Optimization of ozonation process for removal of micropollutants in urban wastewater

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Abstract. This study aims to extend the existing theoretical knowledge to the practical application of ozonation in advanced wastewater treatment. Urban wastewater from a WWTP in a European developed country (Austria) was treated by ozonation technology with different specific doses, varying from 0 g O_3 to 1.0 g O_3/g dissolved organic carbon (DOC), observing an abatement of micropollutants and bromate formation. Based on the ozonation, micropollutants were categorised into 3 groups, namely highly-reactive, medium-reactive, and non-reactive. For ozonation, micropollutants were removed at >80% for three groups at various ozone doses of 0.6 - 1.0 g O_3/g DOC. The results showed that different bromate formations were observed in accordance with different ozone doses and varying between the investigated effluent samples. Bromate formation ranged between 0.65 ± 0.28 and 11.22 ± 9.85 µg/L. The value of ozone dose was regulated by WHO for drinking water (10 µg/L) was only exceeded at > 0.88 ± 0.05 g O_3/g DOC, which is higher than normal applied doses for micropollutant removal (0.6 - 0.7 g O_3/g DOC).

1. Introduction

Currently, most people in Europe need to turn on the faucet to use clean, clear, safe water but do not know where it comes from and how it is treated. Such a water supply requires good and high raw water quality, which will be one of the significant challenges worldwide in the near future. In recent years, the emergence of emerging organic compounds or trace organic compounds (TrOCs) (e.g., pharmaceuticals and personal care products (PPCPs), industrial chemicals, endocrine disrupting compounds (EDCs), and others) threaten our water resources (including surface water and groundwater) [1]. The source of most TrOC is artificial and released into the environment through wastewater. However, the concentration of these TrOCs is so tiny (~µg/L) that they are not treated in urban wastewater treatment plants, including

tertiary treatment [2, 3]. The question is, "How will they harm human health, the ecosystem as well as the economic impact?" [4]. So, they cause adverse effects on aquatic organisms and may limit their additional use as raw water sources for human needs [5-7]. The increasing pressure on water resources due to increased demand for human use on the one hand and the decrease of availability due to climate change, on the other hand, fostered research on technologies to remove organic trace pollutants from wastewater further [8-11].

Ozone technology is considered a suitable technology for removing TrOC from wastewater. This technology has been deployed to remove TrOCs in urban wastewater in several European countries (Germany, Austria, and Switzerland) [12-14]. Actors affecting the effectiveness of TrOC removal include Wastewater composition, ozone dosage, their ability to react with ozone, and hydroxyl radicals (spontaneously formed) [15-17]. Practically, ozonation technique is usually applied for biological (secondary) treatment to reduce the ozone recovery capacity of the organic fraction in wastewater [18]. In biologically treated wastewater, ozone targets electron-rich radicals, such as aromatic rings, amines, olefins, etc. [19] and thus reacts with micropollutants [20, 21].

Oxidation byproducts formed from the oxidative transformation of matrix components involve inorganic (e.g., bromate) as well as organic compounds (e.g., nitrosamines, aldehydes) and, in some cases, are suspected to show a higher toxicological potential as compared to their parent substances. Consequently, the formation of transformation products and/or byproducts is intended to be minimized during the technical operation of ozonation. Besides the chemical matrix and the content of precursor substances in the raw water, the ozone dose is of central importance for the undesired formation of oxidation byproducts. With doses of ozone for DOC removal which is below 0.5g O_3/g DOC, a few bromate formation is found due to the swift decomposition that leads to low exposure of ozone [16].

This study is designed to target and test the elimination of TrOCs and the formation of oxidation byproducts (such as bromate) during ozonation. The effluent of an Austrian WWTP was used. Nine TrOCs usually present in municipal wastewater in wastewater were selected for analysis based on EU regulations. This includes pharmaceuticals, corrosion inhibitors, and artificial sweeteners. The following research questions needed to be answered during the experiments: 1)How is the decomposition performance of ozonation for TrOCs? And 2) How is the bromate formation in the investigated wastewater related to the ozone dose? In order to answer the research questions, batch tests were conducted with different nitrite-compensated specific ozone doses (0.2, 0.4, 0.6, 0.8, and 1.0 g O_3/g DOC).

2. Experiment

The effluent samples from a WWTP in Austria were used for the investigation. The experiments based on the guidelines by the Swiss experts are used in the laboratory to assess and evaluate the processability [22]. The experiment's focus has been to investigate the degradation efficiency of TrOCs at the different specific ozone doses, also considering the formation of bromate (BrO_3^-) as an oxidation byproduct.

2.1. Preparing the ozone stock solution

Preparing the ozone stock solution was based on the guidelines of Zappatini [22]. The structure of the ozone system in the laboratory is illustrated in Figure 1.

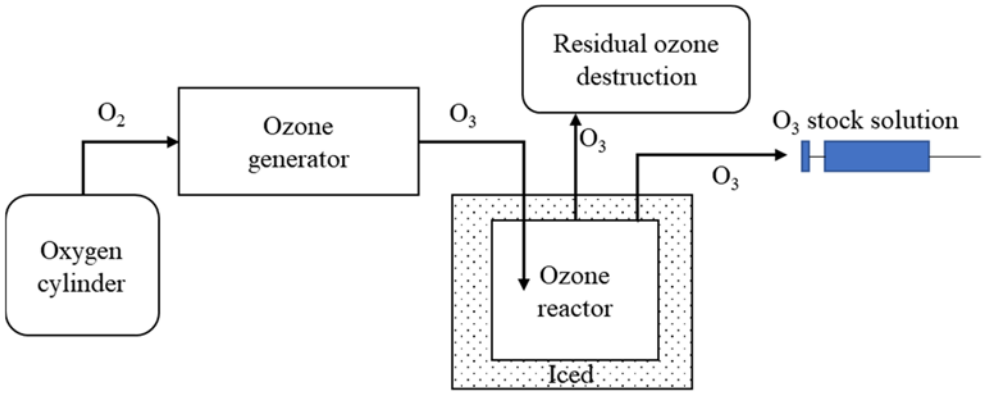

Figure 1. The structure of the ozone system

Ozone is unstable and, therefore, cannot be stored in the same way as oxygen. It is necessary to produce ozone with an ozone generator continuously with the oxygen tank.

Oxygen is supplied to the ozone generator. Deionized water was filled into the ozone reactor, and stored overnight in a frozen condition. Gaseous ozone is introduced into the liquid as fine bubbles through an aeration stone, producing a concentrated solution of O_3 stock. The O_3 stock concentrated solution can vary greatly depending on the temperature condition. Therefore, the concentrated solution of O_3 stock was kept in cool condition in accordance with the procedure suggested by Zappatinoi [22]. The indigo method and photometry were used to determine the ozone concentration [19, 23]. Ice is added to keep the stored ozone stock solution stable. Depending on the experiments, the concentration of ozone in the stock solution varied between 40 and 55 mg O_3/L. A bottle of potassium iodide solution is used to remove excess ozone if it is not entirely dissolved in the water. In addition, an ozone alarm device was used, which provides audible and visual warnings from a concentration of 0.1 ppm in the ambient air. Since ozone is a toxic gas with irritating effects, it needs to be worked inconspicuously and with special attention to safety[11]. Figure 2 shows the ozone system in the laboratory.

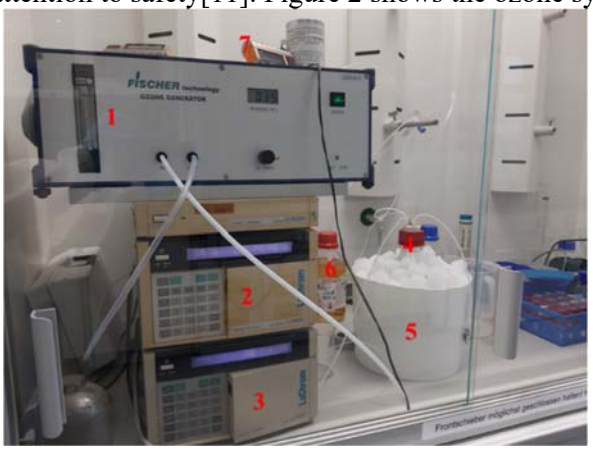

Figure 2. The ozone system in the laboratory
1. Ozone generator
2. Spectrometers
3. Pump
4. Reactor for the O_3 stock solution
5. Ice bath
6. Potassium iodide solution
7. Ozone alarm device

2.2. Experimental setup for micropollutant abatement

Batch testing is applied to determine the degradation of micropollutants. A mixture of wastewater and O_3 solution was prepared according to the ratios (see Table 1). These ratios are much dependent on the content of ozone in the solution of ozone stock, DOC and nitrite in wastewater samples, and the nitrite-compensated targeted Dspec. Figure 3 depicts the preparation of the experimental set-up. All experiments were carried out in duplicates.

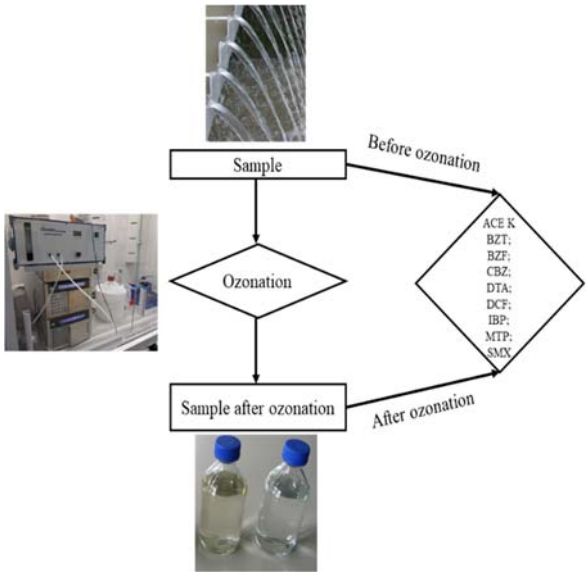

Figure 3. The experimental setup, including analyzed parameters

Table 1. The schematic ratio of wastewater and ozone stock solution in the ozonation batch tests

Applied volumes / sample	**D_{Spec} (g O_3/g DOC)**					
	0	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**
Number of Schott bottles	1	2	3	4	5	6
Total volume (mL)	50	100	100	50	50	50
Volume of ozone stock solution (V_O_3)	V_WW	V_O_3	V_O_3	V_O_3	V_O_3	V_O_3
Volume of the investigated wastewater sample (V_WW)		V_WW	V_WW	V_WW	V_WW	V_WW

3. Analyzed parameters

3.1. Trace organic compounds (TrOCs)

Nine TrOCs were selected for analysis and included pharmaceuticals, corrosion inhibitors, and sweeteners (Table 2) [24].

Table 2. Overview of TrOCs analyzed

Substance	**Acronym**	**Substance class**	**CAS-Number**
Acesulfame K	ACE K	Sweetener	5589-62-3
Bezafibrate	BZF	Lipid regulator	41859-67-0
Benzotriazole	BZT	Corrosion inhibitor	95-14-7
Carbamazepine	CBZ	Anti-convulsant	298-46-4
Diatrizoic acid dihydrate	DTA	Iodinated contrast medium	50978-11-5
Diclofenac	DCF	Analgesic/anti-inflammatory	15307-79-6
Ibuprofen	IBP	Analgesic/anti-inflammatory	31121-93-4
Metoprolol	MTP	Beta blocker	37350-58-6
Sulfamethoxazole	SMX	Antibiotic	723-46-6

3.2. Micropollutant analysis

All testing conditions were duplicated. Micropollutants were analyzed with a liquid chromatograph in tandem with two mass spectrometry (LC/MS/MS).

4. Results and discussions

4.1. Trace organic compounds abatement

4.1.1. Results for abatement

Figure 4 shows the percentage elimination of TrOCs examined for the effluent of WWTP at five D_{spe} (Dspec), whereby the D_{spec} has been rounded to one decimal point for better readability. As expected by the chemical diversity of micropollutants, the results range from 29% to 99%. At the lowest dose of D_{spec} (0.2 gO_3/g DOC), partial removal was observed for most compounds. Meanwhile, half of all compounds were removed for more than 80% with the medium dose of D_{spec} (0.6 - 0.7 g O_3/g DOC). Importantly, all compounds were almost removed (approximately 100%) at the highest dose of D_{spec} (1.0 g O_3/g DOC).

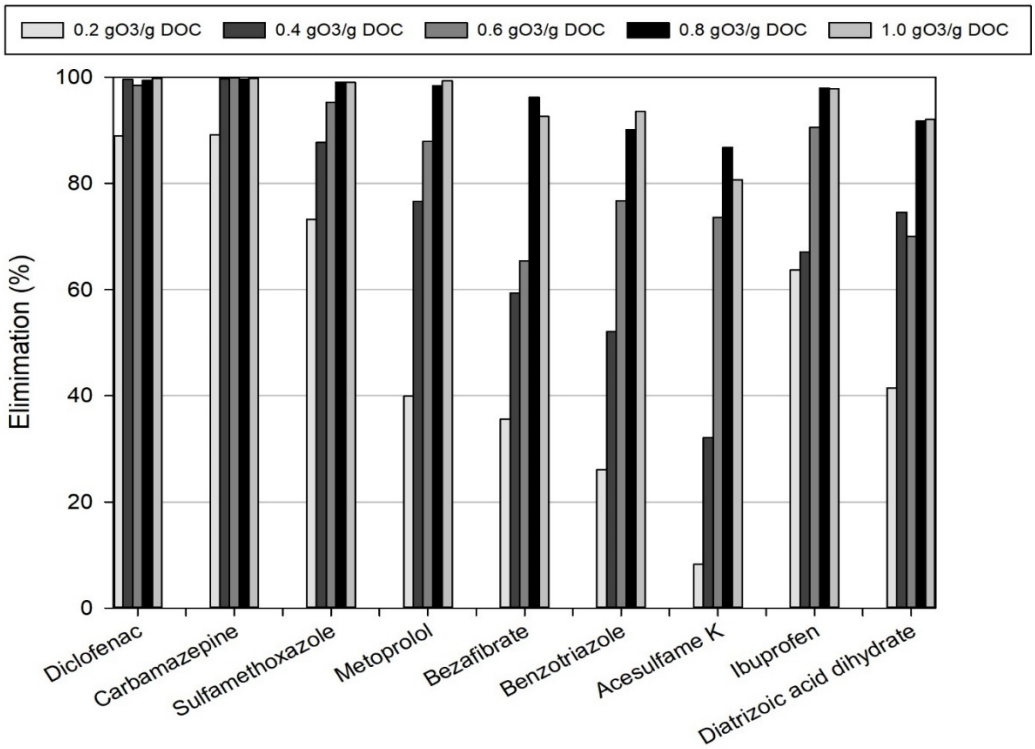

Figure 4. The percentage elimination of TrOCs examined for the effluent of WWTP at five D_{spec}

Micropollutants can be classified into three groups (see Figure 5) based on the studies of Jekel [25], Lee [16], and Stapf [26] Jekel, Dott [25]. Specifically, group I: highly reactive compounds ($k_{O3} \geq 1x10^5$ $M^{-1}s^{-1}$) were easily removed over 90%; group II: medium reactive compounds ($10 \leq k_{O3} \leq 1x10^5$ $M^{-1}s^{-1}$) with moderate removal capacity from 50 to 90%; and group III: low reactive compounds ($k_{O3} < 10$ and $k_{OH} \geq 1x10^9$ $M^{-1}s^{-1}$) that were difficult to remove.

Figure 5 shows the percentage removal of TrOCs studied, for which a specific ozone dose has been rounded to one decimal point for better readability. Removal of diclofenac, carbamazepine, and sulfamethoxazole over 90% can be measured with a defined ozone dose of about 0.45 g O_3/g DOC. These results also agree with data from previous studies [16, 27, 28].

With metoprolol, results showed that >80% removal was achieved from a defined dose of ozone (0.6 - 0.7 g O_3/g DOC). Bezafibrate reacts similarly to metoprolol. The decomposition rate accelerates linearly with the amount of added ozone content. The characteristic degradation performance of the three

compounds, benzotriazole, acesulfame-K, and ibuprofen, showed similarities, although ibuprofen had a low O_3 reactivity for the first two mentioned compounds. In the case of the last two micropollutants mentioned, only >80% removal can be measured from a D_{spec} = 1.0 g O_3/g DOC. In summary, it can be found that a very good decomposition rate (i.e.,> 80%) is achieved for all micropollutants examined at a specific ozone dose in the range of 0.6 - 1.0 g O_3/ g DOC.

Ultraviolet absorbance at wavelength 254 nm (UV_{254}) is relatively stable and straightforward. There is a fact that UV application has been increasingly a promising factor for determining the activity and efficiency of ozone in the secondary treatment method which provides an insight into the correlation between reduced UV absorption, ozone dose, and the efficiency of microscopic pollutants removal [29]. The statistical technique of linear regression was deployed to the correlation evaluation between the relative reduction of UV_{254} (ΔUV_{254}) and the potential oxidation of micropollutants. Figure 6 shows the relative changes of UV_{254} versus D_{spec} for of the investigated micropollutant.

The regression equations for each micropollutant are shown in Figure 6, but the models still indicate rapid response rates with steep slopes or vertical intercepts. The contaminant degradation profiles with group I (highly reactive compounds) were steep. The high slope indicates a fast reaction rate, as expected for these compounds, and the low vertical resistance suggests that the removal of these particular compounds begins at the same time as the removal of the UV_{254} absorption capacity. Therefore, the elimination and ΔUV_{254} correlation is inappropriate (i.e., $R^2 \leq 0.5$). Besides the compounds in group 2 (medium reactive compounds), the slope for micropollutants is lower because their oxidation starts faster than $UV_{25}4$ absorbance. Due to the reduced reactivity, regression analysis was possible for UV_{254} (i.e., $R^2 \geq 0.8$). For group III, oxidation begins later and is slower than changes in UV_{254} absorbance.

The study of Gerrity connected the slope and intercept of the correlations to specific reaction rates of micropollutants: The steeper the slope, the greater the response of particular micropollutants to ozone. and •OH faster, while the low vertical intercepts indicate that removing micropollutants begins when UV_{254} reduction occurs. The blocking of the negative correlation suggests that a minimum of UV_{254} is required before these micropollutants can be removed, which is mainly the case for reactive micropollutants with moderately reactive to ozone and •OH [29]

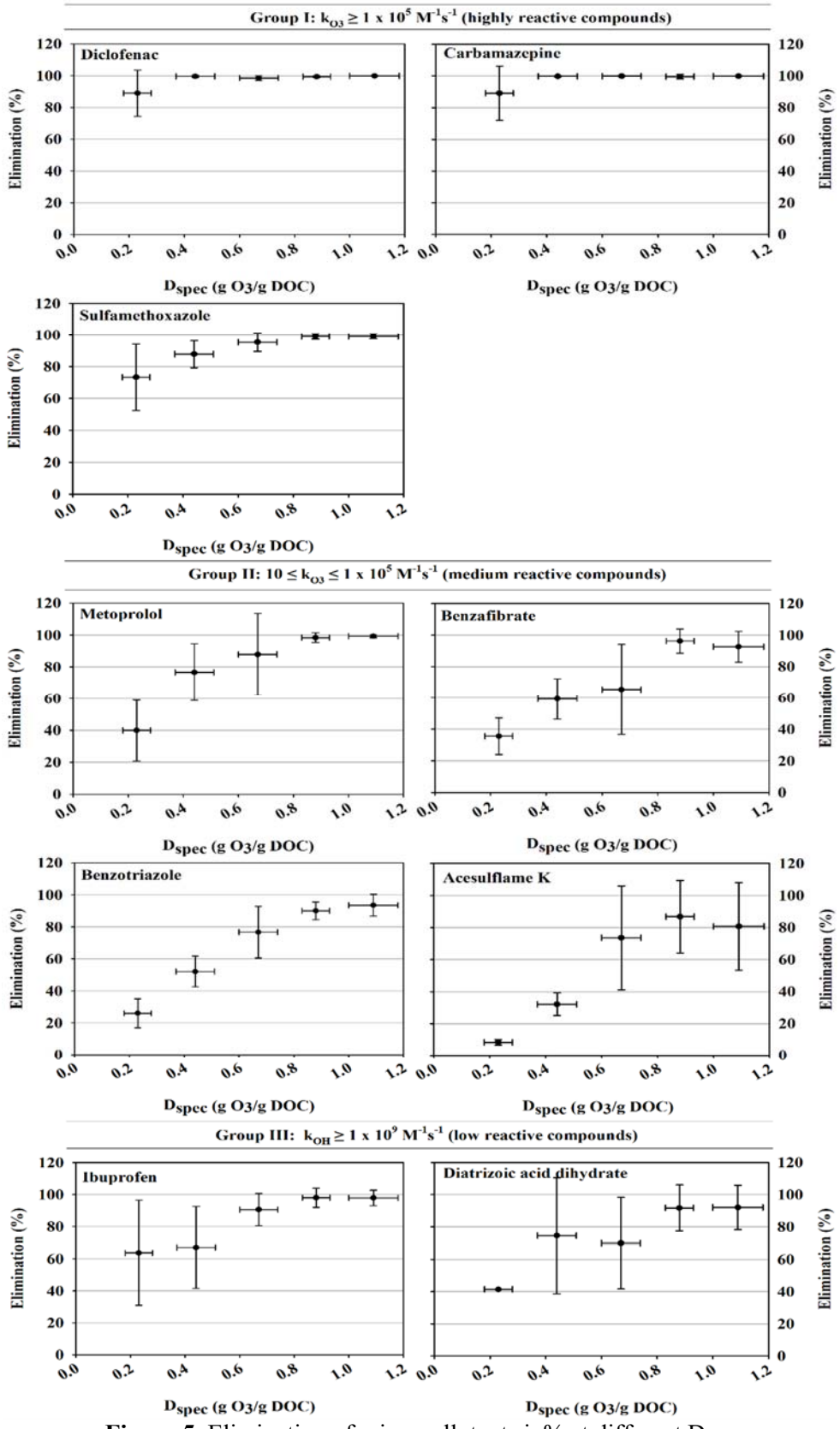

Figure 5. Elimination of micropollutants in% at different D_{spec}

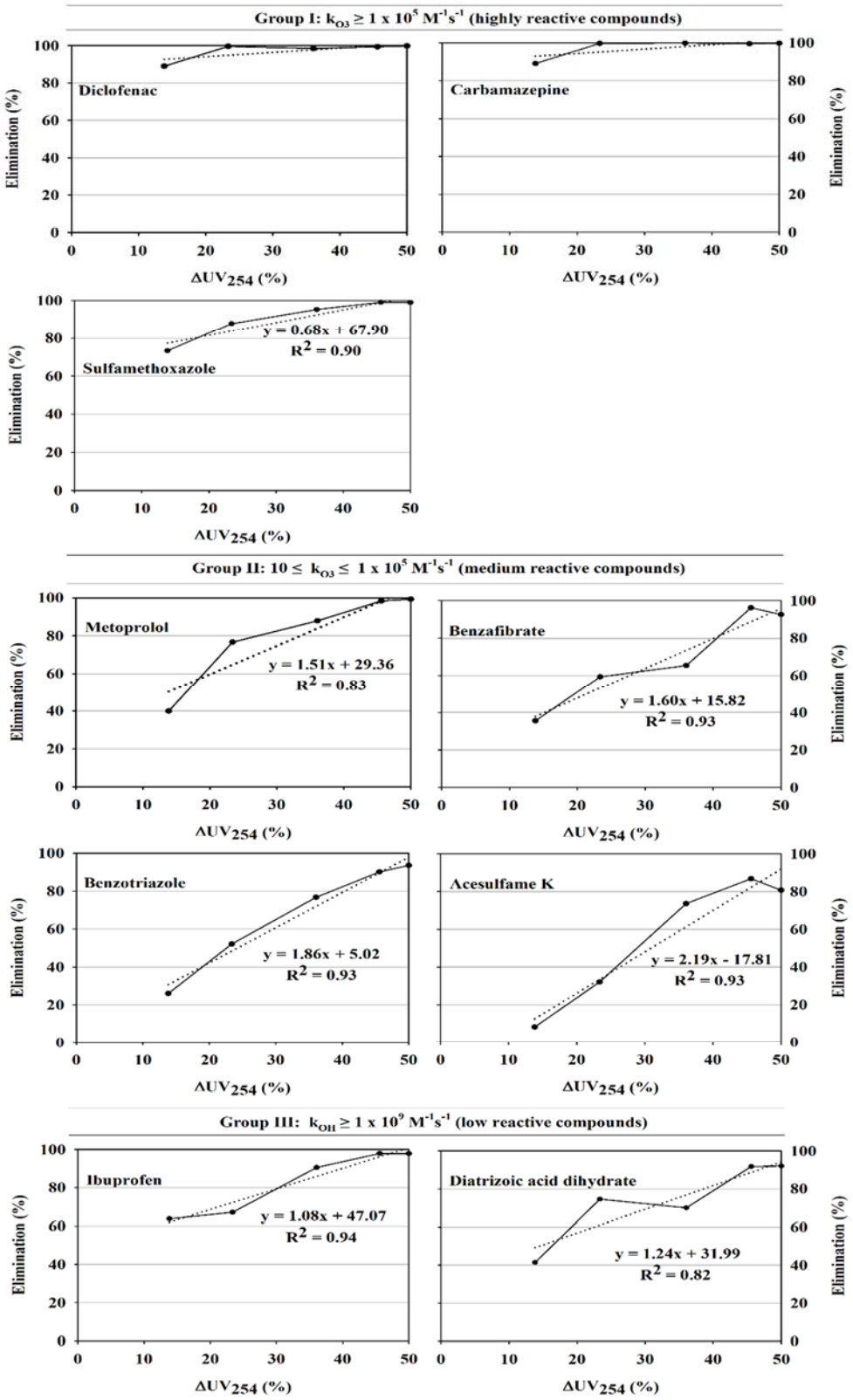

Figure 6. Linear correlation between the reduction in UV_{254} absorbance (ΔUV_{254}) with the elimination of TrOCs

4.1.2. Model for the prediction of the elimination of trace substances

Equation 1 represents the removal of micropollutants during ozonation, as follows. [16]:

$$\ln \frac{C}{C_0} = -k_{O_3} \int [O_3] dt - k_{OH\cdot} \int [OH\cdot] dt \quad (1)$$

c : Concentration of the substance (µg/L)
t : Time (s)
k_{O3} : Reaction constant of substance with ozone ($M^{-1}s^{-1}$)
$k_{\bullet OH}$: Reaction constant of substance with OH radicals ($M^{-1}s^{-1}$)
O_3 : Concentration of ozone (mg O_3/L)
•OH : Concentration of OH radicals (mg O_3/L)

As can be seen in the above-mentioned equation, the reaction constants are necessary for calculation, including: the respective trace substance, the ozone and hydroxyl radical exposure. The reaction rate constants are already known for many micropollutants and are summarized in Table 3 for TrOCs examined in this work.

Table 3. Reaction constants of the selected TrOCs

Substance	Substance class	O_3 - Reaction	pK_a	k_{O3} (M^{-1} s^{-1})	$k_{\bullet OH}$ (M^{-1} s^{-1})	Key reference
DCF	Analgesic/anti-inflammatory	High	4.2	1 x 10^6	7.5 x 10^9	1, 2
CBZ	Anticonvulsant	High	-	3 x 10^5	8.8 x 10^9	1
SMX	Antibiotic	High	1.7; 5.6	5.7 x 10^5	5.5 x 10^9	1
MTP	Beta-blocker	Moderate	9.7	4 x 10^4	7.3 x 10^9	3
BZF	Lipid regulator	Moderate	3.6	590	7.4 x 10^9	1, 4, 5
BZT	Corrosion inhibitor	Moderate	-	230	4.5 x 10^9	1
ACE K	Sweetener	Moderate		88	4.5 x 10^9	6
DTA	Iodinated contrast medium	Low	1.2; 7.9; 11.7	18.65	3 x 10^9	7
IBP	Analgesic/anti-inflammatory	Low	49	9.6	7.4 x 10^9	1, 5

1. Huber, Canonica [30]; 2. Sein, Zedda [31]; 3. Benner, Salhi [32]; 4. Dantas, Canterino [33], 5. Huber, Ternes [34]; 6. Kaiser, Köster [35]; 7. Ning and Graham [36]

For the micropollutants as carbamazepine, diclofenac, sulfamethoxazole, and metoprolol, complete elimination of nearly 100% was calculated with all three D_{spec} (0.6, 0.8 and 1 g O_3/g DOC). The measured values were between 98-100% for carbamazepine, sulfamethoxazole, and diclofenac; and between 87 - 99% for metoprolol. According to Lee, Gerrity [16] and Stapf, Miehe [26], the efficient elimination of carbamazepine and diclofenac is due to the high reaction rate constant k_{O3} (see Table 3). Metoprolol also reacts quickly with ozone, but the O_3 reactivity is more moderate compared to carbamazepine and diclofenac and depends on the pH value of the wastewater; thus, higher D_{spec} of ozone are necessary for almost complete elimination. For bezafibrate, the elimination was between 87-96%, for benzotriazole between 67-81%, for acesulfame K between 58 - 71%, and for ibuprofen between 68 - 79%. The D_{spec} measured values were between 64 - 92% for bezafibrate, 75 - 92% for benzotriazole, 71 - 85% for acesulfame K, and 90 - 97% for ibuprofen. Figure 7 graphically shows the measured elimination with the predicted performance.

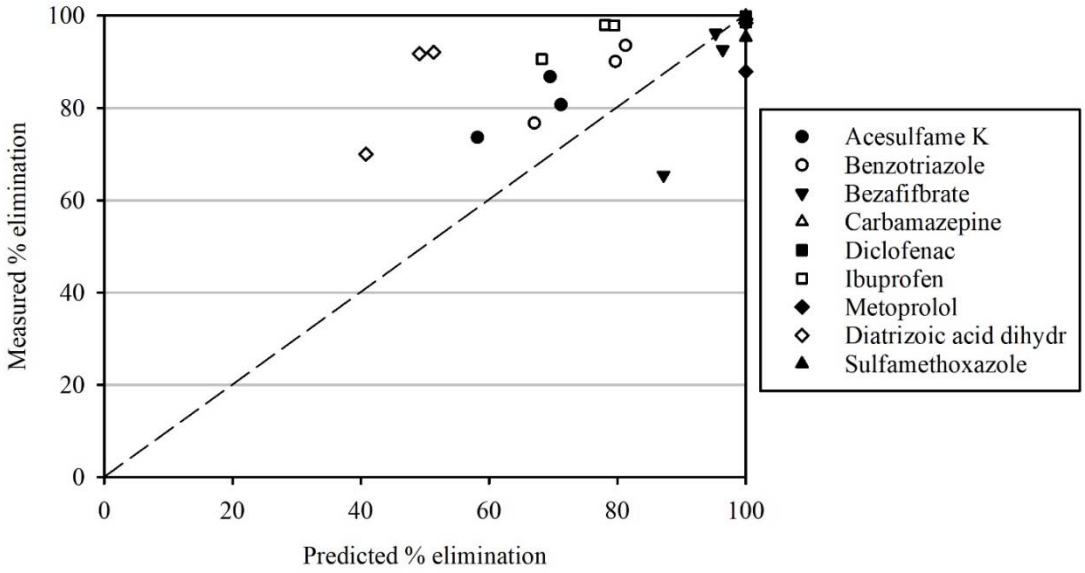

Figure 7. Performance of measured and predicted elimination

The values of micropollutants predicted and measured were the same for the trace substances, which have high reactivity to ozone (diclofenac, carbamazepine, and sulfamethoxazole). In the case of the moderately reacting micropollutants with ozone (see Table 3), a higher elimination is calculated compared to the measured values at low D_{spec}. As the amount of ozone increases, the results of the calculation approach those of the measured values. The prediction of the elimination of micropollutants could be useful for predictions, especially in the case of substances that react moderately with ozone (e.g., bezafibrate and benzotriazole), since substances that have a high reactivity towards ozone (e.g., diclofenac), as a rule, almost at low ozone quantities be completely dismantled. For the exact results of the elimination, however, the measurement should not be dispensed with. In the studies of Schindler, Mestankova [17], the predicted and measured eliminations for all selected micropollutants agree well. These excellent parallels could not be achieved in the course of the present work. The results of the present work confirm that the prediction of elimination can be calculated well for certain micropollutants, but the application does not have the same accuracy for all micropollutants. Deviations of 40-60% between forecast and calculation are possible, see benzotriazole, acesulfame K and ibuprofen in Figure 7. Bourgin, Beck [13] observed in their study that the projection of the elimination of micropollutants with highly reactive ozonation (carbamazepine, diclofenac, and sulfamethoxazole) works extremely well. Deviations from the predicted and calculated elimination have been observed primarily in the case of trace substances, which have a low reactivity to ozone. As was also observed in the present work, these are mainly substances that are mainly broken down via hydroxyl radicals, such as ibuprofen. As a possible cause for the deviation of the measured values compared to the calculated values, Hollender, Zimmermann [27] show that hydraulic behavior is not ideal, which means that ozone and hydroxyl radicals do not come into contact with all micropollutants and are, therefore, not oxidized. Apart from poor mixing, the sorption of micropollutants on other particles and colloids could also prevent oxidation.

4.2. Formation of oxidation byproducts during ozonation

During wastewater ozonation, toxic oxidation byproducts can formate, such as bromates [15, 37]. During the ozonation of bromide-contained water and the involving ozone reactions coupled with secondary oxidant-bearing substances (carbonates and hydroxyl radicals), bromate is produced, a potential human carcinogen [38]. Figure 8 shows the bromate concentration in ozonated samples at D_{spec}. The concentration of bromate increases with D_{sepc} and ranges from 0.23 ± 0.05 g O_3/g DOC to 1.09 ±

0.09 g O_3/g DOC. The dimensionless ratio of the bromate concentration normalized by the initial bromide concentration (µg BrO_3^-/µg Br^-) is the Bromate yield. Table 4 summarizes data on bromide, bromate, and bromate yield in this study.

Table 4. Bromide and bromate concentration, bromate yield

D_{spec} (g O_3/g DOC)	Bromide (µg/L)	Bromate (µg/L)	Bromate yield* (%)
0.23 ± 0.05	220.00 ± 84.71	0.00 ± 0.00	0.00
0.44 ± 0.07	211.75 ± 73.23	0.65 ± 0.28	0.19
0.66 ± 0.09	210.00 ± 18.74	2.52 ± 2.35	0.75
0.88 ± 0.05	169.25 ± 62.32	5.24 ± 5.38	1.94
1.09 ± 0.09	150.00 ± 86.97	11.22 ± 9.85	4.68

*Bromate yield = ([bromate]/[bromide]$_0$)

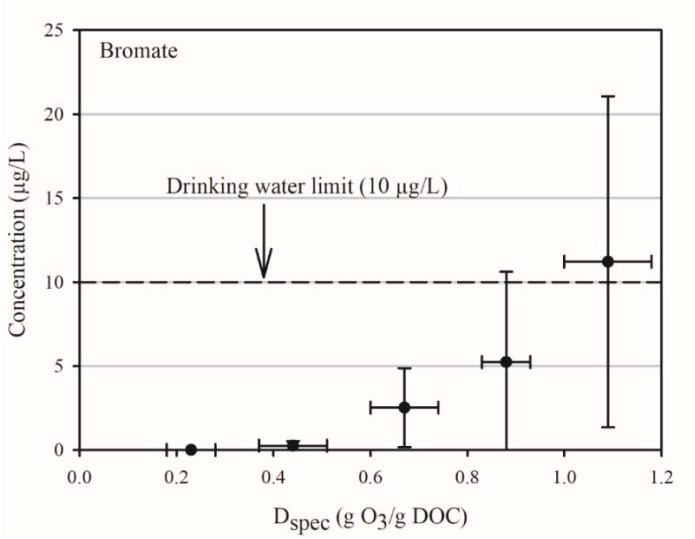

Figure 8. Bromate formation at different D_{spec} (g O_3/g DOC)

With the ozonation experiment, the doses of ozone per dissolved organic carbon (D_{spec} = 0.44, 0.66, and 0.88 g O_3/g DOC) increased bromate concentrations to 0.65 µg/L, 2.52 µg/L, and 5.24 µg/L, respectively (Figure 8). However, at 1.09 ± 0.09 g O_3/g DOC, the bromate concentration was 11.22 ± 9.85 µg/L higher than the guideline value of the drinking water standard (10 µg/L) [39]. D_{spec} should not be used at 1.0 g O_3/g DOC to avoid adverse effects from bromate, even though its effectiveness in removing micropollutants is the highest.

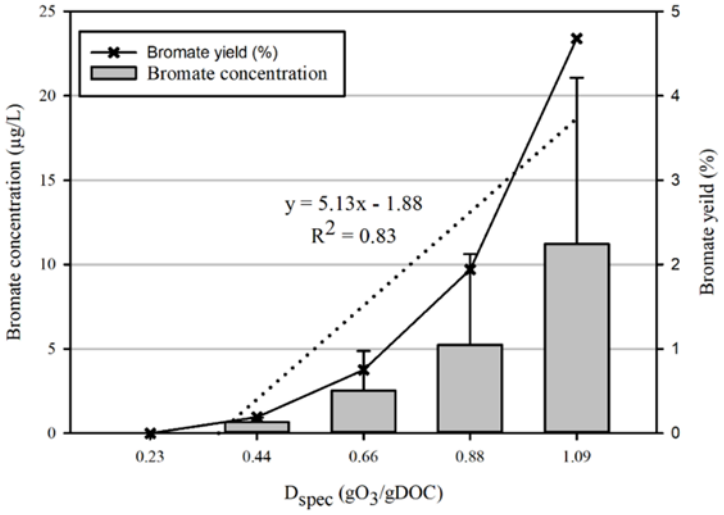

Figure 9. Relationship between bromate and bromate yield and D_{spec}

The previous studies [40-42] demonstrated that bromate production can be described by two stages characterized by D_{spec} range. With the dose of D_{spec} is less than 0.2 g O_3/g DOC, the formation of bromate and a slight influence of bromide concentration are negligible. However, with $D_{spec} \geq 0.4$ g O_3/g DOC, the bromate concentration raises almost linearly with an observed increasing in D_{spec}. Figure 9 shows the relationships between bromate yields and D_{spec}. Therefore, a decrease in bromide concentration usually results in a proportional reduction in bromate concentration.

5. Conclusion

The study focused on evaluating the degradation efficiency of micropollutants at different specific ozone doses (0; 0.2; 0.4; 0.6; 0.8; and 1.0 g O_3/g DOC), with a special focus on considering the formation of bromate as oxidation byproduct. Indicator substances with different reactivity with ozone were applied to monitor the success of ozonation and evaluate the experimental setup. Diclofenac and carbamazepine are the main indicators of the highly reactive group, together with sulfamethoxazole. The representatives of the moderately reactive group are benzotriazole, acesulfame, bezafibrate, and metoprolol. Micropollutants categorized as low ozone reactive compounds were ibuprofen and diatrizoic acid dihydrate. For the investigated ozone doses, the micropollutant abatement for highly reactive compounds ranged from 73 – 99%. The abatement of indicator substances with moderate reactivity (40 – 99%) showed the typical pattern of increasing removal with increasing D_{spec}, mostly due to the contribution of the indirect reaction pathway and increasing •OH formation with increasing D_{spec}. For the representatives of the low reactive compounds, a similar pattern was observed, and an abatement of 41 – 97% was achieved. The predicted removal of micropollutants using ozone and •OH exposure and the corresponding reaction rate constants were higher than observed for moderately reactive compounds due to mechanistic reasons.

Bromate formation ranged between 0.65 ± 0.28 and 11.22 ± 9.85 µg/L. The guideline value for drinking water (10 µg/L) was only exceeded at > 0.88 ± 0.05 g O_3/g DOC, which is higher than usually applied doses for the removal of micropollutants in wastewater (0.6 - 0.7 g O_3/g DOC). At D_{spec} below 0.8 g O_3/g DOC, the limit was not exceeded despite bromide concentrations of approx. 200 µg/L. Thus, the range of ozone doses recommended for micropollutant removal (0.4 – 0.7 g O_3/g DOC) did not only prove successful abatement with regard to micropollutants but are also appropriate to the formation of bromate at the bromide concentrations investigated.

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