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Sonophotolytic degradation of diethyl phthalate (DEP) under different wavelength (UVC/VUV) condition.

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1. Introduction

Phthalates are synthetic compounds widely used as plasticizers for plastics, dope and paint industy to improve flexibility. The phthalates are very unique, spread into natural environemnt as they are released during use and disposal from manufacture plants [1)]. These compounds have been discovered as estrogenic chemicals, which are responsible for the endocrine disruption in the human. Therefore, many researchers suggested advanced oxidation processes (AOPs) is better for more effective phthalae treatment [1),2),3)]. An ultrasound as advaned oxidation process can be applied into environment for toxic micropollutnats disposal due to inducement of thermal (pyrolysis) and chemical (OH radical) reactions. In order to obtain a significant degradation of organic material, some combined advanced oxidation processes were considered with ultrasound [4),5)]. Ultraviolet (UV) radiation has also used the basis of several chemical oxidation technologies, where the action of irradiation and free radicals generated in the process to obtain a high degree degradation of pollutants or disinfection [6),7)]. Especially, vacuum ultraviolet (VUV) was reported a higher rate of degradation or mineralization of pollutants as consequence for formation of hydroxyl radicals and the photolysis of water by 185 nm [7),8)].

Therefore, in this study, diethyl phthalate (DEP) has frequently appeared in enviroment which was selected as a target compound. And, The optimized ultrasonic frequency and main mechanism of DEP degradation in the single sonolysis process were studied in this research. Also, the significant DEP degradation by photolysis and sonophotolysis process was also discussed under different wavelength of ultravilot (UV) condition.

2. Experimental Method

Diethyl phthalate (DEP) was provided from Aldrich (99.5 % pure grade). Hydrogen peroxide (H_2O_2) which produced from ultrasound (US) and ultraviolet (UV) with and without DEP was measured by the analytical procedure described by Beckeet and Hua (2001)[9)]. The reactor used in this system was carried out in a capped cylindrical reactor made entirely of Pyrex glass, as shown in **Fig.1**. Ultrasonic bath equipped with single transducer of 283 and 935 kHz, respectively (produced from Mirae Ultra. Tech., South Korea).

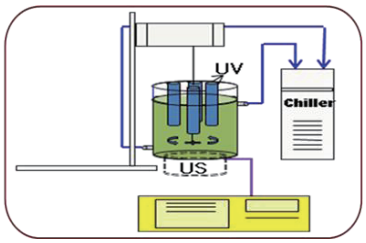

Fig.1 Schematic diagram of the experimental apparatus for sonophotolytic process.

The UV lamps used in this study are emitting a single light at 254 nm (UVC) and emitting combined light at 254 nm (UVC) and 185 nm (vacuum UV-VUV). The powers produced by these lamps are 40 and 36 Watt, respectively. The initial concentration of DEP was fixed at 10 mg/L. The total sample volume throughout an experiment was kept below 5% of the initial volume in the reactor. Temperature in the solution is kept with a cooling water jacket within 15-18℃. The DEP (5mL) concentration was extracted with 10 mL hexane in a 20 mL round cap tube for 24 hrs, 150 rpm to determine the removal rate of DEP according to the single and combined AOPs. After hexane extraction, the 7 mL solvent was removed and concentrated to 200 μl by nitrogen gas blow down prior to GC-MS analysis. The H_2O_2 concentration was determined using a spectrophotometer operated with a wavelength of 350 nm (Specord 40).

3. Results and Discussion

When ultrasound was applied into DEP contaminated solution, **Fig 2 (a)** shows the effect of frequency on the DEP sonolytic degradation rate at input power of 65-70 W/L. An efficient DEP degradation rate was observed at 283 kHz than 935 kHz with operation time. In order to obtain the reason for this result, the H_2O_2 formation rate which as an indirect indicator of free OH radical was measured with and without DEP compound, as shown in **Fig. 2(b)**.

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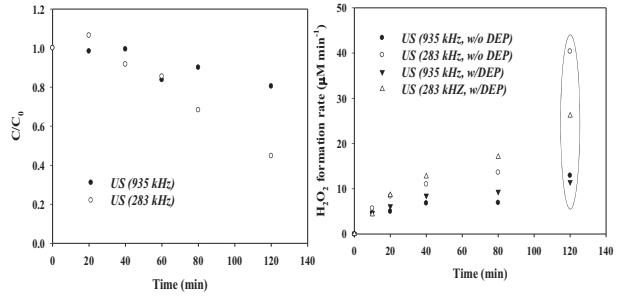

(a) **(b)**

Fig. 2 DEP degradation rate with sonolysis process (a), and H_2O_2 generation rate with and without DEP (b).

The H_2O_2 generation rate in the absence DEP was high at 283 kHz. This agrees with the frequency of the most effective DEP degradation. Moreover, the difference of H_2O_2 formation rate with and without DEP condition was also higher at 283 kHz than 935 kHz after 120 min operation (Fig. 2 (b)). From these results, we can estimate that the optimized frequency is 283 kHz, and sonolytic DEP degradation is more affected by OH radical of ultrasound. Beside the sonolytic degradation of DEP, DEP contaminated solution was irradiated to verify the efficiency of UV photolysis with different wavelength (UVC, VUV) in **Fig. 3**.

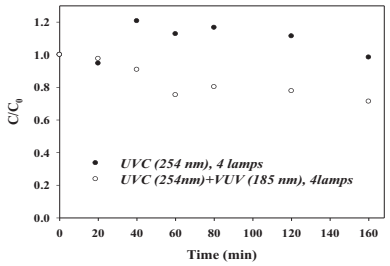

Fig.3 DEP degradation rate by photolysis under different wavelength condition.

Photolytic degradation of DEP by UVC irradiation was more enhanced than that of VUV condition. This is because that the energy photon of UV is different with UV irradiation types, as like UVC =537 kJ Einstein^{-1}, VUV =834 kJ Einstein^{-1} [10]. Furthermore, the combined UVC and VUV system induces a number of OH radicals by ozone production and photolysis of water [6),8)]. The DEP degradation by the combined UVC and VUV photolysis is described as the following reactions (eq. [1]-[5]):

$O_2 \xrightarrow[185\ nm]{} O\cdot + O\cdot$ ----- [1]

$H_2O \xrightarrow[185\ nm]{} O\cdot + OH\cdot$ ----- [2]

; OH, O radicals formation by 185nm

$O\cdot + O_2 \rightarrow O_3$ ----- [3] ; O_3 formation by 185nm

$O_3 \xrightarrow[254\ nm]{} O\cdot + O_2$ ----- [4]

$O\cdot + H_2O \rightarrow OH\cdot + OH\cdot$ ----- [5]

$OH\cdot + DEP \rightarrow$ DEP intermediate formation ----- [6]

Fig. 4 shows the sonophotolytic DEP degradation to confirm the enhancement degree of combined process with different UV wavelength type.

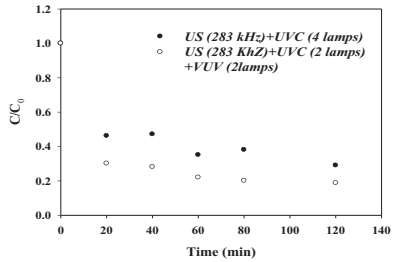

Fig. 4 Sonophotolytic DEP degradation with various UV photolysis.

The DEP degradation by sonophotolytic process was higher than the sum of individual sonolysis and photolysis process (in Fig. 2 and Fig. 3). This means that combined advanced oxidation process is more efficient for DEP degradation. Especially, the sonophotolytic DEP degradation with combined the UVC and VUV irradiation is more enhanced about 25-30 % than that of only UVC photolysis.

From these results, we know that high photon energy and the number of free radical induced from the combined photolysis processes (UVC/VUV) can work to efficient DEP degradation. And sonochemical reaction in combined process can play an active role compare to photolytic and sonophotolytic process.

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