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APPLICATION OF A FLUORINATED SOLVENT TO THE CONVENTIONAL OZONATION PROCESS FOR THE DESTRUCTION OF 2,4-DICHLOROPHENOL

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The removal of 2,4-dichlorophenol from aqueous solution with fluorinated solvent, with ozone, and with fluorinated solvent/ozone combined was investigated. The fluorinated solvent/ozone combined system consists of a chemical extraction from the aqueous phase accompanied by oxidation with ozone in both the solvent and aqueous phase. The results of extraction tests showed that the distribution coefficient decreased with increasing initial pH value of the aqueous phase. The apparent oxidation rate constant of the aqueous ozonation for the initial pH 5.8 was close to that measured of organic phase ozonation. The initial pH value of aqueous phase plays an important role in the fluorinated solvent/ozone combined system for affecting the removal efficiency. The experiment results indicated that 2,4-dichlorophenol was removed at a faster rate at low initial pH value. Although the accumulation of 2,4-dichlorophenol in the organic phase in the fluorinated solvent/ozone combined system was observed under the condition of initial pH 10.0, the overall removal of 2,4-dichlorophenol under the condition of initial pH of 10.0 was close to the condition of initial pH 7.0. Moreover, a comparison test showed that the removal efficiency of 2,4-dichlorophenol by fluorinated solvent/ozone combined system is higher than that by homogeneous phase ozonation or extraction.

INTRODUCTION

Ozone is a powerful oxidant. It is not only capable of sterilizing potable water and municipal wastes, but decomposing many aqueous hazardous organic chemical wastes (Eisenhauer 1968; Glaze 1987; Grasso and Weber Jr. 1988; Harrington and DiGiano 1989; Ferguson et al. 1990). The reaction of ozone with organic compounds has been studied extensively in the development of alternative water or wastewater treatment techniques (Nakagawa et al. 1960; Williamson and Cvetanovic 1968; Hewes and Davison 1971; Rice 1980; Hoigne and Bader 1983a, 1983b; Reckhow et al. 1986; Gurol and Vatistas 1987). A typical contacting system involves bubbling ozonized gas through aqueous solutions containing a hazardous organic. Other systems have been used involving packed columns, jet scrubbers, pressure injectors, and turbine agitated reactors (Langlais et al. 1991). However, the low solubility of ozone in water is a major difficulty associated with these systems. For example, aqueous phase studies indicate that phenolic oxidation is controlled by the ozone mass transfer rather than reaction kinetics (Rice 1981). Another problem is that the process appears to be entirely too energy intensive and expensive to be competitive with alternative treatment processes. In spite of these limitations, the ozonation process remains an attractive prospect for waste treatment and the subject of intense research.

Recent research and development show that gas transfer limitation may be removed if the conventional ozonation process is replaced by combination of ozone with some special kinds of solvent (Stich and Bhattacharyya 1987; Chang and Chen 1993). This process is referred to as two-phase ozonation system. The solvent used in the system was one kind of fluorinated solvents. The fluorinert sol-

vents are produced by a proprietary 3M electrochemical fluorination process and have a unique combination of properties that suit them for specialized applications in the electronics industry. In many cases, the fluorinert liquids can be used as functional alternatives for CFCs due to their stability and inertness.

Basically, the two-phase ozonation system consists of a chemical extraction from the aqueous phase followed by oxidation by ozone in the fluorinated hydrocarbon phase. In a continuing study, a contact flow process is proposed for the removal of organic compounds from water. This process is analogous to the Exxon Donor Solvent (EDS) process for coal liquefaction (Maa et al. 1985) where the solvent is a recirculating hydrogen carrier. In this case the fluorinated solvent is not only a recirculating ozone carrier but also a extractant for organic compounds. Recently, it was reported that the process is indeed feasible for the pretreatment of hazardous organics (Chang and Chen 1994a).

Continuing the study on process design, Stich's process was modified, and a series of experiments were conducted in a stirred reactor on a batch mode (Chang and Chen 1994b). This process consists of a chemical extraction from the aqueous phase accompanied by ozonation in both the aqueous and organic phase. Since ozonation and extraction occur simultaneously in the system, the parameters that affect the extent of extraction/ozonation are worthy of further investigation. For example, the pH value of water phase can affect the partition of an organic solute between water and organic solvent by changing the ionization state of the organic compound (Solomons 1994). On the other hand, the pH can also affect the ozonation by influencing the stability of ozone (Gurol and Singer 1982; Rizzuti et al. 1976; Augugliaro and Rizzuti 1978). At low pH, ozone is relatively stable in water, and it reacts directly with organic material. At high pH, ozone decomposes rapidly to form radicals. For most organic compounds, the radical reaction is several orders of magnitude faster than the direct reaction (Hoigne and Bader 1983b).

Phenols and phenolic compounds are common pollutants of the aquatic system. Many of these materials occur as industrial wastes and direct pollutants in the environment. A number of phenolic compounds, such as 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol, can pose a health hazard and have been designated as priority pollutants by the USEPA (1980). In addition, chlorophenols occur as products in the partial degradation of pesticides. For example, 2,4-dichlorophenol is the hydrolysis product of the widely used herbicide, 2,4-dichlorophenoxy acetic acid (2,4-D).

In this paper, the modified process was used to continue the study and 2,4-dichlorophenol was chosen as a typical pollutant in all our experiments. Since physical extraction and chemical oxidation exist in the process simultaneously, it is of interest to distinguish the independent reaction from the combination. Therefore, this paper presents experimental data for the removal of 2,4-dichlorophenol from aqueous solutions with fluorinert liquid and/or ozone. An important parameter for the determination of solvent extraction efficiency is the distribution coefficient, which describes the partitioning of an organic solute between water and the organic solvent. One of the goals of this study was to measure the pH dependence of the partitioning of 2,4-dichlorophenol between water and fluorinert liquid. In addition, the aqueous and organic phase ozonation were carried out to determine the rate constant. Finally, with respect to the effect of pH value on both the ozone stability and the ionization of organic, the impact of initial pH value of the aqueous phase on the degradation of 2,4-dichlorophenol by the process was examined.

MATERIALS AND METHODS

Materials and apparatus

All solutions were prepared from 18 MΩ/cm resistivity water (Millipore Corp.). 2,4-Dichlorophenol was purchased from R.D.H. Company with 97% purity. The solutions of 2,4-dichlorophenol were prepared by stirring an excess amount of the chemical in water at room temperature. Before measurement, solutions were filtrated with Gelman 0.2 m microfilters to remove the undissolved compound. Then, the amount of 2,4-dichlorophenol dissolved in water was determined by a Gas Chromatograph. More dilute solutions were obtained by mixing a stock solution with water. The solution pH was adjusted with NaOH or H$_2$SO$_4$. The fluorinated solvent used in the experiments was an immiscible fluorinated hydrocarbon manufactured by 3M Company. Table 1 contains pertinent physical properties of the solvent, which is designated as FC77.

Table 1. FC77 solvent properties.

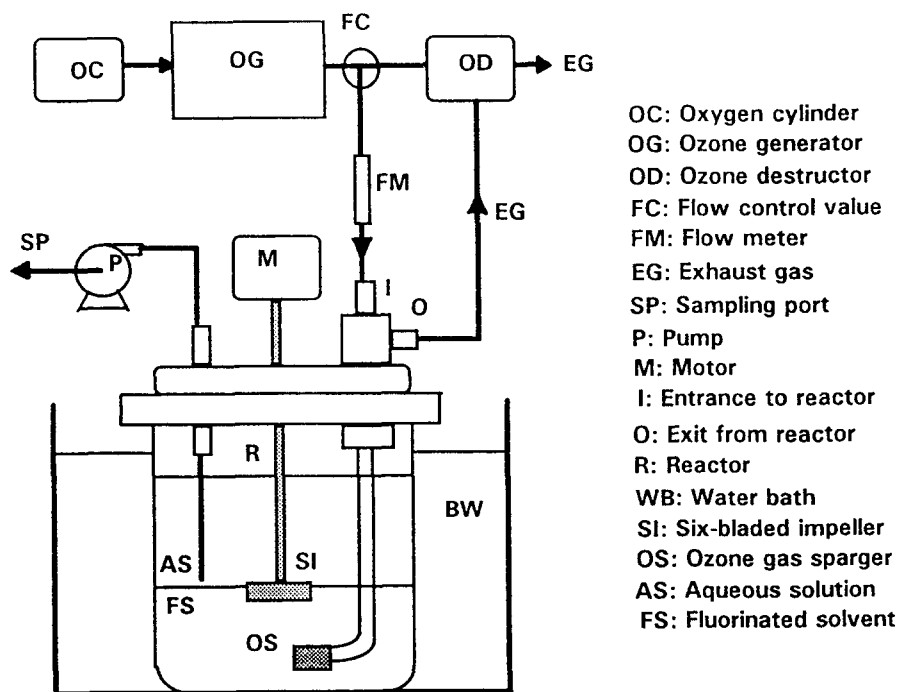| Boiling point	97 °C
Thermal stability	270 °C
Specific gravity	1.78
Vapor pressure at 25°C	42 mm Hg
Avg. molecular weight	415

Fig. 1. Test apparatus.

Three kinds of experiments were performed: the removal of 2,4-dichlorophenol from aqueous solution with fluorinated solvent, with ozone, and with fluorinated solvent/ozone combined. For extraction, the distribution coefficient of 2,4-dichlorophenol was determined by batch test using a 16 ml Pyrex glass tube. The reactor used in the experiments involving ozonolysis was a cylindrical agitated glass vessel as shown in Fig. 1. The vessel had an inside diameter of 11 cm and contained three submerged baffles and a six flat bladed stirrer (7 cm in diameter) for the agitation. The reactor was submerged into a constant-temperature water bath in which the temperature could be controlled to within ±0.5°C. Ozone was produced from oxygen with a high-voltage discharge ozone generator and introduced to the reactor via Teflon tubing at the bottom of the reactor.

Procedures

Batch extraction was conducted in a 16 mL Pyrex glass tube at ambient laboratory temperature in the absence of light with no head space. All tests were performed at solvent-to-water ratio of 1:1. The tubes were tightly sealed and were shaken at 200 rpm for 24 h. At the final equilibrium state, a sample of aqueous phase was withdrawn and analyzed by gas chromatography.

In order to find the apparent oxidation rate constant and removal efficiency in the aqueous and organic phase, experiments were conducted in a homogeneous phase. To start a run, 1000 mL of fluorinated solvent or aqueous solution containing 2,4-dichlorophenol of known concentration were introduced into the reactor. The stirrer was driven at 1000 rpm by a motor, and the reaction was then started by introducing ozone. During the reaction, an aliquot sample (2 mL) was withdrawn from the reaction solution at a chosen time.

For fluorinated solvent/ozone combined system, 500 mL of clean fluorinated solvent was inititally introduced into the reactor; 500 mL of aqueous solution containing 2,4-dichlorophenol of known concentration were then added carefully along the sides of the reactor, so the aqueous solution was not dispersed into the organic phase. The stirrer was driven at 1000 rpm by a motor and the reaction was then started by introducing ozone. During the reaction, an aliquot sample (5 mL) was withdrawn from the reaction solution at a chosen time. Since the fluorinated solvent was insoluble in water, separation was quick and complete. After equilibrium state of separation was achieved, both the two layers were sucked off by using a 2 mL pipette.

The ozone produced rate was maintained at 50 mg/min, and the ozone gas flow rate was maintained at 0.6 L/min by means of a flow controller for all experiments of this study.

Analysis

2,4-Dichlorophenol samples were extracted by methanol and analyzed by Gas Chromatograph (Hewlett-Packard HP 5890 II) with FID detection. HP-1 GC column was used (0.53 mm i.d. 10 m long).
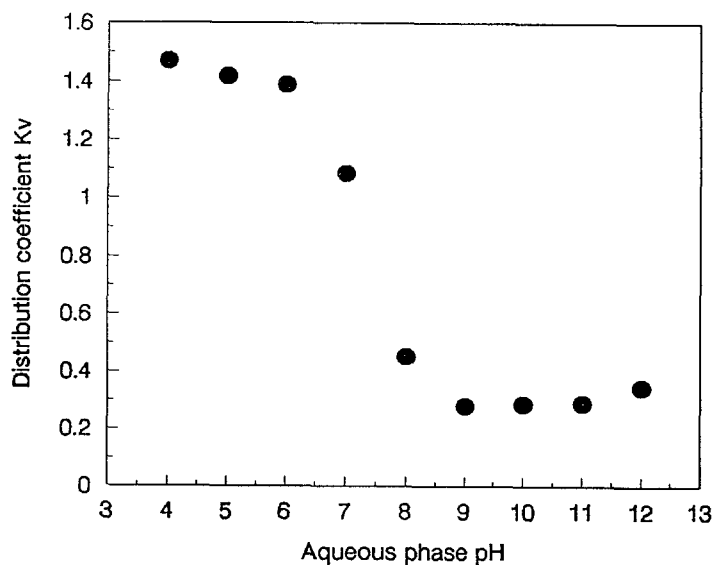
Fig. 2. Distribution coefficient for 2,4-dichlorophenol between fluorinated solvent and water as a function of pH.

RESULTS

The main criterion for a suitable solvent extraction process is the distribution coefficient for the solute in the solvent. The distributions of 2,4-dichlorophenol between water and fluorinated solvent were determined for various initial pH values of the aqueous phase. Figure 2 shows the variation of distribution coefficient of 2,4-dichlorophenol over the range of pH 4.0 to 12.0. The distribution coefficient increases at low side of pH range and approaches a maximum value of 1.47 at a pH of 4.0.

Homogeneous phase ozonation was carried out to determine the apparent oxidation rate constant in the aqueous and organic phase. The reaction of ozone with phenolic compound has been expressed as a second order reaction (Langlais et al. 1991):

$$r = k_1 C_A [O_3] \quad (1)$$

r = rate of reaction of phenolic compound per unit volume
k_1 = reaction rate constant
C_A = liquid phase concentration of phenolic compound
O_3 = liquid phase concentration of ozone

Under conditions of excess O_3, the reaction is assumed to be pseudo-first order, thus Eq. 1 reduces to:

$$r = k_2 C_A \quad (2)$$

To apply this concept to the observed data, the pseudo-first-order kinetic rate constant of the aqueous ozonation was determined from the slope of the straight lines obtained by plotting the ratios of the remaining concentration to the initial concentration on logarithmic scale. From a linear regression of experimental data as shown in

Fig. 3, the rate constant of aqueous ozonation was 9.4 x 10^{-4} min^{-1}. In a similar way, the rate constant of organic phase ozonation was 1.07 x 10^{-3} min^{-1}.

Figure 4 shows the effect of the initial pH value on the overall degradation of 2,4-dichlorophenol by fluorinated solvent/ozone combined system. The results show that 2,4-dichlorophenol is removed at a faster rate at pH 5.8. The concentration profiles of 2,4-dichlorophenol in the aqueous phase and organic phase during the reaction are shown in Fig. 5 and Fig. 6. In the aqueous phase, the least amount of 2,4-dichlorophenol oxidation resulted from an initial pH of 7.0. However, the accumulation of 2,4-dichlorophenol in the organic phase was observed under the condition of initial pH 10.0.

The result of a comparison of the fluorinated solvent/ozone combined system and the homogeneous phase ozonation for the removal of 2,4-dichlorophenol is depicted in Fig. 7. All the experiments were carried out at the initial pH of 5.8. It clearly indicates the superiority of the fluorinated solvent/ozone combined system as compared with the homogeneous phase ozonation.

DISCUSSION

The pH effect on the distribution coefficient

The effect of pH on the distribution coefficient is linked to the solvation characteristics of water. Since 2,4-dichlorophenol is a polar molecule, it forms hydrogen bonds with the water molecules. The water molecules surround the organic molecule because of the strong polar interaction. However, at low pH, the abundance of hydrogen ions causes the water molecules to congregate near these ions. Because the cations are more strongly hydrated than the neutral organic molecule, the organic
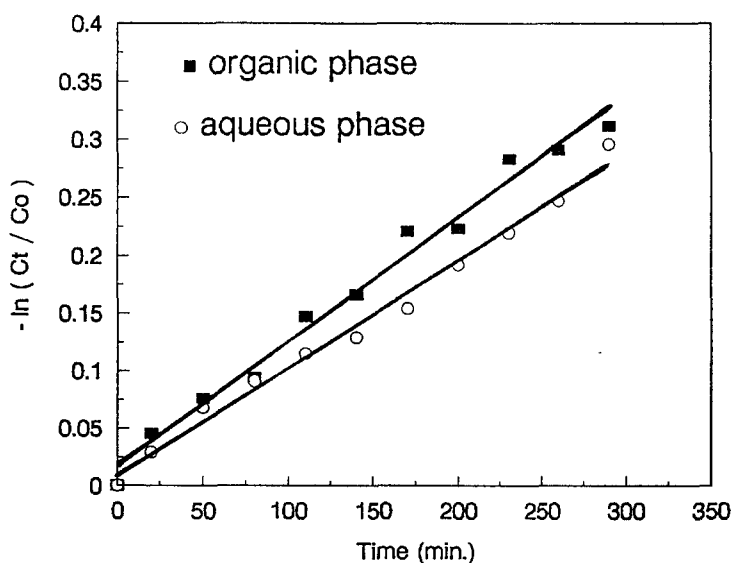
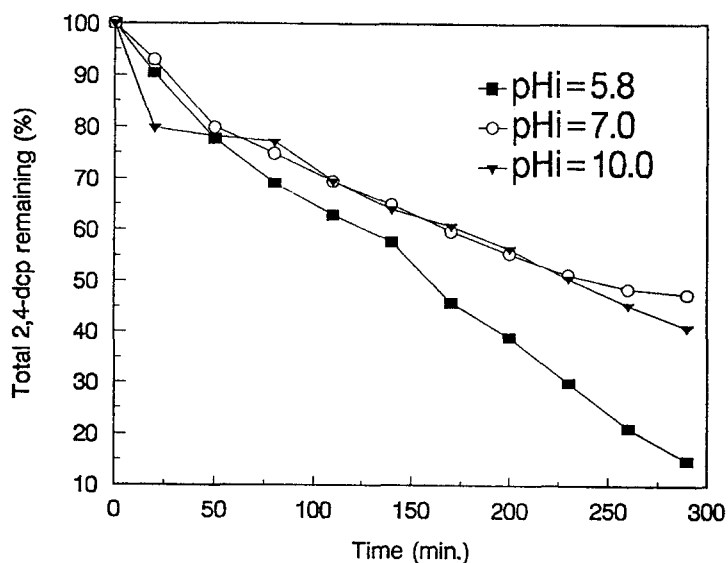Fig. 3. Pseudo-first-order kinetics of 2,4-dichlorophenol ozonation.

Fig. 4. The effect of initial pH on the overall degradation of 2,4-dichlorophenol.

compound becomes less hydrated and thus, it is more freely available to move into the fluorinated solvent.

Greminger et al. (1982) have reported K_V values for phenol, dihydric phenols, and trihydric phenols in MIBK and DIPE as a function of pH. Their data show that at high pH, K_V values are low, primarily due to the existence of phenolate ions.

The solvent commonly used for extraction of phenol and phenolic compounds from wastewater are di-iso-propyl ether and n-butyl acetate. The distribution coefficients for 2,4-dichlorophenol are 351 and 580, respec-

tively. Several alternative solvents and distribution coefficients for 2,4-dichlorophenol are presented in Table 2 (Hwang 1981). It is obvious that polar solvents are better than nonpolar hydrocarbons, and these values are higher than those found in this work. From the standpoint of the distribution coefficient, using the fluorinated solvent as the 2,4-dichlorophenol extractant is not a good choice. However, other properties of the fluorinated solvent such as high specific gravity and low mutual solubility with water are favorable for the fluorinated solvent/ozone combined system.
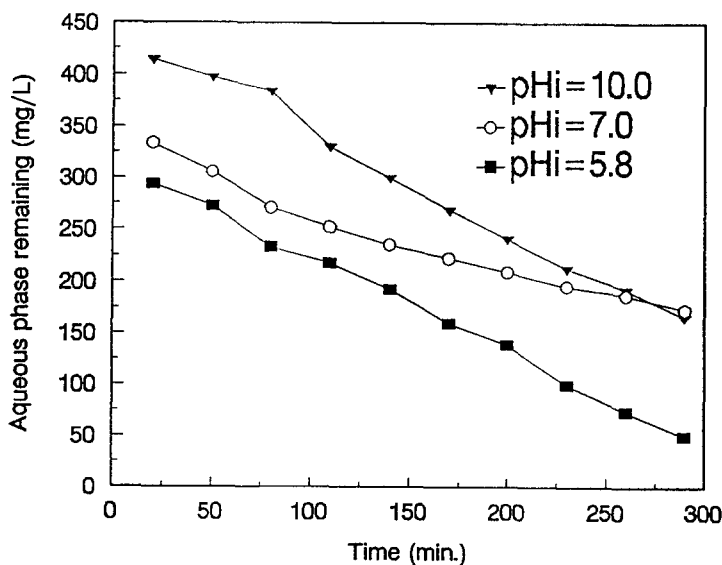
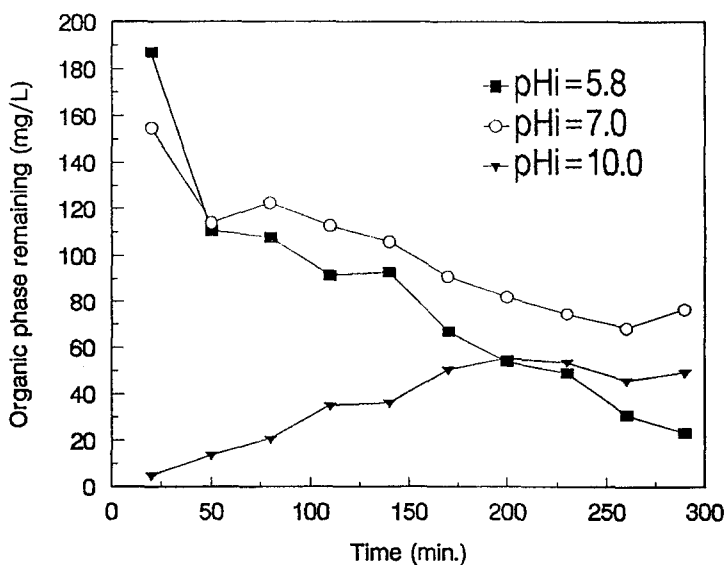Fig. 5. The concentration profiles of 2,4-dichlorophenol in the aqueous phase.

Fig. 6. The concentration profiles of 2,4-dichlorophenol in the organic phase.

Comparison of oxidation rate constants in different homogeneous phases

Several investigators have demonstrated the effect of pH on the chemistry of ozone in water (Gurol and Singer 1982; Rizzuti et al. 1976; Augugliaro and Rizzuti 1978). At high pH, ozone decomposes rapidly to form radicals (R-reaction). At low pH, ozone is relatively stable in water, and it reacts directly with organic material (D-reaction). However, the analysis of data of the aqueous ozonation for the initial pH 5.8 led to a rate value which was close to that measured of organic phase ozonation. It is suggested that the D-reaction mechanism is predominant when the ozonation occurs in the fluorinated solvent.

Table 2. Distribution coefficients (Kv) of 2,4-dichlorophenol in various solvents.

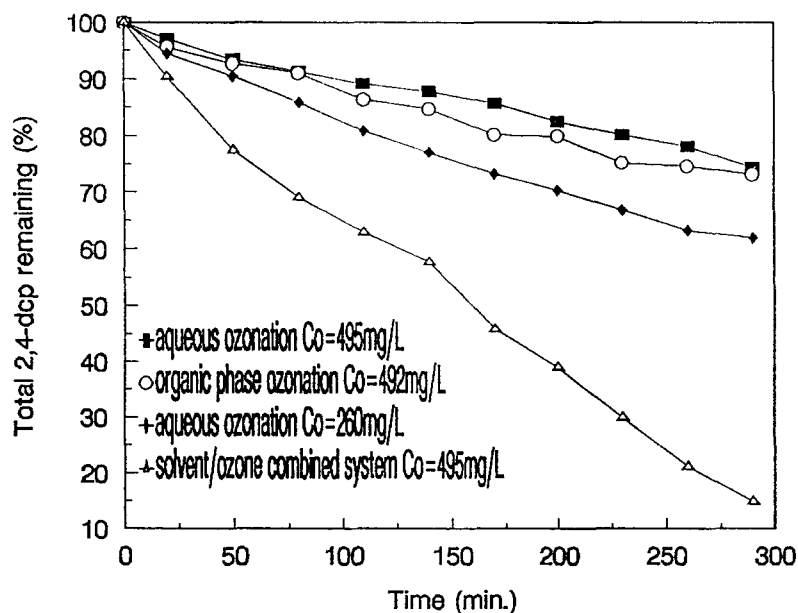| solvents	Kv
MIBK	1080
Benzene	46
Isobutane	3
n-butyl acetate	580
di-isopropyl ether	351
Octanol	562

Fig. 7. Comparison of the solvent/ozone combined system and the single-phase ozonation for the removal of 2,4-dichlorophenol.

Effect of the initial pH value of the aqueous phase

From the observation of Fig. 4, the overall removal of 2,4-dichlorophenol under the condition of the initial pH of 10.0 is close to the condition of the initial pH of 7.0. It should be noted that the distribution coefficient decreasing with the increasing of the initial pH value of the aqueous phase has been presented in our study. So, this result indicates that the overall removal rate of 2,4-dichlorophenol due to oxidation for initial pH of 10.0 is larger than that of the initial pH of 7.0 in the fluorinated solvent/ozone combined system. Otherwise, it is clear that the aqueous removal rate of 2,4-dichlorophenol due to oxidation for initial pH of 10.0 is larger than that of the initial pH of 7.0 in the fluorinated solvent/ozone combined system, as shown in Fig. 5. This observation is in agreement with reports by other authors (Hoigne and Bader 1983b; Hoigne and Bader 1979; Augugliaro and Rizzuti 1978); the increase of the removal rate of organic compounds with pH can be due to either the action of hydroxyl radicals coming from the ozone decomposition (R-reaction) or to the presence of the dissociated form of organic compounds which react with electrophilic agents, such as ozone, faster than its nondissociated form. In fact, the pseudo-first-order kinetic rate constant of aqueous oxidation in the fluorinated solvent/ozone combined system for the initial pH of 10.0 is 3.5 x 10^{-3} min^{-1} and for the initial pH of 7.0 is 2.3 x 10^{-3} min^{-1}. Therefore, the improvement in the removal rate of 2,4-dichlorophenol at a higher pH can be due to the higher ozone absorption efficiency caused by the fast decomposition of ozone

accelerated by phenolate ions. Furthermore, the accumulation of 2,4-dichlorophenol in the organic phase during the reaction was observed under the condition of the initial pH of 10.0. The disappearance of 2,4-dichlorophenol at the initial pH value of 10.0 is mainly due to the oxidation occurring in the aqueous phase rather than that occurring in the organic phase. Summarizing these findings indicates that the efficiency of ozone absorption in the aqueous phase under a high initial pH value condition is higher than that in the organic phase and the oxidation reaction is not predominant in the organic phase during the reaction.

CONCLUSIONS

An innovative extraction/ozonation system for the destruction of organic was investigated. The immiscible fluorinated solvent, inert and highly ozone soluble, was used as the solvent in the extraction/ozonation system. From the standpoint of extractability, the fluorinated solvent is not a good choice as 2,4-dichlorophenol extractant. On the other hand, the result of homogeneous phase ozonation shows that the fluorinated solvent is also not superior to water as an oxidation medium. However, it clearly indicates the superiority of the fluorinert liquid/ozone combined system as compared with the homogeneous phase ozonation. The combination of extraction and oxidation can enhance the removal rate of 2,4-dichlorophenol. Otherwise, the fluorinated solvent, because of its nonpolar characteristic, might play a role in the selective oxidation of ozone during the fluorinated

solvent/ozone combined system. In other words, it is hypothesized that the intermediate oxidation products of 2,4-dichlorophenol often include highly polar acids which diffuse back to the aqueous phase due to their high solubility. This will enhance the oxidation rate of 2,4-dichlorophenol in the fluorinated liquid. Future studies should be conducted to test this hypothesis.

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