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Redox Behavior of Chromium in the Reduction, Coagulation, and Biotic Filtration (RCbF) Drinking Water Treatment—A Pilot Study

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Abstract: The chromium (Cr) limit values are currently tightened to 25 μg L^{-1} (EU), 5 μg L^{-1} (Germany), and possibly 10 μg L^{-1} Cr(VI) (California). The combined process of chemical reduction, coagulation, and biotic filtration (RCbF) efficiently removes Cr(VI) in drinking water. In this study, redox-active substances (O_2, NO_3^-, Fe^{2+}, MnO_2) were investigated concerning their effect on the RCbF process. The experiments were performed at two-stage pilot waterworks for biological iron and manganese removal. O_2 or NO_3^- as oxidants affected the RCbF process, neither by consumption of the reductant Fe(II) nor by re-oxidation of already formed Cr(III) in the supernatant of the filter bed. However, the oxidation of Cr(III) by O_2 to Cr(VI) with MnO_2 as a mediator was identified as potential risk for Cr breakthrough. Up to one third of the initial Cr(III) concentration was oxidized to Cr(VI) in the second filter bed within a contact time of only 5 min. The kinetically relevant mechanism seemed to be the formation of Cr(III)Fe(III)-hydroxides and not the reduction of Cr(VI) by Fe(II). Further, the mixing of Cr(VI) containing raw water with Fe(II) containing groundwater was determined as a chemical-free alternative for the RCbF process, depending on the resulting Fe(II) concentration after mixing.

Keywords: hexavalent chromium; chromate removal; trivalent chromium; drinking water treatment; reduction coagulation biological filtration

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1. Introduction

Chromium (Cr) is a ubiquitously occurring heavy metal in the environment [1]. Its natural appearance in water is limited to the two oxidation states hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) as amphoteric species of chromium hydroxide with much lower solubility and mobility than Cr(VI) [2–5].

There is an ongoing debate among experts about the toxicity of Cr(VI) in drinking water and its mode of action within the human body. While by some a mutagenic mode of action is favored [6–9], others assume a threshold mode of action [10–15] for Cr(VI)-induced carcinogenesis. The latter approach is favored by the World Health Organization (WHO), which assessed data from animal studies by the National Toxicology Program [16] and concluded that hyperplasia in the small intestine for tumor development is to be taken as the most sensitive end point [17]. If a mutagenic mode of action is applied, an assessment in which the data from animal experiments are extrapolated to a lifetime exposure risk for humans would result in a much lower limit value in drinking water [18].

In the latest EU Drinking Water Directive, the limitation value for total chromium (Cr_{tot}) was lowered from 50 μg L^{-1} to 25 μg L^{-1}, whereas the enforcement of this value is postponed to 2036 [19]. In Germany, a limitation value of 25 µg L^{-1} is directly implemented, and further tightening to a limitation value of 5 µg L^{-1} is scheduled for 2030 [20]. In California, as a progressive state for Cr(VI) regulation, a limitation value of 10 µg L^{-1} is proposed by the California Water Boards [21], and therefore this would tighten the current state maximum contaminant level of 50 µg L^{-1} Cr_{tot} (the federal level of 100 µg L^{-1} Cr_{tot}) currently defined in drinking water.

For Cr removal, ion exchange with weak basic anion exchange resins showed sufficient removal at a demonstration scale [22]. However, the water matrix, especially with sulfate as a competing anion, was identified as crucial for the performance [23]. Furthermore, a combination of reduction, coagulation, and filtration (RCF), with divalent iron (Fe(II)) as a reducing agent, showed good performance for Cr(VI) removal at the bench, pilot, and demonstration scales [22,24–26]. The RCF process was further developed by substituting the filtration with a biotic filtration (RCbF), which increased the effectiveness considerably [27]. In the RCbF process, dosed Fe(II) quickly reduces Cr(VI) in the supernatant of the filter bed to Cr(III), which is co-precipitated as an amorphous chromium(III)–iron(III) hydroxide solid solution with a low solubility [5]. This hydroxide is removed in the subsequent biological filter bed, where the excess Fe(II) is also removed very efficiently [27]. The Cr(VI) reduction and the formation of the hydroxide must be completed before entering the filter bed, because the reducing agent Fe(II) is (purposefully) oxidized to Fe(III) very quickly within the filter bed via a contact catalysis and biotic oxidation [28].

In this study, the oxidation/reduction potential (ORP)-dependent behavior of Cr in the RCbF process was investigated. Therefore, the reduction of Cr(VI) with Fe(II) was examined in the presence of competing oxidizing agents O_2 and NO_3^-, which potentially disturb the reduction of Cr(VI). In addition, the re-oxidation of Cr(III) in the process poses a risk for diminished efficiency of the RCbF process, either in the supernatant of the biological filter bed or even after the filter bed, if Cr(III) breaks through the filter. Therefore, the oxidation of Cr(III) with O_2 at a MnO_2 surface within a second filter bed was investigated with different O_2 doses. Further, since the RCbF process requires Fe(II) as a reducing agent, a chemical-free alternative in which Cr(VI)-containing raw water was mixed with Fe(II)-containing groundwater was investigated. The novelty of this study lies in the further investigation of the redox behavior of Cr in the RCbF process on the basis of process engineering variations at a semi-technical scale.

2. Materials and Methods

2.1. Chemicals

Sodium chromate, chromium trichloride hexahydrate, ferrous sulphate heptahydrate, sodium nitrate, potassium dihydrogenphosphate, hydrochloric acid (32%), sodium hydroxide (5 M), nitric acid (65%), and sodium chloride were purchased from Merck (Darmstadt, Germany). All chemicals were analytical grade, except nitric acid which was suprapur. Stock solutions were produced in relatively high concentrations and stored in a fridge. Dosing solution in big volumes were produced next to the pilot waterworks on a daily basis. Cr(VI) stock solution (1 g L^{-1}) was prepared by dissolving 3.20 g of sodium chromate in 1 L ultrapure water. Cr(VI) dosing solutions of 3.0 mg L^{-1} were prepared by transferring 300 mL of the stock solution into 100 L of ultrapure water. Cr(III) stock solution (1 g L^{-1}) was prepared on a daily basis by dissolving 5.1 g of chromium trichloride hexahydrate in 1 L of ultrapure water. Cr(III) dosing solutions of 3.0 mg L^{-1} were prepared by transferring 180 mL of stock solution into 60 L of ultrapure water. Nitrate dosing solution (12.5 g L^{-1}) was prepared by adding 1.25 kg of sodium nitrate into the Cr(VI) dosing solution. Moreover, 375 mg L^{-1} Fe(II) dosing solutions were prepared by dissolving 187.5 g of ferrous sulphate heptahydrate in 100 L of ultrapure water after adjusting the pH to 3.0. For the stabilization of Cr(VI) samples, a phosphate buffer stock solution was prepared by dissolving 17.42 g of potassium dihydrogenphosphate in 200 mL of ultrapure water.

2.2. Pilot Waterworks

Fully automated two-stage pilot waterworks for biological iron and manganese removal (Figure S1, Supplementary Material) were used for the experiments. The waterworks are described in detail elsewhere [27,29].

The continuously operated waterworks usually treat reduced groundwater with 2.4 mg L^{-1} Fe(II) and 0.5 mg L^{-1} Mn(II). The groundwater is oxygenated by mass flow controllers (In-Flow controllers, Bronkhorst, Kamen, Germany) before each filter bed. In filter bed 1 Fe(II) and filter bed 2, Mn(II) is biotically oxidized, precipitated, and retained in the biofilm on the filter material. Before filter 1, O_2 dosage is controlled according to the target redox-potential of 30 mV before filter 2 in order to avoid precipitation of MnO_2 already in filter 1Before filter 2, O_2 dosage is manually adjusted, whereas the O_2 concentration after filter 2 should not exceed 2 mg L^{-1}.

The residence times in the waterworks were determined by a tracer test with NaCl and conductivity measurements, and a 50% breakthrough of conductivity was defined as the residence time until the respective sampling point.

2.3. Experimental Procedure

Before each experiment, both filter columns were backwashed, and raw water was switched from groundwater to oxygen-free drinking water from the technical-scale waterworks in Berlin-Marienfelde, Germany (constituents are shown in Table S1, Supplementary Material). Experiments took one filtration cycle (ca. 50 h) each, and samples were taken on the first and last day of the experiments from various sample tabs. For the evaluation of Cr(VI) removal, the O_2 dosage to the influent of filter bed 1 (1.0, 4.0, 8.0 mg L^{-1}), nitrate concentration (50 mg L^{-1}), and mixture of Cr(VI)-containing raw water with Fe(II)-containing groundwater (1:2 and 1:4) were varied. O_2 dosage variations were first calculated according to the volumetric flow (250 L h^{-1}) and the necessary mass flow of O_2 (setup with mass flow controller 1) to reach the required O_2 concentration. The resulting concentration was measured and verified with an optical dissolved O_2 sensor (FDO 925, WTW—Xylem Analytics Germany Sales GmbH & Co. KG, Weilheim, Germany). For Cr(VI) removal experiments with a nitrate background, Cr(VI) was dosed together with nitrate at dosing point 1, and Fe(II) was subsequently dosed at dosing point 3 (Figure S1, Supplementary Material). For mixing experiments, oxygen-free drinking water was chosen as raw water with a pressure of 2.0 bar and was spiked with Cr(VI) at dosing point 1 to reach the target concentration of 12 μg L^{-1} after mixing the water. At dosing point 3, Fe(II)-containing groundwater under 2.3 bar was mixed in the appropriate ratio (1:2 or 1:4). This way, the sampling of c0 for both Fe(II) and Cr(VI) was possible.

To evaluate the formation of Cr(VI) in the second filter bed, Cr(III) was dosed before entering filter bed 2, and different O_2 doses were applied there (3.0 and 7.5 mL min^{-1}). Reduced groundwater with dissolved Fe(II) and Mn(II) was used as raw water. The O_2 dosage before filter bed 1 was adjusted to the stochiometric O_2 demand for complete Fe(II) oxidation. In filter bed 1, O_2 and Fe(II) (verification by Fe(II) measurements) were completely consumed, while Mn(II) (0.5 mg L^{-1}) was still present in the water.

As standard test setup for all experiments, Cr (12 μg L^{-1}), subsequently Fe(II) (3 mg L^{-1}), and then O_2 (adjusted to the set ORP value of 30 mV after filter bed 1 or with manual control) were dosed into the raw water before entering the relevant filter bed (Figure S1, Supplementary Material). Dosages were controlled with solenoid-driven metering pumps (gamma/X, Prominent; Heidelberg, Germany).

2.4. Analyses

Cr_{tot} samples were directly filtered with membranes (0.45 μm pore size, polyethylene terephthalate, Chromafil, Macherey-Nagel; Düren, Germany) into 50 mL centrifuge tubes (polypropylene (PP)) and stabilized with 300 μL nitric acid (65%). Cr_{tot} was analyzed with a graphite furnace atomic absorption spectroscope (Perkin Elmer 4100ZL, Waltham, MA, United States) with a hollow-cathode lamp (Lumina, Perkin Elmer) at a wavelength of 357.8 nm. The limit of quantification (LOQ) was 2.8 µg L^{-1}, which was determined according to a standardized method, DIN 32645, 2008.

Cr(VI) samples were also directly filtered with membranes (0.45 µm pore size, polyethylene terephthalate, Chromafil, Macherey-Nagel; Düren, Germany) and stabilized by the addition of a 1.5 mL hydrogen phosphate buffer and 450 µL 5 M NaOH into 120 mL bottles (PP) prior to sampling [30]. The samples were again filtered with membranes (0.45 µm pore size, regenerated cellulose, Sartorius; Goettingen, Germany) into 50 mL PP tubes and diluted in a ratio of 1:10 before analyses. Cr(VI) was analyzed with ion chromatography (881 Compact IC Pro, Metrohm; Herisau, Switzerland) with a post-column reaction (Dosino 800) and photometric detector (UV/VIS detector 819, wavelength 530 nm) in accordance with the standardized measurement method US EPA method 218.7. A separation column, A SUPP 5 150/4 (Metrohm; Herisau, Switzerland), was used, and the mobile phase consisted of sodium sulfate/sodium hydroxide solution (15 mmol L^{-1}/0.5 mmol L^{-1}). As a post-column reagent, 2 mmol L^{-1} diphenylcarbazide and 5% methanol with 0.5 mol L^{-1} H_2SO_4 were used. The LOQ was 0.02 µg L^{-1} with a measurement uncertainty of 40% according to a standardized method, DIN 32645, 2008.

Cr(III) concentrations were calculated by subtracting the Cr(VI) concentrations from the Cr_{tot} concentrations.

Fe(II) samples were directly filtered with membranes (0.45 µm pore size, polyethylene terephthalate, Chromafil, Macherey-Nagel; Düren, Germany) into 10 mL glass tubes and immediately analyzed with a UV/VIS photometer (Lambda 35, Perkin Elmer; Waltham, MA, United States) at a wavelength of 510 nm using a triazine-based iron quantification kit (Spectroquant, Merck; Darmstadt, Germany) and a 1 cm quartz cuvette.

Dissolved organic carbon (DOC) was measured with the TOC analysator varioTOC Cube (Elementar Analysensysteme GmbH, Langenselbold, Germany). Samples were directly filtered with membranes (0.45 µm pore size, polyethylene terephthalate, Chromafil, Macherey-Nagel; Düren, Germany), and before measurement, 10 mL of samples were acidified with 80 µL 10% HCl. DOC was fractioned with liquid size-exclusion chromatography with organic carbon detection (LC-OCD) (DOC-Labor GmbH, Karlsruhe, Germany) using a HW50S column (Toyopearl, Japan) according to Huber et al. [31] (2011).

3. Results

3.1. Potential Influences of Oxidizing Water Constituents

First, any critical oxidation agents that potentially could influence the reduction of Cr(VI) with Fe(II) in the supernatant of the filter were identified, and their stabilities were determined by thermodynamic calculations. The lines in Figure 1 display the equimolar distribution of redox pairs (e.g., NO_3^- and NH_4^+), while in the area above the line, the oxidized species dominate, and in the area below, the reduced species dominate. Naturally, only redox reactions are thermodynamically possible when the oxidized species of a redox pair of a higher line reacts with the reduced species of a subjacent line under the formation of the respective redox-pair partners (e.g., Fe(II) reduces O_2 under the formation of $Fe(OH)_3$ and H_2O).

Figure 1 shows that Fe(II) could serve as reducing agent for Cr(VI) over the considered pH range (yellow area) and also that MnO_2 could act as oxidizing agent for Cr(III) for pH values above 3.0 (green area). As Bartlett (1991) [2] and Kotaś and Stasicka (2000) [32] described, MnO_2 constitutes a mediator for Cr(III) oxidation with O_2 in the natural Cr cycle. O_2 and NO_3^- (for pH above 6.0) can act as oxidizing agents towards Cr(III) and therefore could potentially re-oxidize Cr(III) in the RCbF process in the supernatant of filter bed 1 (areas between O_2/H_2O and Cr(III)/Cr(VI) and NO_3^-/NH_4^+ and Cr(III)/Cr(VI)). Furthermore, O_2 and NO_3^- could act as oxidizing agents for Fe(II) over the entire displayed pH range and could therefore negatively influence the targeted Cr(VI) reduction (areas between O_2/H_2O and Fe(II)/Fe(III) and NO_3^-/NH_4^+ and Fe(II)/Fe(III)).

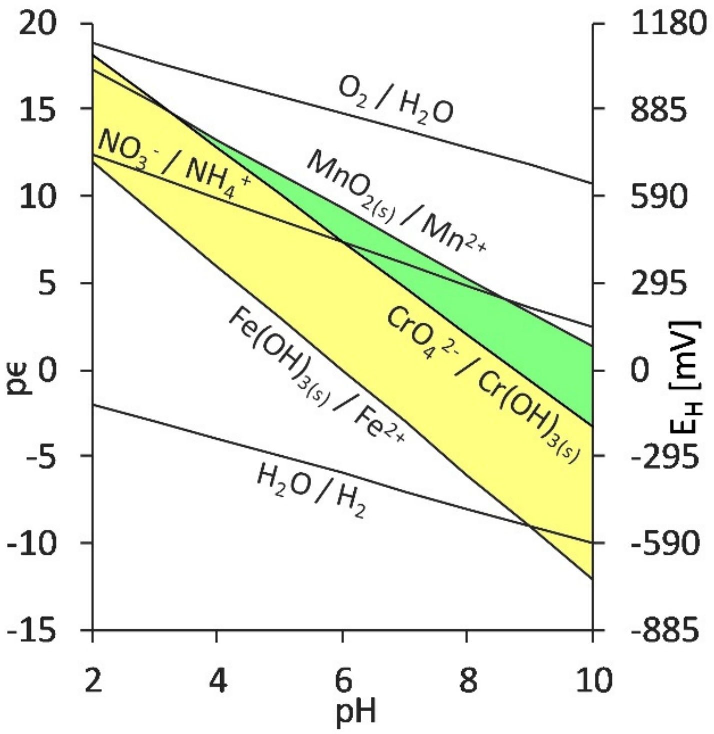

Figure 1. pe pH diagram for relevant redox partners (for 3 mg L^{-1} Fe(II), 0.5 mg L^{-1} Mn(II) and 20 µg L^{-1} Cr(VI)). Yellow area marks pe pH range where Cr(VI) might be reduced by Fe(II) and green area marks pe pH range where Cr(III) might be oxidized by MnO_2.

In the RCbF process, firstly, Cr(VI) is reduced by Fe(II) (Equation (1)), and secondly, the just-formed Cr(III) is coagulated together with an excess of Fe(III) to a Cr(III)–Fe(III) solid solution (Equation (2)) in the supernatant of the filter, which is thirdly filtered out in the subsequent biotic filter bed [27].

$$\mathrm{CrO_4^{2-} + 3Fe^{2+} + 5H_2O \rightleftarrows Cr^{3+} + 3Fe(OH)_{3(s)} + H^+} \tag{1}$$

$$\mathrm{xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \rightleftarrows Cr_xFe_{(1-x)}(OH)_{3(s)} + 3H^+ \ldots (0 < x < 1)} \tag{2}$$

3.2. O_2 or NO_3^- as Competing Oxidants and Potential Drivers for Re-Oxidation of Cr(III)

O_2 is the strongest oxidizing agent in Figure 1, indicated as the highest line in the stability field of water between O_2/H_2O and H_2O/H_2, if O_2 functions in a reaction of four electron transfers [33]. However, O_2 in water, as a covalent homodimer, is hindered from reacting with reduced species due to its strong π-double bond and requires a comparably high activation energy to oxidize. Most likely, the oxidation of Fe(II) with O_2 requires four sequential steps (four electron transmissions), whereas O_2 reacts with $Fe(OH)_{2(aq)}$.($Fe(OH)_{2(aq)}$ represents the Fe(II) species (compared to Fe^{2+} and $FeOH^+$) that O_2 oxidizes the fastest [34,35]. The first step (Equation (3)) represents the slowest reaction (one electron transfer) and therefore the kinetics determining this step are as follows [33]:

$$\mathrm{Fe(OH)_{2(aq)}} + O_2 \rightleftharpoons Fe(OH)_2{}^+ + O_2{}^{-*} \tag{3}$$

To investigate the O_2 dependency on Cr(VI) removal with RCbF, the initial Cr(VI) concentration was set at 12 µg L^{-1} and the Fe(II) dosage was 3 mg L^{-1} at a filtration velocity of 15 m h^{-1}. O_2 reacted poorly with Fe(II) in the supernatant of the filter bed, as shown in Figure 2, but quickly oxidized Fe(II) within the filter bed. As described in the literature, the precipitates on the filter material functioned as an adsorbent for Fe(II) ions and dissolved O_2 and as a catalysator for the required electron transfers due to their semiconductor properties [28,36]. These assumptions explain the occurrence of Fe(II) in the supernatant of the filter bed even though dissolved O_2 is present there, as well as the fast oxidation of Fe(II) and subsequent precipitation in the filter bed (Figure 2). Therefore, in the supernatant of filter 1, two oxidants (Cr(VI) and O_2) competed for the electrons of Fe(II), and after filter bed 1 was reached, no more Fe(II) was present for Cr(VI) reduction. Thus, for an effective RCbF process, the competitive advantage should be attributed to Cr(VI) as an oxidant via the setup of favorable boundary conditions.

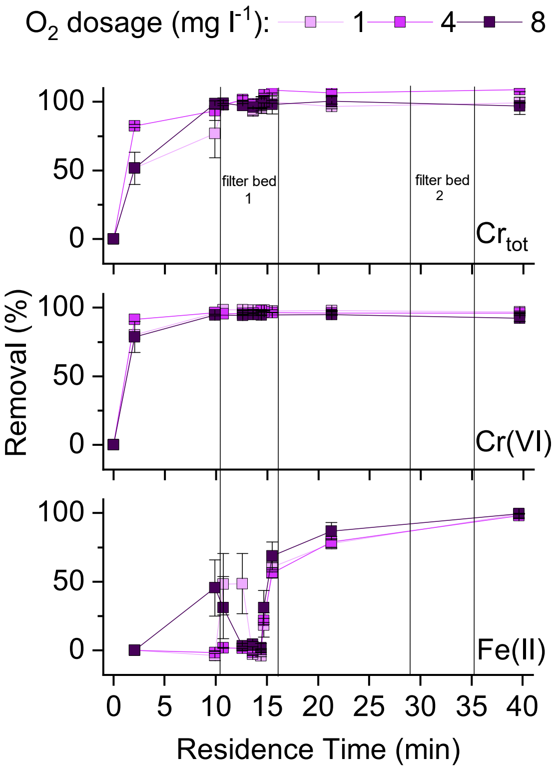

Figure 2. Cumulated removals of Cr_{tot}, Cr(VI), and Fe(II) for different O_2 dosages along the treatment path (given as residence time) at a filtration velocity of 15 m h^{-1}, initial Cr(VI) concentration of 12 µg L^{-1}, Fe(II) dosage of 3.0 mg L^{-1}, pH of 7.0, and a test duration of 50 h. Error bars indicate the maximum and minimum values.

While O_2 is needed in the RCbF process to oxidize excess Fe(II), Figure 2 shows that O_2 did not re-oxidize Cr(III), independent of the O_2 dosage. The removal of Cr was independent of the O_2 dosage, although 8 mg L^{-1} O_2 is, by a stochiometric factor of 19, higher than the amount needed for complete Fe(II) oxidation. In the supernatant of the filter bed, O_2 did not compete with Cr(VI) for the electrons of Fe(II), because the Fe(II) concentration remained almost constant until the filter bed entry. Directly before the filter bed, the Fe(II) concentrations seem to scatter, but this effect was also independent of the O_2 dosage and might have been caused by turbulences at the top layer. The π-double bond probably prevented the dissolved O_2 from exploiting its oxidation potential in the supernatant, and hence Cr(VI) could have been favorably reduced by Fe(II). When the filter bed, with its catalytic surface and microbial activity, was reached, O_2 immediately oxidized Fe(II) and thus did not interfere with the Cr removal. The pH value plays a crucial role in the favored Cr(VI) reduction as opposed to the O_2 reduction in the supernatant. For a pH > 10, the competitive advantage of the electrons changes, and O_2 would be reduced more quickly by Fe(II) compared to Cr(VI). Additionally, the stoichiometric demand for Cr(VI) reduction by Fe(II) would increase (>3 moles Fe(II) per mole Cr(VI)) [37,38]. So in the drinking water pH range, the advantage of Cr(VI) to function as an oxidant is used in the filter supernatant. As for the oxidation of Fe(II) with O_2, the speciation of Fe(II) was described as crucial for the oxidation of Fe(II) with Cr(VI). As for the oxidation with O_2, non-valent $Fe(OH)_{2(aq)}$ was postulated as being the Fe(II) species that reduces Cr(VI) the fastest [37]. As described by Sigg and Stumm (2016) [33], the unhydrolyzed species Fe^{2+} is a weaker reductant because of reduced electron density of the Fe(II) atom. Hence, the valence and electron density, in combination with the hydrolyzation of the Fe(II) species, are crucial for the redox activity of Fe(II). On the other hand, Cr(VI) occurs as a two-valent chromate anion in the drinking water pH range, and its valence was identified as a negligible factor for the reduction kinetics with Fe(II) [37].

NO_3^- is regulated with a limit value of 50 mg L^{-1} (according to the EU Drinking Water Directive [19]) and could provide an oxidant concentration that is by a factor of 5000 higher than the maximal observed Cr concentration in Germany (i.e., in groundwater [39]). NO_3^- has been described as a potent oxidant in groundwater, e.g., for pyrite, that can mobilize heavy metals that might reach drinking water [40]. Since Cr is more mobile as oxidized species (Cr(VI)), the inputs of NO_3^- into aquifers might increase the threat of Cr occurrence. Thus, the co-existence of NO_3^- and Cr(VI) might have negative consequences for Cr(VI) removal in the RCbF process. However, as Figure 3 shows, NO_3^- did not negatively influence the RCbF process. The experimental setup was again 12 µg L^{-1} as the initial Cr(VI) concentration, a Fe(II) dosage of 3.0 mg L^{-1}, and a filtration velocity of 15 m h^{-1}. For pH values higher than 6.0, NO_3^- could potentially re-oxidize Cr(III) to Cr(VI) and compete with Cr(VI) as an oxidant and oxidize Fe(II) to Fe(III) (Figure 1). However, an oxidation of Fe(II) in the supernatant of the filter bed was not observed, and hence, Fe(II) could be utilized to its full extend as a reductant for Cr(VI) reduction. Although the pH was 7.0, no re-oxidation of Cr(III) by NO_3^- could be observed. Cr(III) removal lagged behind Cr(VI) removal in the supernatant of the filter, and consequently, not the Cr(VI) reduction, but the formation of the chromium(III)–iron(III) hydroxide solid solution seemed to be the kinetic determining step in the RCbF process (Figure 3).

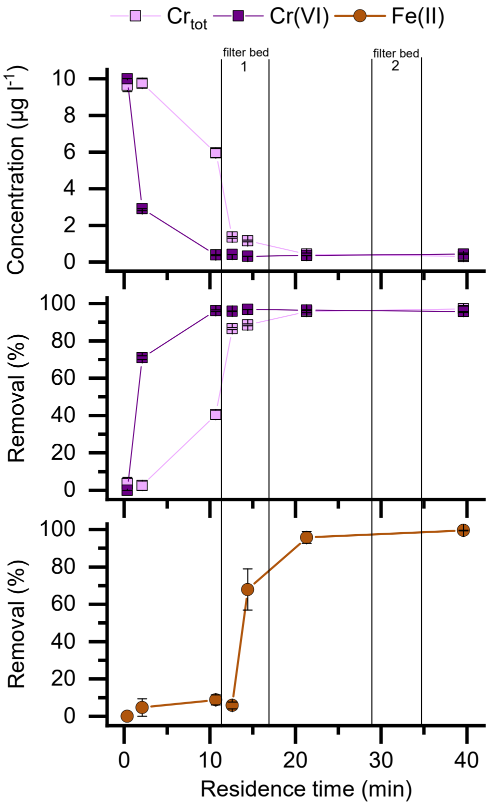

Figure 3. Cr(VI), Cr_{tot}, and Fe(II) removals after nitrate dosage (50 mg L^{-1}) over residence time. Filtration velocity 15 m h^{-1}, initial Cr(VI) concentration of 12 µg L^{-1}, Fe(II) dosage of 3.0 mg L^{-1}, pH of 7.0, and test duration of 50 h. Error bars indicate the maximum and minimum values.

3.3. Oxidation of Cr(III) to Cr(VI) by O_2 with MnO_2 as a Mediator

In the natural Cr cycle, Cr(III) is oxidized to mobile Cr(VI) on MnO_2, which serves as a mediator between O_2 and Cr(III) in soil (Equation (4)) [2].

$$4\,\mathrm{Cr(OH)}_{3(aq)} + 3\,\mathrm{O_2}\ \overset{\rightarrow}{\mathrm{MnO_2}}\ 4\,\mathrm{CrO}_{4^{2-}} + 8\,\mathrm{H}^{+} + 2\,\mathrm{H_2O} \tag{4}$$

Cr(III), with a much lower solubility than Cr(VI), can be mobilized by either a shift in the pH to below 5.0 or by a complexation with natural organic matter [2,32]. The pH very seldom decreases below 5.0 in drinking water treatment, but a complexation by DOC seems a likely mechanism for Cr(III) mobilization. The DOC of the test water was 3.0 mg L^{-1} and showed pronounced fractions of humic acids, which were described to influence the solubility of Cr(III) [32]. The DOC concentrations and composition were not influenced by the treatment process, as is displayed in Figure S2, Supplementary Material. However, no detailed examination of how DOC influences the mobilization of Cr in the context of water treatment is known to the authors, and thus further research on the topic is required. Furthermore, the solubility of Cr(III) at a neutral pH is approx. 4 µg L^{-1} [41], and raw water with dissolved Mn(II) and complexed Cr(III) is chemically stable and thus likely to occur in the environment (Figure 1). The initial Cr(III) concentration was 12 µg L^{-1} at a filtration velocity of 15 m h^{-1}. The Cr(III) was quickly removed in filter bed 2 with biotically generated MnO_2, but Cr(III) was partially oxidized to Cr(VI), which broke through the filter, as shown Figure 4. The ratio of oxidized Cr(VI) increased with an increasing O_2 dosage, and the highest measured concentrations of Cr(VI) in the effluent corresponded with 1/3 of the initial Cr(III) concentration. Thus, the oxidation of Cr(III) to Cr(VI) proceeded very quickly in only a 5 min contact time in the filter bed. Thus, Cr(III) must be fully retained in the filter bed for iron removal to avoid its re-oxidation with O_2 with MnO_2 as a mediator. Most likely, mechanistically, the O_2 was adsorbed onto the MnO_2 surface, and Cr(III) was enriched in the filter, and thus, MnO_2 could catalytically promote the oxidation of Cr(III) with O_2.

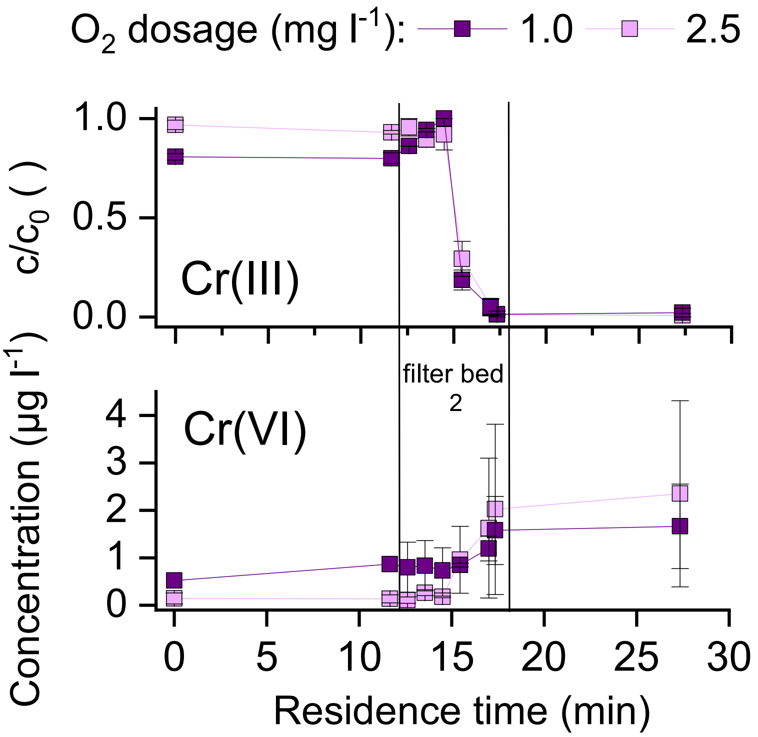

Figure 4. Cr(III) and Cr(VI) concentrations for different O_2 dosages over residence times in the second filter (12 µg L^{-1} Cr(III), with a filtration velocity of 15 m h^{-1}, a pH of 7.0, and 0.5 mg L^{-1} Mn(II)). Error bars indicate the maximum and minimum values during the 50 h operation.

3.4. Mixing of Cr(VI) Containing Water with Fe(II) Containing Groundwater

The continuous chemical consumption due to the dosage of Fe(II) is a disadvantage of the RCbF process. Therefore, the possibility of mixing anoxic Fe(II) containing groundwater with oxic Cr(VI) containing raw water was assessed as a chemical-free treatment. Of course, only if these types of water are locally available is this concept is possible. The experimental setup was an initial Cr(VI) concentration of 12 µg L^{-1} after mixing at a filtration velocity of 15 m h^{-1}. The removal of Cr was made successful by mixing the different waters; however, the Cr removal was dependent on the resulting Fe(II) concentration after mixing (Figure 5), as expected. While a mixing ratio of 1:2 led to a sufficient removal with an effective Fe(II) concentration of 1.2 mg L^{-1}, a ratio of 1:4 led to an insufficient Cr(VI) removal due to a resulting Fe(II) concentration of only 0.6 mg L^{-1}. These results are in line with previous results that identified Fe(II) dosage as a key factor [27].

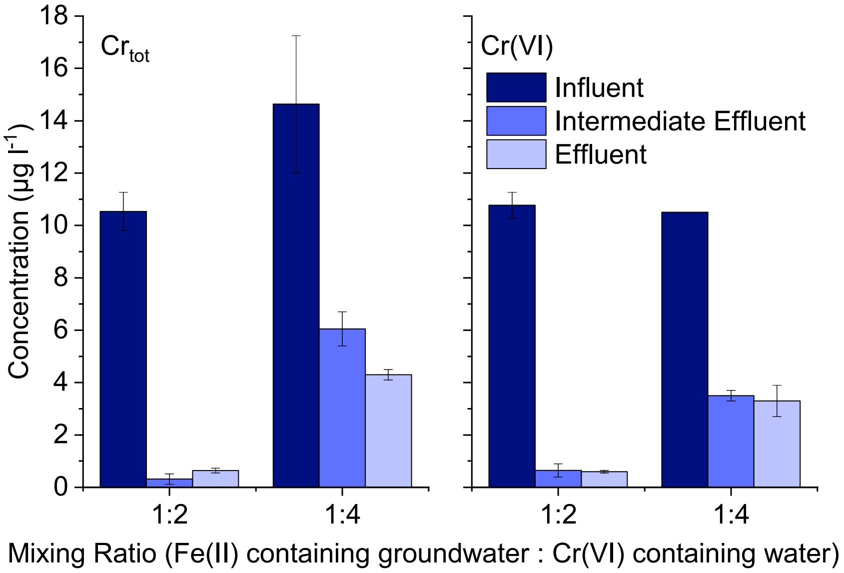

Figure 5. Cr(VI) and Cr_{tot} concentrations after mixing of Cr(VI) spiked water (Cr(VI) concentration after mixing was 12 µg L^{-1}) with Fe(II) containing anoxic groundwater (Fe(II) = 2.4 mg L^{-1}) in different mixing ratios over residence time (filtration velocity: 15 m h^{-1}; pH: 7.0). Error bars indicate the maximum and minimum values during the 50 h operation.

4. Conclusions

The redox pair Cr(VI) and Cr(III) is very reactive, and different reducing and oxidizing agents might affect the oxidation state of Cr and hence its mobility. O_2 (independent of pH), NO_3^- (for pH above 6.0) or MnO_2 (for pH below 9.0) could potentially oxidize Cr(III) to Cr(VI) and thus increase the mobility of Cr. Fe(II) (independent of pH) can reduce Cr(VI) to Cr(III), which consequently precipitates and can be removed via filtration in the RCbF process. If the oxidants O_2 and NO_3^- are present, however, the Cr(VI) reduction by Fe(II) might be affected due to competing oxidation. However, O_2 and NO_3^- did not negatively affect the RCbF process. Neither the oxidation of Fe(II) by O_2 or NO_3^- nor the re-oxidation of just-produced Cr(III) were observed in the supernatant of the filter bed. The oxidation of Cr(III) to Cr(VI) in filter bed 2 happened quickly, dependent on the O_2 dosage. MnO_2 served as a mediator for Cr(III) oxidation with O_2, most likely due to an enrichment of Cr(III) on the filter bed surface and an adsorption of O_2, so that MnO_2 could catalytically promote oxidation. While the Cr(VI) reduction to Cr(III) was completed in the supernatant of the filter bed, the formation of filterable Cr(III) hydroxide happened more slowly, and hence it was identified as a kinetic-determining step for Cr removal with RCbF. If the local conditions allow, a chemical-free variation of the RCbF process is possible by mixing Cr(VI) containing oxic raw water with Fe(II) containing anoxic groundwater; however, this is dependent on the resulting Fe(II) concentration.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w15193363/s1: Figure S1: Simplified scheme of the pilot plant at technical scale; Table S1: Composition of drinking water (groundwater), which was used as test water; Figure S2: DOC development in pilot plant; left: total DOC; right: fractioned DOC with LC-OCD.

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Abbreviations

Cr: chromium, Fe(II): divalent iron, DOC: dissolved organic carbon, LOQ: limit of quantification, Cr(VI): hexavalent chromium, PP: polypropylene, RCF: reduction, coagulation, and filtration, RCbF: reduction, coagulation, and biotic filtration, Cr_{tot}: total chromium, Cr(III): trivalent chromium, UBA: German Environment Agency, ORP: oxidation/reduction potential, WHO: World Health Organization.

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