



Prediction of micropollutant abatement during homogeneous catalytic ozonation by a chemical kinetic model

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ABSTRACT

Prediction of micropollutant abatements by catalytic ozonation is critical for its process design and optimization in water treatment. In this study, a chemical kinetic model based on ozone (O_3) and hydroxyl radical ($\cdot OH$) rate constants (k_{O_3} and $k_{\cdot OH}$) and O_3 and $\cdot OH$ exposures is proposed for the generalized prediction of micropollutant abatement by homogeneous catalytic ozonation. Several micropollutants with k_{O_3} ranging from <0.15 to $1.0 \times 10^6 M^{-1} s^{-1}$ were spiked in water matrices (deionized water and surface water) and then treated by ozonation alone and homogeneous catalytic ozonation with varying transition metals (Ti^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Mn^{2+} , Fe^{2+} , and Fe^{3+}). The addition of the varying catalysts enhanced the kinetics and yield of $\cdot OH$ formation from O_3 decomposition to different extent. Consequently, for the same applied O_3 doses, higher $\cdot OH$ exposures can generally be obtained at the expense of lower O_3 exposures during catalytic ozonation with the varying catalysts compared to ozonation alone. The changes in O_3 and $\cdot OH$ exposures did not considerably influence the abatement of micropollutants with high and moderate O_3 reactivities (diclofenac, gemfibrozil, and bezafibrate), whose abatement efficiencies were generally $>90\%$ during both ozonation alone and catalytic ozonation with the varying catalysts. In contrast, ozone-resistant micropollutants (2,4-dichlorophenoxyacetic acid, clofibric acid, and ibuprofen) were less effectively abated during ozonation (~ 40 – 60% abatement), and the addition of the varying catalysts could enhance their absolute abatement efficiencies to various extent (~ 0 – 10% in the deionized water and ~ 0 – 22% in the surface water) during catalytic ozonation. Despite the differing catalytic mechanisms of the varying transition metals, the abatement efficiencies of micropollutants by catalytic ozonation could be satisfactorily predicted by the chemical kinetic model using the O_3 and $\cdot OH$ rate constants of the micropollutants reported in literature and the O_3 and $\cdot OH$ exposures determined during the treatment processes. These results demonstrate that the chemical kinetic model can provide a useful tool for the generalized prediction of micropollutant abatement by homogeneous catalytic ozonation.

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1. Introduction

The increasing worldwide contamination of the aquatic environment with micropollutants (e.g., pesticides, pharmaceuticals, and personal care products) has aroused considerable international concerns (Michael et al., 2013; Petrie et al., 2015; Schwarzenbach et al., 2006; Ternes and Joss, 2006; Ternes, 1998). Many micropollutants can pose a potential threat to ecosystems and/or human health at environmentally relevant concentrations (e.g., ng – $\mu g/L$).

Moreover, numerous micropollutants often coexist in the water matrix and may result in additive or even synergistic effects, which render their mixtures dangerously potent (Petrie et al., 2015; Schwarzenbach et al., 2006; Ternes and Joss, 2006). To protect ecosystems and human health, effective technologies are needed to sufficiently abate micropollutants (ideally to below detection limits) during water and wastewater treatment (Gerrity et al., 2011; Kasprzyk-Hordern et al., 2009; Klavarioti et al., 2009; Lee et al., 2013; Schwarzenbach et al., 2006; von Sonntag and von Gunten, 2012).

Ozonation has been intensively tested as a potential technology for micropollutant abatement in water and wastewater treatment (Huber et al., 2003; Huber et al., 2005; Rosal et al., 2010;

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von Sonntag and von Gunten, 2012). During ozonation, micropollutants can be abated by oxidation with ozone (O_3) and/or hydroxyl radicals ($\bullet OH$) generated from O_3 decomposition with water constituents (e.g., dissolved organic matter (DOM) in the water matrix) (von Sonntag and von Gunten, 2012). O_3 is a selective oxidant and reacts preferentially with compounds containing electron-rich moieties such as phenols, olefins, deprotonated amines, and reduced sulfur groups. In contrast, $\bullet OH$ is a less selective oxidant and can rapidly oxidize almost all types of organic moieties at diffusion-controlled rates ($\sim 10^8\text{--}10^9\text{ M}^{-1}\text{ s}^{-1}$) (von Sonntag and von Gunten, 2012). Many studies have shown that micropollutants with electron-rich moieties can usually be efficiently eliminated by primarily O_3 oxidation in a variety of water matrices (e.g., natural water and wastewater) during conventional ozonation (Gerrity et al., 2011; Hollender et al., 2009; Huber et al., 2005; Hubner et al., 2015; Kovalova et al., 2013; Lee et al., 2013; Zucker et al., 2016). However, ozone-resistant micropollutants, which can only be oxidized by $\bullet OH$ during conventional ozonation, are usually less effectively abated due to the low $\bullet OH$ yield from O_3 decomposition in real water matrices. Note that the $\bullet OH$ yield is defined as moles of $\bullet OH$ produced per mole of O_3 consumed and reported in the range of $\sim 13\text{--}41\%$ during conventional ozonation of natural water (groundwater and surface water) and municipal wastewater (Lee et al., 2013; Lee et al., 2014; Nothe et al., 2009; von Sonntag and von Gunten, 2012; Yao et al., 2017).

To improve ozone-resistant micropollutant abatements, catalysts (e.g., transition metal ions and metal oxides) can be added during ozonation (i.e., catalytic ozonation) to enhance O_3 transformation to $\bullet OH$ (Kasprzyk-Hordern et al., 2003; Legube and Leitner, 1999; Nawrocki, 2013; Nawrocki and Kasprzyk-Hordern, 2010). When transition metal ions are used (i.e., homogeneous catalytic ozonation), they may react directly with O_3 to produce $\bullet OH$. In addition, they may interact with organics such as humic substances in the water matrix to promote O_3 transformation to $\bullet OH$. When solid catalysts (e.g., metal oxides and metals on supports) are used (i.e., heterogeneous catalytic ozonation), O_3 may be decomposed at the catalyst surface and/or react with organics adsorbed on the catalyst surface to produce $\bullet OH$. Due to the enhanced transformation of O_3 to $\bullet OH$, higher abatement efficiencies can often be obtained for ozone-resistant micropollutants during catalytic ozonation compared to conventional ozonation (Kasprzyk-Hordern et al., 2003; Nawrocki, 2013; Nawrocki and Kasprzyk-Hordern, 2010).

Prediction of the abatement efficiencies of micropollutants is critical for practical applications of catalytic ozonation processes in water and wastewater treatment. Due to the vast number of micropollutants coexisting in the water matrix (many of which have no established analytical methods yet), it is impractical and cost-prohibitive to measure the abatement efficiencies of various micropollutants individually. However, while many studies have demonstrated the superiority of catalytic ozonation for ozone-resistant micropollutant abatement (Nawrocki, 2013; Nawrocki and Kasprzyk-Hordern, 2010), no models have been developed for generalized prediction of micropollutant abatement during catalytic ozonation. This problem can be probably attributed to the complex mechanisms of catalytic ozonation, which have not been fully understood (Nawrocki, 2013; Nawrocki and Kasprzyk-Hordern, 2010). Indeed, numerous catalysts have been tested in catalytic ozonation, and different (or even contradictory) catalytic effects and mechanisms have been reported (Kasprzyk-Hordern et al., 2003; Nawrocki, 2013; Nawrocki and Kasprzyk-Hordern, 2010). Due to the differing catalytic mechanisms of varying catalysts, generalized prediction of micropollutant abatements by catalytic ozonation is challenging.

Notably, recent studies have shown that the abatement of micropollutants by conventional ozonation and ozone-based AOPs such as O_3/H_2O_2 and the electro-peroxone (E-peroxone) process can be satisfactorily predicted using a chemical kinetic model (Eq. (1)) (Lee et al., 2013; Lee et al., 2014; Lee and von Gunten, 2016; Wang et al., 2018).

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

where k_{O_3} and $k_{\bullet OH}$ are the second-order rate constant for the reaction of micropollutant (P) with O_3 and $\bullet OH$, respectively; $\int [O_3]dt$ and $\int [\bullet OH]dt$ are the O_3 and $\bullet OH$ exposures, which are defined as the time-integrated concentration of O_3 and $\bullet OH$ over a given reaction period (Elovitz and von Gunten, 1999).

Over the past decades, the O_3 and $\bullet OH$ rate constants for a great number of micropollutants have been measured (von Sonntag and von Gunten, 2012). In addition, the O_3 and $\bullet OH$ exposures can be readily measured, for example, by following the decay of O_3 and a $\bullet OH$ probe (typically *p*-chlorobenzoic acid (*p*-CBA)) during water treatment processes (Elovitz and von Gunten, 1999). Therefore, this model can provide a relatively easy and convenient way to estimate the abatement levels of many micropollutants by ozone-based processes (Lee et al., 2013; Lee et al., 2014; Lee and von Gunten, 2016).

Considering that catalytic ozonation is in nature also an ozone-based AOP, where O_3 and $\bullet OH$ play a major role for micropollutant abatement (Nawrocki, 2013; Nawrocki and Kasprzyk-Hordern, 2010), it is interesting to evaluate whether similar models can be applied in catalytic ozonation. This may offer a practical way to predict micropollutant abatement by catalytic ozonation with varying catalysts even if the reaction mechanisms (e.g., the catalytic mechanisms of O_3 transformation to $\bullet OH$) are not well understood.

The main objective of this study was to evaluate the applicability of the chemical kinetic model (Eq. (1)) for the prediction of micropollutant abatement by catalytic ozonation. As a first step, homogeneous catalytic ozonation of micropollutants with varying transition metal ions was investigated in this study. Compared with heterogeneous catalytic ozonation, the mechanisms of homogeneous catalytic ozonation are relatively simpler, involving no adsorption effects that can complicate the catalytic mechanisms significantly. Therefore, the chemical kinetic model can be directly applied in homogeneous catalytic ozonation without the need of correction for the adsorption effect. In this study, several model micropollutants with varying reactivities with O_3 (k_{O_3} ranging from <0.15 to $1.0 \times 10^6\text{ M}^{-1}\text{ s}^{-1}$) were spiked in a deionized water and a surface water. The waters were then treated by conventional ozonation and homogeneous catalytic ozonation with varying transition metal ions (Mn^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Ti^{2+} , Zn^{2+} , or Cu^{2+}). The effects of catalysts on O_3 transformation to $\bullet OH$ and micropollutant abatement were evaluated systematically. Based on the O_3 and $\bullet OH$ exposures observed during the treatment, the abatement efficiencies of micropollutants were predicted using the chemical kinetic model.

2. Materials and methods

2.1. Chemicals and water sample

Diclofenac, gemfibrozil, bezafibrate, 2,4-dichlorophenoxyacetic acid (2,4-D), clofibrac acid, ibuprofen, and *p*-CBA with purity $>98\%$ were purchased from Sigma-Aldrich and used as micropollutant model compounds. The properties of these compounds are listed in Table 1. According to their second-order rate constants with O_3 ,

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