Use of organic solution for the removal of hazardous chemicals: the more efficient and zero-emission decomposition processes by extraction, concentration and reaction in organic solutions

M. Okada, Y. Nakano, K. Ohkawa, T.Y. Tsai and W. Nishijima
Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University,
1–4–1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan
(E-mail: mokada@hiroshima-u.ac.jp)

Abstract
We proposed a new process for ozone decomposition of hazardous chemicals in organic solution concentrated from water into the solution by using adsorbent or air-stripping. The target compounds studied were chlorophenols and TCE. Chlorophenols were adsorbed from water and desorbed into organic solutions like acetic acid by GAC and synthetics adsorbents, SP850 and SP207. The best adsorbent both for adsorption and desorption into acetic acid solution was synthetics one, SP850, and percent desorption was 100%. GAC was good for adsorption, but was not for desorption. Although more than 800 mg-TCE L⁻¹ in acetic acid solution was decomposed by ozonation, little decrease in the decomposition rate was noted indicating that acetic acid can be reused for the next step of ozonation in the same acetic acid solution.

Keywords Ozonation; trichloroethylene; chlorophenols; GAC; synthetic adsorbent; acetic acid

Introduction
Contamination of water and soil by hazardous organic chemicals has become a major environmental concern in recent years (Morioka, 1996; Yamamoto et al., 2001). The most common groundwater contaminants in Japan are trichloroethylene (TCE) and tetrachloroethylene (PCE). In case of landfill leachate, chlorophenols and bisphenols are frequently detected. Removals of these chemicals from contaminated waters are urgent needs.

Activated carbon adsorption is the most common process to remove these contaminants from groundwater and landfill leachates (Imamura, 1999; Oba, 1997; Shishida et al. 1999). However, activated carbon saturated with the contaminants is generally incinerated as an industrial solid waste or dumped into landfill sites (Miyake, 1997). Most of contaminants are thermally decomposed, whereas reuse of the activated carbon is impossible. Also, it was pointed out that hydrochloric gas produced by the decomposition of chlorinated organics may damage incinerator (Urano et al. 1998).

Decomposition of organic chemicals by ozonation is one of the most promising processes in water and wastewater treatments (Hoigné et al. 1983a,b; Shishida et al. 1999). Ozonation has been used for the removal of odorous compounds, hazardous chemicals like pesticides and chlorinated organic carbons (Kim et al., 1997). For wastewater treatment, ozonation is also common for the removal of color and dissolved organic substances (Rice et al., 1997; Churchley et al., 1998). Many studies on ozonation have been carried out to remove dissolved organic substances. However, concentrations of most organic chemicals are very low and lower than the concentrations of ozone scavengers like natural organic matter (NOM) and CO₂. The ozonation in water, therefore, is not necessarily an efficient process.
Most hazardous chemicals in water such as pesticides, polycyclic aromatic hydrocarbons, TCE and PCE (Morioka, 1996) are hydrophobic. It is easy, therefore, to separate these substances by extraction using organic solvents directly from water or from activated carbon after adsorbed on it from water. The separated and concentrated chemicals in the solvents might be decomposed by ozonation more efficiently than in water. Also, formations of ozonation by-products in water can be avoided (Neta, et al. 1983; Lawrence et al., 1980). Although it is necessary to select an appropriate organic solution inert with ozone, many organic solutions are known not to react with ozone (Hoigne, et al. 1983a, b).

Here in this study, we propose a new system for the removal of hazardous chemicals from water by (1) adsorption and concentration of chemicals onto activated carbon or synthetic adsorbents, (2) desorption of the chemicals from the adsorbent to organic solution, and (3) ozone decomposition of the contaminant in the organic solution. Both the organic solution and activated carbon are recycled for the following treatments. In case of volatile chemicals like TCE, the process is operated by (1) separation of the chemicals by air stripping, (2) concentration of gaseous chemicals by absorption into organic solution, and (3) ozone decomposition of the chemicals in the organic solution. The organic solution is recycled for the following treatments.

The process has the following advantages over the conventional processes:
(1) the rate of ozone decomposition for concentrated chemicals is higher than that in water with low concentration,
(2) ozone is not consumed by ozone scavengers in water,
(3) ozonation by-products do not contaminate water, and
(4) zero-emission system; organic solution and activated carbon can be regenerated and recycled.

The purpose of this study is to provide basic information and demonstrate possibility of the process mentioned above by chlorophenols and TCE as target chemicals. The most appropriate organic solution and adsorbent were selected based on adsorption and desorption characteristics for the adsorbent-solution system was evaluated. Also, the rate of ozone decomposition of the chemicals in the organic solution was evaluated.

Materials and methods
Adsorption/desorption of chlorophenols
Chlorophenols used in this study are p-chlorophenol (p-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP). Adsorption capacities from water of granular activated carbon (GAC, Calgon F400, diameter = 1.0–1.4 mm) and synthetic adsorbents (styrene-divinylbenzene polymer (SP850 and SP207), Mitsubishi Chemical) were evaluated for chlorophenols. Characteristic features of the adsorbents are shown in Table 1. Organic solutions used for this study are acetonitrile and acetic acid solution based on the following ozonation study in organic solutions. Adsorption isotherm was estimated following to the standard procedure in Japan Industrial Standards (JIS K 1474, 1991).

Desorption of chlorophenols from the adsorbents to organic solution was evaluated. Prior to desorption, absorbent was preloaded with 3.0 mg g⁻¹ of chlorophenol. One gram of the absorbent was placed in a 20 ml vial filled with 20ml of 150 mg L⁻¹ chlorophenol aqueous solution. After sealed with a butyl rubber septum and an aluminium cap, it was shaken at 120 rpm at 20 ±0.5°C. One gram of the adsorbent preloaded with 3.0 mg g⁻¹ of chlorophenols was placed in a 100 ml vial filled with 100 ml of organic solution. After sealing with a butyl rubber septum and an aluminium cap, it was shaken at 120 rpm in 20 ± 0.5°C. Equilibrium concentrations of chlorophenols after desorption were determined in 24 hours.
The organic solvents used for ozonation of chlorophenols were acetic acid, acetone, methyl acetate and acetonitrile. They have low reactivity with ozone and relatively low toxicity. Two hundred millilitres of the solution was placed in a 200 ml Erlenmeyer flask and added with chlorophenol to have initial concentration of 30 mg l–1. Ten milligrams O3 L–1 of ozonated air (Fuji Electric, POX-10) was continuously fed into the solution at a flow rate of 0.2 l min–1 and the change in the concentration of the chlorophenol was monitored. Reaction temperature was controlled at 20±0.5°C.

Organic solutions used for the ozonation of TCE were acetic acid, acetone and methyl acetate. One hundred and fifty ml of each organic solution was added into two 160 mL vial bottles. Ozonated air of 20 mg O3 L–1 was fed into these vials at a flow rate of 500 mL min–1 for 15 min. The one was used to determine initial ozone concentration in the solution and the other was used to study the decomposition of TCE. TCE was added into the vial after the ozonation to give the initial TCE concentration of 5.0 mg L–1. The vial was sealed with a Teflon coated butyl rubber septum and incubated at 20±0.5°C. To determine residual TCE concentration during ozonation, an aliquot of 50 µL was sampled from the vial and was added into a 20 mL of 1 mg L–1 Na2SO3 solution in a 20 ml vial to quench ozone. Residual ozone in the solvent was also determined at the end of experiment.

The effect of ozone concentration on TCE decomposition in acetic acid solution was also evaluated. The ozone concentration ranged from 20 to 200 mg L–1. The initial TCE concentration was 200 mg L–1.

**Analytical procedure**

Chlorophenols were determined by HPLC (JASCO LC-2000 plus, ZORBAX SB-C18) equipped with UV detector (wave length = 280 nm). TCE concentration was determined according to the headspace method (JIS K 0125, 1987) using a gas chromatography with an electron capture detector (Shimazu GC-14B). The iodometric method (APHA-AWWA-WPCF, 1985) was used to determine ozone concentration in feed and exhaust gas and in the solvents. Although these analytical procedures were developed for water analysis, we confirmed that all of them could be applied to the analyses in organic solutions.

**Results and discussions**

**Adsorption of chlorophenols onto GAC and synthetic adsorbents and desorption by organic solutions**

Chlorophenols can be removed from landfill leachate by adsorption. They must be desorbed into organic solution to decompose by ozonation and regenerate the adsorbent. The adsorbent should have high adsorption capacity for chlorophenols and organic solution should desorb almost all the adsorbed chlorophenols. Figure 1 shows the Freundlich adsorption isotherm for GAC, SP850 and SP207 on 2,4,5-TCP in distilled water. Adsorption of 2,4,5-TCP other chlorophenols (not shown here) in distilled water onto GAC, SP850 and SP207 followed the Freundlich adsorption isotherm. Constants for the Freundlich adsorption isotherm for GAC, SP850 and SP207 are shown in Table 2. K values for GAC were from 4 to 5 times as high as those for SP850 and SP207 indicating the higher capacity for the removal of chlorophenols from water.
The percent desorption of chlorophenols by acetic acid solution from GAC, SP850 and SP207 preloaded with 3.0 mg g\(^{-1}\) of chlorophenols are shown in Figure 2. SP850 and SP207 were better than GAC in terms of desorption of chlorophenols by acetic acid solution. Especially, the percent desorption from GAC decreased with the increase in chlorine in chlorophenols. Similar results were also obtained for other organic solutions (not shown here). It is likely that chlorophenols were chemically adsorbed onto GAC. It was reported that chlorophenols adsorbed onto Sep-Pac C18 (a carbonaceous adsorbent) under pH 3 could be desorbed more than those adsorbed under pH 7 because chlorophenols in pH 7 were chemically adsorbed after dissociation (Nishikawa, et al. 1990). In contrast to GAC, the synthetic adsorbent (SP850 and SP207) are known to adsorb chlorophenols physically, because the absorbent does not have carboxyl and phenolic groups on the surface and does not react chemically with chlorophenols. Therefore, they could desorb almost all the chlorophenols into organic solutions (Shimizu, 1993).

The amount of adsorption for 2,4,5-TCP by GAC, SP850 and SP207 were 300 mg g\(^{-1}\), 100 mg g\(^{-1}\) and 70 mg g\(^{-1}\), respectively under equilibrium concentration of 5 mg L\(^{-1}\) in water. GAC had the largest adsorption capacity. However, the amount of recovery were 39 mg g\(^{-1}\), 100 mg g\(^{-1}\) and 70 mg g\(^{-1}\), respectively for GAC, SP850 and SP207 taking the percent desorption by acetic acid solution, i.e. 13% for GAC and 100% both for SP850 and SP207. Therefore, the best adsorbent from water is not necessarily the best adsorbent for desorption into organic solutions. SP850 and SP207 seem to be the better adsorbent than
GAC for this system. Although more studies are necessary to select appropriate adsorbent, it was possible to remove hazardous chemicals from water onto adsorbent and desorb and concentrate into organic solution and regenerate the adsorbent.

**Ozonation of chlorophenols in organic solutions**

Decomposition of 2,4,5-TCP in organic solutions by ozonation is shown in Figure 3. All the decomposition processes followed the first-order reaction kinetics including other chlorophenols not shown in the figure. Acetic acid and methyl acetate solutions showed larger decomposition rates than water in case of 2,4,5-TCP. The first-order reaction constants are summarized in Table 3. Although the decomposition rates of p-CP and 2,4-DCP in organic solutions were lower than those in distilled water, it was possible to decompose these chemicals in organic solutions by ozonation. The fact that the decomposition rates followed the first order reaction kinetics suggests that the concentrated chlorophenols in organic solutions could be decomposed more efficiently than those in water. Acetic acid solution was the best among all the solutions tested including distilled water.

**Ozonation of TCE in organic solutions**

The most common practice for the removal of TCE from groundwater is air stripping followed by GAC adsorption (Imamura, 1999). However, the GAC saturated by TCE must be treated or landfilled properly. If we use organic solution, the air-stripped TCE can be absorbed directly into organic solution without the use of GAC and, therefore, regeneration and/or disposal of GAC are not necessary.

Figure 4 shows ozone decomposition of TCE in organic solutions. Decomposition of TCE also followed to the first order kinetics in all the organic solutions tested. Different from chlorophenols, decomposition rates in the organic solutions were larger than that in water. Especially, the rate constant in acetic acid solution was 5.6 times as high as that in water.

Figure 5 shows effects of dissolved ozone concentration on the reaction constants of TCE in acetic acid solution. The rate constants increased in proportion to the increase in the ozone concentration. The saturated ozone concentrations in acetic acid solution and distilled water by 150 mg L$^{-1}$ of ozonated air were 205 mg L$^{-1}$ and 26 mg L$^{-1}$, respectively.
The ozone concentration in acetic acid solution was 8 times as high as that in water. Therefore, the rate of ozone decomposition in acetic acid solutions is larger than that in water. Figure 6 shows comparison of the rate constants between acetic acid solution and water. The rate constant in acetic acid solution was 60 times as large as that in water due to the higher ozone concentration and reaction rate. Figure 7 shows the rate constant as affected by the progress of TCE decomposition in acetic acid solution. Although more than 800 mg-TCE L⁻¹ in acetic acid solution was decomposed by ozonation, little decrease in the rate constant was noted during decomposition indicating that acetic acid can be reused for the next step of ozonation in the same acetic acid solution.

**Conclusion**

A new process was proposed for the separation and concentration of hazardous chemicals from water into organic solution by adsorbent or air stripping followed by ozone decomposition in the same solution. The target compounds studied were chlorophenols and TCE. This study demonstrated the high efficiency of the proposed process with recycling uses of adsorbent and organic solution.
1. Chlorophenols were adsorbed from water and desorbed into organic solutions like acetic acid by GAC and synthetics adsorbents, SP850 and SP207. The best adsorbent both for adsorption and desorption was SP850. Although GAC was good for adsorption, it was not good for desorption.

2. Both chlorophenols and TCE were decomposed by ozonation in organic solutions. The largest decomposition rate was noted in acetic acid solution. The rate increased in proportion to ozone concentration. Both the high concentration of ozone and the high rate of reaction showed very high (more than 60 times) decomposition rate of TCE in acetic acid solution than in water.

3. Although more than 800 mg-TCE L\(^{-1}\) in acetic acid solution was decomposed by ozonation, little decrease in the decomposition rate was noted. Acetic acid can be reused for another step of ozonation in the same acetic acid solution.

References


