Removal of chromium(VI) from drinking water by redox-assisted coagulation with iron(II)

Giehyeon Lee and Janet G. Hering

ABSTRACT

Batch experiments were conducted to determine whether sub-ppb concentrations of dissolved Cr(VI) could be achieved by redox-assisted coagulation with Fe(II). In this process Fe(II) acts as a reductant for Cr(VI) and, after its oxidation to Fe(III), as a coagulant. With an Fe(II) dose of 30 μM (1.7 mg/l as Fe), dissolved Cr(VI) concentrations in synthetic or natural Colorado River water (CRW) at pH 8.2 could be decreased from an initial value of 1 μM (52 $\mu g/l$) to <0.01 μM (<0.5 $\mu g/l$) corresponding to a >99% removal efficiency. In contrast, removal of Cr(VI) by coagulation with Fe(III) was poor, even at higher Fe(III) doses (up to 100 μM). The efficiency of Cr(VI) removal by redox-assisted coagulation decreased at lower (but still above stoichiometric) Fe(II) doses due to the incomplete reduction of Cr(VI) to Cr(III), which, under our experimental conditions, can be attributed to the competing reaction of Fe(II) with O_2 between pH 7 and 8.2 and to the slow kinetics of reaction of Fe(II) with Cr(VI) between pH 6.5 and 7. Although Cr(VI) was less efficiently removed from natural or synthetic CRW than from the simple electrolyte solution, the desired level of removal could be achieved by increasing the Fe(II) dose.

Key words | chromate, co-precipitation, ferric, ferrous, sorption, water treatment

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INTRODUCTION

The use of chromium in a wide range of industrial applications (and particularly for plating) has resulted in many incidences of soil and groundwater contamination in industrialized areas (Palmer *et al.*, 1990; Powell *et al.*, 1995). Chromium can also occur as a natural constituent in groundwater (Robertson, 1975), rivers (Cox & Mcleod, 1992), and freshwater lakes (Kaczynski & Kiever, 1993). In natural waters, chromium exists in the +VI and +III oxidation states, both of which can be thermodynamically stable in the presence of atmospheric oxygen depending on pH (Stollenwerk & Grove, 1985; Richard & Bourg, 1991). The toxicity, mobility and bioavailability of Cr depend strongly on its redox speciation (Palmer & Wittbrodt, 1991; Richard & Bourg, 1991). Trivalent chromium, Cr(III), is an essential nutrient for glucose metabolism (Vincent, 2000) and one of its organic complexes, chromium picolinate, has been used in the treatment of diabetes (Anderson, 2000). In contrast, Cr(VI) is a

known human carcinogen by inhalation (Langard, 1990) and there is considerable debate regarding its carcinogenicity by ingestion (Flegal *et al.*, 2001). The toxicity of Cr(VI) has engendered interest in processes for its removal from both industrial effluents and potable water. One of the most effective ways to remove Cr(VI) from water is to reduce it to the less toxic and less mobile Cr(III).

The reduction of Cr(VI) to Cr(III) has been observed with various reductants such as subsurface soils (Eary & Rai, 1991), aquifer sand (Anderson *et al.*, 1994), organic matter including phenols and humic and fulvic substances (Elovitz & Fish, 1994; Wittbrodt & Palmer, 1996; Buerge & Hug, 1998), sulphides (Pettine *et al.*, 1994; Kim *et al.*, 2001), zero valent iron (Powell *et al.*, 1995; Blowes *et al.*, 1997; Alowitz & Scherer, 2002), and granular activated carbon (Han *et al.*, 2000). However, the kinetics of the reactions between Cr(VI) and these

reductants are often very slow (in the order of hours to days).

A more important reductant for Cr(VI) in both natural waters and industrial applications is ferrous iron, Fe(II) (Schroeder & Lee, 1975; Sorg, 1979; Eary & Rai, 1988, 1989; Masscheleyn *et al.*, 1992; Loyaux-Lawniczak *et al.*, 2001). The reduction of Cr(VI) by Fe(II) is fast (in the order of minutes to hours) and the rate of the reaction is a minimum at approximately pH 4 and increases at both acidic and alkaline pH (Buerge & Hug, 1997; Sedlak & Chan, 1997; Pettine *et al.*, 1998; Schlautman & Han, 2001).

At pH ≥ 6.5, the redox reaction between Cr(VI) and Fe(II) can be written as:

$$CrO_4^{2-} + 3Fe^{2+} + 8H_2O \rightarrow 4Fe_{3/4}Cr_{1/4}(OH)_{3(s)} + 4H^+ \quad (1)$$

In reaction (1), Cr(VI) is reduced to Cr(III) by Fe(II) as it is oxidized to Fe(III), which rapidly forms ferric hydroxide. The reduced Cr(III) is expected to be sorbed and/or co-precipitated with the ferric hydroxide (Schroeder & Lee, 1975; Sass & Rai, 1987; Eary & Rai, 1988). In oxygenated waters, however, Fe(II) is also oxidized by dissolved oxygen as follows:

$$4Fe^{2+} + O_{2(aq)} + 4H_2O \rightarrow 4Fe(OH)_{3(s)} + 8H^+ \quad (2)$$
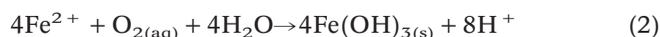
This reaction may decrease the efficiency of reaction (1) due to competition between Cr(VI) and O_2 at pH > 7 (Pettine *et al.*, 1998; Schlautman & Han, 2001).

Although several studies have examined the use of ferrous salts for treatment of Cr(VI)-contaminated groundwater (Philipot *et al.*, 1984; Zotter & Licsko, 1992; Aktor, 1994; El-Shoubary *et al.*, 1998), previous studies have focused on achieving dissolved Cr concentrations in the range of the current drinking water standards, which are 100 µg/l for total Cr for the US and 50 µg/l for California. In California, however, the establishment of a public health goal (PHG) for total Cr of 2 µg/l generated substantial public concern over the occurrence of Cr(VI) in drinking water supplies. Although this PHG was withdrawn, various water supply agencies have chosen not to use groundwater as a source of potable water if the groundwater contains higher Cr concentrations than surface water supplies previously served to consumers. Since

many groundwaters in California contain total Cr at concentrations of 20–30 µg/l (with up to 100% of the total Cr as Cr(VI)) (California Department of Health Service, 2002), this practice excludes from use many water supplies that meet State and Federal standards. The purpose of this study, therefore, was to examine the feasibility of achieving sub-ppb concentrations of total Cr in drinking water by treatment with Fe(II).

MATERIALS AND METHODS

Reagents

All chemicals were reagent grade or better and were used without further purification; $CaSO_4 \cdot 2H_2O$, CrO_3, $CrCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $NaHCO_3$, $NaNO_3$, $NaOH$, Na_2SO_4 and piperazine-N,N′-bis (2-ethanesulphonic acid) (PIPES) were obtained from EM Science and $Ca(NO_3)_2 \cdot 4H_2O$ from Fisher. Solutions were prepared with water purified using a Millipore Milli-Q 18 MΩ system (Milli-Q water). Stock solutions (0.01 M) of Cr(III), Fe(II) and Fe(III) were prepared by dissolving $CrCl_3 \cdot 6H_2O$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, and $FeCl_3 \cdot 6H_2O$, respectively, in 0.01 M HNO_3 (trace metal grade). Cr(VI) stock solutions (0.001 M) were prepared by dissolving CrO_3 in Milli-Q water adjusted to pH 8.4 using 0.01 M NaOH.

Analytical methods

Total chromium and iron concentrations were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Hewlett Packard Model 4500). The minor isotopes [53]Cr and [57]Fe were measured to avoid isobaric interferences between [52]Cr and ArC and between [56]Fe and ArO. Detection limits (determined as three times the standard deviation of the blank) were 0.01 µM for Cr and 0.5 µM for Fe. Samples were acidified to a final concentration of 1% (v/v) with trace metal grade HNO_3 for ICP-MS analysis. In addition, Cr(VI) concentrations of selected samples were determined by ion chromatography (Dionex DX500) using a slightly modified version of EPA

Method 218.6 (Arar *et al.*, 1991). In this method, Cr(VI) stock solution (1000 mg/l) was prepared by dissolving K_2CrO_4 in Milli-Q water, rather than using $Na_2CrO_4 \cdot 4H_2O$ in ASTM Type 1 water. Samples were analysed within 24 h at the Weymouth treatment plant of the Metropolitan Water District of Southern California (MWDSC). Measurements of pH were made with a pH meter (VWR Model 8015) calibrated with pH 4.0, 7.0 and 10.0 buffers.

Experiments

Experiments were conducted to examine the removal of Cr from solution under varying conditions. Parameters examined included Cr and Fe oxidation states, pH and solution composition, and reaction time. Three reaction solutions were used:

1. *Synthetic CRW*. This solution (0.01 M $NaNO_3$, 2 mM $NaHCO_3$, and 2 mM $Ca(NO_3)_2$) mimics the ionic strength, alkalinity and calcium concentration of Colorado River Water (CRW).
2. *Natural CRW*. Raw water was obtained from the MWDSC Weymouth treatment plant. Unfiltered water was used in all experiments. Water composition is given in Table 1.
3. *Simple electrolyte*. A solution of 0.01 M $NaNO_3$ buffered with 1 mM PIPES.

In general, experiments were conducted at room temperature ($23.0 \pm 0.4°C$) using 1-l polyethylene reactors that were open to the atmosphere. Except for a glass pH-electrode, all parts that came in contact with the solutions were made of polyethylene or Teflon. The reactors were cleaned with 1% (v/v) reagent-grade HNO_3 between experiments.

The general procedure for all experiments was as follows. Reaction solutions were adjusted (if necessary) to the desired pH and spiked with Cr at varying concentrations (≤ 1 μM) as either Cr(VI) or Cr(III) and mixed on a magnetic stirrer at 100 rpm. For measurement of the initial Cr(VI) concentrations, a 5-ml aliquot was extracted from each sample before the addition of the Fe(II) dose. Each sample was compensated with the same volume of

Table 1 | Chemical composition of Colorado River Water (CRW)

Constituent	Concentration mol/l eq/l	mg/l
SiO_2	0.19×10^{-3}	11.4
Ca	1.37×10^{-3}	55.0
Mg	0.97×10^{-3}	12.5
Na	3.52×10^{-3}	81.0
K	0.09×10^{-3}	3.50
HCO_3	2.43×10^{-3}	148
SO_4	1.81×10^{-3}	174
Cl	2.48×10^{-3}	88.0
Total hardness	4.68×10^{-3}	234*
Total alkalinity	2.40×10^{-3}	120*
CO_2	43.2×10^{-6}	1.90
Br	1.60×10^{-6}	0.13
NO_3	24.2×10^{-6}	1.50
F	13.2×10^{-6}	0.25
B	12.0×10^{-6}	0.13
TOC		2.38
TDS		512

*as mg/l $CaCO_3$.

an appropriate Cr(VI) concentration prepared separately in the same medium to avoid dilution. Subsequently, the solutions were spiked with Fe(II) to a final concentration of up to 30 μM. Solutions were then immediately amended with appropriate volumes of 0.1 M NaOH to maintain the initial pH against the proton release associated with iron hydrolysis. Base addition was completed within 2–4 min; pH values were maintained at ± 0.03 pH units of the nominal values. Preliminary batch experiments showed that, when no base was added, the pH decreased up to 0.5 pH unit within the first 5 min and remained constant

during the rest of the experiment. The suspensions were mixed at 100 rpm for 30 min and, after a settling time of 15 min, samples were collected using a polyethylene syringe and (for experiments with synthetic CRW) filtered using either 0.2-μm membrane filters (Isopore™, Millipore) or Amicon Type YM-10 Centriplus membrane cones (Millipore) (referred to herein as an ultrafilter) with an effective molecular weight cutoff of 10,000 and an effective pore-size of approximately 0.003 μm. The Amicon membrane cones were pretreated by rinsing with Milli-Q water and then with a small aliquot of the sample to saturate any possible adsorption sites on the filters and filtration containers (Rai *et al.*, 1987). Since the total dissolved Cr and Fe concentrations in 0.2-μm and Amicon membrane filtrates were identical for synthetic CRW samples, the aliquots of the natural CRW and the simple electrolyte were filtered using only 0.2-μm membrane filters.

Filterability of colloidal Cr(III)

The filterability of colloidal Cr(III) was examined using a 1-l solution of 0.01 M $NaNO_3$ spiked with 1.00 μM Cr(III) without any coagulant. The solution was supersaturated with respect to amorphous $Cr(OH)_{3(s)}$ by raising the pH to 8.2. The aliquots of the solution were filtered using 0.2-μm (Isopore™, Millipore) and 0.02-μm (Anodisc™, Whatman) membrane filters, and an ultrafilter in order to determine the filterable Cr(III) concentrations with different pore-sizes.

Kinetics

Redox kinetics between Cr(VI) and Fe(II) in the presence of O_2 were examined at pH 6.5 and 7.0 using simple electrolyte solution. The pH was monitored during the experiments and was constant to within ± 0.01 units. Ten 5-ml samples of each aliquot were collected at time intervals of 1–10 min after the addition of Fe(II) stock solution and filtered with a 0.2 μm filter.

Removal of Cr(VI) with Fe(III)

The efficiency of Cr(VI) removal from synthetic CRW by coagulation with $FeCl_3$ was examined at high ratios of

total Fe to total Cr (Fe_T:$Cr_T = R = 50–200$) in the presence and absence of 3 mM Na_2SO_4. During these experiments solutions were mixed at 45 rpm for 30 min after the addition of Fe(III).

The extent of Cr(VI) sorption onto freshly precipitated $Fe(OH)_{3(am)}$ was also examined at a low Fe_T:Cr_T ratio ($R = 5$). Aliquots of synthetic CRW and simple electrolyte were first amended with an appropriate volume of Fe(III) stock solution and the pH was adjusted to 8.2. Then, 1.00 μM Cr(VI) was spiked into the solutions. The pH was then decreased stepwise by the addition of 0.1 M HNO_3 to a final pH of ~5.0. At each step, the pH was stabilized for 5–10 min before samples were collected.

Modelling

Rate expressions and constants previously reported for the reduction of Cr(VI) by Fe(II) and for oxidation of Fe(II) by O_2 were used to predict the rate and extent of Cr(VI) reduction and Fe(II) oxidation under our experimental conditions. Simulations were performed using SCIENTIST (MicroMath®) considering the reactions of Cr(VI) and Fe(II) according to the rate expressions,

$$-\frac{d[Cr(VI)]}{dt} = k_{Cr,Fe}^{cond} [Cr(VI)][Fe(II)] \qquad (3)$$

and

$$-\frac{d[Fe(II)]}{dt} = 3k_{Cr,Fe}^{cond} [Cr(VI)][Fe(II)] + k_{O_2,Fe}^{cond} [Fe(II)] \qquad (4)$$

where both $k_{Cr,Fe}^{cond}$ ($M^{-1} s^{-1}$) and $k_{O_2,Fe}^{cond}$ (s^{-1}) are dependent on pH and $k_{O_2,Fe}^{cond}$ incorporates a (constant) dissolved oxygen concentration assumed to be in equilibrium with an atmospheric P_{O_2} of 0.22 atm. Since the $k_{O_2,Fe}^{cond}$ values reported by Millero *et al.* (1987) and by Wehrli (1990) were in very good agreement, the former were used in all simulations. The dependence of the conditional rate coefficients ($k_{Cr,Fe}^{cond}$ and $k_{O2,Fe}^{cond}$) on pH reflects the effects of Fe(II) and Cr(VI) speciation as observed (and modelled) in previous studies (Table 2).

Table 2 | Rate coefficients for reaction of Fe(II) with Cr(VI) and O_2^*

Rate coefficient	Value	Conditions	Notes	Ref†
$k_{Cr,Fe}^{cond}$	$0.34 + 10^{9.52}[OH^-] + 10^{16.68}[OH^-]^2$	I = 0.01 M, T = 23 $\pm$ 3°C 1 mM acetate, MES or PIPES buffer, pH: 4.4–7.2	Stoichiometric reaction	(a)
	$10^{3.64}[H^+] + 10^{5.48}[H^+]^2 + 10^{8.97}[OH^-] + 10^{15.5}[OH^-]^2$	I = 0.01 M, T = 25 $\pm$ 1°C 1 mM PIPES buffer, pH: 5.0–8.1	Pseudo first-order reaction	(b)
	$10^{6.70}\alpha(H_2CrO_4)\alpha(Fe^{2+}) + 10^{6.00}\alpha(HCrO_4^-)\alpha(FeOH^+) + 10^{11.70}\alpha(HCrO_4^-)\alpha(Fe(OH)_2)$	I = 0.1 M, T = 10 $\pm$ 0.004°C 9 mM borate buffer, pH: 5.5–8.7	Pseudo first-order reaction	(c)
	$0.68 + 10^{9.85}[OH^-] + 10^{16.85}[OH^-]^2$	I = 0.05 M, T = 23 $\pm$ 2°C No buffer, pH: 4.0–7.2	For anoxic conditions; nonstoichiometric reaction	(d)
$k_{O_2,Fe}^{cond}$	$10^{(36.525 - 21.451pH + 3.4951pH^2 - 0.172083pH^3)}$	T = 25 $\pm$ 0.02°C 0.009 m $NaHCO_3$ buffer, pH: 5.0–9.0	Valid for 6.5 $\leq$ pH $\leq$ 8.5	(e)
	$10^{-8.66} + 10^{-11.66}[H^+]^{-1} + 10^{-17.26}[H^+]^{-2}$		Calculated values; corrected for P_{O_2} = 0.22 atm	(f)

*Rate expressions:
$$-\frac{d[Cr(VI)]}{dt} = k_{Cr,Fe}^{cond}[Cr(VI)][Fe(II)]$$
$$-\frac{d[Fe(II)]}{dt} = 3k_{Cr,Fe}^{cond}[Cr(VI)][Fe(II)] + k_{O_2,Fe}^{cond}[Fe(II)]$$

†References are: (a) Buerge & Hug (1997), (b) Sedlak & Chan (1997), (c) Pettine *et al.* (1998), (d) Schlautman & Han (2001), (e) Millero *et al.* (1987), and (f) Wehrli (1990).

The reaction of Fe(II) with O_2 was explicitly considered in modelling our experiments. Furthermore, it was assumed that all Cr(III) produced by reduction of Cr(VI) and all Fe(III) produced by oxidation of Fe(II) were quantitatively removed by filtration. Thus, the fraction of Cr(VI) removed was taken to correspond to the fraction of Cr(VI) reduced and the fraction of Fe(II) removed to the fraction of Fe(II) oxidized.

Modelling of Cr(VI) sorption onto freshly precipitated $Fe(OH)_{3(am)}$ from the simple electrolyte was performed using MINEQL+ v. 4.5 (Schecher & Mcavoy, 1998). Relevant thermodynamic data for aqueous species and the equilibrium constants for surface complexation reactions were used as g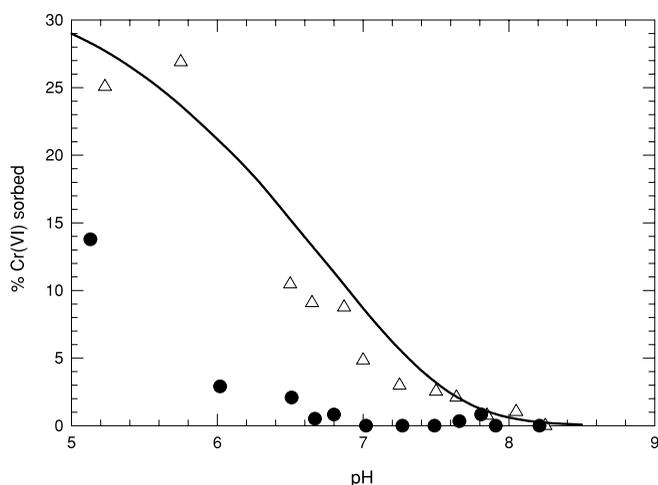iven in MINEQL+ database; MINEQL+ constants for reactions at the hydrous ferric oxide surface are taken from Dzombak & Morel (1990).

RESULTS AND DISCUSSION

The efficiency of Cr(VI) removal by redox-assisted coagulation was examined under varying conditions, including the initial concentrations of Cr(VI) and Fe(II), pH and the presence of various constituents of natural waters. In order to assess the efficiency gained by exploiting the redox chemistry of Cr in the coagulation process, a series of experiments was performed with Fe(III) rather than Fe(II).
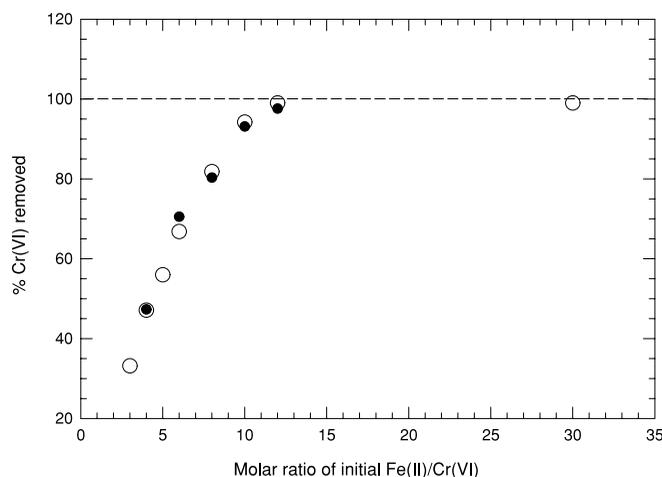
Table 3 │ Removal of Cr(VI) from synthetic CRW at pH 8.2 by coagulation with $FeCl_3 \cdot 6H_2O$

[Cr(VI)]$_T$ (μM)	[Fe(III)]$_T$ (μM)	% Cr(VI) removed	
		No SO$_4$	3 mM SO$_4$
1.0	50	20.2	12.7
1.0	100	9.1	10.2
0.5	100	9.4	20.8

Figure 2 │ Removal of Cr(VI) from synthetic CRW by redox-assisted coagulation with various Fe(II) doses at pH 8.2. Initial Cr(VI) concentrations were 1.08±0.05 μM. Symbols indicate the type of filter used: (○) 0.2 μm filter, (●) ultrafilter.

Figure 1 │ Sorption of Cr(VI) to freshly precipitated Fe(OH)$_{3(am)}$. Conditions: [Cr(VI)]$_T$=1 μM, [Fe(II)]$_T$=5 μM, (△) simple electrolyte, (●) synthetic CRW, (——) modelling for simple electrolyte with MINEQL+.

Cr(VI) removal by coagulation/sorption with Fe(III)

Removal of Cr(VI) from synthetic CRW (pH = 8.2) by addition of Fe(III) as a coagulant was poor (<30%) even with Fe(III) concentrations of 50–100 μM (2.8 to 5.6 mg/l as Fe) (Table 3). Addition of 3 mM sulphate had inconsistent effects. The extent of Cr(VI) sorption to freshly precipitated Fe(OH)$_{(3)(am)}$ at a low Fe$_T$:Cr$_T$ ratio (R = 5) with an initial Cr(VI) concentration of 1.00 μM is shown in Figure 1. At pH>8.0, Cr(VI) did not sorb at all from either synthetic CRW or the simple electrolyte solution. As the pH decreased, the fraction of Cr(VI) sorbed in both solutions increased. Even at pH 6.5, however, only 10.5% of the initial Cr(VI) was sorbed in the simple electrolyte solution and sorption in synthetic CRW was negligible

(2.1%). For the simple electrolyte system, the extent of Cr(VI) sorption is consistent with the values calculated using MINEQL + (Figure 1).

Previous studies have shown that Cr(VI) species followed the characteristic adsorption behaviour of anions with minimal sorption onto amorphous iron oxyhydroxide at alkaline pH values (Davis & Leckie, 1980; Zachara *et al.*, 1987). In addition, bicarbonate, which is present in synthetic CRW, has been shown to depress sorption onto goethite (Van Geen *et al.*, 1994; Villalobos *et al.*, 2001) or amorphous iron oxyhydroxide (Zachara *et al.*, 1987). Although the effect of sulphate was not consistent (Table 3), previous work has shown that Cr(VI) sorption onto amorphous iron oxyhydroxide in solutions equilibrated with elevated P_{CO_2} ($10^{-2.46}$ atm) was depressed by sulphate at pH~5 but not at pH>7.5 (Zachara *et al.*, 1987).

Effect of Fe(II) dose on Cr(VI) removal efficiency

In contrast, excellent Cr(VI) removal (>99%) could be achieved by redox-assisted coagulation with excess Fe(II) (Figure 2). The required Fe(II) concentration (≥12 μM) is substantially in excess of the 3:1 stoichiometric ratio for 1 μM Cr(VI) as described in reaction (1). At lower Fe(II) doses, the fraction of Cr(VI) removed was 94.2% at 10 μM
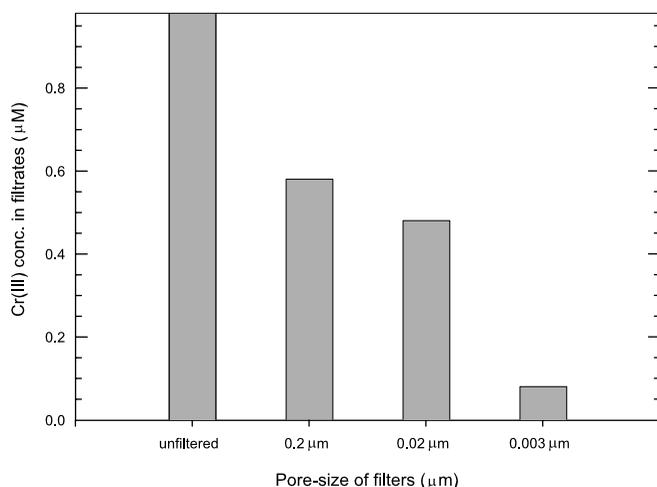
Figure 3 | Cr(III) concentrations in filtrates of a solution supersaturated with amorphous Cr(OH)$_{3(s)}$ obtained with filters having different pore-sizes. Note that the pore size of the ultrafilter (0.003 μm) is estimated. Conditions: [Cr(III)]$_T$=0.98 μM, I=0.01 M, pH=8.2.

Fe(II) but only 33.2% at 3 μM Fe(II). The corresponding total dissolved Cr concentrations were 0.06 and 0.67 μM (3.0 and 34.7 μg/l). The incomplete Cr(VI) removal cannot be attributed to insufficient reaction time since no change in the residual Cr concentrations was observed between 30 and 1500 min (data not shown) (Lee *et al.*, 2002). This observation is consistent with previous reports of rapid reaction of Cr(VI) with Fe(II) at circumneutral pH (*vide infra*).

There are several possible explanations for the poor removal of Cr(VI). The Cr(VI) may have been completely reduced to Cr(III) but either the Fe(III) concentration was insufficient to form filterable solids or the amount of ferric hydroxide formed was not sufficient for all Cr to be sorbed/co-precipitated with the solid. Alternatively, the reduction of Cr(VI) may not have gone to completion because of the competing reaction of Fe(II) with O$_2$. These hypotheses are discussed in the following sections.

Importance of filtration efficiency

In the absence of any coagulant, a substantial fraction of colloidal Cr(III) was found to pass through a 0.2 μm filter (Figure 3). With a solution of 1 μM Cr(III) at pH 8.2

(which was supersaturated with respect to amorphous Cr(OH)$_{3(s)}$), 59.2% of the Cr(III) passed through the 0.2 μm filter, 49.0% through the 0.02 μm filter, and 8.2% through the ultrafilter. On the basis of the solubility product constant ([Cr(OH)$_3$]° = K_{sp}^{conc}<10$^{-6.84}$) for Cr(OH)$_{3(am)}$ reported by Rai *et al.* (1987), the dissolved Cr(III) concentration in the filtrate should be ≤0.14μM (or 14% of the initial Cr(III) concentration). This value corresponds reasonably well to the Cr(III) concentration measured in the ultrafiltrate. However, approximately 80% of the Cr(III) passing through the 0.2 μm filter (corresponding to an operationally-defined 'dissolved' fraction) was actually colloidal. The possible overestimation of truly dissolved Cr should be considered in assessing the speciation of naturally occurring Cr in source waters.

The passage of colloidal Cr through the 0.2 μm filters does not, however, explain the poor Cr(VI) removal observed at low (but still above stoichiometric) doses of Fe(II). As seen in Figure 2, the residual Cr concentrations were identical in both the 0.2 μm filtrate and ultrafiltrate. In addition, Fe was effectively removed (below detection limit) from the 0.2-μm filtrates in every case. These results indicate that the freshly precipitated ferric hydroxide, Fe(OH)$_{3(am)}$, formed filterable solids and that, in the presence of Fe, no colloidal Cr(III) passed through the 0.2 μm filters.

Importance of complete reduction of Cr(VI) to Cr(III)

Removal efficiencies were examined for Cr(III) rather than Cr(VI) so that the efficiencies of the coagulation and redox processes could be distinguished. At low Fe(II) doses, the removal efficiencies of Cr(VI) and Cr(III) were dramatically different (Figure 4). The removal of Cr(III) was >99% even at the lowest Fe(II) dose of 2 μM, which indicates that sufficient ferric hydroxide was formed under these conditions to sorb and/or co-precipitate all of the Cr(III). Note that, since no Cr(VI) was present in these experiments, all Fe(II) oxidized would be due to reaction with O$_2$. For freshly precipitated ferric hydroxide, the total concentration of surface sites available for sorption is approximately 0.2 mol/mol Fe (Dzombak & Morel, 1990). Thus, a 2 μM Fe(II) dose would provide 0.4 μM sorption
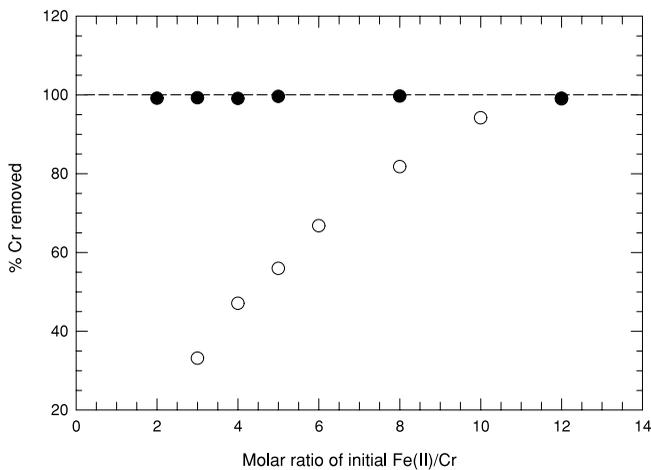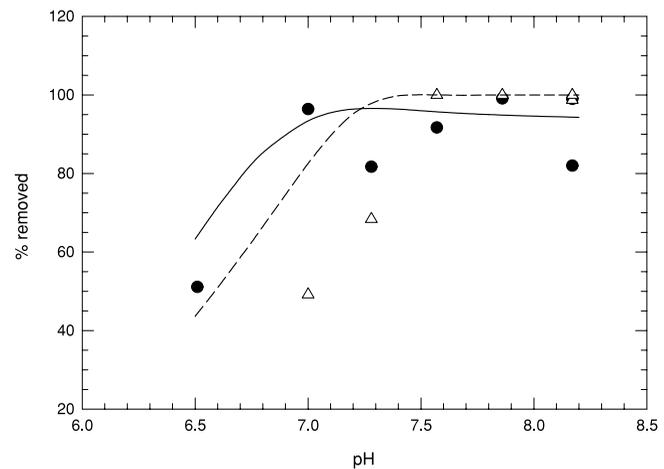
Figure 4 | Removal of Cr added as Cr(III) (●) or Cr(VI) (○) with varying Fe(II) doses from synthetic CRW at pH 8.2. Initial Cr concentrations were 0.97±0.06 μM. Cr removal was determined from residual Cr concentrations (measured as total, dissolved Cr) in 0.2 μm filtrates.
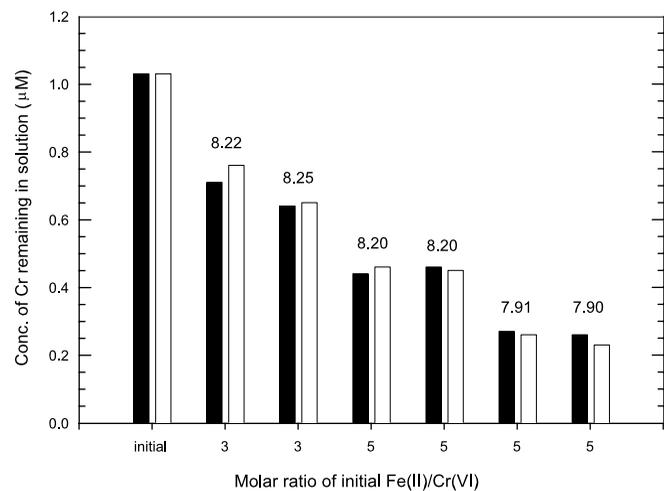
Figure 5 | Speciation of chromium remaining in solution after redox-assisted coagulation with Fe(II). Numbers indicate the final pH of solution. The initial Cr(VI) concentration was 1.03 μM. Symbols: (■) total, dissolved Cr, (□) Cr(VI).

Figure 6 | Effect of pH on the removal of Cr(VI) and Fe(II) from simple electrolyte solutions. Conditions: $[Cr(VI)]_{init}=1.11\pm0.01$ μM, $[Fe(II)]_{init}=5.00$ μM. Symbols: data for (●) Cr(VI) and (△) Fe(II), predictions for (——) Cr(VI) and (– – –) Fe(II) based on Eqns (3) and (4) using values of $k_{Cr,Fe}^{cond}$ from Buerge & Hug (1997) and $k_{O_2,Fe}^{cond}$ from Millero et al. (1987).

sites, which is substantially lower than the initial Cr(III) concentration. This suggests that Cr(III) was removed by both sorption and co-precipitation with $Fe(OH)_{3(am)}$.

Determination of the speciation of Cr remaining in solution after redox-assisted coagulation with Fe(II) at, or in modest excess of, the stoichiometric dose showed that all the residual Cr was present as Cr(VI) (Figure 5). Inconsistencies between total dissolved Cr and Cr(VI) concentrations were <10% in all cases and may be attributed to analytical error. These observations confirm that the poor removal of Cr(VI) was due to its incomplete reduction to Cr(III). The incomplete reduction of Cr(VI) most likely resulted from the competition between Cr(VI) and O_2 for reaction with Fe(II), which decreased the efficiency of reaction (1) at low Fe(II) doses. Previous studies have shown that the reduction rate of Cr(VI) by Fe(II) increases with pH (above pH 5) in the absence (Buerge & Hug, 1997; Sedlak & Chan, 1997; Pettine et al., 1998) and in the presence (Schlautman & Han, 2001) of O_2. However, the rate of oxidation of Fe(II) by O_2 also increases with pH (Millero et al., 1987; Wehrli, 1990). Therefore, a more detailed examination of the pH dependence of the competition between Cr(VI) and O_2 is warranted.

Effect of pH on Cr(VI) removal efficiency

Between pH 7.0 and 8.2, the extent of Cr(VI) removal by redox-assisted coagulation from the simple electrolyte did not vary significantly with pH (Figure 6). The fraction of Cr(VI) removed was $92\pm8\%$ in this pH range. Removal decreased substantially at lower pH values and was only 51% at pH 6.5. Similarly, Fe(II) was completely removed

at pH$\geq$7.3. Below this pH, the fraction of Fe(II) removed also decreased with decreasing pH to 49% at pH 6.5.

These measured values can be compared to those predicted based on Equations (3) and (4) using values of $k_{\text{Cr,Fe}}^{\text{cond}}$ from Buerge & Hug (1997) and $k_{\text{O2,Fe}}^{\text{cond}}$ from Millero et al. (1987) (Table 2). These rate expressions were used to predict the extent of Fe(II) oxidized and Cr(VI) reduced (which was taken, in both cases, to correspond to the extent of removal) after a reaction time of 45 min. In agreement with the observations, the calculations also predicted that Fe(II) removal should be complete and Cr(VI) removal nearly so above 7.2. The slightly lower predicted removal of Cr(VI) than Fe(II) above pH 7.2 is due to the competing reaction of Fe(II) with O_2. The more dramatic decrease in predicted removal efficiency below pH 7 is due primarily to the slow kinetics of reaction of Fe(II) with either Cr(VI) or O_2 and hence the incomplete reaction of Cr(VI) and Fe(II) over the specified reaction time.

The observations (and predictions) of the extent of reaction after a fixed time are, however, sensitive to the initial concentrations of both Cr(VI) and Fe(II). At $[\text{Cr(VI)}]_{\text{init}} = 96$ μM and $[\text{Fe(II)}]_{\text{init}} = 192$ μM, Eary & Rai (1988) observed that Fe(II) was oxidized and Cr(VI) reduced at the stoichiometric ratio of 3:1 between pH 3 and 10 in oxygenated solutions over a reaction time of 5 min and that the side reaction of Fe(II) with O_2 became important only above pH 10. For $[\text{Cr(VI)}]_{\text{init}} = 0.95$ μM and $[\text{Fe(II)}]_{\text{init}} = 39.2$ μM in oxygenated solutions, Pettine et al. (1998) predicted that Fe(II) would react preferentially with Cr(VI) at pH 6 and with O_2 at pH 8. Experimental observations confirmed that competition with O_2 decreased the rate of reaction of Cr(VI) with Fe(II) above pH 7.5. With $[\text{Cr(VI)}]_{\text{init}} = 20$ μM and $[\text{Fe(II)}]_{\text{init}} = 50$ μM, Schlautman & Han (2001) reported that dissolved O_2 had no effect on the observed rate constant for reaction of Cr(VI) with Fe(II) over the pH range from 4 to 6.8.

In our study the effect of the initial Cr(VI) concentration was also examined at pH 8.2 in synthetic CRW with a fixed initial Fe(II) concentration of 4 μM. At low values ($[\text{Cr(VI)}]_{\text{init}} = 0.1$ μM, $R = 40$), 73% of the Cr(VI) was removed (within 45 min); this decreased to 43% for $[\text{Cr(VI)}]_{\text{init}} = 0.84$ μM ($R = 4.8$). This behaviour is generally consistent with the observation of increasing Cr(VI)
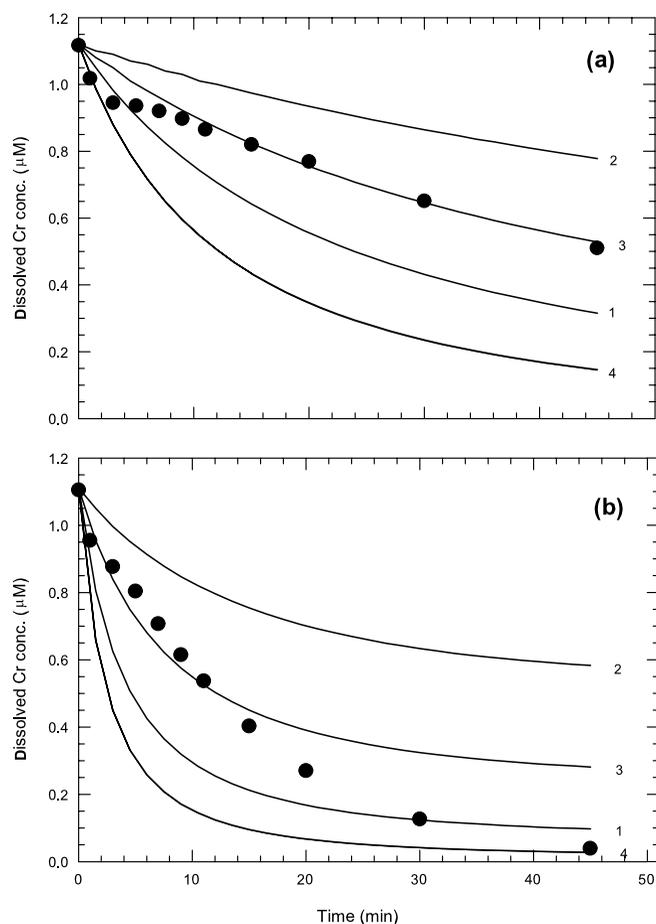

Figure 7 | Concentrations of dissolved Cr as a function of time after addition of Fe(II) in the simple electrolyte solution in the presence of O_2. Conditions: $[\text{Cr(VI)}]_{\text{init}} = 1.1$ μM, $[\text{Fe(II)}]_{\text{init}} = 5.0$ μM. (a) pH=6.5, (b) pH=7.0. Symbols: (●) data. Lines correspond to Cr(VI) concentrations predicted using $k_{\text{O2,Fe}}^{\text{cond}}$ from Millero et al. (1987) and $k_{\text{Cr,Fe}}^{\text{cond}}$ from (1) Buerge & Hug (1997), (2) Sedlak & Chan (1997), (3) Pettine et al. (1998) and (4) Schlautman & Han (2001) (for anoxic conditions).

removal with increasing values of R (cf. Figure 2). At lower $[\text{Cr(VI)}]_{\text{init}}$, however, the removal of Cr(VI) was systematically low compared with that at the same value of R with $[\text{Cr(VI)}]_{\text{init}} = 1$ μM (data not shown). This can be attributed to the increasing importance of the side reaction with O_2 as $[\text{Cr(VI)}]_{\text{init}}$ decreases (at constant R).
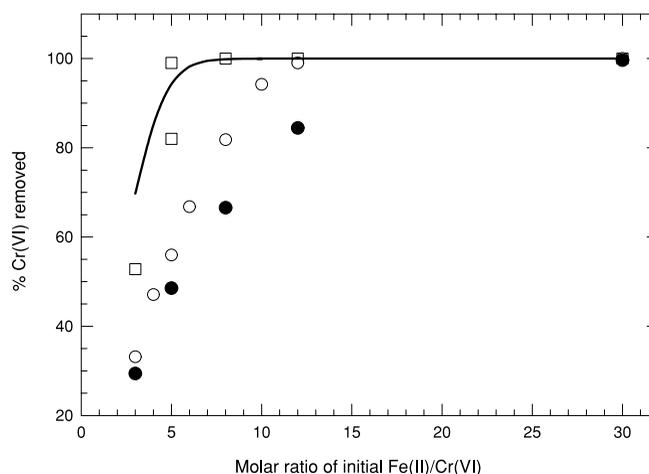
Kinetics and reaction modelling

To compare with the numerous previous studies of the kinetics of reaction of Cr(VI) with Fe(II), the progress of
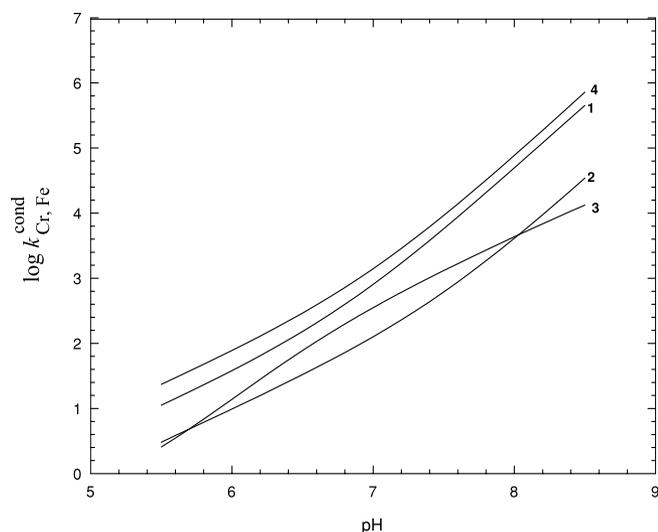
Figure 8 | Rate constants, $k_{Cr,Fe}^{cond}$ for Cr(VI) reduction by Fe(II) calculated using the expressions listed in Table 2. 1. Buerge & Hug (1997), 2. Sedlak & Chan (1997), 3. Pettine *et al.* (1998), 4. Schlautman & Han (2001) (for anoxic conditions). Note: some calculated values are shown outside of the pH range of the original experiments (Table 2) and should be viewed with caution.

Figure 9 | Removal of Cr(VI) with varying Fe(II) doses from different media at pH 8.2. Conditions: [Cr(VI)]$_{init}$=1 μM. Symbols: (□) simple electrolyte, (○) synthetic CRW, (●) natural CRW, (——) prediction for simple electrolyte using values of $k_{Cr,Fe}^{cond}$ from Buerge & Hug (1997) and $k_{O2,Fe}^{cond}$ from Millero *et al.* (1987).

this reaction was followed at pH 6.5 and 7.0 in simple electrolyte solutions open to the atmosphere (Figure 7). As discussed in the previous section, Cr(VI) reduction (with [Cr(VI)]$_{init}$ = 1.1 μM, [Fe(II)]$_{init}$ = 5 μM) was incomplete at pH 6.5 and nearly complete at pH 7.0 within 45 min (Figures 6 and 7). The measurements were compared with a range of predictions based on rate constants reported by different investigators (Table 2). As shown in Figure 7a, the observations agreed well at pH 6.5 with the values calculated using $k_{Cr,Fe}^{cond}$ from Pettine *et al.* (1998) except for the early stage ($t<5$ min) of reaction, in which the observed rate was under-predicted. This initial fast Cr(VI) reduction may be an artifact resulting from base addition and the presence of high-pH microenvironments (Schlautman & Han, 2001). At pH 7.0, however, the value of $k_{Cr,Fe}^{cond}$ from Pettine *et al.* (1998) accurately represented the observed data only for the first 15 min of the reaction (Figure 7b). Note that, in both cases, good agreement was obtained for the first 50% of the reaction of Cr(VI). The further extent of reaction observed at pH 7 was under-predicted by the model. It should be noted that the model does not account for the possible sorption of Cr(VI) onto freshly precipitated Fe^{III} and Fe^{III}-Cr^{III} hydroxides

produced by redox reactions. However, independent sorption experiments (Figure 1) indicate that this effect should not be substantial (particularly at pH 7).

As can be seen in Figure 7, significantly different rates of reaction of Cr(VI) with Fe(II) and, consequently, significantly different extents of reaction of Cr(VI) after 45 min were predicted using the various rate constants reported in the literature. Note that, in all cases, reaction of Fe(II) with O$_2$ was modelled using the rate constant reported by Millero *et al.* (1987).

The discrepancies among reported rate constants for Cr(VI) reduction are further illustrated in Figure 8, which shows values of $k_{Cr,Fe}^{cond}$ as a function of pH. The pH-dependent values of the rate constant vary by a factor of 10 between pH 5.5 and 7 and up to a factor of 100 at pH 8.4. The factors causing the discrepancies in the rates are not clear but probably include different initial concentrations of the reactants, local inhomogeneities associated with chemical (especially base) addition, inaccuracies in measurements, and dissolved oxygen contamination in deoxygenated solutions as also discussed by Pettine *et al.* (1998). The kinetics of reaction of Cr(VI) with Fe(II) were also studied by Fendorf & Li (1996) but were not included in the comparison because fractional order dependence

on [Fe(II)] was reported rather than the first-order dependence observed in all other studies.

As illustrated by Figure 8, the best agreement is between the constants reported by Buerge & Hug (1997) and Schlautman & Han (2001). The constants reported by Sedlak & Chan (1997) show a similar pH dependence but are uniformly lower. In contrast, the constants reported by Pettine *et al.* (1998) exhibit a significantly different dependence on pH and yield the lowest value of $k_{Cr,Fe}^{cond}$ above pH 8. This is probably because their mechanism (and corresponding rate expression) did not include reaction of CrO_4^{2-}, which accounts for more than 90% of total dissolved Cr(VI) species at pH ≥ 7.5. It should be noted, however, that most of these detailed kinetic studies have been performed in aqueous media that did not include common constituents of natural waters. In one study, the major ions in seawater were found to have no effect on the rate of reaction of Cr(VI) with Fe(II) but these experiments were performed at high ionic strength (Pettine *et al.*, 1998).

Effect of source water composition on Cr(VI) removal efficiency

A distinct difference in the efficiencies of Cr(VI) removal by redox-assisted coagulation at pH 8.2 was observed when the simple electrolyte was compared with either synthetic or natural CRW (Figure 9). Although Cr(VI) (at an initial concentration of 1 μM) was completely removed in all case by a Fe(II) dose of 30 μM (*i.e.* 1.7 mg/l as Fe), Cr(VI) was less efficiently removed from synthetic or natural CRW than from the simple electrolyte solution at lower Fe(II) doses.

As discussed above, it has been previously observed that the rate of reaction of Fe(II) with Cr(VI) in the absence of O_2 is influenced by the speciation of Fe(II), particularly by Fe(II) hydrolysis (which is incorporated in the conditional rate constants). In addition, organic ligands that stabilize Fe(III) accelerate the reaction of Fe(II) with Cr(VI) (at pH 4.0–5.5), while those that stabilize Fe(II) inhibit the reaction (Buerge & Hug, 1998). Dissolved organic matter isolated from soils was observed to accelerate the reaction. Such acceleration, however, is

relative to the reaction of Fe^{2+}. At pH 8.2, some organic ligands that accelerate the reaction at low pH would be expected to retard it relative to the reaction with the hydrolysis species $FeOH^+$. Mineral surfaces and soils have also been observed to accelerate the reaction (at pH 5); this effect has been attributed to enhanced reactivity of adsorbed Fe(II) (Buerge & Hug, 1999). Although this effect was observed for solids concentrations above 0.2 g/l, only a small fraction of Fe(II) was adsorbed to the solids at this pH; higher pH values would enhance Fe(II) adsorption and hence the potential contribution of this pathway.

These effects may account for decreased Cr(VI) removal efficiency in natural CRW (which contains 2.4 mg/l TOC) as compared with synthetic CRW, but not for the observed differences between synthetic CRW and the simple electrolyte. The synthetic CRW contained 2 mM $NaHCO_3$. No carbonate was added to the simple electrolyte, and gas-exchange during the course of the experiment (i.e. after pH adjustment to 8.2) would not be expected to achieve full equilibration with the atmosphere. Amendment of synthetic CRW with additional bicarbonate (up to 9 mM) did result in further decrease in Cr(VI) removal efficiency; elimination of added Ca had no effect (Lee, unpublished). Clearly, effects of source water composition, although of modest impact in this study, should be evaluated for individual source waters.

CONCLUSIONS

Redox-assisted coagulation was confirmed to be an effective process for removal of Cr(VI) from drinking water. Dissolved Cr concentrations could be lowered from an initial value of 1 μM (52 μg/l) to the detection limit of 0.01 μM (0.5 μg/l) at pH 8.2 by addition of Fe(II) in moderate excess of the 3:1 stoichiometric dose. Some Fe(II) was lost to reaction with dissolved oxygen and this competing reaction may become comparatively more significant with decreasing initial Cr(VI) concentrations. Nonetheless, efficient Cr(VI) removal can be accomplished with a sufficient Fe(II) dose. Decreased pH (which can result from iron hydrolysis if compensating base

additions are not made) can impair the efficiency of Cr(VI) removal because the rate of Fe(II) reaction with Cr(VI) (and also with O_2) decreases with decreasing pH in the mildly acidic to mildly alkaline pH range.

Published rate coefficients for the reaction of Fe(II) with Cr(VI) and O_2 were used to model Cr(VI) removal in simple electrolyte solutions. Even in these simple systems, however, the range of reported values for the rate coefficients leads to predicted dissolved Cr(VI) concentrations (after a 45 min reaction time) varying by a factor of 5 at pH 6.5 and a factor of 15 at pH 7. A further complication in applying these reported rate coefficients to actual drinking water is the observed differences in the extent of Cr(VI) removal in simple electrolyte solutions as compared with natural or synthetic CRW.

In actual practice, the issues of settleability of the floc and filterability of the precipitated solids may also affect the performance of redox-assisted coagulation. In this study, amorphous $Cr(OH)_3$ solids formed in the absence of Fe were found to be less efficiently retained by a 0.2 μm filter than Cr(III) solids formed in the presence of Fe. The colloidal nature of the Cr(III) solids was demonstrated by their retention on an ultrafilter.

Although all of our experiments were performed in solutions open to the atmosphere, even more efficient reaction of Cr(VI) with Fe(II) would be anticipated in groundwaters containing little or no dissolved oxygen. In these cases, Fe(II) could be added at concentrations closer to the stoichiometric dose since the competing side reaction with O_2 would not be a concern. At low Fe(II) doses, the precipitated Cr(III) and Fe(III) oxyhydroxide solids could be removed by a direct filtration process.

ACKNOWLEDGEMENTS

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