Continuous Flow Process of Cr(VI) Removal from Drinking Water through Reduction onto FeOOH by ISRs

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Abstract

In this study the implementation of an iron oxy-hydroxide (FeOOH) as a surface catalyst for the reduction of Cr(VI) by inorganic sulphur reductants (ISRs) was investigated. Batch Cr(VI) removal tests, performed to evaluate and compare the efficiency of ISRs in the presence of FeOOH, qualified Na₂S₂O₄ as the optimum ISR for drinking water treatment. Application of Na₂S₂O₄ in continuous flow Rapid Small Scale Column Tests (RSSCTs), by practicing FeOOH as adsorbent at pH 7±0.1 and using artificial (resembling natural) water matrix, verified the high potential of this system for Cr(VI) removal at sub-ppb level, since a 15 mg S/L Na₂S₂O₄ dose diminished an initial Cr(VI) concentration of 100 µg/L below the method's detection limit of 1 µg/L at least for 10⁵ bed volumes. EXAFS study showed that Cr(VI) forms outer sphere complexes, while Cr(III) is involved in ²E, ²C and ¹V geometries with the surface Fe-oxyhydroxyl groups. It is, therefore, concluded that FeOOH attracts Cr(VI) to its surface through physisorption, offering a solid surface that promotes the transfer of electrons through bridging ions, and thus, when Na₂S₂O₄ is added to this system, Cr(VI) is reduced to Cr(III), which is subsequently chemisorbed (and removed) onto the FeOOH surface.

Keywords

Cr(VI) removal, drinking water, inorganic sulphur reductants, iron oxy-hydroxides, EXAFS study

INTRODUCTION

The occurrence of Cr(VI) in drinking water resources, whether originating from natural or anthropogenic processes, has attracted wide publicity especially during the last few years. Relevant reports indicate that the problem of non-negligible Cr(VI) concentrations may concern a large number of sites worldwide (Morrison et al., 2009; Kaprara et al., 2015; Kazakis et al., 2015). The initial results from the respective epidemiological studies on the toxicity issue related to Cr(VI) exposure by water consumption (Costa, 2003; Linos et al., 2010) suggest that the re-evaluation of current regulation limit of 50 μ g/L (total chromium) is very likely to take place in the near future. This tendency is signified by the establishment of the very strict maximum level of 10 μ g Cr(VI)/L by the State of California in July 1st, 2014 (California Regulations Related to Drinking Water, 2014).

The potential for a new/lower Maximum Permissible Concentration (MPC) regulation limit enforces the development of novel treatment technologies that can ensure Cr(VI) removal down to single ppb concentrations, can be safely applied in drinking water treatment, can 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 (Mohan et al., 2006), use of biosorbents (Cimino et al., 2000) or metal oxy-hydroxides (Kaprara et al., 2016; Pinakidou et al., 2016), ion-exchange (Dabrowski et al., 2004), membrane separation (Korus et al., 2009), electrodialysis (Nataraj et al., 2007) and phytoremediation (Cervantes et al., 2001). Among them, 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) (Melitas et al., 2001; Niu et al., 2005), ferrous iron salts (Mitrakas et al., 2011), and various inorganic sulphur reductants (ISRs) (Kim et al., 2001, Kaprara et al., 2015b). The method of ZVI use, although very effective in Cr(VI) reduction, suffers from surface passivation, while it enriches the treated water with dissolved ferrous ions, which frequently can overpass the respective drinking water regulation limit. The reduction of Cr(VI) by ferrous iron salts and the 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 as major shortcoming the production of sludge that requires subsequent dewatering and disposal treatment.

The research on Cr(VI) reduction by the use of Inorganic Sulphur Reductants (ISRs) has presented interesting results and led scientists to examine the possible increase of their reactivity though surface catalysis. Kim and co-workers (2007) studied the reaction kinetics of Cr(VI) reduction by hydrogen sulphide through the goethite surface catalytic reaction. They have concluded that surface ferrous irons, produced as a result of goethite surface reduction, following sulphide adsorption, played a key role for the Cr(VI) reduction as the primary electron donors through the Fe(II)–Fe(III) cycle. Elemental sulphur was determined as the stabilized final product of sulphide and it worked as additional catalyst, increasing the Cr(VI) reduction rate at a later stage. The results of a subsequent research, investigating the facilitating role of biogenically produced schwertmannite mineral in the reduction of Cr(VI) by sulphide (Zhou et al., 2012) demonstrated that this mineral was found to markedly accelerate the reduction/removal of Cr(VI) by sulphide and the rates of the reaction were increased by 11, 8 and 6 times at pH 7.5, 8.0 and 8.8, respectively, in comparison with the control samples (i.e. without the presence of schwertmannite). It was concluded that the catalysis of schwertmannite resulted from the activated Fe(III) on its surface, serving as a "bridge" for the transportation of electrons between sulphide and Cr(VI) and leading to the improved reduction of Cr(VI) by sulphide.

Biogenetic jarosite was also tested as a surface catalyst for Cr(VI) reduction by sulphide (Xu et al., 2013); in this case the authors suggest that a cycle process of converting Fe(III) to Fe(II) can occur on the surface of jarosite and markedly accelerate the reduction of Cr(VI) by sulphide. Another approach (Taylor et al., 2000) reports on the removal of chromate by dithionite-reduced clays (Taylor et al., 2000). Chromium K-edge X-ray absorption near edge structure (XANES) suggested that clays containing Fe(II) can reduce Cr(VI) to Cr(III), immobilizing Cr 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 reduced Cr(VI) to Cr(III), it did not immobilize Cr on clay surfaces. Nevertheless, the capacity of clays to reduce Cr(VI) was correlated with the ferrous iron content of the clays (Taylor et al., 2000). Conclusively, the ISRs studied for Cr(VI) removal through surface catalysis are mainly sulphide and dithionite and their efficiency, to best of our knowledge, was evaluated only by batch mode experiments.

Previous findings of the authors on chromate reduction by ISRs (Kaprara et al., 2015b) has provided the motivation of this study, which 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 the full-scale implementation of the process. The reductants examined in this case were NaHSO₃, Na₂S₂O₃, Na₂S₂O₄, Na₂S₂O₅ and Na₂S, while a laboratory synthesized FeOOH, served as a surface catalyst. The Cr(VI) reduction reaction and the sorption mechanism of Cr was investigated by using Extended- (EXAFS) and Near-edge (XANES) X-Ray Absorption Fine Structure spectroscopies at the Cr-*K*-edge.

Iron precursor	Synthesis _{E4}		Fe	SO ²⁻			Surface		Pore	
	pН	Redox mV	wt.%	wt.%	IEP	PZC	Charge, mmol [OH]/g	Area, m²/g	Volume, mL/g	Diameter, Å
FeSO ₄	4	410	50.5	14.8	7.1	3.0	2.8	125	0.18	30

Table 1. Parameters of synthesis and properties of synthesized FeOOH.

MATERIALS AND METHODS

Reagents

A 500 mg/L Cr(VI) stock solution was prepared from reagent grade $K_2Cr_2O_7$. Working standards were freshly prepared by proper dilution of the stock solution in artificial water with composition close to that of natural ones, which was prepared according to National Sanitation Foundation (NSF) standard by dissolving 252 mg NaHCO₃, 12.14 mg NaNO₃, 0.178 mg NaH₂PO₄·H₂O, 2.21 mg NaF, 70.6 mg NaSiO₃·5H₂O, 147 mg CaCl₂·2H₂O and 128.3 mg MgSO₄·7H₂O in 1 L of distilled water. For each ISR examined, 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 mainly consisting of oxyhydroxyl sulfate schwertmannite ([Fe₁₆O₁₆(OH)₁₀(SO₄)₃ ·10H₂O), produced by the method of Tresintsi et al. (2012), was used as the surface catalyst. Details of synthesis parameters and the specific properties of synthesised oxyhydroxyl sulfate, abbreviated hereafter as FeOOH, are presented in Table 1.

Experimental procedure

Batch experiments were conducted at $20\pm1^{\circ}$ C by using 200 mL of 100 µg/L Cr(VI) in artificial water. The influence of FeOOH presence in Cr(VI) reduction was studied at pH 7.0±0.1 for an ISR concentration equivalent to 10 mg S/L and for 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.



Figure 1. Experimental set-up for continuous flow process.

Table 2. FeOOH samples for performing Cr-*K*-edge XAFS experiments (treatment configuration, water pH and Cr-loading).

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Sample	Water pH	Cr-loading (mg/g)			
Batch configuration					
#1	5±0.1	45.1			
#2	7.0±0.1	37.6			
Continuous flow RSSCT with a dose of 15 mg S/L $Na_2S_2O_4$					
#3	7.0±0.1	3.9			

To assess the treatment efficiency under continuous flow conditions, Rapid Small Scale Column Tests (RSSCTs) were practiced. The adsorption columns (ID= 2 cm, H= 16 cm) were filled with FeOOH granules (size: 0.25-0.5 mm) and fed with 1 L/h of 100 μ g/L Cr(VI) solution (EBCT= 3 min) in artificial NSF water and 0.05 L/h of ISR solution (Figure 1). 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 the addition of ISR solution. Process pH was adjusted to 7.0±0.1 and temperature at 20±1°C.

Samples of treated water were periodically collected and analyzed for the residual total chromium concentration as follows: 50 mL of water effluent were acidified with 0.1 mL HNO₃ and 20 mg NaHSO₃ were added for residual Cr(VI) reduction (Tziarou et al., 2015). Chromium concentration was calculated through a Cr(III) calibration curve by Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS). The detection limit of the method, calculated from 7 replicates of 2-5 ug/L, was estimated to be 1ug/L. It must be spotlighted that the residual Cr(VI) concentration was determined by GF-AAS, due to interference of residual ISRs concentration with the commonly applied diphenyl-carbazide spectrophotometric analytical determination method. The residual ISRs concentration was determined as follows: in 100 mL of filtrate 5 mL of concentrated H₂SO₄ were added and titrated with 0.05 N KMnO₄. The end-point of the titration was defined by the persisted weak pink color, indicating that the MnO₄⁻ ions were no longer being reduced. Dissolved oxygen concentration was monitored by using a WTW OXI96 meter. The investigation of Cr(VI) adsorption onto FeOOH was performed by Cr-K-edge XAFS measurements; batch experiments with increased Cr-loading were carried out in absence of ISRs at pH 5.0±0.1 and 7.0±0.1. Cr(VI) uptake mechanism by Na₂S₂O₄ addition was studied for the FeOOH sample by using the continuous flow configuration (Table 2).

X-Ray Absorption Spectroscopy

The Extended (EXAFS) and Near-edge (XANES) X-ray adsorption fine structure 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 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 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 et al., 2005) and calculation of the theoretical phase and amplitude functions for the scattering paths (Rehr at 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 more than 30% for all the ISRs tested, reaching almost 90% for Na₂S (Figure 2).



Figure 2. Influence of FeOOH presence in Cr(VI) removal by ISRs, studied in batch mode experiments (experimental conditions: initial Cr(VI): 100 μ g/L, C_{ISR}: 10 mg S/L, pH: 7.0 \pm 0.1, t: 24 h, T: 20 \pm 1°C).

 $Na_2S_2O_4$ and Na_2S presented the highest efficiency for the reduction of Cr(VI) through surface catalytic reaction, as also observed in the absence of catalyst (Kaprara et al., 2015b). The significant increase in sulphide reactivity is probably attributed to the production of elemental sulphur, as the primary product of sulphide oxidation, which further catalyses Cr(VI) reduction in the heterogeneous system, increasing the Cr(VI) reduction rate (Kim et al., 2007; Lan et al., 2007). However, the residual strong unpleasant sulphur odour presents a significant drawback for Na_2S implementation in drinking water treatment.

In order to assess the FeOOH effectiveness to adsorb Cr(VI) under continuous flow conditions, which in turn can prove its contribution as a surface catalyst, RSSCTs were initially performed without the addition of ISRs. The obtained experimental results showed that, despite its low adsorption capacity (i.e. 0.25 mg Cr(VI)/g) towards Cr(VI) uptake at equilibrium concentration 10 μ g/L), FeOOH presents the ability to decrease residual Cr(VI) concentration down to sub-ppb levels (Figure 3).



Figure 3. Breakthrough curve of Cr(VI) adsorption at FeOOH column (experimental conditions: initial Cr(VI): 100 μ g/L, pH: 7.0 \pm 0.1, EBCT: 3 min, particle size: 0.25-0.5 mm, T: 20 \pm 1°C).

ICD	ISR inflow	ISR _{outflow}	Cr(VI) outflow	O _{2outflow}
ISK	mg S/L	mg S/L	μg/L	mg/L
	20	8	47	3.5
NaHSO ₃	40	26	26	2.5
	20	14	50	3.5
$Na_2S_2O_3$	40	33	28	2.5
	20	13	ND	4.5
$Na_2S_2O_4$	40	31	ND	2.5
	20	4	42	1.5
$Na_2S_2O_5$	40	21	29	<1
	20	<1	ND	<1
Na ₂ S	40	<1	ND	<1

Table 3. Residual^{*} Cr(VI) and ISR concentration during RSSCT experiments, using FeOOH (experimental conditions: initial Cr(VI): 100 μ g/L, pH: 7.0 \pm 0.1, EBCT: 3 min, particle size: 0.25-0.5 mm, T: 20 \pm 1°C).

* Equilibrium concentrations after long-term experimental runs

Continuing the saturation of FeOOH column with Cr(VI), ISRs solution was added to the system at doses of 20 and 40 mg S/L. Data obtained by RSSCTs for each ISR examined are presented in Table 3. In consistence with the respective observations from the batch mode experiments, $Na_2S_2O_4$ and Na_2S presented the highest efficiency for Cr(VI) reduction, holding the ability to decrease residual Cr(VI) concentration below the method's analytical detection limit of 1 µg/L. In contrast, other reductants, such as NaHSO₃, $Na_2S_2O_3$ and $Na_2S_2O_5$, failed to decrease Cr(VI) to single ppb levels, even at high doses (up to 40 mg S/L). However, they still complied with the current European Community regulation limit, regarding Cr(VI) presence in drinking water.

It has to be noted that Na_2S implementation in RSSCTs was accompanied by a strong unpleasant sulphur odour, implying that Cr(VI) removal by Na_2S should be followed by an additional treatment step, considering sulfide elimination that in turn is expected to increase capital and operational costs. Therefore, only $Na_2S_2O_4$ was qualified and further examined at column experiments.



Figure 4. Breakthrough curves of Cr(VI) uptake by FeOOH column for different $Na_2S_2O_4$ concentrations (experimental conditions: initial Cr(VI): 100 µg/L, pH: 7.0±0.1, EBCT: 3 min, particle size: 0.25-0.5 mm, T: 20±1°C).

Figure 4 presents the breakthrough curves of Cr(VI) uptake by FeOOH column, 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) breakthrough concentration bellow 10 µg Cr(VI)/L after the treatment of 35x10³ Bed Volumes (BV), which maintained a loading value of $6\pm 2 \mu g/L$ up to the end of this experiment (100×10^3 BV). This result signifies that a dose of 10 mg/L S-Na₂S₂O₄ is the lowest possible that ensures residual Cr(VI) concentration less than the upcoming regulation limit of 10 µg Cr(VI)/L. In contrast, for Cr(VI) reduction below 10 µg/L by Na₂S₂O₄ in absence of FeOOH, a dose close to 40 mg S/L should be provided (Kaprara, 2015). The addition of 15 and 20 mg S/L Na₂S₂O₄ resulted in residual Cr(VI) concentration below the method's detection limit (1 μ g/L), within 3x10³ BV and 2.5x10³ BV, respectively, that was maintained up to the treatment of 100×10^3 BV. It is obvious that the addition of 15 mg/L S-Na₂S₂O₄ in a column of unsaturated FeOOH can ensure 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 FeOOH column. Experimental results during the implementation of 15 mg/L S-Na₂S₂O₄ dose showed that FeOOH column could uptake Cr(VI) for more than 3 days (~1500BV) without the addition of $Na_2S_2O_4$.

The successful reduction of Cr(VI) to Cr(III) and the mechanism of uptake was further investigated, using XANES spectroscopy at the Cr-*K*-edge. The spectra of the studied samples, including reference Cr(VI) and Cr(III) compounds, are shown in Figure 5(a). The characteristic in all 3d-transition metals pre-edge absorption is related to electronic transitions sensitive to the valence, geometry and distortion of Cr-compounds; it is much more pronounced in tetrahedrally coordinated Cr(VI), as compared to Cr(III) compounds that mostly belong to octahedral geometries (A. Pantelouris et al., 2010).



Figure 5. (a) Cr-*K*-edge XANES spectra of the studied FeOOH and reference $Cr(OH)_3$ and CrO_3 . (b) Fourier transforms (FTs) of the Cr-*K*-edge EXAFS spectra of the studied FeOOH. The figures include the spectra of reference for $Cr(OH)_3$ and CrO_3 . The experimental data and the fitting are shown in thin black and thick (black or coloured) lines, respectively.

As shown in Figure 5(a), a prominent pre-edge peak is present in the XANES spectra of FeOOH samples from the batch experiments in absence of ISRs (#1, #2) and its intensity and position are similar to the respective in reference CrO_3 , suggesting the presence of only Cr(VI) species in tetrahedral coordination. On the contrary, a weaker pre-edge absorption is detected in XANES spectrum of the FeOOH sample from the continuous flow configuration (#3, addition of 15 mg/LNa₂S₂O₄); however, a significantly higher intensity than the respective in reference Cr(OH)₃ was noticed, indicating the existence of both Cr(III) and Cr(VI) species. Therefore, using the aforementioned XANES results, the Cr adsorption mechanism onto the studied FeOOH was investigated by curve-fitting of 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 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 in outer sphere complexing. The Debye-Waller (σ^2) factors were iterated during the fitting in the 1st nearest neighbor (nn) shell, while in case of inner sphere formation, the Fe-comprised nn shells were constrained to be equal, though allowed to vary during the fitting. The Fourier Transforms (FTs) of the $k^2 \times \gamma k$) EXAFS of the studied and reference samples are shown in Figure 3(b). Indeed, the EXAFS analysis results disclosed that in the FeOOH samples in 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 et al, 1994). In the case of samples from continuous flow configuration, where Na₂S₂O₄ solution was added, the EXAFS results reveal the presence of both Cr(VI) and Cr(III) species. More specifically, approximately 40% (±4) of chromium is hexavalent and forms outer sphere complexes. The rest 60% is Cr(III) involved in bidentate cornersharing $({}^{2}C)$, bidentate edge sharing $({}^{2}E)$ and monodentate corner-sharing $({}^{1}V)$ geometries with the surface Fe-oxyhydroxyl groups. In the 1st 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 (2.99ű0.03) results from edge sharing between Cr(III)-oxyanions and surface Fe-oxyhydroxyl groups (²E complexes), the intermediate $(3.39\text{\AA}\pm0.04)$ represents Cr(III) linkage to free corner sites of edge-sharing Fe-octahedra and the longest (3.67ű0.05) corresponds to corner-sharing Cr(III)- and Fe-octahedra (¹V complexes) (S. Fendorf et al., 1997). Thus, it is concluded that FeOOH can attract Cr(VI) to its surface through physisorption, while when Na₂S₂O₄ is added to the system Cr(VI) is reduced to Cr(III) and subsequently chemisorbed onto the FeOOH surface.

CONCLUSIONS

Research results confirmed the significant contribution of FeOOH on Cr(VI) removal by the presence/addition of ISRs. Batch, as well as RSSCT experiments, qualified Na₂S₂O₄ and Na₂S for Cr(VI) removal; however, the application of latter induces a strong unpleasant sulphur odour to treated water, implying that Cr(VI) removal by Na₂S should be followed by an additional treatment step, regarding the removal of residual sulfide. Testing under continuous flow configuration revealed that a dose of, at least 10 mg S/L Na₂S₂O₄ 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. Higher Na₂S₂O₄ dose (15 mg/L) can diminish Cr(VI) concentration below the GF-AAS detection limit of 1 µg/L, while ensuring a "buffer" uptake capacity for more than 3 d (~1.500 BV), i.e. without any supplementary addition of Na₂S₂O₄. EXAFS study showed 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 ¹V geometries with the surface Fe-oxyhydroxyl groups. Conclusively, Cr(VI) removal at sub-ppb level by catalytic reduction onto an iron oxy-hydroxide surface, mainly consisting of oxyhydroxyl sulfate schwertmannite ([Fe₁₆O₁₆(OH)₁₀(SO₄)₃ ·10H₂O), is a very promising technology, presenting the additional advantage of a "buffer" uptake capacity.

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