Continuous flow process of Cr(VI) removal from drinking water through reduction onto FeOOH by inorganic sulfur reductants
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ABSTRACT
In this study, the implementation of an iron oxy-hydroxide (FeOOH) as a surface catalyst for Cr(VI) reduction by inorganic sulfur reductants (ISRs) was investigated. Batch Cr(VI) removal tests, performed to evaluate and compare the efficiency of ISRs in the presence of FeOOH, qualified Na$_2$S$_2$O$_4$ as the optimum for drinking water treatment. Application of Na$_2$S$_2$O$_4$ in continuous flow rapid small scale column tests, using a FeOOH adsorbent at pH 7 ± 0.1 and artificial (resembling natural) water matrix, verified the high potential for Cr(VI) removal at sub-ppb level. Indeed, a 15 mg S/L Na$_2$S$_2$O$_4$ dose diminished an initial Cr(VI) concentration of 100 μg/L below the method’s detection limit of 1.4 μg/L at least for 10$^5$ bed volumes. X-ray absorption fine structure spectroscopy revealed that Cr(VI) forms outer sphere complexes, while Cr(III) is involved in 2E, 2C and 1V geometries with the surface Fe-oxohydroxyl groups. It can, therefore, be concluded that FeOOH attracts Cr(VI) to its surface via physisorption, offering a solid surface that promotes the transfer of electrons through bridging ions. Thus, when Na$_2$S$_2$O$_4$ is added in the system, Cr(VI) is reduced to Cr(III), which is subsequently chemisorbed onto the FeOOH surface.

Key words | Cr(VI) removal, drinking water, inorganic sulfur reductants, iron oxy-hydroxides, XAFS

INTRODUCTION
The occurrence of Cr(VI) in drinking water resources, either originating from natural or anthropogenic processes, has recently attracted wide scientific interest. Reports on relative research suggest that the problem of non-negligible Cr(VI) concentrations concerns a large number of sites worldwide (Kaprara et al. 2015a). The contact of water with ultramafic rocks and soils such as serpentinite, dunites, and ophiolites proved the cause of high Cr(VI) concentrations in numerous cases in California (Gonzalez et al. 2005), Mexico (Robles-Camacho & Armientac 2000), Brazil (Bourette et al. 2009), Italy (Fantoni et al. 2002), Greece (Kazakis et al. 2013), Japan and Indonesia (Saputro et al. 2014). Primary results from epidemiological studies on Cr(VI) toxicity after water consumption (Linos et al. 2011) indicate that a re-evaluation of the current regulation limit of 50 μg/L total chromium (European Commission 1998) is very likely to occur in the near future. This trend is signified by the establishment of strict maximum level of 10 μg Cr(VI)/L by the State of California on July 1st, 2014 (California Regulations Related to Drinking Water 2014).

The potential for a new lower Maximum Permissible Concentration regulation limit enforces the development of novel treatment technologies that will keep Cr(VI) removal down to single parts per billion (ppb) concentrations, be safely applied in drinking water treatment, preserve water quality characteristics and enable environmental friendly and cost...
effective full-scale application. Up to date, numerous chromium remediation methods have been studied, including chemical reduction followed by coagulation/sand filtration (Mitrakas et al. 2011), adsorption onto activated carbons, biosorbents (Mohan & Pittman 2006) or metal oxy-hydroxides (Kaprara et al. 2016; Pinakidou et al. 2016), ion-exchange (Dabrowski & Hubicki 2004), membrane separation (Korus & Loska 2009), electrodialysis (Nataraj et al. 2007) and phyto-remediation (Cervantes et al. 2004). So far, the most efficient and widely practiced treatment technique is the reduction of Cr(VI) to the non-toxic and insoluble Cr(III) form. Reductants that have already been studied include zero-valent iron (ZVI) (Niu et al. 2005), ferrous iron salts (Mitrakas et al. 2011), and various inorganic sulfur reductants (ISRs) (Kaprara et al. 2015b). The method of ZVI is very effective in Cr(VI) reduction, however, it suffers from surface passivation. Furthermore, it enriches the treated water with dissolved ferrous ions whose concentration can frequently overpass the respective drinking water regulation limit. The reduction of Cr(VI) by ferrous iron salts and subsequent co-precipitation as ferric/chromium mixed hydroxides has proven to reduce Cr(VI) concentration to sub-ppb level and it has been successfully applied in pilot (McGuire et al. 2006), as well as in full-scale (Mitrakas et al. 2011) drinking water treatment. However, this reduction method has a major weakness; the production of sludge which requires subsequent dewatering and disposal treatment.

Research on Cr(VI) reduction with the use of ISRs revealed interesting results and led scientists to investigate a possible increase of their reactivity through surface catalysis. Kim et al. (2007) studied the reaction kinetics of Cr(VI) reduction by hydrogen sulfide through the goethite surface catalytic reaction. They concluded that surface ferrous ions, formed as a result of goethite surface reduction after sulfide adsorption, played a key role on Cr(VI) reduction, acting as the primary electron donor through the Fe(II)–Fe(III) cycle. Elemental sulfur was determined as the stabilized final product of sulfide and it worked as additional catalyst, increasing the Cr(VI) reduction rate at a later stage. In the work of Zhou and colleagues, the facilitating role of biogenically produced schwertmannite mineral in the reduction of Cr(VI) by sulfide was investigated (Zhou et al. 2012) and it was demonstrated that such a mineral significantly accelerates the reduction/ removal of Cr(VI) by sulfide; the rates of reaction increased 11, 8 and 6 times at pH values equal to 7.5, 8.0 and 8.8, respectively, in comparison to the control samples (i.e. without the presence of schwertmannite). It was concluded that the catalysis of schwertmannite derived from the activated Fe(III) on its surface, which served as a ‘bridge’ for electron transportation between sulfide and Cr(VI) and led to the improved reduction of Cr(VI) by sulfide. Biogenic jaroite was also tested as a surface catalyst for Cr(VI) reduction by sulfide (Xu et al. 2013). The authors suggested that a cycle process of Fe(III) to Fe(II) conversion can occur on the surface of jaroite and markedly accelerate the reduction of Cr(VI) by sulfide. Another approach (Taylor et al. 2000) reports on the removal of chromate by dithionite-reduced clays. X-ray absorption near edge structure (XANES) at the Cr-K-edge suggested that clays containing Fe(II) can reduce Cr(VI) to Cr(III), via Cr immobilization at the clay/water interface. The adsorption of Cr(VI) by the Fe(II)-containing clay was a prerequisite for the coupled sorption–reduction reaction. However, when sodium dithionite was added directly to aqueous suspensions of non-reduced clays, although it reduced Cr(VI) to Cr(III), it did not immobilize Cr on clay surfaces. Nevertheless, the ability of clays to reduce Cr(VI) was correlated to the ferrous iron content in the clays (Taylor et al. 2000). Conclusively, the ISRs studied for Cr(VI) removal through surface catalysis are mainly sulfide and dithionite and their efficiency was evaluated only by batch mode experiments.

The motivation for this study is the optimization of Cr(VI) removal from drinking water by the addition of ISRs through surface catalysis and under continuous flow configuration. The latter will determine the major design parameters for full-scale implementation of the process. The reductants examined were NaHSO3, Na2S2O3, Na2S2O4, Na2S2O5 and Na2S and a laboratory synthesized FeOOH served as a surface catalyst. The Cr(VI) reduction reaction and sorption mechanism of Cr was investigated using extended- and near-edge X-ray absorption fine structure (EXAFS and XANES) spectroscopies at the Cr-K-edge.

MATERIALS AND METHODS

Reagents

A 500 mg/L Cr(VI) stock solution was prepared from reagent grade K2Cr2O7. Working standards were freshly
prepared by proper dilution of the stock solution in artificial water, resembling natural water matrix. Artificial water was prepared according to National Sanitation Foundation (NSF) standard by dissolving 252 mg NaHCO₃, 12.14 mg NaNΟ₃, 0.178 mg NaH₂PO₄·H₂O, 2.21 mg NaF, 70.6 mg NaSiO₃·5H₂O, 147 mg CaCl₂·2H₂O and 128.3 mg MgSO₄·7H₂O into 1 L of distilled water. For each ISR investigated, fresh solutions were prepared by diluting the appropriate quantity of reagent grade NaHSO₃, Na₂S₂O₃, Na₂S₂O₄, Na₂S₂O₅ and Na₂S in distilled water bubbled with N₂. This procedure was selected for diminishing ISRs oxidation by dissolved oxygen. A FeOOH, consisting mainly of oxyhydroxyl sulfate schwertmannite ([Fe₁₆O₁₆-(OH)₁₀(SO₄)₃·10H₂O) was produced using the method of Tresintsi et al. (2012) and was used as the surface catalyst. The main physicochemical characteristics of FeOOH are as follows: Fe 50.5 wt.%, SO₂⁻/C₄ 14.8 wt.%, isoelectric point 7.1, point of zero charge (PZC) 3.0, surface charge density 2.8 mmol [OH⁻]/g and specific surface area 125 m²/g.

**Experimental procedure**

Batch experiments were conducted at 20 ± 1 °C by using 200 mL of 100 μg/L Cr(VI) in artificial water. The influence of the presence of FeOOH in Cr(VI) reduction was studied at pH 7.0 ± 0.1 for an ISR concentration equal to 10 mg S/L and for a FeOOH dose of 100 and 200 mg/L (fine powder). The reaction solutions were agitated in an orbital shaker for 24 h to reach equilibrium.

To assess the treatment efficiency under continuous flow conditions, rapid small scale column tests (RSSCTs) (Figure 1) were carried out after batch experiments. The adsorption columns (ID = 2 cm, H = 16 cm) were filled with FeOOH granules (size: 0.25–0.5 mm) and fed with a 1 L/h Cr(VI) solution (EBCT = 3 min) in artificial NSF water and a 0.05 L/h of ISR solution. Taken into account that concentrations of typical Cr(VI) containing waters range between 2 and 100 μg/L (Kaprara et al. 2015a) an initial concentration of Cr(VI) solution of 100 μg/L was used. In order to dissociate FeOOH adsorption capacity for Cr(VI) from its contribution as a surface catalyst for Cr(VI) reduction by ISRs, FeOOH columns were saturated with Cr(VI) before addition of the ISR solution. Process pH was adjusted to 7.0 ± 0.1 and temperature at 20 ± 1 °C.

**X-ray absorption spectroscopy**

Samples of treated water were collected every 12 h and analyzed for residual chromium concentration by graphite furnace atomic absorption spectroscopy (GF-AAS) after appropriate preparation as described by Kaprara et al. (2013b). The residual ISRs concentration was determined as follows: in 100 mL of filtrate 5 mL of concentrated H₂SO₄ was added. The solution was then titrated with 0.05 N KMnO₄. The end-point of titration was defined by the persisted weak pink colour, indicating that the MnO₄⁻ ions were no longer being reduced. Competition of dissolved oxygen for ISRs oxidation was evaluated by monitoring its concentration using a WTW OXI96 meter. The investigation of Cr(VI) adsorption onto FeOOH was performed by performing XAFS measurements at the Cr-K-edge; batch experiments with increased Cr-loading were carried out in the absence of ISRs at pH 5.0 ± 0.1 and 7.0 ± 0.1. The Cr(VI) uptake mechanism by addition of Na₂S₂O₄ was studied for the FeOOH sample using the continuous flow configuration.

The EXAFS and XANES measurements were conducted at the BESSY-II storage ring of the Helmholtz Zentrum Berlin. The Cr-K-edge XAFS spectra of the studied FeOOH were recorded at the KMC-II beamline in the fluorescence yield mode. Cr(VI)- and Cr(III)-powder oxide samples (CrO₃ and
Cr(OH)₃, respectively) were recorded in the transmission mode and were used as references. The XANES data were normalized with the intensity of the impinging beam and subjected to linear background subtraction, followed by normalization to the edge jump. After subtraction of atomic absorption in the EXAFS spectra (Ravel & Newville 2005) and calculation of the theoretical phase and amplitude functions for the scattering paths (Rehr et al. 2010), curve fitting was carried out in both R- and k-spaces.

RESULTS AND DISCUSSION

Batch experiments revealed that the presence of FeOOH significantly improved the reduction of Cr(VI) by ISRs. The addition of 200 mg/L of FeOOH resulted in an increase of effectiveness greater than 30% for all ISRs tested (with respect to their performance in the absence of FeOOH) reaching almost 90% in the case of Na₂S (Figure 2). Na₂S₂O₄ and Na₂S presented the highest efficiency for Cr(VI) reduction through surface catalytic reaction. This has also been observed in the absence of a catalyst (Kaprara et al. 2015b). The significant increase in sulfide reactivity is probably attributed to the production of elemental sulfur as the primary product of sulfide oxidation, which further catalyses Cr(VI) reduction in the heterogeneous system increasing the Cr(VI) removal rate (Kim et al. 2007).

However, the residual strong unpleasant sulfur odour remains a significant disadvantage for Na₂S implementation in drinking water treatment.

In order to assess the FeOOH effectiveness to adsorb Cr(VI) under continuous flow conditions, which in turn can demonstrate its contribution as a surface catalyst, RSSCTs were initially performed without the addition of ISRs. The obtained experimental results showed that despite the low adsorption capacity of FeOOH (i.e. 0.2 mg Cr(VI)/g) towards Cr(VI) uptake at equilibrium concentration 10 μg/L, it is possible to achieve a residual Cr(VI) concentration down to sub-ppb levels (Figure 3(a)).
other reductants, such as NaHSO₃, Na₂S₂O₃ and Na₂S₂O₅, ity to decrease residual Cr(VI) concentration below the concentration less than or equal to 2.5 mg/L while Cr(VI) water. The fact that total Cr concentrations in the ef limit (50 μg/L) and 40 mg S/L. However, these reductants still failed to decrease Cr(VI) to single ppb levels, even at high doses (up to 40 mg S/L). However, these reductants still complied with the current European Community regulation and selectivity to Cr(VI) and dissolved oxygen. In par-

table 1 indicate that each ISR presents different reaction distribution of dissolved oxygen concentration (9.2 mg/L) to the sorption of the latter onto FeOOH.

It should be noted that the examined doses of ISRs (20 and 40 mg S/L) were dictated by the competitive contribution of dissolved oxygen concentration (9.2 mg/L) to the ISRs reducing potential for Cr(VI). Experimental results of Table 1 indicate that each ISR presents different reaction rate and selectivity to Cr(VI) and dissolved oxygen. In particular, adding a dose of 40 mg/L of NaHSO₃, Na₂S₂O₃ or Na₂S₂O₅ resulted in the diminishing of dissolved oxygen concentration less than or equal to 2.5 mg/L while Cr(VI) removal efficiency was limited to 72 ± 2%. In contrast, a dose of 20 mg/L for Na₂S₂O₄ succeeded Cr(VI) removal at sub-ppb levels with dissolved oxygen concentration to be maintained at higher values (4.5 mg/L) suggesting a higher selectivity to Cr(VI) removal due to the different dissociation paths of dithionite. Na₂S₂O₄ in water undergoes dissociation and disproportionation reactions to form sulfoxyl radical (SO₂⁻), sulfites (SO₃²⁻) or bisulfites (HSO₃⁻) and thiosulfates (S₂O₅²⁻), via Equations (1) and (2) (Amonette et al. 1994):

\[
2\text{SO}_2^{2-} \leftrightarrow 4\text{SO}_2^{*^\cdot} \quad (1)
\]

\[
4\text{SO}^{2*^\cdot} + \text{H}_2\text{O} \leftrightarrow 2\text{SO}_3^{2-} + \text{S}_2\text{O}_5^{2-} + 2\text{H}^{+} \quad (2)
\]

Sulfites and thiosulfates are oxidized to sulfate and the total reduction capacity of Na₂S₂O₄ is described by the simplified Equation (3):

\[
\text{S}_2\text{O}_4^{2-} \leftrightarrow 2\text{SO}_4^{2-} + 6\text{e}^- \quad (3)
\]

Cr(VI) reduction capacity of Na₂S₂O₄ should be attributed to sulfoxyl radicals formation (Szecsody et al. 2004). The dissociation products such as sulfites may significantly contribute to the long-term reduction of Cr(VI) through the reaction (4) (Ludwig et al. 2007):

\[
2\text{CrO}_4^{2-} + 4\text{SO}_3^{2-} + 6\text{H}^{+} \rightarrow 2\text{Cr(OH)}_3 + 2\text{SO}_4^{2-} + \text{S}_2\text{O}_6^{2-} \quad (4)
\]

It must be pointed out that a strong unpleasant sulfur odour accompanied the implementation of Na₂S in RSSCTs, suggesting that an additional treatment step should be followed when using Na₂S for Cr(VI) removal. This step must incorporate sulfide elimination which in turn is expected to increase capital and operational costs. Therefore, only Na₂S₂O₄ was qualified and further examined at column experiments.

Figure 3(b) presents the breakthrough curves of Cr(VI) uptake by FeOOH columns, initially saturated at the Cr(VI) equilibrium concentration of 100 μg/L for different Na₂S₂O₄ concentrations. As illustrated, the addition of 10 mg/L S-Na₂S₂O₄ solution gradually decreased Cr(VI)

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<th>ISR</th>
<th>ISR&lt;sub&gt;outf&lt;/sub&gt; mg/L</th>
<th>ISR&lt;sub&gt;outf&lt;/sub&gt; mg/L</th>
<th>Cr(VI)&lt;sub&gt;outf&lt;/sub&gt; μg/L</th>
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*Equilibrium concentrations after long-term experimental runs.*
breakthrough concentration below 10 μg Cr(VI)/L after the treatment of 35 × 10^3 bed volumes (BV), which maintained a loading value of 6 ± 2 μg/L up to the end of the experiment (100 × 10^3 BV). This result signifies that a dose of 10 mg/L S-Na_2S_2O_4 is the lowest possible for retaining Cr(VI) residual concentration lower than the upcoming regulation limit of 10 μg Cr(VI)/L. In contrast, for Cr(VI) reduction below 10 μg/L by Na_2S_2O_4 in the absence of FeOOH, a dose close to 40 mg S/L should be provided (Kaprara et al. 2015b). The addition of 15 and 20 mg S/L Na_2S_2O_4 resulted in residual Cr(VI) concentration below the method’s detection limit (1.4 μg/L), within 5 × 10^3 BV and 2.5 × 10^3 BV, respectively, that was maintained up to the treatment of 100 × 10^3 BV. It is clear that the addition of 15 mg/L S-Na_2S_2O_4 in a column of unsaturated FeOOH can provide an effluent Cr(VI) concentration at sub-ppb level even from the first bed volume of treated water. Moreover, it is important to spotlight the ‘buffer’ adsorption capacity of the FeOOH column. Experimental results during the implementation of 15 mg/L S-Na_2S_2O_4 dose showed that FeOOH column could uptake Cr(VI) for more than 3 days (∼1,500 BV) without the addition of Na_2S_2O_4.

The successful reduction of Cr(VI) to Cr(III) and uptake mechanism were further investigated using XAFS (XANES and EXAFS) spectroscopy at the Cr-K-edge. The XANES spectra of the studied samples, including reference Cr(VI) and Cr(III) compounds, are shown in Figure 4(a). The characteristic in all 3d-transition metals pre-edge absorption is related to electronic transitions sensitive to the oxidation state of Cr as well as the geometry and distortion of the bonding environment around Cr atoms in Cr-compounds. The pre-edge absorption is much more pronounced in tetrahedrally coordinated Cr(VI) as compared to Cr(III) compounds that mostly belong to octahedral geometries (Pantelouris et al. 2004).

As shown in Figure 4(a), a prominent pre-edge peak is present in the XANES spectra of FeOOH samples from the batch experiments in the absence of ISRs (#1, #2) and its intensity and position are similar to the respective in reference CrO_3, suggesting the presence of only tetrahedrally coordinated Cr(VI) species. On the contrary, a weaker pre-edge absorption is detected in the XANES spectrum of the FeOOH sample from the continuous flow configuration (#3, addition of 15 mg S/L Na_2S_2O_4); however, the intensity of the pre-edge peak is significantly stronger than the respective in reference Cr(OH)_3, indicating the presence of both Cr(III) and Cr(VI). Therefore, using the aforementioned XANES results, the Cr adsorption mechanism onto the studied FeOOH was investigated by curve-fitting of the Cr-K-edge EXAFS spectra. In samples #1 and #2, where no ISRs was added, it was assumed that Cr(VI) is physisorbed onto the FeOOH surface, while in the case of the column sample, it was assumed that Cr(VI) is partially reduced to Cr(III). In the latter case, Cr(III) forms inner sphere complexes, while Cr(VI) is involved only in outer sphere complexing. The Debye-Waller (σ^2) factors were iterated during the fitting in the first nearest neighbor (nn) shell, while in case of inner sphere formation, the Fe-compromised nn shells were constrained to be equal although allowed to vary during the fitting. The Fourier transforms (FTs) of the k^2 × χ(k) EXAFS spectra of the studied and reference samples are shown in Figure 4(b). The EXAFS analysis results disclosed that in the FeOOH samples in the absence of ISR, Cr(VI) forms outer sphere complexes; the fitted Cr−O interatomic distance is found equal to 1.63 Å (±0.01), indicating the presence of tetrahedrally coordinated Cr(VI) (Pandya 1994). In the case of samples from the continuous flow configuration, where Na_2S_2O_4 solution was added, both Cr(VI) and Cr(III) species are detected. More specifically, approximately 40% (±4) of chromium is hexavalent and forms outer sphere...
Na$_2$S$_2$O$_4$ dose (15 mg/L) can diminish Cr(VI) concentration. The remaining 60% is Cr(III) involved in bidentate corner-sharing (2°), bidentate edge sharing (2E) and monodentate corner-sharing (1V) geometries with the surface Fe-oxyhydroxyl group. In the first nn shell, the Cr(III)-O bond length is equal to 1.98 Å (±0.02), which suggests the presence of chemisorbed Cr(III) in octahedral coordination. In the next shells, the shortest Cr(III)-Fe distance (2.99 Å ± 0.03) results from edge sharing between Cr(III)-oxanions and surface Fe-oxyhydroxyl group (2E complexes), the intermediate (3.39 Å ± 0.04) represents Cr(III) linkage to free corner sites of edge-sharing Fe-octahedra and the longest (3.67 Å ± 0.05) corresponds to corner-sharing Cr(III) and Fe-octahedra (1 V complexes) (Fendorf et al. 1997). Thus, it is concluded that FeOOH can attract Cr(VI) to its surface through physisorption, while when Na$_2$S$_2$O$_4$ is added to the system, Cr(VI) is reduced to Cr(III) followed by chemisorption onto the FeOOH surface.

CONCLUSIONS

Research results confirmed the significant contribution of FeOOH on Cr(VI) removal by the addition of ISRs. Batch, as well as RSSCT, experiments qualified Na$_2$S$_2$O$_4$ and Na$_2$S as the best candidates for Cr(VI) removal. However, the application of Na$_2$S induces a strong unpleasant sulfur odour to treated water, indicating that Cr(VI) removal by Na$_2$S should be followed by an additional treatment step for the removal of residual sulfide. Testing under continuous flow configuration revealed that a dose of at least 10 mg S/L Na$_2$S$_2$O$_4$ should be applied in order to ensure the reduction of an initial 100 μg/L Cr(VI) concentration below the upcoming drinking water regulation limit of 10 μg/L. A higher Na$_2$S$_2$O$_4$ dose (15 mg/L) can diminish Cr(VI) concentration below the GF-AAS detection limit of 1.4 μg/L, while ensuring a ‘buffer’ uptake capacity for more than 3 d (~1.500 BV), i.e. without the need of any supplementary addition of Na$_2$S$_2$O$_4$. XAFS analysis results at the Cr-K-edge revealed that chromium uptake onto FeOOH proceeds via both physisorption and chemisorption. Cr(VI) forms outer sphere complexes, while Cr(III) is involved in 2E, 2C and 1 V inner sphere complexing with the surface Fe-oxyhydroxyl groups. Conclusively, Cr(VI) removal at sub-ppb level by catalytic reduction onto an iron oxy-hydroxide surface, consisting mainly of oxyhydroxyl sulfate schwertmannite ([Fe$_{16}$O$_{16}$(OH)$_{10}$(SO$_4$)$_3$ · 10H$_2$O], is a very promising technology with the additional advantage of a ‘buffer’ uptake capacity.

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