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DEGRADATION OF TOLUENE
USING UV/HYDROGEN PEROXIDE PROCESS

Toluene in wastewater is volatile and difficult to degrade, and the longer it stays in the water, the higher is the risk. An advanced oxidation process (AOPs) has been used to degrade toluene rapidly and efficiently in wastewater by using ultraviolet light and hydrogen peroxide. Toluene in solution (initial concentration – 180 mg/dm^3) with hydrogen peroxide (H_2O_2 dose – 2022 mg/dm^3) was almost decomposed within 150 min. pH as well as the presence of various ions in wastewater did not affect the degradation process. However, under strongly acidic conditions (pH less than 3), the chloride ions reduced the degradation efficiency of toluene. Based on the UV spectrophotometer and GC-MS analyses, the degradation pathways were observed: first, the methyl group was oxidized leading to the generation of benzoic acid, the benzene ring was subsequently opened by the action of hydroxyl radical, followed by the gradual decomposition of the intermediate products into small molecules such as water and carbon dioxide.

1. INTRODUCTION

Toluene is a commonly used organic solvent and important raw material for a variety of chemicals, mainly obtained by catalytic reforming of petroleum or extraction from pyrolysis gasoline. However, the toxicity and physicochemical properties of toluene have made its discharge processes a matter of concern.

Specifically, the toxicity level of toluene is classified as low. Exposure to toluene for a short time can irritate the eyes and upper respiratory tract, along with headache and dizziness. The long-term exposure can lead to a weakened nervous system, with an effect on organs such as the liver, kidney, and heart as well as circulatory and nervous

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systems. The studies have indicated that long-term exposure to toluene affects the reproductive system of rats, along with the nervous system of male rats [1]. Besides, toluene also inhibits the biological activity of microorganisms [2].

Toluene in water exhibits a volatile character, with its vapor forming an explosive mixture with air with an explosion limit of 1.2–7.0% by volume. The as-produced volatile products are one of the important components of the atmospheric VOCs [3–5].

Industrially, toluene is usually discharged with wastewater sent to the wastewater treatment plants (WWTPs). A fraction of mixed toluene is evaporated during the transportation process. The conventional wastewater treatment plants cannot usually deal with such substances, and the biochemical process at the treatment station is inhibited by toluene, thus, affecting the normal operation [6]. Therefore, this study has adopted an advanced oxidation process (AOPs), to achieve the degradation and elimination of toluene in the early stages of emission.

The AOPs represent the process of oxidative degradation of pollutants in wastewater by generating hydroxyl radicals [7–9]. In this study, hydrogen peroxide was used as an oxidant to generate hydroxyl radicals under irradiation with ultraviolet light, thus, leading to toluene degradation by utilizing the strong oxidizing property of the hydroxyl radicals.

The methods generally employed for the analysis of toluene are gas chromatography [10–14] and TOC analysis [15]. However, these methods are cumbersome and expensive. In this study, the traditional ultraviolet spectrophotometry method has been adopted. The method has the characteristics of simple operation and low cost, thus, enabling the comprehensive analysis of the degradation process of toluene. As the addition of hydrogen peroxide significantly interferes with the toluene analysis, the experiments have been designed to deal with such effects.

2. MATERIALS AND METHODS

Materials. Toluene (purity > 99%) was provided by Shandong Taihe Water Treatment Technologies Co., Ltd. (China). Hydrogen peroxide (H_2O_2) was 30 wt. % solution with a density of 1.11 g/cm^3. NaCl, $MgSO_4 \cdot 7H_2O$, Na_2SO_4, and $CaCl_2$ were provided by Tianjin Guangcheng Chemical Reagent Co., Ltd. (China).

Experimental setup and procedure. A UV germicidal equipment, purchased from Shenzhen Ruixing Water Treatment Equipment Co., Ltd. (China), was employed. A 10 W UV lamp was positioned at the center of the equipment (Fig. 1). Before starting the experiment, aqueous solutions were add006ed through the inlet, followed by blocking the inlet and sampling port with corks to form a closed system. During the experiment, ca. 5 cm^3 of the solution was taken through the sampling port at different intervals for carrying out the measurements.
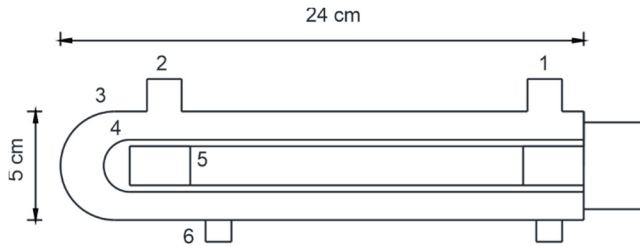
Fig. 1. Schematic diagram of the UV germicidal equipment: 1 – inlet, 2 – sampling port,
3 – stainless steel cover, 4 – quartz protection tube, 5 – UV lamp, 6 – bracket, 7 – cover

The toluene aqueous solution was firstly prepared by adding a sufficient amount of toluene to water in a beaker, followed by heating and stirring for 12 h. It was found through repeated measurements that the toluene concentration of 180 mg/dm^3 resulted in a stable solution. Subsequently, the toluene aqueous solution (100 cm^3) and hydrogen peroxide were mixed in the equipment. Every 30 min, a small amount of solution was taken for absorbance measurement by using a UV-Vis spectrophotometer (UV-2450, Shimadzu, Japan). The UV absorption peak at 261 nm was chosen for developing the standard curve and calculating the degradation efficiency of toluene (Fig. 2).
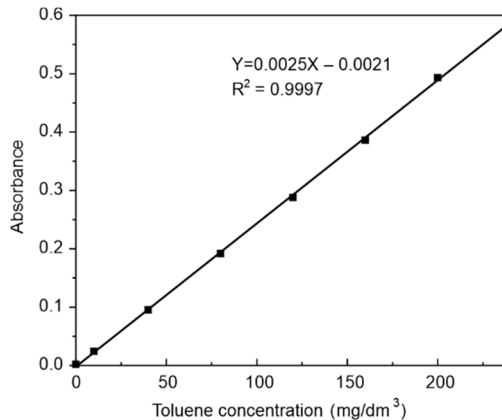

Fig. 2. The calibration curve of toluene

For a constant dose of hydrogen peroxide, its absorbance (at 190–400 nm) can be completely ignored. The absorbance of the toluene solution was measured before the addition of hydrogen peroxide (A_0, considering the error, the volatile toluene during degradation was subtracted), followed by the absorbance of the solution after UV irradiation (A_i). The toluene degradation efficiency can be written as:

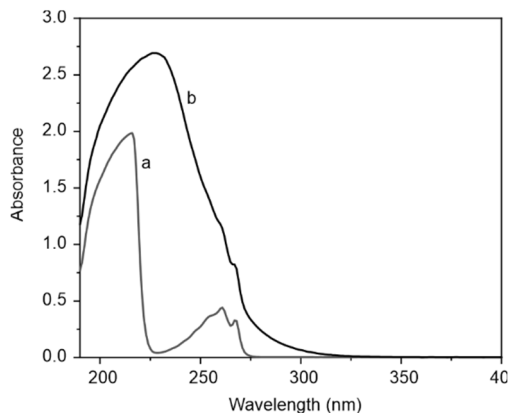$$n = \frac{A_0 - A_i}{A_0} \qquad (1)$$

Fig. 3. The ultraviolet absorption spectrum of:
a) toluene, b) toluene mixed with hydrogen
peroxide (toluene concentration 180 mg/dm^3,
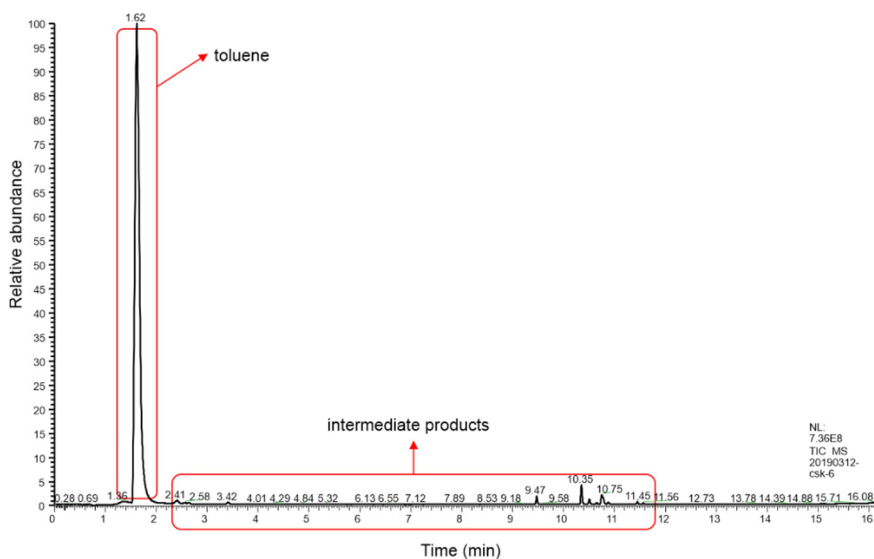hydrogen peroxide dosage 2022 mg/dm^3)

Fig. 4. Total ion chromatogram for toluene degradation for 2.5 h (GC-MS)

For various doses of hydrogen peroxide (Fig. 3), its addition could influence the measured concentration. However, the total ion chromatogram of toluene (Fig. 4) and decomposition efficiency of hydrogen peroxide (Section 3.1) revealed that after 2.5 h degradation, the dosages of residual hydrogen peroxide and intermediate products in the solution were sufficiently lower than the residual toluene. Besides, the absorbance of the solution could replace the absorbance of the residual toluene. Therefore, the degradation efficiency of toluene could still be calculated by using equation (1).

The toluene degradation was examined by: a) adding hydrogen peroxide to the toluene solution, b) irradiating the toluene solution with UV light for a certain time, and c) adding hydrogen peroxide to the toluene solution and irradiating it with UV light for a certain

time. Toluene solution (180 mg/dm^3) without any subsequent treatment was used as the blank control sample.

To determine the cost of practical application, the effect of hydrogen peroxide concentration on toluene degradation was investigated. For this, hydrogen peroxide solution (30 wt. %) in various amounts (0.4–1.0 cm^3) was added to the toluene solution, resulting in the following H$_2$O$_2$ initial concentrations: 1348; 1685; 2022; 2359; 2696; 3033 and 3370 mg/dm^3. pH of actual wastewater can vary, thus, it is necessary to investigate the effect of pH on toluene degradation [16]. In the experiment, the pH of the solution was adjusted as 1, 3, 5, 7, 9, and 11 by adding hydrochloric acid, sulfuric acid, and sodium hydroxide.
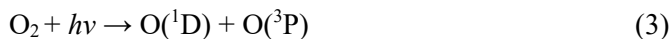
The experiment also investigated the influence of various inorganic ions present in the wastewater [17] on toluene degradation. For this, different ion solutions of calcium, magnesium, sulfate, and chloride (200, 400, 600, and 800 mg/dm^3) were mixed with toluene and hydrogen peroxide, respectively.

Gas chromatography-mass spectrometry (GC-MS) from Thermo Scientific TSQ 9000 (United States) was used to investigate the degradation process and corresponding intermediates. The data was obtained from the Analysis and Testing Center, School of Environmental Science and Engineering, Shandong University (China).

The temperature program for the oven was as follows: heating at 40 °C and hold for 3 min, ramping from 40 °C to 280 °C at 10 °C/min and holding at 280 °C for 3 min; the total run time was about 30 min. Splitless modes conditions: time (1 min); split ratio (33.3); split flow (20.0 cm^3/min). The MS operated in the electron ionization mode and the ion source temperature was maintained at 200 °C, methane was used as the carrier gas at a constant flow rate of 1.00 cm^3/min, the detection was achieved with electron ionization (70 eV) in the full scan monitoring mode (50–350 m/z).

3. RESULTS AND DISCUSSION

When only ultraviolet light was applied to degrade toluene (Fig. 5), the absorbance of the solution changed very slowly, approaching zero 48 h later. The absorbance of toluene increased during the first 6 h, then it decreased, which was attributed to the high absorbance of the benzene series (specifically benzoic acid identified through GC-MS). The degradation mechanism was attributed to the ultraviolet light activating the water molecules and dissolved oxygen to generate hydroxyl radicals [18]. The efficiency of the reaction was low, thus, the toluene degradation efficiency was correspondingly low.

$$H_2O + h\nu \rightarrow {}^{\bullet}OH + {}^{\bullet}H \tag{2}$$

$$O_2 + h\nu \rightarrow O(^1D) + O(^3P) \tag{3}$$

$$O(^1D) + H_2O \rightarrow 2{}^{\bullet}OH \tag{4}$$

$$O(^3P) + 2O_2 \rightarrow O_3 + O_2 \tag{5}$$

When hydrogen peroxide was added without any irradiation, the absorbance of the solution exhibited a weak tendency to decrease. By comparing with the blank control, the decreasing tendency was associated with the volatilization of toluene. Thus, it could be concluded that the toluene degradation efficiency almost tended to be absent under this condition. When UV light and hydrogen peroxide were used together, toluene could be quickly degraded owing to the ultraviolet light activating hydrogen peroxide to generate hydroxyl radicals in the process [19]. Based on UV spectrophotometric analysis, the toluene degradation efficiency was calculated to be 95.47% (eq. (1)).
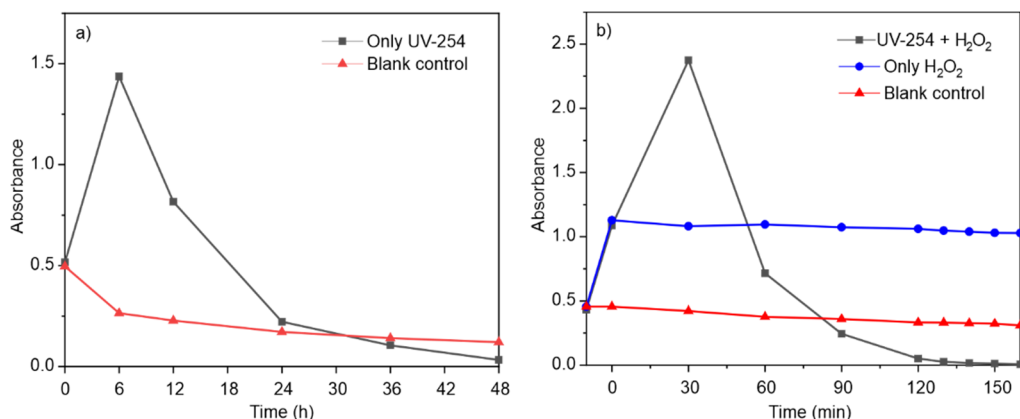
$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \qquad\qquad (6)$$

Fig. 5. The degradation process of toluene: a) on irradiation with UV-254, b) on mixing with hydrogen peroxide (2022 mg/dm^3) as well as on combining UV-254 irradiation and hydrogen peroxide (2022 mg/dm^3). The blank control was used to investigate the effect of toluene volatilization (initial toluene concentration 180 mg/dm^3)
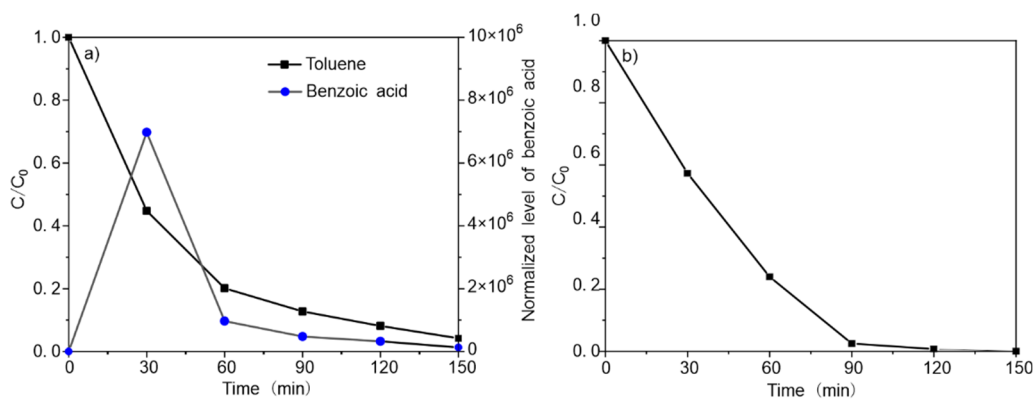

Fig. 6. Toluene and benzoic acid concentrations during degradation by the GC-MS method (a), and decomposition efficiency of hydrogen peroxide during the degradation process (b); initial toluene concentration – 180 mg/dm^3, initial hydrogen peroxide dosage – 2022 mg/dm^3

The results of the UV spectrophotometric analyses did not show any differences between toluene and intermediate products formed during the degradation process; however, GC-MS provided more insights. The changes in toluene, hydrogen peroxide, and intermediate benzoic acid concentrations during the degradation process are presented in Fig. 6. The amount of residual toluene (after 150 min) in the solution was higher than that of other substances (c toluene – 7.4 mg/dm^3, c hydrogen peroxide – 0.505 mg/dm^3). The toluene degradation efficiency determined based on GC-MS was 95.91%, like that established from spectrophotometric measurements. Therefore, it was feasible to replace the absorbance of residual toluene with the absorbance of the solution. The error mainly came from the volatilization of toluene and the residue intermediate products in the solution.
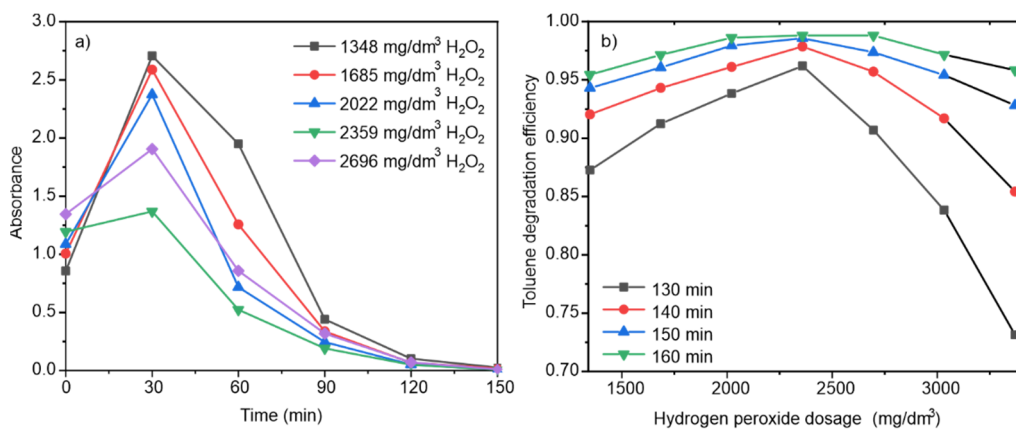

Fig. 7. Effect of hydrogen peroxide concentration on toluene degradation: a) the curve of solution absorbance as a function of time under different hydrogen peroxide dosages, b) effect of different hydrogen peroxide dosage and different process duration on toluene degradation efficiency (initial toluene concentration: 180 mg/dm^3; irradiation with UV-254)

For the dosage of hydrogen peroxide of 2359 mg/dm^3, the degradation of toluene was observed to be the fastest (Fig. 7a). As the dosage of hydrogen peroxide increased, the initial absorbance of the solution also increased correspondingly. It indicated that the influence of hydrogen peroxide was significant. To diminish the contents of the residual hydrogen peroxide in the solution, illumination with UV light was extended. After 160 min, for the hydrogen peroxide dosages lower than 2022 mg/dm^3, toluene in the solution did not decompose completely (Fig. 7b). For hydrogen peroxide dosages of 2022–2696 mg/dm^3, toluene in the solution was entirely decomposed, along with the decomposition of the excess amount of hydrogen peroxide under the irradiation of UV light. At the concentration of hydrogen peroxide higher than 2696 mg/dm^3, toluene decomposed completely, however, the residual hydrogen peroxide in the solution was not decomposed, thus, the curve exhibited a drop. The dose of hydrogen peroxide of 2022 mg/dm^3

has proven to be optimal. The mass ratio of hydrogen peroxide to toluene in the solution was 11:1. The toluene degradation efficiency after 150 min was 95%. Although the observed rate was not the fastest, it was the most economical. Compared with the theoretical value (612:92), the effective utilization rate of hydrogen peroxide was noted to be 60%.
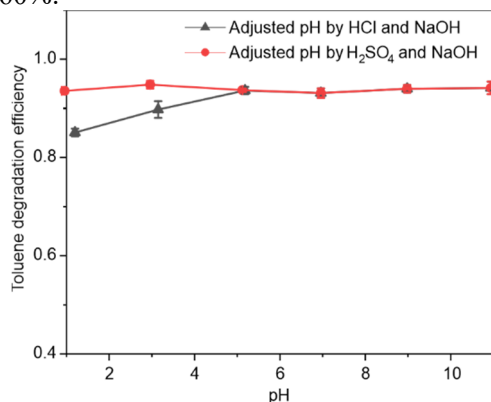

Fig. 8. Effect of pH on toluene degradation; initial toluene concentration – 180 mg/dm^3, degradation time – 150 min, hydrogen peroxide dosage – 2022 mg/dm^3

As wastewater samples may vary in pH, the effect of different pH conditions on the degradation of toluene was investigated. When sulfuric acid and sodium hydroxide were used to adjust pH, the degradation rate of toluene remained unaffected (Fig. 8). However, for pH < 3 adjusted by using hydrochloric acid, the degradation efficiency of toluene decreased. This may suggest that chloride ions and hydroxyl radicals react to form weakly oxidizing chlorine radicals, thus, leading to a low degradation efficiency of toluene [20, 21]
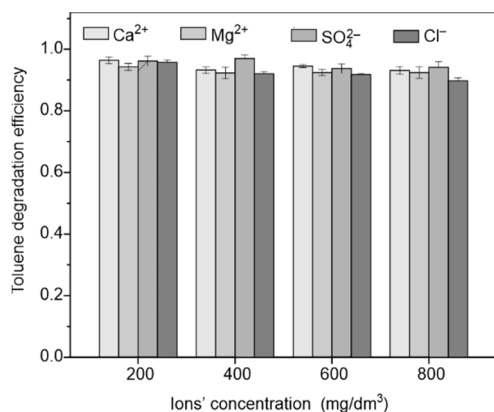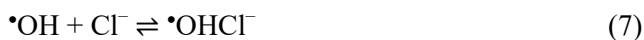
$$^\bullet OH + Cl^- \rightleftharpoons {^\bullet}OHCl^- \tag{7}$$

$$^\bullet OHCl^- + H^+ \rightleftharpoons Cl^- + H_2O \tag{8}$$

Fig. 9. Effect of various ions on toluene degradation; initial toluene concentration – 180 mg/dm^3, degradation time – 150 min, pH – 6.96, hydrogen peroxide dosage – 2022 mg/dm^3

As a large number of inorganic salt ions are present in wastewater, it is necessary to investigate the effect of these ions on toluene degradation. In this study, calcium, magnesium, sulfate, and chloride ions were mixed with toluene and hydrogen peroxide, and the degradation rate of toluene was calculated after UV light irradiation. As shown in Fig. 9, investigated ions had no impact on the photodegradation of toluene.
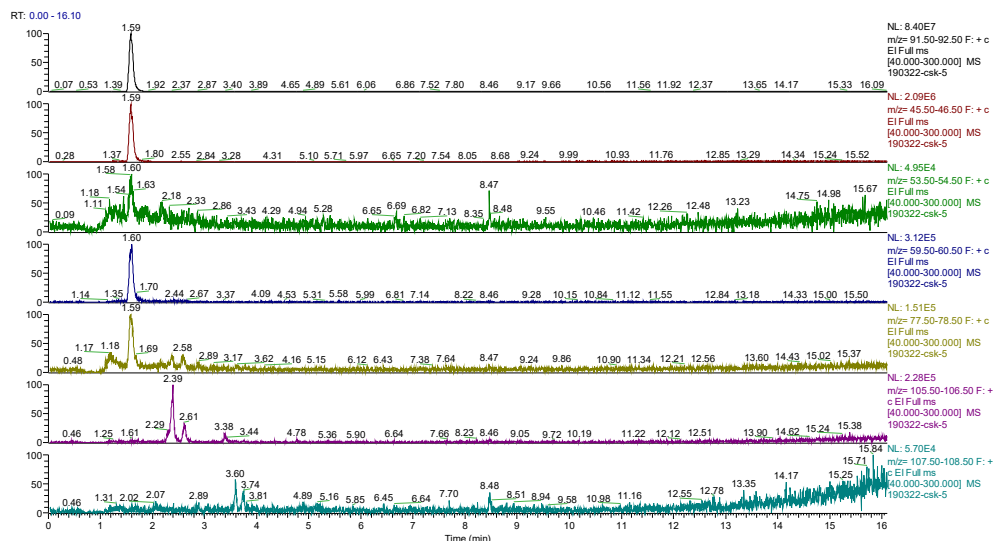

Fig. 10. Extracted ion chromatogram for toluene degradation for 2 h (GC-MS)

As has already been suggested, toluene derivatives were produced during an early stage of its degradation, which was followed by breaking benzene rings into small molecules. Therefore, GC-MS was used to further determine the specific intermediate products. Aqueous solutions of toluene (180 mg/dm^3) degraded for 2 h and 2.5 h under UV light were analyzed. The total ion chromatogram (Fig. 10) indicated mainly the presence of toluene among the last remaining products, along with a small amount of benzaldehyde (oxidized swiftly to benzoic acid). It seems that the intermediate products also contained benzene, acetic acid, and other substances.
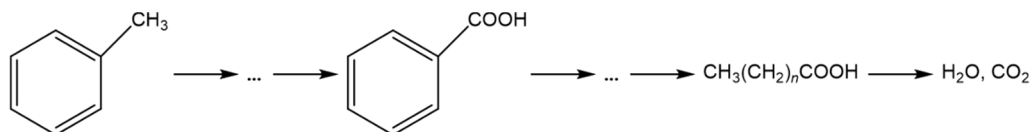

Fig. 11. Toluene degradation pathways

Therefore, by combining the findings from UV spectrometry and the GC-MS analyses, the degradation mechanism of toluene was considered to be as follows (Fig. 11):

first, the methyl group on the benzene ring was oxidized, leading to the generation of benzoic acid. Subsequently, the benzene ring opened, and formed a chain, followed by conversion into small molecules like acetic acid. Finally, the intermediate products were transformed into water and carbon dioxide.

4. CONCLUSION

UV spectrophotometry and GC-MS were employed to investigate the degradation of toluene, along with the effect of interfering factors. It was found that the mixture of hydrogen peroxide and toluene did not react. Irradiation of the toluene solution with UV light led to the degradation of toluene after 48 h, while the use of both ultraviolet light and hydrogen peroxide resulted in complete degradation of toluene within 2.5 h, thus, indicating high efficiency. The optimal ratio of hydrogen peroxide to toluene was 11:1. Using this condition, hydrogen peroxide in the solution was observed to completely react with toluene, pointing to the most economical scenario. The reaction was basically independent of the presence of other inorganic ions and pH, however, at pH < 3 the toluene degradation efficiency decreased in the presence of the chloride ions in the solution.

The degradation pathways of toluene could be investigated by combining the GC-MS and UV spectrophotometer analyses. In addition, the amount of the intermediate products in the final products also confirmed the superior effect of UV light and hydrogen peroxide on toluene degradation.

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