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Degradations of organic pollutants by US/H₂O₂ and UVC/H₂O₂ processes

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1. Introduction

Advanced oxidation processes (AOPs) such as US, UV, US/H_2O_2 and UV/H_2O_2 produced oxidizing species, generally OH radicals which are very powerful and unselectively oxidized without causing secondary pollutant [1-5]. US/H_2O_2 and UV/H_2O_2 processes were more fastly degraded than the US and UV processes. It was concluded that the reaction were enhanced by the synergistic effects.

In the case of ultrasound, the volatile and hydrophobic species directly diffused into the cavitation bubble, which were then decomposed in the bubble mainly due to pyrolysis, non-volatile and hyrdophillic compounds which were mainly degraded at the interfacial region by the reaction with OH radicals generated from the cavitation [5,6].

There were few studies on the mechanisms of degradation for organic pollutants by US/H_2O_2 and UV/H_2O_2 according to characteristics of pollutants such as Henry's Law constant, vapor pressure and solubility, and species such as aliphatic, aromatic, halogenated hydrocarbons, azo dyes and pesticides, however, the mechanisms of degradation related with characteristics of pollutants was not clear. In this study, the two organic pollutants had different characteristics. Bisphenol A among aromatic compounds has been regarded as a representative pollutant among endocrine disruptors and chloroform related with halogenated aliphatic compounds.

The objectives in this research were to investigate the degradation and mineralization of Bisphenol A and chloroform by US, UV, H_2O_2, US/H_2O_2 and UV/H_2O_2 processes and then compare the synergistic effects between US/ H_2O_2 and UV H_2O_2 processes at same electric power.

2. Materials and Methods

The highly pure chemicals were used in this study as follows: Bisphenol A (BPA, Sigma Aldrich, USA), Chloroform (CF, Samchun, Korea) and hydrogen peroxide (28%, Duksan, Korea). And the initial concentrations of BPA, CF and H_2O_2 were 10mg/L. Experiments were performed in a pyrex

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reactor with cylindrical water jacket, temperature of the reactor was controlled at 16±2℃. Fig.1 shows a schematic diagram of batch reactor.

Ultrasound was emitted from a transducer (Tamura corp.) with ultrasonic controller (Mirae Ultrasonic Tech., Korea) placed on a cup horn type reactor. The frequency and the electric power of ultrasound were fixed at 300 kHz and 40W.
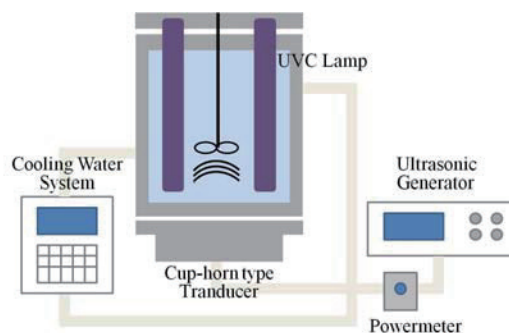

Fig. 1 Schematic diagram of batch reactor.

UVC lamps (λ= 254nm, Philips, Holland) were placed in the solution and electric power was fixed at 40W. All of the experiments were carried out at least twice to obtain the precise data. Samples were taken from the reactor for analysis of BPA, CF and TOC(Total Organic Carbon) concentrations at predetermined interval (i.e. 20, 40, 60, 80, 100 and 120min). The concentrations of BPA, CF and TOC were immediately determined by use of a HPLC-UV (Prostar, Varian, USA), a GC-FID (6890N, Agilent, USA) and a TOC analyzer (SEIVERS 5310 C laboratory analyzer, GE, USA).

3. Results and Discussion

The degradation of BPA was more rapid than CF by all process except US alone. The results were explained according to characteristics of BPA and CF. Henry's Law constant (atm m³ mole⁻¹) and vapor pressure (mmHg) of BPA and CF were 1.0×10^{-11}, 3.7×10^{-3} and 3.9×10^{-7}, 1.9×10^{2}, respectively. It was indicated BPA was less volatile and more hydrophilic organic compound than CF, respectively. So, BPA reacted with OH radical more faster than CF and it was matched with previous study related with mechanism of degradation [6]. The changes of concentration of BPA and CF were shown in the Fig. 2 and the first order kinetic

constants were summarized in the Table 1.

The order of degradation rate of BPA was $UVC/H_2O_2 > UVC > US/H_2O_2 > H_2O_2 > US$. The first order kinetic constants for degradation of BPA were 7.0×10^{-3} min^{-1} and 3.6×10^{-3} min^{-1} by UVC and H_2O_2 alone, respectively. The best kinetic constant was 1.6×10^{-1} min^{-1} and removal of TOC was 61% by UVC/H_2O_2 while the kinetic constant was 5.6×10^{-3} min^{-1} and removal of TOC was 21% by US/H_2O_2.

highly soluble in water [7]. Therefore, H_2O_2 affinity towards the gas phase of the cavitation bubble was low [8].

Table 1. First order kinetic constants (min^{-1})

Process	Bisphenol A	Chloroform
US	1.6×10^{-3}	2.3×10^{-3}
UVC	7.0×10^{-3}	3.0×10^{-4}
H_2O_2	3.6×10^{-3}	9.0×10^{-4}
US/H_2O_2	5.6×10^{-3}	2.4×10^{-3}
UVC/H_2O_2	1.6×10^{-1}	7.0×10^{-4}

The synergistic values of the combined process (US/H_2O_2 and UV/H_2O_2) divided by the single processes (US, UVC and H_2O_2) are defined with first order kinetic constant as given below:

$$\frac{k(combined\ process)}{k(single\ process; US\ and\ UV) + k(single\ process; H_2O_2)}$$

In the case of BPA, synergistic value of UV/H_2O_2 and US/H_2O_2 processes were 15.09 and 0.11, respectively. In case of CF, UV/H_2O_2 and US/H_2O_2 processes were 0.58 and 0.75, respectively. It was indicated BPA was best degraded by UV/H_2O_2 process among all processes. because BPA was non-volatile pollutant, it reacted with OH radicals from photolysis of peroxide and the highest OH radicals were yielded at 254nm of UV radiations.

And CF didn't react with OH radicals generated from H_2O_2 in aqueous phase because CF was volatile pollutant and it indicated the main mechanism of degradation for CF in aqueous phase was pyrolysis [7].
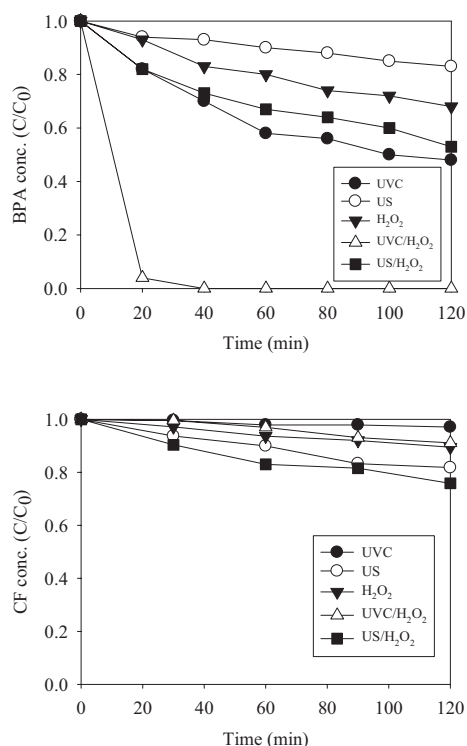
Fig. 2 Degradations of Bisphenol A and Chloroform by US (300kHz,40W), UVC (254nm,40W), H_2O_2 (10mg/L), US/H_2O_2 and UVC/H_2O_2 processes.

The results were explained with previous study, in UV/H_2O_2 process the UV light was absorbed directly by H_2O_2, OH radicals were generated by photolysis of peroxide bond and the highest OH radical yields were obtained when short wave ultraviolet radiations (200-280nm) were used [3,4].

And the order of degradation rate of CF was $US/H_2O_2 > US > UVC/H_2O_2 > H_2O_2 > UVC$. The first order kinetic constants for degradation of CF were 2.3×10^{-3} min^{-1} and 9.0×10^{-3} min^{-1} by US and H_2O_2 alone, respectively. The best kinetic constant for was 2.4×10^{-3} min^{-1} and removal of TOC was 18% while the kinetic constant was 7.0×10^{-4} min^{-1} and removal of TOC was 5% by UVC/H_2O_2. From Shemer et al. [2], explains the addition of H_2O_2 on sonolysis which was not significantly affected by the presence of aqueous chloroform, it could be concluded that H_2O_2 neither oxidized the chloroform nor affected their ultrasonic irradiation. The sonolysis of the H_2O_2 itself in the aqueous solution was slow; thus, H_2O_2 is non-volatile and

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