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Photochemical Degradation Performance of Quinoline Aqueous Solution in the Presence of Hydrogen Peroxide

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ABSTRACT

Photochemical degradation performance of quinoline aqueous solution in the presence of H_2O_2 was carried out, and some intermediates produced during quinoline degradation were also identified tentatively. The experimental results showed that the advanced oxidation of quinoline by UV/H_2O_2 process accorded well with the pseudo first order kinetics, and the dependence of concentrations of H_2O_2 and quinoline, and pH value on the photodegradation kinetics has been investigated in detail. It is found that the concentrations of hydrogen peroxide and quinoline have opposite effect on photodegradation kinetics. That means the photodegradation rate of quinoline increased significantly as the hydrogen peroxide concentration increasing, while the photodegradation rate decreased critically as the initial concentration of quinoline increasing. It also concluded that the photodegradation of quinoline by H_2O_2/UV process is more favorable under alkali solution than acid solution.

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Key Words: UV/H_2O_2 process; AOPs; Quinoline; Photodegradation; Kinetics.

INTRODUCTION

The main sources of polycyclic aromatic nitrogen heterocycles (PANHs) to the aquatic environment are discharges from tar plant and coke oven plant,[1,2] waste from synthetic fuel production,[3] and spill from oil drilling, refining, and storage.[4] Hence, PANHs are now widespread in the aquatic environment. However, PANHs have been shown to be very toxic, mutagenic, and carcinogenic.[5] Quinoline and their derivatives are typical PANHs, and are ubiquitous environmental contaminants because they are widely served as raw materials and solvents in the manufacture of dyes, paints, and pesticides.[6,7] Due to the presence of heterocyclic structure, quinoline and other PANHs are more soluble in water than their homocyclic analogues and can be transported easily through soils, sediments, and aquifer materials.[8] As a consequence, quinoline and their derivatives have been detected in groundwater or soil very often, especially those adjacent to coal tar distillation and creosote wood preservation facilities.[6] Owing to their toxicity, carcinogen and mutagenic, there has been increasing concern about the public health risks posed by quinoline and their derivatives.[9] Therefore, it is important to develop novel methods for complete degradation of them.

One promising technology is commonly referred to advanced oxidation processes (AOPs).[10] Hydroxyl radicals, the main oxidative species in AOPs, can be generated by both photochemical processes (for example, ultraviolet radiation in combination with O_3, H_2O_2, or a photosensitizer) and nonphotochemical processes (for example, dark H_2O_2 oxidation, and Fenton reagent). Hydroxyl radicals can react nonselectively with organic pollutants via addition to carbon–carbon unsaturated bonds and H-abstraction.[10] The application of AOPs to mineralizing toxic and hazardous organic pollutants to inorganic materials, such as carbon dioxide and water, or converting them to readily biodegradable intermediates has been reviewed by Hoffmann et al. and Legrini et al.[11,12]

Though the photolysis of quinoline in natural water bodies showed that the degradation of quinoline was very slow and inefficient,[2] a few researchers have reported about the degradation of quinoline by AOPs, including ozonation,[13] dark H_2O_2 oxidation,[14] Fenton system,[15] UV–TiO_2 system,[15] respectively. However, few reports on the removal of quinoline by UV/H_2O_2 AOPs have been studied to date. Hence, in the study, the photochemical degradation performance of quinoline in water by UV/H_2O_2 AOPs was mainly investigated, and some intermediates produced during the degradation of quinoline were also identified.

MATERIALS AND METHODS

Materials

Quinoline (98%) was purchased from Sigma. 1H-2-Oxo-1,2-dihydroquinoline (99%) was obtained from Aldrich. 8-Hydroxy-2-oxo-1,2-dihydroquinoline (>98%),

7-hydroxycoumarin (99%), 3-(2-hydroxyphenyl)propionic acid (98%) were obtained from Lancaster. *N,O-bis*-(Trimethylsilyl)trifluoroacetamide (BSTFA) was from Pierce. Ethyl acetate was re-distilled using glass system, and the water employed in all preparations was purified by a Film Tec RO TW30-40404 system, and the conductivity was lower than 5.37×10^{-6} s cm^{-1}. All other chemicals used in the experiments were analytical reagent grade.

Photoreactor and Light Source

The photoreactions were carried out in an annular glass reactor with an available volume of 1.5 L (35 cm high, 7.8 cm o.d.). A low pressure UV lamp (S2-Q-PA12, Canada R-Can Environmental Inc.), with a monochromatic radiation at 254 nm and a nominal power of 14 W, was housed in a quartz sleeve inside the glass reactor. The photon flux (at 254 nm) entering the reactor from the UV lamp was 3.14×10^{-6} Einstein s^{-1} determined by potassium ferrioxalate actinometry.[16] The reactor was wrapped with an aluminum foil to improve the efficiency of photoreaction.[17]

Procedures

The desired initial concentration of quinoline and hydrogen peroxide were fed in the reactor. A magnetic stirrer was placed at the bottom of reactor to provide the necessary agitation. Most experiments were performed at the natural pH of quinoline dissolved in water. For the experiments of pH effect on the degradation of quinoline, the pH of the reaction solution was adjusted using sulphate acid or sodium hydroxide solution. Samples were taken at desired intervals for analysis once the lamp was turned on. For the identification of intermediates, the initial quinoline concentration was 5 mmol L^{-1} and the irradiation time was 10, 20, and 40 min. The reaction mixtures were extracted with ethyl acetate at neutral and acid pH value, respectively. Then the extracts were mixed and dried over anhydrous sodium sulfate, filtered, and blown to dryness under a gentle N_2 stream. Then the dried extract was dissolved into 0.2 mL dichloromethane for GC/MS analysis. One portion of the treated samples was also silylated by addition of BSTFA and analyzed by GC/MS.

Analysis

Absorption spectra were measured with a Helios Alpha UV/Visible spectrophotometer (Thermo Spectronic). The concentration of hydrogen peroxide was obtained iodometrically.[18] Progress of all reactions was monitored by HPLC. Analysis was achieved by a Hewlett-Packard 1100 system equipped with a UV/Vis detector and a reverse phase C_{18} column (Dieckman, 250 × 4.6 mm i.d.). The column was eluted with a mixture water–methanol 40:60 v/v with a flow rate of 1.0 mL min^{-1}. The detection was performed by UV absorption at 225 nm.

A Hewlett-Packard (HP) 5890 gas chromatograph (GC) with a flame ionization detector was used with a HP-5 fused-silica capillary column (50 m × 0.32 mm i.d. × 0.17 μm film) to learn the primary distribution of the intermediates. The temperature of the column was programmed at 60°C for 5 min, and then ramped up to 130°C at the rate of 10°C min^{-1} and ramped up to 260°C at the rate of 20°C min^{-1}.

Identification of the intermediates during quinoline degradation was carried out using a GC (HP 5890 series II) with a 5972 mass selective detector (MSD) operated on the scan mode. The column is the same as that used in GC analysis. The column temperature program was 60°C for 5 min and then 7°C min^{-1} to 300°C isothermal 20 min.

RESULTS AND DISCUSSION

Synergistic Effect in the Combined UV/H_2O_2 Process

The photochemical degradation of quinoline in the presence of hydrogen peroxide was conducted and shown in Fig. 1. The changes in the UV spectra of quinoline degradation were investigated and the selected UV spectra for the photodegradation is also shown in Fig. 2. It is easy to see from Fig. 2 that the adsorption spectra of quinoline decreased rapidly, companying that the solution changed from colorless to yellowish as the reaction time increased. The degradation of quinoline in water and the significant decrease in UV spectra indicated that the photodegradation of quinoline in the presence of hydrogen peroxide was completely achieved within 120 min. Moreover, control experiments were also conducted, that is, when the UV irradiation or hydrogen peroxide was used alone, from Fig. 1, the degradation of quinoline is very slow, 0.5% and 6.3% of degradation efficiencies at 80 min, 1.1% and 12.2% of degradation efficiencies at 120 min were obtained,

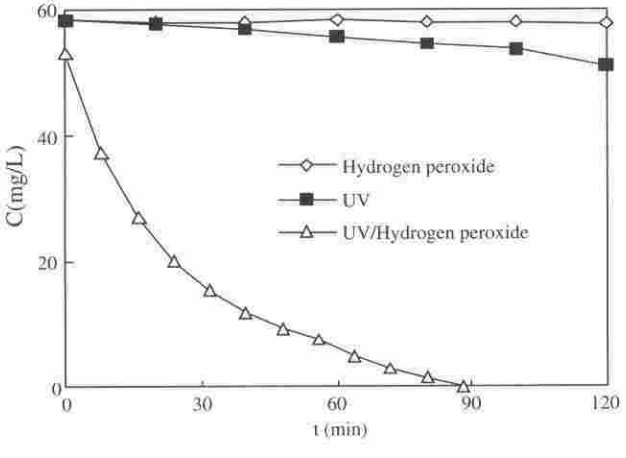

Figure 1. The comparison efficiencies of combined UV/H_2O_2 with single process.

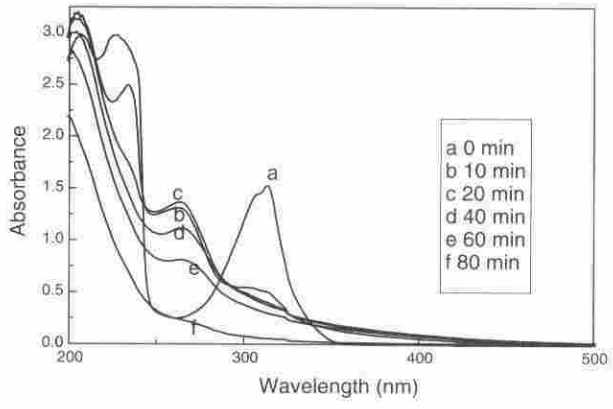

Figure 2. The UV spectra change during quinoline degradation.

respectively. This indicated that the single process was relatively inefficient in the degradation of quinoline by hydrogen peroxide or UV irradiation alone. On the contrary, as for the combined UV/H_2O_2 process, high degradation efficiency up to 97.5% was obtained at 80 min, indicating that the combined process has an efficient removal of quinoline from the reaction solution. Thus, we can conclude that there is an apparent synergistic effect existed in the combined UV/H_2O_2 process.[19]

It is well recognized that photodegradation of organic pollutants accords with pseudo first-order kinetics.[20] The photodegradation of the organic pollutants can be described as a function of irradiation time and the equation below is often used to express the variation of reactant:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t$$

where k_1 (min^{-1}) is the first-order rate constant, C_t and C_0 are the concentrations at irradiation time t and initial concentration, respectively.

The experimental data showed that more than 97.5% of quinoline was decomposed within 80 min. After the linear transform of the data from Fig. 1, we can conclude that both photodegradation of quinoline in the presence of hydrogen peroxide and direct oxidation by hydrogen peroxide accord with the pseudo first-order kinetics, and the apparent rate constants are $0.03813\,min^{-1}$ and $7.98 \times 10^{-4}\,min^{-1}$, respectively. From Fig. 3, it is found that the kinetics in the photodegradtion reaction in the presence of hydrogen peroxide was far faster than that in the direct oxidation by hydrogen peroxide. The rate constant of the former is 48.3 folds of the latter. The enhancement in rate constant also indicated that an apparent synergistic effect in the degradation of quinoline was achieved in the combined process. The reason why the photodegradation of quinoline is much faster than the direct oxidation by hydrogen peroxide is that more hydroxyl radical was generated from hydrogen peroxide when the UV light illuminated on the solution, and hydroxyl radical has a higher reaction rate than hydrogen peroxide.[21]

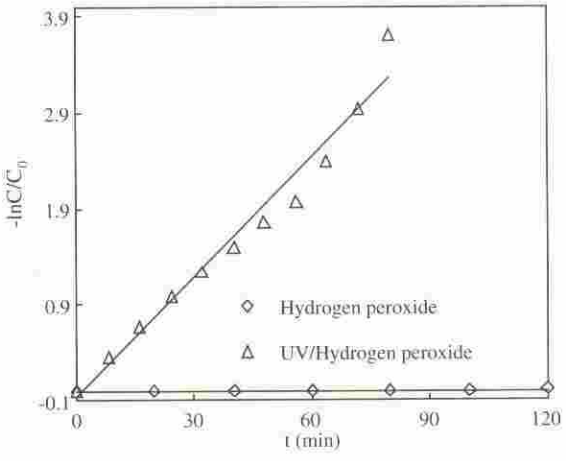

Figure 3. The kinetics curves of UV/H_2O_2 and single H_2O_2 oxidation process.

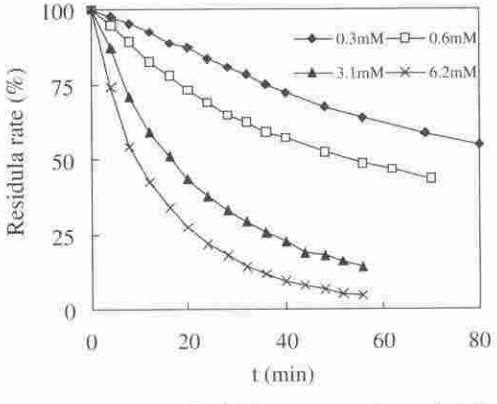

Figure 4. Effect of initial concentration of H_2O_2.

Dependence of Photodegradation Kinetics on H_2O_2 Concentration

From above comparison, it is easy to see that hydrogen peroxide plays an important role in the photooxidation of organic pollutants. Thus, in order to clearly learn the effects of initial concentration of hydrogen peroxide, the experiments of the relationship of initial hydrogen peroxide concentration with quinoline degradation kinetics were conducted and the profiles obtained are shown in Fig. 4. It can be observed from Fig. 4 that the photodegradation rate of quinoline is significantly increased as the increase in hydrogen peroxide concentration. The apparent rate constant increased from $7.8 \times 10^{-3}\,\mathrm{min}^{-1}$ at concentration of 0.312 mM to $59.15 \times 10^{-3}\,\mathrm{min}^{-1}$ at concentration of 6.24 mM. The apparent rate constant increased 7.6 folds when the initial concentration of hydrogen peroxide increased 20 folds. The result can be interpreted by that more ·OH will be generated to

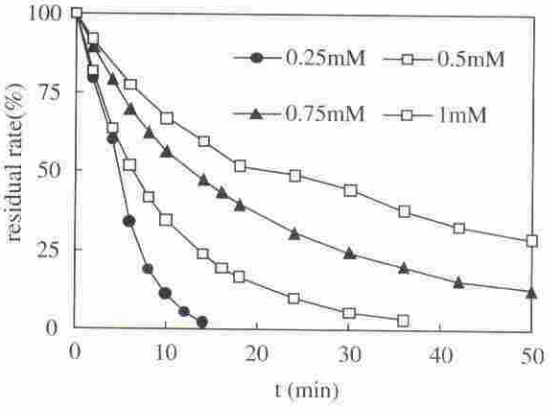

Figure 5. Effect of initial concentration of quinoline.

accelerate the degradation of quinoline if more hydrogen peroxide were added into the reaction solution to some extent. However, differing from the photochemical degradation of 4-NP,[22] we have not observed the scavenging effect of hydrogen peroxide on ·OH in the photodegradation of quinoline in the present study.

Dependence of Photodegradation Kinetics on Quinoline Concentration

The photochemical degradation was also studied by changing the initial concentration of quinoline solution from 0.25 to 1 mmol L^{-1}. The kinetic profiles at various initial concentrations of quinoline are shown in Fig. 5. It was observed that, as the same as hydrogen peroxide, initial concentration of quinoline also has a significant effect on the photochemical degradation kinetics. However, from the Fig. 6, it is easy to see that the effects of concentration of quinoline and hydrogen perioxide present opposite trendy on photodegradation kinetics. The apparent rate constant decreased critically from 0.2262 min^{-1} at 0.25 mM to 0.0272 min^{-1} at 1 mM as initial concentration of quinoline increasing. The rate constant decreased 8.3 folds when the initial concentration of quinoline increased four folds. The decrease in the apparent rate constant may be partly due to that, when the concentration of quinoline increased, more intermediates would be produced, resulting in a competition of quinoline with the hydroxyl radicals.

Dependence of Photodegradation Kinetics on pH Value

The effect of pH value on the photodegradation of quinoline by UV/H_2O_2 process is shown in Fig. 7. It is found that the degradation rate of quinoline increased significantly with the increase of pH value. That is, the apparent rate constant is increased from 0.0494 min^{-1} at pH 2.0 to 0.0699 min^{-1} at pH 10.0. This is due to that under strong alkali conditions, generally speaking, alkaline

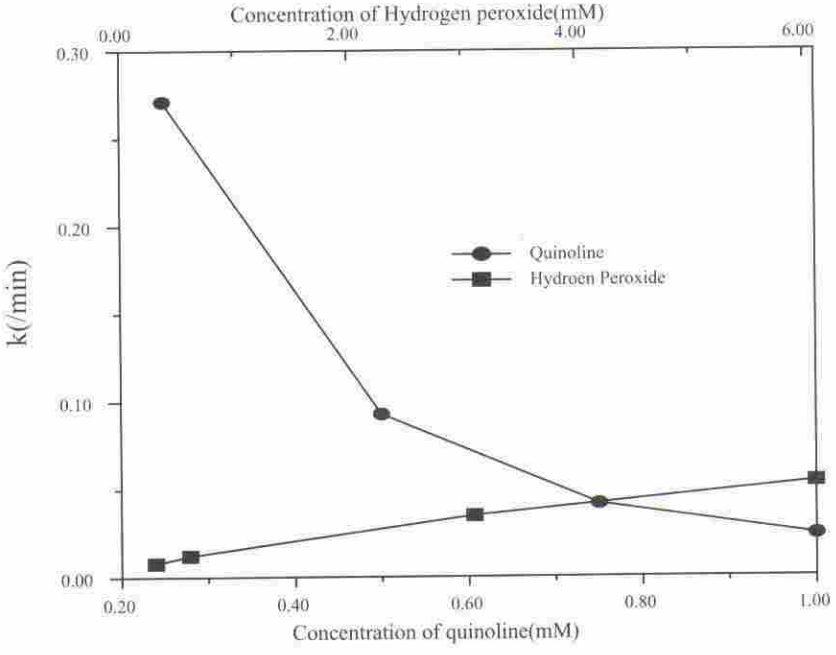

Figure 6. Different effects of initial conentration of quinoline and H_2O_2 on rate constant.

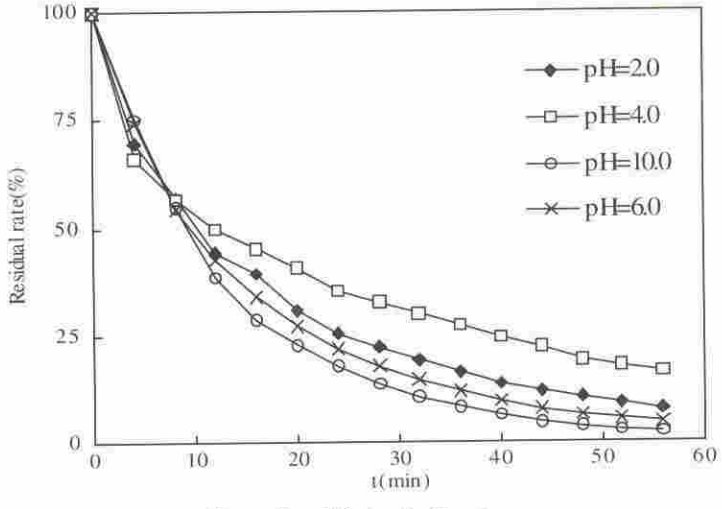

Figure 7. Effect of pH value.

pH values have been found to be favorable for the formation of hydroxyl radical from the direct photolysis of hydrogen peroxide since at 254 nm the extinction coefficiency of ionic form of hydrogen peroxides, the hydroperoxide ions (major peroxide species at alkali conditions), is higher than that of the nonionic form.

Though there also existed two disadvantageous effects with the increase of solution pH,[23] first one is the degradation of quinoline will be retarded as the increase of CO_3^{2-}, HCO_3^-, and the pH value of reaction solution increased; and the second one is that alkali conditions are also favored to the dissociation of hydrogen peroxide to form hydroperoxide ions (HO_2^-) that has a higher reactivity with hydroxyl radical, we did not observe this phenomena in all tested pH range. About this issue, Beltran et al.[24] thought that the scavenging effect did not become stronger until the pH value was higher than 11.8, pKa of hydrogen peroxide dissociation equilibrium. Thus it can be concluded that the photodegradation of quinoline by H_2O_2/UV process is more favorable under alkali solution than acid solution.

Intermediates Identification

It is well known that when hydrogen peroxide is under the irradiation of UV light chain reactions will occur in the solution. Hydroxyl radical generated by the photolysis of hydrogen peroxide will initiate the degradation reactions of the organic pollutants through H-abstraction and the addition of hydroxyl radicals to unsaturated bonds of organic molecule. Since the hydroxyl radical is an electrophilic reagent, degradation of organic pollutants by this radical should be initiated through a preferential attack onto the position with higher electron density.[25] In the case of quinoline photooxidation, the pyridine ring has a lower electron density than the benzene ring because of the larger electron affinity of the nitrogen atom. So, the benzene ring will be attacked preferentially.

By GC/MS and HPLC analysis, the main intermediates from the oxidation of quinoline by UV/H_2O_2 process are listed in Fig. 8. 2-Quinolinone (the most stable tautomer of 2-hydroxyquinoline in water) and 8-hydroxyquinoline were identified not only by comparing HPLC retention times but also by mass spectrum of standards derivatized or not derivatized by BSTFA, while 4-quinolinone (the most stable tautomer of 4-hydroxyquinoline in water), 5- and 6-hydroxyquinolines and 2,8-dihydroxyquinoline are identified both by silylation and without silylation. Similar to the study by Cermenati et al.,[26] we also observed several intermediates with molecule mass of 161 (quinoline + 2O) but with different mass spectrum. One of these intermediates has a very strong mass peaks, $m/z = 142$, which was considered to be the fragment obtained by the loss of H_2O from the intermediates. GC/MS analysis of these intermediates silylated by BSTFA further confirmed the presence of two hydroxyl radicals in the compounds. So we consider that this intermediate may be 7,8- or 5,6-dihydroxyquinoline where two hydroxyl radicals added to quinoline molecule are adjacent (in Fig. 8). Minute amounts of a trihydroxyquinoline with molecular mass of 393 (quinoline + 3O-3H + $3Si(CH_3)_3$) were also found only after silylation followed by GC/MS analysis. 7-Hydroxycoumarin and 3-(2-hydroxyphenyl)propionic acid often found in the biodegradation of quinoline[27] were not observed in our study. The mass spectrum of 2,8-dihydroxyquinoline and the trihydroxyquinoline are shown in Figs. 9 and 10, respectively, from which we can see that the typical fragment at $m/z =$ 147 corresponding to $(CH_3)_2Si{=}O\text{-}Si(CH_3)_3^+$, indicating the formation of multihydroxylated compounds.

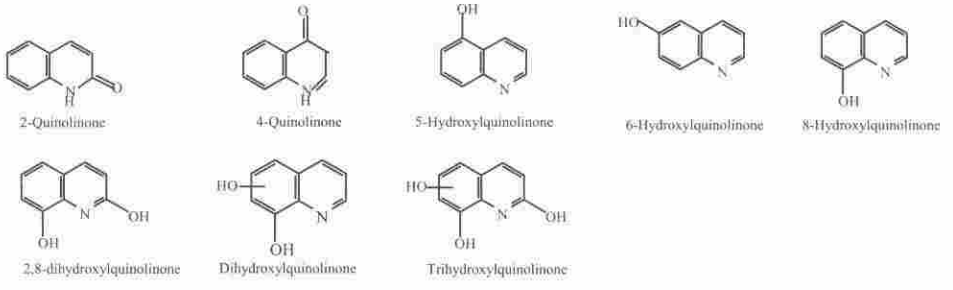

Figure 8. Intermediates identified tentatively during the degradation of quinoline.

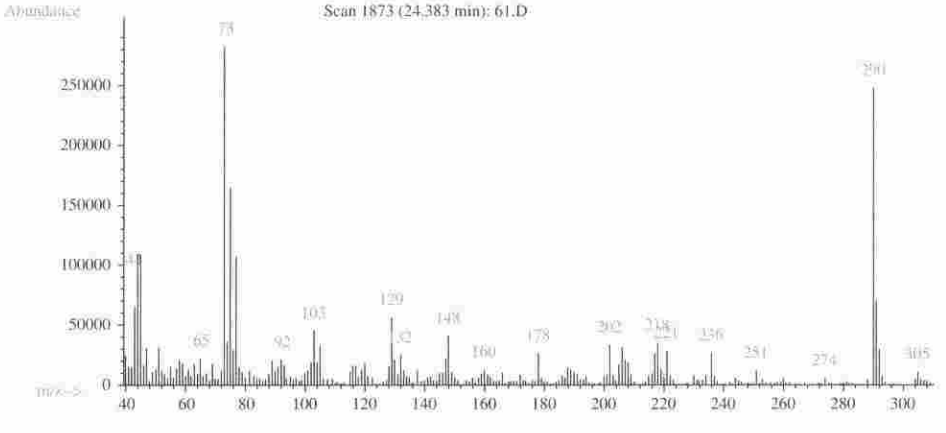

Figure 9. The mass spetrum of 2,8-dihydroxylquinoline indentified during the degradation of quinoline.

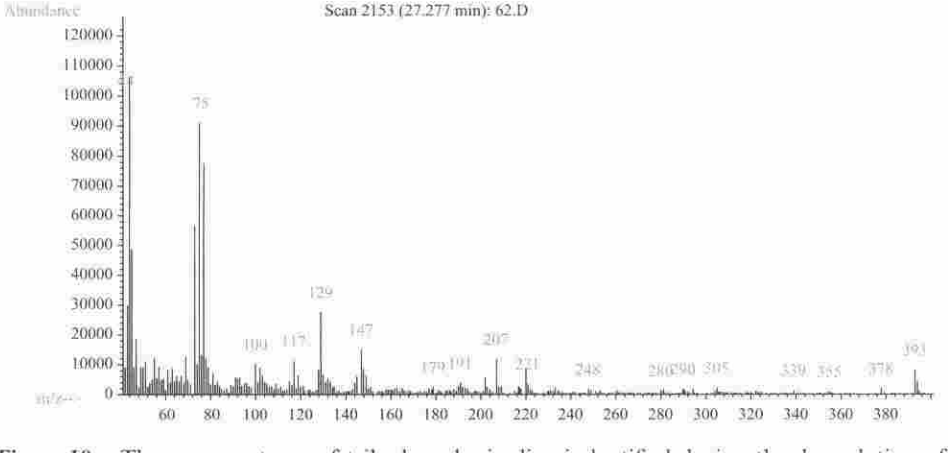

Figure 10. The mass spetrum of trihydroxylquinoline indentified during the degradation of quinoline.

The benzene ring would be attacked preferentially, however, small amount intermediates such as 2- and 4-quinolineones are produced by attack at the less electron-rich pyridine ring. Further oxidation of these intermediates would lead to more addition of hydroxyl radicals to the parent molecule. For example, 2,8-dihydroxylquinoline is formed by the addition of hydroxyl radical to 8-hydroxyquinline. Other dihydroxyquinolines may be produced during the degradation of quinoline. One of these is tentatively identified as 7,8-dihydroxyquinoline (representative of the dihydroxyquinoline whose hydroxyl radicals are adjacent). Although the presence of the trihydroxyquinoline is not further confirmed, it can be speculate from the mass fragments of the intermediates silylated by BSTFA and it is plausible that further oxidation of dihydroxyquinoline will yield trihydroxyquinolines. However, the complete understanding of the degradation pathway and reaction mechanism needs to wait for further researches.

CONCLUSIONS

Photochemical degradation of quinoline in the presence of hydrogen peroxide can be reached within 80 min, and the degradation reaction accorded well with the pseudo first order kinetics. The photodegradation rate of quinoline increased significantly as the hydrogen peroxide concentration increasing, while the photodegradation rate decreased critically as the initial concentration of quinoline increasing, and the photodegradation of quinoline by H_2O_2/UV process is more favorable under alkali solution than acid solution. A series of intermediates produced from the photodegradation of quinoline were also identified tentatively.

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