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Study of optimal parameters of the H_2O_2/O_3 method for the decomposition of acetic acid

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HIGHLIGHTS

- The decomposition path of acetic acid was experimentally investigated.
- A simplified reaction model was built concerning the decomposition path.
- The optimum ratio of the H_2O_2 supply rate to the O_3 absorption rate was determined.
- The main reaction path for each condition was revealed.

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ABSTRACT

Advanced oxidation processes (AOPs) constitute one of the most effective methods to decompose persistent organic pollutants in water using OH radicals. In this study, the parameters of the H_2O_2/O_3 method in the decomposition of acetic acid were investigated through a combination of experiments and numerical simulations. A simplified reaction model was built based on the analysis of the decomposition path. The simulation results showed that effective treatment of acetic acid can be achieved when the H_2O_2 supply rate is half of the O_3 absorption rate as one H_2O_2 and two O_3 molecules are necessary to produce two OH radicals.

1. Introduction

There is much demand for the treatment of wastewater generated during oil and gas extraction, called produced water [1,2]. In offshore oil plants, a flocculation magnetic separation system is used to remove oil and solid matter from produced water; however, the treated water still contains soluble organic compounds. Three types of organic acids are typically found as soluble organics in produced water: acetic, formic, and propionic acids, and acetic acid makes up the bulk of the acid mass [3]. Table 1 shows the values of total organic carbon (TOC) concentration, pH, and conductivity of produced waters released from two different offshore oil plants, and measured after a flocculation magnetic separation treatment [4]. The produced waters were close to neutral, with TOC values ranging from several ten to several hundred mg_{TOC}/L. It has been confirmed that the major organic compound in the abovementioned two types of produced water was acetic acid, as same as reported in [3]. In the USA, a monthly average limit of 29 mg/L is set for oil and grease in the produced water of offshore oil plants [5]; however, there is no regulation on the TOC concentration so far. Thus, a large amount of produced water with high TOC concentration is discharged to the environment as long as it meets offshore regulations [2]; however, it is expected that the regulation will become more stringent for the produced water of onshore oil plants as well. Therefore, it is necessary to establish effective water treatment technologies for TOC reduction.

Acetic acid is known as one of the persistent organic compounds and cannot be decomposed by O_3. The advanced oxidation process (AOP) is an effective method for decomposing persistent organic compounds in water using OH radicals (·OH) [6–8]. There are several types of AOPs; e.g., the H_2O_2/O_3 method [6,8–15], H_2O_2/ultraviolet light (UV) method [6–9], UV/O_3 method [6,8,9], and O_3/catalyst method [16]. The O_3/catalyst method has been investigated as a candidate for the treatment of produced water [16]. The H_2O_2/O_3 method is another candidate because it is possi-

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Table 1
Values of different parameters of produced waters taken from two different locations [4].

	Produced water A	Produced water B
TOC concentration [mg/L]	424	56.8
pH	7.6	8.2
Conductivity [mS/cm]	39	1.0

ble that the TOC reduction rate increases with increasing supply rate of oxidants [13,15]. The generation of plasma in contact with water is another example of an AOP, and it has been investigated by many researchers for several decades [17,18]. Although plasma processes can decompose persistent organic compounds, H_2O_2 produced by the self-quenching reaction of ·OH has been found to scavenge ·OH, thereby limiting the processing speed and energy efficiency [19]. Thus, we proposed a combined O_3/plasma system that reacts O_3 and H_2O_2 to reproduce ·OH upon adding O_3 to the plasma-treated solution [4,20]. This system is suitable to treat wastewater from isolated locations such as offshore oil plants since transportation and storage of H_2O_2 are not needed. The addition of O_3 to treat a highly concentrated acetic acid solution was shown to drastically improve the processing speed and efficiency. Flocculation magnetic separation systems have a treatment capacity of about 100 m^3/h, which means that the treatment capacity of an AOP should be 1 kg_{TOC}/h if more than 90% TOC reduction is needed for the produced water containing 100 mg_{TOC}/L soluble organic compounds. Our current target with lab-scale equipment is 1 g_{TOC}/h for the decomposition of acetic acid.

In AOPs employing H_2O_2 and O_3, including the O_3/plasma system, the ratio between the amount of supplied H_2O_2 and the amount of O_3 absorbed in the solution is an important factor to be considered [8,10–13] since H_2O_2 and O_3 are scavengers of ·OH and excess H_2O_2 or O_3 causes ·OH consumption. Glaze et al. [8] decomposed tetrachloroethylene by the H_2O_2/O_3 method and the highest decomposition rate was obtained at a H_2O_2/O_3 molar ratio of about 1 with greater than 90% O_3 utilization. Tuhkanen et al. [10] showed that the optimum removal of the precursors of mutagenic compounds was achieved with a H_2O_2/O_3 molar ratio of 1. Adams et al. [11] decomposed 1,4-dioxane under three different H_2O_2/O_3 molar ratios of 0, 0.5, and 1.0. Their results showed that the effective decomposition of 1,4-dioxane was achieved at both 0.5 and 1.0 ratios, and they concluded that less O_3 and more H_2O_2 required at the higher ratio. Zwiener and Frimmel [13] conducted a treatment of pharmaceuticals in distilled water and neutral surface water at a H_2O_2/O_3 molar ratio of 1. They showed that dissolved organic carbon in the surface water significantly constrained the degradation of pharmaceuticals. The degradation rate could be improved by increasing the amounts of O_3 and H_2O_2 at the same ratio. In [14,21], the reaction in the H_2O_2/O_3 method was summarized as follows:

$$2O_3 + H_2O_2 \rightarrow 2{\cdot}OH + 3O_2 \quad (1)$$

However, the details of the reaction path using the H_2O_2/O_3 method with a wide range of H_2O_2/O_3 ratio are still not fully understood and there is no analytical confirmation for the optimum H_2O_2/O_3 ratio.

In this study, the appropriate H_2O_2/O_3 ratio was investigated through experiments and numerical simulations for treating model water containing acetic acid at an initial concentration of 100 mg_{TOC}/L. First, the decomposition of acetic acid was conducted by AOP by injecting H_2O_2 solution and bubbling O_3 gas. Then, a numerical simulation was performed to investigate the optimum ratio of the H_2O_2 supply rate to the O_3 absorption rate by analyzing the main reaction path.

2. Experimental apparatus and methods

2.1. Experimental plan and modeling

Acetic acid solution (1 L) at an initial concentration of about 100 mg_{TOC}/L was treated as model water in a lab-scale experimental setup for the H_2O_2/O_3 method. The experiment was carried out by bubbling O_3 generated by an ozonizer and injecting H_2O_2 solution into the model water. During the treatment, the by-products in liquid and gas phases were analyzed to investigate the decomposition path of acetic acid. Then, the supply rates of H_2O_2 and O_3 were varied to investigate the optimum condition for TOC reduction. The O_3 concentration was varied between 50 and 100 g/m^3, which is within the operation range of the ozonizer. Meanwhile, the H_2O_2 concentration was varied from 19.7 to 197.2 g/L to make the supply rate of H_2O_2 almost same as that of O_3. The treatment time was set to 90 min.

A model of the decomposition path of acetic acid was built based on the experimental results. In Chapter 4, the rate equations for liquid-phase species were solved under the variation of the supplied H_2O_2/O_3 ratio. By analyzing the main reaction path using the simulation model, the appropriate ratio of H_2O_2/O_3 and the reason were revealed.

2.2. Description of lab-scale experimental setup

Fig. 1 shows a schematic diagram of the experimental setup. An acrylic cylinder with a diameter of 80 mm and a height of 400 mm was used with 1 L model water. O_3 was generated by an ozonizer (Ecodesign, ED-OG-R5) from pure oxygen and supplied to the model water as fine bubbles through an aeration diffusor at a flow rate of 1 L/min. The ozone concentrations at the inlet and outlet were measured with an ozone monitor (EBARA JITUGYO, EG-600). H_2O_2 was supplied to the model water by injecting the water with highly concentrated H_2O_2 at a flow rate of 169 μL/min using a syringe pump (AS ONE, SPE-1).

2.3. Chemicals and methods

The model water was prepared by adding 1 mol/L acetic acid (Showa Kagaku Kogyo Co., Ltd., Japan) to ultrapure water, and then neutralized by using 1 mol/L NaOH (Wako Pure Chemical Industries, Ltd., Japan) or a phosphate buffer (a mixed solution of NaH_2PO_4 and Na_2HPO_4; Wako Pure Chemical Industries, Ltd., Japan) since the pH values of the produced waters were close to neutral, as shown in Table 1. The H_2O_2 solution injected to the

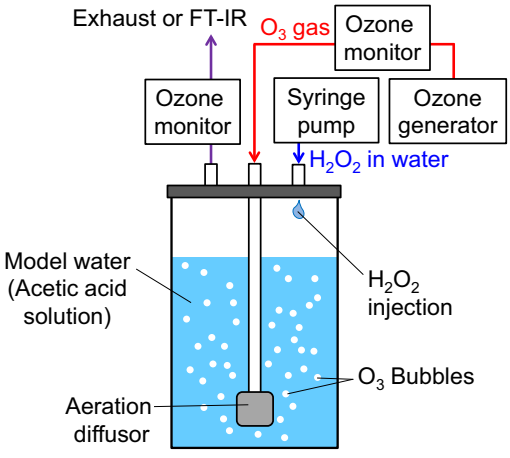

Fig. 1. A schematic diagram of an experimental setup.