

Kinetics of 1,4-Dioxane Oxidation during O₃-H₂O₂ Treatment

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Abstract

The removal of 1,4-dioxane and the biodegradability enhancement of dioxane contaminated water was investigated using O₃-H₂O₂ based advanced oxidation process. Experiments were conducted using a bubble column reactor under different dioxane and peroxide concentrations as well as pH. The O₃-H₂O₂ process effectively converted dioxane to more biodegradable intermediates and increased the biodegradability and average oxidation state of dioxane in the solution.

Introduction

1,4-Dioxane (dioxane), a cyclic ether, is a problematic water pollutant with significant impacts on human health and the environment. Dioxane is used widely as a degreasing agent, as a component of paint and varnish removers, and as a wetting and dispersion agent in the textile industry¹⁾.

Conventional water treatment techniques are limited in their effectiveness for the treatment of dioxane contaminated water. Biological processes often cannot oxidize this compound effectively due to its high resistance to biotransformation²⁾.

Advanced oxidation technologies (AOTs) offer effective alternative to the removal of dioxane from contaminated water. In particular, ozone based advanced oxidation has resulted in promising outcomes on the removal of 1,4-dioxane in aqueous solutions.

In this study, with the aim of using O₃-H₂O₂ based advanced oxidation as pretreatment to conventional biological water treatment, the oxidation kinetics of 1,4-dioxane removal was investigated.

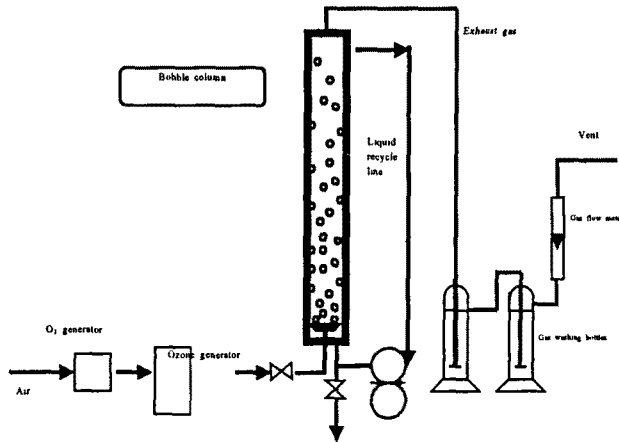


Figure 1. Experimental set-up for the O_3 - H_2O_2 oxidation of 1,4-dioxane.

Materials and Method

The experimental set-up included a bubble column reactor made of Plexiglas (160 cm H \times 10 cm D), a circulating pump, and oxygen and ozone generator (Figure 1). A peristaltic pump (Masterflex, Cole Parmer) provided circulation and complete mixing of the dioxane solution through the column. Ozone was produced from pure oxygen and using the ozone generator (Model RMU16-16, AZCO Ind., Canada). The oxygen generator (Model AS-12, AIRSEP Corp., USA) operated based on pressure swing adsorption (PSA) and produced the oxygen fed to the ozone generator. 1,4-Dioxane and hydrogen peroxide (30% v/v) were purchased as analytical reagent grade (Fisher certified ACS).

Results and Discussion

All the O_3 - H_2O_2 treatments provided significant removal of dioxane from the contaminated water. The experiments were carried out at different initial dioxane concentrations and with varying pH and peroxide concentrations. Figure 2 shows the concentrations of dioxane in the solution as a function of ozonation time for various conditions. Ozonation alone resulted in little dioxane degradation, indicating that OH radical is the main species oxidizing dioxane. This is in agreement with the information reported in the literature (Adams *et al.*, 1994) and the rate constants of the reactions of dioxane with ozone ($0.32 \text{ M}^{-1}\text{s}^{-1}$) and OH radical ($1.1\text{-}2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). As shown in Figure 2, significantly higher destruction of dioxane was achieved when hydrogen peroxide was present in the solution. Also, the apparent rate of dioxane removal increased with increasing peroxide concentration as well as with the initial concentration of dioxane in the solution.

The destruction of dioxane during each O_3 - H_2O_2 experiment did not correspond to any TOC decrease in the solution. Figure 3 shows the average oxidation state (AOS) of the solution for three of the experiments conducted with different initial dioxane and peroxide concentrations. AOS was estimated according to the following equation (Scott and Ollis, 1995):

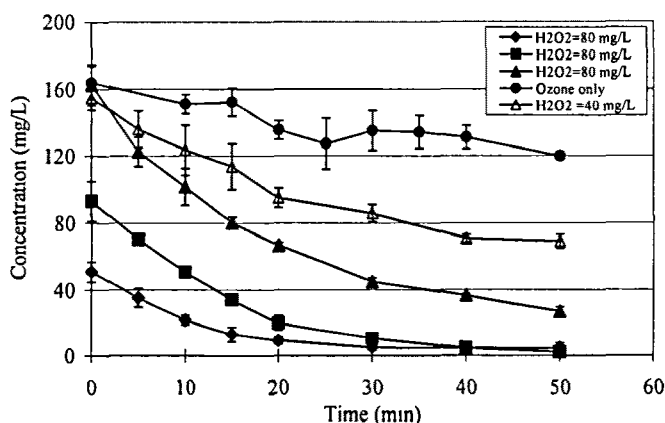


Figure 2. Destruction of dioxane during the O₃-H₂O₂ oxidation experiments for three different initial dioxane concentrations; pH=8, ozone dosage=40 mg/min.

$$\text{Average oxidation state (AOS)} = 4 \frac{\text{TOC} - \text{COD}}{\text{TOC}} \quad (1)$$

where TOC and COD are expressed in moles of C L⁻¹ and moles of O₂ L⁻¹, respectively. AOS takes values between +4 for CO₂, the most oxidized state of C and -4 for methane, the most reduced state of carbon. Figure 3 shows that AOS of the solution increases with ozonation time for both concentrations of dioxane. Formation of acidic oxidation intermediates was evident from the gradual decline of pH in the solution for all the experiments. Also, in our studies AOS did not significantly increase after about 20 min of ozonation, suggesting that the chemical nature of the intermediates did not vary considerably beyond this time which corresponds to an approximate ozone dosage of 160 mg/L.

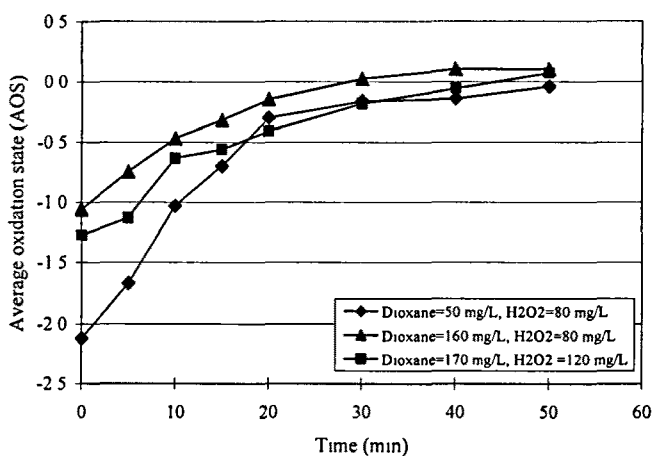


Figure 3. Average oxidation state improvements during the ozone-peroxide process; pH=8, ozone dosage=40 mg/min.

Conclusion

Ozone in combination with hydrogen peroxide is an efficient method in eliminating dioxane from contaminated water. The conversion of dioxane into more biodegradable intermediates provides an opportunity for integrating advanced oxidation with more conventional biological treatment, with the overall aim of complete elimination of harmful organic compounds at lower operating and capital expenditure.

References

- 1) Grant R, and C. Grant, *Grant and Hackh's Chemical Dictionary*. R. Grant and C. Grant, eds. 5th ed. (New York: McGraw-Hill Book Co. 1987), p. 189.
- 2) Kosaka K., H. Yamada, S. Matsui, and K. Shishida, "The effects of the co-existing compounds on the decomposition of micropollutants using the ozone/hydrogen peroxide process", *Wat. Sci. Technol* 42: 353-361 (2000).