Comparison of Fenton and US/Fenton for degradation of DEP and effect of power density on degradation

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1. Introduction

Advanced oxidation processes (AOPs) had been proposed as an attractive alternative method for the treatment of polluted waters. These processes were known to generate OH radical which were able to oxidize almost all toxic and non-biodegradable pollutants [1].

Diethyl phthalate (DEP) was one of the most frequently identified phthalates with high water solubility and short-chain in diverse environmental samples including surface water, drinking water, sea water and so on. Since DEP was difficult to degrade biologically and photo-chemically[2], DEP degradation by Fe(III)-solar process [3], Fenton reaction [4] and biological process [5] was a strong need to look for effective treatment processes for such pollutants.

However, few reports on DEP removal by ultrasound (US) and US/Fenton could be found for degradation effectively. These processes were successfully applied for degradation of aliphatic, aromatic, polycyclic aromatic and halogenated hydrocarbons, azo dyes and for some pesticides as well [6].

The aim of this study was to compare the degradation of DEP between US and US/Fenton processes and the effect of electric power density on degradation has been investigated at same frequency and volume.

2. Materials and Methods

DEP obtained from Sigma Aldrich (USA, purity > 99%), characteristics of DEP are shown in

Molecular formula	$C_{12}H_{14}O_4$
Molecular weight (g/mol)	222.24
Water solubility at (mg/L)	1080
Log K _{ow}	2.42
Henry's law constant (atm-m ³ /mole)	6.10×10 ⁻⁷
Vapor pressure (mmHg)	2.10×10 ⁻³

Table1. Characteristics of DEP (at 25 °C)

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the Table 1 and it was indicated DEP was non-volatile pollutant. The chemical reagents used in the study were ferrous sulfate (FeSO₄·7H₂O, Samchun, Korea) and an aqueous solution of hydrogen peroxide (28%, Duksan, Korea).

To keep a constant temperature $(16\pm2^{\circ}C)$, the experiments were performed in a pyrex reactor with cylindrical water jacket, and Fig.1 was shown a schematic diagram of batch reactor. Ultrasonic waves were emitted from a transducer (Tamura corp.) with ultrasonic controller (Mirae Ultrasonic Tech., Korea) placed on a cup horn type reactor. The frequency and the density was 500 kHz and the electric power of ultrasound was fixed at 80, 180 and 330W/L.



Fig. 1 Schematic diagram of batch reactor.

The initial concentration of DEP was 10mg/L and total volume of aqueous phase was 300mL. Fenton process was carried out using FeSO₄ $(1.67 \times 10^{-5} \text{ mol/L})$ and H₂O₂ $(5.0 \times 10^{-5} \text{ mol/L})$. Samples were taken from the reactor for analysis of DEP and TOC concentrations at predetermined interval (i.e. 10, 20, 30, 40, 50 and 60min). The concentrations of DEP and TOC were immediately determined by use of a HPLC-UV (Prostar, Varian, USA), and a TOC analyzer

(SEIVERS 5310 C laboratory analyzer, GE, USA).

3. Results and Discussion

Fig. 2 was shown degradations of DEP by Sono, Fenton and Sono-Fenton. The first order kinetic constants of degradation for DEP were 5.01×10^{-3} , 2.04×10^{-2} , 3.67×10^{-2} , 1.40×10^{-2} , 4.28×10^{-2} , 9.24×10^{-2} and 1.02×10^{-2} min⁻¹ at US(80W/L),US(180W/L),US(330W/L),US(80W/L) /Fenton, US (80W/L)/Fenton, US(330 W/L)/Fenton and Fenton, respectively. And the combined effect was high at US(180W/L)/Fenton and the synergistic value was 1.97.



Fig. 2 Degradations of DEP by \bullet US (80W/L), \circ US (180W/L), \forall US (330W/L), \triangle US (80W/L)/Fenton, \bullet US(180W/L)/Fenton, \Box US (330W/L)/Fenton, \diamond (Fenton).

The faster degradation of DEP with Sono-Fenton as compared to Fenton was due to the higher efficiency for the OH radical production (1) as well as to the ultrasonic physical (bubble collapse and mixing) and chemical (OH radical) processes.

$$\operatorname{Fe}^{2^+} + \operatorname{H}_2\operatorname{O}_2 \rightarrow \operatorname{Fe}^{3^+} + \operatorname{OH}^- + \operatorname{OH}^{\bullet}$$
 (1)

The mineralization of DEP was highest at US (330W/L)/Fenton process and the reduction of TOC was 23% while Fenton alone was 5% and US alone was 19%, respectively.

Fig. 3 shows a plot of the k values against power density. For the range of experimental conditions, the rate constant of DEP degradation did



Fig. 3 Dependence of reaction rate constant k on power density.

indeed appear to vary linearly with power density. The beneficial effect of power on degradation rate was due to increasing cavitational activity occurred at higher levels of power. As power increased, the number of collapsing cavities also increased, thus leading to enhanced degradation rates[6]. Conversely, the rate of degradation decreased with increasing liquid volume at a constant power. This was presumably the amount of energy transmitted per unit volume decreased with increasing volume [7].

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