

Photochemical Degradation of Oxytetracycline Hydrochloride in the Presence of H₂O₂

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Abstract—Advanced oxidation process (AOPs) are technologies based on the intermediacy of hydroxyl radical and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products. In this paper, Oxytetracycline hydrochloride (OTC) was degraded inside a UV-H₂O₂ system which utilize hydroxyl radical generated from H₂O₂ to attack OTC. Concentration of H₂O₂, temperature and pH was varied in this experiment. To monitor OTC degradation, TOC and UV-VIS spectra analysis were carried out. Constant OTC concentration at 250 ppm was used. About 93.06% of TOC removal was achieved at 40°C and 1 eq mole ratio H₂O₂ to OTC. After 180 min irradiation, UV-Vis spectra of OTC have shown total disappearance of OTC peak. HPLC analyses has shown about 93.08% of OTC were degraded after 180 min irradiated inside UV-H₂O₂ system.

Keywords- Environmental, AOPs, Oxytetracycline, UV/H₂O₂

I. INTRODUCTION

In our society, antibiotic were widely used for treating bacterial infections in humans and animal [1]. This high increment has lead to the increased concentration of antibiotic in our environment. The contamination may come from excretion of metabolized or unmetabolized antibiotics from the human and animal body which have been detected in surface and ground water, drinking water, tap water, ocean water, sediments and soil [2-4]. It can accumulate in the natural ecosystem which may produce antibiotic-resistant bacteria, modification of the indigenous microbiota and may damage internal organ of the aquatic organism [5-8].

Several classes of antibiotics were known namely: β-lactams, Tetracyclines, Aminoglycosides, Quinolones, Macrolides, Glycopeptides, and Sulfonamides. OTC is the most widely used antibiotics in livestock productions [9-11]. Therefore, in this study is chosen as the source of antibiotics contaminant (Fig.1). OTC is belonging to Tetracycline classes of antibiotics.

Antibiotics have extreme resistances toward biological degradation process. Therefore, many research works concentrated on non-biological processes for antibiotic destruction. One of them is advanced oxidation processes

(AOPs) which utilize highly reactive species (i.e. hydroxyl radical) for transforming organic pollutant into non toxic substances such as CO₂ and H₂O [3, 12].

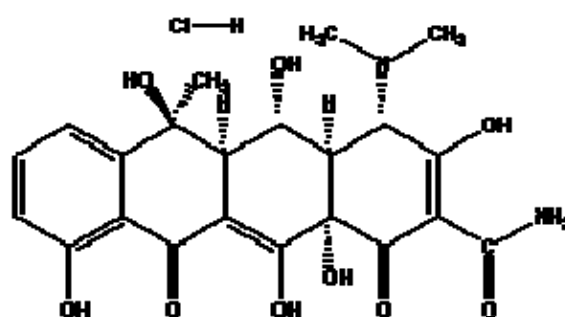


Figure 1 Chemical structure of OTC

To date, most of the studies on pharmaceuticals degradation using UV/H₂O₂ have been done, but only few pharmaceuticals such as carbamazepine, diclofenac, sulfamethoxazole, clofibric acid and 17β-estradiol have been studied [3, 13]. Several systems have been used to study OTC degradation such as water hydrolysis, fenton process, ozone process, UV photolysis, UV-TiO₂-zeolite photocatalytic, enzymatic degradation and γ and pulse irradiation [10- 25]. However, limited studies have been conducted in studying OTC degradation inside UV/H₂O₂ system. In this study, OTC degradation was investigated inside a UV-H₂O₂ system. The experiments were conducted by varying temperature at 20,30, 40°C; pH at 3,7 and 10; as well as H₂O₂ to OTC mole ratio at 0.5;1.0 and 1.5 eq.

II. MATERIALS AND METHODS

A. Materials

Oxytetracycline hydrochloride (Merck, Germany) was used as the source of antibiotics contaminant. Hydrogen peroxide 30% (Merck, Germany) was used as the source of •OH radical.

For pH adjustment, NaOH (Merck, Germany) and H₂SO₄ 98% (Merck, Germany) were used.

B. Methods

UV/H₂O₂

The experiments were carried out inside a glass reactor which irradiated with low pressure UV lamp. During irradiation, the solution was magnetically stirred and cooled using water flows inside the reactor jacket. Antibiotic and H₂O₂ were added inside the reactor with 400 mL working volume. Concentrations of H₂O₂, initial pH, as well as temperature were varied. To monitor the progress of degradation, about 5 mL of liquid samples are drawn from the reactor at scheduled times.

Analyses

UV/H₂O₂

The experiments were carried out inside a glass reactor which irradiated with low pressure UV lamp. During irradiation, the solution was magnetically stirred and cooled using water flows inside the reactor jacket. Antibiotic and H₂O₂ were added inside the reactor with 400 mL working volume. Concentrations of H₂O₂, initial pH, as well as temperature were varied. To monitor the progress of degradation, about 5 mL of liquid samples are drawn from the reactor at scheduled times. Initial pH was adjusted by adding drops of concentrated NaOH or H₂SO₄. TOC analyses are carried out using a TOC V-CSH analyzer (Shimadzu, Japan) while the amount of H₂O₂ inside the solution is analyzed by colorimetric method using KMnO₄. UV-VIS spectra analyses were carried out using UV-VIS Spectrophotometer (Shimadzu, Japan). OTC concentrations were measured using HPLC (Agilent 1100 Series) equipped with a Zorbax SB-C18 column (250mm x 4.5 mm, 5 μm) at 30°C. Mobile phase of 70% H₂C₂O₄ 0.01M, 20% acetonitrile and 10% methanol were used. OTC peak detection was performed with UV detector at 355 nm.

III. RESULTS AND DISCUSSIONS

A. Effect of H₂O₂ concentrations

In this study, concentrations of H₂O₂ were varied at 0.5, 1.0 and 1.5 x theoretical ratios. The mole ratio was based on the chemical equation below (Eq. 1):

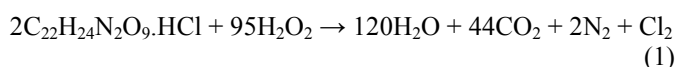


Fig. 2 describe the TOC profile of OTC at various H₂O₂ concentrations. It was shown that the lowest TOC value was achieved at 1x eq ratio of H₂O₂. About 79.2, 86.18 and 84.08% TOC degradation were observed for 0.5, 1 and 1.5 x theoretical ratios. Increment of the TOC removal at 0.5 and 1 eq ratio is due to the higher amount of hydroxyl radical concentration inside the solution. At higher ratio, H₂O₂ acts as hydroxyl radical scavenger (Eq.2 and 3), thus lowering the TOC removal.



Consumption of H₂O₂ as the source of OH radical is shown in Fig. 3. The highest consumption was occurred during the 40-120 min of degradation time which was shown for all different H₂O₂ concentrations.

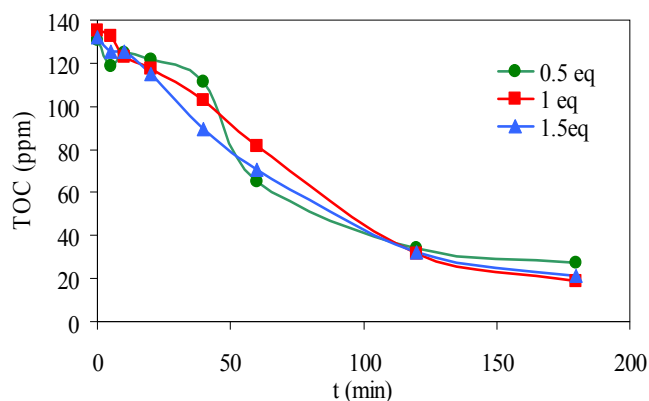


Figure 2. TOC profile of OTC at different H₂O₂ concentrations

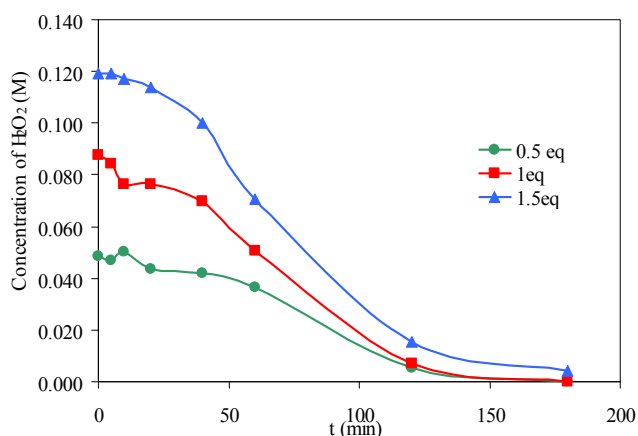


Figure 3 H₂O₂ consumption profile

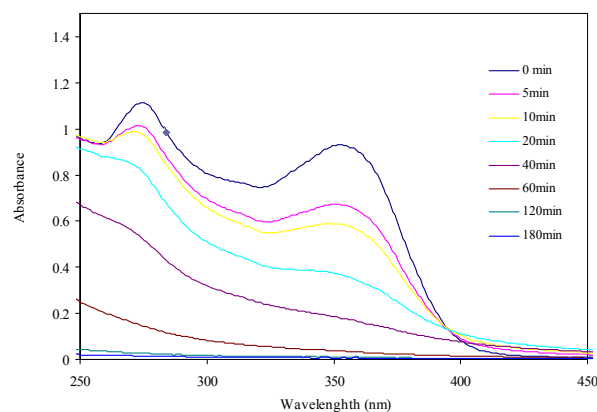


Figure 4 UV-Vis Spectra of 250 ppm OTC after 180 min degradation at 0.5 eq ratio

TABLE I. OTC CONCENTRATION AT CERTAIN T FOR 250PPM OTC AND 1.5 EQ RATIO OF H₂O₂-OTC

Time (min)	OTC (ppm)
0	196.9
5	106.9
10	78.9
20	33.1
40	6.3
60	4.1
120	3
180	2.3

Degradation of OTC is also shown by the disappearance of UV-Vis peak at 355nm (Fig. 4). After 180 min, total disappearances of OTC peaks were observed. This implied that the OTC concentration inside the system is too small to be detected by the instrument. Based on HPLC analyses, OTC concentration was reduced by 98.7% at 2.3 ppm (Table 1).

Effect of pH

Generation of hydroxyl radical inside the solution was affected by the pH value. Dissociations of H₂O₂ molecules into hydroxyl radical is the most commonly accepted mechanism for photolysis of H₂O₂ (Eq. 4) which was found to be pH dependent [26]. Higher photolysis rate would increase at alkaline pH which might be mainly due to higher molar absorption coefficient (at 253.7 nm) of the hydroperoxy anion (HO₂⁻ 240 M⁻¹ cm⁻¹) compared to H₂O₂ (18.6 M⁻¹ cm⁻¹). Deprotonation of H₂O₂ produced a conjugated base, mentioned as hydroperoxy anion (Eq. 5) which was regulated by acid-base reaction [27]. The degradation processes were conducted at pH 3, 7 and 11 using 1 eq mole ratio of H₂O₂. Based on Fig.5, the highest TOC removal was observed at pH 11. Higher pH increases the hydroxyl radical generation which lead to higher reduction of TOC. Since the adequate mole ratio of H₂O₂ to OTC was used, H₂O₂ will not undergo a self decomposition rate as was described by Eq. 6.

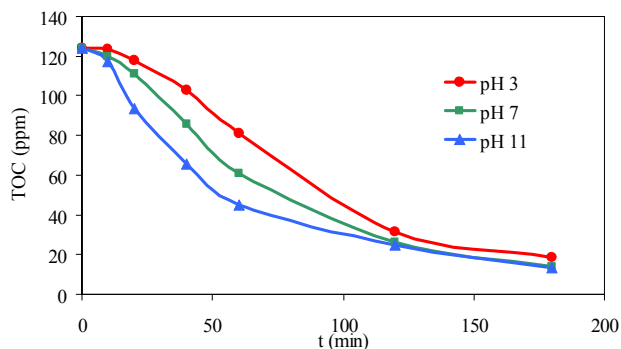


Fig.5 TOC profile of 250 ppm OTC degradation at different pH

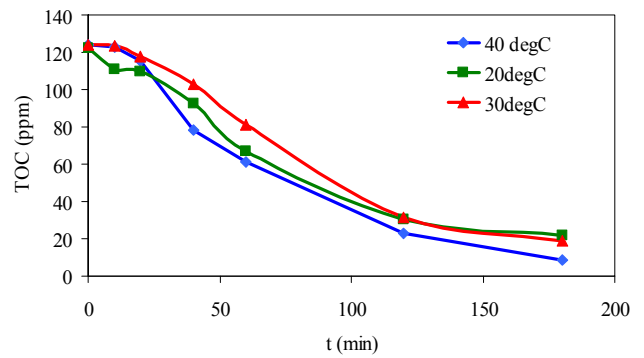
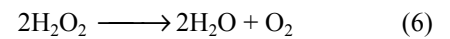
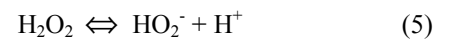
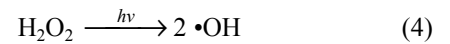


Fig. 6 TOC profile of 250 ppm OTC at different temperature



Effect of temperature

Three different temperature were applied, 20, 30 and 40°C. According to kinetic theory, number of molecular collisions increases as the temperature rise [21]. Therefore, in this study the highest TOC degradation was reached at 40°C. About 93.06% of TOC was degraded at the end of the experiment. This study was also conducted at 1 eq mole ratio of H₂O₂. TOC degradation profile of OTC at various temperatures is shown in Fig. 6.

IV. CONCLUSIONS

In this study, OTC degradation inside UV/H₂O₂ system were observed by varying three parameters, H₂O₂ mole ratio, pH and temperature. Different TOC degradation percentages were observed for all parameters. Degradation of OTC could be evaluated from the peaks disappearances of UV-VIS spectra. HPLC analyses capable of determining the exact concentration of OTC after irradiation time ended. About 93.06% of TOC were degraded after 180 min of UV irradiation. This highest TOC degradation efficiency was achieved at 40°C and 1 eq H₂O₂ mole ratio. Therefore, UV-H₂O₂ systems can be used to degrade OTC with high efficiency. These preliminary results can be used for further process optimization of OTC degradation.

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