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RADIATION TREATMENT OF CHLORINATED ETHYLENES

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Introduction

The pollution of groundwater with chlorinated ethylenes is becoming a serious problem in industrialized areas of Korea. As a result, the government limited trichloroethylene (TCE) and perchloroethylene (PCE) concentrations in groundwater to less than 30 and 10 ppb, respectively, since 1993. However, the contamination of groundwater with these pollutants did not decreased due to increasing industrialization and poor groundwater conservation. Thus, many techniques have been proposed for the reclamation of groundwater. Among them, adsorption onto activated carbon and air-stripping are found to be efficient and economic, however, they just remove the contaminants but do not decompose them.¹

An attractive solution of TCE and PCE pollution is radiation-induced decomposition. The organic pollutants can be completely decomposed by gamma-rays or electron-beam irradiation, and the decomposition is more efficient in the presence of ozone.²⁻⁴ In this system, ozone has been known to accelerates the gamma-ray decomposition of TCE and PCE by the action as an additional hydroxyl radical source. However, there is no report that directly proves this enhancement of hydroxyl radical production by ozone. Thus, in this work, the enhancement of TCE and PCE decomposition by ozone in radiation treatment was investigated and the role of ozone was evaluated by an electron paramagnetic resonance (EPR) spectroscopy and spin-trapping technique. The EPR/spin-trapping method is known to be a sensitive and selective technique to detect unstable hydroxyl radicals.⁵ The effect of catalysts such as TiO_2 on the gamma-ray decomposition of TCE and PCE was also investigated because there are few reports that evaluate the catalytic mechanism of TiO_2 in radiation treatment while the mechanism is clearly characterized in photocatalytic oxidation processes using UV or visible light.

Methods and Materials

Pollutant stock solutions (about 100 mg/l) were prepared by dissolving spectrophotometric grade 99.5 % TCE and 99 % PCE (Aldrich) in distilled and deionized water (DD water). Ozone-saturated water (OS water) was made by bubbling ozone through DD water, which was prepared

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from pure dioxygen using a laboratory ozonizer (Won Jeon Technical Development Co. Ltd., Korea). An Al-TiO₂ catalyst was made using a sol-gel method described in detail elsewhere⁶ and calcined at 700 °C. The Al content in TiO₂ was around 0.05 w/w %. For the decomposition of TCE and PCE, irradiation was performed at room temperature (around 20 °C) in a ⁶⁰Co source (Paranomic, UK). The radioactivity of the source is about 270 Ci. Irradiation samples were prepared in 120 ml glass bottles with the pollutant stock solutions in DD water (γ -rays alone) or in OS water (γ -rays/O₃). For irradiation combined with O₃ and TiO₂ (γ -rays/O₃/TiO₂), the Al-TiO₂ powder was suspended into the γ -ray/O₃ samples. The irradiation bottles were filled up to zero-headspace in order to minimize air contamination. After irradiation, residual TCE and PCE contents were measured by a Younglin M600D (Korea) gas chromatograph that is equipped with an electron capture detector. The column used was a 30-m DB-624 from J & W.

For the determination of hydroxyl radicals, a spin-trapping reagent DMPO (5,5-dimethylpyrroline-N-oxide) from Aldrich was used. The γ -rays alone, γ -rays/O₃ and γ -rays/O₃/TiO₂ samples were mixed with DMPO in phosphate buffer (0.1 M, pH 7.4) just before gamma-irradiation. Irradiation was performed at room temperature in the low-level ⁶⁰Co source. Immediately after irradiation, around 25 μ l of the sample solution was transferred into a capillary tube, and EPR spectra were recorded in the X-band on a Bruker EMX spectrometer at room temperature. The change of Al-TiO₂ catalyst after gamma-irradiation was also examined by the Bruker EMX spectrophotometer at 77 K.

Results and Discussion

Figure 1(a) shows the decomposition of TCE and PCE by gamma-rays. Compared to gamma-irradiation alone, the combination of ozone and gamma-rays greatly increased the TCE and PCE decomposition. However, the addition of Al-TiO₂ catalyst extraordinarily deteriorates the ozone/gamma-ray treatment. The concentration of liberated chloride ions from TCE and PCE during gamma-irradiation was given in Figure 1(b). Similar to TCE and PCE decomposition, γ -rays/O₃ system showed more efficient chloride ion removal than γ -rays alone. Although, the addition of Al-TiO₂ catalyst into γ -rays/O₃ samples did not enhance the decomposition (see Figure 1), γ -rays/O₃/TiO₂ system increased the removal of chloride ions from TCE and PCE. In this respect, the γ -rays/O₃/TiO₂ system is more favorable than the γ -rays/O₃ system since chlorinated byproducts of TCE and PCE decomposition may be still dangerous to environment.

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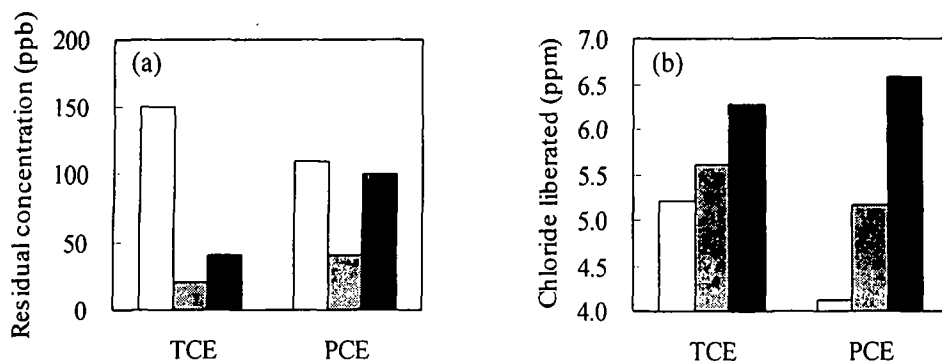


Figure 1. The concentration of (a) residual TCE and PCE (b) chloride ions liberated from TCE and PCE. White, gray and black bars are γ -rays alone, γ -rays/ O_3 and γ -rays/ O_3 / TiO_2 , respectively. Conditions: initial TCE and PCE; 10 ppm, O_3 ; 6 ppm, Al- TiO_2 ; 4 g/l, total absorbed dose; 300 Gy.

An EPR/spin-trapping technique was used to determine hydroxyl radicals since the radicals have been known to play an important role in the oxidative decomposition of TCE and PCE by gamma-rays. Figure 2 shows the typical EPR spectrum of DMPO-OH adduct that is composed of quartet lines having a peak height ratio of 1:2:2:1. Extraordinarily, gamma-irradiation alone showed the highest hydroxyl radical production. In the presence of ozone, the intensity of the DMPO-OH signal was largely suppressed and additionally reduced by adding Al- TiO_2 catalyst. For TCE, the percent of relative intensities of γ -rays alone, γ -rays/ O_3 and γ -rays/ O_3 / TiO_2 were 100, 61 and 60 %, respectively, and 100, 79 and 66 %, respectively, in the case of PCE. This directly indicates that ozone does not increase hydroxyl radical concentration but consumes the hydroxyl radicals. This result is contrary to the current assumption that ozone enhances the TCE and PCE decomposition by producing additional hydroxyl radicals. The enhancement might be caused by acceleration of chain reaction occurred in TCE and PCE decomposition by gamma-rays. The inhibition effect of Al- TiO_2 catalyst on hydroxyl radical production is somewhat extraordinary. As indicated in Figure 3, the intensity of EPR peaks of Al- TiO_2 catalyst was largely decreased after gamma-irradiation. The relationship between the peaks and hydroxyl radical production should be further clarified.

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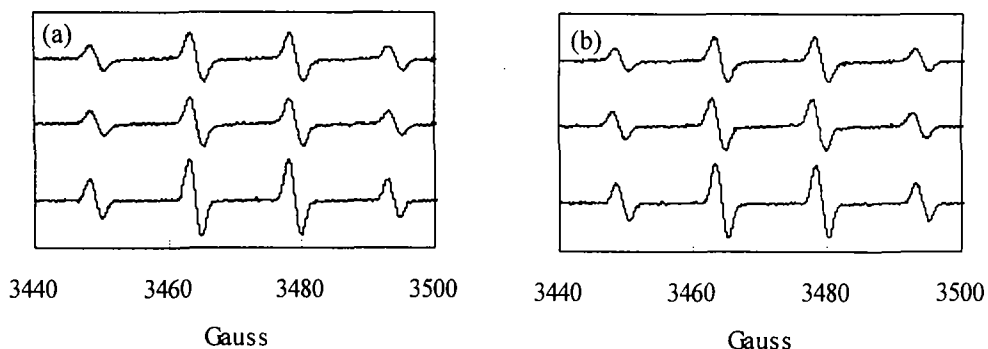


Figure 2. EPR spectra of DMPO-OH adduct in (a) TCE and (b) PCE decomposition. From bottom to top are γ -rays alone, γ -rays/ O_3 and γ -rays/ O_3 / TiO_2 , respectively. Conditions: initial TCE and PCE; 1.0×10^{-5} M, DMPO; 1.0×10^{-2} M, O_3 ; 10 ppm, Al- TiO_2 ; 4 g/l, total absorbed dose; 200 Gy.

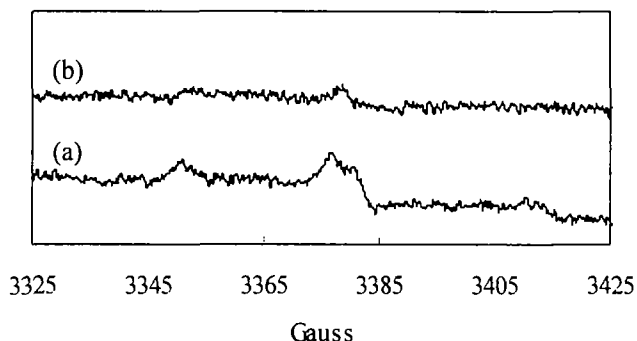


Figure 3. EPR spectra of Al- TiO_2 catalyst powder (a) before and (b) after gamma-irradiation.

References and Notes

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