Effect of Light Intensity on the Photodegradation of PCB 153 in Aqueous Solution using UV and UV/H₂O₂

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ABSTRACT
This study examines the photodegradation of PCB 153 under ultraviolet radiation and ultraviolet radiation combined with hydrogen peroxide (H₂O₂) using a batch tubular recirculating photoreactor equipped with 17 W and 24 W UV-C lamps emitting at 254 nm. PCB 153 solutions with various concentration of 50 ppb, 80 ppb and 100 ppb were prepared for experiments conducted under photolysis (UV only) while 25 \( \mu \)L (0.221 mM), 50 \( \mu \)L (0.441 mM), 75 \( \mu \)L (0.662 mM) of 30% (w/w) H₂O₂ were individually added to an 80 ppb PCB 153 solution and used as samples for UV/H₂O₂ experimental runs. Under ultraviolet radiation, the increase of light intensity from 17 W to 24 W increased the degradation from 90.43% to 94.71% of an 80 ppb aqueous PCB 153 solution after 2 hrs of irradiation. The addition of 50 \( \mu \)L (0.441 mM) of 30% wt H₂O₂ resulted into a drastic decrease of the same concentration of PCB 153. After 30 minutes of irradiation using 17 W UV lamp, 95.95% PCB degradation was observed while complete degradation was attained with the 24 W UV lamp. The pH of the solutions was closely monitored and it was observed that it decreases during photodegradation. The decrease of the sample’s pH was a result of inorganic chlorides and acidic metabolites formation as measured using High Performance Liquid Chromatography (HPLC) - Conductivity Detector. Likewise, the PCB concentration of irradiated samples was measured using Gas Chromatography equipped with Electron Capture Detector (GC-ECD).

Keywords: advanced oxidation process, PCB 153, UV/H₂O₂

INTRODUCTION
Polychlorinated Biphenyls (PCBs) is a group of halogenated organic compounds that has caused potential adverse health effects to humans by contact with PCB contaminated soil, water, air, plants, and animals (Barro et al., 2005). Among the 209 PCB congeners that dominate the commercial PCB mixtures, the 2,2’,4,4’,5,5’-Hexachlorobiphenyl or PCB 153 is most resistant to degradation (Safe, 1994).

Various advanced oxidation processes, such as UV photolysis and UV/H₂O₂ have been applied successfully in wastewater treatment to mineralize many synthetic organic chemicals such as PCBs. The purpose of advanced oxidation process is to produce hydroxyl radicals, a highly reactive oxidizing agent that reacts with and destroys most organic pollutants in water. These are generated even in natural waters under the influence of sunlight (Haag and Hoigne, 1985).

Several studies have been done on the use of UV on the degradation of PCBs. Bunce et al. (1978) cited that, under ultraviolet light irradiation, PCB was significantly decomposed. For this reason, many investigations started to focus on the use of high
energy, low wavelength (254 - 300 nm) radiation for dechlorination of PCBs. Lin et al., (2004) observed the effect of diethyamine and xenon simulated on the photodegradation of PCBs in transformer oil and PCB 138. Xenon lamp of 150 W was used in the study which resulted to a significant photodegradation of PCBs. The mechanism of congener 138 dechlorination favored a nucleophilic aromatic substitution reaction. Chang et al., (2003) also carried out photodegradation study of 22 individual PCB congeners by irradiation using 15 W (254 nm) ultraviolet lamp in n-hexane solution. They reported that the photodechlorination of PCBs is apparently related to the charge distribution of the chlorinated carbon. The higher the charge distribution for chlorine attached carbon, the easier for photodechlorination to occur.

Light intensities emitted by 17 W and 24 W lamps were measured at $6.714 \times 10^{-6}$ Einstein/min and $1.284 \times 10^{-5}$ Einstein/min respectively (Macawile et al., 2007) using potassium ferrioxalate chemical actinometry (Murov et al., 1993)

The Asian Regional Research Programme on Environmental Technology (ARRPET) - De La Salle University (DLSU) conducted a study on the photodegradation of PCB (Aroclor 1260) using UV/H$_2$O$_2$ system (Centeno et al., 2005). To further enhance the degradation of PCB in water matrix using advanced oxidation process, this study aims to investigate the effect of UV light intensity, 17 Watts and 24 Watts, on PCB 153 aqueous solution using UV photolysis and UV/H$_2$O$_2$ processes.

**MATERIALS AND METHODS**

**Photoreactor**

To investigate the effect of light intensity on photodegradation of PCB 153, experiments were carried out in an aluminum cased batch tubular recirculating photoreactor (Sterilight Ultraviolet Sterilizer System) equipped with 17W (S330RL) and 24W (S463RL) low-pressure UV lamps that were vertically mounted at the center of quartz sleeves. The UV lamps were imported from Canada and locally distributed by Wet Industries Inc, Philippines. The 2.5 L stainless steel reactor was fabricated with various ports for the sample feed, for sampling and for the gas vent. Recirculation pump and thermocouple were installed into the reactor allowing continuous flow in clockwise direction and monitoring the temperature of solution. Fig. 1 shows the schematic diagram (A) and actual photo (B) of the batch circulating photoreactor.

**Preparation of Feed Stock Solutions**

Two sets of three various PCB 153 solutions (50 ppb, 80 ppb and 100 ppb) were prepared and used as feed stock for experiments conducted under photolysis (UV only). For photodegradation of PCB 153 under UV/H$_2$O$_2$ system, six solutions of 80 ppb PCB153 were prepared. Two of these six solutions were added with 25 μL (0.221 mM), 50 μL (0.441 mM), 75 μL (0.662 mM) of 30% (w/w) H$_2$O$_2$. Methanol was added in each solution to enhance the solubility of PCB 153 in water since PCB 153 has a solubility of 0.95 ppb. Before irradiation of sample to 17 W and 24 W UV lamps, solution was mixed and kept uncovered inside a hood to allow the solvent to evaporate. The stock solutions were wrapped on with aluminum foil and mixed using a polytetrafluoroethylene (PTFE) magnetic stirrer for 30 minutes. Fresh feed solution was observed for every experimental run.
Experimental Procedure

All experiments were carried out in batch mode. The UV lamp was warmed for 10 minutes to ensure stable lamp output. The PCB 153 solution was placed in the reactor and exposed to UV (17 W and 24 W) radiation for four (4) hours (UV) and one (1) hour (UV/H₂O₂). Five (5) mL samples were withdrawn each from two (2) sampling ports of the operating reactor. The collected samples were represented as sample 1 and sample 2. 

The samples withdrawn were immediately extracted using 5 mL of hexane, 100 μL of non-ionic surfactant Tween 80 (polyoxyethylene sorbitan monooleate) and sodium sulfate.

Instrumentation

Concentrations of PCB 153 in each experimental runs were measured using Gas Chromatography - Electron Capture Detector (GC 14B, Shimadzu, Japan). Temperature of the injection port and detector was maintained at 300°C. Temperature of the column started at 180°C and held for two minutes, ramped to 190°C at 1°C/minute, and 215°C at 2°C/minute. The chloride ion generation was quantitatively analyzed using High Performance Liquid Chromatography (LC-10AT, Shimadzu, Japan) equipped with conductivity detector (CDD 6A, Shimadzu, Japan)

RESULTS AND DISCUSSION

Degradation of PCB 153 Using UV Radiation

Experimental results on direct UV photolysis using 17 W and 24 W UV lamps are presented in Figs. 2 and 3. After 30 minutes exposure to 17 W UV radiation, the 80 ppb PCB 153 aqueous solution degraded significantly up to 77.84%. The same observation, at shorter irradiation time of approximately 17 minutes was exhibited on 80 ppb PCB 153 sample exposed under 24 W UV lamp. These can be attributed on the high amount
of energy, amounting to 470 kJ/mol, from ultraviolet light that caused the cleavage of organic compound bonds, which led to the formation of more radical intermediates and lowering of parent organic compound concentration (Tokumaru and Coyle, 1992). The free radicals produced from the cleavage of organic compound, which are often extremely reactive, explains the drastic decrease in the PCB 153 concentration during the first few minutes of irradiation. Conversely, the nearly stable behavior of PCB 153 degradation curve at $t = 30$ minutes and onwards can be accounted from the UV absorption of not only by PCB 153 but as well by the intermediate products generated during the photodegradation process.

**Degradation of PCB 153 Using UV Radiation: Effect of PCB Concentration**

Experimental results reveal that increasing the concentration of PCB 153 from 50 ppb to 100 ppb resulted into a decrease of percentage degradation from 91.95% to 87.66% and
97.80% to 93.92% for samples irradiated for two (2) hours under 17 W and 24 W respectively. These observations showed that for a fixed UV radiation intensity emitted by 17 W or 24 W UV lamps, the number of photons emitted were also fixed. Thus, at higher concentrations, more PCB molecules were capable of absorbing the fixed amount of photons and consequently lowered the percent degradation of PCB 153. The same results were observed in AOP treatment of various organic pollutants in wastewater such as humic acid (Wang et al., 2000), reactive azo dye (Muruganandham and Swaminathan, 2004), and acid orange 7 (Behnajady et al., 2003).

**Degradation of PCB 153 Using UV/H$_2$O$_2$: Effect of Peroxide Concentration**

Results on photodegradation of PCB 153 using three different concentrations of H$_2$O$_2$ irradiated under 17 W and 24 W are presented in Figs. 4 and 5 respectively. As shown in Fig. 4, the PCB degradation increased with increasing H$_2$O$_2$ concentration under 17 W UV lamp. The highest percent degradation (> 98%) of PCB 153 was achieved upon addition of 0.662 mM hydrogen peroxide at $t = 20$ minutes using 17 W UV lamp. While

![Fig. 4 - Degradation of PCB 153 using UV/H$_2$O$_2$ system (17 W UV Lamp)](image)

![Fig. 5 - Degradation of PCB 153 using UV/H$_2$O$_2$ system (24 W UV Lamp)](image)
as shown in Fig. 5, the highest percentage degradation of PCB 153 was achieved at $t = 30 \text{ minutes} \ (24 \text{ W})$ UV lamp. The complete degradation of PCB 153 at shorter reaction time was brought by the hydroxyl ($'OH$) radical attack. According to Wang et al., (2000), hydroxyl radicals attack organic compounds non-selectively with a rate constant ranging from $10^6$ to $10^{10}/\text{Ms}$. The same observation was reported in the study by Woods and Pikaev, (1994) in which the radicals produced from UV/H$_2$O$_2$ reacted with the first collided molecule and abstracted hydrogen from any one of the C-H bonds present in an organic molecule.

In Fig. 5, the PCB 153 samples with 0.441 mM of H$_2$O$_2$ exhibited higher percent degradation compared to PCB 153 samples spiked with a higher peroxide concentration of 0.662 mM. This result is in contrast from the observations and discussions made using 17 W in UV experimental runs. This occurrence can be explained by the two opposing effects and functions of peroxide concentration that is to be a UV light photon absorber and $'OH$ scavenger. At higher H$_2$O$_2$ concentrations, more hydroxyl radicals were available to attack aromatic rings and consequently increase the PCB degradation. However in excess of H$_2$O$_2$ concentration, depleted the generation of $'OH$ radicals and form hydroperoxyl radicals (HO$_2^*$) as shown in equation 1. The same observation was noted in the photochemical degradation study of 1,3-dinitrobenzene, the excess spiked of H$_2$O$_2$ in aqueous solution will likely acts as $'OH$ scavenger to produce the much less reactive HO$_2^*$, which consequently caused the decrease of initial reaction rate (Chen et al., 2004).

\[
'OH + H_2O_2 \rightarrow HO_2 + H_2O \quad (1)
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Likewise, Centeno et al., (2005) reported on photodegradation of Aroclor 1260 in which peroxide concentration reacted with hydroxyl radicals as inhibiting agent and by Lopez et al., (2000) on photodegradation of 4-chloro-3,5-dinitrobenzoic acid in which addition of H$_2$O$_2$ produced $'HO_2$ radicals which was less reactive than $'OH$.

**Degradation of PCB 153 Using UV and UV/H$_2$O$_2$: Effect of Light Intensity**

To determine the effect of light intensity on photodegradation of PCB 153, two Hg lamps were used as source of UV radiation. Experimental results show that the percent photodegradation of PCB 153, in both direct UV and UV/H$_2$O$_2$ experimental runs increased from 17 W to 24 W UV lamps. This observation is evident in Figs. 2 and 3 for direct UV and Figs. 4 and 5 for UV/H$_2$O$_2$ experimental runs. The results showed that more excited PCB molecules were produced and destroyed as the light intensity of the UV lamp increased from 17 W to 24 W. Likewise, more hydroxyl radicals were generated upon photo dissociation of H$_2$O$_2$ followed by degradation of more PCB 153 in UV/H$_2$O$_2$ system.

The observed increase on the photodegradation efficiency relative to the light energy applied was similar to the results obtained in photodestruction studies of acid orange 7 (Behnajady et al., 2003), reactive azo dye (Muruganandham and Swaminathan, 2004) and 4-chloro-3,5-dinitrobenzoic acid (Lopez et al., 2000).
Chloride Ion Analysis
A test for chloride ion concentration was conducted using irradiated samples from UV/H$_2$O$_2$ experimental runs. The initial PCB 153 concentration and H$_2$O$_2$ concentration used were 80 ppb and 0.221 mM respectively. Five (5) ml of irradiated sample was withdrawn at specified time interval. The amount of chloride ion released during the experiment is illustrated in Fig. 6.

Experiments conducted under UV/H$_2$O$_2$ system showed that the generation of chloride ions increases with increasing percentage PCB degradation. Prolonged irradiation time resulted to increase in chloride ion concentration and eventually has stabilized. This result could be possibly explained by the process of reductive dechlorination, which is the usual primary process in photoreaction experiments. In general, the chloride ion generation increases with an increase of light exposure and UV light intensity to PCB 153. This result is similar to the observation on chloride ion produced during the photodegradation of permethrin (Hidaka et al., 1992). After 240 minutes of irradiation, the 80 ppb PCB 153 water sample exposed to 24 Watt UV lamp generated a higher concentration of chloride ion compared with sample exposed to 17 Watt UV lamp. PCB 153 was not detected in the final concentration of the water samples however there were more PCB metabolites present in the sample exposed in 17 Watt UV lamp. The different amount of PCB metabolites present at $t = 240$ minutes affects the final chloride ion concentration in the solution.

CONCLUSIONS
Experimental results reveal that UV and UV/H$_2$O$_2$ are efficient processes for the degradation of PCB 153 in water matrix. Higher percentage degradation of PCB 153 was obtained on the UV/H$_2$O$_2$ system. It was observed that the reactive species involved in the degradation of PCB 153 is brought by the generation of hydroxyl (’OH) radicals. The increase of light intensity from 17 W to 24 W increased the PCB 153 degradation.
Other operational parameters also showed that the increase in initial PCB concentration led to a lower percentage degradation of PCB 153 while an increase in peroxide concentration to the solution led to a higher degradation of PCB 153. The addition of more peroxide concentration resulted into a lower percentage degradation of PCB 153 due to the scavenging of the hydroxyl radicals (‘OH).

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