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Sonophotolytic diethyl phthalate (DEP) degradation with UVC or VUV irradiation

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ABSTRACT

This study investigated the degradation of diethyl phthalate (DEP) by sonolytic, photolytic and sonophotolytic processes. Two types of UV lamps, UVC (254 nm) and VUV (185 nm + 254 nm), were combined with ultrasound (283 kHz). The pseudo-first order degradation rate constants were in the order of 10^{-1}–10^{-3} min^{-1} depending on the processes. The sonolytic DEP degradation rate increased with increasing applied power. Photolytic or sonophotolytic degradation of DEP when using a VUV lamp appeared to be effective because the photo II (UVC/VUV) resulted in a significantly faster degradation than the photo I (UVC) processes due to the higher photon energy and higher hydroxyl radical generation by homolysis of water by VUV. Significant degradation and mineralization (TOC) of DEP were observed with the combined sonophotolytic processes. Moreover, synergistic effects of 1.68 and 1.23 were exhibited at DEP degradation of the sonophoto I and sonophoto II processes, respectively. This was attributed to the UV-induced dissociation of hydrogen peroxide (H_2O_2) generated by the application of US to hydroxyl radicals. Therefore, US in sonophotolytic processes can play an important role in enhancing DEP degradation. Moreover, the sonophoto II process is more effective on the mineralization and biodegradability of DEP.

1. Introduction

Diethyl phthalate (DEP), which is used as a plasticizer and solvent, is an estrogenic chemical that has been considered a cause of endocrine disruption in humans [1]. DEP was reported to be the major proportion of micro-pollutants in the Han River that runs through Seoul, South Korea over a five year period [2]. Integration of the Advanced Oxidation Process (AOP) to the conventional process in treatment facilities to ensure the safety of surface water containing micropollutants as a source of drinking water has attracted increasing attention.

For the AOP, the generation of hydroxyl radicals ($^{\cdot}OH$) is the most critical step, which is carried out by chemical, photochemical and sonochemical methods. When ultrasound (US) is applied to an aqueous solution with organic pollutants, cavitation provides the pyrolysis mechanism (1) inside the cavitation bubbles and generates hydroxyl radicals (2) [3].

$$\mathrm{DEP}\ \underset{\text{Pyrolysis}}{)))}\ \text{by product of DEP} \tag{1}$$

$$\mathrm{H_2O}\ \underset{\text{Pyrolysis}}{)))}\ {}^{\cdot}\mathrm{H} + {}^{\cdot}\mathrm{OH} \tag{2}$$

On the other hand, ultrasound shows better results when combined with other techniques [3–5]. Ultraviolet (UV) radiation can be used for the direct and indirect oxidation of pollutants as well as for disinfection [6,7]. In particular, vacuum ultraviolet (VUV) with a wave length of 185 nm is quite effective in the degradation of pollutants due to the higher rate of hydroxyl radical production by the water homolysis (3) and water ionization (4) [7–9].

$$\mathrm{H_2O} \xrightarrow[185\ \mathrm{nm(VUV)}]{} {}^{\cdot}\mathrm{H} + {}^{\cdot}\mathrm{OH} \tag{3}$$

$$\mathrm{H_2O} \xrightarrow[185\ \mathrm{nm(VUV)}]{} {}^{\cdot}\mathrm{H}^{+} + {}^{\cdot}\mathrm{OH} + e^{-} \tag{4}$$

For the treatment of phthalates, a range of oxidation processes have been attempted, adopting chemical, photo-chemical, Fenton, photo-Fenton, and sonochemical mechanisms [10–14]. The applications of the combined sono–photo process in various UV wavelength have not been reported despite their effectiveness [15–17]. In particular, there have been no reports of sonophotolytic pollutant degradation when using the VUV lamp. Therefore, this study examined the kinetics of the sonolytic, photolytic and sonophotolytic degradation of DEP using UVC and VUV. In addition, the mineralization (TOC) and biodegradability (BOD_5/COD) of DEP after the application of each process were also studied.

2. Experimental methods

2.1. Material

DEP was obtained from Aldrich (99.5% pure grade), while hexanes (99.5%, HPLC grade) and iodine stock solution (I_2, 0.05 mol L^{-1}) were purchased from Fisher and Fluka, respectively.

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Purified water was obtained using a Milli-Q system (Millipore) and had a resistivity of 18.2 MΩ cm.

2.2. Experimental procedure and analysis method

The degradation of DEP (45 μM) was carried out in a capped cylindrical glass batch reactor. The reactor had an inner diameter, height and volume of 12.5 cm, 22 cm and 1 L, respectively.

Four UVC lamps, each with a wavelength of 254 nm and power of 10 W, or two UVC and two VUV lamps, each with a wavelength of 185 and 254 nm and power of 10 W were placed in the reactor. A US frequency of 283 kHz with a nominal power of 40, 65 and 85 W L^{-1} was applied by placing a cup horn type single transducer beneath the reactor. The delivered ultrasound energy to react was analyzed by power meter (Metex). Fig. 1 shows a schematic diagram of the experimental set-up. The temperature in the reactor was kept within 15–18 °C using a water jacket around the reactor. The mixing rate was controlled at 100 rpm during the experiment.

A 7 mL of aliquot was sampled from the reactor and the concentrations of DEP, total organic carbon (TOC) and hydrogen peroxide (H_2O_2) were analyzed. The total sample volume throughout the experiment was kept below 5% of the initial volume in the reactor. To analyze the DEP concentration, a 5 mL sample was extracted with 10 mL hexane in a 20 mL round cap tube in a shaking bath for 24 h. Subsequently, 7 mL of the solvent was removed and concentrated to 200 μL by blowing with nitrogen gas prior to GC–MS analysis (Agilent 6890 plus GC-5973 Mass). The hydrogen peroxide concentration was measured using a spectrophotometer [18].

Tri-iodide ion (I_3^-) was measured using the KI method [19,20]. In addition, the TOC was analyzed using a TOC meter (Sievers 5310 C laboratory TOC analyzer) including a Sievers 900 auto sampler. The biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) were also measured as a biodegradability index of DEP [21].

3. Results and discussion

3.1. Sonolytic degradation of DEP

Fig. 2(a) and (b) shows the effect of intensity (40, 65, or 85 W L^{-1}) on the DEP sonolytic degradation constants at a frequency of 283 kHz. The degradation rate increased with increasing applied power. The degradation kinetic constants of DEP were 2.8, 7.2 and 8.9 × 10^{-3} min^{-1} at 40, 65 and 85 W L^{-1}, respectively. The number of active cavitation bubbles and their implosive energy increase with increasing applied power, leading to an increase in the amount hydroxyl radical generated [22–24]. To observe the amount of generated hydroxyl radical, tri-iodide ion (I_3^-) as an indirect indicator was measured using a potassium iodide (KI) solution after US irradiation at each applied power (Fig. 2(a)) [19]. The difference of the measured tri-iodide ion concentration at each power density is similar to the result of the sonolytic degradation rate of DEP. Therefore, the higher degradation rate of DEP is believed to result in increased hydroxyl radicals at a high power density.

t-BuOH, which is known to be a hydroxyl radical scavenger [25,26], is added to the aqueous solution of contaminated DEP to confirm whether or not there is a hydroxyl radical reaction (Fig. 2(b)). The added *t*-BuOH concentration was 0.45 mM, which is 10 times more than the initial DEP molar concentration. The degradation rate constant of DEP including *t*-BuOH was 5.0 × 10^{-4} min^{-1} at 65 W L^{-1}, which differs from that without *t*-BuOH by being approximately 10 times greater. From this result, we know that the main reaction of DEP is affected by hydroxyl radical.

3.2. Direct photolysis of DEP

Fig. 3 shows the degradation profile plotted against the irradiation time of DEP contaminated solution when the solution was irradiated with either UVC (photo I) or UVC/VUV (photo II) radiation with different UV intensities (20 and 40 W L^{-1}). Under UVC irradiation, the degradation of DEP was not significant (approximately 5–15% after 120 min of irradiation). The degradation constant of DEP in the photo I process was 2.3 × 10^{-3} min^{-1} and this is slightly larger than the result of Olmez-Hanci et al. (2010), who observed a low DEP degradation rate (6.0 × 10^{-4} min^{-1}, about 5%) in direct UVC photolysis [27]. Photolysis of DEP by UVC radiation may be described by the following reactions (5)–(10) [28].

$$\mathrm{DEP} \xrightarrow[\text{UVC or VUV}]{} \mathrm{DEP}^* \qquad (5)$$

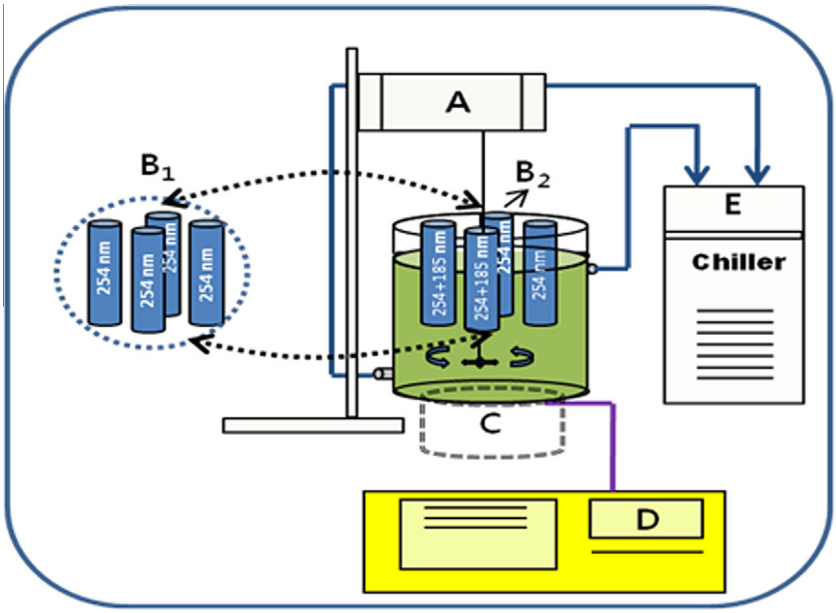

Fig. 1. Schematic diagram of the experimental set-up; (A) Mixer, (B) UV lamps (B_1-photo I, B_2-photo II), (C) US transducer, (D) US generator, (E) Cooling water.