



Significant diethyl phthalate (DEP) degradation by combined advanced oxidation process in aqueous solution

Seungmin Na^a, Yun-Gyong Ahn^b, Mingcan Cui^a, Jeehyeong Khim^{a,*}

^a School of Civil, Environmental and Architectural Engineering, Korea University, 5 Anam-dong, Seoul 136-701, South Korea

^b Korea Basic Science Institute, 126-16 Anam-Dong, Sungbuk-Ku, Seoul 136-701, South Korea

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ABSTRACT

Ultrasound (US) combined with ultraviolet (UV) irradiation and a titanium dioxide (TiO₂) catalyst was used to effectively remove diethyl phthalate (DEP) from aqueous solutions. Single (sonolysis, photolysis, photocatalysis) and combined (sonophotolysis, sonophotocatalysis) processes were performed to confirm the synergistic effects and DEP degradation mechanism. Using only US, the optimum frequency for DEP degradation was 283 kHz. At this frequency a high rate of hydrogen peroxide (H₂O₂) formation was observed of approximately 0.32 mM min⁻¹. The pseudo-first order degradation rate constants were 10⁻²–10⁻⁴ min⁻¹ depending on the process. Significant degradation and mineralization (TOC) of DEP were observed with the sonophotolytic and sonophotocatalytic processes. Moreover, synergistic effects of 1.29 and 1.95 were exhibited at the sonophotocatalytic and sonophotolytic DEP degradation, respectively. Furthermore, additional advantageous reactions may occur in the heterogeneous sonophotocatalytic process due to interactions between US, UV, and the photocatalyst.

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1. Introduction

Phthalates are widely used as polymer plasticizers and in the paint and coating industries to improve flexibility. Phthalates are estrogenic and are responsible for endocrine disruption in humans (Jobling et al., 2005), and possess carcinogenic properties. Phthalates are present in concentrations ranging from 0.1 to 300 µg L⁻¹ in various environments including surface water and river sediments (Yuan et al., 2002; Chen and Sung, 2005). Oh et al. (2006) reported phthalates to be the major proportion (53.4%) of micro-pollutants detected in the Han River that runs through Seoul, South Korea. Surface water such as the Pal-Dang reservoir on the Han River main stream provides approximately 70% of the drinking water in South Korea. Therefore, the removal of phthalates is essential to maintaining safe drinking water.

Various advanced oxidation processes (AOPs) may be applied to contaminated systems to effectively treat micro-pollutants (Gogate et al., 2002; Chen et al., 2003; Berberidou et al., 2007; Selli et al., 2008; Joseph et al., 2009). Combined AOPs such as sonophotocatalysis are more effective than single-mode processes such as sonolysis, photocatalysis, or chemical treatment with hydrogen

peroxide, ozone and Fenton reagent (Selli et al., 2005; Yang et al., 2005; Muruganandham and Swaminathan, 2006(b); Oh et al., 2006; Berberidou et al., 2007; Selli et al., 2008). However, most research on decomposition processes has focused on photolysis or chemical treatment (Bajt et al., 2001; Tawabini and Al-Suwaiyan, 2004; Lau et al., 2005; Yang et al., 2005; Xu et al., 2007), with only a few studies suggesting sonochemical degradation of phthalates (Yim et al., 2002; Psillakis et al., 2004). To date, no reports have been conducted concerning the sonophotocatalytic degradation of phthalate.

Ultrasonic irradiation (US) of aqueous solutions induces acoustic cavitation effects that generate high local temperatures (>5000 K) and pressures (>1000 atm) and produce strongly oxidizing hydroxyl radicals (Hua and Hoffmann, 1997; Thompson and Doraiswamy, 1999). Yim et al. (2002) observed the degradation rate of DMP, DEP, and DBP during sonolysis at pH levels from 4 to 12. Psillakis et al. (2004) examined the effects of ultrasonic power, reaction time, salt concentrations, and temperature on phthalate degradation rate without frequency. The kinetics of the degradation reaction are sensitive to the operating frequency. However, the optimum frequency still needs to be determined, and we attempted to determine the optimum frequency during single-mode sonolysis experiments. Photolytic degradation of phthalates at short wavelengths (below 300 nm) is also feasible (Bajt et al., 2001). Therefore, a wavelength of 254 nm was selected

* Corresponding author.

E-mail address: hyeong@korea.ac.kr (J. Khim).

for the photolytic degradation of phthalate. Other combined processes with photolysis also considered for the complete degradation and mineralization of phthalates within a set treatment time, including sonophotolytic (US/UV) and sonophotocatalytic processes (US/UV/TiO₂).

Moreover, in this study, diethyl phthalate (DEP) was selected as the target compound because it is a common pollutant. Titanium dioxide (TiO₂) was also selected as a semiconductor for photoexcitation. Therefore, the DEP degradation reaction constants and mineralization (TOC) rate at combined each processes were investigated to understand efficient degradation process. In addition, biodegradability (BOD₅/COD) of mineralized DEP after the application of each processes were also studied.

2. Experimental details

2.1. Material

DEP was obtained from Aldrich (99.5% pure grade). Methanol (100%, HPLC grade) and hexanes (99.5%, HPLC grade) were purchased from Fisher. Reagent grade potassium bi-phthalate (C₆H₄ (COOK) COOH, 99.7%, Samchun Chemical), potassium iodide (KI, 99.5% Jusei), ammonium molybdate ((NH₄)₆Mo₇·4H₂O, 99%, Samchun chemical) and hydrogen peroxide (35%W/V, Samchun chemical) were used as received. The TiO₂ (Degussa P25, consisting of 80% anatase and 20% rutile) used in this study had a surface area of 50 m² g⁻¹ and a mean particle size of 30 nm. Purified water was obtained using a Milli-Q system (Millipore) and had a resistivity of 18.2 MΩcm.

2.2. Experimental procedure

The reaction was carried out in a capped cylindrical reactor made entirely of Pyrex glass with a volume of 1.8 L, an inner diameter of 12.5 cm and a height of 22 cm. The ultrasonic bath was equipped with a single cup horn type transducer (produced by Mirae Ultra. Tech., South Korea). The transducer was located at the bottom of the reactor with the energy provided by an external generator. Ultrasonic frequencies of 35, 283, 450, or 935 kHz were delivered at a power between 65 and 70 W. The delivered ultrasound energy to react was analyzed by power meter (Metex). Four UV lamps (Sankyo Denki) predominantly emitting at 254 nm were used as the radiation source. The lamps were encased in quartz tubes, and were each rated at 10.5 W. The length and intensity of the UV lamps were 28 cm and 2.5 mW cm⁻², respectively, and the lamps were centered axially and immersed in the solution.

The initial DEP concentration was fixed at 45 μM. The total sampling volume throughout the experiment was maintained below 5% of the initial volume in the reactor. A reference sample ($t = 0$) was collected from the reactor to determine the catalyst adsorption of DEP before the addition of a known amount of TiO₂. The amount of DEP adsorbed onto TiO₂ was ignored if it was ≤2% of the initial DEP concentration. In experiments involving the catalyst, a turbine agitator was used to maintain the catalyst particles uniformly suspended in the reaction mixture. The reactor was equipped with a cooling water jacket to maintain a solution temperature at approximately 15–18 °C. The pH was uncontrolled, but remained between 6.2 and 7 during the reactions.

2.3. Analytical determinations

Samples were filtered through a 0.45-μm membrane filter to remove suspended TiO₂ prior to analysis. The samples were analyzed immediately to avoid further reaction.

DEP was extracted from 5 mL samples using 10 mL of hexane in a 20 mL sealed tube for 24 h at 150 rpm. A 7 mL portion of the extraction solution was concentrated to a final volume of 200 μL under a nitrogen gas flow prior to gas chromatography–mass spectrometry (GC/MS).

GC/MS analysis was performed using an Agilent 6890 Plus gas chromatograph equipped with a 5973N quadrupole mass spectrometer system (Agilent, Palo Alto, CA). A DB-5 MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, 5% diphenyl-95% dimethylsiloxane stationary phase) was obtained from J&W Scientific (Folsom, CA, USA). The mass selective detector was operated in electron impact (EI) mode with an electron energy of 70 eV.

Hydrogen peroxide (H₂O₂) was monitored using the analytical procedure described by Beckett and Hua (2001). The total organic carbon (TOC) content of the treated samples was analyzed using a Sievers 5310 C laboratory TOC analyzer including a Sievers 900 auto sampler. The biochemical oxygen demand (BOD) was measured for 5 days using an Hg free WTW 2000 Oxitop unit thermostated at 20 °C.

3. Results and discussion

3.1. Frequency optimization of sonolytic process

Fig. 1(a) depicts the effect of frequency (35, 283, 450, or 935 kHz) on the DEP sonolytic degradation rates at a power of 65–70 W L⁻¹.

The degradation rate for DEP exhibited behavior similar to a pseudo first order reaction. Table 1 summarizes the degradation kinetic constants of DEP under different frequencies.

Of the frequencies examined, the highest DEP degradation constant (k_{US}) was $6.9 \times 10^{-3} \text{ min}^{-1}$ at 283 kHz. For the effective treatment of DEP, the optimal frequency in this process was 283 kHz. However, this degradation constant ($k_{US, 283 \text{ kHz}}$) was a lower result than that ($k_{US, Yim} = 1.0 \times 10^{-1} \text{ min}^{-1}$) reported by Yim et al. (2002) (Table 1). This is estimated to be possibly due to the difference of applied US power and of the US type and reactor configuration used.

When US is applied to an aqueous solution, organic pollutants may be degraded through either pyrolysis or oxidation by the hydroxyl radical (Hua and Hoffmann, 1997; Mason and Lorimer, 1988; Thompson and Doraiswamy, 1999).

Several researchers (Kotronarou et al., 1992; Pètrier et al., 1994; Hua and Hoffmann, 1997; Pètrier and Francony, 1997; Kang et al., 1999; Keck et al., 2002; Wayment and Casadonte Jr., 2002; Inoue et al., 2006; Torres et al., 2008; Chand et al., 2009) have used the rate of hydrogen peroxide formation as an indirect indicator of the number of hydroxyl radicals produced during cavitation bubble collapse. Inoue et al. (2006) reported that the maximum amount of hydrogen peroxide is produced at approximately 404 kHz, which is coincident with the frequency of maximum degradation of organic materials. Kang et al. (1999) reported that hydrogen peroxide and tri-iodide ion (I₃⁻) formation at 358 kHz was greater than at higher frequencies (618 kHz or 1078 kHz) during sonochemical degradation of methyl tert-butyl ether (MTBE). Chand et al. (2009) examined the rate of hydrogen peroxide formation with and without phenol at various frequencies (20–520 kHz). They also observed maximum hydrogen peroxide formation near 300 kHz. Pètrier et al. (1997, 1994) reported that hydrogen peroxide formation and the sonochemical degradation effect of phenol, which is less volatile than carbon tetrachloride, were greater at high frequencies (500 or 487 kHz >20 kHz). We also investigated the rate of hydrogen peroxide formation at various frequencies (Fig. 1(b) and Table 1).

The formation rates were frequency dependent, decreasing in the order 283 kHz >450 kHz >935 kHz >35 kHz. The frequency of

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