3
				Bicarbonate buffered chromium(VI) solution			
5	1	0	0.04	4.2	0.049	5.6	0.068
	5	0	0.04	4.3	0.046	5.5	0.054
	8	0	0.04	4.4	0.042	5.5	0.054

not form oxides, as indicated by the presence of the Cu^0 peak ($2\theta = 43.7°$) in Fig. 2(b). The XRD pattern in Fig. 2(b) corresponds to Cu–ZVI particles ($Q_{Cu/Fe} = 8\%$) that were exposed to 50-mg/L

Fig. 7. Pseudo first-order plots for chromium(VI) reduction [initial chromium(VI) concentration $= 50$ mg/L; solids:solution ratio $= 2{:}100$]
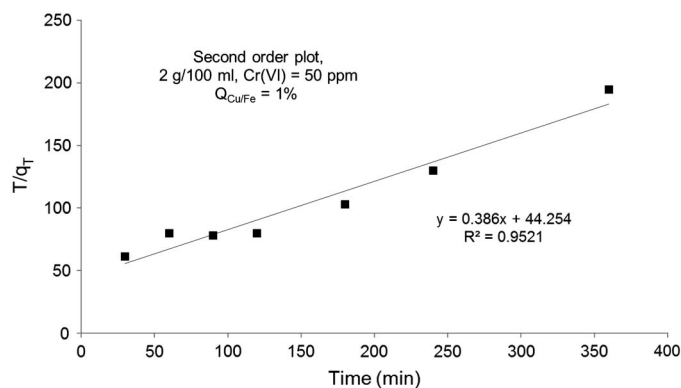
Fig. 8. Pseudo second-order plots for chromium(VI) reduction [initial chromium(VI) concentration $= 50$ mg/L; solids:solution ratio $= 2{:}100$]

chromium(VI) solution. Besides reflections for Fe^0 and Cu^0, peaks at $2\theta = 26.72$ and $35.5°$ were observed. The peak at $26.72°$ is ascribed to FeOOH, whereas the peak at $35.5°$ is ascribed to $Fe_2O_3(s)$ and $Cr_2FeO_4(s)$, respectively. The synthetic chromite (Cr_2FeO_4) is formed according to the reaction

$$Fe^{2+} + 2Cr^{3+} + 4H_2O \qquad Cr_2FeO_4 + 8H^+ \qquad (6)$$

The scanning electron micrograph [Fig. 3(c)] of Cu–ZVI particles ($Q_{Cu/Fe} = 8\%$) exposed to 50-mg/L chromium(VI) solution shows deposition of discrete precipitates that are possibly the mixed Cr–Fe oxide identified earlier in the XRD pattern [Fig. 2(b)]. Similar trend of results were observed at lower chromium(VI) concentrations (10 and 30 mg/L); for brevity, the results are not presented in this paper.

Table 3 reveals that the pH of the 50-mg/L chromium(VI) solution markedly increased from 4.36 to 7–10.8 on equilibration with Cu–ZVI particles, apparently because of the absence of the buffering influence of bicarbonates that are encountered in groundwater. The role of bicarbonates is demonstrated from results obtained with

Table 3. pH and Eh Values of Nonbuffered Chromium(VI) Solution before and after Equilibration with Cu–ZVI Particles

$Q_{Cu/Fe}$ (percentage)	Initial pH	Final pH	Initial Eh (mV)	Final Eh (mV)
	ZVI or bimetal content $= 2$ g/100 mL			
8	4.36	10.8	578.8	464.2
5		10.4		468.5
1		8.5		478.3
0		7.6		483.8
	ZVI or bimetal content $= 1$ g/100 mL			
8	4.36	9.8	578.8	470.5
5		9.6		472.0
1		7.8		486.0
0		7.2		490.2
	ZVI or bimetal content $= 0.5$ g/100 mL			
8	4.36	7.8	578.8	488.7
5		7.6		488.0
1		7.0		502.6
0		6.8		518.7

Note: Initial concentration of nonbuffered chromium(VI) solution $= 50$ mg/L.

Table 4. pH and Eh Values of Bicarbonate (250 mg/L) Buffered Chromium(VI) Solution before and after Equilibration with Cu–ZVI Particles

$Q_{Cu/Fe}$ (percentage)	Initial pH	Final pH	Initial Eh (mV)	Final Eh (mV)
ZVI or bimetal content = 0.5 g/100 mL				
8	7.9	8.75	717	191
5		7.52		336
1		7.89		230
0		9.62		179
ZVI or bimetal content = 1 g/100 mL				
8	7.9	8.2	717	199
5		8		137
1		7.5		193
0		9.69		162
ZVI or bimetal content = 2 g/100 mL				
8	7.9	9.1	717	27
5		9.25		95
1		8.9		166
0		9.67		158

Note: Initial concentration of bicarbonate buffered chromium(VI) solution = 5 mg/L.

bicarbonate buffered chromium(VI) solutions (Table 4); the pH of the buffered solutions varies between a narrower range of 7.5 and 9.7 after contact with Cu–ZVI particles (initial value = 7.9).

Conclusions

Deposition of 1–8% of copper on the surface of ZVI particles enhances chromium(VI) reduction by 11–233% owing to stronger corrosion of ZVI particles, as evidenced by the lower Eh and higher pH values. The enhanced electron activity and release of hydroxyl ions converted chromium(VI) to mixed Fe–Cr oxide, supported by X-ray diffraction and scanning electron micrograph studies. The chromium(VI) reduction was accomplished in periods ranging from 60–240 min in the batch experiments. Chromium(VI) reduction obeyed the pseudo first-order kinetics at copper loadings of 5 and 8% and pseudo second-order kinetics at copper loading of 1% [initial chromium(VI) concentration = 50 mg/L]. The copper-loaded ZVI particles were able to lower chromium(VI) levels to drinking water limits (≤0.05 mg/L) only when the initial concentration corresponded to 10 mg/L and a minimum solids:solution ratio of 1:100 was used. The residual chromium(VI) levels were 20–400 times higher than the permissible chromium(VI) limit in drinking water when 30- and 50-mg/L chromium(VI) solutions were used in the batch experiments (solids:solution ratio = 1–2 g/100 mL). Buffering with bicarbonates caused narrower variations in pH of treated solutions in comparison with nonbuffered solutions.

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