



## Research article

# Effective degradation of methylisothiazolone biocide using ozone: Kinetics, mechanisms, and decreases in toxicity



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## ABSTRACT

Methylisothiazolone (MIT) is a common biocide that is widely used in water-desalination reverse-osmosis processes. The transformation of MIT during water treatment processes is poorly understood. The kinetics and mechanisms involved in the degradation of MIT during ozonation were investigated in this study. Ozonation was found to be a useful way of degrading MIT in water, and the degradation rate constant was  $0.11 (\pm 0.1) \times 10^3 \text{ L}/(\text{mol} \cdot \text{s})$ . The degradation rate constant did not change when the pH was increased from 3 to 9. The pre-exponential factor  $A$  and the activation energy  $E_a$  for the ozonation process were  $7.564 \times 10^{13} \text{ L}/(\text{mol} \cdot \text{s})$  and  $66.74 \text{ kJ}/\text{mol}$ , respectively. The decrease in the MIT concentration and the amount of ozone consumed were measured, and the stoichiometric factor  $\alpha$  for the ozone consumption to MIT removal ratio was found to be 1.8. Several ozonation products were detected using time-of-flight mass spectrometry. Almost 32% of the organic sulfur in the MIT was oxidized to release sulfate ions, which caused a decrease in pH. Sulfur atoms were oxidized to sulfone species and then hydrolyzed to give sulfate during ozonation. Addition reactions involving carbon-carbon double bonds and the oxidation of  $\alpha$ -carbon atoms also occurred. MIT was found to be lethal to *Daphnia magna* Straus (*D. magna*) with a median lethal concentration of  $18.2 \mu\text{mol}/\text{L}$ . Even though the primary ozonation products of MIT still showed some toxicity to *D. magna*, ozone could minimize the toxic effect after a long reaction time.

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## 1. Introduction

Methylisothiazolone (MIT) was one of the most widely used nonoxidizing biocides. Both in wastewater reclamation and treatment plants (i.e. reverse osmosis) and in cosmetic personal care products, MIT acted as an important ingredient because of its biocidal properties. To suppress the microbial contamination of

reverse osmosis (RO) membranes, MIT is used alone or with other compounds (Isaksson et al., 2014) such as 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT) in continuous (40–90  $\mu\text{mol}/\text{L}$ ), intermittent (260–700  $\mu\text{mol}/\text{L}$ ), or pulse (approximately 2.6  $\text{mmol}/\text{L}$ ) addition mode. According to U.S. Department of Health & Human Services database (Services, 2012), some laundry detergent contained MIT as high as 1 percent.

MIT can not only cause skin allergies (Lundov et al., 2011; Uter et al., 2013), but also lead to immune responses in the respiratory tract of rats (Devos et al., 2015). Meanwhile, MIT was a kind of potential neurotoxicant (He et al., 2006). MIT concentrations in cosmetics are regulated in many countries. MIT concentrations in cosmetics in China cannot exceed 0.01% Ministry of Health (2007). MIT in cosmetics, pharmaceuticals and personal care products (PPCPs) can enter the wastewater system after use. MIT also could leak into environment from the usage of roof paint (Jungnickel

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et al., 2008). This biocide remained in the RO concentrate (ROC), leading to high toxicity (Perez-Gonzalez et al., 2012; Sun et al., 2014; Tang et al., 2013). Some research has been performed to evaluate the potential risks to marine environment, when the isothiazolinone biocides was widely used in aquaculture (Guardiola et al., 2012). Therefore, the study on the degradation of MIT is very meaningful.

The structure of MIT is shown in Fig. 1. The MIT molecule contains a sulfur atom that can have a biocidal effect because it can undergo nucleophilic reactions with sulfur-containing enzymes (Collier et al., 1990; Morley et al., 1998; Morris et al., 1984). In previous studies of the removal of biocides from water it has been found that it takes a long time for MIT and its derivatives to be degraded. Krzeminski and his colleagues measured the degradation products of  $^{14}\text{C}$ -labeled MIT in rat feces, aquatic plants, and rivers, and showed that only up to 75% of the MIT originally present can be degraded by a natural biological system in 4 d (Krzeminski et al., 1975). It has been found that divalent ferric ions can cause CMIT to be degraded in 2 days (Tanji et al., 2007). MIT can be degraded using nanocrystalline  $\text{TiO}_2$  and  $\text{ZnO}$  photocatalysts with UV irradiation applied, but the reaction time would be 800 min (Kandavelu et al., 2004). It also took 300 min for CMIT to be removed using electrochemical methods (Han et al., 2011).

Ozonation processes are widely used in drinking water and wastewater treatment plants (Margot et al., 2013; Martins et al., 2015; Zou, 2015). During the ozonation process, ozone and hydroxyl radicals, which have high oxidation potentials, are able to decompose organic pollutants. A pilot study on the ozonation of wastewater containing biocides has previously been performed (Poberznik et al., 2011). Catechol (Aghapour et al., 2015), 2,4,4'-trichloro-2'-hydroxydiphenyl ether (Arslan-Alaton, 2007), ibuprofen and clofibrac acid (Quero-Pastor et al., 2014), N, N-diethyl-mtoluamide (DEET) (Liu et al., 2016) and four pharmaceutical compounds (atenolol, hydrochlorothiazide, ofloxacin and trimethoprim) (Rodriguez et al., 2013) could be degraded by ozonation or catalytic ozonation. Benzisothiazolone (BIT) recently found could be degraded by ozone (Li et al., 2016). However, the degradation kinetics and intermediate products of the ozonation of MIT and the effects of using different ozone dosages have not been studied.

The removal of MIT from water by ozonation was investigated in the study. The products of the ozonation of MIT were identified, which indicate possible pathways through which MIT is removed during the ozonation process. Moreover, the effects of ozonation on the toxicity of MIT to *Daphnia magna* were assessed. The kinetics of the ozonation process under different conditions (different pH values and different temperatures) were also studied.

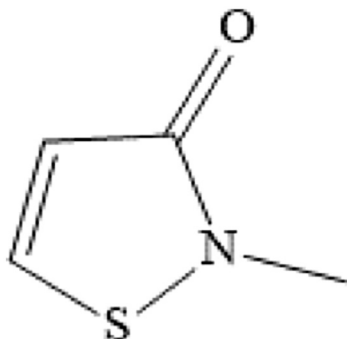


Fig. 1. Molecular formula of methylisothiazolinone.

## 2. Materials and methods

### 2.1. Materials and chemicals

The MIT used in the experiments was >95% pure and was purchased from Sigma-Aldrich Corporation (St Louis, MO, USA). All solutions were diluted with ultra-pure water (with a conductance of 18.2  $\text{M}\Omega\text{ cm}$ ) produced using a Milli-Q purification system (Millipore Corporation, MA, USA). The TBA, Sodium thiosulfate,  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  reagents were purchased from J&K Scientific Ltd. (Beijing, China). The purity of all chemicals was above 99%.

### 2.2. Batch MIT ozonation experiments

Batch ozonation experiments were performed by mixing aqueous ozone and MIT solutions in reaction bottles (with a volume of 100 mL). An aqueous ozone solution was produced by aerating ultrapure water in an ice bath with ozone generated using an ozone generator (NL-20; Newland Digital Equipment Corporation, Fujian, China) for more than 1 h. The dissolved ozone concentration in the solution was determined using a portable aqueous ozone meter (PTH 043; Palintest<sup>®</sup>, Gateshead, UK) and was found to be between 1 mmol/L and 1.25 mmol/L. The illustration of obtaining ozone solution was shown in Fig. S1 (a) in Supporting Information.

An MIT solution with an initial concentration of 10  $\mu\text{mol/L}$  was added to each reaction bottle, and the bottles were kept in a thermostatic water bath. The solution in each bottle was adjusted to a selected pH value, of between pH 3 and pH 9, by adding a  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$  buffer. *Tert*-butanol (TBA) was added (with a concentration of 10 mmol/L) before ozonation to act as a  $\cdot\text{OH}$  radical scavenger (Deborde et al., 2005), to allow the rate constant  $k_{\text{O}_3}$  for the ozonation of MIT to be determined without the presence of  $\cdot\text{OH}$  radicals affecting the results. The initial ozone concentration (0.5 mmol/L) was 50 times higher than the MIT concentration, and the reaction time was 50 s. The amount of ozone lost during the experiment could therefore be neglected, and the soluble ozone concentration in each MIT solution could be assumed to be constant. After the reaction time had elapsed, sodium thiosulfate was added to give a concentration of 10 mmol/L (i.e., 20 times the ozone concentration), to quench the residual ozone.

Experiments were performed using different initial MIT concentrations (43  $\mu\text{mol/L}$  to 350  $\mu\text{mol/L}$ ) and ozone concentrations (0 mmol/L to 0.625 mmol/L) to allow the stoichiometric factor  $\alpha$  for the ozonation of MIT to be determined.

### 2.3. Semi-batch MIT ozonation experiments

An MIT solution with an initial concentration of 350  $\mu\text{mol/L}$  was added to a semi-batch reactor (with a volume of 3 L). The solution was mixed with a magnetic stirrer. The solution was 0.6 m deep. Gaseous ozone was added to the semi-batch reactor, and the ozone concentrations in the gases passing through the inlet and outlet were monitored using an IDEAL-2000 ozone analyzer (Zibo, China). The amounts of ozone consumed during the experiments are shown in Fig. S2 in Supporting Information. The MIT solution used in each ozonation experiment was adjusted to a specified pH, a pH range of 3–9, by adding a  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$  buffer. The reaction time was 30 min. All samples stored in 4  $^\circ\text{C}$  refrigerator and analyzed in 48 h. The illustration of semi-batch experiment was shown in Fig. S1 (b) in Supporting Information.

### 2.4. Batch ozonation experiments vs semi-batch ozonation experiments

Semi-batch ozonation experiments are more similar than batch

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