




Article

Removal of Chromium Species from Low-Contaminated Raw Water by Different Drinking Water Treatment Processes

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† This article is dedicated to our dear colleague Ralph Hobby, who unfortunately passed away suddenly and unexpectedly while writing this article. Ralph, we miss you!

Abstract: The occurrence of Cr (VI) in drinking water resources in low but toxicologically relevant concentrations requires the development of reliable and industrially applicable separation processes in drinking water treatment. There is little information in the literature on the removal of chromium species at concentrations below 10 µg/L. Therefore, in this study, the removal of chromium in the concentration range ≤ 10 µg/L was investigated using three separation processes, activated carbon filtration (ACF), reduction/coagulation/filtration (RCF) and low-pressure reverse osmosis (LPRO), in both laboratory- and pilot-scale tests. In ACF treatment, Cr (III) was removed by deep bed filtration over 1.5 m of anthracite at a pH of 7.5 (which was used as a prefilter prior to ACF), while Cr (VI) was removed up to 75% via ACF at a filter bed depth of 2.5 m. Fresh activated carbon (AC) exhibited the highest adsorption capacity for Cr (VI), while reactivated AC had a significantly lower capacity for Cr (VI), which was attributed to calcium and iron deposits. In technical filters, where multiple reactivated activated carbon is used, this led to a low removal rate for Cr (VI). Using the RCF process with Fe (II) dosing in a continuous flow reactor at a specific coagulant dosing ratio, high Cr (VI) removal, down to a concentration of 0.1 µg/L, was achieved within minutes. The subsequent anthracite filtration ensured the complete removal of Fe (III) and Cr (III) precipitates. The RCF process was limited by the oxygen side reaction with Fe (II), which dominated at Cr (VI) concentrations below 1 µg/L. In addition, a four-step LPRO process with concentrate recycling showed effective removal (>99%) of both Cr (III) and Cr (VI) species in raw water as well as a negligible effect of pH in the testing pH range of 5.6 to 8.3 on the Cr (VI) removal. Nevertheless, the water hardness and pH of the LPRO permeate must be increased to make it available as drinking water. The three separation processes were found to be able to meet the expected more stringent future regulations for Cr (VI) level in drinking water. The most suitable technology, however, can be selected with respect to the raw water quality/characteristics, site-specific conditions and the already existing equipment.

Keywords: chromium removal; drinking water treatment; activated carbon adsorption; low-pressure reverse osmosis; reduction coagulation flocculation



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1. Introduction

Chromate contamination of drinking water and its impact on human health became known worldwide through the several-award-winning movie “Erin Brockovich” starring Julia Roberts [1]. With a few exceptions, the contamination of groundwater is caused by the industrial and commercial use of chromates for galvanic processes (chromium plating) and their use in corrosion protection [2]. Depending on the redox conditions and pH, chromium presents in groundwater as Cr (III) and/or Cr (VI) [3]. While Cr (III) is considered an essential trace nutrient, all Cr (VI)-based compounds are classified as toxic and carcinogenic substances [4]. According to WHO guidelines, the maximum allowed limit for total chromium substances in drinking water is 50 µg/L [5]; the EU drinking water directive specifies a limit value of 25 µg/L [6]. Nevertheless, stricter regulations regarding Cr (VI) are expected in the near future. However, it is already necessary to examine and/or develop the technical possibilities for reducing the naturally occurring chromium content in drinking water treatment. This is in line with the EU action plan “Towards Zero Pollution for Air, Water and Soil” by 2050 [7] and the specifications in the document “Chemicals Strategy for Sustainability” [8] with the aim of reducing the use and release of chemicals that are persistent, mobile and harmful to the environment.

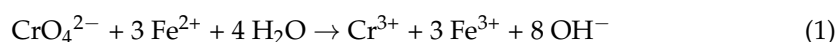
In the past, it was assumed that Cr (VI) is unstable in the aquatic environment and that it transforms into Cr (III) due to the strong oxidizing potential [9]. Nevertheless, recent studies have revealed that Cr (VI) is stable at low concentrations (µg/L) and a neutral pH value [10,11] because its redox potential in that case is low compared to other oxidants naturally present in water in high concentrations such as oxygen (see also Section 3.2).

In addition, Cr (VI) species can be formed in the natural environment by manganese (III) catalysis [12]. Cr (VI) can also be formed in water treatment as a result of oxidative processes, e.g., ozonation and chlorination [13,14].

Several separation techniques for the removal of Cr (VI) substances from contaminated groundwater and wastewater were reported in the literature [15–18], for instance, activated carbon filtration (ACF), reduction/coagulation/filtration (RCF) with iron (II) salts, membrane filtration, ion exchange and electrochemical treatment. Recent studies on the removal of Cr (VI) from industrial wastewater using new adsorbents based on biomass wastes, microalgae and co-immobilized microbial biochar beads were reported in the literature [19–21]. Moreover, recent review articles on advances in separation technologies for Cr (VI) removal were reported [22–24]. Brandhuber et al. studied reverse osmosis, nanofiltration, adsorbent resins and RCF for low-level Cr (VI) treatment [25], while Giagnorio et al. reported on nanofiltration for achieving low concentrations of Cr (VI) in drinking water [26].

Activated carbon (AC) is a very well-known adsorbent for metal species; the main governing mechanisms include physical adsorption and/or chemical reduction. The removal of Cr (VI) by chemical reduction to Cr (III) at low pH values was reported [27,28]. In addition, Han et al. determined the adsorption capacity of granular activated carbon (GAC) using artificial groundwater with 5 mg/L Cr (VI); the loading was 0.13 mg Cr (VI)/g AC, which was increased to 0.38 mg Cr (VI)/g AC by acid treatment [29].

In RCF treatment, Cr (VI) is reduced to Cr (III) and then removed by coagulation and precipitation [30]. Reducing agents including sulfur compounds (e.g., sulfur dioxide and sodium metabisulfite [31,32]) and metal salts (e.g., tin (II) [33] and iron (II) [16]) were reported. Both iron (II) sulfate and sodium metabisulfite are approved additives for drinking water treatment [34]. Therefore, ferrous sulfate was used as a reducing agent in this study. Basically, ferrous sulfate reduces Cr (VI) to Cr (III) according to the following reaction [30,35]:



The formed Fe (III) acts as a coagulant for Cr (III) species, and the coprecipitated particles are subsequently removed via filtration. Chemical-kinetic investigations showed

that the rate-determining step is the reduction of Cr (VI) to Cr (V) along with the subsequent reduction to Cr (III) [35].

Reverse osmosis (RO), a pressure-driven membrane separation process commonly used for water desalination [36,37] and for micropollutant removal [36,37], was also examined for chromium elimination. Chromium species can already be retained by less-dense low-pressure thin-film composite (LP-TFC) membranes in a low-pressure reverse osmosis (LPRO) process that requires less energy; therefore, it is more cost-efficient than typical RO desalination processes. Examples of the removal of Cr (VI) species by LPRO in the ppm concentration range are reported in the literature [26,38,39]. The separation mechanism is generally described by combined size exclusion and electrostatic effects resulting in a strong pH dependence of chromic acid species retention, since chromic acid (H_2CrO_4) is a medium-strong acid with a pK_a of 6.5. In the respective pH range, LP-TFC membranes can effectively retain hydrated multivalent anions as chromate (CrO_4^{2-}) due to electrostatic repulsion with the deprotonated surface functional groups on the membrane surface, making this technology ideal for Cr (VI) separation [40]. Mnif et al. [39] reported an increase in Cr (VI) rejection from 99.2% at pH 4.0 to 99.9% at pH 10 using the RO-SG 2514 membrane. Furthermore, in an AWWA study [25], the LFC-1 RO membrane showed Cr (VI) rejection of ~87% at pH 5.6 and ~90% at pH 8.3, whereas the ESNA NF membrane had Cr (VI) rejection of ~72% at pH 5.7 and ~90% at pH 8.3. This reveals that LPRO retention of chromate species can be significantly decreased at low pH values because of the larger fraction of hydrogen chromate (HCrO_4^-) in the total chromium concentration, which is less efficiently retained than the divalent CrO_4^{2-} anions (see Table 1 and Supplementary Materials, Section S1).

Table 1. The percentage of main Cr (VI) species in total chromium (VI) as a function of pH¹.

pH	Chromate (%)	Hydrogen Chromate (%)
5.6	13.7	86.3
6.5	50.0	50.0
7.6	92.6	7.4
8.3	99.4	1.6

Note(s): ¹ Calculated with pK_a of 6.5 for chromic acid and c_{Cr} 520 $\mu\text{g}/\text{L}$ (0.01 mmol/L) [41]. The corresponding species diagram is shown in Figure in Section S1.

There are relatively few studies in the literature on the removal of Cr (VI) in drinking water treatment, especially for raw water with a Cr (VI) concentration in the $\mu\text{g}/\text{L}$ range and neutral pH range, which is to be expected. In addition, no information was found on the removal of Cr (III) and Cr (VI) species at low concentrations by ACF, RCF or LPRO. For drinking water suppliers, however, it is of utmost importance to know whether trace concentrations of chromium (i.e., 1–10 $\mu\text{g}/\text{L}$), which is becoming legally relevant, can be removed with the existing technology (in this case, ACF) or RCF, which is easy to upgrade, or whether a high-end solution such as LPRO needs to be provided. For this reason, laboratory-, pilot- and full-scale experiments, described below, were conducted to investigate, for the first time to the authors' best knowledge, the removal of Cr (III) and Cr (VI) species by ACF, RCF and LPRO processes in a concentration range of 1–10 $\mu\text{g}/\text{L}$.

2. Materials and Methods

2.1. Materials

All chemicals used in this work were of analytical grade and were used as supplied. A full description, including purity and suppliers, can be found in Supplementary Materials, Section S2. Two types of ACs and their reactivated forms were used in this work; the main characteristics are listed in Table 2. Spiral wound LPRO membrane elements of type TMH 10A (each 4 inches and 8 m²) were obtained from Toray Membrane Europe AG, Münchenstein, Switzerland. TMH 10A is a TFC membrane consisting of a fully crosslinked aromatic polyamide supported on a macroporous polysulfone carrier; salt rejection reported by the manufacturer is 99.3%, measured at operating conditions: pressure

of 6.9 bar, temperature of 25 °C, feed concentration of 500 mg/L NaCl, recovery of 15%, feed water pH 7 and permeate flow rate of 9.1 m³/d [42].

Table 2. Characteristics of activated carbons employed in this study.

Parameter	F300	F300, Multiple Reactivated	F207c
Base material	hard coal	hard coal	coconut
Iodine Number (mg/g)	974	n.a. ³	1100
Abrasion number (min)	85	n.a. ³	97
Ash, weight (%) ¹	31.8	25.2	3.29
Apparent density (g/mL)	0.538	0.542	0.565
Calcium (mg/kg) ²	695	5000	594
Chromium (mg/kg) ²	640	422	557
Iron (mg/kg) ²	5660	5790	3090
Manganese (mg/kg) ²	48.1	83.9	44.1

Note(s): ¹ Ash according to DIN 51719. ² Investigation in aqua regia digestion using ICP-OES according to ISO 11885 based on the dry substance. ³ Not analyzed.

2.2. Raw Water

The raw water was pumped from five wells and comprised of approx. 70% Rhine riverbank filtrate and ~30% groundwater. A complete chemical analysis and the main characteristics of the raw water are given in Supplementary Materials, Section S3. The raw water can be regarded as hard water (mean calcium concentration was 82.5 mg/L) and well mineralized (mean electric conductivity was 760 µS/cm). This was particularly caused by two wells; one contained significant amounts of groundwater with relatively high hardness and acidity, while the other had an elevated sodium chloride content (due to a second aquifer). Elevated iron and manganese concentrations were also measured in the raw water from two other wells. In addition, the raw water contained ~0.3 µg/L Cr (VI), while the Cr (III) content was below 0.15 µg/L.

2.3. Pilot Plant

The pilot plant was designed by Stadtwerke Düsseldorf (SWD) and made by Cornelsen Umwelttechnologie GmbH, Essen, Germany. The LPRO unit was built by Grünbeck Wasseraufbereitung GmbH, Höchstädt a.d. Donau, Germany (GENO Nano RKF1800 S). Electric installation, plant control and data management were installed by SWD. A detailed description of the system was reported elsewhere [37]. The pilot plant consisted of two treatment lines, ACF and LPRO, with 16 sampling points on the ACF line and 10 sampling points on the LPRO line. A detailed description of the sampling points is provided in Supplementary Materials, Section S4. A schematic illustration of the ACF line is shown in Figure 1.

Raw water (1.1) was continuously pumped into the storage tank (1.2) with built-in ventilation. Aeration and anthracite filtration (3.1 in Figure 1) as well as anthracite sand filtration (3.1.2 in Figure 2) were used as pretreatment for the removal of iron and manganese species prior to ACF and LPRO operations. During aeration, the raw water pH increased by ~0.2 because of carbon dioxide stripping.

The spiking of the pretreated raw water with Cr (III)/Cr (VI) solutions (cf. Section 2.4) was carried out at dosing points 2 and 2A for ACF using a DDA Smart Digital Pump (Grundfos GmbH, Erkrath, Germany). The multiphase pump (2.2.1) (PBU 201-E10-Cr Edur Pumpenfabrik, Kiel, Germany) delivered the water to the continuous flow reactor (CFR; 2.3), and the booster pump (2.4) increased the pressure to 6.5 bar. The water was then pressed through the anthracite filter (3.1) and the AC filter (4.1). Biological processes on the anthracite filter led to a reduction of the pH value by 0.1; hence, a pH value of 7.4 was determined at the filter outlet. Due to the aeration, the oxygen content in the anthracite filter inlet was increased from 8.5 to 9.0 mg/L. A pressure control valve was installed in the outlet to maintain the pressure at 5.0 bar, the typical network pressure in the city of Düsseldorf, Germany. The removal of Cr (VI) using ACF was affected by various operating

parameters, e.g., specific throughput and empty bed contact time, which were controlled by the volumetric flow rate at 2.0 m³/h.

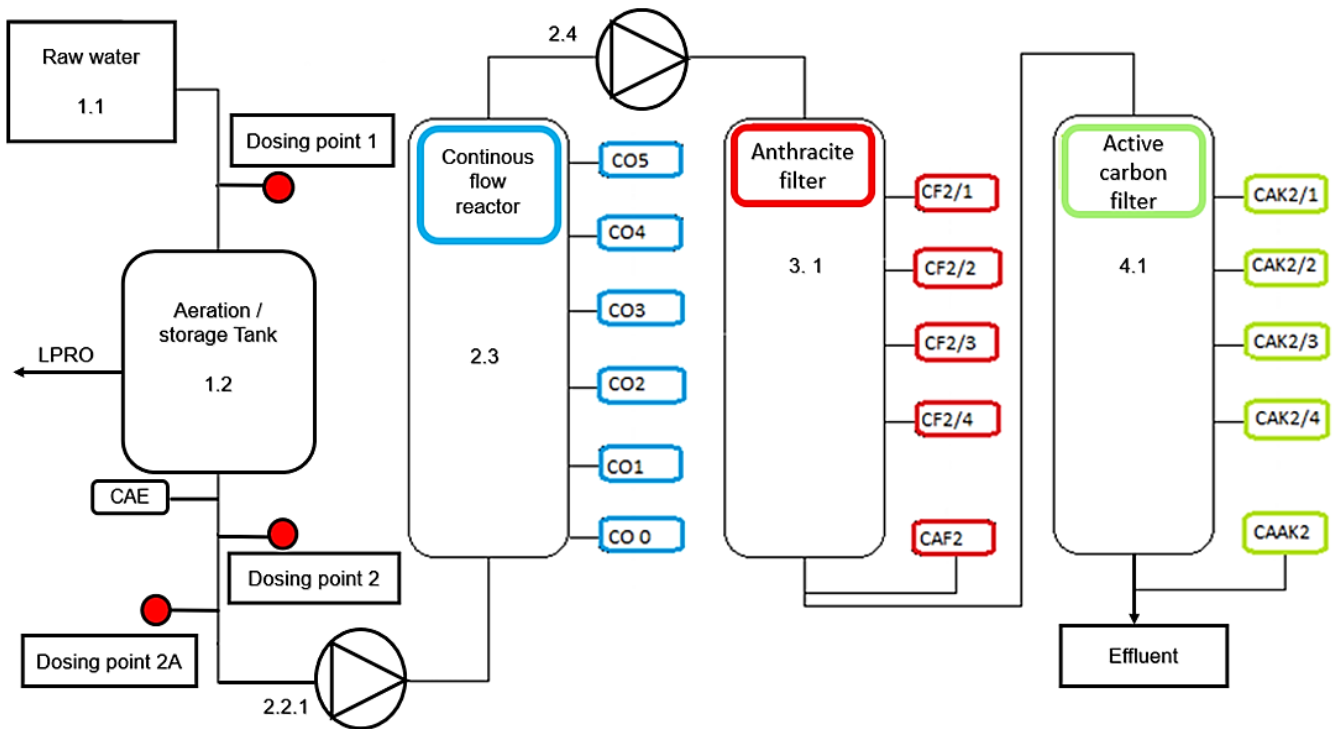


Figure 1. Schematic illustration for the pilot plant—ACF line with a CFR, anthracite filter and activated carbon filter with sampling points. A detailed description of the sampling points is provided in Supplementary Materials, Section S4.

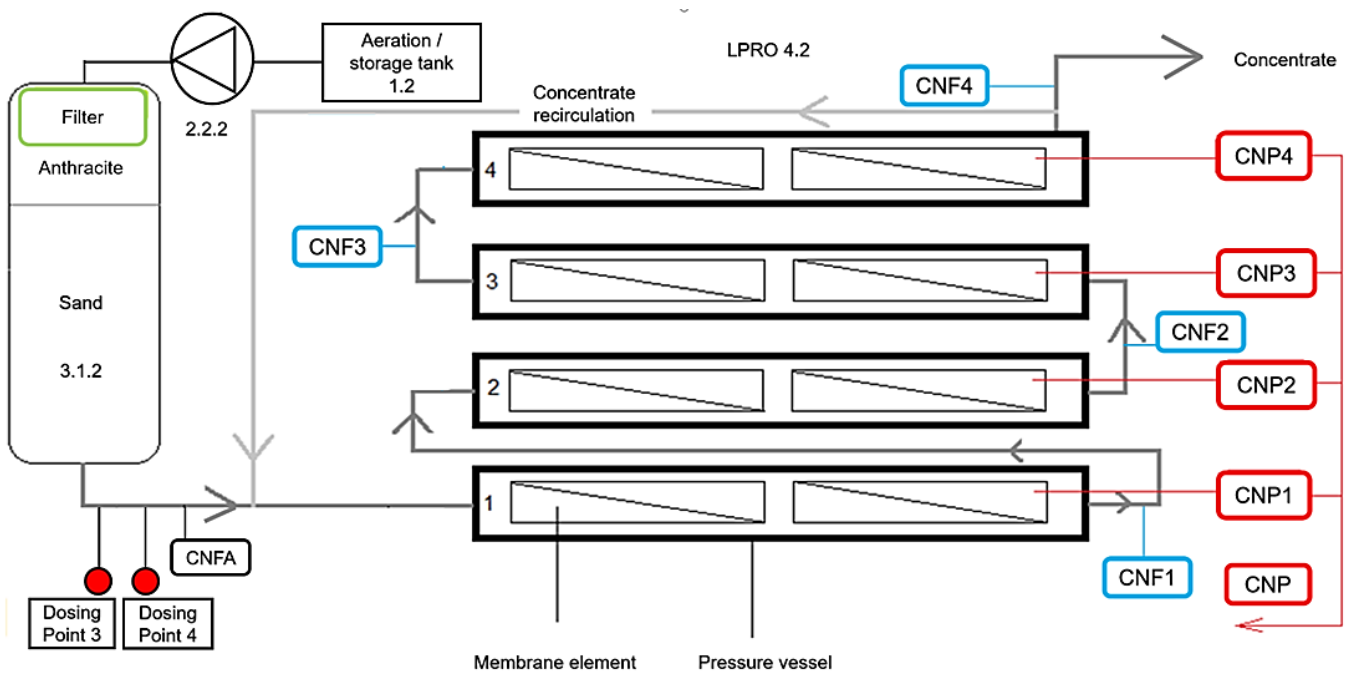


Figure 2. Schematic illustration for the pilot plant—LPRO line with several sampling points. A detailed description of the sampling points is provided in Supplementary Materials, Section S4.

For RCF, a Cr (VI) solution was injected at dosing point 1 and mixed with raw water in the aeration tank. An iron (II) sulfate solution was then added at dosing point 2. The specifications of the major system components are listed in Table 3.

Table 3. Specifications for the main pilot plant components (ACF and LPRO lines).

Component	Specification
Aeration/storage tank	Cylindrical tank, height: 120 cm, diameter 160 cm; filling height (control size): 70 cm, with built-in ventilation (air/water ratio = 1:3).
Continuous flow reactor (CFR)	Height 250 cm, diameter 75.5 cm; flow time from dosing point 2 to CO5 at a flow of 2 m ³ /h is 22 min.
Anthracite filter (ACF line)	Height: 150 cm, diameter 75.5 cm. Supporting layer: 10 cm gravel, grain size 30 mm; 150 cm anthracite (Aquazit N, Type I), grain size 0.8–1.6 mm; from Euroquarz, Dorsten, Germany; flow time from dosing point 2 to CAF2 at a flow of 2 m ³ /h is 48 min.
AC filter	Height 250 cm, diameter 75.5 cm filled with Hydraxin XC 30 (8 × 30), bulk density 450 kg/m ³ , 318.6 kg; reagglomerated activated carbon based on hard coal (Donau Carbon GmbH, Frankfurt, Germany); flow time from dosing point 2 to CAAK2 at a flow of 2.0 m ³ /h is 84 min.
Multilayer filter (LPRO line)	Height 150 cm, diameter 75.5 cm. Supporting layer: 10 cm gravel, grain size 30 mm; 80 cm silica sand, grain size 0.71–1.25 mm; and 70 cm anthracite, grain size 1.4–2.5 mm (Aquazit N, Type II); from Euroquarz, Dorsten, Germany.
Antiscalant	Cublen D 5113 (active substance: Diethylenetriamine pentakis(methyl phosphonic acid), DTPMP) at 0.2 g P/m ³ in feed; from Zschimmer & Schwarz Chemie GmbH, Lahnstein, Germany.

A schematic illustration for the LPRO line is shown in Figure 2. Pretreated raw water from the storage tank (1.2) was pressurized to 5 bar with a booster pump (2.2.2), passed through an anthracite sand filter (3.1.2) and used as feed for the LPRO (4.2) unit. Before membrane filtration, the feed was pretreated using two sequential cartridge filters with 80 and 5 µm nominal cutoff points. An antiscalant (cf. Table 3) was added before the sampling point CNFA (cf. Supplementary Materials, Section S4). The specifications of the main components of the pilot plant are listed in Table 3. The membrane unit consisted of four pressure vessels, each equipped with two 4-inch elements (cf. Figure 2). The pressure vessels were connected in series with recirculation of concentrate flow to increase the recovery rate. In large-scale RO systems, multiple-stage RO systems are usually installed; comparable concentration profiles can be achieved on a semitechnical scale by partially recirculating the concentrate [36]. This enables simulation of the bulk concentration at any point within an RO operated in continuous flow at a technical scale. The circulation of the concentrate resulted in an increase in the pH value in the feed by about 0.2.

Typical operating parameters of the LPRO line are shown in Table 4. Since certain operating parameters were varied during the pilot plant experiments, detailed operational data for LPRO are also given in Supplementary Materials, Section S5. Cr (III)/ Cr (VI) solutions were injected at dosing point 3, while pH was adjusted at dosing point 4 by acid or base.

Table 4. Typical operating parameters of LPRO without pH variation.

Parameter	Unit	Value
Medium flux	L/m ² /h	22
Raw water flow	m ³ /h	1.7
Feed flow	m ³ /h	2.1
Total permeate flow	m ³ /h	1.4
Total concentrate flow	m ³ /h	0.29
Recirculation flow	m ³ /h	0.44
Recovery	%	83

Table 4. *Cont.*

Parameter	Unit	Value
Feed conductivity	μS/cm	736–822
Permeate conductivity	μS/cm	32–62
Feed pH		7.4–7.5
Operating pressure	bar	6.7
Temperature	°C	13

2.4. Spiking Experiments with the ACF Line

In the first pilot-scale ACF experiment, a 20 mg/L Cr (VI)/ Cr (III) solution prepared from potassium chromate and chromium (III) chloride was dosed at dosing point 2 and a CFR influent flow rate of 2.0 m³/h, resulting in concentrations of 10 μg/L in the CFR influent (see Table 5). Because the stock solution became discolored, a second experiment was conducted in which potassium chromate and chromium (III) nitrate were added separately with the same concentrations as in the first experiment at dosing points 2 and 2A. A third experiment was conducted in this arrangement with concentrations of 1 μg/L Cr (VI) and 1 μg/L Cr (III). The fourth experiment was performed at a higher specific flow rate of the AC filter.

Table 5. Chromium spiking experiments in the ACF line.

Experiment	Dosage	Specific Load (m ³ Water/kg AC)
1.	10 μg/L Cr (VI) as potassium chromate + 10 μg/L Cr (III) as chromium (III) chloride	29.5
2.	10 μg/L Cr (VI) as potassium chromate + 10 μg/L Cr (III) as chromium (III) nitrate	38.5
3.	1 μg/L Cr (VI) as potassium chromate + 1 μg/L Cr (III) as chromium (III) nitrate	43.0
4.	10 μg/L Cr (VI) as potassium chromate	86.5

In a tracer experiment with sodium chloride to determine the residence time distribution in the pilot plant, a value of approx. 2.5 h was determined for CAAK2. Therefore, sampling was carried out after an equilibration period of 5 h. Samples for chromium analysis were taken at the sampling points marked in Figure 1 (CFR: CO1, CO2, CO3, CO4 and CO5; anthracite filter: CF2/1, CF2/2, CF2/3, CF2/4 and CAF2; activated carbon filter: CAK2/1, CAK2/2, CAK2/3, CAK2/4 and CAAK2). Samples were stored at 4 °C ready for IC-ICP-MS analysis of individual chromium species or acidified with nitric acid (1%) for total chromium analysis using ICP-MS. The removal ratios of Cr (III) and Cr (VI) were calculated from the analysis of chromium species concentrations at the sampling points. The removal was calculated according to Equation (2), where c_i and c_e are the influent and the effluent concentrations, respectively.

$$\text{Removal (\%)} = \left(1 - \frac{c_e}{c_i}\right) \times 100 \quad (2)$$

Deviations of the removal values, calculated using the measurement uncertainty for the chromium analyses (cf. Section 2.10) in the permeate and the effluents of the pressure vessels, were all below 0.2%.

2.5. Spiking Experiments under RCF Conditions

In the pilot-scale RCF experiments, potassium chromate was used to prepare the 2 mg/L and 20 mg/L Cr (VI) dosing stock solutions. At dosing point 1, with a flow rate of 2 m³/h and a dosing rate of 1 L/h, concentrations of 1 and 10 μg/L Cr (VI) were achieved (cf. Figure 1). Ferrous sulfate solutions containing 10, 20 and 60 g/L Fe (II) were added at dosing point 2 at a rate of 1 L/h to obtain Fe (II) concentrations of 1, 2 and 6 mg/L,

respectively (Table 6). Samples for chromium analysis were taken from the sampling points marked in Figure 1 (CFR: CAE, CO1, CO2, CO3, CO4 and CO5; anthracite filter: CF2/1, CF2/2, CF2/3, CF2/4 and CAF2). As the water collected at the sampling points (CO1 to CO5) was slightly brownish in color, the samples were filtered through a syringe filter (0.45 μm) immediately before stabilizing with nitric acid (1%). The removal was calculated as described in Section 2.4 and according to Equation (2).

Table 6. Chromium spiking experiments under RCF conditions.

Experiment	Dosage
1.	10 $\mu\text{g/L}$ potassium chromate and 6 mg/L ferrous sulfate
2.	1 $\mu\text{g/L}$ potassium chromate and 2 mg/L ferrous sulfate
3.	10 $\mu\text{g/L}$ potassium chromate and 1 mg/L ferrous sulfate
4.	10 $\mu\text{g/L}$ potassium chromate and 2 mg/L ferrous sulfate

2.6. Spiking Experiments with the LPRO Line

Potassium chromate and chromium (III) chloride (or chromium (III) nitrate) were used to prepare Cr (IV) and Cr (III) dosing stock solutions with 17 mg/L chromium, which were injected at dosing point 3 (into LPRO influent, cf. Figure 2) at a flow rate of 1 L/h for a period of 3 h. Employing an adjusted flow of 1.7 m^3/h , the influent concentrations of Cr (III) or Cr (VI) species were 10 $\mu\text{g/L}$. The spiking experiments with the LPRO line were carried out in one campaign within three months; see Table 7.

Table 7. Chromium spiking experiments in the LPRO line.

Experiment	Dosage	pH Value
1.	10 $\mu\text{g/L}$ chromium (III) chloride	7.7
2.	10 $\mu\text{g/L}$ potassium chromate	7.7
3.	10 $\mu\text{g/L}$ chromium (III) nitrate	7.4
4.	10 $\mu\text{g/L}$ potassium chromate	7.6
5.	10 $\mu\text{g/L}$ potassium chromate	6.5
6.	10 $\mu\text{g/L}$ potassium chromate	5.6
7.	10 $\mu\text{g/L}$ potassium chromate	8.3

In order to investigate the pH dependence of chromate removal by LPRO, the pH was adjusted to different values by dosing hydrochloric acid or sodium hydroxide at certain rates at dosing point 4. Hydrochloric acid (16%) was dosed at a rate of 330 mL/h and 770 mL/h for 21 h to achieve pH values of 6.5 and 5.7, respectively. When a pH of 6.5 was reached, the chromate solution was injected at dosing point 4, and samples were taken after 3 h. The pH of the feed was then equilibrated to 5.6, and samples were taken after an equilibration period of 3 h. The pH value was adjusted to 8.3 with sodium hydroxide solution (10%) at a dosing rate of 70 mL/h. Samples for chromium analysis were collected from the sampling points described in Supplementary Materials, Section S4. Chromium retention by one pressure vessel and the overall retention by the LPRO line were calculated according to Equation (3), where c_b and c_p are the average bulk and the permeate concentrations, respectively.

$$\text{Rejection (\%)} = \left(1 - \frac{c_p}{c_b}\right) \times 100 \quad (3)$$

The average bulk concentration was calculated as the arithmetic mean value of the concentration at the inlet and outlet of the respective pressure vessel or the entire LPRO line. The deviations of the values for the retentions were all below 0.2%, calculated with the measurement uncertainty for the chromium analyses in the permeates and concentrates of the pressure vessels. For chromium species concentrations that were below the limit of quantification (LOQ), the values in the permeates were set to LOQ, and the respective rejection rates were calculated using LOQ values and marked with “>”.

2.7. RCF Laboratory Experiments

Prior to the pilot-scale RCF experiments (cf. Section 2.5), the operating parameters were adapted in laboratory experiments to determine the required concentration of ferrous sulfate for the complete reduction of Cr (VI). Certain amounts of ferrous sulfate were added into 100 mL of raw water containing 0.1 mmol/L Cr (VI) at 15 °C and a pH value of 7.3 under stirring to achieve the final concentrations of 0.2, 0.5 and 0.6 mmol/L Fe (II). After a reaction time of 30 min, the samples were collected and filtered through a syringe filter (0.45 µm) into a 1 cm quartz cuvette (Hellma GmbH & Co. KG, Müllheim, Germany). Then, the Cr (VI) concentration was analyzed by a UV/Vis spectrophotometer (Perkin Elmer Lambda 35, PerkinElmer Inc., Waltham, MA, USA) at a wavelength range of 200–700 nm to determine the decrease in Cr (VI) absorption at 375 nm. Analytical characteristics of the UV/VIS detection method for Cr (VI) are given in Supplementary Materials, Section S6.

The kinetics of the RCF process were investigated by adding 1 mmol/L ferrous sulfate to the raw water with 0.1 mmol/L Cr (VI) at pH 7.3 under stirring at 15 °C. Samples were collected after 1, 5 and 10 min, filtered and analyzed by the UV/Vis spectrophotometer as described above.

2.8. Laboratory Experiments on the Kinetics of Adsorption on Activated Carbon

Granular AC samples were ground using an ultra-centrifugal mill with a sieve diameter of 80 µm (Retsch GmbH, Hann, Germany). Carbon doses (500 ± 5 mg) were suspended in 250 mL raw water under stirring at 23 ± 2 °C. An inline filter (5 µm) was inserted into the suspension, and the filtrate was pumped continuously using a cassette pump into a 5 cm cuvette and then returned to the suspension. After stabilization, the background was recorded and set to zero. The time-dependent measurement of Cr (VI) was performed at 375 nm for 30 min. After stirring for 3 min, 0.5 mL of 0.1 mol/L Cr (VI) in deionized water was added to the suspension to give a final concentration of 0.02 mmol/L Cr (VI). The decrease in Cr (VI) concentration was calculated as c_t/c , where c_0 represents the concentration of 0.02 mmol/L Cr (VI) in raw water without AC addition.

2.9. Investigation on the Transferability of Pilot Plant Results into Technical Scale

The examined technical-scale drinking water treatment plant (DWTP) has 24 technical activated carbon filters; each has dimensions of 800 cm (height) and 500 cm (diameter). They are designed as a pressurized two-layer filter with an upper 150 cm filling with anthracite of a grain size of 1.4–2.5 mm (Aquazit N, Type II, Euroquarz, Dorsten, Germany) and a lower AC layer of 250 cm height (either Chemviron F300 or Norit GAC 830 EN, both reactivated several times) on a base layer of 20 cm gravel with a grain size of 30 mm. The AC layer includes 10% fresh AC on top to compensate for the reactivation loss. Depending on the requirement for the treatment volume, the flow rate of the filter was between 200 and 250 m³/h. Samples for total chromium analysis were taken from the outlet of 19 anthracite filters and the corresponding AC layers. The samples were acidified with 1% nitric acid and analyzed using ICP-MS.

2.10. ICP-MS Analytics

The total multielement analysis was performed according to ISO 17294 [43] using ICP-MS (Agilent 7900, software ICP-MS MassHunter 4.2, Agilent Technologies Germany GmbH & Co., Waldbronn, Germany). The calibration was carried out using certified standards on the same working day (cf. Supplementary Materials, Table in Section S2). The analytical characteristics are given in Supplementary Materials, Section S7. The measurement uncertainties are provided in Supplementary Materials, Section S8.

Chromium species analysis in the ng/L to µg/L range can be performed using different methods [44,45]. In this study, the separation and quantification of Cr (III) and Cr (VI) were achieved by coupling a low-pressure IC column (ESI Chrom Speciation Column) with ICP-MS. Separation was performed using an autosampler with a peristaltic pump (SC DX FAST MP2-4-52, Elemental Scientific, Omaha, NE, USA) coupled with an

ion chromatography column (ESI chromFAST speciation kit, CF-KIT-Cr36). The chromium species eluted separately from the anion-exchange column (CF-Cr-01, Elemental Scientific, Omaha, Nebraska, USA) were determined using ICP as Cr (VI) at 2.75 min and as Cr (III) at 5.67 min. The analytical characteristics and the chromatogram of the Cr (III)/Cr (VI) speciation method with an IC-ICP-MS chromatogram are included in Supplementary Materials, Section S9. A 10-point calibration was carried out in the concentration range of 0.1–1 µg/L in deionized water. Calibration solutions were diluted from certified standards, and the accuracy was checked with chromium-certified water prepared on the same working day. The eluent phase consisted of 15 mL of 69% nitric acid and 23 mL of 22% ammonia in 500 mL of deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$), which was adjusted to pH 2.0 with 65% nitric acid. The analytics was carried out within 24 h after sampling.

2.11. Acid Treatment of Reactivated Activated Carbon

The ground reactivated AC (0.5 g) was stirred with 60 mL of 10% hydrochloric acid for 2 days. Thereafter, the AC suspension was filtered through a 0.45 µm filter, and the filtrate was analyzed for impurities/trace elements by ICP-MS; the results are provided in Supplementary Materials, Section S10.

3. Results and discussion

3.1. Chromium Removal by ACF Treatment

3.1.1. Pilot Plant Experiments

The results from the first spiking experiment with 10 µg/L Cr (III) and 10 µg/L Cr (VI) in the ACF line revealed that the Cr (III) concentration in the raw water at pH > 7 was reduced by about 90% in the aeration/storage tank (cf. Figure 1, point 1.2). The residual 10% passed the CFR without further reduction and was completely removed in the top 30 cm of the anthracite filter. Since the Cr (III) equilibrium concentration at neutral pH was normally below 1 µg/L [10], at higher concentrations, Cr (III) hydroxide precipitates were formed because of its low solubility product ($k_{\text{SP}} = 6.3 \times 10^{-31} \text{ mol}^4 \text{ L}^{-4}$ at 25 °C) [46]. For this reason, Cr (III) could be completely eliminated as a precipitate from the neutral raw water by the filtration step. Therefore, it can be assumed that Cr (III) removal can also occur by natural filtration processes, for instance, riverbank filtration or groundwater recharge.

In contrast, a Cr (VI) concentration of ~13 µg/L in the inflow could not be separated in the anthracite filter; it was removed by about 70% in the subsequent activated carbon filter (cf. Figure 3).

The following spiking experiments displayed more or less the same performance. Detailed numerical data on the measured chromium concentrations in the ACF line are provided in Supplementary Materials, Section S11. Complete removal of Cr (III) and removal of Cr (VI) by about 60% with reference to the concentration at CAF2 were measured (cf. Figure 4). The increase in Cr (VI) concentration from CO5 to CF2/1 by about 3.5 µg/L could be due to the oxidation of Cr (III) to Cr (VI) through contact with the filter material since the Cr (III) concentration was reduced to approx. 3 µg/L at the same time. The filter was flushed three days before the spiking experiments and operated without dosing. It is known that the reaction of manganese (II) species with oxygen in raw water can result in the formation of γ -manganite (manganese (II/IV) oxide hydrate) that deposits on the filter and catalytically oxidize Cr (III) to Cr (VI) in the presence of oxygen [12]. Although the filter flushing was supposed to remove most of the solid deposits including manganese (III/IV) oxides, some residues may be responsible for the formation of Cr (VI) on the upper filter layer. In both experiments, Cr (VI) was not removed in either the CFR or in the anthracite filter, but it was partially removed in the AC filter down to ~60–70% of the concentration at CAF2. A partial removal of Cr (VI) was also observed in the batch adsorption tests using AC in the mg/L range and a contact time of 60 min by Attia et al. [47]. Here, the highest removal of Cr (VI) was achieved at pH 1.5, while at pH 7.5, a Cr (VI) removal of 50% was measured.

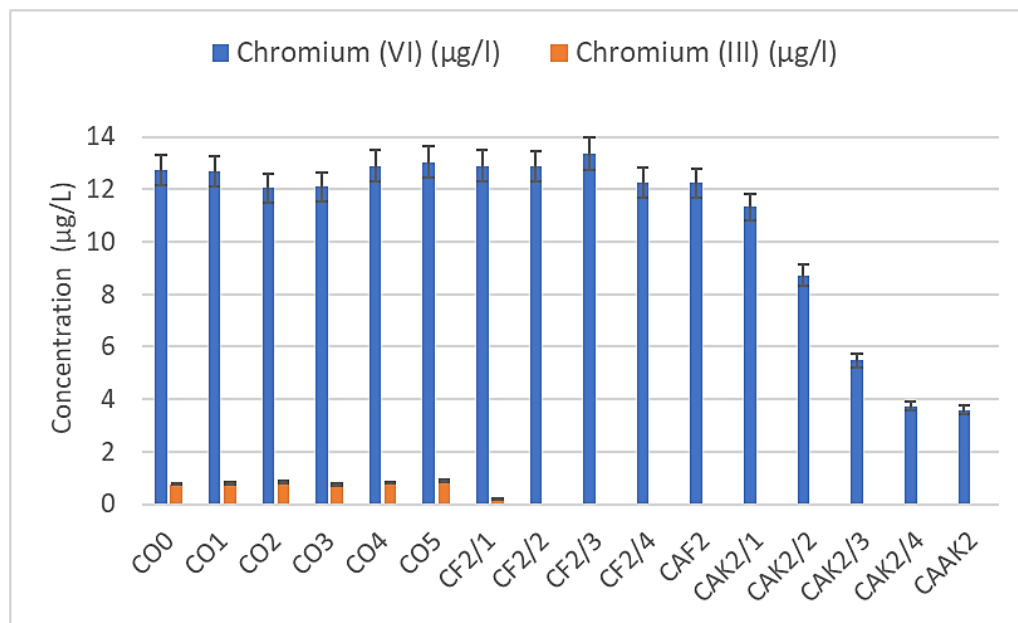


Figure 3. Concentration of chromium in the ACF line (dosing concentrations of Cr (III) and Cr (VI): 13 µg/L; specific throughput AC filter: 29.5 m³ water/kg AC). Sampling points are illustrated in Figure 1 and listed in Supplementary Materials, Section S4. The absence of a result for Cr (III) means that the concentration was below the limit of quantification (LOQ).

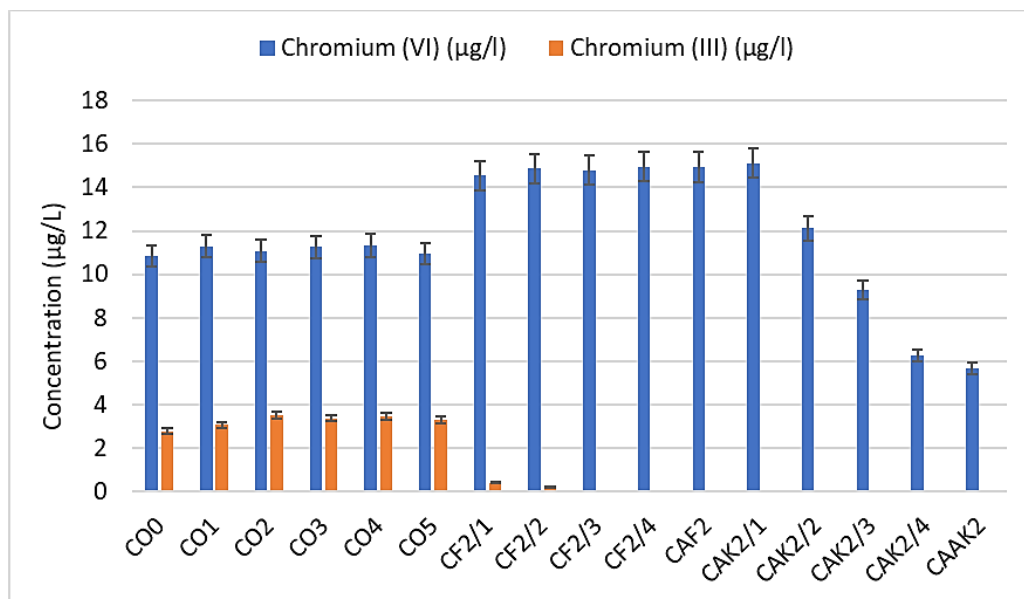


Figure 4. Concentration of chromium in the ACF line (dosing concentrations of Cr (III) and Cr (VI): 10 µg/L; specific throughput AC filter: 38.5 m³ water/kg AC). Sampling points are illustrated in Figure 1 and listed in Supplementary Materials, Section S4. The absence of a result for Cr (III) means that the concentration was below the LOQ.

Further experiments were carried out at a lower initial chromium concentration of 1 µg/L, which was close to the real raw water contamination level, i.e., 0.3 µg/L (cf. Figure 5). In this case, Cr (III) was completely eliminated in the aeration/storage tank and did not reach the CFR in a measurable concentration, while Cr (VI) was removed by ~60% in the AC filter relative to the concentration at CAF2.

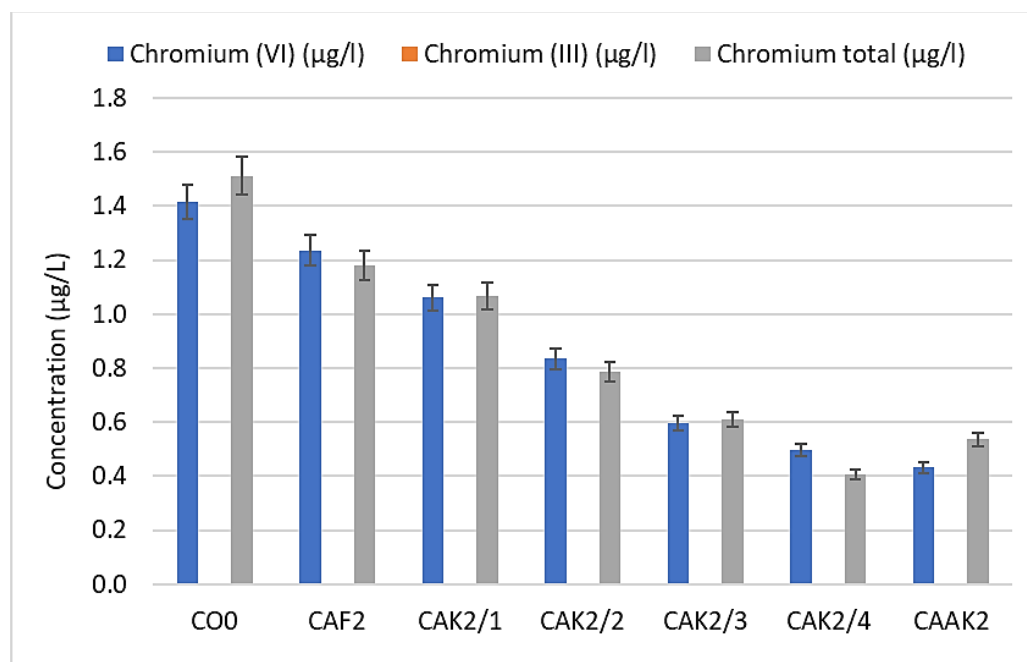


Figure 5. Concentration of chromium in the ACF line (dosing concentrations of Cr (III) and Cr (VI): 1 µg/L; specific throughput AC filter: 43 m³ water/kg AC). Sampling points are illustrated in Figure 1 and listed in Supplementary Materials, Section S4. The absence of a result for Cr (III) means that the concentration was below the LOQ.

Moreover, the decrease in Cr (VI) concentration within the AC filter showed a linear relationship with the filter depth, as can be seen in Figure 5 (the sampling points are equidistant). This agrees with the behavior reported by Attia et al. [47], where a linear relationship between Cr (VI) removal up to 75% and the contact time was found in batch adsorption experiments.

3.1.2. Transferability Investigations

The total chromium removal data in the 19 AC filters of the DWTP as a function of the specific throughput of the filters and using two different AC products are plotted in Figure 6. With an influent total chromium concentration of ~0.3 µg/L, the effluent concentrations varied strongly depending on the specific loading. However, in addition to a total chromium removal of up to 55%, a release of chromium species was also observed.

To gain more insight into the reasons for the different removal results in pilot-scale and technical-scale experiments, a series of bench-scale kinetic adsorption tests were conducted to measure Cr (VI) removal using two commercially available fresh ACs, two reactivated ACs and one acid-washed AC (cf. Section 2.8). The removal of Cr (VI) during a 30 min experiment, which corresponds roughly to the retention time of a typical AC filter in a drinking water treatment plant, was plotted against time (cf. Figure 7). With the addition of Cr (VI) after 3 min, its concentration increased sharply, although some Cr (VI) species were adsorbed immediately. The Cr (VI) adsorption rate decreased with time for most AC samples until saturation was reached. The process was almost completed within the run time of 30 min. The maximum Cr (VI) removal achieved by AC samples increased in the following order: multiple reactivated F300 < reactivated and acid-washed F300 < reactivated F207c < fresh F207c < fresh F300.

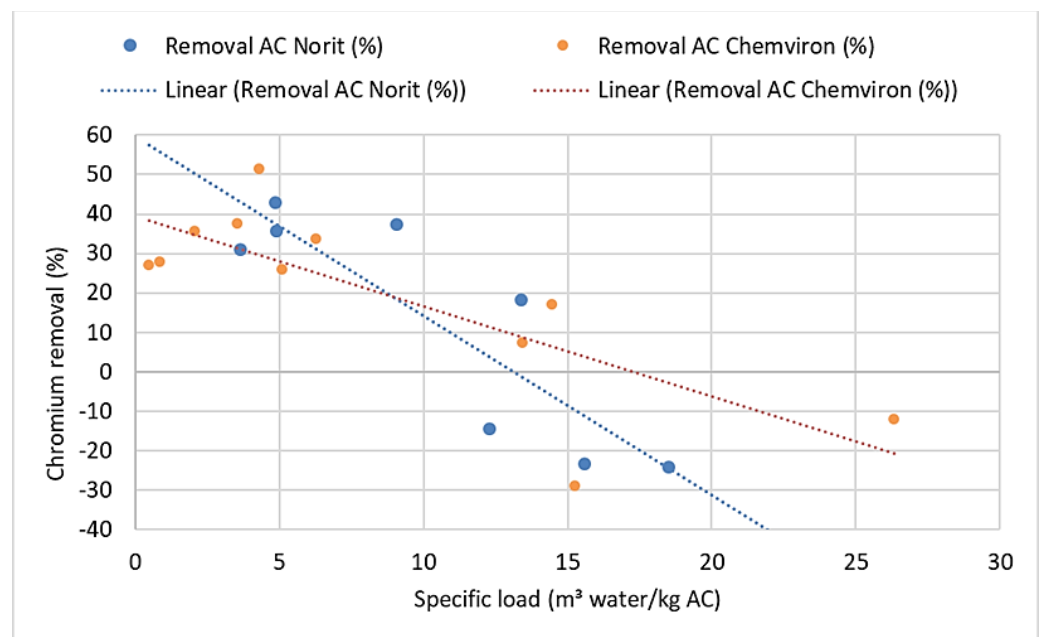


Figure 6. Total chromium removal in 19 AC filters of the DWTP depending on the specific throughput (Cr (VI) removal data are listed in Supplementary Materials, Section S12). The lines are intended for better eye guidance.

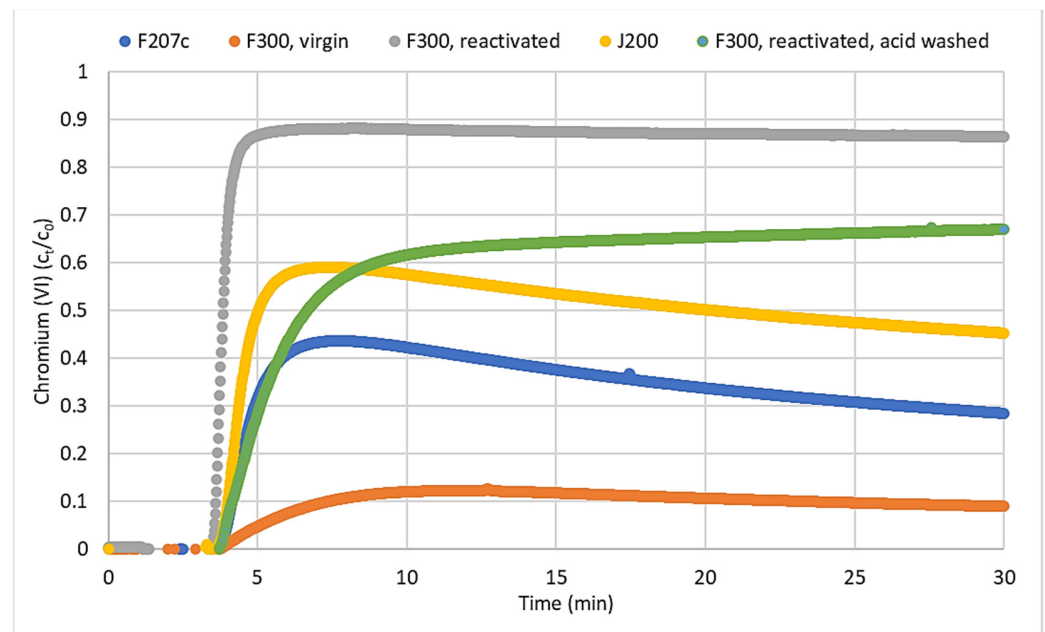


Figure 7. Decrease in relative Cr (VI) concentration by applying fresh and reactivated commercially available AC samples; $c_0 = 1.04$ mg/L Cr (VI) (0.02 mmol/L); and solution added after 3 min.

In parallel, the adsorption capacities for the bench-scale tested AC samples were calculated from the final Cr (VI) concentrations (cf. Figure 7) and are listed in Table 8. They were found to be significantly different.

Table 8. Maximum Cr (VI) adsorption capacity for the AC samples shown in Figure 7.

Activated Charcoal	Cr (VI) Adsorption Capacity (mg/g)
F300, fresh	1.89
F300, reactivated	0.28
F300, reactivated, acid-treated	0.34
F207c, fresh	1.49
F207c, reactivated	1.16

The two fresh AC samples, Chemviron F300 and Aquasorb F207c, showed the highest adsorption capacities for Cr (VI) with 1.89 and 1.49 mg/g AC, respectively. These values were lower than those reported by Di Natale et al. [48], who measured an adsorption capacity of ~7.2 mg/g for Aquasorb F207 EA at a higher Cr (VI) concentration of 0.5 mM (~25 mg/L), low salinity and neutral pH value. In addition, An et al. [49] determined the Cr (VI) adsorption capacity by powdered wood-based AC of 2.64 mg/g at pH 7, which is comparable to the measured adsorption capacity for the coal-based F300 in the current study.

On the other hand, the reactivated AC samples showed a strong decrease in the adsorption capacity by ~22% after single reactivation (F207c) and ~85% after multiple reactivation (F300). It was evident that multiple reactivation of AC significantly reduced the adsorption capacity. The acid treatment of the reactivated F300 with 10% hydrochloric acid (see Section 2.11) led to an increased Cr (VI) adsorption capacity compared to the unwashed reactivated F300. However, this result was unsatisfactory because the performance of fresh AC could not be achieved. Analysis of the acid extracts by ICP-MS provided an interpretation for the reduced adsorption capacity for the reactivated F300 samples (see Supplementary Materials, Section S10). High concentrations of calcium and iron were found in the acid extracts, which negatively affected the adsorption capacity of the reactivated F300 samples. These elements can occupy (and thus deactivate) the active sites on F300 and limit its adsorption capacity for Cr (VI) species. Therefore, the observed decrease in the adsorption capacities (by ~10%) for the technical plant AC filters can be explained by the use of reactivated AC. The measured partial chromium removal in the AC filters within short runtimes was due to the 10% share of fresh AC placed on the top of the reactivated AC, since the high removal values could be detected only for a short period of time (about 80 days for 0.3 µg/L Cr (VI) influent concentration).

In summary, these experiments demonstrated the limitations of the ACF process for total chromium removal. In pilot-scale experiments, a Cr (VI) removal of 60–70% was achieved for an influent Cr (VI) concentration of 1–10 µg/L at an average flow velocity of 4.5 m/h and an AC filter depth of 2.5 m. That means that, if a final Cr (VI) concentration of 0.3 µg/L is required, the inlet Cr (VI) concentration must not exceed 1 µg/L. In addition, the use of reactivated AC cannot be recommended because the loading with chromium and other elements increased with more reactivation times, resulting in a decreased adsorption capacity towards Cr (VI) species. Thus, the ACF process can only be applied as a reliable method in drinking water treatment for the removal of Cr (VI) if fresh AC is used and the influent concentration does not exceed a certain concentration.

3.2. Chromium (VI) Removal by RCF Treatment

In principle, the removal (reaction) of Cr (VI) with ferrous sulfate should follow the stoichiometric ratio of 1:3 (Cr (VI) to Fe (II)) in an inert atmosphere (see Equation (1)). However, oxidizing agents present in the medium can also increase Fe (II) demand. For this reason, different Fe (II) to 0.1 mM Cr (VI) concentration ratios were examined in laboratory experiments (cf. Section 2.7). As expected, the intensity of the Cr (VI) absorption band at 375 nm decreased with increasing Fe (II) concentration; see Figure 8. The data obtained indicated a minimum ratio of 1:6 (Cr (VI) to Fe (II)) for the raw water to ensure complete Cr (VI) removal, which is twice the ratio reported in the literature [30,35], but it is in accordance with the AWWA study [25].

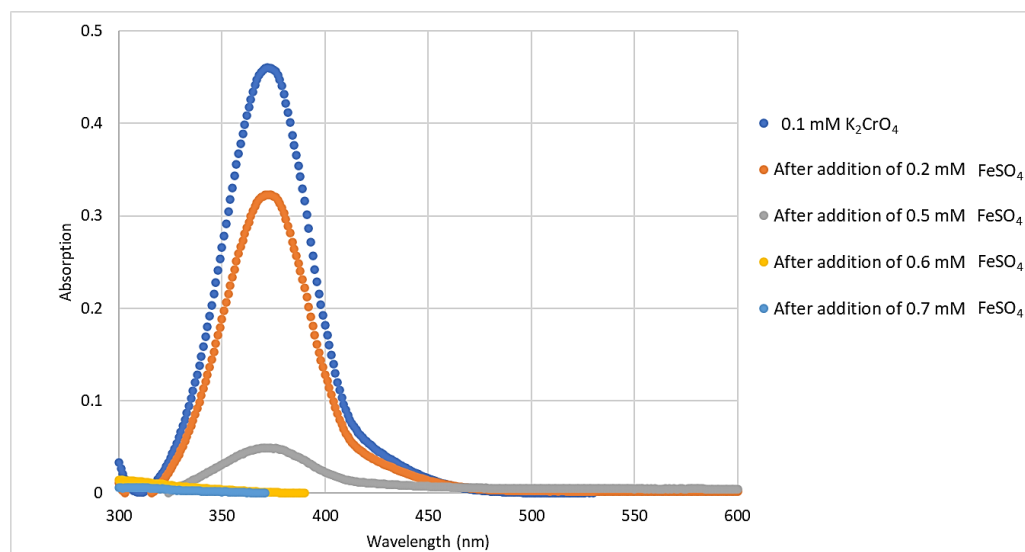


Figure 8. Change in the intensity of the absorption band for Cr (VI) (0.1 mmol/L) at 375 nm due to the reaction with iron sulfate at different Fe (II) concentrations.

Given that the low Cr (VI) concentrations in the pilot plant experiments were in the range of 1.9×10^{-3} mM to 1.9×10^{-4} mM (i.e., lower by a factor of 500 to 5000 than in case of laboratory experiments), an initial Cr (VI) concentration of 10 $\mu\text{g/L}$ and a Fe (II) concentration of 6 mg/L were chosen for RCF, which corresponds to a ratio of 1:600 (see Table 9).

Table 9. Concentrations of the employed Cr (VI) and Fe (II) concentrations and ratios besides the removal in pilot plant experiments.

Concentrations of Reactants	Ratio of Cr (VI)/Fe (II)	Removal of Cr (VI) (%)
10 $\mu\text{g/L}$ Cr (VI) + 6 mg/L Fe (II)	1:559	complete ¹
10 $\mu\text{g/L}$ Cr (VI) + 2 mg/L Fe (II)	1:186	complete ¹
10 $\mu\text{g/L}$ Cr (VI) + 1 mg/L Fe (II)	1:93	97.5
1 $\mu\text{g/L}$ Cr (VI) + 2 mg/L Fe (II)	1:1862	complete ¹

Note(s): ¹ Chromium (VI) concentration in the effluent < LOQ (0.15 $\mu\text{g/L}$).

Furthermore, kinetic tests revealed that the intensity of the Cr (VI) absorption band at 375 nm disappeared at a 10-fold Fe (II) excess concentration within minutes (cf. Figure 9). The continuous decrease in the nonspecific absorption intensity, especially at lower wavelengths, can be explained by the formation of iron (III) hydroxides.

The reduction rate constant (k) of Cr (VI) by Fe (II) was calculated according to Pettine et al. [50] using Equation (4), which was derived for a pH range of 5.0–8.7, temperature (T) range of 5–40 $^{\circ}\text{C}$ and ionic strength (I) range of 0.01–2 M.

$$\log k = 11.93 + 0.95 \text{ pH} - \frac{4260.1}{T} - 1.06 I^{0.5} \quad (4)$$

In laboratory experiments, at a pH of 7.6, temperature of 25 $^{\circ}\text{C}$, ionic strength of 0.013 M and Fe (II) concentration of 1 mM (60 mg/L), a half-life time of 1.1 s was calculated for the pseudo-second-order reaction, which was in a good agreement with the experimental data of almost complete removal after 1 min.

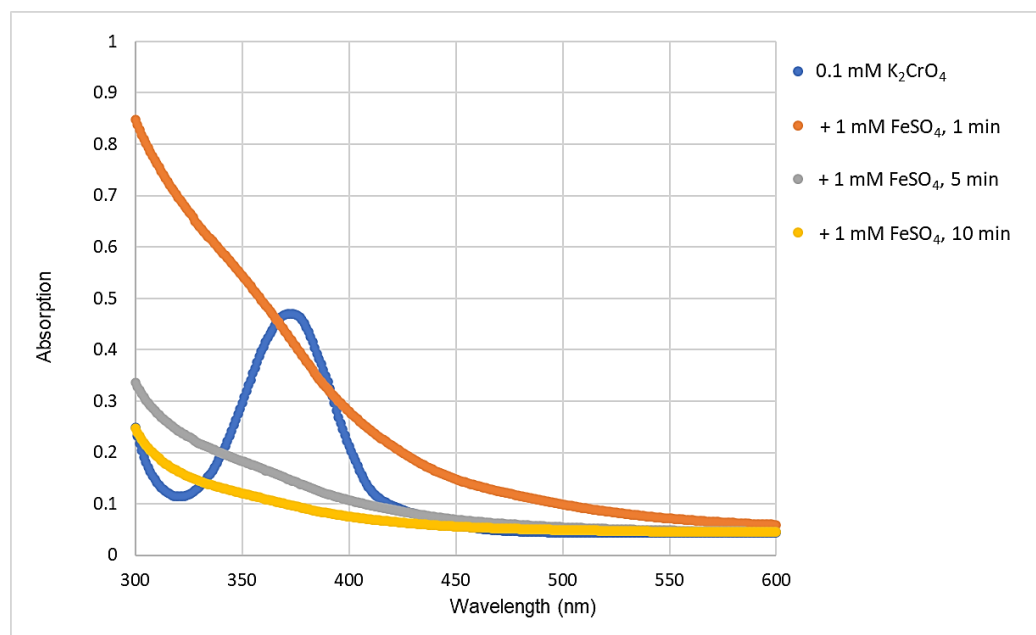


Figure 9. Reduction kinetics of Cr (VI) (0.1 mmol/L) by ferrous sulfate (1 mmol/L) at 15 °C and pH of 7.6.

In the pilot plant, the calculated half-life increases to 3.2 min at a temperature of 15 °C and Fe (II) concentration of 1 mg/L (0.18 mM). Pilot plant tests at different Fe (II) concentrations were carried out on this basis at concentration range of 1–6 mg/L. The removal rates along with different Cr (VI)/Fe (II) concentration ratios are listed in Table 9; detailed analytical results are included in Supplementary Materials, Section S13.

Post-treatment concentrations were below the LOQ in the case of an initial Cr (VI) concentration of 10 µg/L and Fe (II) doses of 6 and 2 mg/L, while reducing the Fe (II) concentration to 1 mg/L lowered the Cr (VI) removal to 97.5%. Therefore, it can be concluded that the Cr (VI)/Fe (II) ratio for complete removal was slightly higher than 1:100. Moreover, for a lower initial Cr (VI) concentration and Fe (II) dosage of 2 mg/L, the Cr (VI) concentration was also below the LOQ. Regarding the location of the reduction reaction (cf. Figure 10), it was found that the reaction started during the mixing in the multiphase pump, and it was completed in the CFR. The reduction reaction was almost completed after 10 min, as the Cr (VI) concentration at CO1 was <1 µg/L (8 min), while the Cr (VI) concentration at CO2 (16 min) was below the LOQ. The coprecipitated iron chromium hydroxide was subsequently removed using the deep bed filter (CF/1–CF/4), resulting in a Cr (VI) concentration below the LOQ at the filter effluent (CAF2).

In summary, RCF treatment was proven to be an effective method for the elimination of Cr (VI) species from raw water with a low influent Cr (VI) concentration in the range of 1–10 µg/L, using an Fe (II)-based coagulant with a dosing concentration of 2 mg/L Fe (II). For a complete reduction reaction, ferrous sulfate might be dosed with a minimum Cr (VI)/Fe (II) molar ratio of about 1:200 (but at least above 1:100). This is significantly higher than the typical stoichiometric ratio reported in the literature (i.e., 1:3), probably due to the additional side reaction of Fe (II) with dissolved oxygen. The reaction rate constant of the redox reaction between Fe (II) and oxygen at pH 7.2 was reported to be slower by a factor of 1000 than the reaction of Fe (II) and Cr (VI) at the same concentrations [29]. In the current work, the Cr (VI) concentration ranged from 10 to 1 µg/L (i.e., 1.9×10^{-4} – 1.9×10^{-5} mM), while the oxygen concentration ranged from 8.5 to 9.0 mg/L (~0.25 mmol/L), corresponding to a molar ratio of 1:1300 and 1:13,000, respectively. Therefore, in oxygen-saturated input water, as the Cr (VI) concentration decreases, the competition for the Fe (II) becomes more important and makes the RCF process inefficient.

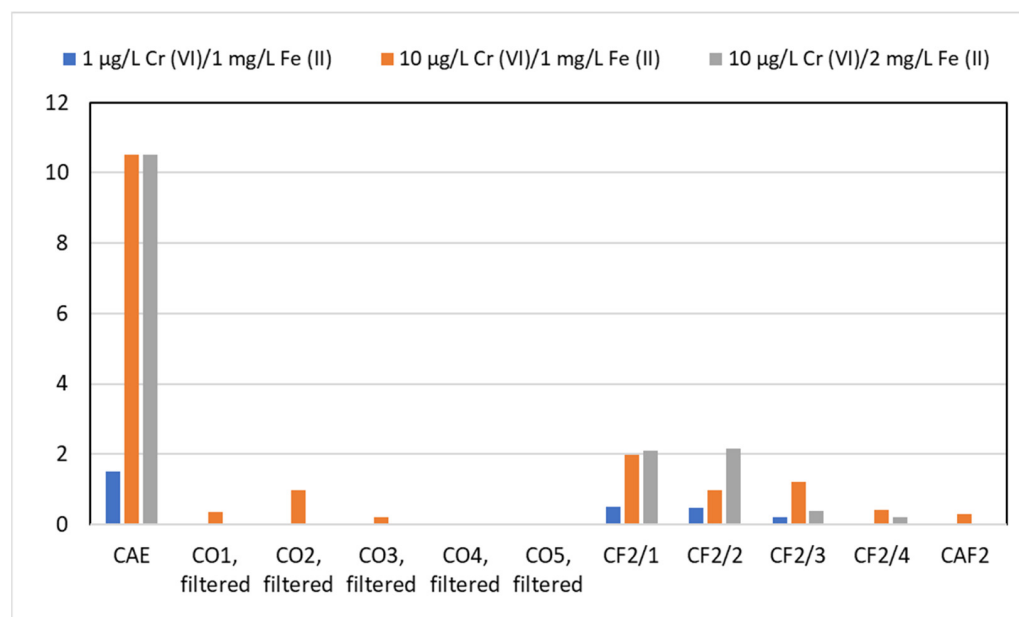


Figure 10. Removal of Cr (VI) during RCF treatment at different Cr (VI) to Fe (II) concentration ratios.

After the chemical reduction of Cr (VI) to Cr (III), coprecipitation with Fe (III) hydroxide took place, and the resulting precipitates were separated by deep bed filtration. In the present study, a filter depth of 1.5 m and an average flow rate of 4.5 m/h were used to ensure the complete removal of chromium iron hydroxide precipitates in the filter effluent (CAF2) (see Table 10). The total iron concentration in the effluent was below the LOQ of 0.02 mg/L because the raw water was aerated resulting in the oxidation of the residual Fe (II). In the case of anoxic raw water, the drinking water limit for iron would have to be monitored, for example, 0.200 mg/L in the EU [6]. In this case, RCF treatment with biological iron removal introduced by Mahringer et al. may be employed [51].

Table 10. Total chromium removal by RCF treatment for raw water containing 10 µg/L chromium (VI) and 2 mg/L ferrous sulfate.

Sampling Point	Total Chromium (µg/L)
CAE	10.5
CO1, filtered	<0.15
CO2, filtered	<0.15
CO3, filtered	<0.15
CO4, filtered	<0.15
CO5, filtered	<0.15
CF2/1	2.11
CF2/2	2.16
CF2/3	0.39
CF2/4	0.22
CAF2	<0.15

Additionally, the RCF process was found to be fast enough for use in drinking water treatment. For instance, an influent Cr (VI) concentration of 10 µg/L was reduced to <1 µg/L in about 8 min and was completely removed after 16 min. To achieve these results, good mixing and a minimum reaction time of 10 min were necessary. In this study, a multiphase pump and CFR were sufficient. Therefore, the RCF process demonstrated very good reliability for application in drinking water production under the employed operating conditions. Moreover, the RCF process can be adapted to further changes in the influent Cr (VI) concentrations. It is also advantageous that ferrous sulfate is already approved as an additive chemical for drinking water treatment (EN 889, chemicals for treating water for

human consumption—iron (II) sulfate [46], and the reaction products (precipitates) can be effectively separated.

3.3. Chromium Removal by LPRO Process

The rejection of Cr (III) and Cr (VI) by the LPRO process was studied using the operating data listed in Table 4 and Supplementary Materials, Section S5 and at a chromium concentration of 10 µg/L. Rejections for Cr (III), sodium and calcium are given in Table 11. Detailed analytical data for further ions are provided in Supplementary Materials, Section S14. Cr (III) rejections were higher than monovalent sodium and comparable to divalent calcium. As explained in Section 3.1.1, Cr (III) is not stable in raw water, and chromium hydroxide is formed at neutral pH values. Since concentrate recirculation and carbon dioxide permeation caused an alkaline pH shift in the LPRO feed, the probability increased that a considerable proportion of Cr (III) species might be present in the particle form and could be, therefore, easily separated.

Table 11. Rejection of chromium (III) species and other major cations using the LPRO process in the pilot plant with respect to bulk inlet and permeate outlet concentrations ¹.

Dosage	Sodium Rejection (%)	Calcium Rejection (%)	Chromium Rejection (%)
10 µg/L Cr as Cr(NO ₃) ₃ , pH 7.4	96.0	>99.3	>99.5
10 µg/L Cr as CrCl ₃ , pH 7.7	96.2	>99.1	98.9

Note(s): ¹ Relative combined uncertainty of 4.5–6.5% (cf. Supplementary data, Table in Section S8).

Experiments on removing Cr (VI) by LPRO also resulted in high rejections of >99% (see Table 12).

Table 12. Rejection of chromium (VI) using the LPRO process in the pilot plant with respect to bulk inflow and permeate outlet concentrations.

Dosage	pH-Value	Chromium (VI) Rejection (%)
10 µg/L Cr as K ₂ CrO ₄	5.6	>99.2
10 µg/L Cr as K ₂ CrO ₄	6.5	>99.1
10 µg/L Cr as K ₂ CrO ₄	7.6	99.2
10 µg/L Cr as K ₂ CrO ₄	7.7	>99.3
10 µg/L Cr as K ₂ CrO ₄	8.3	>99.2

Moreover, since the raw water pH can change depending on the environmental conditions, it was relevant to examine the rejection rate of Cr (VI) by LPRO as a function of pH. Cr (VI) was spiked in the feed to achieve a concentration of 10 µg/L. The pH in the feed was adjusted to different inflow values of 5.6, 6.5, 7.6 and 8.3. The rejection of Cr (VI) and other ions was measured at each pressure vessel at the different applied pH values. Detailed concentration data are provided in Supplementary Materials, Section S14. For all applied pH values, Cr (VI) was rejected to such an extent that Cr (VI) concentrations in the permeates were very close to or below the LOQ of 0.25 µg/L. Only in the case of pH 5.6, the rejections were slightly lower, which agreed with expectation (cf. Table 13). At pH values < 6.5, chromate was increasingly protonated to hydrogen chromate (HCrO₄⁻), which, as a monovalent anion should be less well retained, could explain the lower rejection at pH 5.6.

Table 13. Influent and permeate Cr (VI) concentrations for all pressure vessels at initial Cr (VI) feed concentration of 10 µg/L and pH 5.6 as well as the corresponding Cr (VI) rejection values ^{1,2}.

Sampling Point	Influent (µg/L)	Average in Bulk (µg/L)	Permeate (µg/L)	Rejection (%)
Influent LPRO with antiscalant	9.5			
Pressure vessel 1	18.3 ²	21.9 ²	<0.25	>98.9
Pressure vessel 2	25.6	28.5 ²	0.34	98.8
Pressure vessel 3	31.4	33.8 ²	0.29	99.2
Pressure vessel 4	36.1	43.9 ²	0.30	99.3
Outlet LPRO (brine)	51.6			
Total		30.0 ²	0.25	99.2

Note(s): ¹ Inlet flow LPRO with antiscalant: 1686 L/h, and flow recirculation: 442 L/h; ² calculated concentrations (with LPRO operation data given in Supplementary Materials, Section S5 (01.06.2016 @12:15)).

In summary, LPRO technology was shown to be an efficient method for the removal of Cr (III) and Cr (VI) at low concentrations of ≤ 10 µg/L. Total chromium removal was >98% for Cr (III) and >99% for Cr (VI), and it was almost independent of pH. Since permeate conductivities were mostly below 50 µS/cm and pH values were below 6.5 (see Supplementary Materials, Section S5), they require further treatment before they can be used as drinking water. Additionally, in order to reduce the corrosion of cement-lined and metallic pipes, it is important to raise the pH and hardness. Alternatively, it can be mixed with another type of water, for instance, water produced by activated carbon filtration.

4. Conclusions

Because stricter regulations for the Cr (VI) content in drinking water are expected in the future, three separation technologies, activated carbon filtration (ACF), reduction/coagulation/filtration (RCF) and low-pressure reverse osmosis (LPRO), were investigated in laboratory tests, pilot plant tests and partially in full scale for the removal of Cr (III) and Cr (VI). These tests were essentially performed at low chromium concentrations ≤ 10 µg/L as present in raw water resources. It can be concluded that all investigated separation processes were capable of fulfilling the set task; however, the most appropriate technology should be selected taking into account the raw water properties and the existing equipment.

Deep bed filtration through an anthracite filter used as a prefilter for ACF was sufficient to remove Cr (III) as chromium (III) hydroxide precipitate at neutral pH. In contrast, Cr (VI) species were not removed in the prefiltration but only in the subsequent ACF. Fresh AC at a filter bed depth of 2.5 m was able to remove ~75% of the influent Cr (VI) concentration. Thermally reactivated AC was found to be insufficiently effective. Therefore, the application of the ACF process for Cr (VI) elimination is only appropriate if AC filters are already installed for other purposes, e.g., for the elimination of organic micropollutants [31].

The RCF process for Cr (VI) elimination, started at an initial Cr (VI) concentration of 10 µg/L by adding ferrous sulfate with a molar ratio of Cr (VI)/Fe (II) of 1:200, was finished in minutes. The chromium-iron hydroxide precipitates formed were completely removed in a filter with a depth of ≥ 1.0 m. In addition, it was revealed that molecular oxygen in the water competed with Cr (VI) for Fe (II) ions, which negatively affected the process efficiency. The RCF process is easy to install and can be adapted to different Cr (VI) concentrations. With a dosing station, a reaction tank and a deep bed filter, the equipment requirements are relatively low.

Cr (VI) was completely eliminated by the LPRO process in the investigated pH range (from 5.6 to 8.5), achieving removal rates of at least 99%. In addition, Cr (III) rejection was as high as Cr (VI) rejection, probably due to the formation of Cr (III) hydroxide colloids, which can be completely rejected by the TFC membrane.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15030516/s1>, S1. Species diagram of chromic acid in the pH range relevant to the study, S2. Full description for chemicals purity and suppliers, S3. Chemical analysis of the raw water, S4. A detailed description of the sampling points in the semitechnical pilot plant,

S5. Specific operation data for LPRO, S6. Analytical characteristics of UV/VIS method for Cr (VI) at 375 nm, S7. Analytical characteristics of chromium and iron analytics with ICP-MS, S8. Relative combined uncertainties for analytics with ICP-MS, S9. Analytical characteristics and chromatogram of Cr (III)/Cr (VI) speciation method with IC-ICP-MS, S10. Acid treatment of multiple reactivated activated charcoal, S11. Detailed numerical data on chromium removal in the ACF line, S12. Cr (VI) adsorption on full-scale AC filters, S13. Analytical data for the chromium removal with RCF treatment, S14. Detailed analytical data for elements during LPRO trials, S15. Stability of Cr (III) in raw water.

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