REMOVAL OF 1,4-DIOXANE FROM WASTEWATER

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Summary

Chemical methods were evaluated for the treatment of 1,4-dioxane in industrial process wastewaters. The compound was rapidly oxidized by a combination of hydrogen peroxide and ferrous iron, although the rate of organic carbon removal was considerably slower than the disappearance of 1,4-dioxane from solution. Chlorine oxidation at 75°C was also found to be highly effective. The rate of the reaction was greatest at pH 5.2, suggesting that hypochlorous acid was the preferred oxidant. 1,4-Dioxane appeared to be completely oxidized during chlorination, although the removal of organic carbon was somewhat slower than the disappearance of the parent compound.

Introduction

1,4-Dioxane (1,4-diethylene dioxide) is used for a variety of industrial applications including, as a solvent for cellulosics and a wide range of organic products, a wetting and dispersing agent for textile processing and printing, and as a stabilizer in certain chlorinated solvents. Process waters arising from these operations may contain 1,4-dioxane as a result of spills or through the routine discharge of wastes. Although the levels of 1,4-dioxane present in plant effluents are likely to be low, under certain conditions it may be desirable to pretreat more concentrated process waste streams to remove the compound. However, methods for the removal of 1,4-dioxane from such wastewaters have not been described.

1,4-Dioxane is generally considered to be nonbiodegradable. Results of the biochemical oxygen demand test for 1,4-dioxane indicate that negligible oxygen is consumed over a 20-day test period [1]. Mills and Stack [2] have also noted that degradation of the compound was not observed in cultures of sewage microorganisms exposed for 1 year to wastewater treatment plant effluents adjusted to contain 1,4-dioxane at concentrations ranging from 100 to 900 mg/L. Thus, it appears unlikely that significant removal of 1,4-dioxane will occur in conventional biological treatment systems.

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As an alternative to biological treatment, physical or chemical methods can be considered for the removal of 1,4-dioxane from industrial process wastes. However, in view of the infinite water solubility and low vapor pressure (30 mm at 20°C) [3] of the compound, physical treatment by air-stripping or activated carbon adsorption is not likely to be highly effective. Preliminary studies conducted in our laboratory have indeed confirmed this observation. As a result, the present study was conducted to evaluate chemical methods, including chlorine and hydrogen peroxide oxidation for the treatment of industrial wastewaters containing 1,4-dioxane.

Experimental

The oxidation of 100 mg/L of 1,4-dioxane by hydrogen peroxide in combination with a ferrous iron salt (Fenton's reagent) [4] was examined in aqueous solutions containing 115, 230 and 465 mg/L of H_2O_2. These levels correspond to H_2O_2:dioxane molar ratios of 3:1, 6:1 and 12:1, respectively. Reaction mixtures were prepared by combining the appropriate amount of a 30% H_2O_2 solution with distilled water, and adjusting the pH of the solution to pH 5.5 ± 0.2. Test reaction mixtures were supplemented with 200 mg/L of $FeSO_4:7H_2O$. Control reaction mixtures were prepared as above, except that the ferrous iron was omitted. Solutions (final volume of 200 mL) were transferred to amber bottles and incubated at an ambient temperature (25°C). Reactions were initiated by the addition of 20 mg of 1,4-dioxane (neat). Samples were removed periodically, diluted with an equal volume of 60 mM Na_2SO_3 to quench the reaction, and analyzed as described below.

Chlorine oxidation of 100 mg/L of 1,4-dioxane was initially examined in water solutions containing 1000 mg/L of NaOCl (corresponds to NaOCl:dioxane molar ratio of 12:1). Reaction mixtures were prepared by combining the appropriate amount of a 5% NaOCl solution with distilled water, and adjusting portions of the mixture to a pH of 2, 6 and 11. Test solutions (final volume of 200 mL) were transferred to amber bottles and incubated at an ambient temperature (25°C) or in a water bath at 75°C. Reactions were initiated by the addition of 20 mg of 1,4-dioxane (neat). Samples were removed periodically, diluted with an equal volume of 60 mM Na_2SO_3 to quench the reaction, and analyzed as described below.

The effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine was examined in reaction mixtures prepared using 1.0 M NaH_2PO_4 buffers adjusted to a pH ranging from 5 to 6.5. Portions of the appropriate buffer were transferred to amber bottles and supplemented with 100 mg/L of 1,4-dioxane and 2000 mg/L of NaOCl. Reaction mixtures (final volume of 200 ml each) were incubated in a water bath at 75°C.

1,4-Dioxane was analyzed by gas chromatography by direct injection of aqueous samples. Chromatography was performed using a Hewlett—Packard model 5730 gas chromatograph with a flame ionization detector. The analytical column (glass; 10 ft. × 0.25 in.) was packed with Tenax GC (Supelco,

Inc., Bellefonte, PA). Compounds were eluted from the column isothermally at an oven temperature of 150°C with a helium carrier gas at a flow rate of 30 mL/min. Output of the flame ionization detector was connected to a Hewlett—Packard model 3380 recording integrator. All values were calculated from peak height measurements by comparison with an external standard of 1,4-dioxane prepared in water.

Total organic carbon was determined using either a Beckmann model 915B or Dohrmann model 80 total carbon analyzer. Total organic carbon concentrations were calculated from the difference of the total carbon and inorganic carbon concentrations of a sample. The instruments were calibrated using potassium biphthalate and sodium carbonate as standards.

Results and discussion

1,4-Dioxane was rapidly degraded by a combination of hydrogen peroxide and ferrous iron, as shown in Fig. 1. No degradation was observed in the control. The compound was rapidly oxidized during the first hour in all test solutions; however, the rate of the reaction decreased thereafter in reaction mixtures containing 3 or 6 moles H_2O_2 per mole 1,4-dioxane. Complete removal of the compound occurred within 10 h in test solutions containing 12 moles H_2O_2 per mole 1,4-dioxane. During incubation, the pH of all test solutions rapidly decreased from pH 5.7 to pH 2.9 due to acid formation during the reaction. These conditions are within the optimum range (pH 2.5–4.0) reported for the oxidation of organic compounds by Fenton's reagent [5].
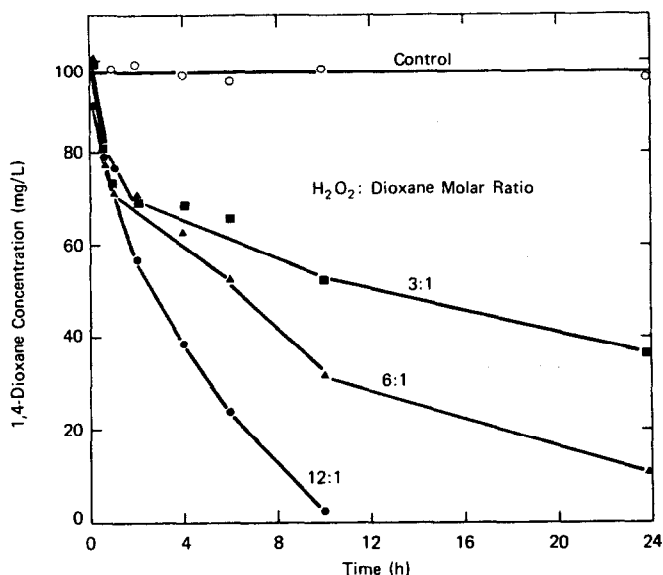

Fig. 1. Oxidation of 1,4-dioxane by a combination of hydrogen peroxide and ferrous iron.
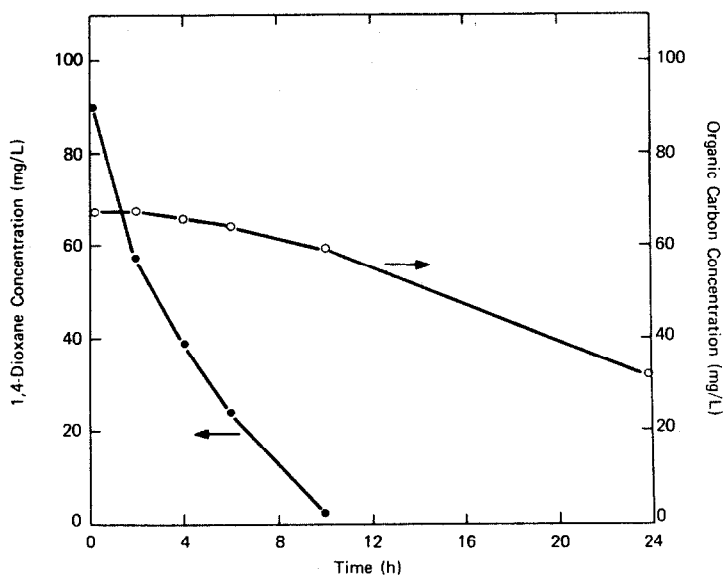
Fig. 2. Removal of 1,4-dioxane and organic carbon during hydrogen peroxide oxidation.

To determine whether 1,4-dioxane was completely oxidized during the reaction, samples of the test solution containing 12 moles H_2O_2 per mole compound were periodically analyzed for the concentration of organic carbon remaining in solution. As shown in Fig. 2, the rate of organic carbon removal was considerably slower than the disappearance of 1,4-dioxane from solution. After 10 h of incubation, removal efficiencies were 97% and 10.5% for 1,4-dioxane and organic carbon, respectively. Following 24 h of incubation, the organic carbon concentration of the reaction mixture was decreased by 48%.

The stoichiometry calculated for the oxidation of 1,4-dioxane,

$$C_4H_8O_2 + 10\ H_2O_2 \rightarrow 4\ CO_2 + 14\ H_2O \tag{1}$$

suggests that 10 mol hydrogen peroxide are required for the complete degradation of 1 mol 1,4-dioxane. While removal of the parent compound occurred rapidly in test solutions containing a 12:1 molar ratio of H_2O_2 to 1,4-dioxane, the oxidation of the residual organic carbon was considerably slower. The incomplete oxidation of organic compounds by a combination of hydrogen peroxide and ferrous iron has been previously described [6], and appears to be due to the formation of low molecular weight organic aldehydes and acids which are resistant to further chemical oxidation. However, such products are known to be readily removed by conventional biological treatment processes.

A series of experiments were also conducted to examine the chlorine oxidation of 1,4-dioxane in aqueous solution. Preliminary studies indicated that the compound was not degraded at 25°C in reaction mixtures prepared at a
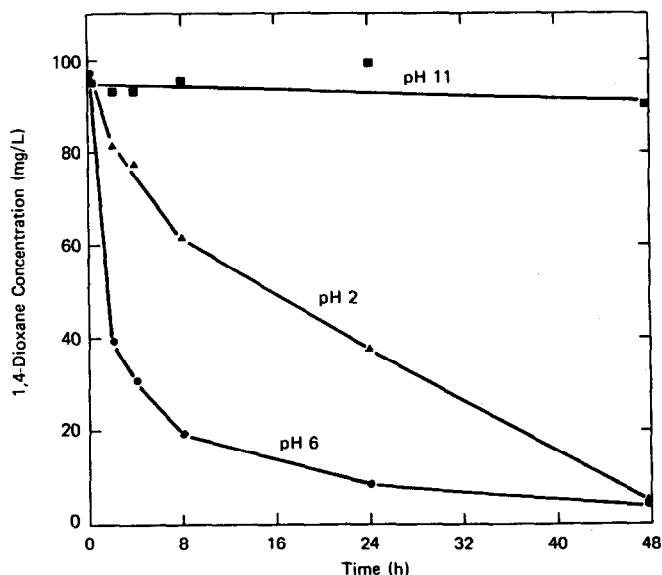
Fig. 3. Chlorine oxidation of 1,4-dioxane in water at 75°C.

pH of 2, 6 or 11. However, when solutions containing 100 mg/L of 1,4-diox-
ane and 1000 mg/L of NaOCl were adjusted to pH 2 or pH 6 and incubated
at 75°C, the compound was rapidly degraded as shown in Fig. 3. The rate of
the reaction at pH 6 changed with time. This was presumably due to a de-
crease in the pH of the solution from pH 6 to pH 2.8 as a result of acid for-
mation during the reaction. The rate of oxidation was negligible in test solu-
tions prepared at pH 11.

The effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine at
75°C was subsequently examined in reaction mixtures prepared using 1.0 M
NaH_2PO_4 buffers over the range from pH 5.2 to 6.5. Results of the study are
shown in Fig. 4. Destruction of 1,4-dioxane at 75°C proceeded rapidly at
pH 5.2, with an initial removal rate of approximately 32.6 mg of 1,4-dioxane
consumed per hour. The rate of oxidation decreased as the pH of the reac-
tion mixture was increased, and was negligible at a pH of 6.5 (see Inset, Fig.
4).

To determine whether 1,4-dioxane was completely oxidized during the
reaction with chlorine, samples of the reaction mixture prepared at pH 5.2
were periodically analyzed for the concentration of organic carbon remain-
ing in solution. As shown in Fig. 5, the rate of organic carbon removal was
somewhat slower than the disappearance of 1,4-dioxane from solution. After
8 h of incubation, removal efficiencies were 97% and 70% for 1,4-dioxane
and organic carbon, respectively. Following 24 h, the organic carbon concen-
tration of the reaction mixture was decreased by 85%.

Chlorine oxidation was found to be highly effective for the removal of
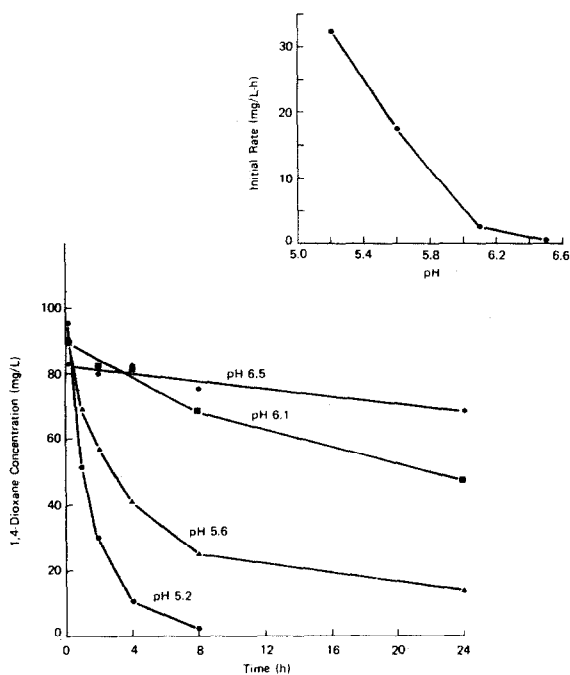1,4-dioxane from water, although the reaction rates were shown to be

Fig. 4. Effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine in 1.0 M NaH$_2$PO$_4$ buffer at 75°C.
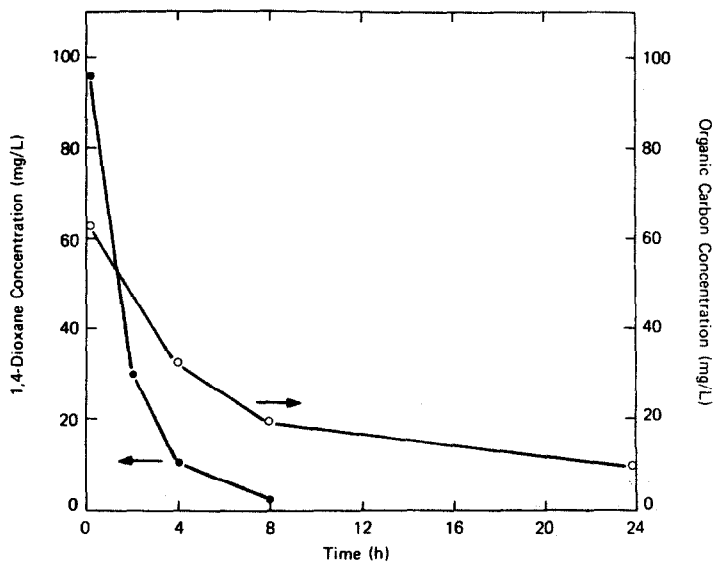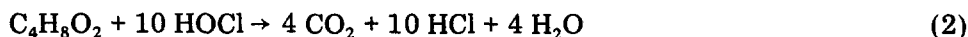

Fig. 5. Removal of 1,4-dioxane and organic carbon during chlorine oxidation chlorination at pH 5.2 at 75°C.

strongly influenced by temperature and pH. The effect of pH is reasonable in view of the chemistry of chlorine [7]. In aqueous solution, chlorine can exist as molecular chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) depending on the pH of the system. Preliminary studies conducted with unbuffered solutions adjusted to pH 2 or pH 6 indicated that molecular chlorine and hypochlorous acid were capable of oxidizing 1,4-dioxane. No reaction was observed with hypochlorite ion at a pH 11. Oxidation of the compound was fastest at pH 6; however, in unbuffered mixtures the rate of the reaction rapidly decreased with time, presumably due to a decrease in the pH of the solution from pH 6 to pH 2.8 as a result of acid formation during the reaction. This observation suggests that hypochlorous acid is the preferred oxidant.

The stoichiometry of the reaction of 1,4-dioxane with hypochlorous acid is given by the following equation:

$$C_4H_8O_2 + 10\ HOCl \rightarrow 4\ CO_2 + 10\ HCl + 4\ H_2O \qquad (2)$$

1,4-Dioxane appeared to be completely oxidized during the reaction, although the removal of organic carbon from solution was not as fast as the disappearance of the parent compound. However, the formation of intermediate degradation products was not detected during gas chromatographic analysis of test solutions for 1,4-dioxane.

In an attempt to optimize the reaction with respect to pH, the oxidation of 1,4-dioxane by chlorine was examined in solutions buffered with $1\ M$ NaH_2PO_4. Note that since phosphate buffers are not highly effective over the range from pH 5 to 6.5 ($pK_a = 7.2$), solutions had to be strongly buffered to prevent changes in pH during the reaction. The rate of the reaction was greatest at pH 5.2, which approximately corresponds to the maximum dissociation of chlorine to hypochlorous acid [7]. Further attempts to study the reaction at lower pH using an acetate buffer system ($pK_a = 4.76$) were unsuccessful due to the competitive reaction of available chlorine with acetate. However, in view of the fact that the rate of the reaction with molecular chlorine at pH 2 (unbuffered reactions) was slower than the reaction with hypochlorous acid at pH 5.2 (buffered solutions), the oxidation of 1,4-dioxane is likely to be optimal under conditions which favor the dissociation of chlorine to hypochlorous acid.

Conclusions

In contrast to biological or physical methods, chemical treatment can be used effectively for the removal of 1,4-dioxane from industrial process wastewaters. Oxidation of the compound by a combination of hydrogen peroxide and ferrous iron occurs within 10 h, and requires greater than a 10-fold molar excess of hydrogen peroxide. Chlorine oxidation of 1,4-dioxane proceeds rapidly at 75°C in the presence of a 12-fold molar excess of hypochlorous acid. The reaction was optimal under conditions favoring the dissociation of chlorine to hypochlorous acid.

References

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