Article

Chromium Removal in the Presence of NOM during Fe(II) Reductive Precipitation for Drinking Water Treatment

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Abstract: Cr(VI) is toxic and carcinogenic, which fuels discussions on reducing existing standards for maximum Cr concentrations in drinking water. Fe(II) reductive precipitation is a common and economical method for achieving very low Cr(tot) concentrations (<5 μg/L). While Cr(VI) is reduced to Cr(III), Fe(II) is oxidized to Fe(III). The resulting Cr(III) and Fe(III) have low solubilities at neutral pH, precipitate as hydroxides, and can be removed by conventional media filtration. The presence of natural organic matter (NOM) in the raw water source can, depending on pH, concentration, type of NOM, and contact time, affect this process in various ways, from promoting Cr(VI) reduction, to re-reducing Fe(III), to forming stable complexes with Cr and Fe, thus, impairing chromium removal. The presented data showed that NOM, whether dominated by terrestrial humic acid, or of aquatic origin, could substantially impair chromium removal at neutral pH conditions. In particular, the ultimate removal of Cr(III) was affected. Soluble complexes and/or colloids of Cr(III), Fe(III) and NOM in the size range of 10 kDa–0.1 μm were formed, that could not be removed by conventional media filtration. Presence of iron sludge (>50 mg/L Fe(III)) mitigated the negative impacts of NOM on Cr(VI) reduction and Cr(III) removal. However, even 100 mg/L Fe(III), the highest applied sludge concentration, did not lead to a decrease in Fe(II) dosing requirements under the given conditions. A molar ratio higher than the given stochiometric ratio of [Fe(II)]:[Cr(VI)] = 3 was necessary for sufficient Cr(VI) removal.

Keywords: chromium removal; Fe(II); reductive precipitation; humic acid; NOM; drinking water

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1. Introduction

Chromium is commonly used in industrial applications such as leather tanning, production of steel and other alloys, and textile processing. Depending on production conditions chromium can often be found in soil and groundwater, e.g., through uncontrolled emission of fly ashes and wastewater [1,2].

Apart from anthropogenic contamination, natural chromium sources can be washed into groundwater by erosion of ophiolitic and metamorphic rocks [3]. In aqueous solutions, hexavalent (Cr(VI)) and trivalent chromium (Cr(III)) are the predominant redox species. The most relevant Cr(VI) species at pH values >6.5 is chromate (CrO_4^{2-}), while $Cr_2O_7^-$ and $HCrO_4^-$ are only present at pH values <6.5 and high Cr(VI) concentrations [4,5]. In the pH range of 6.5–8.5, Cr(III) forms stable complexes with hydroxides ($Cr(OH)_3^0$), resulting in a low solubility (<5 μg/L) [6]. Kaprara et al. (2015) found that most dissolved chromium in natural waters is Cr(VI) [3].

While Cr(III) is considered essential for human metabolic processes, Cr(VI) is highly toxic due to its carcinogenic and mutagenic properties even at low concentration in the

range of several μg/L Cr(tot) [5,7–10]. This fact has triggered an ongoing discussion of severely reducing the current international standards for maximum Cr concentrations in drinking water. The World Health Organization has long been assessing a potentially stricter guideline value for Cr(tot), and had proposed a transitional period before reducing the current value of 50 μg/L, which has now been withdrawn [11]. However, the European Parliament complies with the former resolution and stated in the latest Drinking Water Directive (EU/2020/2184) the intention to reduce the limit from 50 to 25 μg/L Cr(tot) by 2036 [12]. Some countries consider the introduction of a separate limit for Cr(VI), e.g., 10 μg/L in California [13] and 20 μg/L in Switzerland [14].

Chromium in the form of Cr(VI) can directly be removed by ion exchange, adsorption (e.g., onto iron oxides or activated carbon) or solution–diffusion membrane filtration such as reverse osmosis or nanofiltration [15–17]. These processes make use of its anionic properties/low diffusion coefficients and are able to achieve very low residual chromium concentrations (<5 μg/L). Nevertheless, these technologies produce problematic concentrate streams, require further pre-treatment, have high energy demand, high investment and operating costs, or need highly trained operators [15–17].

Another common way to decrease Cr(VI) to very low concentrations is the reduction of Cr(VI) to the less toxic and less mobile Cr(III), followed by precipitation and filtration. Zero- and divalent iron, especially ferrous sulphate, are possible reducing agents for Cr(VI) reduction. During the chemical reduction of Cr(VI), Fe(0) or rather Fe(II), are oxidized to Fe(III). The resulting Cr(III) and Fe(III) have low solubilities at neutral pH and readily precipitate as hydroxides. Cr(III) can either co-precipitate with Fe(III) or adsorb onto $Fe(OH)_3$ flocs, while with increasing Fe to Cr ratio, the relevance of co-precipitation increases [18]. Solid residuals can then be removed by conventional filtration or microfiltration [15,16,19,20]. The redox reaction between Fe(II) and Cr(VI) results in the following equation.

$$Cr(VI) + 3\ Fe(II) \rightarrow Cr(III) + 3\ Fe(III) \tag{1}$$

$$x\ Cr(III) + (1 - x)\ Fe(II) + 3\ H_2O \rightarrow Cr_xFe_{1-x}(OH)_{3\ (s)} + 3\ H^+\ (0 < x < 1) \tag{2}$$

Three mole Fe(II) are needed to reduce one mole of chromate (Equation (1)). In general, Cr(VI) is rapidly reduced by Fe(II) to Cr(III) [19,21,22]. Resulting Fe(III)-hydroxide offers large surface floc area for Cr(III) adsorption. In addition to the formed flocs, Cr(III) may be included by trapping it into the hydroxide (Equation (2)). Moreover, there is also a certain potential for Cr(IV) adsorption on $Fe(OH)_3$ [23]. If optimized, this mechanism may lead to final Cr(tot) concentrations below 5 μg/L. It is an effective and simple option for chromium removal. However, operating conditions must be adjusted to water quality to minimize chemical consumption and sludge production [17,19,22,24].

Fe(II) reductive precipitation in natural organic matter (NOM)-free waters is a stable process. This might not be the case at elevated NOM concentration. In natural waters, a major part of the total organic carbon (TOC) consists of NOM. As a consequence, both parameters are often used as synonyms. Bulk quantification of TOC is performed by measuring the organic content in mg/L carbon. With respect to its quality and chemical composition, NOM is highly complex [25]. Due to the diversity of molecules, organic particles and the relatively low concentration of NOM in natural waters, characterization is difficult. At neutral pH conditions NOM is generally negatively charged, and analytical characterization according to its hydrophobicity, molecular weight distribution, fluorescence and content of functional groups are options for describing its quality. A large fraction of freshwater NOM (50–80%) consists of dissolved humic substances [26], and in streams and shallow groundwater, the particulate fraction of NOM plays an important role for both biotic and abiotic processes.

NOM representatives, such as humic substances, fulvic acids and humic acids (HA), are omnipresent in surface and groundwaters (0.5–100 mg/L TOC or after 0.45 μm filtration as dissolved organic carbon, DOC) and can play an important role for metal complexation, adsorption and redox processes [27,28]. Humic substances often comprise elevated amounts

of oxygen-containing functional groups, e.g., carboxylic and phenolic groups that have a strong affinity to complex with Fe(II) and Fe(III) due to their anionic nature [28–30].

The influence of NOM on drinking water production is a topic of growing concern as climate change will lead to an increased release of NOM in surface and groundwaters in the near future, due to temperature-induced intensified biodegradation of soil organic matter and a facilitation of transport into water bodies as a result of flooding events [31]. Apart from changes in temperature and precipitation, progressing urbanization and land sealing might also increase organic loads in groundwaters, thus, impeding water treatment [32]. Naturally occurring dissolved organic matter comprises a wide variety of heterogeneous structures with high and low molecular weight, typically below 10 kDa (=10,000 g/mol) [28].

With regard to chromium removal by means of Fe(II) reductive precipitation, adverse effects of NOM have been observed. Agrawal et al. (2009), Buerge and Hug (1998) and Hori et al. (2015) found that, depending on the pH (low to near neutral) and composition of NOM, Cr(VI) could slowly (within hours to days) be reduced to Cr(III) by NOM [33–35]. However, it was observed by Mak and Lo (2011) that HA did not interact with Cr(VI) at neutral pH in the presence of Fe(0), probably due to the fast reaction of Cr(VI) with Fe(0) [36]. Furthermore, Fe(III) generated during the reduction of Cr(VI) might be recycled by a re-reduction to Fe(II) by NOM at pH $\leq$6, resulting in a decreased Fe(II) dosing demand [34,37].

On the other hand, due to metal complexation, NOM might either stabilize Fe(II) [38] or enhance oxidation of Fe(II) by oxygen instead of Cr(VI) [29]. Both effects can lower the amount of Fe(II) accessible for Cr(VI) reduction. Additionally, the presence of HA as part of NOM can lead to the formation of stable, hardly-aggregating complexes and colloids containing Cr(III), HA and Fe(III) [22,29,35]. Liu and Lo (2008) found that when zero-valent iron was used for chemical reduction, HA did not necessarily lower Cr(VI) reduction, but led to formation of soluble and colloidal Fe-HA complexes [39]. Pan et al. made similar observations during electrocoagulation at a pH of 8 [29]. The presence of HA decelerated Cr(VI) reduction and induced the formation of colloidal complexes containing Fe(III), HA and Cr(III), which were not removed by filtration (>0,22 μm). They assumed that supporting HA coagulation, e.g., by increasing Fe(II) dosing might improve total Cr removal.

In a former study we also observed that negative impacts of HA could be compensated by increasing the dosage of Fe(II) during reductive precipitation [22]. The increased amount of Fe(II) led to an increased amount of Fe(III), which could catalyze reduction [34,37] and adsorption of Cr(VI) [23], as well as enhance NOM removal. The amount of Fe(III)-sludge in the reactor was established by dosing with Fe(III)-salts instead of waiting until the dosing rate of Fe(II) achieved the desired Fe(III)-sludge concentration. By using a hybrid process (reduction reactor coupled with submerged porous membrane) as suggested by Stylianou et al. (2017), where a microfiltration membrane was submerged into the coagulation tank, the produced $Fe(OH)_3$ sludge was completely retained and accumulated to reach higher concentrations in the reactor [40].

The aim of this study is to produce more insights into the role of natural organic matter on the performance of the Fe(II) reductive precipitation process, as well as the fate of Cr and Fe in the presence of NOM in the form of two different major representatives of NOM: (i) terrestrial HA and (ii) aquatic NOM, that differ among other parameters mainly in molecular weight as the latter is smaller than terrestrial HA [41].

2. Materials and Methods

2.1. Examined Waters

HA (terrestrial origin) was chosen as representative of NOM. In order to validate whether the observed effects can also be transferred to NOM of aquatic origin, additionally, water from "Hohlohsee" was used for some experiments. In general, all experiments were conducted with an ion matrix based on NSF challenge water, an artificially compiled groundwater described by the National Sanitation Foundation (NSF) (see Table 1). NSF

challenge water was set-up with ultrapure water one to two days before the experiment. This water was either spiked with natural terrestrial HA (from alkaline extraction of brown coal) or water from "Hohlohsee" (aquatic NOM). The stock solution of HA was prepared by adding 20 g of HA salts (Carl Roth) to 2 L of ultrapure water. The solution's pH was adjusted to 7.0, stirred for at least 12 h and then filtered through a 0.45 μm filter. The resulting stock solution had a DOC of 2.1 g/L and was used to set the DOC of the test water to approx. 1, 3 or 5 mg/L. "Hohlohsee" is a bog lake in a nature reserve near Karlsruhe, Germany. The water has a high DOC concentration and low conductivity [42]. After membrane filtration (0.45 μm), a DOC of 15.7 mg/L was measured (for original water composition, see Table 1). For experiments with NOM, the original sample from "Hohlohsee" was diluted with NSF challenge water (1:3) to reach a DOC concentration of approx. 5 mg/L. Cr(VI) concentrations of 100 or 300 μg/L were reached by adding dichromate salt ($K_2Cr_2O_7$, Carl Roth $\geq$ 99.5% p.a.).

Table 1. Composition of NSF challenge water, and water from "Hohlohsee".

Substance	NSF Challenge Water [43]	Hohlohsee * [41]
Na^+ (mg/L)	88	0.5
Mg^{2+} (mg/L)	12.5	0.15
Ca^{2+} (mg/L)	40	0.79
HCO_3^- (mg/L)	183	-
SO_4^{2-} (mg/L)	50	0.4
Cl^- (mg/L)	71	2.0
NO_3^- (mg/L)	2	<0.1
F^- (mg/L)	1	<0.1
SiO_2 (mg/L)	20	-

Note: * Undiluted.

2.2. Experimental Set-up and Procedures

2.2.1. General Jar Test Procedure for Reductive Precipitation of Chromium

All experiments were set-up as jar tests with 1.8 L batch volume, electronic overhead stirrer (Hei-Torque Precision 100, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) with a paddle stirrer in a 2 L beaker (tall form) with baffles (according to DVGW W 218 standard [44]). After filling the beaker with 1.8 L of Cr(VI)-spiked water, and adjusting the pH to 7.5 with 0.2 N H_2SO_4, the stirring speed was set at 150 rpm (G-value of 270 s^{-1}) for dosing Fe(II). After 2 min of intense mixing, the stirring speed was reduced to 50 rpm (G-value of 50 s^{-1}). Slow stirring was continued for 60 min. After 1 min of settling, samples were taken, filtered by 0.45 μm membrane filtration (cellulose nitrate, 47 mm diameter, Sartorius AG, Göttingen, Germany) under vacuum suction, and then analyzed. Almost all experiments have been conducted twice (n = 2).

$FeSO_4 \cdot 7H_2O$ was used for stock solutions of Fe(II) (min 99.5%, Merck KGaA, Darmstadt, Germany). Stock solutions of Fe(II) were prepared in acidified ultrapure water on every experimental day and degassed with nitrogen to avoid oxidation. All other chemicals used during the experiments were at least of reagent grade.

2.2.2. NOM Fractionation Tests

For the fractionation experiments, the coagulated water (see Section 2.2.1) was first filtered by 0.45 μm (cellulose acetate, 47 mm diameter, Sartorius AG, Göttingen, Germany) and then by 0.1 μm membrane (cellulose nitrate, 47 mm diameter, Sartorius AG, Göttingen, Germany) vacuum driven filtration (see Figure 1). Each of these filtrations was conducted in parallel by means of two batches in order to avoid a too severe cake layer formation. An amount of 1.6 L of the filtrate was then split into portions of 400 mL and transferred to the pressure driven membrane filtration cells (Amicon Stirred Cell Model 8200, max 200 mL, effective membrane area 28.7 cm^2, EMD Millipore, Burlington, MA, USA) that were loaded with 4 ultrafiltration membranes of different molecular weight cut-offs: 10,

5, 3 and 1 kDa (1 kDa = 1000 g/mol). The stirred filtration cells were pressurized with nitrogen gas at 2 bars. The stirring speed was set to 3000 rpm. After collecting approx. 40 mL permeate, the filtration was paused to refill the cells to 200 mL in order to avoid concentration build-up. The filtration was stopped as soon as the permeate reached 80 mL. Prior to the experiments, the ultrafiltration membranes (Ultracel® regenerated cellulose, 25 mm diameter, MilliporeSigma, Burlington, MA, USA) were stored in ultrapure water for a minimum of 24 h and subsequently flushed with 2 L of ultrapure water.
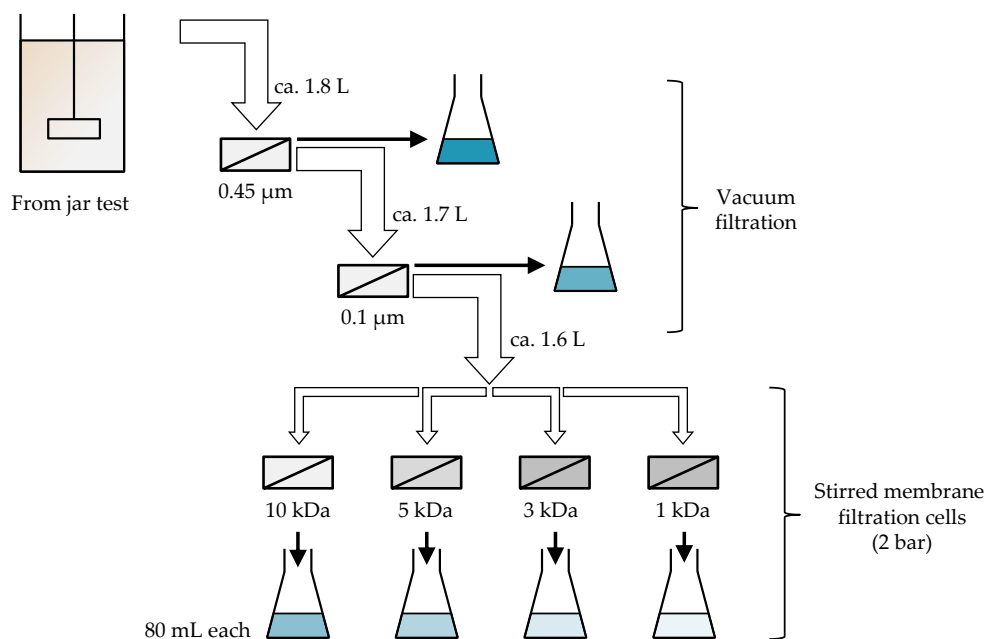

Figure 1. Scheme of the fractionation procedure.

2.2.3. Jar Tests with Pre-Formed FeOH$_3$ Sludge

Fe(OH)$_3$ sludge was produced by adding varying amounts of Fe(SO)$_4$ to the NSF challenge water, adjusting the pH to 7.5, and aeration with air overnight to ensure complete oxidation and precipitation of Fe. After re-adjusting the pH to 7.5 on the next day, Cr(VI) and HA were added and the jar test started by dosing Fe(II) as described in Section 2.2.1. This procedure was chosen in order to imitate the sludge generation in a continuously operated hybrid process with a reduction reactor coupled with a submerged porous membrane that also uses Fe(SO)$_4$ as a reducing agent.

2.3. Analytical Methods

Cr(tot) was measured by inductively coupled plasma mass spectrometry (NexION 300D, PerkinElmar, Waltham, MA, USA) with a detection limit of 0.4 µg/L. Ion chromatography (Eco IC 925, Metrohm AG, Herisau, Switzerland) with post-column derivatization and UV-visible spectroscopic detection was used for the determination of Cr(VI). The limit of detection (LOD) was 0.1 µg/L. Fe(II) and Fe(tot) were determined colorimetrically with the 1,10-phenanthroline method according to DIN 38 406 (50 mm cuvette, UV 1601, Shimadzu Deutschland GmbH, Duisburg, Germany). The LOD for Fe(II) and Fe(tot) were 0.005 mg/L and 0.02 mg/L. For characterizing organic water compounds, the high-temperature catalytic oxidation technique with a nondispersive infrared (NDIR) detection (TOC-LCPH, Shimadzu Deutschland GmbH, Duisburg, Germany) with LOD of 0.05 mg/L, and liquid chromatography with organic carbon detection (LC-OCD-UVD, DOC Labor Dr. Huber, Karlsruhe, Germany) were used.

3. Results and Discussion

3.1. Impairment of Chromium Removal by NOM

The effect of NOM representatives HA vs. "Hohlohsee" aquatic NOM (HSNOM) on chromium removal by Fe(II) reductive precipitation was examined in jar tests. Figure 2a shows residual Cr(VI) and Cr(III) concentrations after reductive precipitation with Fe(II), at different DOC levels of both NOM representatives. The background DOC concentration was 0.2 mg/L when no HA or HSNOM was added and a Fe(II) dose of 1 mg/L was sufficient to fully convert the initial 100 μg/L Cr(VI) to Cr(III). Final Cr(tot) concentration below 10 μg/L was achieved. As no Cr(VI) could be detected, it was assumed that all residual Cr was Cr(III). With increasing amounts of HA resulting in initial DOC concentrations of 1.0–5.5 mg/L, the residual concentrations of both Cr(VI) and Cr(III) increased. The total chromium removal was clearly impaired: 44–85 μg/L of dissolved Cr(tot) remained in the water. However, removal rates for Cr(VI) of >90% were achieved at all DOC concentrations tested. When HSNOM was added, residual Cr(VI) concentration was below 2 μg/L while approx. 90 μg/L of Cr(tot) was detected. Compared with terrestrial HA, HSNOM seemed to have a less pronounced effect on Cr(VI) reduction, though the impact on Cr(III) removal was slightly more distinct.
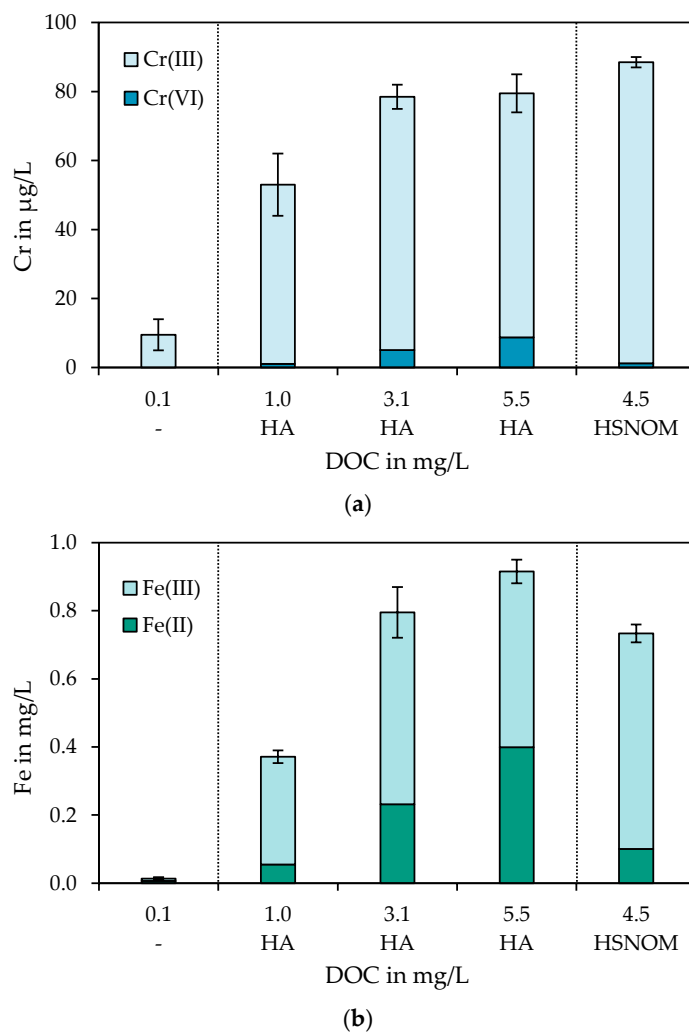

(a)

(b)

Figure 2. Mean residual concentrations of (**a**) Cr(VI) and Cr(III), and (**b**) Fe(II) and Fe(III), at increasing initial DOC concentrations of terrestrial humic acid (HA) and natural aquatic NOM from "Hohlohsee" (HSNOM). Test conditions: 100 μg/L Cr(VI), 1.0 mg/L Fe(II), pH 7.5, t = 60 min, n = 2; error bars indicate minimum and maximum.

Without addition of organic matter, almost all Fe(II) was oxidized to Fe(III) and removed from the solution (see Figure 2b). Here, Fe(II) and Fe(tot) were barely detectable. In contrast, high amounts of dissolved iron were observed during treatment in the presence of organic matter. At the highest HA dose (5.5 mg/L DOC), up to 0.46 mg/L Fe(II) and 0.95 mg/L Fe(tot) remained in the solution. Only 5% of the initially dosed 1.0 mg/L Fe(II) was removed from the water that contained HA. With HSNOM this effect was similar, although a little less distinct.

These data suggest that under the given conditions, NOM primarily affects the fate of Cr(III), while the reduction of Cr(VI) to Cr(III) is only slightly inhibited. Organic matter seems to prevent Cr(III) and Fe(III) from coagulating and, thus, being removed by conventional filtration. As Cr(III) might easily be re-oxidized to Cr(VI) in subsequent treatment steps of drinking water production, e.g., oxidation for disinfection [45], it is mandatory to remove all Cr(VI) as well as all Cr(III) from water.

Additionally, Fe(II) is restrained from being fully oxidized to Fe(III), although oxygen and Cr(VI) are present, as the relatively high pH of 7.5 reduction of Fe(III) to Fe(II) by organic ligands, as described by Hori et al. (2015) [34] and Agrawal et al. (2009) [33], is negligible. Thus, it might be possible that a fraction of Fe(II) is stabilized by complexation with HA or HSNOM, as observed by Daugherty et al. (2017) [38], decreasing its availability for Cr(VI) reduction, as was seen in the increasing residual concentrations of Cr(VI). Incomplete Cr(VI) reduction paired with incomplete Fe(II) oxidation at high HA concentration might also be a consequence of decreased reaction speed, as Pan et al. (2017) observed [29].

3.2. Fate of Residual Chromium, Iron and Organic Matter

In order to gain more insight into the fate of Cr, Fe and DOC, the water was further fractionated (see Section 2.2.2 for procedure) after reduction, precipitation and filtration (0.45 µm). In comparison with the experiments presented in Section 3.1, the initial concentration of Cr(VI) was increased to 300 µg/L, and the Fe(II) dosage increased to 3 mg/L, in order to facilitate detection after fractionation while maintaining a constant molar ratio of [Fe(II)]:[Cr(VI)] = 9.3. The fractionation experiments were conducted with both types of NOM. With 5.5 mg/L (HA) and 4.7 mg/L HSNOM, similar initial DOC concentrations were applied. This resulted in Fe(II) to DOC mass ratios of 0.55 for HA and 0.64 for HSNOM. While Cr(tot) removal was significantly improved from 20 to 78% for the experiments with HA (see Figure 2a last column and Figure 3a), the higher mass ratio of Fe(II) to DOC did not affect Cr(tot) removal when HSNOM was applied (Cr(tot) removal of 12% compared with 13%). The experiments with HA also showed better removal of Fe and DOC from the solution, i.e., better incorporation into flocs that remained in the jar after precipitation and filtration. HA was removed by 45%, whereas for HSNOM, no DOC removal at all, was observed. It seems that in the case of HSNOM a Fe(II) dose higher than 1 mg/L might be necessary to initiate coagulation and, thus, noteworthy removal of Cr(III) and DOC.

A reduced affinity to coagulation of HSNOM can also be seen in the results from the fractionation. Significant amounts of Fe, DOC and Cr were detected in the size fraction 0.1–0.45 µm for HA, while for HSNOM, the amounts of Fe, DOC and Cr in this fraction were negligible (see Figure 3c,d). This, and the overall better removal observed in the experiments with HA presented in Figure 2a, indicate that reductive precipitation of Fe(II) and Cr(VI) resulted in flocs and colloids with larger size in the presence of HA compared with the presence of HSNOM. This may be due to the inherently larger molecular weight portion of HA compared with HSNOM [41], which theoretically leads to a higher potential for coagulation of HA [46]; 68% of dissolved HA and only 16% of HSNOM are >10 kDa [41].
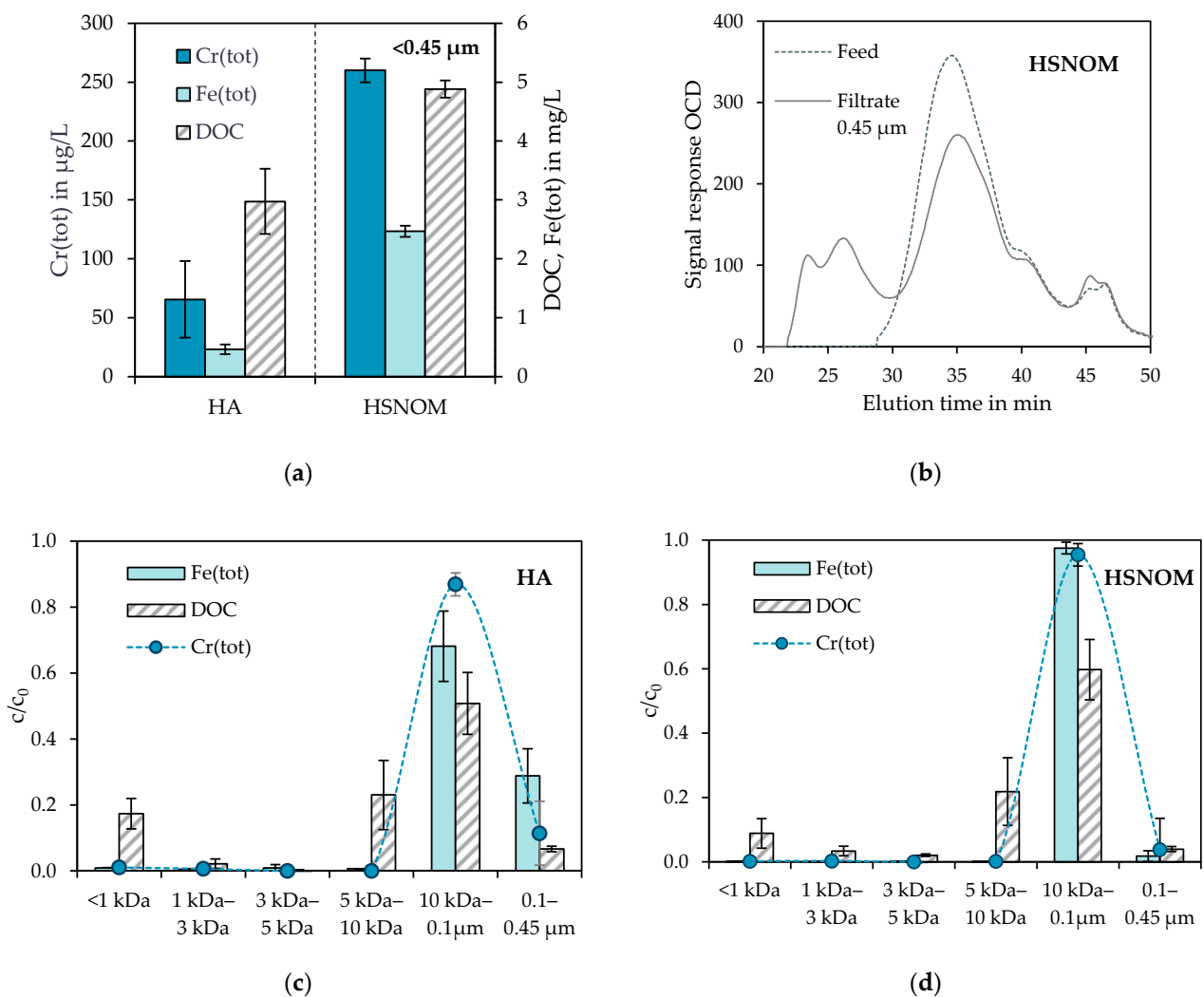
(**a**)

(**b**)

(**c**)

(**d**)

Figure 3. DOC fractionation experiments. Test conditions: 300 µg/L Cr(VI), 3.0 mg/L Fe(II), 5.5 mg/L DOC for humic acid (HA) or 4.7 mg/L DOC for "Hohlohsee" NOM (HSNOM), pH 7.5, t = 60 min, n = 2; error bars indicate minimum and maximum. (**a**): Mean absolute concentrations of Cr(tot), Fe(tot) and DOC after reduction, precipitation and filtration (0.45 µm), which equal c_0 in (**c**,**d**). (**b**) LC-OCD plot of the feed and the 0.45 µm filtrate from the reduced and precipitated water when HSNOM was present. (**c**,**d**): Mean distribution of Cr(tot), Fe(tot) and DOC for HA and HSNOM over different size fractions/filter sizes (related to concentration of precipitated and filtered (0.45 µm) water).

However, the given distributions of Cr(tot), DOC and Fe(tot) showed a similar pattern, for the experiments with HA and HSNOM. Residual Cr, Fe and DOC were mainly detected in size fraction 10 kDa–0.1 µm, suggesting complexation or other aggregation in colloidal form of all three components. Cr and Fe were barely detectable in the size fractions <10 kDa. This was also observed by Pan et al. (2017) during electrocoagulation of Fe, Cr and HA [29]. After treatment with Fe(II), only 64% of HSNOM was found in the size range between 10 kDa and 0.45 µm; 84% of dissolved HSNOM from untreated "Hohlohsee" water was <10 kDa [41]. Thus, coagulation seems to take place to some extent.

A shift from smaller to larger molecule size of HSNOM was also discernable in the LC-OCD plot (see Figure 3b). While the fraction of humic substances (peak at 35 min) clearly decreased from 3130 to 2520 ppb by precipitation and filtration, the fraction of hydrophilic biopolymers, that is, ≥10 kDa [47], and the largest fraction detectable through LC-OCD, grew from 40 to 930 ppb.

Both HA and HSNOM formed complexes/colloids with Cr and Fe. However, an overall colloid size <0.1 μm was too small for removal by conventional filtration or even microfiltration.

3.3. Removal of Residual Chromium in Presence of Precipitated $Fe(OH)_3$

Former pilot experiments for reductive precipitation that included continuous Fe(II) dosing and submerged microfiltration to accumulate and recycle iron sludge in the reaction tank suggested an improved Cr removal efficiency and process stability [40]. The influence of $Fe(OH)_3$ on Cr removal was, thus, investigated by adding increasing concentrations of pre-formed iron sludge made from $FeSO_4$ (for procedure, see Section 2.2.3) to batch tests at varying HA concentrations. In all tests, 1 mg/L of fresh Fe(II) was added for Cr(VI) reduction to Cr(III). When no HA or only low concentrations (2.1 mg/L DOC) were present, the sludge had little impact on Cr(VI) removal (see Figure 4a), as Cr(VI) reduction was complete (>98%) without any sludge addition under the given conditions. Only at high initial HA concentrations was the Cr(VI) reduction impaired. Here, a clear improvement was observed by addition of $Fe(OH)_3$ sludge: without pre-formed sludge, final Cr(VI) concentrations amounted to 26 μg/L, while Cr(VI) was barely detectable at sludge concentrations of $\geq$50 mg/L Fe.

(a)　　　　　　　　　　　　　　　　　　　　　　　(b)
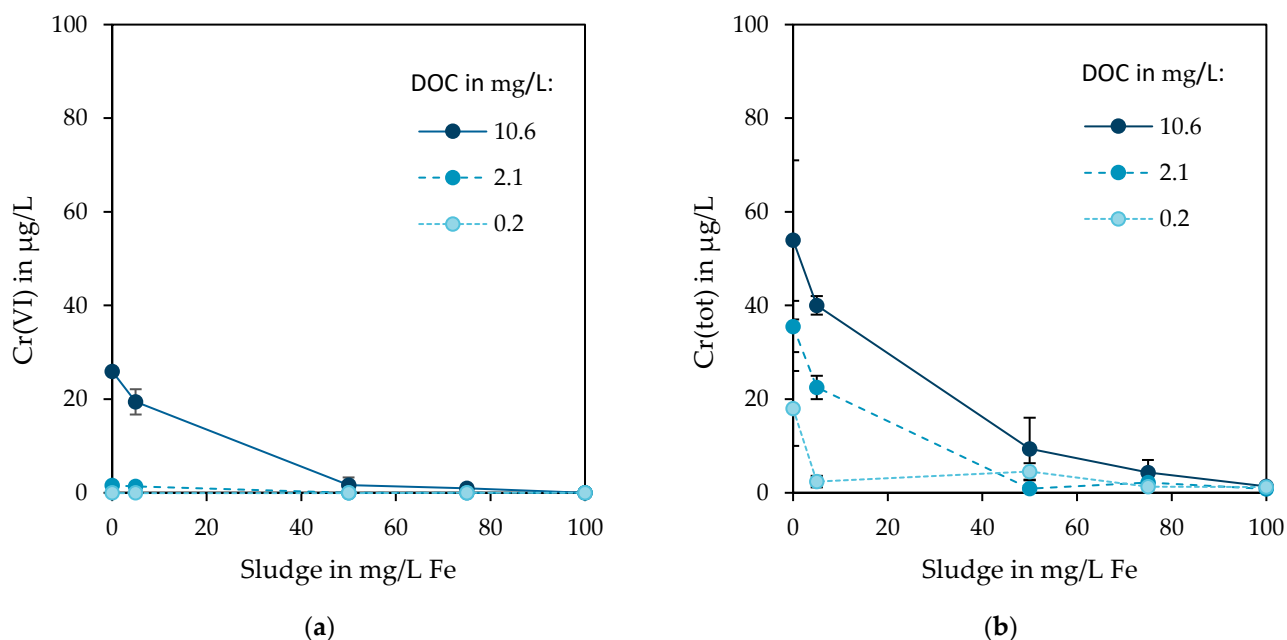
Figure 4. Mean residual concentrations of (**a**) Cr(VI) and (**b**) Cr(tot), in batch tests with increasing dosages of pre-formed sludge from $FeSO_4$ and a fixed dose of fresh Fe(II) at different DOC concentrations (HA). Test conditions: 100 μg/L Cr(VI), 0–100 mg/L Fe(III), 1.0 mg/L Fe(II), pH 7.5, 0.2–10.6 mg/L DOC, t = 60 min, n = 2; error bars indicate minimum and maximum.

With regard to residual Cr(tot) concentrations, which mainly consisted of Cr(III), even the lowest sludge concentration (5 mg/L of Fe) led to an improved removal at all initial HA concentrations (see Figure 4b). At a sludge concentration of 100 mg/L Fe, the negative impacts caused by HA could be fully compensated. All residual Cr(tot) concentrations were below 2 μg/L, even at an initial HA of 10.6 mg/L DOC. Additionally, the DOC removal improved when increasing sludge concentrations: from 39 to 50% when the initial DOC amounted to 2.1 mg/L, and from 47 to 88% for an initial DOC concentration of 10.6 mg/L. At the highest sludge concentration, a residual Fe(tot) concentration of maximum 0.2 mg/L was detected in the presence of HA.

The increasing amounts of Fe-sludge enhanced HA removal. Thus, HA seems to be detained from stabilizing Fe(II), as described by Daugherty et al. (2017) [38], keeping Fe(II) available for Cr(VI) reduction. During the experiments, a distinctive improvement of Cr(VI)

removal was observed with the highest DOC concentration (10.6 mg/L), when the sludge concentration amounted to 50 mg/L Fe. The decreasing residual Cr(tot) concentration implies that the formation of soluble/colloidal complexes containing Cr(III), Fe(III) and HA was also noticeably reduced or even fully prevented, as observed at sludge concentrations of 100 mg/L Fe.

Aoki and Munmorah (1982) observed that Cr(VI) can directly adsorb onto Fe(OH)$_3$ and, hence, be removed from the solution under optimized conditions [23]. Thus, tests were run to see if the dosage of fresh Fe(II) could be reduced without affecting Cr removal when sludge concentration was as high as 100 mg/L Fe. However, decreasing the Fe(II) dose resulted in decreasing Cr(tot) removal (see Figure 5a). Already at a dose of 0.5 mg/L Fe(II), which equals a molar ratio of [Fe(II)]:[Cr(VI)] = 4.7 and exceeds the stochiometric ratio of 3 (compare Equation (1)), residual Cr(tot) concentrations increased from 0.5 to 7.3 and 23 µg/L, respectively, in the presence of HA. Without dosing any fresh Fe(II), only 2–10% of Cr(tot) could be removed, depending on the HA concentration. From the experiments with an initial HA of 2.1 mg/L DOC (see Figure 5b), it was apparent that nearly all residual Cr was Cr(VI). Thus, there was only little evidence for Cr(VI) adsorption onto Fe(OH)$_3$ flocs.
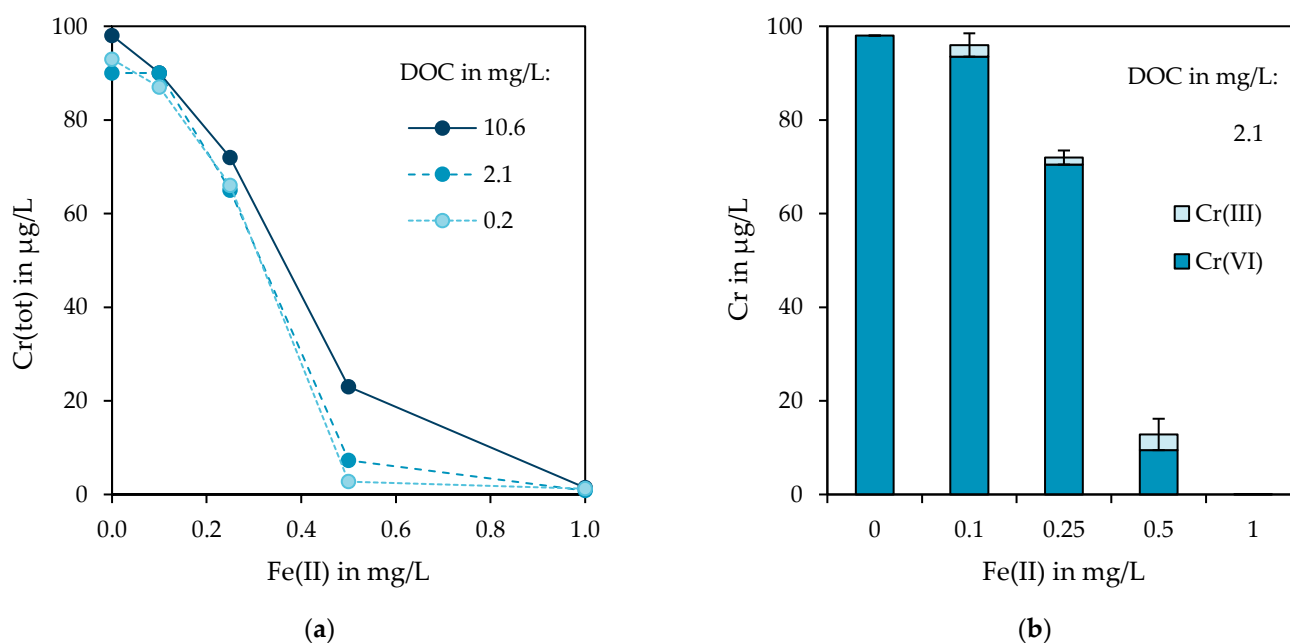

(**a**)   (**b**)

Figure 5. Residual concentrations of Cr(tot) (**a**), and Cr(VI) and Cr(III) (**b**), in batch tests with a fixed dose of pre-formed sludge and increasing dosages of fresh Fe(II) at different HA concentrations (0.2–10.6 mg/L DOC). Test conditions: 100 µg/L Cr(VI), 100 mg/L Fe(III), 0–1.0 mg/L Fe(II), pH 7.5, 0.2–10.6 mg/L DOC, t = 60 min, n = 1/2; error bars indicate minimum and maximum.

Under the given conditions (pH 7.5, t = 60 min, 100 mg/L Fe(III)), there was no evidence that the presence of Fe(III) further supports Cr(VI) reduction to Cr(III). It is unlikely that Cr(VI) might be reduced by HA, as suggested by Wittbrodt and Palmer (1996) for low pH waters [37], or by Fe(II) that arose from Fe(III) reduction by HA (compare Hori et al. (2015) [34]), as all Fe(III) was precipitated. The applied concentrations of Fe-sludge could not even reduce the amount of Fe(II) from 1.0 to 0.5 mg/L, which would still exceed the stoichiometrically required molar ratio without clearly decreasing Cr removal.

Fe(II) is still required for chemical reduction, as hardly any Cr(VI) removal was observed when only Fe(III) was added to the water. Here, it was evident that no Cr(VI) adsorption took place within 60 min and that longer contact times of several hours to days would probably be necessary. In order to reduce Fe(II) consumption and sludge production, the integration of Fe-recycling into the process may be an option. Fenton or Fenton-like reactions, for example, provide the opportunity to reduce Fe(III) to Fe(II) and

use the iron repeatedly for Cr(VI) reduction. Huang et al. (2017) [48] and Rahmani et al. (2015) [49] already proved the efficiency of chromium removal at pH 3 by electro-Fenton, where hydrogen peroxide is produced in situ and iron added to the process in the form iron-based nano-catalysts or electrodes material.

4. Conclusions

Toxic Cr(VI) can effectively be removed from groundwater by Fe(II) reductive precipitation. However, the presence of NOM, whether dominated by terrestrial HA or of aquatic origin ("Hohlohsee" NOM), can substantially impair chromium removal during this treatment process. In particular, the removal of Cr(III) that is produced by chemical reduction of Cr(VI), is affected. Soluble complexes and/or colloids of Cr(III), Fe(II)/Fe(III) and NOM, in the size range of 10 kDa–0.1 μm, are formed that cannot simply be removed by microfiltration (0.1 μm). The presence of Fe(OH)$_3$ sludge can mitigate negative impacts of HA on both Cr(VI) and Cr(III) removal. Then, a larger portion of Fe(III), Cr(III)/Cr(IV) and DOC can be incorporated in ferric hydrolyte flocs instead of remaining in the colloidal fraction (10 kDa–0.1 μm). This can ease their removal in a subsequent porous membrane filtration treatment. For an optimized combined Cr(IV)-reductive precipitation and adsorption removal by Fe(III)-sludge, a hybrid process of a submerged porous membrane filtration is an effective solution. However, continuous Fe(II) dosage would be needed for complete Cr(VI) reduction. Even the presence of high Fe(III)-sludge concentration is not suitable to reduce the Fe(II) dosing requirement. This would also imply a replacement strategy for iron sludge, with high Cr loading, which requires further research.

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