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Study on the removal of benzisothiazolinone biocide and its toxicity: The effectiveness of ozonation

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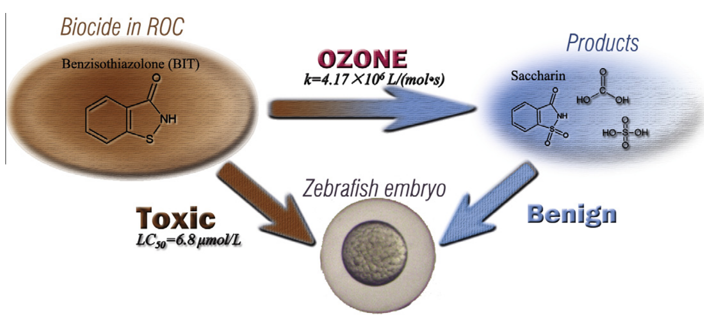
HIGHLIGHTS

- Ozone could remove benzisothiazolinone (BIT) rapidly and effectively.
- Toxicity of BIT solution was eliminated by ozone as soon as no BIT remained.
- An ozonation pathway was proposed using MS detection and energy calculation.
- Municipal ROC matrix showed little negative effect on BIT ozonation process.

GRAPHICAL ABSTRACT



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ABSTRACT

Benzisothiazolinone (BIT) is widely used as a biocide in different industries, and, in particular, in wastewater reclamation plants in which reverse osmosis (RO) is used. BIT can cause dermatitis in humans and is toxic to fish. It is therefore significant to control BIT concentrations in water that is being treated, however, appropriate methods for BIT control and removal have not yet been developed. This study investigated the changes in the concentrations and toxicities of aqueous solutions of BIT, caused by ozonizing the solutions. It was found that BIT was rapidly degraded by ozonation effect, and the rate constant $k_{O_3,BIT}$ was 4.17×10^6 L/(mol s). Samples were analyzed using time-of-flight mass spectrometry, and a possible ozonation pathway was proposed from the results. Besides, free energy calculations were performed for characterization of possible products of BIT ozonation. One product, saccharin, was identified, which was produced through the sequential oxidation of sulfur atoms in BIT. The specific ultraviolet absorbances of the BIT solutions decreased and sulfate ions were produced during ozonation. Furthermore, BIT was found to be toxic to zebrafish embryos, with a median lethal concentration of

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6.8 μmol/L. Nevertheless, ozonation markedly decreased the toxic effects of BIT to zebrafish embryos, making the toxic effects undetectable. This indicated that the oxidized products were ecologically benign. Since the kinetic rate of BIT ozonation is very fast, compared with (bi)carbonate or humic acid, there is no observable negative interference on BIT ozonation process. Even in the RO concentrate matrix, namely existing complex organic/inorganic components, ozone is still able to quickly degrade BIT as in pure water system. Consequently, ozonation can be considered as an effective method for removing BIT from RO concentrates.

1. Introduction

The biocide benzisothiazolinone (BIT) (structural formula was shown in Fig. 1) is commonly used both in domestic and industrial products [1]. For instance, building exterior wall paints [2], paper based materials [3] and laundry detergents [4] can contain BIT to inhibit the proliferation of bacteria. The presence of BIT in such products leads to BIT being unintentionally emitted into the aquatic environment. As a result, BIT has been detected in surface water at concentrations of several nanograms per liter, and a single house could emit 1 μg of BIT during a storm event [2].

In water and wastewater treatment field, biocide (such as BIT) was increasingly applied to reverse osmosis (RO) systems which are effective advanced treatment approaches in water reclamation, for prevention of biofilm growth on the membranes. Therefore, RO concentrates contain highly toxic pollutants (from the influent wastewater) and dosing agents (including biocides and antiscalants). Tang et al. [5] found that the non-oxidizing biocide isothiazolone was at concentrations up to 160 mg/L in RO concentrates (ROCs) from wastewater reclamation plants.

Bacteria, algae, and even fish can be effectively inhibited by BIT because BIT contains a reductive sulfur atom that can form a disulfide bond (–S–S–) with cysteine, deactivating proteins containing cysteine [6–8]. Both growth and activity of bacteria could be inhibited by BIT depending on concentration. E. coli growth rate could be inhibited by BIT at a concentration as low as 15 μg/mL [9]. The median lethal BIT dose for rainbow trout is 1.6 mg/kg [10]. BIT can induce severe chronic dermatitis in humans [11]. BIT may also inhibit the activity of human orphan phosphatase (which may be involved in skeletal mineralization), with a half-maximum inhibition concentration of 0.14 mg/L [12]. Therefore, the potential risk from BIT should be addressed.

It has been found that BIT is hydrolytically stable and has a half-life of more than 30 days in the environment [13]. BIT may be transported through soil and reach surface water [13], and it can still retain its biocidal qualities for 3 months when exposed to sunlight [3]. Due to the toxicity of BIT and its presence in the aquatic environment and resistance to degradation, it is vital and essential to control BIT concentrations in wastewater. Currently, little research has been performed on the removal of BIT during wastewater reclamation processes. Yang et al. [14,15] found that modified resins didn't perform good enough to adsorb BIT from aqueous solutions.

Ozonation processes are widely used in wastewater reclamation and treatment plants as advanced treatment technologies [16]. Ozone could decompose to produce hydroxyl radical in water, with the participation of hydroxyl ion [17]. The oxidative ability of hydroxyl radical is superior to that of ozone. In general, the oxidation by ozone is selective (direct oxidation), and the oxidation by hydroxyl radical is non-selective (indirect oxidation). And the oxidation rate of hydroxyl radical is much faster than that of ozone [18]. Ozone is effective at removing endocrine disruptors, pharmaceuticals, and pesticides from water [19–21]. Since RO processes are increasingly being used in wastewater reclamation plants, it is important to find ways of removing pollutants from ROC. Notably, ozone based advanced oxidation processes have been found to be effective to remove pollutants from ROC [22]. However, its effectiveness on the removal of BIT from ROC is still not yet to be known.

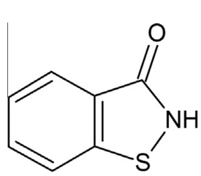

Fig. 1. Structural formula of BIT.

The objectives of this study were to investigate the kinetics of BIT removal by ozone and to characterize the products of BIT ozonation so as to further propose the possible reaction pathways. Changes in toxicity during the ozonation process were also determined, and the effects of the presence of (bi)carbonate ions and humic acid on the removal of BIT were analyzed. Furthermore, ozone was used to remove BIT from a municipal ROC sample.

2. Materials and methods

2.1. Materials and chemicals

The BIT used in this study was >98% pure and was purchased from J&K Scientific (Beijing, China). A Milli-Q purification system (Millipore, MA, USA) was used to produce ultra-pure water (conductance 18.2 MΩ cm), which was used to prepare the samples. All other chemical reagents were of analytical or high-performance liquid chromatography (HPLC) grade.

2.2. Determining the rate of the reaction between BIT and ozone

The rate of the reaction between BIT and ozone in an aqueous solution was determined using the competition kinetics method, which has been described previously [23,24]. An aqueous solution containing ozone at a concentration of 1–1.5 mmol/L was prepared by ozonizing ultrapure water in an ice bath for more than 1 h. The ozone solution was then added to a solution containing 15 μmol/L BIT and 15 μmol/L phenol. The BIT and phenol solution contained phosphate buffers and 10 mmol/L *tert*-butyl alcohol (to act as a hydroxyl radical scavenger), and was at pH 7. The BIT, phenol, and ozone mixture was kept at 22 ± 2 °C in a thermostatic water bath for a specified time, then the residual BIT and phenol concentrations were determined and the rate constant for the reaction between BIT and ozone was calculated using Eq. (1).

$$\ln\left(\frac{[\text{Phenol}]}{[\text{Phenol}]_0}\right) = \ln\left(\frac{[\text{BIT}]}{[\text{BIT}]_0}\right)\frac{k_{O_3,\text{Phenol}}}{k_{O_3,\text{BIT}}} \quad (1)$$

In Eq. (1), [Phenol] is the endpoint phenol concentration, $[\text{Phenol}]_0$ is the initial phenol concentration, [BIT] is the endpoint BIT concentration, $[\text{BIT}]_0$ is the initial BIT concentration, $k_{O_3,\text{Phenol}}$ is the mean rate constant for the reaction between phenol and