EFFECT OF SCAVENGING RATE OF WATER ON THE ENERGY REQUIREMENTS FOR MICROPOLLUTANT TRANSFORMATION BY CONVENTIONAL OZONATION AND THE AOPs O$_3$/H$_2$O$_2$ and UV/H$_2$O$_2$

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ABSTRACT

In the present study we investigated the effect of scavenging rate of water on the energy efficiency of conventional ozonation and the AOPs O$_3$/H$_2$O$_2$ and UV/H$_2$O$_2$ for transformation of organic micropollutants. For the investigations we used three lake waters and a wastewater. We experimentally determined the rate constants of organic matter for their reaction with OH-radicals (k$_{OH,DOM}$), and based on these data we calculated scavenging rates of the various water matrices, which varied from 6.1 to 20 x 10$^{-4}$ s$^{-1}$ and energy requirements for efficient oxidation. For 90% pCBA transformation by ozonation, energy consumption was 0.035 (in ZH. and NW. water), 0.065 (GF. water) and 0.2 (DW. water) kWh/m$^3$. Application of O$_3$/H$_2$O$_2$ increased the energy consumption by approximately 22%. UV/H$_2$O$_2$ efficiently oxidized pCBA in all waters but energy requirements were substantially higher.

Μελέτη και σύγκριση των ενεργειακών απαιτήσεων της οξείδωσης οργανικών μικρορρύπων από υδατικά διαλύματα με την εφαρμογή οξιονισμού και προχωρημένων μεθόδων οξείδωσης O$_3$/H$_2$O$_2$ και UV/H$_2$O$_2$

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ΠΕΡΙΛΗΨΗ

Στην εργασία αυτή παρουσιάζονται αποτελέσματα εφαρμογής όζοντος και προχωρημένων τεχνολογιών οξείδωσης, όπως O$_3$/H$_2$O$_2$ και UV/H$_2$O$_2$ με σκοπό την σύγκριση των ενεργειακών απαιτήσεων για την οξείδωση οργανικών μικρορρύπων σε διαφορετικά υδατικά υποστρώματα. Τα αποτελέσματα έδειξαν ότι η χρήση όζοντος είναι μια μέθοδος με χαμηλές ενεργειακές απαιτήσεις, αλλά όταν το νερό περιέχει υψηλές συγκεντρώσεις οργανικής ύλης, αλκαλικότητας και βρωμίων, τότε για να επιτύχουμε αυξημένη οξείδωση, χρησιμοποιούμε αυξημένες ποσότητες όζοντος, με αποτέλεσμα να έχουμε σχηματισμό βρωμικών, τα οποία είναι πιθανός καρκινογόνες ουσίες και αυξημένες ενεργειακές απαιτήσεις. Στις περιπτώσεις αυτές, η χρήση ακτινοβολίας UV με υπεροξείδιο του υδρογόνου είναι πιο συμφέρουσα, παρόλο που είναι πιο ενεργοβόρα, γιατί αποτρέπει την δημιουργία βρωμικών και επιτυγχάνει εξίσου αποτελεσματική οξείδωση.
1. INTRODUCTION

Ozone (O$_3$) is used widely in water treatment as disinfectant and oxidant. Transformation of organic compounds with O$_3$ occurs either via direct reaction with O$_3$ or with hydroxyl radicals (•OH), which is the result of ozone decay in water. O$_3$ reacts selectively with organic compounds and kinetic constants vary over 10 orders of magnitude, whereas •OH is 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 H$_2$O$_2$, comprises an Advanced Oxidation Process (AOP). Thus the combined use of O$_3$/H$_2$O$_2$ can accelerate ozone conversion to •OH and can reduce the reaction time required for micropollutant transformation [1]. The combined use of UV and hydrogen peroxide results in the generation of hydroxyl radicals and represents an AOP as well. It can lead to pollutant transformation by direct photolysis and oxidation by •OH radicals [2].

In general, AOPs are more energy intensive than conventional ozonation. However, because not all micropollutants are susceptible to direct ozone oxidation (in 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 [3]. The efficiency of ozonation and AOPs is greatly dependent on the water matrix composition and particularly on the concentrations of DOC and alkalinity, which consume •OH or influence the ozone decomposition. There has been little research in comparing the energy requirements of ozonation and AOPs to transform micropollutants in different waters. 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 consideration [4]. Furthermore, in this study we examined the methods in several water matrices, covering a broader range of scavenging rates (the scavenging of •OH occurring by the presence of DOC and alkalinity).

2. EXPERIMENTAL PART

2.1. Experimental setup

Ozonation experiments were performed in a 500 mL batch reactor. The solution preparation was 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 H$_2$SO$_4$ or NaOH 1M. Next, pCBA was spiked to a final concentration of 1 µM and 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 O$_3$ concentration. Samples were taken after 24 hours to measure pCBA transformation after complete ozone consumption. The experiments with O$_3$/H$_2$O$_2$ were performed exactly as the ozonation experiments with the addition of H$_2$O$_2$ (1:2 molar basis H$_2$O$_2$:O$_3$) prior to the addition of ozone in the solution. For the UV/H$_2$O$_2$ investigations, a merry-go-round photoreactor was used. The methodology for irradiation kinetics experiments has been described elsewhere [2]. For most irradiations a low-pressure (LP) mercury arc lamp (Heraeus Noblelight model TNN 15/32, nominal power 15 W) was used in combination with a quartz cooling jacket. Pure water with negligible light absorption was recirculated in the temperature-controlled photoreactor. Fluence rate values were determined by chemical actinometry at low optical density [2] using 5µM atrazine as an actinometer (solution buffered at
pH=7.0 with 5 mM phosphate). The determined fluence rate was $2.73 \times 10^9$ Einstein cm$^{-2}$ s$^{-1}$.

Another photoreactor setup, with a medium-pressure (MP) mercury arc lamp (Heraeus Noblelight model TQ718, nominal power 500 – 700 W) and a UVW-55 glass band pass filter ($\lambda = 308 – 410$ nm) in the cooling jacket (Huber et al., 2003), was employed for the determination of $k_{\text{OH,DOM}}$.

2.2 Analytical methods

pCBA concentrations were measured by HPLC with UV/vis detection. An eluent consisting of 50%:50% methanol:H$_2$O was used for pCBA measurement. Bromate was measured with Ion Chromatography and UV detection after post column reaction [5].

3. RESULTS AND DISCUSSION

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

Three lake waters and a wastewater 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. Therefore, we need to assess the oxidation capacity of O$_3$ towards oxidation of micropollutants for specific water systems. This can be done by calculating the scavenging rate of water from the concentration of DOC and alkalinity and the respective $k_{\text{OH}}$ values ($k_{\text{OH, HCO}_3}$ = $8.5 \times 10^6$ M$^{-1}$ s$^{-1}$). Increasing the scavenging rate of the water source reduces the fraction of hydroxyl radicals, which are 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. DOC and alkalinity concentrations of waters examined in this study; experimentally determined rate constants ($k_{\text{OH,DOM}}$) for the reaction of NOM with OH-radicals; calculated scavenging rates for the different water matrices.

<table>
<thead>
<tr>
<th></th>
<th>Lake Zürich water (ZH-water)</th>
<th>Lake Greifensee water (GF-water)</th>
<th>Lake Jonsvatnet water (NW-water)</th>
<th>Wastewater Dübendorf (DW-water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DOC] ((mg of C) L$^{-1}$)</td>
<td>1.3</td>
<td>3.1</td>
<td>3</td>
<td>3.9</td>
</tr>
<tr>
<td>$k_{\text{OH,DOM}}$ (L (mg of C)$^{-1}$ s$^{-1}$)</td>
<td>$2.7 \times 10^4$</td>
<td>$2.1 \times 10^4$</td>
<td>$1.95 \times 10^4$</td>
<td>$3.5 \times 10^4$</td>
</tr>
<tr>
<td>Alkalinity (mM)</td>
<td>2.6</td>
<td>4.0</td>
<td>0.35</td>
<td>6.5</td>
</tr>
<tr>
<td>Scavenging rate (s$^{-1}$)</td>
<td>$6.1 \times 10^4$</td>
<td>$10.4 \times 10^4$</td>
<td>$6.2 \times 10^4$</td>
<td>$20 \times 10^4$</td>
</tr>
</tbody>
</table>
3.2. pCBA transformation by conventional ozonation as a function of ozone dose in different water matrices and comparison with the AOP O₃/H₂O₂

The extent of pCBA transformation as affected by ozone dose and the water matrix is illustrated in Figure 1, showing that the higher the ozone concentration, the higher the pCBA transformation. This is mainly ascribed to the higher OH-radical exposure resulting from higher ozone concentrations. For the same ozone dose, the extent of pCBA formation depends on the scavenging rate of the water matrix. Apparently, the higher the scavenging rate of the water matrix, the higher the scavenging rate of hydroxyl radicals will be scavenged resulting in lower micropollutant transformation. Consequently, in waters with higher scavenging rates, like the GF and DW-water, higher ozone doses will be required to achieve a pre-defined micro-pollutant transformation level, thus higher energy requirements for efficient treatment.

The use of AOP O₃/H₂O₂ mostly affects the kinetics of pCBA transformation, for equal ozone doses. 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 2. For different ozone doses the use of AOP can reduce bromate formation up to 70%. However, the use of AOP eliminates the disinfection capability of ozonation.

![Figure 1. pCBA transformation by conventional ozonation as a function of ozone dose in waters with different composition and scavenging rates (pH = 8, T = 20°C)](image-url)
Figure 2. Bromate formation by conventional ozonation and AOP O$_3$/H$_2$O$_2$ in lake Zürich water (pH 8, T= 20 °C, initial bromide = 80 µg/L)

3.3 pCBA transformation by UV/H$_2$O$_2$ at different water matrices

The use of UV/H$_2$O$_2$ generates hydroxyl radicals through the light absorption and subsequent photolysis of H$_2$O$_2$. Figure 3 shows the transformation of pCBA in the four different water matrices, by using a low pressure mercury lamp and constant hydrogen peroxide concentration (0.2 mM; 6.8 mg/L). It can be seen that the scavenging rate of water plays an important role in this case as well. However, in addition to that, the absorption coefficient of the water plays an additional part. ZH- and NW-waters have quite different absorption coefficients at 254 nm (0.037 and 0.1 cm$^{-1}$, respectively) and despite the similar scavenging rates, the removal of pCBA is significantly faster in the case of ZH-water. Use of UV/H$_2$O$_2$ does not induce bromate formation, but as it will be discussed later, it is more energy intensive than the conventional ozonation or the AOP O$_3$/H$_2$O$_2$. 
Figure 3. Transformation of pCBA in different water matrixes as a function of time by LP-UV/H₂O₂ at 20°C and pH 8, applying H₂O₂ concentration of 0.2 mM.

3.4. Energy calculations and concluding remarks

Results of energy calculations for the examined treatment methods in the different waters are shown in Table 2 and depict that ozonation requires in general much less energy than UV/H₂O₂ for 90% pCBA transformation in all waters examined in this study.

Table 2. Energy requirements (kW/m³) for 90% pCBA transformation in diverse water matrices by conventional ozonation and UV/H₂O₂, employing a 5 cm path length and 0.2 mM H₂O₂.

<table>
<thead>
<tr>
<th>Water Matrix</th>
<th>Ozonation</th>
<th>UV/H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZH-water</td>
<td>0.035</td>
<td>0.23</td>
</tr>
<tr>
<td>NW-water</td>
<td>0.035</td>
<td>0.45</td>
</tr>
<tr>
<td>GF-water</td>
<td>0.065</td>
<td>0.61</td>
</tr>
<tr>
<td>DW-water</td>
<td>0.2</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Note: a Experimental conditions: Target compound concentration = 0.5 µM, pH = 8, T= 20 °C.
Table 2 also shows, the pronounced effect of scavenging rate of water on the energy efficiency of the methods. In the case of O$_3$/H$_2$O$_2$, the energy for H$_2$O$_2$ production has to be considered. If we assume a molar ratio 2:1 (O$_3$:H$_2$O$_2$), then for 90% pCBA transformation in ZH-water, the energy consumption will be increased from 0.035 to 0.045 kWh/m$^3$, corresponding to approximately 22% increase in energy requirements. However, this increase in energy requirements was compensated by reduced bromate formation and smaller contact times in the reactor.

Treatment of pCBA with UV/H$_2$O$_2$ in all waters required more energy than when applying conventional ozonation for the same degree of pollutant transformation. In this case, absorption coefficient of the water plays also a significant role, in determining the required energy. As already demonstrated, between waters with comparable scavenging rates but with different absorption coefficients (e.g., ZH- and NW-water) the removal of pCBA requires substantially less energy when doing the experiments in ZH-water.

4. REFERENCES