

Degradation of 1,4-Dioxane using O_3/H_2O_2

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1,4-dioxane is a recalcitrant pollutant found in contaminated ground waters and industrial effluents. Conventional water treatment techniques are limited to treat this compound effectively. In this study, O_3/H_2O_2 oxidation process was used to eliminate 1,4-dioxane in water and to enhance the biodegradability. Several factors affecting biodegradability enhancement were investigated. The relationship between initial oxidation rate of 1,4-dioxane and BOD enhancement rate has been determined, a kinetic model has been proposed. H_2O_2 concentration and pH had a proportional relation with biodegradability of 1,4-dioxane, but in case of ozone, there was no relationship with biodegradability. 1,4-Dioxane removal efficiencies had good agreement with the biodegradability.

Key words: Advanced Oxidation Technology, O_3/H_2O_2 Process, 1,4-Dioxane, Initial Reaction Rate, Biodegradability,

1. Introduction

1,4-Dioxane is an extraordinary solvent, capable of solubilizing most organic compounds, water in all proportions, and many inorganic compounds (internet) and, thus, is widely used in industry. 1,4-Dioxane is mainly produced as a by-product from process of synthesizing ethylene glycol or ethylene oxide¹. 1,4-Dioxane causes liver damage and kidney failure, has been shown to be carcinogenic to animals, and is a potential carcinogen for humans and, hence, is classified as a hazardous waste and a priority pollutant². 1,4-Dioxane has been set a discharge limit of 30 L-1 by Environmental Protection Agency(EPA), if not removed from industrial wastewater effluents, can occur as a xenobiotic constituent of groundwater and in drinking water³.

Carbon adsorption purification of water containing 1,4-dioxane has limited practicality because of the high ratio of carbon to adsorbed 1,4-dioxane required for complete removal. Aeration of water containing 1,4-dioxane is inefficient because of its extreme solubility and low vapor pressure. Distillation is also inefficient and expensive process for 1,4-dioxane due to a

boiling point of 101 C. Conventional industrial biotreatment process cannot oxidize 1,4-dioxane effectively because of its highly resistant to biotransformation^{4,5}.

In general, it is considered that routine treatment of organic contaminants by chemical oxidation is frequently less economic than biological treatment. Under certain circumstance, however, chemical oxidation systems can be used cost effectively to treat organic chemicals that are normally toxic or refractory to microorganisms⁶. Especially, advanced oxidation processes(AOPs) are considered as an effective treatment for nonbiodegradable organic materials such as phenol, chloride, and ether compounds^{2,7,8}. Ozone and hydrogen peroxide combined process is one of the commonly used AOPs, which has recently shown promise for recalcitrant material due to its capability to produce high levels of hydroxyl radical (OH), a strong oxidant^{9,10}. This process has been also applied for several toxic nonbiodegradable compounds such as methyl-tert-butyl ether^{11,12}, atrazine¹³, and alachlor¹⁴, and has shown significant high removal efficiency because the reaction between ozone and the ion form of peroxide lead to hydroxyl radicals well. Several studies have examined the ozone and hydrogen peroxide combined process for removal of 1,4-dioxane in aqueous solution^{3,15,16}. The authors showed the optimum O_3/H_2O_2 molar ratio and competition effects with alkalinity and capability as a pretreatment process combined

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with conventional bioreactor, but no systematic study of reaction rate of 1,4-dioxane required to enlarge and apply this system to the industrial scale was explored.

In this study, with the aim of using O_3/H_2O_2 process as a pretreatment of conventional wastewater treatment, several factors affecting the biodegradability increase of 1,4-dioxane during ozonation were examined. The relationship between initial reaction rate of 1,4-dioxane and BOD enhancement rate has been proposed in order to estimate the rate of BOD enhancement at a given initial 1,4-dioxane concentration.

2. Experimental Methods

2.1 Chemicals and Materials

1,4-Dioxane, potassium indigotrisulfonate, and potassium iodide were purchased from Fisher Scientific Ltd. (Canada). Hydrogen peroxide (30% v/v) was purchased as analytical reagent grade (Fisher certified ACS. All reagents used in this experiment were at least reagent grade.

2.2 Apparatus

A bubble column (160 cm L x 10 cm i.d) was operated in a batch mode for the oxidation experiments as shown in fig. 1, and the column was made of polymethylmethacrylate (PMMA). The 1,4-dioxane solution was circulated through the column using Masterflex peristaltic pump (Cole Parmer). Ozone was produced by an ozone generator (Model RMU16-16, AZCO ind., Canada) fed with at least 95% oxygen which was produced by an oxygen generator (Model AS-12, AIRSEP corp., USA).

2.3 Experimental procedure

All the experiments were carried out in a bubble column as depicted in Fig. 1 in a batch mode. The bubble column was charged with 5L water containing appropriate concentrations of 1,4-dioxane and hydrogen peroxide. The solution in the column was circulated continuously by a peristaltic pump during the operation at a rate of 1 L/min. Ozone was introduced continuously into the aqueous phase at the bottom of the column through a glass sparger. Samples were taken at regular intervals corresponding to known applied ozone dosage and analyzed for concentration of

1,4-dioxane and hydrogen peroxide. Ozone in the samples was discharged immediately with nitrogen gas and the catalyst was added to each sample to deactivate the residual hydrogen peroxide for BOD analyses. Excess ozone discharged from bubble column during the operation was entrapped in the 2% KI solution contained in the glass trap, and was analyzed. All the experiments were finished at 50 minutes because the 1,4-dioxane concentration was almost reached at equilibrium state at that time (data not shown). The initial pHs in the column were varied using sodium hydroxide.

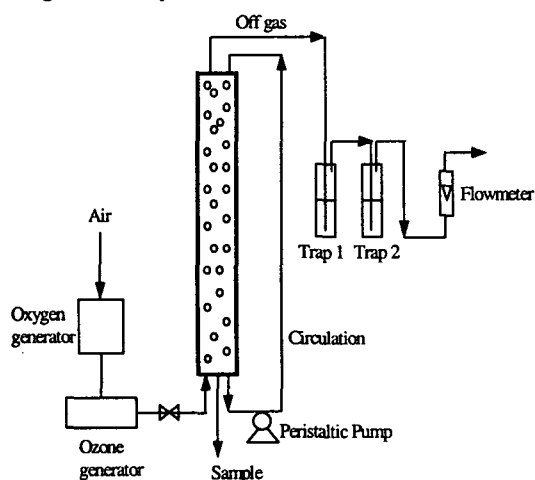


Fig. 1. Schematic diagram of experimental apparatus for oxidation of 1,4-dioxane using ozone and hydrogen peroxide.

In this experiment, temperature was not controlled because it has two different effects on ozonation. The one is positive to enhance the organic material removal rate due to an increase of rate constants of chemical reactions, the other is to reduce the ozone solubility. Therefore, for a practical case, ambient temperature is recommended¹⁴⁾.

2.4 Analysis

Gas chromatography (Hewlett Packard 5890) with flame ionization detector was used to measure the 1,4-dioxane concentration. BOD₅ analyses were performed in accordance with Standard Method 5210¹⁷⁾ using 300 mL BOD bottles. The biological seed for the BOD₅ test was obtained from the return activated sludge line of

the sewage treatment plant. The amount of ozone consumption was calculated from the following equation :

$$(\text{total mass of ozone consumed}) = (\text{total mass of ozone fed}) - (\text{total mass of dissolved ozone in the column} + \text{total mass of ozone off gas})$$

The masses of ozone in the reactor feed and off gas were analyzed with Standard Method 2350 E¹⁷) and the analysis of ozone dissolved in water was performed with Standard Method 4500-O₃ B¹⁷). Hydrogen peroxide concentrations in the samples were analyzed by iodide method¹⁸). The assessment of the biodegradability for 1,4-dioxane was considered as the amount of BOD₅ enhancement during the experiment.

3. Results and Discussion

The results of the pH effects on the BOD₅ concentrations were shown in Fig. 2. Fig. 2 shows the dependence of BOD₅ enhancement on initial

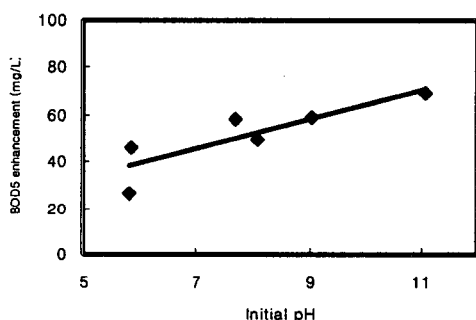


Fig. 2. Relationship between initial pH and the amount of BOD₅ enhancement. Initial concentrations of 1,4-dioxane and H₂O₂ were 200 mg/L and 120 mg/L, respectively.

pH. In the ranges of the pH (5.8-11.0) examined in this experiment, BOD₅ enhancement was proportionally increased with initial pH, and the trend between the initial pH and BOD₅ enhancement showed almost linear relationship.

Fig. 3 shows the effect of initial H₂O₂ concentration on the amount of BOD₅ enhancement during the ozonation process. In Fig. 3, at all H₂O₂ ranges examined (0, 40, 80, and 120 mg/L), BOD₅ enhancement was increased at high initial H₂O₂ concentrations. There existed a linear relationship with acceptable data scattering. However, there was no significant difference in

BOD₅ enhancement at high initial H₂O₂ concentration ranges (80-120 mg/L) and the difference in H₂O₂ consumption amount was also not observed. Kamenev et al.¹⁹) investigated the effect of H₂O₂ dose on the removal of phenol in O₃/H₂O₂ combined system. They observed that changes in the H₂O₂ doses (10-30 mg/L) had no notable effect on the oxidation efficiency. However, they used extremely low initial phenol concentration (3.3 mg/L), which maybe is excess amount of H₂O₂ responsible for treatment of phenol. Gulyas et al.⁹) reported that there was a significant difference in efficiency according to the variation of H₂O₂ concentration for removal triethylene glycol dimethylether (TEGDME) during ozonation. It was also observed that H₂O₂ had no influence on the removal rate of TEGDME

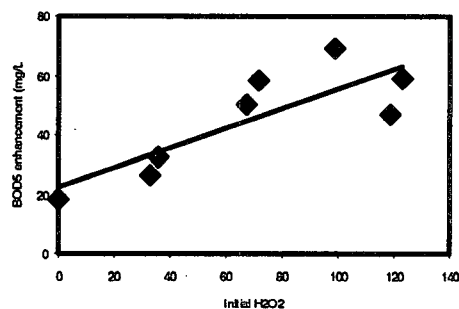


Fig. 3. Relationship between initial H₂O₂ and the amount of BOD₅ enhancement.

in the presence of humic acid at a certain concentration. As pointed out by Safarzadeh-Amiri¹²), the effect of H₂O₂ on the rate of destruction of methyl-tert-butyl ether (MTBE) was not straightforward since it is both a promoter and a scavenger of hydroxyl radicals. The oxidation rate and treatment efficiency of MTBE increased initially (approximately 10 %) with increasing concentration of H₂O₂, reached a maximum value followed by decreased with further increasing of H₂O₂ concentration. Therefore, it is likely that there exists an optimum H₂O₂ concentration according to the amount of ozone introduced, initial organic compounds concentration, and the presence of additives as inhibitors or initiators. This is resulted from different rate constant of ozone and OH radical

with different organic materials such as scavengers and intermediate.

The effect of ozone consumption on the BOD₅ enhancement was presented in Fig. 4. This Figure showed that there was no clear trend between ozone consumption and BOD₅ enhancement. The ozonation was performed for 50 min under the same gas flowrate, and the ozone consumption was calculated from the value of ozone in solution, in inlet and outlet gas. In contrast, Safarzadeh-Amiri¹²⁾ reported a different result in MTBE treatment process, in that the decay profile as a function of consumed ozone concentration appeared to be a biphasic, particularly at high MTBE concentration ([MTBE] > 100 mg/L). The first-phase covers MTBE concentrations greater than 10 mg/L and the second-phase covers MTBE

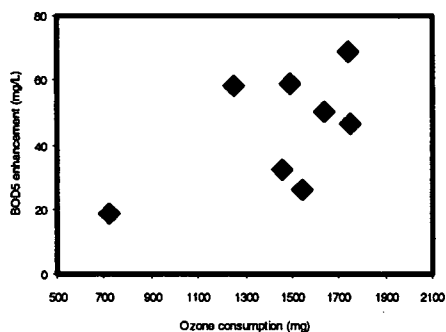


Fig. 4. Effect of ozone consumption on the BOD₅ enhancement at different experimental conditions.

concentration below 10 mg/L. Kitis et. al.²⁰⁾ pointed out that higher oxidant dosages significantly increased the biodegradability (presented by DOC removal). However, there was no difference in the value of DOC removed at high ozone dose over 1 mg ozone/mg compound. This result suggest that there could be no remarkable change in biodegradability although the ozone dose increased, after the biodegradability reached maximum point, and also it could be dependent on the kind of organic material and its initial concentration. This is likely that the amount of ozone consumption could not be consistent with the biodegradability increase because the ozone could affect not only 1,4-

dioxane decomposition but also continuous degradation of intermediate.

Fig. 5 shows that there was a linear relationship between 1,4-dioxane removal percentage and BOD₅ enhancement. The 1,4-dioxane removal efficiencies significantly increased the BOD₅ value (e.g. biodegradability of 1,4-dioxane). This result suggests that most of the intermediate materials from 1,4-dioxane are biodegradable, which was observed by Stefan et al.²⁾ for UV/H₂O₂ process. Therefore, it can be easily checked the biodegradability of 1,4-dioxane with just monitoring its removal efficiencies, if this process applied to the conventional wastewater treatment as a pretreatment unit.

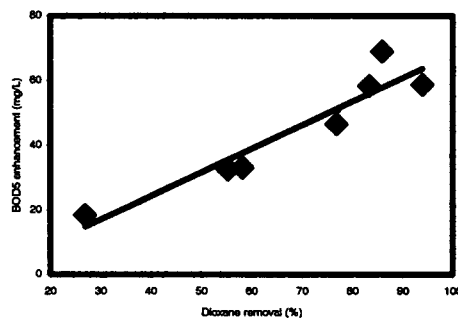


Fig. 5. Relationship between removal percentage of 1,4-dioxane and BOD₅ enhancement.

In order to apply O₃/H₂O₂ system investigated in the present study to industrial wastewater plant, the capability of treatment should be essentially investigated. In addition, treatment speed of organic material is also one of the important factors. In this regard, the reaction rate would be an important measurement to check the time needed for removal of organic material by this process because it would be possible to compare with other system specifically and help to determine the adaptability or which process could be better for given organic material.

The method used in this experiment for determining reaction rate was simply measured from the 1,4-dioxane concentration for 10 min by varying the initial concentration (3–180 mg/L), and then, calculated on the basis of the initial rate method²¹⁾.

The reaction rate of 1,4-dioxane for O₃/H₂O₂ system used in this study was shown in Fig. 6. The reaction rate increased linearly at low initial 1,4-dioxane concentrations (below 55 mg/L), thereafter the rates were nearly leveled off. This result can be represented with the following equation (1) which is similar to the Langmuir-Heinswood kinetics:

$$r = (r_{\max} C_0)/(a + C_0) \quad (1)$$

Where, r is the initial reaction rate of 1,4-dioxane, r_{\max} is the maximum reaction rate of 1,4-dioxane (mg/L-min), C_0 is the initial 1,4-dioxane concentration (mg/L), a is constant of reaction rate (mg/L). According to the least square fitting method, the values of r_{\max} and a were found to be 8.82 mg/L-min, 80.71 mg/L, respectively. Thus, the reaction rate with calculated constants could be shown as following equation (2):

$$r = (8.82 C_0)/(80.71 + C_0) \quad (2)$$

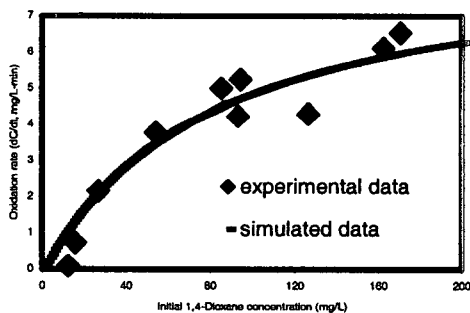


Fig. 6. Reaction rates of various initial concentrations of 1,4-Dioxane.

As can be seen in Fig. 6 (represented by solid line), results profile simulated from eq. (2) were fitted well with experimental data. The value of maximum reaction rate of 8.82 mg/L-min, r_{\max} is considered as the maximum degradation speed of 1,4-dioxane in this O₃/H₂O₂ system. In the judgment of reaction rate concept, it was revealed that equilibrium state was almost reached at over 200 mg/L of initial 1,4-dioxane concentration. Therefore, there was no economic profit to

operate this system at high initial 1,4-dioxane concentrations over 200 mg/L.

References

- 1) Alnaizy, R. and A. Akgerman, 2000, Advanced oxidation of phenolic compounds. *Advanced in Environmental Research* 4, 233-244.
- 2) Stefan M. I. and J. R. Bolton, 1998, Mechanism of the degradation of 1,4-dioxane in the dilute aqueous solution using the UV/hydrogen peroxide process. *Environ. Sci. Technol.* 32, 1588-1595.
- 3) Adams, C. D., P. A. Scanlan and N. D. Secrist, 1994, Oxidation and biodegradability enhancement of 1,4-dioxane using hydrogen peroxide and ozone. *Environ. Sci. Technol.* 28, 1812-1818.
- 4) Sandy, T., C. P. Grady Jr., S. Meininger and R. Boe, 2001, Biological treatment of 1,4-dioxane in wastewater from an integrated polyethylene terephthalate(PET). *Annual Industrial Wastes Technical and Regulatory Conference, Conference Proceeding 7th, Charleston, SC, USA*, 88-117.
- 5) Kelley, S. L., E. W. Aitchison, M. Deshpande, J. L. Schnoor and P. J. J. Alvarez, 2001, Biodegradation of 1,4-dioxane in planted and unplanted soil: effect of bioaugmentation with *Amycolata* sp. CB1190. *Wat. Res.* 35(16), 3791-3800.
- 6) Weber, W. J. Jr. and E.J. LeBoeuf, 1999, Process for advanced treatment of water, *Wat. Sci. Tech.*, 40, NO. 4-5, 11-19.
- 7) Bose, P., W. H. Glaze and D. S. Maddox, 1998, Degradation of various advanced oxidation processes : 1. Reaction rates. *Wat. Res.* 32, 997-1004.
- 8) Hirvonen, A., T. Tuhkanen, M. Ettala, S. Korhonen and P. Kalliokoski, 1998, Evaluation of a field-scale UV/HO₂ oxidation system for the purification of groundwater contaminated with PCE. *Environ. Technol.* 19, 821-
- 9) Gulyas, H., R. von Bismarck and L. Hemmerling, 1995, Treatment of industrial wastewaters with ozone/hydrogen peroxide. *Water Sci. Technol.* 32(7), 127-134.
- 10) Shishida, K., H. Haruki, K. Kamio, H. Yamada, K. Kosaka and S. Matsui, 1999, Comparison of the ozone/hydrogen peroxide process, the ozone/ultraviolet process, and the hydrogen peroxide/ultraviolet process in the treatment of

- landfill leachate. *J. Jpn. Soc. Waste Manage. Experts* 10(5), 247-256.
- 11) Acero, J. L., S. B. Haderlein, T. C. Schmidt, M. Jr. F. Suter and U. V. Gunten, 2001, MTBE oxidation by conventional ozonation and the combination ozone/hydrogen peroxide: efficiency of the processes and bromate formation. *Environ. Sci. Technol.* 35, 4252-4259.
 - 12) Safarzadeh-Amiri, A. 2001, O₃/H₂O₂ treatment of methyl-tert-butyl ether (MTBE) in contaminated waters, *Wat. Res.* 35(15), 3706-3714.
 - 13) Nelieu, S., L. Kerhoas and J. Einhorn, 2000, Degradation of atrazine into ammeline by combined ozone/hydrogen peroxide treatment in water. *Environ. Sci. Technol.* 34, 430-437.
 - 14) Beltran, F., B. Acedo and J. Rivas, 1999, Use of ozone and hydrogen peroxide to remove alachlor from surface water. *Bull. Environ. Contam. Toxicol.* 63, 9-14.
 - 15) Kosaka, K., H. Yamada, S. Matsui and K. Shishida, 2000, The effects of the co-existing compounds on the decomposition of micropollutants using the ozone/hydrogen peroxide process. *Water Sci. Technol.* 42, 353-361.
 - 16) Bowman, R. H., P. Miller, M. Purchase and R. Schoellerman, 2001, Ozone-peroxide advanced oxidation water treatment system for treatment of chlorinated solvents and 1,4-dioxane. Extended Abstracts at the ACS National Meeting, American Chemical Society, 41(1), 1064-1074.
 - 17) APHA (American Public Health Association) 1998, Standard Methods for the Examination of Water and Wastewater, 20th ed, Donnelly and Sons, New York.
 - 18) Klassen, N. V., Marchington D. and McGowan H. C. E. 1994, H₂O₂ determination by the I₃-method and by KMnO₄ titration. *Anal. Chem.* 66, 2921-2925.
 - 19) Kamenev, S., J. Kallas and R. Munter, 1995, Chemical oxidation of biologically treated phenolic effluents. *Waste Management* 15(3), 203-208.
 - 20) Kitis M., C. D. Adams, J. Kuzhikannil and G. T. Daigger, 2000, Effect of ozone/hydrogen peroxide pretreatment on aerobic biodegradability of nonionic surfactants and polypropylene glycol. *Environ. Sci. Technol.* 34, 2305-2310.
 - 21) Fogler, H. S. 1992, Elements of chemical reaction engineering. 2nd ed., PTR prentice Hall, 205-207.