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Oxidation and Biodegradability Enhancement of 1,4-Dioxane Using Hydrogen Peroxide and Ozone

Craig D. Adams,* Patricia A. Scanlan,† and Neal D. Secrist

Department of Environmental Systems Engineering, Clemson University, Clemson, South Carolina 29634

Ozone in combination with hydrogen peroxide has been shown to effectly oxidize 1,4-dioxane in synthetic solutions representing groundwater or industrial wastewater to more readily biodegradable oxidation products that could be treated using conventional biological treatment. Bicarbonate alkalinity and competition by 1,3-dioxolane and 2-methyl-1,3-dioxolane were found to increase the oxidant dosages required for 1,4-dioxane oxidation. The results of this study suggest that anaerobic pretreatment prior to advanced oxidation may be a viable means of reducing the ozone and hydrogen peroxide dosages required for biodegradability enhancement.

Introduction

1,4-Dioxane, a suspected carcinogen (*1*), is an industrial solvent used for dyes, oils, waxes, resins, cellulosic esters and ethers, and polyvinyl polymers (*2–5*). 1,4-Dioxane is also a common byproduct of chemical processes such as those involving ethylene glycol or ethylene oxide (*4, 6*). If not removed from industrial wastewater effluents, 1,4-dioxane can occur as a xenobiotic constituent of groundwater (*7, 8*) and in drinking water (*9*). 1,4-Dioxane is essentially nonbiodegradable by microorganisms under conditions typically occurring in conventional industrial biotreatment processes. No significant aerobic biodegradation was achieved by microorganisms acclimated to municipal wastewater (*10, 11*), to soils (*12*), or to other synthetic organic chemicals (SOCs) (*13, 14*). In addition, others have observed that 1,4-dioxane is apparently not biodegradable under anaerobic conditions (*7, 15*). Cultures of naturally occurring organisms have been isolated, however, that are capable of degrading 1,4-dioxane (*16–18*).

Carbon adsorption and air stripping are not effective treatment processes for 1,4-dioxane. Therefore, distillation has been employed to remove 1,4-dioxane from industrial wastewaters although, due to a boiling point of 101 °C (*5*), this is an expensive means of removing 1,4-dioxane.

Other treatment options have also been examined. Klécka and Gonsoir (*19*) found that, while chlorination at 25 °C resulted in no reaction with 1,4-dioxane, at 75 °C and the optimum pH of 5.2 oxidation of 1,4-dioxane did occur. Although the chlorination byproducts of 1,4-dioxane were not reported by the authors, others have shown that five chloro derivatives of 1,4-dioxane are from 12 to 1000 times more toxic than 1,4-dioxane (*20*), thus bringing into question the potential value of chlorination as a viable treatment alternative.

Basic chemical structural features of organic compounds such as the position, type, and number of substituents can significantly affect the biodegradability of organic compounds (*21*). For the case of 1,4-dioxane, recalcitrance is enhanced by its cyclic structure and by the presence of oxygen in the carbon chain. Minor modification of the chemical structure through redox reactions, therefore, may markedly alter 1,4-dioxane's biodegradability.

The use of ozone (O_3) in water treatment processes has been shown to significantly increase the assimilable organic carbon (AOC) fraction of the total organic carbon (TOC) pool in natural waters (*22–24*) and in secondary effluents (*25, 26*). Further, Duguet *et al.* (*27*) showed that ozonation with the addition of hydrogen peroxide (H_2O_2) (thus forming hydroxyl radicals, •OH) resulted in an increase in the AOC fraction of the natural organic matter.

Oxidation has also been shown to increase the biodegradability of many (but not all) SOCs. For example, Suzuki and co-workers (*28*) ozonated five biorefractory polymeric SOCs and measured a significant increase in biodegradability for polyethylene glycol, poly(vinyl alcohol), poly(vinylpyrrolidone), and sodium polyacrylate. Similarly, Medley and Stover (*29*) found that ozonation increased the biodegradability of 1,2-dichloropropane and 2,4-dinitrophenol while concluding that treatability studies are necessary for each compound due to differences in reactivities. Ozone also was shown by Somich *et al.* (*30*) to significantly increase the biodegradability of an agricultural wastewater containing 0.46 mM atrazine. Decreases in biodegradability have been reported upon ozonation of acrylonitrile (*29*) and polyacrylamide (*28*) even though a decrease in molecular weight was achieved. Thus, treatability studies are often required to assess the effectiveness of ozonation for increasing the biodegradability of specific compounds.

Treatment processes that utilize •OH as the primary oxidant are often referred to as advanced oxidation processes (AOPs) (*31, 32*). While ozone is a strong though relatively selective oxidant, the hydroxyl radical is a much stronger and nonselective oxidant with reaction rate constants often 9 orders of magnitude greater than ozone for the same organic compound (*33, 34*). While some hydroxide ion-catalyzed autodecomposition of ozone in aqueous solution may naturally occur, the conversion of ozone to •OH by the addition of H_2O_2 and/or UV irradiation can often be used to increase oxidation rates and efficiency, especially for compounds not readily degraded by ozone alone.

Ozone-based AOPs form hydroxyl radicals in an autodecomposition cycle catalyzed by the hydroxide ion (high pH), by H_2O_2, and/or by UV (*35–37*). Competition for radicals in such systems occurs between the target organic substrate, other organic substrates, bicarbonate ions ($k_{\cdot OH,HCO_3^-} = 2 \times 10^7\ M^{-1}\ s^{-1}$) (*38, 39*), carbonate ions ($k_{\cdot OH,CO_3^{2-}} = (2 \times 10^8 - 4 \times 10^8)\ M^{-1}\ s^{-1}$) (*40, 39*), hydrogen peroxide ($k_{\cdot OH,H_2O_2} = 3 \times 10^7\ M^{-1}\ s^{-1}$) (*41–43*), and other reactive compounds. Rate constants for the reaction of 1,4-dioxane with ozone have been reported as $0.32\ M^{-1}\ s^{-1}$ at pH 2 (*34*). By comparison, the reported rate constants for the reaction

* Corresponding author; Telephone: (803) 656-1005; FAX: (803) 656-0672; e-mail address: acraig@ese.clemson.edu.

† Present address: Black & Veatch, Engineers-Architects, 4800 Ward Parkway, Kansas City, MO 64114.

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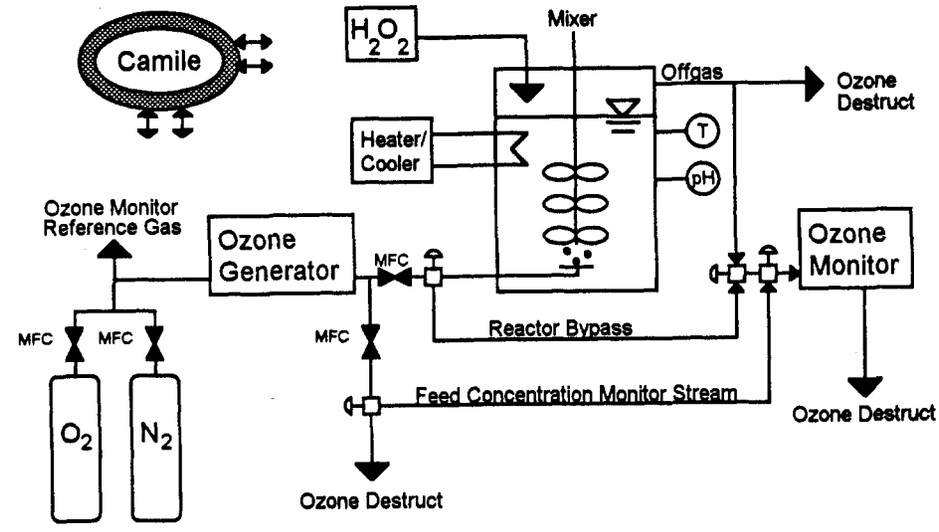

Figure 1. Oxidation apparatus used for ozonation and advanced oxidation experiments. Mass flow controllers (MFC) were used to monitor the mass flow to the reactor and other flows. A Camile data acquisition and control system was used to monitor and control process parameters. The reference gas humidification system for the ozone monitor is not shown.

of 1,4-dioxane with •OH are (1.1×10^9)–(2.4×10^9) M^{-1} s^{-1} (*44*, *42*).

Klécka and Gonsoir (*19*) used Fenton's reagent, another AOP, to oxidize 1.14 mM solutions of 1,4-dioxane at 25 °C. The authors reported that at the optimum pH of 3–4 for the Fenton reaction, the 1,4-dioxane and TOC concentrations were reduced 97% and 11% in 10 h, respectively (*45*).

The purpose of our research was to examine the use of H_2O_2 in combination with O_3 to increase the biodegradability of 1,4-dioxane in synthetic groundwater and industrial wastewaters, thus allowing subsequent conventional biological wastewater treatment. This research examined the effect of H_2O_2/O_3 ratio, bicarbonate alkalinity, anaerobic metabolic byproducts (primarily volatile fatty acids), other organic wastewater constituents, and initial dioxane concentration on the oxidant dosages required to achieve biodegradability enhancement of the synthetic aqueous solutions of 1,4-dioxane.

Experimental Methods

Chemicals. 1,4-Dioxane (HPLC grade) and potassium indigotrisulfonate were obtained from Aldrich Chemical. D-Glucose, ferrion indicator, sulfuric acid, and ammonium, magnesium, potassium, and sodium salts were obtained from Mallinckrodt. TOC standards, ferrous ammonium sulfate, and potassium dichromate were obtained from Ricca Chemical. All reagents were at least reagent grade.

Apparatus. A 6-L, 14-cm i.d., completely mixed reactor (New Brunswick Scientific) was operated in a semi-batch mode for the oxidation experiments (Figure 1) and was mixed with three axially mounted, 4.5-cm impellers operated at 750 (±10) rpm. Reactor materials of construction were glass, Teflon, or 316 stainless steel. The reactor temperature was continuously monitored *in situ* with a Type J thermocouple (Omega) and maintained at 20 °C using a RC20 recirculating heater/cooler (Lauda). Reactor pH was monitored *ex situ* with a Model 476540 probe and a Model 220 pH meter (Corning).

Ozone was initially produced using a Model PWCIA CD corona-type generator (Pure Water Corp.) from a 80: 20 (v/v) mixture of oxygen and nitrogen and then using a Model GTC-1B ozone generator (Griffin Technics) from pure oxygen. Gas flows were controlled using FC-280 mass flow controllers (Tylan General). Ozone concentrations in the feed and off gas from the reactor were determined using an HC12 monitor (PCI Corp.) modified to permit continuous sample flow. Ozone in the off gas was catalytically destroyed prior to discharge using a OTG-20001 destruction unit (Emery Trailigaz). Hydrogen peroxide was fed to the reactor using a 7550-90 Masterflex drive (Cole Parmer) through a Teflon diaphragm pump head and lines.

With the exception of a few initial experiments, all temperature, ozone feed and off gas concentrations, and mass flow data were acquired and processed using a Camile 2000 data acquisition and control system (Dow Chemical USA). The absorbed ozone rate and mass transfer efficiency were continuously calculated from the difference between the mass of ozone in the reactor feed and off gas and were used to maintain a constant H_2O_2/O_3 ratio throughout an experiment.

Experiment Procedure. All of the oxidation experiments were performed in the 6-L semi-batch reactor with ozone (and hydrogen peroxide when applicable) fed continuously into the batch-mode aqueous phase. Execution of each experiment entailed charging the reactor with 1,4-dioxane, and sodium bicarbonate (and additional organic compounds for competition runs) and then adjusting the reactor temperature to the desired temperature, which was maintained throughout the experiment. All experiments were conducted under isothermal conditions, typically at 20 °C. Prior to initiating an experiment, the ozone generation, control, and monitoring systems were turned on and allowed to stabilize with the gas stream bypassing the reactor. To initiate an experiment, the ozone and hydrogen peroxide flows were routed to the reactor, and the determination of the cumulative absorbed ozone (mM) was initiated. Applied ozone rates were approximately 0.05 and 0.4 mM/min with the PWC and Griffin Technics ozone generators, respectively. Periodically, samples were withdrawn for immediate analysis of pH and alkalinity, with the eventual analysis of 1,4-dioxane concentration (in all experiments) and COD, TOC, and BOD_5 concentrations (in selected experiments).

Typical baseline experiments were conducted on solutions containing 2.3 mM (200 mg/L) 1,4-dioxane and 4–5 mM carbonate alkalinity. This alkalinity represented the lower end of the alkalinity range expected from an anaerobic pretreatment unit. Other initial parameters for each experiment including the H_2O_2/O_3 molar ratio are presented in the appropriate sections below.

In the initial experiments, which were designed to investigate the effect of H_2O_2/O_3 molar ratio, the pH of the initial solution was adjusted to pH 7.0 (±0.1) using HCl. In the remaining experiments, the initial pH was not adjusted. While the pH was not controlled, it was monitored throughout each experiment.

An additional experiment was also run with hydrogen peroxide as the sole oxidant at a concentration of 45 mM, a dioxane concentration of 2.3 mM, and an alkalinity of 0.17 mM. The applied H_2O_2 represented more than a 100% excess of the total cumulative mass of applied H_2O_2 for an entire H_2O_2/O_3 experiment. This experiment resulted in negligible removal of dioxane.

Bioassay Procedures. BOD_5 analyses were performed in accordance with Standard Method 5210 (*46*) using 60-mL BOD bottles. The biological seed for the BOD_5 tests was obtained from the return activated sludge (RAS) line of the Pendleton-Clemson Wastewater Treatment Plant.

While BOD_5 measurements were used as the primary bioassay in these experiments, a second bioassay was also performed. A 2.27 mM 1,4-dioxane solution (initial bicarbonate alkalinity of 5.0 mM and pH of 7.0) was oxidized using a H_2O_2/O_3 molar ratio of 1.0 according to the procedure described above. For use in the bioassays, 300-mL samples were withdrawn after application of 0.0, 1.2, 2.6, and 4.3 mol of both absorbed ozone and H_2O_2/mol of 1,4-dioxane. The residual H_2O_2 was quenched by the addition of sodium sulfite in excess of the applied H_2O_2 and subsequent aeration on a shaker table to convert any excess sulfite to sulfate. Seed for the bioassay was prepared by spiking nutrients and a protein broth solution (containing yeast extract, beef extract, phytone peptone, and casitone) with biomass from the Pendleton-Clemson (SC) Wastewater Treatment Plant and providing aeration until the top of the growth curve was achieved.

Duplicate samples of the unoxidized 1,4-dioxane solution and each oxidized mixture were bioassayed. Additionally, single samples of distilled water and glucose and duplicate samples of ethylene glycol and an industrial wastewater (from a plant utilizing ethylene glycol) were also tested. The initial COD of each bioassay sample was adjusted to 4.1 mM by dilution to normalize the analysis. Then 27 mL of biological seed was spiked along with nutrients into each sample. The samples were aerated on a shaker table over a 3-day period and 3–5-mL samples were periodically removed for COD analysis. The resulting COD values were plotted versus time, and the maximum COD removal rate (q) was calculated based on initial biomass total suspended solids (TSS) as

$$q = \frac{dCOD/dt}{TSS_{biomass}}\left(\frac{\text{mg of COD}}{\text{mg of TSS h}^{-1}}\right) \quad (1)$$

Analytical Procedures. Gas chromatography (Hewlett Packard 5880a) with flame ionization detection was used to measure 1,4-dioxane concentration. Injection volumes were 0.50 μL using a Chaney adapter (Hamilton) for reproducibility. The method quantitation and detection limits were 0.011 and 0.005 mM (1 and 0.5 mg/L), respectively, with the former being determined using Standard Method 1030E (*46*). COD measurements provided a measure of the relative oxidation of the organic mixture and were measured in duplicate using COD ampoules (Hach, 0–150 mg/L) with titration with ferrous ammonium sulfate. TOC measurements provided a measure of mineralization and were performed in duplicate or triplicate using Standard Method 5310 (*46*) with a Model 915C TOC analyzer (Beckman). Ozone residual concentrations were measured using the indigo method (Standard Method 4500 (*47*)).

Results and Discussion

Baseline Experiments. 1,4-Dioxane was the sole organic compound in the initial solutions in these experiments which examined H_2O_2/O_3 molar ratios including 0.0 (ozone only), 0.5, and 1.0. Samples were periodically withdrawn and analyzed for 1,4-dioxane concentration, TOC, COD, and BOD_5 as a function of cumulative absorbed ozone and hydrogen peroxide.

For the 0.0 H_2O_2/O_3 molar ratio, a negligible reaction rate was achieved due to an ozone transfer efficiency (defined as ozone absorbed per ozone fed) of less than 4%. This was consistent with reaction rate constants 9 orders of magnitude lower for the reaction of 1,4-dioxane with ozone versus with hydroxyl radical (*35, 43, 44*).

1,4-Dioxane was readily oxidized by ozone in combination with hydrogen peroxide at both the 0.5 and the 1.0 H_2O_2/O_3 oxidant ratios. Average steady-state mass transfer efficiencies of 57% were achieved for both oxidant ratios at the typical impeller speed of 750 rpm. Due to mass transfer limitations, the mass transfer efficiency was a strong function of impeller speed.

Examination of Figure 2 shows that the BOD_5 data rapidly increased to their maximum values after application of nominally 1.0 mol of absorbed ozone/mol of initial dioxane (m:m). The COD and TOC data decreased linearly relative to the absorbed ozone throughout the experiments after an initial lag in the TOC reduction. This lag period for TOC removal suggests that the initial oxidation reactions of 1,4-dioxane did not result in mineralization, that is, in the production of carbon dioxide. The rapid rise in BOD_5 compared with the limited coincident COD reduction suggests that the initial oxidation byproducts have significantly enhanced biodegradability relative to 1,4-dioxane for the mixed microbial cultures obtained from a municipal wastewater treatment plant and used in these bioassays. The required oxidant dosage for biodegradability enhancement of a wastewater or groundwater, therefore, may correspond to the dosage required to reduce the 1,4-dioxane's concentration to its effluent guideline (including subsequent dilution effects downstream). Further chemical oxidation may simply waste oxidant and, therefore, increase net treatment costs. This also implies that the 1,4-dioxane concentration itself (easily monitored using gas chromatography) might be an appropriate control parameter for a full-scale process.

While effective oxidation of 1,4-dioxane was achieved at both the 0.5 and 1.0 H_2O_2/O_3 molar ratios, less ozone but more hydrogen peroxide was required at the higher ratio to remove the 1,4-dioxane. The optimum ratio should be based on (1) the relative total costs (capital and operating) associated with delivering a mole of absorbed

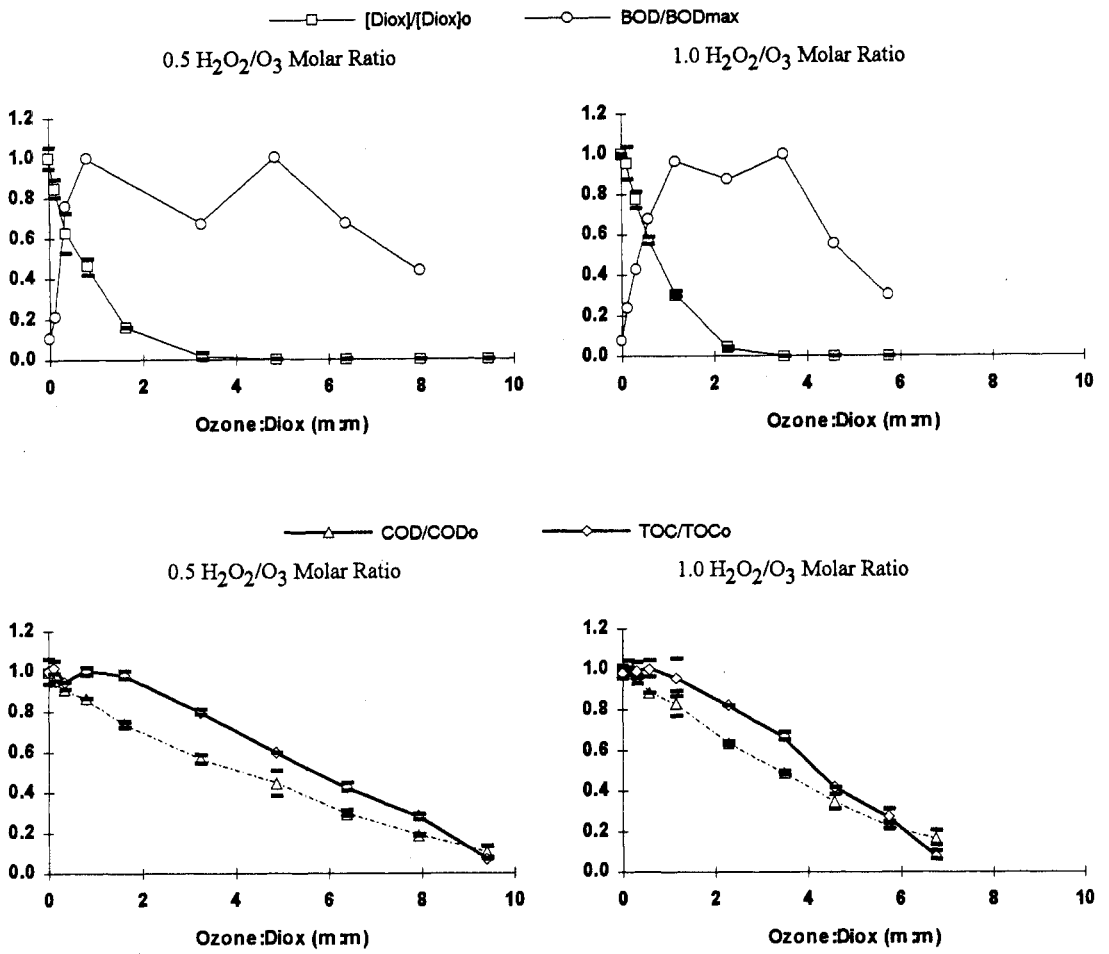

Figure 2. TOC, BOD, COD, and dioxane concentration results for pure solution experiments executed with 0.5 and 1.0 H_2O_2/O_3 molar ratio experiments and initial dioxane concentrations of 2.2 and 2.5 mM, respectively. Error bars indicate ±2 standard deviations about the mean. The initial carbonate alkalinities were 4.2 ± 0.1 mM.

ozone versus a mole of hydrogen peroxide and (2) the allowable residual H_2O_2 concentration with regard to subsequent biotreatment. The oxidant ratio can be adjusted in full-scale treatment processes to minimize costs. A low residual H_2O_2 effluent concentration may simply provide a supplemental oxygen source while larger concentrations may be inhibitory to the indigenous microorganisms.

Shaker Table Bioassay Results. The biodegradability of the mixture of 1,4-dioxane oxidation byproducts was also determined through shaker table bioassays designed to measure the relative COD removal rates of solutions oxidized using a 1.0 H_2O_2/O_3 molar ratio. Little or no biodegradation was achieved with the sample which received no (0 m:m) oxidant reflecting the biorecalcitrance of 1,4-dioxane (Figure 3). The COD for the samples receiving oxidant dosages (normalized to initial dioxane) of 2.6 and 4.3 (m:m) achieved an 85% reduction in COD in 57 h (Figure 3). The residual COD at these dosages was approximately 15% and may be due exclusively to metabolic byproducts. The sample receiving 1.2 m:m exhibited a residual COD of about 37% of the original COD due to residual 1,4-dioxane still present in the sample. The specific COD removal rates were 0.0002, 0.0053, 0.0087, and 0.0069 h^{-1} [(mg of COD) (mg of TSS)$^{-1}$ h^{-1}] for oxidant dosages of 0.0, 1.2, 2.6, and 4.3 m:m, respectively.

For comparison, the COD removals for ethylene glycol, glucose, and an industrial wastewater were also determined (Figure 3). Glucose, a readily degradable substrate

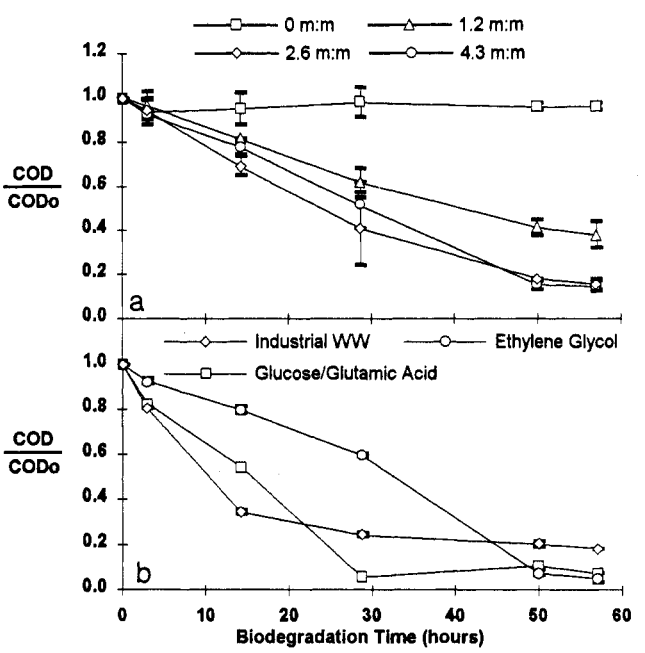

Figure 3. Biodegradation by conventional wastewater treatment plant biomass of (a) dioxane solutions treated with 0.0, 1.2, 2.6, and 4.3 mol of both ozone and hydrogen peroxide/mol of 1,4-dioxane (1.0 molar ratio) and (b) ethylene glycol, glucose, and an industrial wastewater. The initial dioxane concentration and carbonate alkalinity of the solution treated with the combined oxidants were 2.6 and 4.4 mM, respectively. Error bars indicate ±1 standard deviation about the mean.

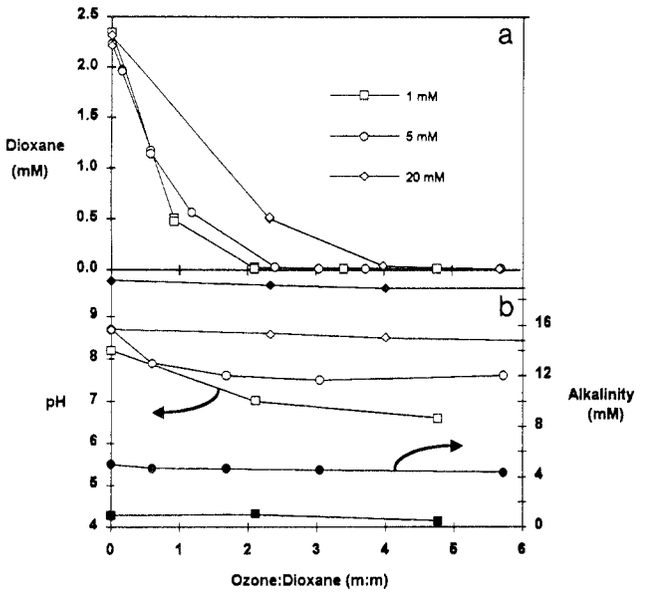

Figure 4. Effect of bicarbonate alkalinity (1, 5, and 20 mM carbonate alkalinity) on (a) the removal of 1,4-dioxane from solution and (b) the pH (open symbols) and alkalinity removal (closed symbols).

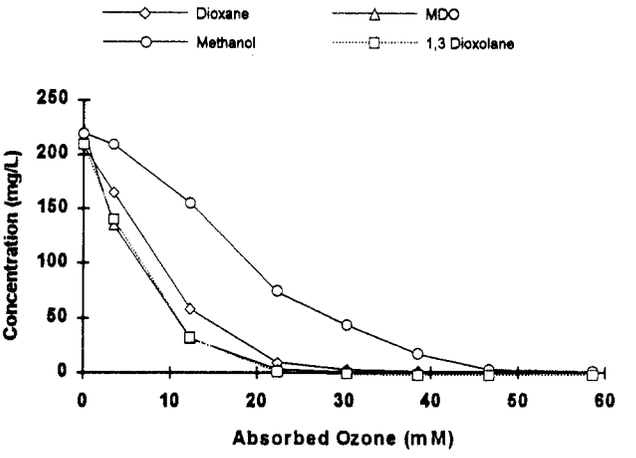

Figure 5. Effect of other potential synthetic organic wastewater constituents (methanol, 2-methyl-1,3-dioxolane (MDO), and 1,3-dioxolane) on the removal of 1,4-dioxane from solution oxidized at a 0.5 H_2O_2/O_3 molar ratio. Initial carbonate alkalinity was 5.0 mM.

exhibited a COD removal rate of 0.013 h^{-1} while the ethylene glycol solution exhibited a specific COD removal rate of 0.0054 h^{-1}. From these tests, it may be concluded that the mixed oxidation byproducts of 1,4-dioxane are readily biodegradable. It should be emphasized that the biological seed used was not acclimated to any of these substrates and, therefore, a higher specific COD removal rate would be anticipated from a biomass acclimated to 1,4-dioxane oxidation byproducts.

Effect of High Initial Dioxane Concentration. The effect of initial 1,4-dioxane concentration was examined by comparing the oxidant dosage required to reduce the 1,4-dioxane concentration to the detection limit in solutions containing 2.3 mM (200 m/L) versus 23 mM (2000 mg/L) using a 1.0 H_2O_2/O_3 molar ratio. The results showed that equivalent oxidant dosages were required to reduce 1,4-dioxane to the detection limit, that is, approximately 3 m:m (moles of ozone and hydrogen peroxide per mole of dioxane).

In the low and high initial concentration experiments, alkalinity reductions of 0.4 and 2.3 mM, respectively, were achieved from an initial alkalinity of 5 mM (500 mg/L as $CaCO_3$). More alkalinity was removed in the high concentration experiment due to extended reactions times required to achieve 1,4-dioxane removal.

Effect of Competition with Bicarbonate Alkalinity. The effect of bicarbonate alkalinity on the oxidant demand was examined in a series of experiments with initial 1,4-dioxane concentrations of 2.3 mM and initial alkalinities of 1, 5, and 20 mM. The oxidant dosages required to reduce the 1,4-dioxane concentration to the detection limit were compared to assess the significance of carbonate system alkalinity as a process parameter.

The results showed that an increased solution alkalinity resulted in an increase in the oxidant requirements for reduction of the 1,4-dioxane concentration to below the detection limit (Figure 4). This is consistent with the fact that 1,4-dioxane, bicarbonate ions, and carbonate ions all compete for hydroxyl radicals in the system. Rate constants reported for these reactions were cited above. Also presented in Figure 4 are the corresponding alkalinity and pH data, which show a decrease in both alkalinity and pH during the experiments.

Effect of Competition with Volatile Fatty Acids and Synthetic Organic Compounds. Industrial wastewaters containing 1,4-dioxane may also contain other organic constituents including 2-methyl-1,3-dioxolane, 1,3-dioxolane, and methanol. An experiment was performed to compare the relative competition for oxidant exerted by these compounds versus 1,4-dioxane. A solution containing 220 (±10) mg/L of each compound and 5 mM (500 mg/L as $CaCO_3$) was prepared and oxidized using a 0.5 H_2O_2/O_3 molar ratio. The concentration of each compound was subsequently determined for samples periodically obtained using gas chromatography and plotted versus absorbed ozone dosage (mM). Examination of Figure 5 shows that 2-methyl-1,3-dioxolane and 1,3-dioxolane were oxidized more rapidly than 1,4-dioxane but that methanol was removed significantly less rapidly. These relative removal rates are consistent with the second-order rate constants for the reaction of hydroxyl radical with 2-methyl-1,3-dioxolane, 1,3-dioxolane, and methanol of 3.5×10^9 (*48*), 4×10^9 (*48*), and 7.8×10^8 M^{-1} s^{-1} (*49*), respectively. In this matrix, nominally 15 mol of ozone and 7.5 mol of hydrogen peroxide/mol of 1,4-dioxane were required to reduce the 1,4-dioxane concentration from 200 to 1 mg/L.

A parallel study on the anaerobic pretreatment aspects of this project was conducted in a anaerobic fluidized bed reactor by Cowan *et al.* (*15*). They reported that while 1,4-dioxane was not removed in the anaerobic reactor, other organic constituents of the synthetic industrial wastewater were effectively converted to metabolic byproducts, primarily volatile fatty acids (VFAs). For example, after steady-state operation of the anaerobic reactors was achieved, anaerobic pretreatment of a synthetic wastewater containing approximately 10% (as COD) 1,4-dioxane and 90% (as COD) other organic compounds typically resulted in an effluent containing over 90% (as COD) 1,4-dioxane with the remainder being volatile fatty acids (primarily acetic acid) with no measurable 1,4-dioxane removal. To examine competition with significantly greater relative VFA concentrations than in the actual reactor effluents, oxidation of synthetic solutions with equal concentrations (COD basis) of 1,4-dioxane (360 mg/L as COD) and VFAs (360 mg/L as COD) was performed. This represented a

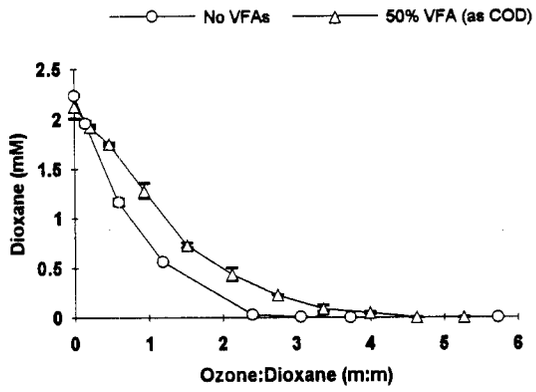

Figure 6. Effect of volatile fatty acids (acetic acid, 70% (as COD), propionic acid, *n*-butyric acid, and isobutyric acid, 10% each (as COD)) on the removal of 1,4-dioxane from solution. Initial solution contained equal COD concentrations of 1,4-dioxane and total VFAs (360 mg/L as COD). Error bars indicate ±2 standard deviations about the mean.

solution with 5 times the VFA concentration relative to 1,4-dioxane as the actual reactor effluent.

The acetic acid:propionic acid:*n*-butyric acid:isobutyric acid ratio was 70:10:10:10 (as COD), and the alkalinity was adjusted to 5.0 mM using sodium bicarbonate. The solution was oxidized with a 0.5 H_2O_2/O_3 molar ratio, and the 1,4-dioxane concentration was measured as a function of oxidant dosage. The results showed that VFAs substantially in excess of the actual relative amounts occurring in the effluents from the anaerobic pretreatment studies resulted in nominally a 50% increase in required oxidant dosage for 1,4-dioxane oxidation (Figure 6). Additional advanced oxidation experiments (not shown) on actual anaerobic reactor effluents were consistent with these results.

Conclusions

The oxidant combination hydrogen peroxide plus ozone was found to be effective at enhancing the biodegradability of 1,4-dioxane by conventional wastewater treatment plant microorganisms. Neither hydrogen peroxide nor ozone alone readily oxidized 1,4-dioxane. The optimum H_2O_2/O_3 molar ratio will depend on economic criteria but may lie in the range of from 0.5 to 1.0 for most wastewaters to be treated. Below this range, less than the stoichiometric amount of hydrogen peroxide is added precluding efficient conversion of ozone to hydroxyl radicals. Above this range, hydrogen peroxide may (1) increase scavenging by hydroxyl radicals while offering no extra oxidation efficiency or (2) cause excessive residual effluent H_2O_2 concentrations.

The results of this research provide estimates of the oxidant dosages for biodegradability enhancement of 1,4-dioxane. The optimum applied total oxidant may correspond to the dosage required to reduce the 1,4-dioxane concentration below the effluent guidelines with further oxidation more economically achieved using conventional biological treatment. An order of magnitude increase in the initial 1,4-dioxane concentrations did not have a significant effect on oxidant dosage requirements per mole of 1,4-dioxane.

Significant competition for oxidants during advanced oxidation was observed from bicarbonate alkalinity and also from SOCs. From the competition studies between 1,4-dioxane and volatile fatty acids, it appears that anaerobic pretreatment of an industrial wastewater containing 1,4-dioxane and other organic constituents may be a viable means of reducing the net chemical oxidant demand. Other AOPs (e.g., UV/O_3, H_2O_2/UV or Fenton's reagent) may also be viable and may offer certain advantages as hydroxyl radical sources for this process and therefore, may merit further study.

Acknowledgments

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