

오존/광화학 산화공정과 오존/촉매 고급산화공정의 조합 및  
순차적 적용을 통한 프탈산 함유 폐수의 처리

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**Combination and Sequence of Ozone assisted Photo-Chemical and Catalytic Ozonation Process  
for the Treatment of Phthalic acid Containing Wastewater**

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**Introduction**

Terephthalic acid (TPA) is widely used for a raw material in making polyester fiber, polyethylene terephthalate (PET), polyester films, paints, engineering plastics etc. Due to its good thermostable, abrasion resistance, insulating properties. Therefore, as growing of the TPA demand the production of wastewater was also increased annually. The main organic components in the wastewater are terephthalic acid (TPA), isophthalic acid (IPA) and benzoic acid (BA) and it brings high COD and BOD value in the water environment [1,2]. TPA wastewater is traditionally treated by biological process but it is not very effective. It is slow and activity of the biomass is lost during biodegradation, strongly rate limiting and inhibition of micro-organisms by high organic concentration and in the presence of antiseptic compounds like as benzoic acid and sodium benzoate. Recently, Advanced oxidation process (AOP), Radiation Treatment using gamma-ray, Supercritical water oxidation processes are studied for the effective destruction of Phthalic acid containing wastewater [3,4]. The AOPs can be operate under ambient conditions and generate highly reactive oxidizing free radicals, which oxidizes the organics either completely mineralizing the organic or converting it into less harmful or lower chain compounds, which can be treated more easily by the biological process. Nowadays, some kinds of researchers investigate for the increase of oxidation ability in the AOPs by the recombination and modification of known advanced process like as photo-fenton oxidation, photo catalytic ozonation, ozone assisted photo-fenton oxidation. In this study investigate the degradation of TPA wastewater by several AOPs. Main oxidation processes such as UV assisted ozonation (UV/O<sub>3</sub>), ozone assisted photo-chemical oxidation (UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), photo-fenton oxidation (UV/H<sub>2</sub>O<sub>2</sub>/FeSO<sub>4</sub>), ozone assisted photo-fenton oxidation (UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/FeSO<sub>4</sub>) were studied [5,6,7]. And direct and indirect oxidation of each system also compared.

**Experiments**

The schematic diagram of the AOP system is shown in Figure 1. The main organics contained in TPA wastewater are TPA 2,800 ppm, IPA 4,000 ppm, BA 10,000 ppm. And it has color and 35,000

ppm of  $\text{COD}_{\text{cr}}$ . The initial pH of the wastewater was around 6.5. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 35 %) was purchased from Daejung Chemicals & Metals Co. Ltd., Korea and ferrous sulfate ( $\text{FeSO}_4$ ), Tert-butyl alcohol from Junsei Chemicals Co. Ltd., Japan. Tert-butyl alcohol was used for the radical scavenger. The wastewater suspension (1 L) was irradiated in the photo reactor by six quartz tube mercury vapor ultraviolet lamps (TUV 36 SP T5, Philips, USA) with a power input of 40 W. The irradiation intensity was  $144 \mu\text{W}/\text{cm}^2$  and the wavelength was 253.7 nm. Constant amount of ozone (0.26 g/min) was introduced, when required. The each concentration of TPA, IPA and BA in the aqueous solution were analyzed by high-performance liquid chromatography HPLC (Shimadzu LC-10 VP, Japan) equipped with a UV detector (240 nm, Shimadzu SPD-10A VP) and a Shim-pack CLC-ODS column. Initial and final  $\text{COD}_{\text{cr}}$  was measured by COD reactor digestion method using spectrophotometer (Model Odyssey, HACH, USA). The elutant used was a solvent mixture of 1 % acetic acid and acetonitrile (85:15, v/v %). The flow rate of the mobile phase was 1 ml/min. The samples were filtered through syringe filter ( $0.25 \mu\text{m}$ , Adventec, Japan) before analyzing by HPLC.

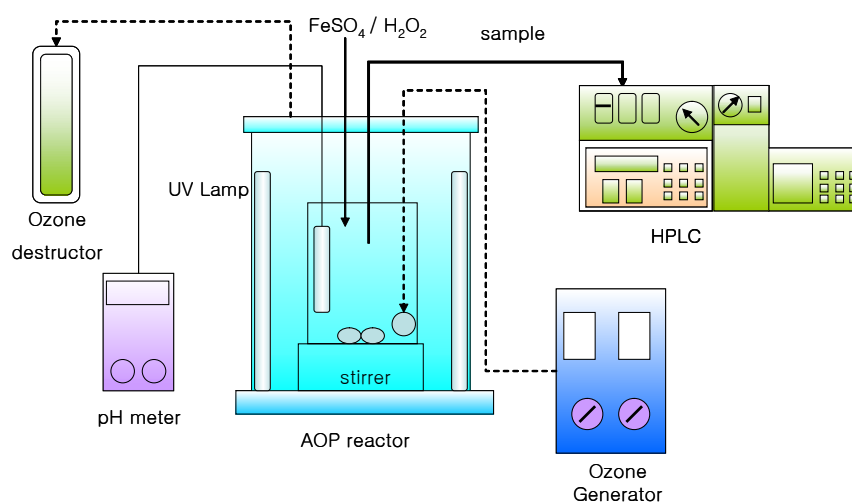


Fig. 1. Schematic diagram of the AOP system.

## Results and discussions

TPA containing wastewater would begin to precipitate at low pH (around pH 4). Hence care was taken not to operate the system at low pH (less than pH 4) in order to avoid any precipitation and evaluate the actual destruction of these target materials in the aqueous solution. Fig. 2 shows the effect of  $\text{H}_2\text{O}_2$  dosage on the organic degradation in the UV/ $\text{O}_3$ / $\text{H}_2\text{O}_2$  system. In the UV/ $\text{O}_3$  system, COD was lineally decreased to 180 min and slowly decreased to 240 min but UV/ $\text{O}_3$ / $\text{H}_2\text{O}_2$  system shows linear decrease until 240 min. UV/ $\text{O}_3$  system shows 70 % degradation efficiency during 240 min, but UV/ $\text{O}_3$ / $\text{H}_2\text{O}_2$  system shows 85 % at the same time. The effect of  $\text{H}_2\text{O}_2$  dosage on the degradation of organic was not significant. Fig. 3 shows the effect of  $\text{FeSO}_4$  dosage on the organic degradation in the

UV/O<sub>3</sub>/FeSO<sub>4</sub> system. Degradation efficiency was increased with increase of FeSO<sub>4</sub> dosage from 0.25 to 0.76 mM but similar degradation efficiency was shown before 180 min. Fig. 4 shows the combination effect of ozone assisted photo chemical (UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) and photo catalytic ozonation (UV/O<sub>3</sub>/FeSO<sub>4</sub>) system. UV and all of oxidants (H<sub>2</sub>O<sub>2</sub>, FeSO<sub>4</sub>, O<sub>3</sub>) were introduced in the initial time and pH was not controlled. UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/FeSO<sub>4</sub> system shows similar organic degradation efficiency with UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system, even added the FeSO<sub>4</sub>.

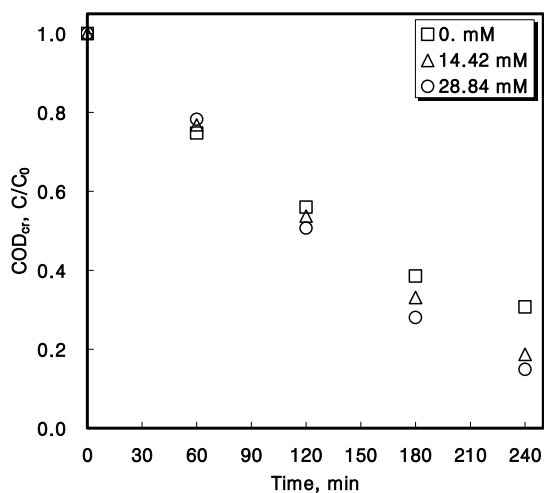


Fig. 2. Effect of H<sub>2</sub>O<sub>2</sub> dosage in the UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system.

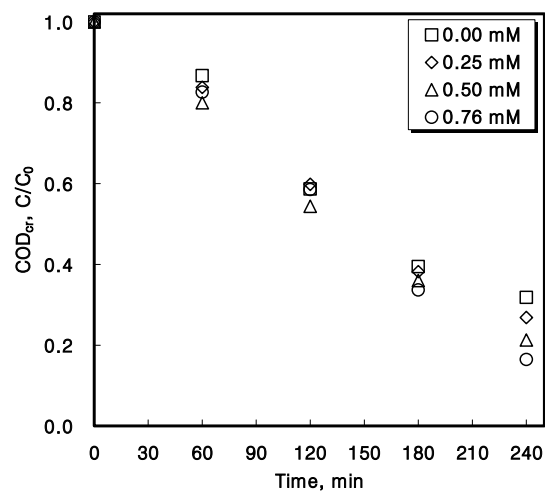


Fig. 3. Effect of FeSO<sub>4</sub> dosage in the UV/O<sub>3</sub>/FeSO<sub>4</sub> system.

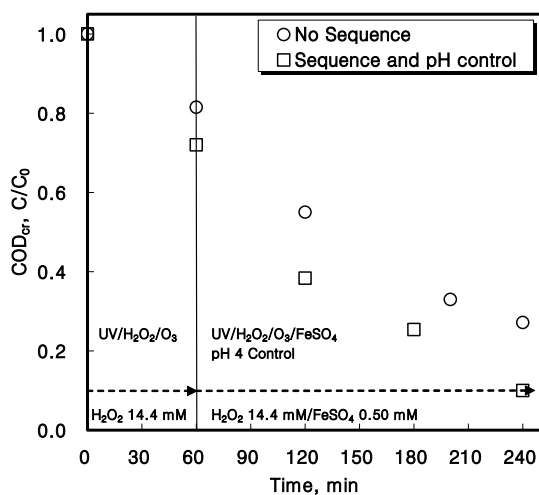


Fig. 4. Effect of sequence and pH control in the UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/FeSO<sub>4</sub> system.

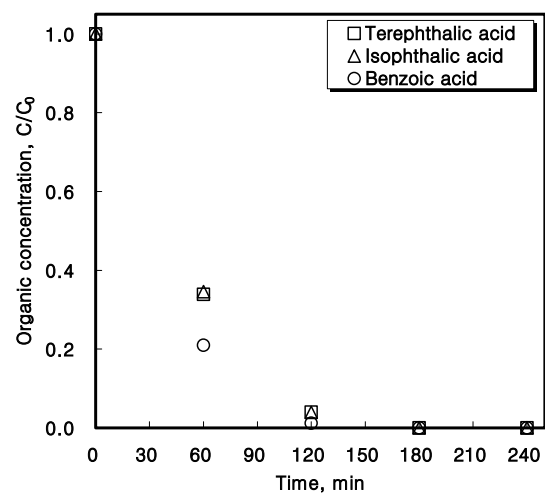


Fig. 5. Degradation of organic compound in the UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/FeSO<sub>4</sub> system.

But, sequence and pH control method in the UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/FeSO<sub>4</sub> system shows enhanced degradation efficiency. First UV and H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, FeSO<sub>4</sub> were input at once in the initial stage, which system shows more less degradation efficiency compare with UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system. But, sequence and

pH control method shows significant effect on the degradation of organic compare with UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system. UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> System was adopted initial stage from 0 to 60 min and that time 14.4 mM of H<sub>2</sub>O<sub>2</sub> was continuously supplied. From 60 min 14.4 mM of H<sub>2</sub>O<sub>2</sub> and 0.5 mM of FeSO<sub>4</sub> were added again and pH was controlled at 4. Fig. 5 shows the degradation of main organic compounds such as TPA, IPA, BA by the UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/Fe sequence method. Three main organic compounds were successfully destructed and go to low range molecular materials before 180 min. From first-order kinetic, destruction of TPA wastewater by direct with indirect oxidations and direct oxidation of rate constant  $k$  was calculated the values 0.0073 and 0.0036 respectively in the sequence UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/FeSO<sub>4</sub> system.

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