# The Effect of Hydrogen Peroxide Concentration in Degradation of 2,4,6-Trichlorophenol Using UV Light

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***Abstract*—The highly toxic of organic contaminant had caused problems to human health and the environment. Hence, it was very compulsory to do a research on method how to degrade the toxic compound from the environment. The method proposed was by using the presence of an oxidizing agent which was $H_2O_2$ solution together with UV light. In order to study effect on $H_2O_2$ concentration, the concentration of $H_2O_2$ solution was varied to three different concentrations. Those were 5%w/v, 15%w/v and 25%w/v respectively. The initial concentration of 2,4,6-TCP was prepared at 30 and 60 ppm to study the effect between different initial concentration. The period of exposure of the sample to the UV light was 6 hours. The experiment was conducted in a 25mL sealed glass bottle which act as batch reactor. Six sample solutions were prepared. The instrument used to analyze the degradation was High Performance Liquid Chromatography (HPLC). From the analysis, different $H_2O_2$ concentration gives big influence to the degree of degradation of the 2,4,6-TCP compound. From the research study, increasing concentration of $H_2O_2$ solution, cause the percent of removal of the persistent organic compound also increasing for both initial concentration of 2,4,6-TCP. The highest degree of degradation for 30ppm and 60ppm concentration were 100% and 99.62% respectively. The combination of $H_2O_2$/UV by AOPs shows high efficiency in the degradation process.**

***Keywords*— 2,4,6-Trichlorophenol (2,4,6-TCP), Hydrogen peroxide ($H_2O_2$), degradation, UV light.**

## I. INTRODUCTION

This research study comes with two objectives which were to investigate the effect of $H_2O_2$ concentration in the degradation of 2,4,6-Trichlorophenol (TCP) using UV light and to optimize the efficiency of the combination of both $H_2O_2$ with the UV light ($H_2O_2$/UV). In the recent years, there was growing concern from the public on the quality of wastewater since it was likely to contaminate from various organic compounds. The effluent from the manufacturing industries like the pulp and paper industry, and thermal power plants discharged into the environment had poses a threat to the ecosystems and drinking water quality [1]. They become released into the environment from the numerous anthropogenic activities [2].

The organic contaminant often discovered in the environment of most industrialized countries was chlorophenols which highly in toxicity, hazardous and probable human carcinogen [3]. They had been considered as highly pollutants due to their toxicity, unusual and caustics [4]. Wood preservation industry used large quantities of CPs for pressure treatment in the mentioned industry [1]. Although for the past few years, the use of CPs in industries had been restricted, large quantities of CPs still produced by some of the related industries. Meanwhile, lower quantities of CPs acts as intermediates in the production of pesticides [3].

Among various types of CPs, 2,4,6-trichlorophenol was commonly found in the wastewater and has most stable structure compared to its own aromatic compound, phenol. CPs had poses threat to human health and all other living things. Inhalation, ingestion and dermal contact are the routes of potential human exposure to this recalcitrant organic contaminant. 2,4,6-TCP was abundant in effluent from the pulp bleaching process [5]. It was commonly found in drinking water as a by-product from the chlorination [2]. 2,4,6-TCP has been widely used in the industrial production of pesticides, herbicides, dyes, pigments and paper. The present of 2,4,6-TCP in water poses problems to the quality of water, human health and may harm the all living things as well as the ecosystem. The position of chlorine atoms relative to the hydroxyl group are responsible for its toxicity and carcinogenic properties. The properties of 2,4,6-TCP cause it very crucial to degrade the 2,4,6-TCP from the environment.

Nowadays, different alternative of methods had been created for safely degradation of this persistent compounds from wastewater. The methods include of biological, chemical and thermal treatment methods [6]. The biological method need long reaction times since the degradation was done by the microorganisms [6]. Chemical treatment methods including precipitation, flocculation, reverse osmosis, and activated carbon adsorption require post treatments to remove the pollutants from the contaminated environment [6]. Besides, other conventional methods were chemical and photooxidation, adsorption on activated charcoal, solvent extraction, and microbial degradation [4]. Those methods can be differentiated easily by their cost and efficiency of degradation as well as the formation of hazardous by-products [4].

Advanced oxidation process (AOP) had been proposed as one of the potential method for reducing toxic and recalcitrant compounds compared to other conventional treatment method [7]. It was a kind of process which reducing the persistent hazardous compound by oxidation through reaction with hydroxyl radicals, $OH^+$ [3]. It was capable in achieving complete mineralization of persistent compound [5]. AOP was very effective in eliminating the hazardous compounds compared to other various ways of water purification. However, the reaction time for AOP was long and often require strong doses of oxidant [1]. The combination of UV/$H_2O_2$ was one of the method by AOP which also known as photooxidation process.

## II. METHODOLOGY

All of the degradation research study was carried out in a batch photoreactor system [8]. The photoreactor system consist of a direct UV light supplied from UV light source with fixed distance about 15cm to the samples and sealed glass bottles with 25mL

volume. High Performance Liquid Chromatography (HPLC) was used to analyze the initial and final concentration of the 2, 4, 6-TCP in the prepared solution. The purity of the $H_2O_2$ was 33%. The experiment was performed for six hours and samples were taken for every one hour to six hours of irradiation. The starting of the experiment was the time at which the UV lamp was turned on.

### *A. Materials and chemicals*

The model compound used in the present study was 2, 4, 6-TCP and was supplied from Merck. The oxidant used was $H_2O_2$ solution supplied from Merck/System which was in liquid form with the concentration of 30%w/v. Methanol solution was supplied from System and used to prepare the stock solution of the 2,4,6-TCP.

### *B. HPLC Analyses*

Fig.1 High Performance Liquid Chromatography (Perkin Elmer)

Fig. 1 above shows the HPLC Perkin Elmer Model Series 200. HPLC was one of the instrument with the principle of identification of organic compounds in solution.

Results from the HPLC analyzes were used to identify and evaluate peaks that appeared during course of reaction. The chromatogram was also used to monitor the disappearance of 2,4,6-TCP.

The intermediate peaks of all compound present in the sample solution was identify by quantitative and qualitative analyses. The concentration of the solution was initially determined from the prepared calibration charts with known concentrations of the analyte.

Below shows the condition of HPLC system [10]:

HPLC system: Hewlett-Packard HP 1050 Liquid Chromatography with Ultraviolet absorbance detector.
Column : 15 cm x 150 mm
Mobile phase : Solvent A – Deionized water
Solvent B – Methanol and water(7:3%,v/v)
Flow Rate : 1.2 mL/min
Injection Volume : 1microL
Stop / Post time : 5min
Detection Wavelength: 290nm

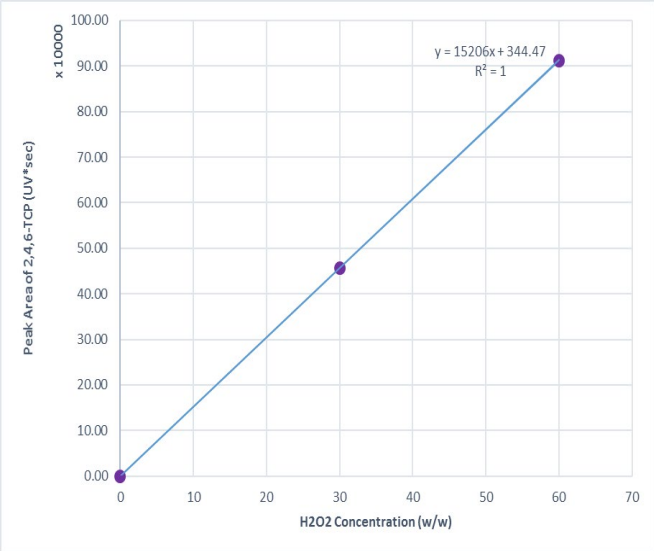


Fig.2. Standard curve of 2,4,6-TCP concentration with wavelength 290nm.

Fig.2. shows the calibration curve for the 2,4,6-TCP initial concentration. The graph of calibration was constructed from the injection of all initial concentration of 2,4,6-TCP which were 30 and 60ppm respectively. Calibration curve was compulsory to determine the final concentration of a single analyte. It is a kind of graphical representation of the amount and data responses of that compound. The amount is obtained from one or more samples of calibration.

### *C. Preparation of 2,4,6-Trichlorophenol solution*

In this experiment, two different concentration of 2,4,6-TCP were studied, as 30ppm and 60ppm, to investigate the effect of concentration of 2,4,6-TCP on the extent of degradation. The stock solution of 500ppm was prepared with small volume of methanol as solvent and 0.25 g of 2,4,6-TCP in powder form. Methanol solution was then added up to the volume of 500mL. The stock solution was stirred using magnetic stirrer and was fully wrapped with aluminum foil and placed at dark space. Both initial concentrations were prepared from the dilution of stock solution just prior to start the reaction.

### *D. Hydrogen Peroxide Concentration Preparation*

Reagent grade $H_2O_2$ solution (30%w/v) was used. 5%, 15% and 25% by volume of $H_2O_2$ stock solution was prepared from the 30% standard solution by dilution. The stock solution was prepared by adding the calculated amount of $H_2O_2$ into the glass bottle containing calculated 2,4,6-TCP sample solution.

### *E. UV/hydrogen peroxide system*

The prepared 30ppm and 60ppm of initial concentration of 2,4,6-TCP were initially analyzed using HPLC. All samples were added with three varied $H_2O_2$ concentration by volume, 5%w/v, 15%w/v and 25%w/v. Sealed glass bottles with parafilm were used and act as batch reactor.

All other operating parameters such as pH and temperature were kept constant. The UV light source used was Airstream Horizontal Laminar Flow Cabinets, model AHC-4A1 with serial number 2004-8150. The light intensity of the UV lamp was 1527 lux. The ambient temperature of the batch systems was maintained at room temperature.

All those six sealed glass bottles are placed under direct UV lamp. The experiments were performed for period of six hours. The glass bottles were placed closer with the source of UV light and the distance was fixed. Liquid samples were collected at 60-min intervals. The samples were stored in small glass bottles until the concentrations of the contents were analyzed by the HPLC instrument.

An aliquot of the sample was injected into the HPLC with 10microL for analysis at 290nm. Qualitative and quantitative analysis were performed to identify the peak of 2,4,6-TCP compound. The retention time of 2,4,6-TCP was observed from 3.5min to 5.5 min (2.0 min of appearance). Blank solution of methanol and $H_2O_2$ were injected to identify their retention time. The influence of concentration of $H_2O_2$ solution was studied on the degradation.

### *F. Determination of degradation efficiency*

The percentage of rate of removal of 2,4,6-TCP was calculated as follows:

$$\% \text{ Degradation} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where $C_0$ is the initial concentration of 2, 4, 6-TCP present in the solution. C is the final concentration of 2,4,6-TCP present after photo-irradiation.

## III. RESULTS AND DISCUSSION

### *A. Effect of $H_2O_2$ concentration on degradation of 2,4,6-TCP with UV light.*

To obtain a deeper understanding towards the effective reactivity of the hydroxyl radicals due to the addition of $H_2O_2$ solution, the degradation of 2,4,6-TCP was studied with different amounts of hydrogen peroxide ($H_2O_2$/UV system) in aqueous solution.

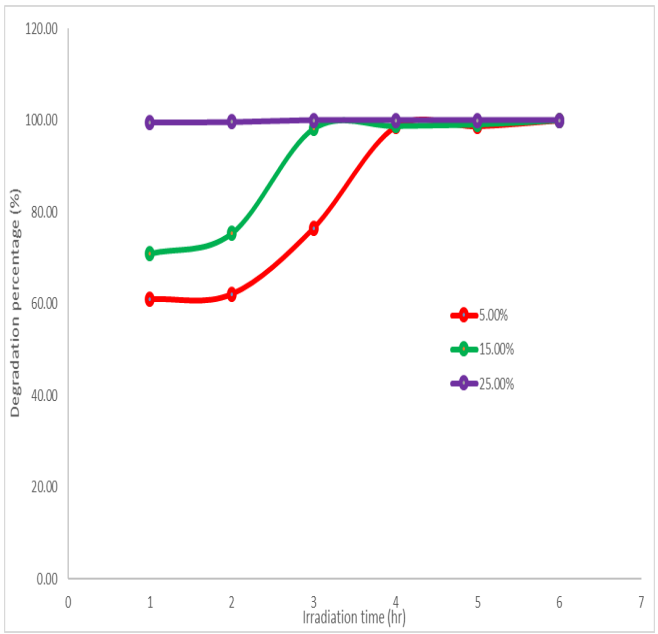


Fig.3. Effect of varied $H_2O_2$ concentration on 2,4,6-TCP removal via direct source of UV light. ($C_0$ = 30ppm)

Fig.3 shows the changes in the degree of degradation of degradation percentage versus time exposed to UV light source for 30ppm concentration of 2,4,6-TCP. The degradation was very fast under the $H_2O_2$/UV condition compared to UV light alone [10]. In order to enhance the degree of degradation and study the effect of $H_2O_2$ (%w/v) concentration, varied concentration of the oxidant was introduced into the photolysis system to help the UV light in supplying more hydroxyl radicals.

At the first hour of exposure, shows that the degradation percentage of 2,4,6-TCP was the lowest at 5%w/v of $H_2O_2$ concentration followed with 15%w/v and 25%w/v of $H_2O_2$ concentration. The figure obviously shown that all the curve was kept increasing form the first hour till six hours of exposure. This indicates that the longer the time of exposing the sample solution to the UV light source, hence the higher the rate of removal of 2,4,6-TCP. At the same time, also can be concluded that the higher the concentration of $H_2O_2$ concentration added, the higher the percentage degradation of 2,4,6-TCP [8].

From the graph, approximately shows that when the 2,4,6-TCP was treated with the highest concentration of $H_2O_2$ which was 25% (w/v), the 2,4,6-TCP obtained fully degradation at first 180 min of irradiation which was 100%. However, the rate of removal was decreased when the solution treated with lower concentration of $H_2O_2$. Meanwhile, 5% and 15% (w/v) $H_2O_2$ concentration also gained 100% degradation but after being exposed for about six hours which means longer irradiation time was required.

The optimum time of degradation for 30ppm concentration 2,4,6-TCP was at 180 min when treated with 25% $H_2O_2$(w/v) which was able to obtain fully degradation. Meanwhile, for both 5%(w/v) and 15%(w/v), the optimum time for degradation was at six hours exposure.

According to Nguyen et. al, 2015, [6], removal of $H_2O_2$ was only 59% within 180min when treated with 2.0mM $H_2O_2$ and increased up to 99% within 150min after adding 20.0mM $H_2O_2$. Besides, Pera-Titus et. al, 2004, [11] also had the same hypothesis which stated that as concentration of $H_2O_2$ increases, the degradation of CPs also increases. This was mainly due to the amount of oxidant present in the reaction system.

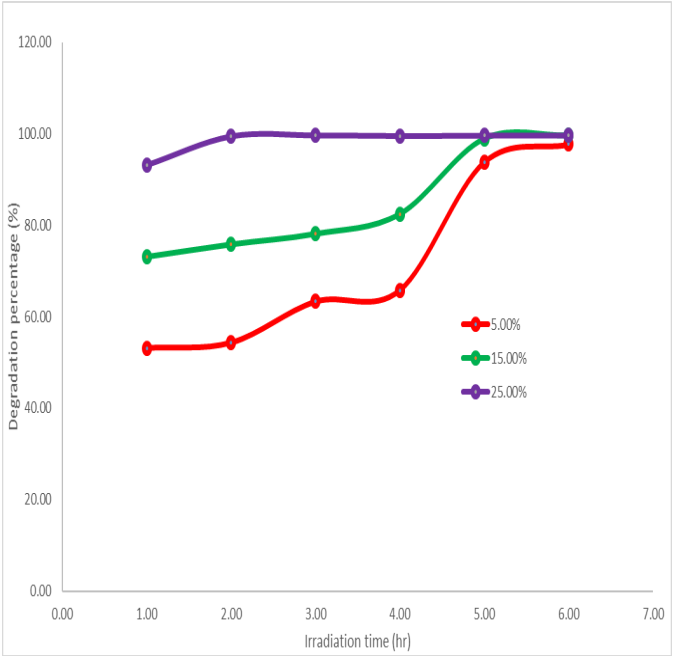


Fig.4. Effect of varied $H_2O_2$ concentration on 2,4,6-TCP removal via direct source of UV light. ($C_0$ = 60ppm)

Fig.4. above shows the rate of removal of 60ppm concentration of 2,4,6-TCP with also three varied concentration of $H_2O_2$; 5%w/v, 15%w/v and 25%w/v respectively.

Fig.5. above shows the graph of effect of $H_2O_2$ concentration on percentage degradation of 60ppm concentration 2,4,6-TCP. Generally, all three graphs in the figure kept increasing starting from the first hour till six hours exposed. This graph of 60ppm concentration 2,4,6-TCP obviously show the same hypothesis as the 30ppm concentration of 2,4,6-TCP.

The highest degree of degradation was only 99.62% when treated with 25%w/v of $H_2O_2$ which was at six hours irradiation compared to 30ppm concentration 2,4,6-TCP which able to degrade 100% at early of 180min. This result was might due to the high concentration of 2,4,6-TCP in the 60ppm concentration 2,4,6-TCP which require strong doses of oxidant to produce more hydroxyl radicals to attack the recalcitrant compound. High concentration of 2,4,6-TCP make it more persistent to biodegradation and persistent to degradation.

It was known that $H_2O_2$ able in enhanced the degradation of several recalcitrant organic compound. In previous study by Antonaraki et.al (2002) [3], $H_2O_2$ has been used as an additional source of hydroxyl radicals generation with higher degree of removal and up to certain optimum concentration.

The observed results for both initial concentration of 2,4,6-TCP showed the action of scavenging by the $H_2O_2$ which lead to the higher degree of degradation [6]. As the irradiation time increased, the $H_2O_2$ became more volatile and it then undergoes dissociation which cause the formation of hydroxyl radicals.

Below shows the mechanism of reactions occur during the process of degradation under $H_2O_2$/UV are [13]:

$$OH^+ + H\text{-}R \longrightarrow R^+ + H_2O \quad (2)$$

$$R^+ + O_2 \longrightarrow RO_2^+ \quad (3)$$

$$R^+ + H_2O_2 \longrightarrow R\text{-}OH + OH^+ \quad (4)$$

$$RH + OH^+ \longrightarrow R+ + H_2O \quad (5)$$

$$RH + OH^+ \longrightarrow R+ + H_2O \quad (6)$$

$$H_2O_2 \xrightarrow{hv} OH^+ \quad (7)$$

Eqn. (2) shows the $OH^+$ generated from the $H_2O_2$/UV system. The $OH^+$ produce will act as an oxidant and not as catalyst. It will function in enhanced the rate of degradation. However, it will not speed up the reaction rate like what catalyst do. The UV light alone able to degrade the persistent compound but only in small percentage and is low degradability. Besides, the degradation time is often longer. Hence, heterogeneous combination is a must to enhance the degradation. $H_2O_2$ is added to increase the production of $OH^+$. $OH^+$ will then degrade the pollutant organic compound. Higher $OH^+$ generate, hence higher removal of persistent compound in percentage.

Eqn. (2) also indicates the first reaction of $OH^+$ with the pollutant organic compound by the removal of hydrogen atom from the recalcitrant organic compound which then forming water and alkyl radical ($R^+$). The produced $R^+$ typically then will react with oxygen which then produce a peroxy radical in eqn. (3) [11]. Besides, the produced alkyl radical also reacts with the $H_2O_2$ to regenerate more $OH^+$. At the same time the $R^+$ will combine with the $OH^+$.

Eqn. (6) above shows further oxidation of the organic substance. In the propagation of further oxidation, the $OH^+$ and the active reactant are regenerated. The generated $OH^+$ capable in attracting a hydrogen atom from many present pollutant organic molecules. Besides it also offers the addition of the abstract hydrogen atom into any carbon to carbon double bond [11]. At the same time, the $OH^+$ can produce a wide spectrum of products by accepting an electron [11]. The phenol aromatic ring in the molecule of 2, 4, 6 - TCP reacts with the $OH^+$ in water at various rate. On the other hand, the rate of the oxidation of substrate is dependent on type of radical oxidation processes. This will then determine the concentration of generate $OH^+$ in the degradation [11].

Eqn. (7) above represent photoactivation reaction where with the presence of UV light, the $H_2O_2$ generated free $OH^+$. Without the photoactivation reaction, $H_2O_2$ is not able to degrade the persistent organic compound [11].

From the same view, UV alone may only exhibit bond cleavage of the organic compound but slowly attract other molecules [11]. Besides the formation of free radical when UV light alone is focused on certain molecules only and at a rate slower than $H_2O_2$/UV combination [13]. UV light alone was a method based on the energy supply to the organic compound as radiation. The radiation was absorbed by the molecules and increase into their excited states.

Photolysis system or UV light alone is a type of process which supplies direct sunlight to the aqueous solution alone. The UV light alone able to degrade the persistent compound but only in small percentage and is low degradability. Besides, the degradation time is often longer. Hence, heterogeneous combination is a must to enhance the degradation. From the same view, UV alone may only exhibit bond cleavage of the organic compound but slowly attract other molecules. Besides the formation of free radical is focused on certain molecules only and at a rate slower than $H_2O_2$/UV combination.

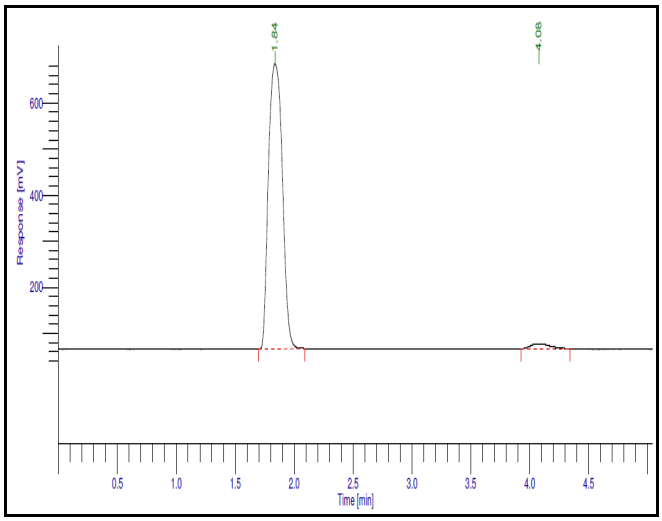


Fig. 5. HPLC chromatogram showing the peaks of both $H_2O_2$ and 2,4,6-TCP.

Fig.5. above shows the HPLC chromatogram showing the peaks of both $H_2O_2$ and 2,4,6-TCP. Both retention time and peak of compound were identified from qualitative and quantitative analysis. First peak at 1.84 min was the $H_2O_2$ compound and another one at 4.08 time would be the retention time for 2,4,6-TCP compound.

Along the experiment conducted, the chromatogram shows the retention time of 2,4,6-TCP always changed and would be between the range of 3.50 to 5.50 min. This is because the $Cl^-$ from 2,4,6-TCP compound tends to move from its position when gained heat which was from the UV light source and then will attached to other carbon bond. Then produce another isomer of trichlorophenol such as 2,3,4-TCP and 2,3,6-TCP as time of exposure passed. Hence, produced different retention time.

### *B. Effect of initial 2,4,6-TCP concentration on degradation of 2,4,6-TCP.*

To gain better understanding regarding on the concentration effect, two different initial concentration of 2,4,6-TCP, 30ppm and 60ppm, were analyzed using also the $H_2O_2$/UV system.

| Irradiation time (hr) | 2,4,6-TCP Concentration (ppm) | |
|---|---|---|
| | 30 | 60 |
| 1 | 60.90 | 53.17 |
| 2 | 61.99 | 54.34 |
| 3 | 76.45 | 63.33 |
| 4 | 98.59 | 65.80 |
| 5 | 98.72 | 93.84 |
| 6 | 100.00 | 97.73 |

Table 1. .Effect of initial 2,4,6-TCP concentration on percentage degradation of 2,4,6-TCP (5%w/v $H_2O_2$)

Table 1. shows the comparison of graph between both concentration of 2,4,6-TCP at 5%w/v $H_2O_2$ addition. At six hours of exposure, the highest degree of degradation was obtained by 30ppm 2,4,6-TCP which was 100% and 60ppm 2,4,6-TCP was 97.73%. 30ppm 2,4,6-TCP sample solution obtained higher rate of removal since it contained less concentration of toxic compound compared to the 60ppm 2,4,6-TCP. Less concentration of recalcitrant compound was easier to degrade.

## IV. CONCLUSION

As a conclusion, exposing the sample solution containing 2,4,6-TCP to the UV light alone was a poor method. Meanwhile, the addition of oxidant which was $H_2O_2$ solution can enhanced the rate of degradation. The higher the concentration of $H_2O_2$ added, the higher the hydroxyl radicals generated and hence contribute to higher degree of degradation. Besides, also can be concluded that higher $H_2O_2$ concentration take shorter time to reached fully degradation. The optimum degree of degradation for both 30ppm and 60ppm concentration were 100% at early of 180min exposed to irradiation and 99.62% at six hours.

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