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Fate of Cr(III) during ozonation of secondary municipal wastewater effluent

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Abstract

In the present study, the fate of trivalent chromium (Cr(III)) during ozonation of ultrapurified water and wastewater effluent was investigated. In experiments conducted in phosphate buffered ultrapurified water, O_3 alone in excess was inefficient to oxidize Cr(III) (only about 10 – 15 % of total Cr(III) content), while in presence of the secondary oxidant, OH radical, almost all Cr(III) was oxidized to hexavalent chromium (Cr(VI)). In a wastewater effluent, spiked with Cr(III), only about 10 to 20% of Cr(III) was oxidized with specific ozone doses in the range 0.15 to 1.5 gO_3/gDOC, although O_3 and OH radical were both available for reaction. Cr(VI) formation was monitored in parallel with the abatement of some common micropollutants, reacting with differing apparent second order rate constants with ozone, decreasing in the order carbamazepine>> benzotriazole> atrazine> pCBA. Carbamazepine and benzotriazole were abated to > 80% for specific O_3 doses of 0.3 gO_3/gDOC, and 0.8 gO_3/gDOC, respectively. The more ozone-resistant compounds (atrazine and pCBA) required a specific ozone dose of about 1.25 gO_3/gDOC for the same relative abatement. At this specific ozone dose (i.e., 1.25 gO_3/gDOC) only about 20% of Cr(III) was oxidized to Cr(VI), whereas, only 10% of Cr(III) was oxidized to Cr(VI) at a more realistic specific ozone dose for enhanced wastewater treatment for micropollutant abatement (0.5 gO_3/gDOC). Therefore, for typical Cr(III) levels in municipal wastewaters, effluent ozonation only leads to toxicologically insignificant Cr(VI) concentrations.

Keywords: Cr(III), chromate, Cr(VI), ozonation, hydroxyl radical, micropollutants

1. Introduction

Cr(III) and Cr(VI) are the most common forms of chromium in natural and engineered aquatic systems (Richard and Bourg 1991). Chromium compounds are widely used in electroplating, stainless steel production, leather tanning, textile manufacturing, and in wood preservation and therefore, chromium compounds are present in the respective industrial wastewaters (Mohan and Pittman 2006). Cr(VI) usually exists as oxyanions such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) in industrial wastewater and does not precipitate easily using conventional precipitation methods. Therefore, chemical reduction to Cr(III) followed by precipitation is the most widely used technique for Cr(VI) removal (Mitrakas et al. 2011; Gröhlich et al. 2017), because Cr(III) has a low solubility in water ($\log K_{sp}$ of $Cr(OH)_3$ < -32.2) (Rai, Sass and Moore 1987).

Figure 1 shows the simulated Cr(III) speciation as a function of pH in presence of phosphate (5 mM), similarly with the experiments conducted in this study. The $CrH_2PO_4^{2+}$ complex plays a dominant role up to pH 5, where the $Cr(OH)_2^+$ starts to increase and is the main species until a pH of about 6.5. For further increasing pH values, the $Cr(OH)_3(aq)$ complex predominates up to a pH of about 11.5. Therefore, under the experimental conditions of this study (i.e., circumneutral pH values), the presence of phosphate is not expected to affect the oxidation rates. Cr(III) complexes are very inert with low water exchange rates (2.4×10^{-6} s^{-1} for $Cr(H_2O)_6^{3+}$ and 10^{-5} s^{-1} for $Cr(H_2O)_4(OH)_2^+$ at 25 ^oC, Helm and Mehrbach 2005). This may affect the rates of Cr(III) oxidation by ozone, if an inner sphere complex needs to be formed. In Cr(III)-containing solutions, the potential formation of polynuclear complexes is also of concern, especially if kinetics is investigated. However, it seems that they are formed very slowly at room temperature and even at elevated temperatures (35-50 ^oC) long equilibration times are required (ca. 100 days) (Rai et al. 1987).

Industrial wastewaters, which have been chemically reduced, might contain trivalent chromium in either dissolved or in the various particulate forms, which are mostly removed at industrial wastewater treatment plants (Stasinakis et al. 2003). This wastewater is then discharged to municipal wastewater treatment plants and some of the particulate, dissolved and possibly complexed Cr(III) might be carried through the biological treatment system. Stasinakis et al., 2003 showed that around 5% of the initial Cr(III) can be carried through this process to the

effluent. Imai and Glonya (1996) demonstrated that Cr(III) can form complexes with organic matter and remain in the effluent of activated sludge process.

Oxidative treatment of such wastewaters, i.e., with O_3, which is a potential option for an enhanced treatment of effluents to reduce the load of organic micropollutants (Hollender et al. 2009; Zimmermann et al. 2011; Margot et al. 2013; Eggen et al. 2014), might lead to re-oxidation of Cr(III) to the more toxic Cr(VI), which is afterwards discharged to the natural aquatic environment. This might be problematic for ecosystem or for human health if such waters are used as resources for drinking water production, because Cr(VI) is 100 times more toxic than Cr(III) and is known to exert carcinogenic, mutagenic and teratogenic action in biological systems (WHO, 1996).

The US Environmental Protection Agency (US EPA) and the EU have set a maximum contaminant level of 100 μg/L and 50 μg/L for total chromium, respectively and the World Health Organization (WHO) has a guideline value of 50 μg/L for total Cr in drinking water (W.H.O. 1996). However, because of its severe toxicity, the Department of Public Health in California established a Cr(VI) Maximum Contaminant Level (MCL) in drinking water of 10 μg/L (effective July 1, 2014), which however on May 31 2017, was judged invalid by the court because the California Department of Public Health (which was responsible for the drinking water program before it was transferred to the State Water Board) failed to properly consider the economic feasibility of complying with the MCL. (California Water Boards announcement, https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Chromium6.html, acessed on February 22 2018). However, some European Union countries have set even more stringent guidelines as Environmental Quality Standards for Cr(VI) to protect the ecological status of inland surface water systems such as lakes and rivers (2008/205/EC). For example, in Greece the respective value for Cr(VI) is 3 μg/L (ΦΕΚ 1909/B/08-12-2010, Annex I, Part B, Table 2).

This is important, because Cr(VI) is very mobile and does not adsorb efficiently onto most relevant solid surfaces such as iron oxides. Therefore, it is remaining in the water, especially under oxic conditions (Stanin, 2004). Its reduction to insoluble Cr(III) usually requires the presence of Fe(II). However, Fe(II) is not present in fully oxic aquatic environments at circumneutral pH values (Stumm and Morgan, 1996).

Reactions of metal/metalloid ions with O_3 in their low oxidation states have been studied for As(III), Fe(II), Mn(II), Co(II) and other metals but only to a limited extent for Cr(III). In general, these reactions are governed by ozone adducts with an oxygen transfer leading to the highest oxidation state of these metals or metalloids (von Sonntag and von Gunten 2012).

Cr(VI) formation during ozonation of Cr(III)-containing materials in aqueous suspension was investigated previously (van der Merwe, Beukes and van Zyl 2012). It was observed that Cr(VI) was formed during ozonation and the corresponding reaction was pH-dependent. These results have implications for water treatment and therefore, there is a need to further investigate the oxidation of Cr(III) during ozonation. In the present study, Cr(III) oxidation was studied in ultrapurified water and in municipal wastewater effluent.

The key objective was to investigate Cr(III) oxidation during ozonation of municipal wastewaters in parallel with the abatement of selected common micropollutants with different reactivities with ozone and/or hydroxyl radicals. The goal was to determine if with the applied specific ozone doses for micropollutants elimination, Cr(III) oxidation could lead to toxic levels of Cr(VI) in the treated waters, ready to be disposed in the natural aquatic systems.

2. Materials and Methods

2.1 Reagents and solutions

All chemicals used were of the best available quality. Stock solutions of Cr(III), ozone (O_3) and analytical reagents were prepared in ultrapurified water (Milli-Q Advantage). A Cr(III) stock solution of 8 mg/L was prepared by dissolving $Cr(III)Cl_3 \times 6H_2O$ (96% Sigma-Aldrich) at pH 2, where Cr(III) has higher solubility (Figure 1). A concentrated O_3 stock solution was prepared by bubbling ozone-containing oxygen continuously through a flask of ice-cooled ultrapurified water (Bader and Hoigne, 1981). O_3 concentrations in the stock solutions were in the range 1.0–1.3 mM, determined several times daily with direct photometry at 260 nm (ε = 3200 $M^{-1}cm^{-1}$) (von Sonntag and von Gunten 2012). Stock solutions of pCBA (258 μM), carbamazepine (69 μM) benzotriazole (201.5 μM), atrazine (100 μM) and iopromide (147 μM) were prepared by dissolving these compounds in ultrapurified water.

2.2 Experimental approach and dosage experiments

To measure the efficiency of the O_3-Cr(III) reaction in ultrapurified water, batch experiments were performed in aquatic solutions for a range of O_3 and Cr(III) concentrations. An appropriate volume of the Cr(III) stock solution was transferred to a 100 mL volumetric flask, which already contained ultrapurified water buffered with 5mM phosphate under vigorous stirring. The resulting Cr(III) concentration was oversaturated according to Figure 1, to allow the maximum soluble Cr(III) concentration in equilibrium. It is assumed that the kinetics are

controlled by the dissolved species and that the contribution of Cr(III)(s) is minimal. The flask was then filled up to 100 mL and the pH of the solution was subsequently adjusted with very low quantities of 1 M H_3PO_4 or 1 M NaOH under stirring. A sample was taken at time zero. Thereafter, O_3 from a stock solution was injected under stirring to achieve the desired O_3 dose. Samples were taken after 24h to perform the various measurements after complete O_3 depletion (no ozone residual could be measured at this point). Some experiments were performed in presence of *t*-BuOH (50 mM), to examine the reaction of O_3 with Cr(III) in absence of $^{\bullet}OH$ radicals, since t-BuOH scavenges $^{\bullet}OH$ radicals ($k_{t\text{-}BuOH,OH} = 6 \times 10^8$ $M^{-1}s^{-1}$) (Buxton et al. 1988).

The experiments with secondary effluent municipal wastewaters were performed with treated wastewater obtained from the treatment plant in Vidy, Lausanne, Switzerland (VD). No significant pH changes were observed before and after ozonation experiments of wastewaters (i.e., less than 0.1 pH unit). Cr(III) was added to the wastewater 24h prior to the experiments, to allow time for equilibration of the solution. In these experiments the critical parameter was the specific ozone dose, expressed as $gO_3/gDOC$ (Margot et al. 2013). The VD wastewater effluent after the biological treatment stage contained 6.4 mg DOC/L. pCBA was also spiked to the wastewater together with Cr(III), as a probe compound to assess the $^{\bullet}OH$ oxidation efficiency during ozonation. The abatement of selected spiked micropollutants (atrazine, benzotriazole, carbamazepine), with initial concentrations of 1 μM, was also assessed to compare their abatement with the Cr(III) to Cr(VI) conversion. Samples were taken after 24h to perform the various measurements after complete O_3 depletion (no ozone residual could be measured at this point). Table 1 shows the respective second order rate constants k_{O3} and k_{OH} of the studied micropollutants.

2.3 Analytical methods

Total chromium was measured by ICP-OES (Shimadzu ICPE-9000) (LOD = 7 μg/L, SD= 4%). A Cr(VI)-selective determination was performed by the standard colorimetric method (3500-Cr D) based on the reaction of Cr(VI) with diphenylcarbazide (DPC) (LOD=4 μg/L, SD = 4%) (Clesceri, Greenberg and Trussell 1989) using a UV/Vis Shimadzu UV-1800 at 540 nm. The Cr(III) concentration was calculated from the difference between the total and hexavalent chromium Cr(VI). The DOC concentration of the wastewater effluent was measured with a total organic carbon analyser (Shimadzu TOC-V CPH) (LOD=0.1 mg/L, SD= 6%). Organic micropollutants and pCBA were measured by HPLC Dionex Ultimate 3000, equipped with a UV

detector and Nucleosil 100-5 C18 EC 125/3 Ref. 720002.30 column with pre-column. The eluents used were phosphate buffered water 10 mM, pH 2.3 and acetonitrile in various gradient ratios. Measurements were made for carbamazepine at 285 nm, atrazine at 225 nm, benzotriazole at 262 nm, pCBA at 240 nm. Calibration curves were for pCBA from 0.5 to 3 μM and for carbamazepine, atrazine and benzotriazole from 1 to 3 μM.

3. Results and discussion

3.1 Oxidation of Cr(III) by ozone

Figure 2 shows the oxidation of Cr(III) to Cr(VI) as a function of O_3 dose in ultrapurified water at pH 7, in the presence or absence of *t*-BuOH, respectively.

The results show a distinct difference of the Cr(III) oxidation efficiency when O_3 was used in presence (i.e., only O_3 reaction) or absence of *t*-BuOH (combined reactions of O_3 and $^{\bullet}OH$). The over-stoichiometric O_3 doses required for the formation of Cr(VI) indicate that Cr(III) is an O_3 refractory compound, which is oxidized mainly through the $^{\bullet}OH$ route. This is demonstrated by the higher Cr(VI) yield in absence of *t*-BuOH, which resulted in a more efficient oxidation of Cr(III) by $^{\bullet}OH$. In absence of *t*-BuOH, the total dosed Cr(III) was oxidized to Cr(VI). This is most likely due to a dissolution of $Cr(OH)_3(s)$ by the depletion of $Cr(OH)_3(aq)$, which is caused by its oxidation ot Cr(VI). This provides more aqueous Cr(III) species available for oxidation, before ozone is completely consumed.

3.2 Cr(III) oxidation during ozonation of municipal wastewater effluent

Based on the results presented above, it can be assumed that Cr(III) oxidation during ozonation occurs preferentially by hydroxyl radicals with low efficiency. Wastewaters contain quite high concentrations of dissolved organic matter, which lead to a fast transformation of O_3 to $^{\bullet}OH$. At the same time also a large fraction of the formed $^{\bullet}OH$ are scavenged by the effluent organic matter (Katsoyiannis, Canonica and von Gunten 2011; Lee et al. 2013), thereby limiting the oxidation efficiency, e.g, for Cr(III) to Cr(VI). Previous results for enhanced wastewater treatment with O_3 have shown that specific ozone doses in the range of 0.5-1.0 $gO_3/gDOC$ were sufficient to achieve approximately 80% abatement of the micropollutant load (Hollender et al. 2009; Margot et al. 2013; Bourgin et al. 2018). Based on these observations, we examined the extent of Cr(VI) formation and pCBA abatement (probe compound for an ozone-resistant compound, $k_{O3} < 0.1\ M^{-1}s^{-1}$, $k_{OH} = 5 \times 10^9\ M^{-1}s^{-1}$) by applying specific ozone doses in the range

0.15 to 1.5 gO_3/gDOC for various initial Cr(III) concentrations (20 to 200 µg/L). The aim was to examine, if for conditions optimized for micropollutant abatement, Cr(VI) concentrations higher than the potential drinking water standard of 10 µg/L would result (Figure 3).

Figure 3 shows that for Cr(III) concentrations of 20 µg/L and for specific ozone doses ≤ 1 gO_3/gDOC, the produced Cr(VI) was < 10 µg/L for all initial Cr(III) concentrations. *p*CBA abatement of about 60 or 80% was observed for specific ozone doses of 0.5 or 1.2 mgO_3/mgDOC, respectively. In the cases of an initial Cr(III) concentration of ≥ 100 µg/L, concentrations of Cr(VI) significantly higher than 10 µg/L are formed for specific ozone doses ≥ 0.5 gO_3/gDOC. The fact that the Cr(VI) formation is not proportional to the Cr(III) dose is an indication that Cr(VI) is a result of mixed kinetics of the oxidation of Cr(III) aqueous complexes and dissolution $Cr(OH)_3$(s).

To further investigate the potential of Cr(VI) formation during ozonation of secondary wastewater effluent under realistic conditions for micropollutant abatement, carbamazepine, benzotriazole and atrazine were selected as representative micropollutants. The choice of the micropollutants was based on their different k_{O3} values, while their k_{OH} values were in a similar range (Table 1). The results for Cr(VI) formation (Cr(III) dose 50 µg/L) and micropollutant abatement are shown in Figure 4.

Figure 4 shows, that under the current experimental conditions, Cr(VI) concentrations of 10 µg/L are only reached for specific ozone doses > 1.25 gO_3/gDOC. However, these specific ozone doses are significantly higher than those applied in practice to achieve overall 80% micropollutant abatement without a significant bromate formation (Soltermann et al. 2016; Soltermann et al. 2017). Typically, specific O_3 doses between 0.5-0.6 gO_3/gDOC are optimal to achieve the best overall goal (Bourgin et al. 2018). For a specific ozone dose of 0.6 gO_3/gDOC, about 8 µg/L of Cr(VI) are formed in the case of this wastewater, for an initial Cr(III) concentration of 50 µg/L. To this end, total chromium concentrations were measured in wastewater effluents of >50 wastewater treatment plants in Switzerland and more than 95 % of the samples contained a total chromium concentration of <1 µg/L (Vriens et al. 2017). These results and the determined oxidation efficiency from this study suggest that, ozonation of secondary wastewater effluents with typical doses for micropollutant abatement will not lead to problematic Cr(VI) concentrations in the treated effluents.

4. Conclusions

In the present study the oxidation of Cr(III) by ozone and hydroxyl radicals was investigated to assess the extent of Cr(VI) formation during ozonation of wastewater effluents. The results showed that Cr(III) is poorly oxidized directly by O_3 but can be completely oxidized by hydroxyl radicals. Experiments performed in a secondary wastewater effluent containing a DOC concentration of 6.4 mg/L showed that only when the wastewater contained Cr(III) concentrations >50 μg/L, specific ozone doses of about 1 mgO_3/mgDOC could result in Cr(VI) concentrations higher than 10 μg/L. This suggests that ozonation of secondary effluent wastewaters containing < 50 μg/L of Cr(III) and lower specific ozone doses, will not result in a significant Cr(VI) contamination of the receiving water bodies and the connected drinking water resources.

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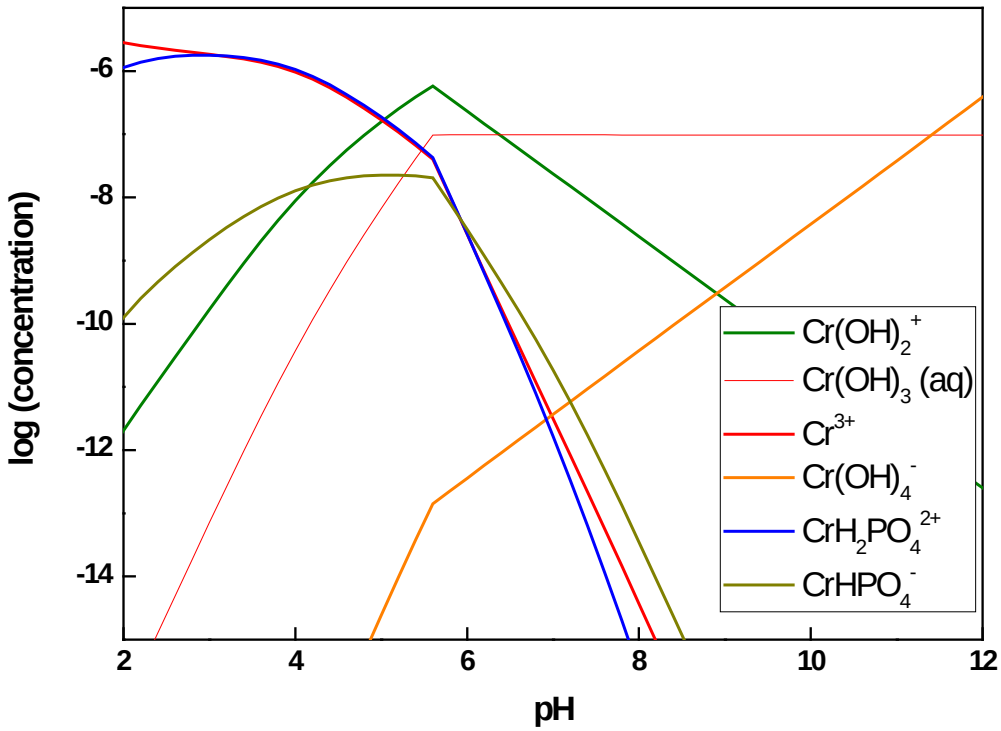

Figure 1. Cr(III) speciation as a function of pH in ultrapurified water. The calculations are based on visual Minteq version 3.1 (Gustafsson 2015). Both hydroxo- and phosphate complexes are considered, with a total phosphate concentration of 5 mM.

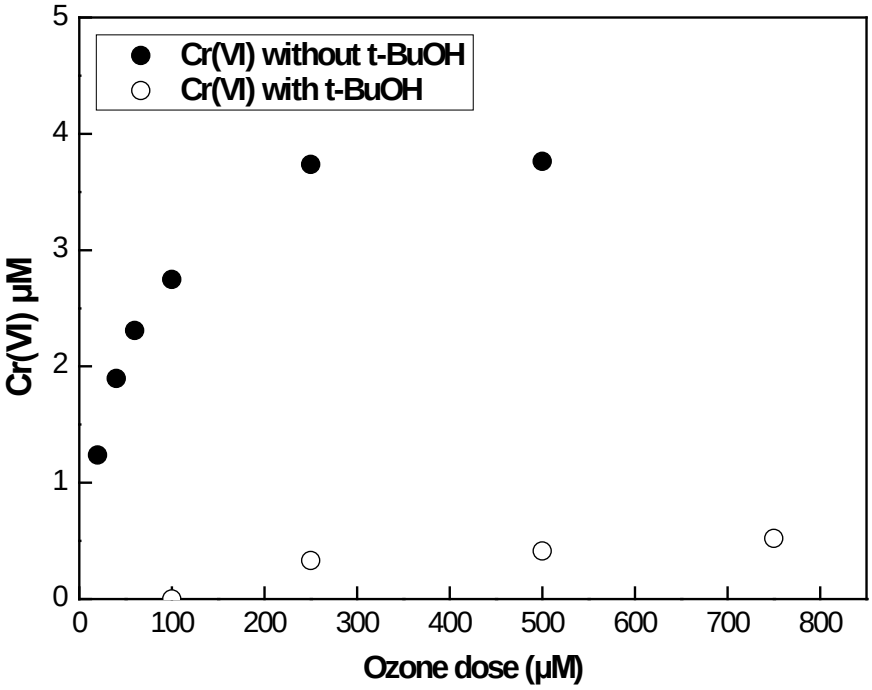

Figure 2. Cr(VI) formation from Cr(III) oxidation as a function of the ozone dose in presence and absence of *t*-BuOH. Cr(III) dose 200 μg/L (ca. 4 μM), pH 7, *t*-BuOH 50 mM. Experiments were conducted in buffered ultrapurified water (5 mM phosphate).

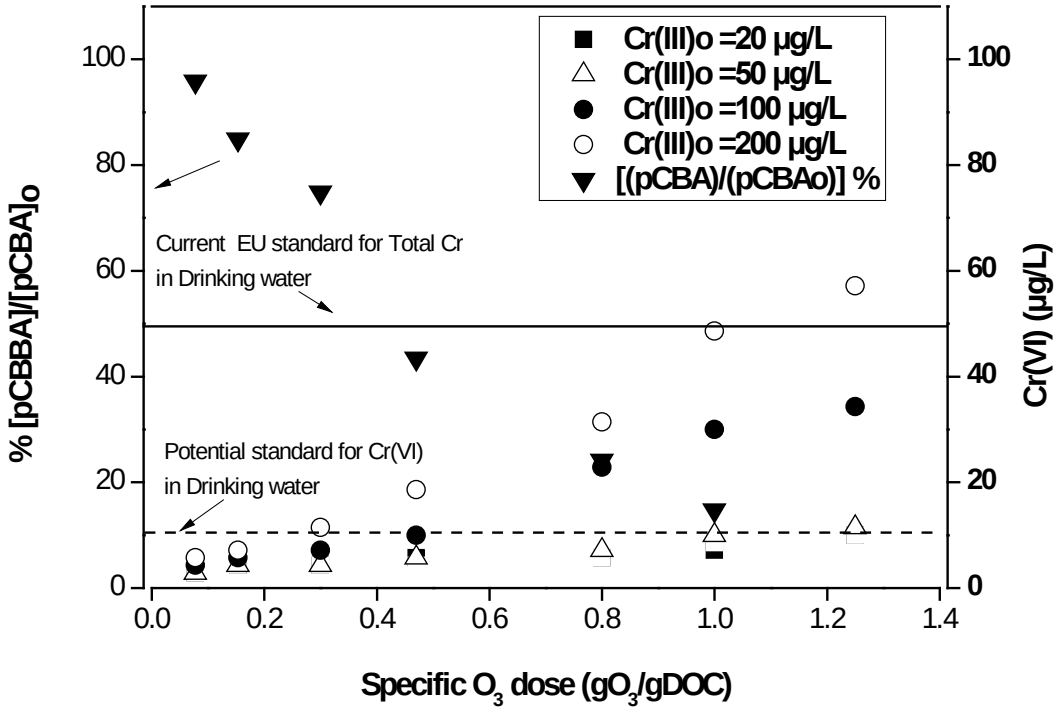

Figure 3. Cr(VI) formation and pCBA abatement during ozonation of a secondary wastewater effluent (VD) as a function of the specific O_3 dose (gO_3/gDOC) for varying Cr(III) doses (20, 50, 100, 200 µg/L). Experiments were conducted at pH 7.7, which was the pH of effluent wastewater. *t*-BuOH was not added and the solution was not buffered. The pH was constant over the course of the reaction. The solid and dashed horizontal lines indicate the current EU drinking water standard for total Cr and the probable Cr(VI) drinking water standard of 10 µg/L, respectively.

<u>Note:</u> The points regarding the 20 µg/L of Cr(III) injection are covered by the other higher initial concentrations

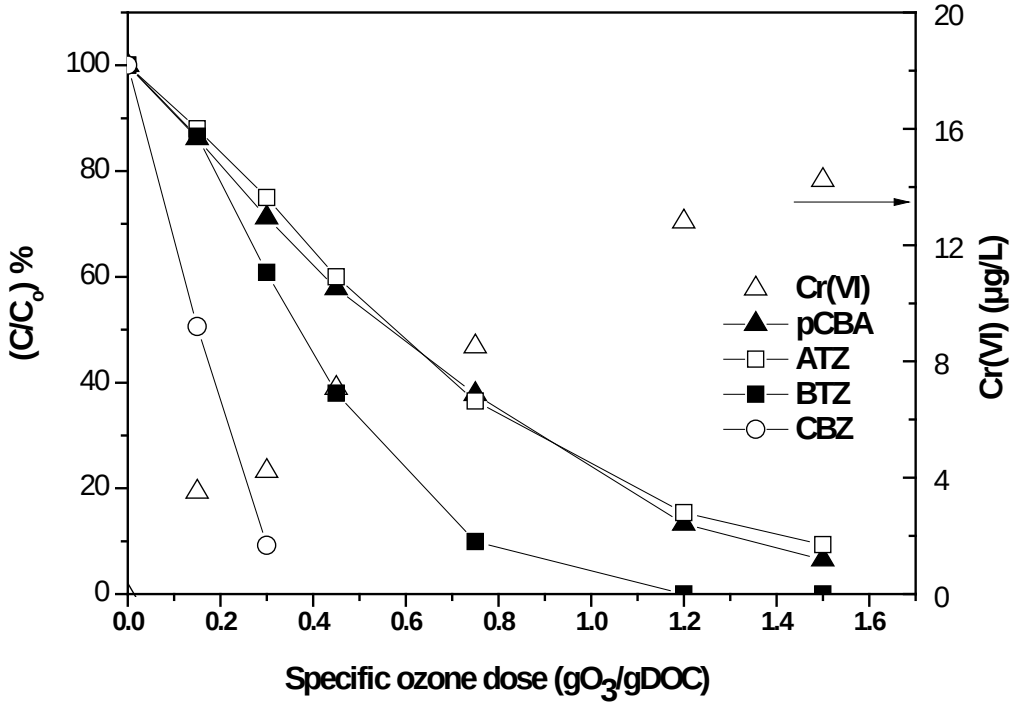

Figure 4. Ozonation of secondary wastewater effluent: Micropollutant abatement (carbamazepine, benzotriazole, atrazine and pCBA) and Cr(VI) formation as a function of the specific ozone dose. $[Cr(III)]_o$ = 50 µg/L (dosed) at the pH of VD wastewater (7.7).

Table 1. Second order rate constants for the reactions of the selected micropollutants with O_3 and •OH

Organic compound	k_{O3} ($M^{-1}s^{-1}$)	k_{OH} ($M^{-1}s^{-1}$)	Reference
pCBA	< 0.1	5×10^9	Elovitz and von Gunten 1999
Atrazine	6	3×10^9	Acero, Stemmler and von Gunten 2000
Benzotriazole	36 at pH 2 159 at pH 7	6.2×10^9 at pH 10 1.7×10^{10} at pH 2	Vel Leitner and Roshani 2010 von Sonntag and von Gunten 2012
Carbamazepine	3×10^5 at pH 7	8.8×10^9 at pH 7	Huber et al., 2003