

COMPARISON OF ENERGY REQUIREMENTS OF CONVENTIONAL OZONATION AND THE AOP O₃/H₂O₂ FOR TRANSFORMATION OF TARGET MICROPOLLUTANTS IN DIVERSE WATER MATRICES

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ABSTRACT

We used conventional ozonation and the AOP O₃/H₂O₂ to estimate the required energy to achieve the desired pre-defined level of oxidation of target organic micropollutants by hydroxyl radicals. We used the probe compound para-chloro benzoic acid (pCBA) to assess the fraction of •OH available for oxidation of micropollutants. pCBA reacts slowly with O₃ but reacts very fast with •OH ($k_{OH,pCBA} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). For our investigations we used three lake waters: Lake Zürich (ZH) and Lake Greifensee water (GF) from Switzerland and Lake Jonsvatnet water (NW) from Norway. The DOC concentrations were 1.4, 3.5 and 3 mg/L for ZH, GF and NW waters respectively and alkalinity was 2.7, 3.4 and 0.3 mM correspondingly. The results showed that for 90% pCBA transformation, the O₃ consumption was roughly 2 mg/L (40 µM) for ZH and NW waters and approximately 4 mg/L (80 µM) for GF water. Bromate formation in ZH water was much higher than in GF and NW waters and exceeded the EU drinking water standard of 10 µg/L for all examined O₃ concentrations, for initial bromide concentration 80 µg/L. The energy requirement to achieve 90% transformation was in the range 6.4 – 12.8 Wh/person/day for conventional ozonation of ZH-water and slightly higher for the use of AOP O₃/H₂O₂. The use of O₃/H₂O₂ however, reduces the required contact times and bromate formation.

1. INTRODUCTION

Ozone (O₃) is used widely in water treatment as disinfectant and oxidant. Transformation of organic compounds with O₃ occurs either via direct reaction with O₃ or with hydroxyl radicals (•OH), which result from ozone decay in water. O₃ reacts selectively with organic compounds and kinetic constants vary over 10 orders of magnitude, whereas •OH is an unselective oxidant and its reaction with the majority of organic compounds is nearly diffusion controlled. The enhanced formation of •OH, i.e., by addition of H₂O₂, comprises an Advanced Oxidation Process (AOP). Thus the combined use of O₃/H₂O₂ can accelerate ozone conversion to •OH and can reduce the reaction time required for micropollutant transformation [1].

In general, AOPs are more energy intensive than conventional ozonation. However, because not all micropollutants are susceptible to direct ozone oxidation (in the

time scale of interest in water treatment) and moreover extensive ozonation of bromide containing waters leads to bromate formation, AOPs can serve as a feasible alternative to ozonation [2]. The efficiency of ozonation and AOPs is greatly dependent on the water matrix composition and particularly on the concentrations of NOM and alkalinity, which consume $\bullet\text{OH}$ or influence the ozone decomposition [1]. There has been little research in comparing the energy requirements of ozonation and AOPs to transform target micropollutants. In a recent study by Rosenfeldt and co-workers, some of these issues were addressed; however the issue of bromate formation was not taken into account [3]. Furthermore, in this study we used several water matrices, covering a broader range of scavenging rates (the scavenging of $\bullet\text{OH}$ occurring by the presence of NOM and alkalinity), thus connected energy requirement not only to ozone dosage but to the scavenging of hydroxyl radicals.

2. EXPERIMENTAL PART

2.1. Experimental setup

Ozonation experiments were performed in a 500 mL batch reactor. The solutions were prepared as follows: firstly we filled the reactor with the desired water matrix, adjusted the temperature at 20 °C and buffered with 5 mM borate and pH adjustment was following, using 1M H₂SO₄ or NaOH. Next, pCBA was spiked to a final concentration of 1 μM and a sample was taken at time zero. Ozone was afterwards injected under vigorous stirring from a stock solution of approximately 1.5 mM to achieve the desired initial O₃ concentration. Samples were taken after 24 hours to measure pCBA transformation after complete ozone consumption. The experiments with O₃/H₂O₂ were performed exactly as the ozonation experiments with the addition of H₂O₂ (1:2 molar basis H₂O₂:O₃) prior to the addition of ozone in the solution.

2.2 Analytical methods

pCBA concentrations were measured by HPLC with UV/vis detection. An eluent consisting of 50%:50% methanol:H₂O was used for pCBA measurement. Bromate was measured with Ion Chromatography and UV detection after post column reaction [4].

3. RESULTS AND DISCUSSION

3.1. Calculation of scavenging rates of water matrices used in this study

Three lake waters were used in the present study to assess the effect of water composition on the efficiency of pCBA transformation, thus on the fraction of hydroxyl radicals which are available for transformation of target compounds. The basic constituents of water affecting the hydroxyl radical availability are the concentration of organic matter and the alkalinity. This can be estimated by calculating the scavenging rate of the system from the concentration of DOC and alkalinity and the respective k_{OH} values ($k_{\text{OH, DOC}}=2.5 \times 10^4 \text{ L mg}^{-1} \text{ s}^{-1}$, $k_{\text{OH, HCO}_3^-}=8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{OH, CO}_3^{2-}}=3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Increasing the scavenging rate of the water source, reduces the fraction of hydroxyl radicals, available for oxidation of target micropollutants. Table 1 shows the

concentration of DOC and alkalinity and the calculated scavenging rates of the examined surface waters.

Table 1. Water composition and calculation of scavenging rates of the lake waters used in this study

	Lake Zürich water (ZH)	Lake Greifensee water (GF)	Lake Jonsvatnet water (NW)
DOC (mg/L)	1.4	3.5	3
Alkalinity (mM as HCO ₃)	2.7	3.4	0.3
Scavenging rate (s ⁻¹)	5.7 x 10 ⁴	11.5 x 10 ⁴	7.75 x 10 ⁴

3.2. pCBA transformation by conventional ozonation as a function of ozone dosage in different water matrices and comparison with the AOP O₃/H₂O₂

The extent of pCBA transformation as a function of ozone dosage and the water matrix is illustrated in Figure 1. It shows an increase of pCBA transformation with increasing O₃ concentrations. This is ascribed to the resulting higher OH-radical exposure. For the same ozone dosages, the extent of pCBA transformation depends upon the scavenging rate of the water matrix. Apparently, the higher the scavenging rate of the water matrix, the higher fraction of hydroxyl radicals will be scavenged resulting in lower pCBA transformation. Consequently, in waters with higher scavenging rates, like the GF water, higher ozone dosages will be required to achieve a pre-defined micro-pollutant transformation level, thus higher energy requirements for the same degree of oxidation.

The use of the AOP O₃/H₂O₂ mostly affects the kinetics of pCBA transformation and the kinetics of ozone transformation to hydroxyl radicals (Figure 2) and not the extent of transformation. The additional use of H₂O₂ increases the energy requirements and the treatment costs, but substantially reduces the required contact times in the reactor and bromate formation, in bromide containing waters, as shown in Figure 3. For different ozone dosages the use of AOP can reduce bromate formation up to 70%. However, the use of AOP eliminates the disinfection capability of ozonation. Therefore, to ensure disinfection and reduce bromate formation, H₂O₂ is usually spiked in the reactor after ozone addition. In this case disinfection is ensured and bromate formation is reduced by 30% (data not shown), which in some cases might be sufficient to keep bromate concentration below 10 µg/L. This depends strongly on the initial bromide concentration and ozone dosages. Ozonation of GF and NW waters resulted in reduced bromate formation (data not shown), most likely because of reduced ozone exposure, due to increased rates of ozone decay.

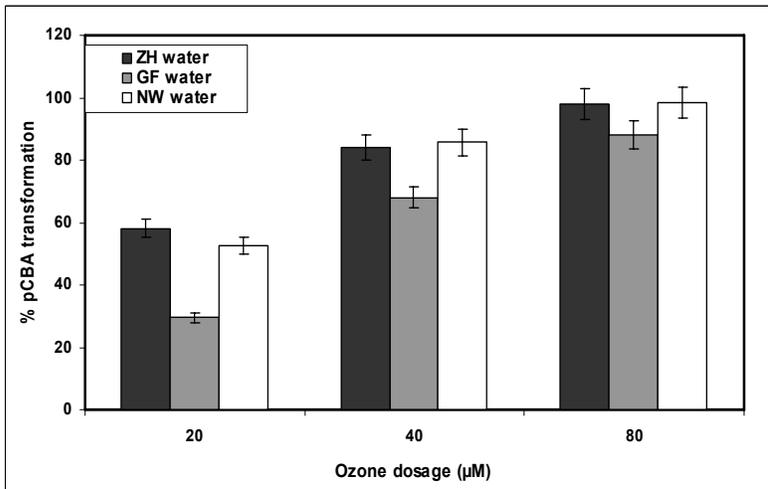


Figure 1. pCBA transformation by conventional ozonation as a function of ozone dosage in waters with different composition and scavenging rates (pH = 8, T = 20°C)

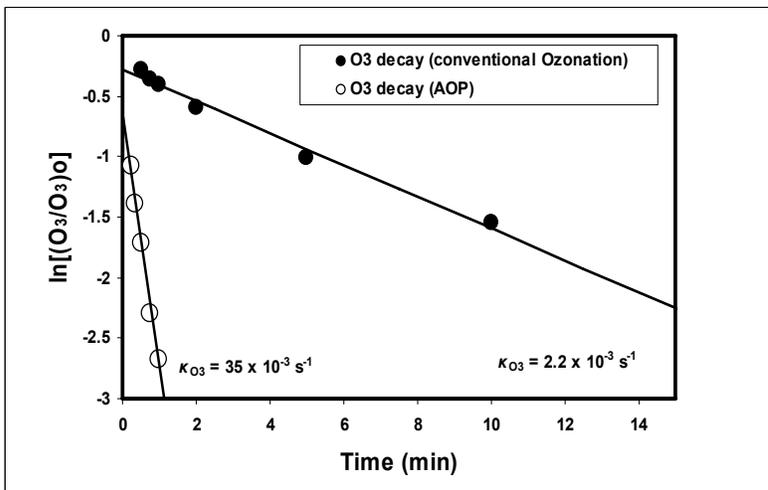


Figure 2: Rate of O₃ depletion using conventional ozonation and the AOP O₃/H₂O₂ in Lake Zürich water, 20°C, pH 8

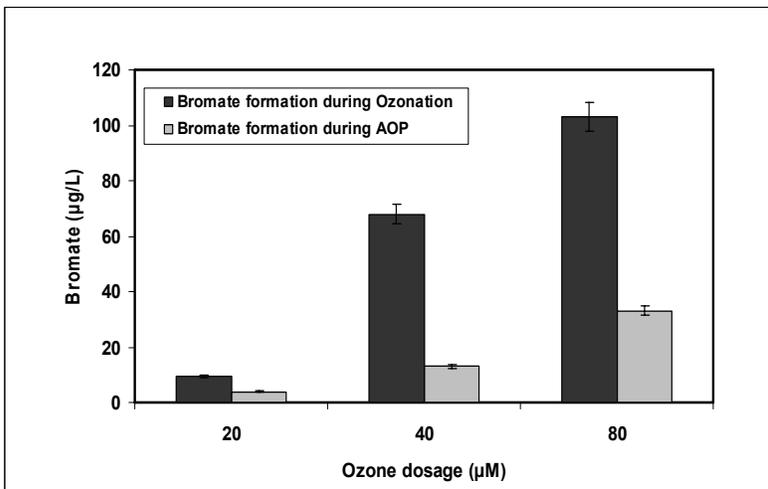


Figure 3. Bromate formation by conventional ozonation and AOP O₃/H₂O₂ in lake Zürich water (pH 8, T= 20 °C, initial bromide = 80 µg/L)

3.3. Energy calculations and concluding remarks

Assuming that for the production of ozone, 10 – 20 kWh/kg O₃ are consumed and of H₂O₂ 10 kWh/kg [3] and that for drinking water treatment a 90% removal of contaminants would be desirable, we can calculate the amount of energy required for complete elimination of pCBA and correlate it to bromate formation. For ZH water at pH 8, a rough estimate would be a 6.4 – 12.8 Wh/person/day with conventional ozonation and 7.5 – 14 Wh/person/day with AOP (assuming 160 L consumption of drinking water/person/day). However, the use of O₃/H₂O₂ reduces bromate formation by 70% but eliminates the disinfection capacity of ozone. Therefore, use of H₂O₂ after ozone addition reduces bromate formation by 30% and ensures disinfection. The treatment of the Norwegian water would require the same energy for oxidation as the ZH-water but bromate formation would be much lower, because of lower ozone exposure. Greifensee water would require more energy than ZH water to achieve the same oxidation efficiency. Compounds which are susceptible to direct oxidation with ozone, such as olefins, activated aromatics and deprotonated amines, will require 10 times less energy for 90% transformation. The use of UV/H₂O₂ as an alternative to O₃/H₂O₂ is expected to be roughly 10 times more energy intensive than ozonation but circumvents bromate formation and ensures disinfection. This would be a viable solution for waters with high concentrations of bromide and scavengers and organic micropollutants, not susceptible to direct ozone oxidation.

4. REFERENCES

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