Removal of hexavalent chromium from contaminated ground water using zero-valent iron nanoparticles

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Abstract Batch experiments were conducted on ground water samples collected from a site contaminated with Cr(VI) to evaluate the redox potential of zero-valent iron (Fe^0) nanoparticles for remediation of Cr(VI)-contaminated ground water. For this, various samples of contaminated ground water were allowed to react with various loadings of Fe^0 nanoparticles for a reaction period of 60 min. Data showed 100% reduction of Cr(VI) in all the contaminated ground water samples after treatment with 0.20 gL^{-1} of Fe^0 nanoparticles. An increase in the reduction of Cr(VI) from 45% to 100% was noticed with the increase in the loading of Fe^0 nanoparticles from 0.05 to 0.20 gL^{-1}. Reaction kinetics of Cr(VI) reduction showed pseudo first-order kinetics with rate constant in the range of 1.1×10^{-3} to 3.9×10^{-3} min^{-1}. This work demonstrates the potential utility of Fe^0 nanoparticles in treatment and remediation of Cr(VI)-contaminated water source.

Keywords Cr(VI) · Remediation · Reaction kinetics · Zero-valent iron (Fe^0) nanoparticle · Batch experiments

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Introduction

Chromium (Cr) is a well-known heavy metal having wide range of application in metal plating, leather tanning, metal corrosion inhibition, pigment production, and wood-preserving industries. Cr exists in primarily two-valence states, i.e., trivalent Cr(III) and hexavalent Cr(VI). Cr(III), a micronutrient important in the biological activity of insulin, is relatively stable and has low solubility in aqueous solution (Puls et al. 1999). In contrast, Cr(VI) is highly toxic, soluble, and mobile in the aquatic systems (Cheryl and Susan 2000). Moreover, Cr(VI) has been classified as a potential carcinogen, mutagen, and teratogen and has acute toxicity for different biological systems. According to BIS (Bureau of Indian Standards) desirable limit for drinking water, the maximum acceptable limit for Cr (VI) in drinking water is 0.05 mgL^{-1}.

Several techniques for Cr(VI) removal such as ion exchange, filtration, electrochemical precipitation, activated carbon adsorption, bioremediation, etc., have been reported in literature. However, these conventional methods are relatively expensive and

complicated. In this context, zero-valent iron (Fe^0) nanoparticle technology offers a potential advantage over conventional methods because of its unique physico-chemical properties, non-toxicity, and economy (Zhang 2003; Li et al. 2006). A key advantage of this technique is its relative simplicity with the requirement of only two common reagents and no need for any special equipment. Furthermore, due to its nano size it can be injected and transported effectively into contaminated groundwater and aquifers for in situ treatment. The fate and transport of Fe^0 nanoparticles in environment are greatly affected by the geochemical factors such as pH, dissolved oxygen, oxidation-reduction potential, and concentration of competing oxidants. Besides these factors, some other factors which influence the fate of nanoparticles include contaminant concentration, age and agglomeration of nanoparticles, particle density, ionic strength of groundwater, aquifer's hydraulic properties, organic matter, etc. (Keane 2009). Fe^0 nanoparticles provide a high surface-to-volume ratio, which promotes mass transfer to and from the solid surface resulting in high potential for contaminant removal and degradation (Martin et al. 2008). As a strong reductant, Fe^0 nanoparticles can degrade a wide range of pollutants by adsorption and chemical reduction. Fe^0 nanoparticles has been successfully used for the treatment of chlorinated hydrocarbons (Lien and Zhang 2005; Liu et al. 2005), polychlorinated biphenyls (Varanasi et al. 2007), organochlorine pesticides (Elliott et al. 2009), and inorganic pollutants such as perchlorate (Xiong et al. 2007), chromate (Xu and Zhao 2007; Franco et al. 2009), nitrate (Liou et al. 2005), arsenic (Morgada et al. 2009), etc.

The transformation of heavy metals such as Cd, Cr, Ni, Zn, Pb, etc., by Fe^0 nanoparticles has been extensively documented (Ponder et al. 2000; Li et al. 2006). Reduction of Cr(VI) by Fe^0 nanoparticles has been investigated in various bench- and field-scale studies (Elliott and Zhang 2001; Singh and Singh 2003; Wilkin et al. 2005; Franco et al. 2009). Fe^0 rapidly reduces and immobilizes Cr(VI), accompanied by the formation of insoluble chromium compounds (Ponder et al. 2000; Lee et al. 2003; Cao and Zhang 2006). In view of the above, Fe^0 nanoparticles synthesized by borohydride reduction was tested for its potential to remove Cr(VI) from contaminated ground water samples and also to determine the reaction kinetics involved in the process.

Materials and methods

Chemicals

Ferric chloride anhydrous ($FeCl_3$), sodium borohydride ($NaBH_4$), and potassium dichromate ($K_2Cr_2O_7$) were obtained from CDH, India. 1,5-Diphenylcarbazide ($C_{13}H_{14}N_4O$) was procured from SD Fine Chemicals Ltd., India, and ethanol (C_2H_5OH) from Loba Chemie Pvt. Ltd. Perchloric acid ($HClO_4$, 72%), nitric acid conc. (HNO_3, 70%), and acetone (CH_3COCH_3) were purchased from Merck, India. Fe^0 nanoparticles used for the study were synthesized in the laboratory by reduction of $FeCl_3$ with $NaBH_4$ (Sun et al. 2006).

Study area

Khanpur, Rania, is located at latitude 26º24′40″ N and longitude 80º05′57″ E in Kanpur Dehat of Uttar Pradesh at an elevation of 126 m from mean sea level. Rania is an industrial area having many large- and small-scale industries. The site selected for study had been used for many years as a dumping ground for the waste generated from basic chrome sulphate industries, which are the main generators of wastes in this area.

Sampling site

Ground water samples were collected from 12 sites at various locations within study area on the basis of Global Positioning System coordinates in the month of March, 2010. The geographical location of study area and sampling locations are shown in Fig. 1. All the samples were collected manually in plastic containers and then acidified with conc. nitric acid (5 mL L^{-1}). The physico-chemical parameters of collected samples were performed as per the standard methods described in APHA (2005), and the results were compared with BIS for drinking water (Tables 1 and 2).

Methods of analysis

Cr(VI) was estimated by colorimetric method specified in Method 7196A of USEPA (1,5-diphenylcarba-
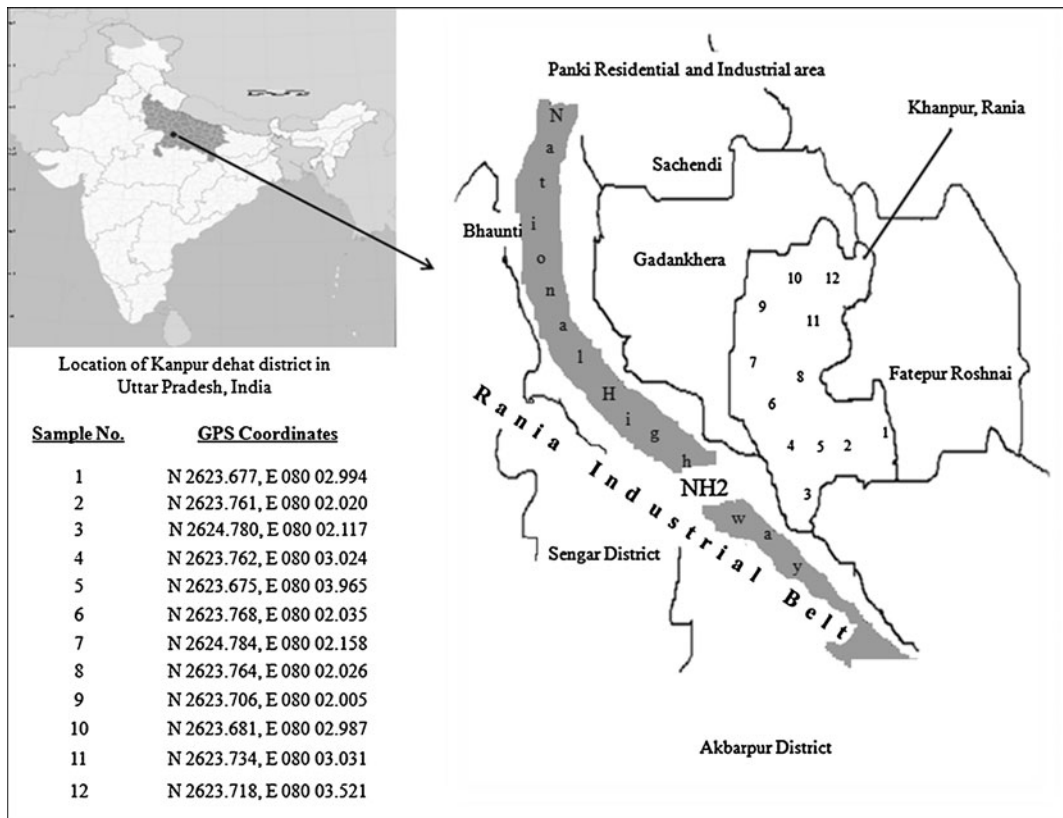
Fig. 1 Geographical location of Rania, Kanpur Dehat

Table 1 Physico-chemical parameters of water samples collected from Rania in (μg mL^{-1}) except pH

Sample no.	pH	TDS	Fluoride	Nitrite	Sulphate	Hardness	Alkalinity	Chloride
1	7.27	379	0.4	6.98	140	88	26	180
2	7.35	341	0.6	6.34	172	106	28	23
3	7.43	56	0.6	6.15	81.2	66	6	130
4	7.59	407	0.6	19.2	112	70	30	110
5	7.50	79	0.2	16	210	32	58	210
6	7.39	367	4.4	4.46	224	26	8	20
7	7.24	48	0.4	7.62	110	34	12	170
8	7.49	363	0.3	8.2	149	112	22	140
9	7.35	523	0.7	0.43	57.3	61	6	230
10	7.11	526	0.9	6.44	98	19	38	110
11	7.16	434	0.4	7.99	252	40	14	32
12	7.41	370	0.5	6.42	140	65	8	190
BIS desirable limit for drinking water	6.5–8.5	500	1.0	45	200	200	200	250

BIS Bureau of Indian Standards (2003), *TDS* total dissolved solids

Table 2 Heavy metals ($\mu g\ mL^{-1}$) present in water samples collected from Rania

Sample no.	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	n.d.	0.01	4.65	0.02	0.23	0.04	0.02	0.02	0.23
2	n.d.	0.01	5.64	0.02	0.22	0.02	0.01	0.03	0.23
3	n.d.	0.03	7.51	0.01	0.25	0.10	n.d.	0.02	0.09
4	n.d.	0.01	9.25	0.01	0.04	0.01	n.d.	0.01	0.01
5	n.d.	0.01	12.36	0.02	0.26	0.09	0.01	0.02	0.01
6	n.d.	0.04	12.98	0.02	0.16	0.37	0.01	0.02	0.06
7	n.d.	0.02	14.11	0.03	0.25	0.02	0.02	0.03	0.30
8	n.d.	n.d.	20.19	0.01	0.06	0.04	n.d.	0.01	0.03
9	n.d.	0.05	21.81	0.02	0.17	0.22	n.d.	n.d.	0.02
10	0.01	0.01	26.79	0.02	0.17	0.05	0.01	0.02	0.06
11	n.d.	0.03	27.28	0.03	0.12	0.01	n.d.	0.03	0.27
12	n.d.	0.03	33.88	0.03	0.08	n.d.	0.02	0.03	0.18
BIS desirable limit for drinking water	0.01	–	0.05	0.05	0.3	0.1	0.02	0.05	5.0

n.d. not detected, *BIS* Bureau of Indian Standards (2003)

zide method). The 1.0 mL of extract to be tested was transferred to a 10.0-mL volumetric flask. Two hundred microliters of diphenylcarbazide solution was added to it and mixed properly. Then, 5 drops of 1 N HNO_3 was added to maintain its pH=2±0.5. The volume was made up to 10 mL with distilled water and allowed to stand for 5–10 min for full color development. For quantification, an appropriate portion of it was transferred to a cuvette, and the absorbance was measured at a wavelength of 540 nm using Thermo Spectronic GENESYS 10 UV–vis Spectrophotometer. Heavy metals present in sample were determined by digesting the sample with 10 mL of digestion mixture (conc. HNO_3+conc. $HClO_4$ in 5:1 ratio) in 250-mL conical flasks. The mixture was heated at 90–95°C till the completion of digestion. It was then filtered and transferred into a 10-mL volumetric flask. Finally, the volume was made up to the mark with 1% HNO_3. The samples were then analyzed on atomic absorption spectrophotometer. Cr(III) was estimated by subtracting Cr(VI) from total Cr.

Batch studies

To evaluate the efficiency of Fe^0 nanoparticles in removing Cr(VI) from ground water samples, batch experiments with varied loading of Fe^0 (0.05, 0.10, 0.15, 0.20 gL^{-1}) were carried out in 15-mL glass vials. The reaction mixture was allowed to react for 1 h with continuous shaking. During the reaction, at predetermined time intervals (0, 15, 30… min), the reaction mixture was withdrawn and transferred to centrifuge tubes and centrifuged at 5,000 rpm for 15 min. Because the reaction has not stopped during centrifugation, this time was also included in total reaction period. The supernatant obtained was filtered using a 0.22-μm syringe-driven micropore filter. Cr(VI) in the filtrate was analyzed via the colorimetric technique. Control tests were also carried out in the absence of nanoparticles but otherwise under identical conditions. All the experiments were conducted in triplicate. In further experiments, percent reduction was studied for the above said loading of Fe^0 at two time points (30 and 60 min).

Kinetic studies of Cr(VI) reduction

To determine the rate of Cr(VI) reduction by Fe^0, various loading of Fe^0 nanoparticles (0.05, 0.10, and 0.15 gL^{-1}) were added to the contaminated water sample. At selected time intervals, samples were taken out, filtered, and tested for residual Cr(VI).

Results and discussion

Physico-chemical parameters

All the ground water samples collected from the study area were analyzed for their physico-chemical properties. A comparison between various physico-chemical parameters of ground water samples and desirable limit for drinking water set up by BIS was shown in Table 1. Results showed that the value of pH, total dissolved solids, fluoride, nitrate, sulphates, total hardness, total alkalinity, and chloride are well within the desirable limits. Table 2 shows the concentration of various heavy metals present in samples. Analysis of the data revealed that the concentration of heavy metals Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn lies within the BIS desirable limits. However, the concentrations of Cr present in all the samples and Mn in one of the samples (sample no. 6) exceed BIS desirable limits for drinking water. Table 3 represents the concentration of Cr(VI) along with the concentration of Cr(III) and total Cr. The presence of high levels of Cr(VI) in groundwater suggests a definite adverse impact on the environment and a considerable risk on human health in the exposed areas.

Reduction of Cr(VI) by Fe^0 nanoparticles

Results of the experiments conducted with different loading of Fe^0 nanoparticles (0.05, 0.10, 0.15, and

Table 3 Concentration of Cr(VI), Cr(III) and total Cr ($\mu g\ mL^{-1}$) in water samples collected from site Rania at Kanpur Dehat

Sample no.	Cr(VI)	Cr(III)	Total Cr
1	4.65	15.67	20.32
2	5.64	67.24	72.88
3	7.51	43.13	50.64
4	9.25	31.65	40.90
5	12.36	28.04	40.40
6	12.98	47.23	60.21
7	14.11	34.99	49.10
8	20.19	77.61	97.80
9	21.81	85.29	107.10
10	26.79	126.91	153.70
11	27.28	83.92	111.20
12	33.88	148.72	182.60

0.20 gL^{-1}) showed that 0.20 gL^{-1} of Fe^0 reduces the concentration of Cr(VI) in samples below the permissible limit within a reaction period of 60 min only (Fig. 2). It is also indicated in Fig. 2 that Cr(VI) reduction increases with the increase in the loading of Fe^0 nanoparticles and reaction period. A similar increase in Cr(VI) reduction with increased Fe^0 loading was reported by Franco et al. (2009). This increase in reduction may be attributed to the fact that, as the loading of Fe^0 nanoparticles increases, the number of reactive sites also increases which, in turn, enhances the reduction of Cr(VI) in samples. Control tests did not show any Cr(VI) reduction. In further experiments, an average of percent reduction was calculated for the above said loading of Fe^0 nanoparticles (Fig. 3). Results showed that 0.05, 0.10, 0.15, and 0.20 gL^{-1} of Fe^0 resulted in 32%, 41%, 58%, and 93% reduction in 30 min, respectively. However, when the reaction period increased from 30 to 60 min, percent reduction also increased and reached up to 45%, 63%, 79%, and 100% for 0.05, 0.10, 0.15, and 0.20 gL^{-1} of Fe^0 nanoparticles, respectively. Figure 4 shows the reaction kinetics of Fe^0 nanoparticle-mediated Cr(VI) reduction. The results revealed that Cr(VI) reduction follows a pseudo first-order kinetic model which can be represented by the following equation.
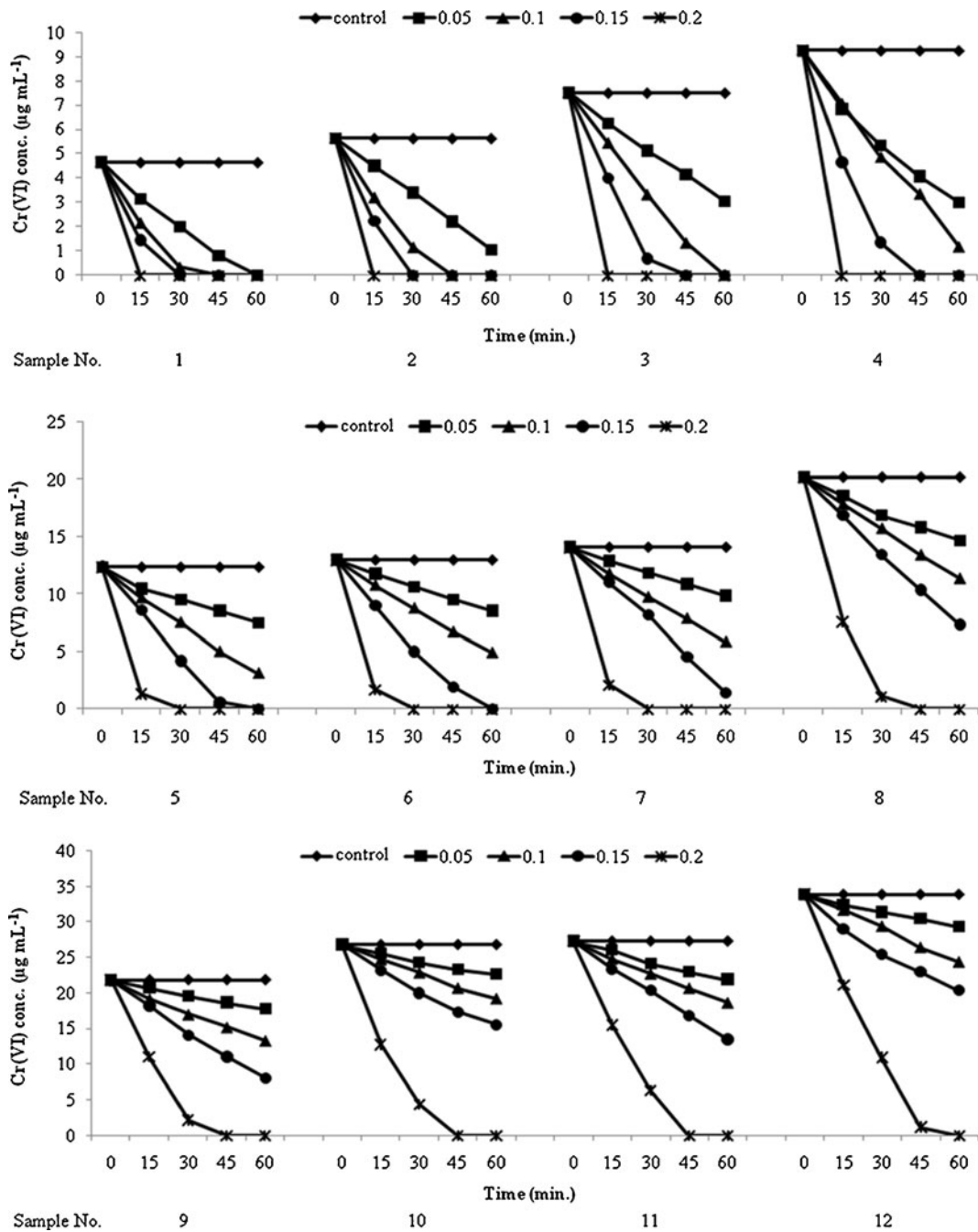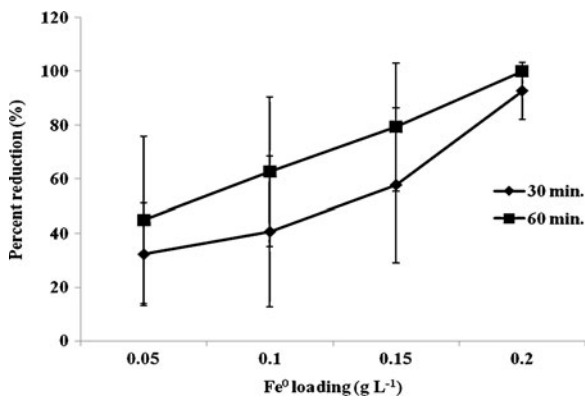
$$\ln[Cr(VI)]/[Cr(VI)]_0 = -k_{obs}t \qquad (1)$$

where [Cr(VI)] and $[Cr(VI)]_0$ are the instantaneous and initial concentration of Cr(VI) in micrograms per milliliter, respectively; t is the reaction period in minutes, and k_{obs} (slope of the plot of In Cr(VI)/Cr (VI)$_0$ versus time t) is the observed rate constant representing the overall removal rate for remediation (per minute). The values of observed rate constant (k_{obs}) were obtained with regression coefficient (R^2) around 0.99 (Table 4). Analysis of the data reveals that the rate constant increases from 1.1×10^{-3} to $3.9 \times 10^{-3}\ min^{-1}$ as the loading of Fe^0 increases from 0.05 to 0.15 gL^{-1}. The results obtained are in agreement of the results of previous studies conducted on Cr(VI) reaction kinetics (Xu and Zhao 2007; Liu et al. 2008).
     Li and Zhang (2007) explained the reduction of metal cations on the basis of the standard electrode potential (E^0) of the metal ions. For the metals having E^0 greatly positive than E^0 of Fe^0 such as Cu^{2+}, Hg^{2+},

Fig. 2 Reduction of Cr(VI)-contaminated water samples collected from Rania by Fe^0 nanoparticles; Fe^0 loading=0.05, 0.10, 0.15, and 0.20 gL^{-1}

and Ag^+, predominant removal mechanism is reduction. Removal via sorption and reductive precipitation is followed by metals having E^0 slightly more positive than that of Fe^0 (Pb^{2+}, Ni^{2+}) and the metals having E^0

more negative than Fe^0, such as Zn^{2+} and Cd^{2+} removed by sorption or surface complexation procedure. The standard electrode potential of Fe^0, Cr(VI), and Cr(III) are (−0.41), (1.36), and (−0.74 V),
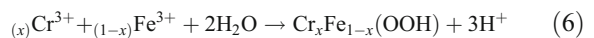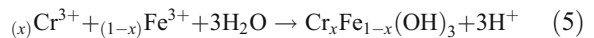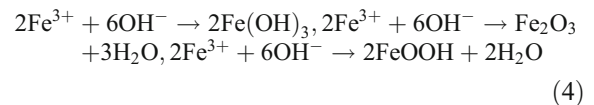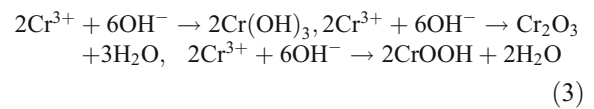
Fig. 3 Percent reduction of Cr(VI) (*error bars* represent the standard deviation)

Table 4 The rate constant of Cr(VI) reduction at different loading of Fe^0 nanoparticles

Loading of Fe^0 nanoparticles (gL^{-1})	Pseudo first-order kinetics	
	k_{obs} (min^{-1})	R^2
0.05	1.1×10^{-3}	0.9976
0.10	2.1×10^{-3}	0.9951
0.15	3.9×10^{-3}	0.9975

respectively. Removal of Cr(VI) by Fe^0 follows the pathway of sorption and reductive precipitation/immobilization (Lai and Lo 2008; Liu et al. 2008). Initially, Cr(VI) gets adsorbed on the surface of Fe^0 where electron transfer takes place. After sorption, Cr(VI) is reduced to Cr(III) with oxidation of Fe^0 to Fe^{2+} and Fe^{3+}. Spectroscopic data showed that Cr(III) precipitates in the form of Cr or Cr–Fe mixed oxides/hydroxides/oxyhydroxides (Ponder et al. 2000; Powell et al. 1995; Pratt et al. 1997). These precipitates were most likely in the form of irregular strips, chick–footmark-like or boulder-like forms (Lai and Lo 2008). Due to the similar ionic radii of Cr^{3+} and Fe^{3+} [r (Cr^{3+})=0.615 Å, r (Fe^{3+})=0.645 Å] and same charge, Cr^{3+} substitutes Fe^{3+} and gets incorporated into iron oxy-hydroxide shell of iron, forming Cr–Fe mixed oxides/hydroxides/oxyhydroxides with general

chemical formula $Cr_xFe_{1-x}(OH)_{3(s)}$. The overall redox reaction can be represented by the following equation:

$$Cr_2O_7^{2-} + 2Fe^0_{(s)} + 7H_2O_{(1)} \rightarrow 2Cr^{3+} + 14OH^- \quad (2)$$

$$2Cr^{3+} + 6OH^- \rightarrow 2Cr(OH)_3, 2Cr^{3+} + 6OH^- \rightarrow Cr_2O_3 + 3H_2O, \quad 2Cr^{3+} + 6OH^- \rightarrow 2CrOOH + 2H_2O \quad (3)$$

$$2Fe^{3+} + 6OH^- \rightarrow 2Fe(OH)_3, 2Fe^{3+} + 6OH^- \rightarrow Fe_2O_3 + 3H_2O, 2Fe^{3+} + 6OH^- \rightarrow 2FeOOH + 2H_2O \quad (4)$$

$$_{(x)}Cr^{3+} + _{(1-x)}Fe^{3+} + 3H_2O \rightarrow Cr_xFe_{1-x}(OH)_3 + 3H^+ \quad (5)$$

$$_{(x)}Cr^{3+} + _{(1-x)}Fe^{3+} + 2H_2O \rightarrow Cr_xFe_{1-x}(OOH) + 3H^+ \quad (6)$$
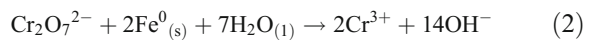
On the basis of solution chemistry and X-ray photoelectron spectroscopy data, Li et al. (2008) determined the average value of x, and it was found to be approximately 0.667. This Cr–Fe oxy-hydroxide shell is stable and serves as a sink for Cr(VI).

Lai and Lo (2008) reported that Fe^0 reactivity toward Cr(VI) is susceptible to the influence of the dissolved groundwater constituents such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-) ions. They further found that hardness and carbonate exerts a declining effect on the removal capacity of Fe^0, and this effect increases when both hardness and carbonate were present together. This was explained by the formation of passive layer of precipitates such as $CaCO_3$ and $MgOH_2$ on the surface of Fe^0, which hinders the electron transfer to metal ion resulting in decreased reactivity. Several
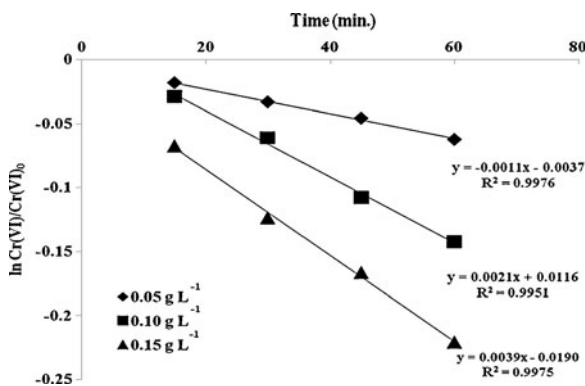
Fig. 4 Reduction kinetics of Cr(VI); Cr(VI) initial conc.= 33.88 µg mL^{-1}; Fe^0 loading=0.05, 0.1, and 0.15 gL^{-1}; reaction time=60 min.; pH=7.41

authors have investigated the influence of natural organic matter (NOM) on Fe^0 reactivity and suggested that NOM compete with the contaminants for the reactive sites on Fe^0 surface and alter the reduction potential of neighboring surface sites (Liu et al. 2008). Liu et al. (2008) have investigated the individual and combined effect of humic acid and hardness on Cr(VI) reduction by Fe^0 at initial pH of 6 and 9.5. The results showed that 5–20 mg L^{-1} of humic acid has slight inhibitory effect on Cr(VI) reduction which becomes more pronounced in the presence of 0.8 mM of $CaCO_3$ hardness. In contrast to these findings, humic acid has not shown any significant inhibitory effect on Fe^0 reactivity towards chromate ($Cr_2O_4^{2-}$) removal (Tsang et al. 2009). As the samples studied in this work showed significant value of hardness, it may affect the reduction efficacy of Fe^0 nanoparticles. Furthermore, the presence of other heavy metals in contaminated sites may also play detrimental role in Cr(VI) reduction.

Although the unique properties of Fe^0 nanoparticles make them a remarkably effective tool for cleaning up contaminated soil, sediments, and groundwater, the ecotoxicity of Fe^0 nanoparticles is an area of concern in the scientific community (Keenan et al. 2009). Along with the toxicity of Fe^0 nanoparticles, toxic implications of boron/boron oxide nanoparticles (Liu et al. 2009; Strigul et al. 2009) which may form during the synthesis of Fe^0 nanoparticles as by-products also needs attention. These studies suggest that the environmental fate, transport, and toxicological aspects of Fe^0 nanoparticles should also be addressed while doing environmental remediation studies with Fe^0 nanoparticles.

Conclusions

The results of this study clearly suggest that Fe^0 nanoparticle is extremely effective for the removal of Cr(VI) from Cr(VI)-contaminated ground water. The results obtained showed that a minimal loading of 0.20 gL^{-1} of Fe^0 nanoparticles is needed to reduce the concentration of Cr(VI) in groundwater below the permissible limit set up by standard agencies. However, to increase the reactivity and longevity of Fe^0 nanoparticles, the role of factors such as pH, alkalinity, hardness, etc., needs to be studied in greater detail.

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