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Prediction of micropollutant elimination during ozonation of a hospital wastewater effluent

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ABSTRACT

Determining optimal ozone doses for organic micropollutant elimination during wastewater ozonation is challenged by the presence of a large number of structurally diverse micropollutants for varying wastewater matrice compositions. A chemical kinetics approach based on ozone and hydroxyl radical (•OH) rate constant and measurements of ozone and •OH exposures is proposed to predict the micropollutant elimination efficiency. To further test and validate the chemical kinetics approach, the elimination efficiency of 25 micropollutants present in a hospital wastewater effluent from a pilot-scale membrane bioreactor (MBR) were determined at pH 7.0 and 8.5 in bench-scale experiments with ozone alone and ozone combined with H_2O_2 as a function of DOC-normalized specific ozone doses (gO_3/gDOC). Furthermore, ozone and •OH exposures, •OH yields, and •OH consumption rates were determined. Consistent eliminations as a function of gO_3/gDOC were observed for micropollutants with similar ozone and •OH rate constants. They could be classified into five groups having characteristic elimination patterns. By increasing the pH from 7.0 to 8.5, the elimination levels increased for the amine-containing micropollutants due to the increased apparent second-order ozone rate constants while decreased for most micropollutants due to the diminished ozone or •OH exposures. Increased •OH quenching by effluent organic matter and carbonate with increasing pH was responsible for the lower •OH exposures. Upon H_2O_2 addition, the elimination levels of the micropollutants slightly increased at pH 7 (<8%) while decreased considerably at pH 8.5 (up to 31%). The elimination efficiencies of the selected micropollutants could be predicted based on their ozone and •OH rate constants (predicted or taken from literature) and the determined ozone and •OH exposures. Reasonable agreements between the measured and predicted elimination levels were found, demonstrating that the proposed chemical kinetics method can be used for a

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generalized prediction of micropollutant elimination during wastewater ozonation. Out of 67 analyzed micropollutants, 56 were present in the tested hospital wastewater effluent. Two-thirds of the present micropollutants were found to be ozone-reactive and efficiently eliminated at low ozone doses (e.g., >80% for $gO_3/gDOC = 0.5$).

1. Introduction

In recent years, ozonation has been intensively tested as an advanced wastewater treatment technology from laboratory- to full-scale studies and demonstrated to be a useful, economically feasible method to improve the quality of municipal wastewater effluents (Flyborg et al., 2010; Gerrity et al., 2011, 2012; Hollender et al., 2009; Huber et al., 2005; Lee et al., 2013; Margot et al., 2013; Nakada et al., 2007; Reungoat et al., 2012; von Sonntag and von Gunten, 2012; Zimmermann et al., 2011). These studies have shown that ozonation of secondary wastewater effluents can achieve significant abatement of many organic micropollutants and inactivation of bacteria and viruses at reasonable specific ozone doses (e.g., $gO_3/gDOC = 0.5–1.0$ in which the mass-based ozone to dissolved organic carbon ratio is a common operating parameter for ozone applications). Significant reductions of *in vitro* and *in vivo* toxicities were also demonstrated after ozonation or ozonation followed by biological filtration (Escher et al., 2009; Macova et al., 2010; Reungoat et al., 2012; Stalter et al., 2010a,b).

The presence of a large number of structurally diverse micropollutants in wastewater matrices from various sources has been found to be challenging for ozonation process design for micropollutant elimination (Lee et al., 2013). The number of organic micropollutants in wastewaters is up to several hundred (Oulton et al., 2010), which makes it cost-prohibitive and impractical to measure their elimination efficiencies individually. Wastewater quality parameters such as effluent organic matter (EfOM) or pH can vary considerably depending on the wastewater sources or operating conditions of wastewater treatment plants. EfOM is the main sink for ozone and OH radicals (•OH), thus it has been difficult to predict the micropollutant elimination efficiency in wastewater effluents containing EfOMs with different concentration and characteristics.

A previous study showed that these challenges can be solved using an approach based on chemical kinetics (Lee et al., 2013). The elimination of a micropollutant (P) during ozonation is achieved by its reaction with ozone and •OH, the latter is produced from the ozone decomposition (von Sonntag and von Gunten, 2012). The elimination of P in terms of logarithmic relative residual concentration of P can be predicted if the ozone and •OH rate constant (i.e., k_{O_3} and $k_{\bullet OH}$) and the ozone and •OH exposures ($\int[O_3]dt$ and $\int[\bullet OH]dt$) are known (Eq (1)).

$$-\ln\left(\frac{[P]}{[P]_0}\right) = k_{O_3}\int[O_3]dt + k_{\bullet OH}\int[\bullet OH]dt \quad (1)$$

Ozone reacts selectively with compounds containing electron-rich moieties (ERMs), such as phenols, anilines, activated aromatics, amines, organic sulfurs, and olefins with k_{O_3}-values typically ranging from $10^3–10^7\ M^{-1}\ s^{-1}$ at pH 7 (Lee and von Gunten, 2010). Quantitative structure–activity relationships (QSARs) have been found between the logarithmic k_{O_3}-values for the ozone reactions with compounds having a common ERM vs. Hammett or Taft sigma constants as substituent descriptor variables. These QSARs were found to be able to predict the k_{O_3}-values for various organic compounds within a factor of 1/3–3 compared to measured values (Lee and von Gunten, 2012). •OH is a less selective oxidant with $k_{\bullet OH}$ values generally differing within only a factor of 3 for most organic compounds ($k_{\bullet OH} = 3 \times 10^9 - 10^{10}\ M^{-1}\ s^{-1}$, Buxton et al., 1988; NDRL/NIST Solution Kinetic Database, http://kinetics.nist.gov/solution/). A group contribution method has been developed and demonstrated to be able to predict the $k_{\bullet OH}$ values for various compounds within a factor of 1/2–2 compared to measured values (Minakata et al., 2009). Based on Eq (1), ozone-reactive micropollutants with ERMs can be more efficiently eliminated than ozone-resistant ones without ERMs due to the combined reaction with ozone and •OH.

It was shown previously that similar •OH exposures were achieved at the same specific ozone dose (i.e., $gO_3/gDOC$) during ozonation of 10 municipal wastewater effluents from Australia, Switzerland, and the USA regardless of water qualities (Lee et al., 2013). Variations of the ozone exposures for the same $gO_3/gDOC$ were within a factor of 4 and were larger than the variations of the •OH exposures that were within a factor of 2. Nevertheless, the large variations of the ozone exposure affected only the elimination efficiency of ozone-reactive micropollutants with elimination levels already close to the quantification limits (i.e., >95% elimination) for low ozone doses (e.g., $gO_3/gDOC < 0.5$). Overall, it was concluded that the elimination of micropollutants having the same or similar k_{O_3}- and $k_{\bullet OH}$-values was comparable at the same specific ozone dose ($gO_3/gDOC$) during ozonation of wastewater effluents (Lee et al., 2013). Therefore, the specific ozone dose, and the k_{O_3}- and $k_{\bullet OH}$-values were identified as the key parameters to predict and generalize the elimination efficiency of micropollutants during ozonation of municipal wastewater effluent. To further test, validate, and upgrade the afore-described chemical kinetics approach, more measurements of the ozone and •OH exposures in wastewater effluents with a range of matrix characteristics are recommended considering the still limited information for these parameters. Studies for comparing the measured and predicted elimination of micropollutants covering a broader range of chemical structures are also needed.