



Determination of oxidant exposure during ozonation of secondary effluent to predict contaminant removal



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ARTICLE INFO

Article history:

Received 20 January 2016

Received in revised form

6 May 2016

Accepted 14 May 2016

Available online 17 May 2016

Keywords:

Trace organic compound

Probe compound

Quench flow

Depletion

Oxidant exposure

ABSTRACT

The use of kinetic models to predict oxidation performance in wastewater is limited due to fast ozone depletion during the first milliseconds of the reaction. This paper introduces the Quench Flow Module (QFM), a bench-scale experimental technique developed to measure the first 5–500 milliseconds of ozone depletion for accurate determination of ozone exposure in wastewater-ozonation processes. Calculated ozone exposure in QFM experiments was up to 24% lower than in standard batch experiments, strongly depending on the initial sampling point for measurement in batch experiments. However, oxidation rates of slowly- and moderately-reacting trace organic compounds (TrOCs) were accurately predicted from batch experiments based on integration of ozone depletion and removal of an ozone-resistant probe compound to calculate oxidant exposures. An alternative concept, where ozone and hydroxyl radical exposures are back-calculated from the removal of two probe compounds, was tested as well. Although the QFM was suggested to be an efficient mixing reactor, ozone exposure ranged over three orders of magnitude when different probe compounds reacting moderately with ozone were used for the calculation. These effects were beyond uncertainty ranges for apparent second order rate constants and consistently observed with different ozone-injection techniques, i.e. QFM, batch experiments, bubble columns and venturi injection. This indicates that previously suggested mixing effects are not responsible for the difference and other still unknown factors might be relevant. Results furthermore suggest that ozone exposure calculations from the relative residual concentration of a probe compound are not a promising option for evaluation of ozonation of secondary effluents.

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1. Introduction

Ozonation reduces the concentrations of many trace organic compounds (TrOCs) from secondary wastewater effluent (Hollender et al., 2009; Huber et al., 2005; Ternes et al., 2003; Wert et al., 2009b; Zucker et al., 2015b) via direct and indirect oxidation reactions. Optimization of ozone dosing in tertiary treatment is commonly based on selected fast-, moderately- and slowly-reacting TrOC elimination requirements (e.g. Lee et al., 2013). Hence, modeling and predicting the elimination of TrOCs is an essential tool for controlling ozonation systems. The relative

residual compound concentration (c) following ozonation can be determined by second-order kinetics with ozone and hydroxyl ($\cdot\text{OH}$) radicals, using second-order rate constants $k(\text{O}_3)$ and $k(\cdot\text{OH})$, ozone exposure ($\int(\text{O}_3)dt$) and $\cdot\text{OH}$ -radical exposure ($\int(\cdot\text{OH})dt$), as expressed in Eq. (1) (von Gunten and von Sonntag, 2012). Oxidation of TrOCs can be adequately predicted when the rate constants are known – either derived from the literature (e.g. Huber et al., 2003) or determined based on direct measurements or competition kinetics method (von Gunten and von Sonntag, 2012). Oxidant exposures are determined specifically for every application since they are directly affected by water quality parameters. However, oxidant exposure measurement is a significant obstacle due to low $\cdot\text{OH}$ -radical concentration and fast ozone depletion during ozonation.

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$$\frac{c}{c_0} = \exp\left(-k_{O_3} \int [O_3] dt - k_{\cdot OH} \int [\cdot OH] dt\right) \quad (1)$$

Oxidation performance in drinking and surface waters can be predicted from batch experiments by calculating ozone and $\cdot OH$ -radical exposures (Elovitz and von Gunten, 1999). $\cdot OH$ -radical exposure can be back-calculated from the removal of an ozone-resistant probe compound (e.g. pCBA) (Elovitz and von Gunten, 1999; Pi et al., 2005; Wert et al., 2009a). The direct reaction of the resistant probe compound with ozone is negligible, hence its contribution to compound removal can be eliminated from the equation, according to Eq. (2). This method can be referred as ' $\cdot OH$ -radical probe method'. Ozone exposure can be determined by integrating measured ozone concentrations in batch experiments over time (referred here as 'direct indigo method'). Hence, the evaluation of oxidation performance can be determined from the ozone depletion in conjunction with removal of the probe compound.

$$\frac{c}{c_0} = \exp\left(-k_{\cdot OH} \int [\cdot OH] dt\right) \quad (2)$$

However, an accurate ozone exposure measurement in wastewater effluents is problematic. The rapid reaction of effluent organic matter and even effluent particles (Zucker et al., 2015a) with ozone results in very rapid ozone depletion in the first milliseconds of the reaction and hence inaccurate determination of the ozone exposure (Buffle et al., 2006b; Schindler Wildhaber et al., 2015). Thus, sensitive and advanced methods, such as quench- or stopped-flow systems (Buffle et al., 2006b; Nöthe et al., 2009), are required to determine the accurate ozone exposure.

An alternative concept suggests that ozone exposure can be back-calculated from the removal of a probe compound that reacts with both ozone and $\cdot OH$ -radicals (Huber et al., 2005; Hübner et al., 2013). This concept involves indirect determination of oxidant exposures; where $\cdot OH$ -radical exposure is back-calculated from the removal of ozone-resistant probe compound (i.e. ' $\cdot OH$ -radical probe method'), and ozone exposure is back-calculated from removal of moderately- (or fast-) reacting probe compound (referred here as 'ozone probe method') following ozonation of wastewater effluents. The methods suggested to determine oxidant exposure are summarized in Table 1. However, predicting the elimination of fast-reacting TrOCs ($k(O_3) > 10^4 \text{ M}^{-1} \text{ s}^{-1}$) was not feasible. The reasons suggested for the poor prediction were either selective TrOC sorption to wastewater particles leading to some protection against ozone attack (Huber et al., 2005), mixing effect of aqueous ozone to the entire water (in batch systems), or gas-liquid mass-transfer limitation (in diffuser-based systems) which may lead to a similar oxidation degree for all fast-reacting TrOCs despite the different rate constants (Hübner et al., 2013). However, diffusion (i.e. gas-liquid mass-transfer) limitation was ruled out based on film theory by Huber et al. (2005). Consequently, it is assumed that the consumption of low ozone dosages is faster than the time required for volumetric sample homogenization in the experimental batch, semi-batch or diffuser-based pilot systems. To overcome this

limitation, other mixing alternatives in ozone systems must be taken into consideration, such as venturi ozone-injection or quench-flow systems.

In the present study, a quench-flow system was used to determine ozone exposure in wastewater effluents using the two proposed methods: (1) the quench-flow system is used as a tool to measure ozone depletion in the first milliseconds (5–500 ms) of the reaction in the 'direct indigo method' and (2) the system is used as an efficient mixing tool to overcome limitation through mixing in the 'ozone probe method'. Then, the feasibility of predicting oxidation of TrOCs by these methods was evaluated. Finally, different ozone-injection techniques were compared (stock solution mixing, diffusion, venturi injection) with respect to mixing and mass-transfer efficiency.

2. Materials and methods

2.1. Standards and reagents

Eleven TrOCs were selected for this study, based on the availability of established rate constants with ozone and $\cdot OH$ -radicals and their occurrence and concentration in secondary effluents. The TrOCs were separated according to their apparent second order rate constants at pH 8 for the reaction with ozone into fast-reacting ($k(O_3) > 10^4 \text{ M}^{-1} \text{ s}^{-1}$), moderately-reacting ($10 \text{ M}^{-1} \text{ s}^{-1} < k(O_3) < 10^4 \text{ M}^{-1} \text{ s}^{-1}$) and slowly-reacting ($k(O_3) < 10 \text{ M}^{-1} \text{ s}^{-1}$) compounds (Table 2). Stock solutions ($2\text{--}10 \text{ mg L}^{-1}$) were prepared separately for each TrOC in ultrapure water and kept in the dark at $4 \text{ }^\circ\text{C}$.

2.2. Experimental procedures

Six sets of experiments were conducted using a Quench Flow Module (QFM-400, Bio-Logic, Tennessee, USA) and an ozone batch reactor to evaluate the determination of oxidant exposure by the two concepts. Quench-flow experiments using similar system were described earlier by Lee et al. (2013). Experiments were performed in triplicates and conducted at room temperature ($\sim 22 \text{ }^\circ\text{C}$) with grab samples of secondary effluent from a wastewater treatment plant in Berlin (Ruhleben). General effluent parameters were: pH = 7.94 ± 0.05 , dissolved organic carbon (DOC) = $11.4 \pm 0.6 \text{ mg L}^{-1}$, nitrite (NO_2^-) = $72.8 \pm 29.8 \text{ } \mu\text{g L}^{-1}$, UV absorbance at 254 nm (UV_{254}) = $30.3 \pm 3.3 \text{ m}^{-1}$, TIC = $63.9 \pm 5.4 \text{ mg L}^{-1}$. A concentration of $10 \text{ } \mu\text{g L}^{-1}$ for all TrOCs (with the exception of para-chlorobenzoic acid [pCBA] at $100 \text{ } \mu\text{g L}^{-1}$) was spiked directly before starting the experiments to ensure reliable analysis of removal rates.

An ozone stock solution ($\sim 70 \text{ mg L}^{-1}$) was prepared by continuously bubbling ozone gas, produced from a pure oxygen-fed generator (Modular 8 HC generator, Wedeco (Xylem), Herford, Germany), in a stirred glass reactor filled with chilled ($4 \text{ }^\circ\text{C}$) ultrapure water to improve ozone solubility.

In the QFM, three syringes driven by independent motors introduce ozone stock solution, effluent and ultrapure water at different ratios into a mixing chamber. The reacting mixture then

Table 1
Summary of methods suggested for oxidant-exposure determination.

Exposure	$\cdot OH$ -radical	Ozone	
Method name	$\cdot OH$ -radicals probe method	1. Direct indigo method	2. Ozone probe method
Technique	Back-calculation from the removal of a probe compound	Integration of ozone depletion over time	Back-calculation from the removal of a probe compound
Probe compound used	Ozone-resistant TrOCs (pCBA, IOP or PRI)	Indigo quenching	Moderately-reacting TrOCs (ACS, BTA, MTP, BZF or VLX)

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