Effect of Organic Matter on Cr(VI) Removal from Groundwaters by Fe(II) Reductive Precipitation for Groundwater Treatment

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Abstract: Due to its toxicity, Cr(VI) is undesirable in groundwater. Its chemical reduction to Cr(III) species, followed by precipitation is the most widely practiced treatment technique for the removal of Cr(VI) from polluted waters. The resulting Cr(III) species present low solubility, is much less toxic, and can be subsequently removed either by precipitation, or by adsorption onto iron oxy-hydroxides and co-precipitation. The effects of several parameters, such as the pH value of water to be treated, the applied Fe(II) dose, and the presence of appropriate mineral surfaces, are well investigated and understood. However, the impact of the presence of humic acids (HAs) in this process has only been considered by rather few studies. The main aim of this study was to determine the effect of humic substances on Fe(II) reductive precipitation of Cr(VI) within a pH range relevant for drinking water treatment. Jar test experiments were performed, using artificial groundwater of defined composition and initial Cr(VI) concentration 100 µg/L, ferrous sulphate dosages 0.25–2 mg Fe(II)/L, and pH values 6.5–8. It was found that Cr(VI) and total chromium (Cr(total)) can be reliably removed in the absence of HAs in the tested pH range with the addition of Fe(II) dosage of 1 mg Fe(II)/L. Further on, the results indicated that the reduction of Cr(VI) is only slightly affected by the presence of HAs. However, increased residual total Cr concentrations were found at lower Fe(II) dosages and/or higher pH values. Additionally, the removal of the Cr(III) species formed during Cr(VI) reduction was strongly inhibited by the presence of HAs under the examined experimental conditions, since residual concentrations higher than 60 µg/L were determined. The results of this study will have implications to the ongoing discussion of a new, stricter, European Union regulation limit, regarding the presence of total chromium in drinking water.

Keywords: Cr(VI) removal; Fe(II) dose; Cr(total); humic acids; groundwater

1. Introduction

Chromium and its compounds present unique properties, which are used in a broad range of industrial applications, such as leather tanning, pigment production, gas/oil well drilling, etc. [1]. Due to this wide range of applications, Cr is discharged into the environment by several sources and its presence in widely documented in several groundwaters and soils [1,2]. Moreover, hexavalent chromium (Cr(VI)) can occur naturally in soils and groundwaters. Increased Cr(VI) concentrations
in aquifers can be formed due to erosion of ophiolithic and metamorphic rocks, as reported by Kaprara et al. (2015) [3] and Kazakis et al. (2015) [4]. The toxicity of chromium is mainly related to Cr(VI), while the second important redox species, the trivalent chromium (Cr(III)), is considered to be 100 times less toxic [5]; Cr(VI) is toxic, mutagenic, and carcinogenic to humans by inhalation and oral intake [6]. The other redox species are not stable and therefore, not relevant for treatment processes [7]. The higher relevance of Cr(VI), when compared to Cr(III), can be also explained by the different solubility in the pH range of drinking water. While Cr(III) has a low solubility (<1 µg/L) due to the formation of insoluble hydroxide ($K_{sp}$ for Cr(OH)$_3$ = $6.3 \times 10^{-31}$ [8,9]), in the pH range between 7 and 10, Cr(VI) is highly soluble. The most important redox species at pH values >6.5 is chromate (CrO$_4^{2-}$), while Cr$_2$O$_7^{2-}$ and HCrO$_4^{-}$ are mainly relevant to pH values <6.5 [10] and its speciation depends on Cr(VI) concentration and pH value.

Chromium is an important parameter, regarding its presence, in drinking water regulations. However, there is only a limit concentration value for the presence of total chromium (Cr(total)). For example, a value of 50 µg Cr(total)/L is defined as the maximum allowable limit in the drinking water regulations of European Union [11]. However, due to recent findings about the toxicity of Cr(VI) for oral intake [5], there is an ongoing discussion in research and policy about introducing lower limit values for Cr(total), as well as a separate concentration limit value for Cr(VI). At the moment, only the US state of the California has already established a limit value of 10 µg/L for Cr(VI), which has been in place since 1 July 2014 [12].

Reductive precipitation, commonly by adding Fe(II), is a well-known treatment process for the removal of Cr(VI) from water. Firstly, Cr(VI) is reduced to Cr(III), while Fe(II) is oxidized to ferric iron (Fe(III)) [13]. This step is displayed in the chemical reaction (1),

$$\text{Cr(VI)}_{aq} + 3 \text{Fe(II)}_{aq} \rightarrow \text{Cr(III)}_{aq} + 3 \text{Fe(III)}_{aq} \quad (1)$$

Afterwards, Cr(III) and Fe(III) precipitate either as combined hydroxides, or Cr(III) is adsorbed to produced ferric hydroxides [13], as shown by the reaction (2).

$$x \text{Cr(III)} + (1 - x) \text{Fe(II)} + 3\text{H}_2\text{O} \rightarrow \text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s}) + 3\text{H}^+ \quad (0 < x < 1) \quad (2)$$

The type of precipitate is hereby dependent on the specific pH value [14]. Moreover, the reduction of Cr(VI) by Fe(II) has a minimum reaction rate at pH 4 and the reaction rate increases with increased pH value [15]. Thus, a fast reaction for the commonly encountered pH range in drinking water (6–8.5) is expected [13]. From the respective chemical Equation (1), it is further derived that stoichiometrically a molar ratio of 1 [Cr(VI)] to 3 [Fe(III)] is needed for the optimum removal of Cr(VI) [13]. However, this molar ratio may vary in a relatively broad range, considering the findings of different researchers. A molar ratio [Cr(VI)]:[Fe(II)] = 1:3 was found by several researchers in batch tests at pH range 6.0–8.0 [16] and 3.5–6.0 [17], as well as in full scale application at pH range 3.7–4.7 [18]. In contrast, higher molar ratios up to 1:10 were also found at pH range 6.5–8.2 [19]. Moreover, the process is influenced by several parameters, such as the presence of oxygen, temperature, and specific water composition [13,14].

Only a few studies have investigated the combined effects of humic acids (HAs) and Fe(II) presence. Buerge and Hug [20] claimed that the removal of Cr(VI) by different Fe(II)-organic ligand complexes depends strongly on the characteristics of the used ligand, for example, on its capacity to stabilize Fe(II) and Fe(III) in an aqueous solution [20]. Depending on the pH of the water, the presence of other ligands that stabilize Fe(III) (e.g., by the creation of bi- and/or multia-dentate carboxylates) may accelerate the respective reaction, whereas ligands that can stabilize Fe(II) (e.g., phenanthroline) may even stop the reductive reaction of Cr(VI) [20]. Further on, the removal of Cr(VI) with a combination of Fe(II) and humic substances was previously tested by Hori et al. [21] and Agrawal et al. [22]. They found a catalysing effect on the reductive reaction by the presence of HAs at pH values lower than 6, through a cycling process of iron [21]. Fe(II) is in a first step oxidized by Cr(VI) and the formed
Fe(III) was subsequently reduced by humic substances so that Fe(II) was again available for Cr(VI) reduction. Due to this, the removal of Cr(VI) was found to be effective at Fe(II) dosages lower than the aforementioned 1:3 molar ratio ([Cr(VI)]:[Fe(II)]) \cite{21,22}. The kinetics of a combined reduction by the co-presence of Fe(II) and HAs are hereby different from the kinetics of experiments where only Fe(II) or only HAs were available \cite{22,23}. It is claimed that this effect is dependent on the specific type of humic substance \cite{22} and it is also limited by the lower solubility of Fe(III) at higher pH values, which would lead to a precipitation of ferric hydroxide(s), so that no further recycling of Fe can take place \cite{24}. Therefore, there is a need for further investigation, regarding the effect of HAs or of natural organic matter on Cr(VI) and on total chromium removal by the application of Fe(II) reductive precipitation. In this study, the main objective was to evaluate the impact of dissolved organics carbon (DOC), present as humic acids (HAs), in synthetic groundwater spiked with Cr(VI) on the removal of Cr(VI) and of total chromium by applying the Fe(II) reductive precipitation treatment. The synthetic groundwater according to the NSF-challenge water from the National Sanitation Foundation (NSF International) is a model for natural groundwater and has already been applied in many other studies.

Additionally, the removal behaviour was compared with experiments conducted using tap water containing natural DOC and spiked with Cr(VI).

2. Materials and Methods

2.1. Examined Waters

Two different types of water were examined. Unless otherwise stated, all experiments were performed using NSF water; its composition is displayed in Table 1 and is based on the composition of the NSF-challenge water, as described by Amy et al. \cite{25}. Additional experiments were performed with tap water from northern Germany. The groundwater source of the tap water naturally contains organic matter. Due to the high initial iron concentration, the treated water was used for the experiments, which has a DOC concentration of 1.3 mg/L. The pH value of water was 7.8 and it was not adjusted prior to the experiments.

| Substance       | NSF-Water | Tap Water |
|-----------------|-----------|-----------|
| Na\(^+\) (mg/L) | 88        | 26        |
| Mg\(^{2+}\) (mg/L) | 12.5     | 4         |
| Ca\(^{2+}\) (mg/L) | 40       | 67        |
| HCO\(_3^-\) (mg/L) | 183      | -         |
| SO\(_4^{2-}\) (mg/L) | 50       | 15        |
| Cl\(^-\) (mg/L) | 71        | 35        |
| NO\(_3^-\) (mg/L) | 2        | <0.4      |
| F\(^-\) (mg/L) | 1         | 0.15      |
| SiO\(_2^-\) (mg/L) | 20       | Not specified |
| SO\(_4^{2-}\) (mg/L) | -        | 15        |
| Carbonate alkalinity (mmol/L) | Not specified | 1.7 |

2.2. Set-Up and Procedure

All experiments were conducted as jar test experiments using two different set-ups (compare Table 2). For set-up A, jar tests were performed with 1.8 L batch volume, a Hei-Torque Precision 100 (programmable) stirrer (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany), and a 2 L beaker (tall shape) with baffles (according to DVGW W 218 standard \cite{26}). For set-up B, a jar test apparatus with six stirrers (Aqualytic, Dortmund, Germany) was used with 1 L batch volume in 1 L beakers (tall shape).
The jar test procedure was identical for both set-ups. The pH value of artificial groundwater was adjusted prior to the addition of Fe(II) with drops of 0.2 N H$_2$SO$_4$ using a WTW pH 340i pH meter (Xylem Analytics Germany Sales GmbH & Co. KG, Weilheim, Germany) for set-up A and with a Crison MultiMeter MM 41 (Crison Instruments, Barcelona, Spain) for set-up B. For the experiments without the presence of HAs, rapid stirring was performed for 2 min after the addition of Fe(II) (Figure 1a)—note that, if necessary, the pH was consistently adjusted during this stirring phase. Afterwards, slow stirring was performed for another 60 min. For the experiments with the presence of HAs, an additional 2 min of rapid stirring was added to the procedure, prior to the addition of Fe(II) based on DVGW (Deutscher Verein des Gas- und Wasserfachs e.V.) working sheet W 218 [26] (Figure 1b). Although operational parameters differ slightly between the two set-ups, random tests showed very good comparability between both approaches.

All samples received after the performance of experiments and prior to analytical determinations were filtered using a 0.45-µm filter directly after sampling to remove precipitates. For experimental set-up A, a cellulose nitrate filter and a vacuum filtration unit was used, whereas for set-up B, a nitro-cellulose mixed ester filter and a Buchner funnel was applied.

Stock solutions of Cr(VI) were prepared from potassium dichromate salt (K$_2$Cr$_2$O$_7$, for set-up A: Carl Roth (≥99.5% p.a.), for set-up B: Carlo Erba Reagents (99%)). FeSO$_4$·7H$_2$O was used for stock solutions of Fe(II) (for set-up A: Merck KGaA (min 99.5%), for set-up B: Chem-Lab NV (99%)). Stock solutions of Fe(II) were prepared in acidified ultrapure water during every experimental day.
and degassed with nitrogen to avoid oxidation. The same stock solution of HAs was used for both experimental set-ups. The stock solution was prepared by adding 20 g of HA salts (Carl Roth) to 2 L of ultrapure water. The solution was stirred for at least 12 h and filtered through a 0.45-µm filter. The stock solution had a dissolved organic carbon (DOC) content of 1.74 g/L. All other chemicals used during the experiments were at least of reagent grade.

2.3. Tested Reaction Conditions

The concentration of Cr(VI) was kept constant at 100 µg/L for all the experiments performed. For the experiments without the presence of HAs, ferrous sulphate dosages of 0.25, 0.5, 1.0, 1.5, and 2.0 mg Fe(II)/L (molar ratios from 1:2.3 to 1:18.6 [Cr(VI)]:[Fe(II)] were tested in a pH range of 6.5–8. Most experiments were performed with artificial groundwater, termed as NSF water (see Section 2.1), spiked with Cr(VI). All experiments without the presence of humic acids were performed by using experimental set-up A. Tables 3 and 4 display a detailed overview of which set-up was used in each experiment. Experiments with the presence of HAs were performed at pH values of 6.5, 7, and 8 at ferrous sulphate dosages of 0.25, 1.0, and 2.0 mg Fe(II)/L. HA concentrations are expressed as mg DOC/L and concentrations of 1, 3, 5 mg DOC/L were examined. The removal of chromium was additionally tested in tap water containing natural organic matter (tap water A, used for comparison in Section 2.3).

| HA (mg DOC/L) | 0.25 mg Fe(II)/L | 1 mg Fe(II)/L | 2 mg Fe(II)/L |
|---------------|-----------------|---------------|---------------|
| 0             | A               | A             | A             |
| 1             | A *, B          | A *           | A, B          |
| 3             | B               | A *           | A, B*         |
| 5             | A, B *          | A *           | A, B          |

Note: * two repetitions.

| HA (mg DOC/L) | pH 6.5 | pH 7  | pH 8  |
|---------------|--------|-------|-------|
| 0             | A      | A     | A     |
| 1             | B *    | A, B  | A, B *|
| 3             | -      | A, B  | -     |
| 5             | B *    | A, B  | B *   |

Note: * two repetitions.

2.4. Analytical Methods

Cr(total) was measured with Inductively Coupled Plasma-Mass Spectrometry (NexION 300D ICP-MS, PerkinElmar, Waltham, Massachusetts, USA, [27]) for the experiments performed the set-up A and with Graphite Furnace-Atomic Adsorption Spectroscopy (AAnalyst 800, PerkinElmer, Waltham, Massachusetts, USA [28]) for the experiments performed with set-up B. The detection limit for Cr(total) is 0.4 µg/L for ICP-MS and 1 µg/L for GF-AAS. Cr(VI) was measured spectrophotometrically, following its complexation with 1,5-Diphenylcarbazide, according to method 3500 Cr B, as described by the American Public Health Association [29]. The respective measurements for set-up A were performed with a UV 1601 photometer (Shimadzu Deutschland GmbH, Duisburg, Germany) in a 100 mm cell; in this case, the detection limit was 1.5 µg/L. A DR 3900 photometer (Hach Lange GmbH, Berlin, Germany) with a 50 mm cell was used for experimental set-up B, where the respective detection limit was 3.8 µg/L.

Regarding the Cr(VI) determination in the presence of HAs, the applied spectro-photometric measurement method (3500 Cr B) needed to be modified accordingly, due to background values
caused by HAs, which can otherwise lead to an over-estimation of Cr(VI) concentrations. Due to this, a standard addition method was integrated into the measurement method, according to DIN 32633. Additions of 25 and 50 µg Cr(VI)/L were applied. Moreover, the background values caused by the presence of HAs were subtracted from the adsorption value, caused by the addition of 1,5-diphenylcarbazide. Due to these necessary adjustments, the detection limit for Cr(VI) in the presence of HAs was increased to 10 µg/L. The measurements of Cr(total) by the application of ICP-MS or GF-AAS procedures were not affected by the presence of HAs.

3. Results

3.1. Removal of Cr(VI) in the Absence of HAs

3.1.1. Kinetics of Cr(VI) Removal

The reduction of Cr(VI) was found to be a fast process. Remaining concentrations of Cr(VI) > 5 µg/L were measured after 2 min of slow stirring (Figure 2a, <0.25 mg Fe(II)/L). The further decrease in concentrations of Cr(VI) during the following slow mixing phase (60 min) was generally not significant for all the tested dosages of ferrous sulphate; e.g., the addition of 1 mg Fe(II)/L led to [Cr(VI)] residual concentration of 1.93 µg/L after 2 min of mixing (contact) and to [Cr(VI)] 1.07 µg/L after 60 min. A rapid initial decrease of Cr(VI) concentrations was also found for all tested pH values (i.e., 6.5 to 8) and for all applied dosages of Fe(II) (i.e., 0.25–2 mg Fe(II)/L). Moreover, as it can be derived from Figure 2a, low residual concentrations of Cr(VI) can be found for all Fe(II) dosages, except for 0.25 mg/L. At 0.25 mg Fe(II)/L, the residual Cr(VI) concentration after 60 min was 10.2 µg/L, while it was below 5 µg/L for Fe(II) dosages ≥0.5 mg Fe(II)/L. The rapid reduction of Cr(VI) is well matching with the relevant results reported in literature. For example, Mittrakas et al. [13] found a reduction of Cr(VI) within 5 min after the addition of Fe(II). A rapid reaction rate was also found by Sedlak and Chan [30]. Increased residual Cr(VI) concentrations might also be well explained by literature, as an applied Fe(II) dosage of 0.25 mg Fe(II)/L for an initial Cr(VI) concentration of 100 µg/L is equal to a molar ratio lower than 1:3 (1:2.3: [Cr(VI)]:[Fe(II)]). As derived from the respective literature review, this ratio would be needed for the complete reduction of Cr(VI) to Cr(III) if all Fe(II) is exclusively used for Cr(VI) reduction [13]; therefore, this might explain the increased residual Cr(VI) concentrations at Fe(II) dosage 0.25 mg Fe(II)/L. Moreover, Cr(VI) removal was found to be effective by applying a molar ratio of 1:5 or even higher ([Cr(VI)]:[Fe(II)]), which corresponds to a Fe(II) dosage of 0.5 mg Fe(II)/L.

![Figure 2](image-url)  
**Figure 2.** Removal kinetics of (a) Cr(VI) and (b) Cr(total) concentrations at pH value 7 and Fe(II) dosages 0.25, 0.5, 1, 1.5, and 2 mg/L. All experiments were performed using set-up A.
However, the residual Cr(total) concentrations displayed a decrease more similar to an exponential decline (Figure 2b). Especially for the dosages of 0.25 and 0.5 mg Fe(II)/L, the decrease of Cr(total) concentrations is delayed. Since the concentrations of Cr(VI) were below 5 µg/L for the Fe(II) dosage of ≥0.5 mg Fe(II)/L, these concentrations can be most likely attributed to the removal of Cr(III). Thus, it was assumed that the removal of Cr(III) was the rate-determining step for the removal of Cr(total) under the applied experimental conditions. This could be attributed to the application of a two-step treatment process, in which the precipitation of Cr(III) is the second step and can only take place when a sufficient amount of Fe(III) and Cr(III) is formed during the process [13]. From the residual concentrations of Cr(total), it might be derived that the adsorption/co-precipitation of Fe(III) and Cr(III) is more efficient at Fe(II) dosages of 1 mg Fe(II)/L or higher.

Fe(II) dosages of ≥0.5 mg/L were able to remove Cr(total) below the concentration of 5 µg/L within 60 min of slow stirring. The increase from 30 to 60 min of slow stirring at a Fe(II) dosage of 1 mg Fe(II)/L is considered as an outlier. Increased concentrations of Cr(total) after 60 min of slow stirring were only found at the Fe(II) dosage of 0.25 mg Fe(II)/L. At this dosage of Fe(II), Cr(VI) is the highest fraction of Cr(total), i.e., (Cr(total) = 18 µg/L; Cr(VI) = 10 µg/L, and Cr(III) = 8 µg/L). This result indicates that at low dosage of Fe(II) the reduction of Cr(VI) is less efficient.

### 3.1.2. Influence of pH and Fe(II) Dose

The residual concentrations of Cr(VI) after 60 min of slow stirring are displayed in Figure 3a for the pH range of 6.5–8.0 and for Fe(II) dosages 0.25–1.0 mg/L. For all pH values, the highest residual Cr(VI) concentrations can be found for the Fe(II) dosage 0.25 mg/L. When dosing 1 mg Fe(II)/L or more, all residual Cr(VI) concentrations were below 5 µg/L. In contrast, for lower ferrous sulphate dosages (i.e., 0.25 and 0.5 mg Fe(II)/L) a strong dependency of the residual Cr(VI) concentrations on the respective pH value was recorded (Figure 3). At these Fe(II) dosages and at pH 8, residual Cr(VI) concentrations increased up to 58 µg/L (for 0.25 mg Fe(II)/L), or to 23 µg/L (for 0.5 mg/L Fe(II)/L), respectively. Moreover, for the Fe(II) dosage 0.25 mg/L, the lowest residual concentration can be found at pH 7.

![Figure 3](#)  
**Figure 3.** Residual concentrations of (a) Cr(VI) and (b) Cr(total) after 60 min of slow stirring as a function of pH value. Fe(II) dosages of 0.25, 0.5, 1, 1.5, and 2 mg/L and pH values of 6.5, 7, 7.5, and 8 were examined; all experiments were performed using set-up A.

Similar to Cr(VI), the residual Cr(total) concentrations decreased with increasing Fe(II) dosages (Figure 3b). The strongest dependency on the pH value was again found for the lower Fe(II) dosages (0.25 and 0.5 mg/L). For these dosages, the lowest residual concentrations can be found at pH 7, and...
the highest residual concentrations at pH 8 (71 µg/L for 0.25 mg Fe(II)/L and 37 µg/L for 0.5 mg Fe(II)/L). For the higher Fe(II) dosages (1.5 and 2 mg/L), the residual concentrations of Cr(total) slightly increased with increased pH values, but the residual concentrations after 60 min still remained below 6 µg/L. It is assumed that a similar effect might be also observed for the Fe(II) dosage of 1 mg/L. Residual Cr(III) concentrations are influenced by the low solubility of Cr(III) in the tested pH range (6.5–8) [9].

Due to these results, it is assumed that at pH 7 the Fe(II) dosage of 0.5 mg/L is sufficient for an effective removal of Cr(VI), as well as for Cr(III) (equals to a molar ratio of approx. 1:5 [Cr(VI)]:[Fe(II)]). However, to assure a sufficient removal of both species over the whole examined pH range (i.e., 6.5–8), a dosage of 1 mg Fe(II)/L is needed, which corresponds to a molar ratio of 1:10 [Cr(VI)]:[Fe(II)]. These increased molar ratios might be explained by competing reactions, for example, the oxidation of Fe(II) by oxygen taking place simultaneously with increasing rates as the pH of water increases. The precise influence of competing reactions could not be determined within the frame of this study, since, for example, the effect of dissolved oxygen was not investigated.

3.2. Removal of Chromium in the Presence of HA

3.2.1. Influence of Fe(II) Dosage

Three different Fe(II) dosages (0.25, 1, and 2 mg/L) were tested in the presence of HA concentrations ranging between 0 and 5 mg DOC/L. The residual concentrations of Cr(VI) were found below the detection limit for all the tested concentrations of HAs (and for dosages 1.0 or 2.0 mg Fe(II)/L), noting the aforementioned higher detection limit of Cr(VI) in the presence of HAs. In contrast, the residual concentrations of Cr(VI) in the presence of HAs increased for the dosage of 0.25 mg Fe(II)/L (10 µg/L Cr(VI) at 0 mg DOC/L) up to approximately 58 µg/L of Cr(VI) (at 1 mg DOC/L), (Figure 4).

![Figure 4. Cr(VI) residual concentrations after 60 min of slow stirring, as a function of the presence of HAs (concentrations: 0, 1, 3, 5 mg DOC/L) at pH 7 and for Fe(II) dosages 0.25, 1, and 2 mg/L. Mean values with vertical bars indicate the range. The results were obtained with the application of both set-ups A and B.](image)

These results are not in good agreement with the results reported by other researchers. Jiang et al. [23] showed that HAs by themselves are capable of reducing Cr(VI) to Cr(III). Prior to the tests with Fe(II), several batch tests were conducted to verify if the presence of HAs influences the oxidation state of chromium. At the given test conditions and initial concentrations of Cr(IV) and Has, no reduction of Cr(VI) was observed within 60 min of stirring.

According to the results by Agrawal et al. [22], under anoxic conditions a catalysing effect for the reductive reaction is expected, due to a redox recycling process for iron and hence a lower Fe(II) demand is expected, as compared to experiments without HAs (at a stoichiometric ratio lower than 1:3
[Cr(VI)]:[Fe(II)]. However, at the tested pH range, Fe(III) is practically insoluble (with the respective Ksp = $6 \times 10^{-38}$ [8]) and is therefore removed from the solution, indicating that redox cycling might not take place in this case [24].

Additionally, at the dosage of 0.25 mg Fe(II)/L it can be observed that the residual Cr(VI) concentrations remained almost constant with the increased HA concentrations. This indicates that the reduction of Cr(VI) at lower Fe(II) dosages is inhibited by the presence of HAs, but also that this inhibitory effect is almost independent from the concentration of HAs. Finally, it is assumed from the obtained results that a Fe(II) dosage of 1 mg/L is needed to efficiently remove 100 µg/L Cr(VI) in the presence of 1–5 mg DOC/L, similar to the results obtained in the absence of HAs in solution.

3.2.2. Influence of pH Value

The removal of Cr(VI) is strongly influenced by the pH value in the range 6.5–8, as Figure 5 depicts. Cr(VI) residual concentrations at pH values of 6.5 and 7 were below the respective detection limit for all the examined dosages of HAs. However, the most remarkable results were obtained for pH 8, where the residual Cr(VI) concentrations increased strongly with increasing HA concentrations, i.e., residual Cr(VI) concentrations were below 5 µg/L at 0 mg DOC/L, up to 16 µg/L at the presence of 1 mg DOC/L, and increased further to 25 µg/L in the presence of 5 mg DOC/L (Figure 5).

![Figure 5. Cr(VI) residual concentrations as a function of HA presence (concentrations: 0, 1, 3, 5 mg DOC/L) at pH values 6.5, 7, and 8 at for Fe(II) dosage 2 mg/L. Mean values with vertical bars indicate the range of values. The results were obtained by using both set-ups A and B.](image)

The observed increase of residual Cr(VI) concentrations at the pH value 8 is of particular significance when the dosage of Fe(II) would also be considered, as it was also found for the lower applied Fe(II) dosages (0.25 and 0.5 mg Fe/L). However, the results displayed in Figure 5 were obtained with the Fe(II) dosage of 2 mg/L, which is up to 8 times higher when compared with the experiments performed without the presence of HAs. The results therefore indicated that the influence of increased pH values on the reduction of Cr(VI) was stronger in the presence of HAs. However, it can be confirmed that the Fe(II) demand significantly increased at pH 8 and in the presence of HAs and consequently, Fe(II) dosages > 2 mg/L are needed to achieve comparably high reduction and removals of Cr(VI).

3.3. Influence of HAs on the Removal of Cr(total)

3.3.1. Influence of Fe(II) Dosage

For all the examined dosages of Fe(II), the residual concentrations of Cr(total) increased with increasing concentrations of HAs (Figure 6). Fe(II) dosages of 0.25 and 1.0 mg/L were not able to reduce
the Cr(total) concentrations below 60 µg/L at pH 7. Even with a Fe(II) dosage of 2.0 mg/L, the residual Cr(total) concentration was 31 µg/L for waters containing 1 mg DOC/L and up to 86 µg/L for waters containing 5 mg DOC/L. Moreover, it is remarkable that at 0.25 and 1.0 mg Fe(II)/L concentrations, the respective Cr(total) concentrations remained roughly constant, even with increased concentrations of HAs (Figure 6).

![Figure 6](image1.png)

**Figure 6.** Cr(total) residual concentrations as a function of the presence of HAs (0, 1, 3, 5 mg DOC/L) at pH 7 and with Fe(II) dosages of 0.25, 1.0, and 2.0 mg/L. Mean values with vertical bars were used to indicate the range. The results were obtained with both set-ups A and B.

For Fe(II) dosages of 1.0 and 2.0 mg/L, the results indicated that a relatively high amount of Cr(III) still remained dissolved after 60 min of slow stirring (Figure 7). This fact reduces the acute toxic potential of chromium in solution. However, due to the possible re-oxidation of it, for example, through disinfection with chlorine, there is still a considerable risk of the re-formation of Cr(VI) [31,32]. In particular, Lindsay et al. [32] showed that Cr(III) complexed with ethylenediaminetetraacetic acid was very rapidly oxidized to Cr(VI) when in contact with chlorinated water during the disinfection of New York Tap water.

![Figure 7](image2.png)

**Figure 7.** Cr(III) residual concentrations as a function of the presence of HAs (0, 1, 3, 5 mg DOC/L) at pH 7 and Fe(II) dosages 0.25, 1.0, and 2.0 mg/L. Mean values with vertical bars indicate the respective range. The results were obtained with both set-ups A and B.

A significantly higher amount of residual Cr(VI) was measured for all examined concentrations of HAs, but only when a smaller concentration of Fe(II) (0.25 mg/L) was dosed. An increase in residual
Cr(VI) concentration was also observed in the experiments without the presence of HAs for the smaller Fe(II) dosage (0.25 mg/L). This effect seems to be strongly intensified in the co-presence of HAs, leading to a higher residual amount of toxic Cr(VI).

Thus, the reduction of Cr(VI) was strongly inhibited in the presence of HAs at the smaller Fe(II) dosages (0.25 mg/L), while Cr(VI) was shown to be reduced effectively by applying higher Fe(II) dosages (1.0 and 2.0 mg/L). However, at dosages of 1 or 2 mg Fe(II)/L the removal of Cr(III) was strongly inhibited. This effect was also reported by Buerge and Hug [20]. They attributed their observations to the formation of complexes between HAs and Cr(III), which lead to a higher fraction of soluble Cr(III) in the presence of HAs [20]. Finally, all of these effects were shown to lead to higher residual concentrations of Cr(total) at pH 7 and Fe(II) dosages between 0.25 and 2.0 mg/L.

3.3.2. Influence of pH Value

The effect of increasing pH values cannot be clearly characterized for the removal of Cr(total) (Figure 8). For all the tested pH values, the residual concentrations of Cr(total) were found to increase similarly with the increased concentrations of HAs. Indeed, it is difficult to clearly differentiate between the examined pH values, because of the relatively large variability of results. Moreover, it is remarkable that the residual concentrations increased again with the increased concentrations of HAs, even when the relatively higher dosage of 2 mg Fe(II)/L was applied. As a comparison, in the experiments without the presence of HAs, the residual Cr(VI) concentrations were found below 6 µg/L, indicating high increase of Cr(VI) concentrations in the presence of HAs for all the examined pH values.

![Figure 8](image_url)

**Figure 8.** Cr(total) residual concentrations as a function of the presence of HAs (0, 1, 3, 5 mg DOC/L) at pH values 6.5, 7, and 8 and at Fe(II) dosage 2 mg/L. Mean values with vertical bars indicate the range. The results were obtained by the application of both set-ups A and B.

Again, a higher fraction of Cr(VI) was found in this case with increased pH values. The fraction of Cr(VI) was lower at pH 8, with the application of the low Fe(II) dosage (0.25 mg/L). This indicates a lower inhibitory effect of pH value as compared to the application of lower Fe(II) dosages. In contrast, an efficient reduction (and removal) of Cr(VI) was shown to be possible at lower pH values (7 and 6.5). However, at higher Fe(II) dosages, a relatively high amount of Cr(III) still remained dissolved, representing an inhibition of the second reaction step at lower pH values (Figure 9).
with a water matrix of tap water containing NOM of 1.3 mg/L. Due to the pH of the examined water (7.8), the effect of pH value was only found when lower Fe(II) dosages (0.25 or 0.5 mg/L) were applied. The removal of Cr(VI) in the presence of HAs showed residual concentrations below the detection limit of 10 μg/L in NSF water, indicating high increase of Cr(VI) concentrations in the presence of HAs for all the examined pH values. The effect of increasing pH values cannot be clearly characterized for the removal of Cr(total) as compared to Cr(VI). With Fe(II) reductive precipitation was confirmed to be an effective process for the removal of 100 μg/L Cr(VI), Cr(total), and Cr(III) from tap water (pH 7.8, 1.3 mg DOC/L) and from NSF water (pH 7 and 8, 1 mg DOC/L) at the Fe(II) dosage 2 mg/L. All experiments were performed using set-up A.

Residual concentrations of Cr(total) were lower compared to the results in NSF water at pH 8, which might be attributed to the slightly lower pH values. Certainly, the chemistry of Chromium removal depends also on the type of DOC which varies between natural waters and model humic substance.

3.4. Cr(VI) Removal in Tap Water Containing NOM, Spiked with Cr(VI)

To further determine if the results obtained with the artificial groundwater (NSF water) can be transferred to water containing natural organic matter, a first trial was conducted with the use of a water matrix of tap water containing NOM of 1.3 mg/L. Due to the pH of the examined water (7.8), the results were compared with the results obtained using NSF water at pH 7 and 8 and with HAs (1 mg DOC/L). Figure 10 shows that the reduction of Cr(VI) in the tap water was equally efficient when compared with NSF water at pH 8 (16 μg/L residual Cr(VI) concentration in tap water, as compared with 17 μg/L in NSF water), but higher as compared with the respective residual concentrations at pH 7 in NSF water.

3.3.2. Influence of pH Value

Again, a higher fraction of Cr(VI) was found in this case with increased pH values. The fraction of soluble Cr(III) in the presence of HAs [20]. Finally, all of these effects were found for Fe(II) dosages lower than 2 mg/L, the residual chromium concentrations remained at levels around 10 μg/L Cr(VI) in the absence of HAs, at the pH range between 6.5 and 8 and for Fe(II) dosages 1 mg/L or higher. A significant effect of the pH value was only found when lower Fe(II) dosages (0.25 or
0.5 mg/L) were applied. At these (lower) dosages, the residual Cr(VI) and Cr(total) concentrations increased at pH 8 (Cr(total) was also increased at lower pH value of 6.5). For all examined pH values, the highest residual concentrations were found for the lower Fe(II) dosage (0.25 mg/L). Moreover, the reduction of Cr(VI) was quite fast and practically completed within 4 min after the addition of Fe(II) for all the examined dosages of Fe(II). A rapid rate of removal of subsequently formed Cr(III) was also found for Fe(II) dosages 1 mg/L or higher, although this was decreased when the lower Fe(II) dosages (0.25 or 0.5 mg/L) were applied. The removal of Cr(VI) in the presence of HAs showed residual concentrations below the (higher in this case) detection limit of 10 µg/L, while the respective reductive reaction was strongly inhibited for the smaller examined Fe(II) dosage (0.25 mg/L).

The removal of Cr(total) was more inhibited by the presence of HAs as compared to Cr(VI). With Fe(II) dosages lower than 2 mg/L, the residual chromium concentrations remained at levels around 60 µg/L. At Fe(II) dosages 1 or 2 mg/L, where the decrease of Cr(VI) concentrations below 10 µg/L is possible, the high residual concentrations of Cr(total) observed are mainly attributed to high residual Cr(III) concentrations. This coincides with relevant literature data, since a formation of soluble complexes between Fe(III), Cr(III) and organic substances is possible in this case.

Residual iron concentration was not measured in all experiments, so a reliable analysis concerning remaining iron concentration cannot be given. However, a tendency of higher iron content in organically loaded waters was seen, probably due to complexation reactions taking place between Fe and NOM. This issue is currently under further investigation.

The results from experiments using tap water containing natural organic matter spiked with Cr(VI) indicated that similar results were obtained when using artificial groundwater. While the removal of Cr(VI) was similar for both cases, Cr(III) was more efficiently removed from the natural water, eventually leading to lower Cr(total) concentrations.

The results of the current study demonstrated the necessity for further optimization of the treatment processes applied for Cr(total) removal, especially in the presence of HAs. During this process, the removal of Cr(III) was shown to be an important step of the process in the presence of HAs, which is indicated through the higher residual concentrations of Cr(III). Contrary, the removal of Cr(VI) seems to be less affected by the presence of HAs.

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