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Investigation of Degradation Mechanism for Dimethyl Phthalate (DMP) in Aqueous Solution by Using Analytical Methods

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Abstract

Organic compounds called endocrine disruptors cause health problems by altering the functioning of the endocrine system in a healthy organism or its future generation. In this study, phthalate acid esters (PAE's) type of endocrine disruptors were chosen as model compounds and the degradation of dimethyl phthalate (DMP) in aqueous solution was investigated under a variety of reaction conditions using hydrogen peroxide. In order to increase the efficiency of degradation of DMP and intermediates which may be toxic, H_2O_2 was used as hydroxyl radical (oxidizing agents) sources in addition to water radiolysis products. To examine the effect of hydrogen peroxide concentration to decompose of DMP, different hydrogen peroxide concentrations (0.6-4.8 mM) was chosen and as a result of the findings obtained from the comparison of the results, 4.8 mM hydrogen peroxide was determined to provide the optimum condition for decomposition of 25 mg L^{-1} DMP solution. Changes in amounts of the remains DMP, dissolved oxygen (DO), total acidity, and formaldehyde with irradiation time were followed. The qualitative analysis of the DMP and the intermediates resulted from degradation of DMP were performed using a high performance liquid chromatography (HPLC), gas chromatography associated to mass spectrometry (GC–MS) and ion chromatography (IC). The results showed that 99.44% of DMP can be removed during 20 min UV radiation time in the presence of 4.8 mM hydrogen peroxide.

Keywords: Endocrine disruptors, degradation of dimethyl phthalate (DMP), advanced oxidation process (AOP's), phthalate acid esters (PAEs), (UV/H_2O_2).

1. INTRODUCTION

Endocrine disrupting chemicals are found in the plastics, detergents, insecticides and industrial chemicals. Some of them are lipophilic and accumulate in fat tissue so they can stay in the environment, some just for only a short time, but during a critical period of growth. DMP is a substance found in toys, nail polish, plastic materials, adhesives and medicines and is soluble in ether, benzene, organic substances and water [1-4]. DMP cannot easily decompose in water and soil so it causes pollution in groundwater, surface waters and wastewater which is one of the most important pollution problems in the world. The common methods for pollutant removal in wastewater are the adsorption and conventional water treatment methods, but by

using these methods pollutants in the water are transferred from one medium to another, therefore the removal of impurities from this concentration requires further processing.

Radicals produced during further oxidation processes can lead to the conversion of organic contaminants into numerous new species. The processes leading to the formation of hydroxyl radicals to be used for the decomposition of pollutants are generally referred to as AOP's [5]. AOP's are characterized by the production of oxidative hydroxyl radicals at the environmental temperature which will provide the formation of CO_2, H_2O and mineral acids, which are indicators of complete mineralization. AOP's can be developed by combining a single treatment process such as ultrasonic irradiation, electron beam irradiation, gamma irradiation and Fenton processes, with various catalysts such as hydrogen peroxide, ozone and titanium dioxide [6].In UV/H_2O_2 process hydrogen peroxide is photo chemically degraded as a result of UV irradiation. Irradiation of the solution with UV light in the presence of H_2O_2 results in a greater number of •OH radicals than other processes [7, 8].

Hancı et al.found that organisms are oxidized very efficiently by UV irradiation and they mentioned that hydrogen peroxide (H_2O_2) is an effective and easy-to-use oxidant but H_2O_2 is not an excellent oxidant alone [9]. For this reason, hydrogen peroxide is often used in combination with oxidants such as ozone and UV. Kun Zhao et al was used the Fenton process which there is transfer of electrons between peroxide and iron, and iron acts as a homogeneous catalysis to increase the oxidation ability of hydrogen peroxide [10]. This process can be used for the purification of many industrial wastewaters (such as wastewaters containing textiles, paper, phenol compounds, antibiotics and pesticides).Many investigations carried out to investigate the synergistic effect of radiation and other oxidants [11].

The use of AOP's techniques for the removal of phthalates has been also tested by many researchers. Belgiornoa and colleagues concentrated on ultrasonic radiation and photolysis techniques to remove EDC in waste water [12].Bolonga et al used nanofiltration methods for the effects of endocrine disruptors on living organisms and their elimination [13]. Li and his group examined the degradation of the structure using dibutyl phthalate over TiO_2 film and the degradation of phthalates using UV/Ozone [14]. In Hacettepe University, Chemistry Department, gamma-radiation technology is being used to remove textile dyes in wastewater [15]. Factors affecting the radiolysis of the dye such as dye concentration, irradiation dose, dose rate, solution pH were studied.

In this study, DMP, a phthalate from EDC which cannot be broken down by the conventional methods and cannot be removed from the medium, has been determined by UV irradiation technique and its decomposition in the presence and absence of hydrogen peroxide. The aim of the study is to investigate the degradation of DMP by synergistic effects of various experimental factors, such as H_2O_2, and to detect the resulting intermediates and degradation mechanisms. In addition, in this study, the irradiation of DMP was tried to be followed up until mineralization occurred. The crucial point in this study, all analytical techniques are used and the results are given such as some chromatograms and the results which related techniques are compared with each other after these steps the degradation mechanism are suggested according to the intermediates species and final products. The mechanistic experiments and results such as the changes in the total acidity and formaldehyde concentration during the degradation of DMP at different processes were studied first time by our group.

2. EXPERIMENTAL

2.1 Chemicals

Dimethyl phthalate (DMP, purity 99.7%), hydrogen peroxide (30% w/w), purchased from Fisher Scientific (New Jersey, USA) and RieldeHaen (Seelze, Germany) were used without further purification. Acetic acid/sodium acetate buffer and methyl alcohol was used as mobile phase for HPLC and also purchased Fisher Scientific Company, USA. The initial concentration and pH of DMP in all experiments was 25 mg L^{-1}and9.13, respectively. The aliphatic acids which are possible intermediates produced during the irradiation of DMP in the presence of air and H_2O_2 , malic acid, malonic acid, maleic acid, itaconic acid were obtained from Fluka (Steinheim, Germany). Acetic acid, oxalic acid dehydrate and formic acid were used from Sigma-Aldrich (Steinheim, Germany) and BDH (Poole, England), respectively. The chemicals used in the tests of formaldehyde and total acid yield are, formaldehyde, acetylacetone, ammonium acetate, sodium hydroxide which were obtained from Merck, BDH, Sigma-Aldrich and Merck, respectively.

2.2 Apparatus and methods

The UV reactor volume was 2 L. Experiments were performed in an immersion-type reactor equipped with an external water jacket to keep a constant temperature and the low pressure monochromatic mercury lamp (the UV lamp was in the quartz glass tube in the photoreactor and was placed vertically) with maximum radiation emission at 16 W power and 254 nm wavelength was used as the UV light source. The height and diameter of the UV reactor was 380 mm and 15 mm, respectively. To ensure mixing at a constant speed, the magnetic stirrer was placed below the UV reactor to ensure that the solution mixes at a constant rate. A Varian Carry 100 UV-vis spectrophotometer was used to measure absorption spectra of DMP aqueous solutions before and after irradiation and formaldehyde complexes. Before and after irradiation, pH value of the solutions was measured by a JENWAY 3010 model pH meter. Possible organic aliphatic acids were determined using DX-3000 Ion Chromatography from Dionex. The High performance liquid chromatography determinations of DMP were performed using Dionex-DX3000 series equipment, with a Deuterium-UV detector. For extraction of DMP and intermediates Varian (vacuum manifold Varian 20) solid phase extraction system was used by using Varian octadecyl (C18) one way cartriges [16].The DMP residues were analyzed by gas chromatography-mass spectrometry (GC-MS) method using Thermo Trace 1300 Gas Chromatograph with an ISQ LT Single Quadruple Mass Spectrometer from Thermo instruments operated in electron ionization (EI) mode. Dissolved oxygen was determined with WTW Microprocessor Oxi 3000 Oxygen Meter. Formaldehyde was measured according to Hantzsch reaction, recording complex absorption at 412 nm [17]. The total acid yield was determined with titrimetric method.

3. RESULTS AND DISCUSSION

3.1 UV, UV/H_2O_2 Processes

Whether the endocrine disruptors are in any environment and how much they are found, is very important to the removal of these species from the medium. UV-Vis spectra of aqueous solutions of DMP in the presence and absence of H_2O_2 as a function of irradiation time are recorded. Since there is no significant change in UV-vis spectra, it has been decided that UV irradiation alone is not sufficient for DMP degradation [18].

Hydrogen peroxide concentration is an important parameter on UV/H_2O_2. In order to investigate the effect of H_2O_2 on the degradation of the DMP, 25 mg L^{-1} DMP solutions containing different hydrogen peroxide concentrations (0.60 mM, 1.20 mM, 2.40 mM, 4.8 mM) were irradiated at different irradiation times (20, 40, 60, 80, 120, 180, 240 minutes) in UV photocatalytic reactor (16 Watt). The changes of the UV-absorbance of DMP aqueous solutions were monitored before and after irradiation. Attempts have been

made to detect intermediate products and final degradation products in intermediate irradiation times and in the last irradiation period. To investigate the effect of hydrogen peroxide, UV-Vis spectra of irradiated 25 mg L^{-1}DMP solutions in varying amounts of hydrogen peroxide medium are recorded. The results showed that 4.8 mM H_2O_2 is most effective for degradation of DMP. In the presence of 4.8 mM hydrogen peroxide, DMP was thought to degrade without forming too much of an intermediate products. Absorbance changes at 300 nm of DMP solutions at different hydrogen peroxide concentrations as a function of irradiation time are shown in Figure1.

The pH values and dissolved oxygen (DO) of the unirradiated and UV irradiated of DMP solutions in the absence and presence H_2O_2 are given in Figurers 2 and 3 . It was observed that the pH values of the unirradiated and irradiated solutions decreased with the irradiation time. Also it was showed that the pH values of DMP solutions in the presence of H_2O_2 are lower than in the absence of H_2O_2 since DMP is more degraded in the presence of H_2O_2.It was showed that in the presence of 4.8 mM hydrogen peroxide, the decrease in dissolved oxygen is more pronounced than in the case of hydrogen peroxide-free DMP solutions as the irradiation time increases. This reduction is due to the more degradation of DMP in the presence of H_2O_2, the depletion of more dissolved oxygen, and the further uptake of mineralization [19]. In order to study the effect of hydrogen peroxide concentration and UV-irradiation on the degradation of DMP, 25 mg L^{-1}DMP solutions were exposed to UV-irradiation for different times (20-240 min) in the presence and absence of hydrogen peroxide and HPLC chromatograms were recorded (Figure 4, Figure 5) . Changes in the amount of DMP during the UV irradiation under all conditions are given in Figureure 6.

In UV/H_2O_2(0.0 mM) process: After 60 and 240 minutes irradiation, 1.92 % and 4.87 % of DMP in aqueous solution was degraded in the aqueous solutions, respectively(Figure). These results suggest that DMP is resistant to direct UV-photolysis [20].

In UV/H_2O_2(4.8mM) process: 100 % of DMP was degraded in 25 mg L^{-1} DMP aqueous solution which is subjected to UV irradiation for 60 and 240 minutes (Figure 7).

In no UV irradiation/H_2O_2 (4.8mM) process: To examine the effect of only H_2O_2 on the degradation of unirradiated DMP in aqueous solution, Experiments were repeated with 25 mg L^{-1} DMP aqueous solution in 4.8 mM H_2O_2 at different waiting periods which are as equal to UV-irradiation times (2-240 min). The results showed that after 60 and 240 minutes UV irradiation ~9.5 % of DMP was degraded (Figure 7). Observation indicates that DMP cannot be oxidized by hydrogen peroxide alone (Figure 7).

These results showed that UV irradiation alone and H_2O_2oxidation alone processes have little effect on the decomposition of DMP and the synergistic effects of UV/H_2O_2 process is more effective on the DMP degradation. When these results are compared, the irradiation time required for complete decomposition of DMP is found to be lower in the presence of hydrogen peroxide. Hydrogen peroxide concentration effectively increases and accelerates degradation. In addition, in the presence of hydrogen peroxide, hydroxyl radicals are more effective in radically degrading organics. Hydrogen peroxide can also react with $^{\bullet}H$ ($k\ (20\ ^{\circ}C) = 2.4 \times 1010\ M^{-1}\ s^{-1}$) and e^-_{aq}($k\ (20\ ^{\circ}C) = 1.5 \times 107\ M^{-1}\ s^{-1}$) [21]. Since UV radiation is selective, it can be said that only UV rays are inadequate to decompose DMP. UV rays cause hydrogen peroxide to photo chemically break down to form hydroxyl radicals. As a result, there are more radicals in the medium to allow degradation of DMP [22]. In this way, there are more radicals and the activation of these radicals with UV rays increases the percentage of DMP degradation.

3.2 Evaluation of Gas Chromatography - Mass Spectrometry Results

GC-MS analyzes were performed for identification of the intermediates formed in DMP solutions exposed to UV light. It was showed that no intermediate was found in aqueous DMP solutions exposed only to UV radiation. GC spectroscopy recorded from DMP solutions irradiated with UV for 20 minutes in the presence of 4.8 mM hydrogen peroxide and retention times of Silyl ester structures of possible intermediates identified (Figure 8).

GC chromatogram of UV-irradiated DMP solution containing hydrogen peroxide (4.8 mM) for 60 minutes is given (Figure 9). It was showed that DMP appears to be completely degraded.

The amount of formaldehyde was determined spectrophotometrically by the Hantzsch method [23]. Formaldehyde formation was quantitatively and qualitatively determined by spectrophotometric method at λ_{max} = 412 nm. Although the complex formed in the presence of acetyl acetone and acetate buffer shows maximum absorbance at 412 nm, acetaldehyde does not give absorbance under the same conditions [17]. Therefore, only the amount of formaldehyde can be detected in this method and no aldehyde penetration is caused. To investigate the effect of irradiation time on formaldehyde formation, changes in formaldehyde concentration as a function of UV irradiation time of 25 mg L^{-1}DMP solutions containing 4.8 mM hydrogen peroxide were followed (Figure 10). It was showed that the amount of formaldehyde increases as the UV-irradiation time increases, but the amount of formaldehyde decreases significantly at higher UV-irradiation times. The reason is that formaldehyde is converted to formic acid during or after irradiation. Supporting assays for this confirmation were made by ion chromatography and the results are given in further sections.

3.3 Evaluation of Gas Chromatography - Mass Spectrometry Results

After irradiation with UV, the total acidity of the media was determined by titration using phenolphthalein indicator with 0.0092 M NaOH (standardized with oxalic acid dihydrate). Total acidity values were monitored as a function of UV- irradiation time. Total acidity values of 25 mg L^{-1}DMP aqueous solution containing 4.8 mM hydrogen peroxide as a function of irradiation time were measured (Figure 11). The total acidity value of the solution increased due to the presence of hydrogen peroxide and the presence of small structured acids (hexanoic acid, pentanoic acid, oxalic acid, formic acid, muconic acid, acetic acid, etc.) These acids are mainly formed by the breakdown of the benzene ring. The pH of the medium decreases due to the acids formed (Figure 2). Therefore, the measured pH values are consistent with the total acidity values obtained.

3.4 Determination of Aliphatic Acids

Organic and inorganic anions containing different aliphatic acids have been identified by ion chromatography (IC Dionex DX3000). Ion chromatograms of 25 mg L^{-1}, DMP aqueous solutions were exposed to UV light for different durations (2-240 min) in order to detect the intermediates resulting from decomposition of DMP in the presence of 4.8 mM hydrogen peroxide (Figure 12). In DMP aqueous solutions which exposed only to UV rays, no intermediate product resulting in degradation of DMP was detected.

The changes in acetic acid concentration as a function of UV-irradiation time, in 25 mg L^{-1} DMP solutions containing 4.8 mM hydrogen peroxide were reported (Figure 13). Acetic acid formation was observed in samples exposed to UV irradiation in the presence of hydrogen peroxide. In the samples without hydrogen peroxide, no intermediate product formation was observed as a result of UV irradiation. In the presence of hydrogen peroxide, more OH radicals are formed in the medium, which leads to further decomposition of DMP. As shown in Figure13, acetic acid was formed in the UV irradiated DMP aqueous for 2 minutes in the solutions containing hydrogen peroxide (4.8 mM) and after 20 minutes irradiation, the amount of acetic acid decreased and remained constant.

The changes in the formic acid concentration occurring as a function of UV irradiation time were reported in 25 mg L^{-1} DMP solutions in the presence and absence of 4.8 mM hydrogen peroxide (Figure 13). Formic acid formation is the next conversion step of formaldehyde. In solution which containing hydrogen peroxide and irradiated by UV for 2 minutes, formic acid is formed and the amount of formic acid is reduced after irradiation for 10 minutes (Figure 13).

In DMP solutions exposed to UV irradiation, maleic acid concentrations are shown as a function of UV irradiation time in the presence and absence of 4.8 mM H_2O_2 (Figure 13) . In solutions containing 4.8 mM hydrogen peroxide, greater amounts of maleic acid are formed. Maleic acid formation was observed in DMP solutions containing and without hydrogen peroxide as the irradiation time increased. Concentration is reduced by irradiation with maleic acid after irradiation for 120 minutes in solutions containing hydrogen peroxide and 180 minutes in solutions without hydrogen peroxide.

In DMP aqueous solutions were exposed to UV irradiation, oxalic acid concentrations are shown as a function of irradiation time in the presence and absence of 4.8 mM H_2O_2 (Figure 13). Oxalic acid was formed in higher concentrations in solutions containing 4.8 mM hydrogen peroxide. In DMP solutions containing hydrogen peroxide, oxalic acid formation increased as irradiation time increased. No oxalic acid were found in solutions without hydrogen peroxide. Oxalic acid is an intermediate product in the last stages of DMP degradation. Oxalic acid is then likely to break down into CO_2 and carbonate species [24].

$$C_2O_4^{2-} + OH^{\cdot} \longrightarrow OH^- + CO_2 + COO^- \quad (1)$$

$$COO^- + O_2 \longrightarrow O^{2-} + CO_2 \quad (2)$$

3.5 Degradation Mechanism in UV / H_2O_2 Process

As a result of exposure of aqueous solution of DMP to UV irradiation, the most effective oxidizing agent are hydroxyl radicals. The hydroxyl radicals formed by UV rays attack the DMP molecules. Dihydroxybenzene-1,2-dicarboxylate, 3,4,5-trihydroxy benzoic acid, 2,4,5-dihydroxy benzoic acid, methyl-3-hydroxy-2-phenylpropanoate, hydroxy (4-hydroxyphenyl) acetic acid are aromatic intermediate products. These structures are converted to 2-hydroxy propanoic acid and butanedioic acid as a result of UV irradiation, and in forward UV irradiation formic acid, acetic acid, formaldehyde and formic acid. Formaldehyde, formic acid and acetic acid is oxidized and carbon dioxide and water form over oxalic acid, the last intermediate product before mineralization (Figure 14).

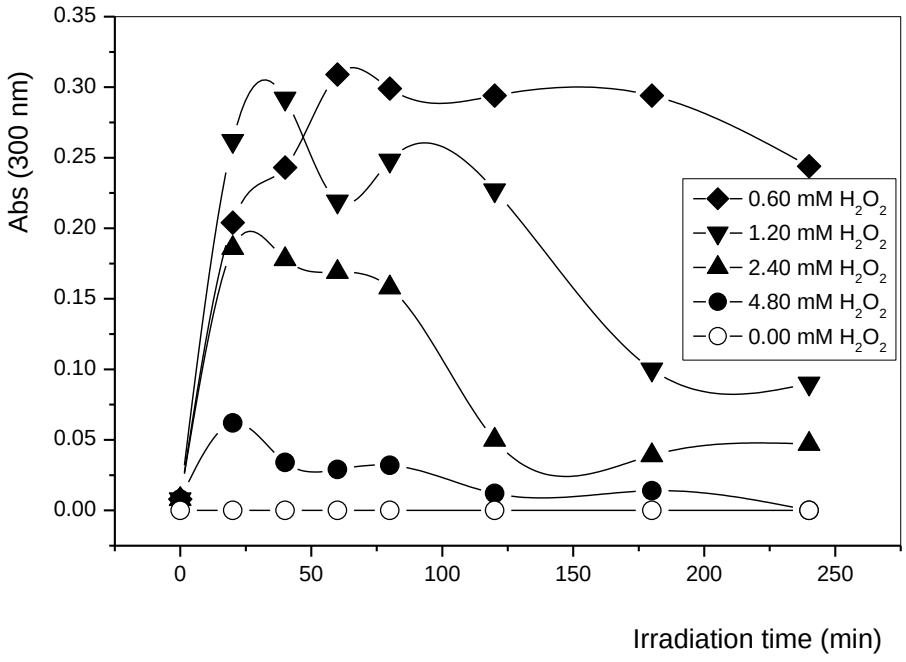

FIG. 1. Absorbance changes at 300 nm of DMP solutions at different hydrogen peroxide (0.6-4.8 mM) concentrations as a function of UV irradiation time, [DMP]: 25 mg L^{-1}.

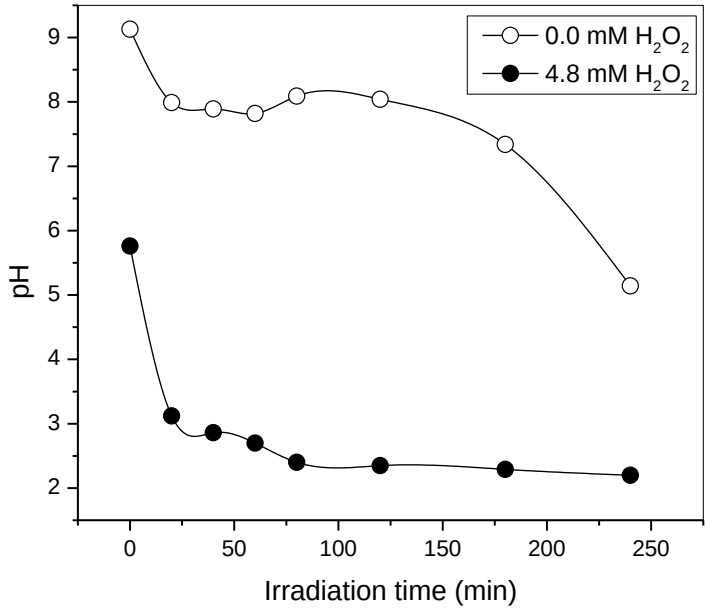

FIG. 2. The change in pH value as function of UV irradiation time in DMP aqueous solutions. [DMP]: 25 mg L^{-1}.

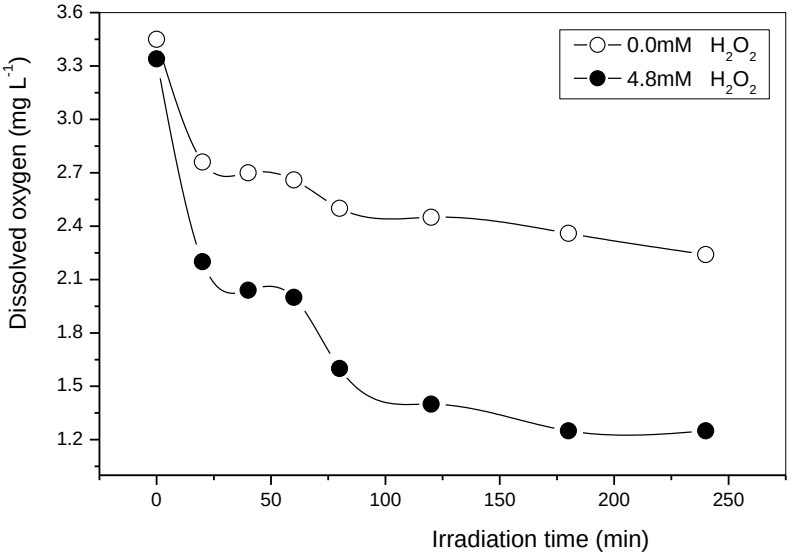

FIG. 3. Change in the amount dissolved oxygen (DO) with the irradiation time in the absence and presence of hydrogen peroxide (4.80 mM) during irradiation of DMP (25 mg L^{-1}).

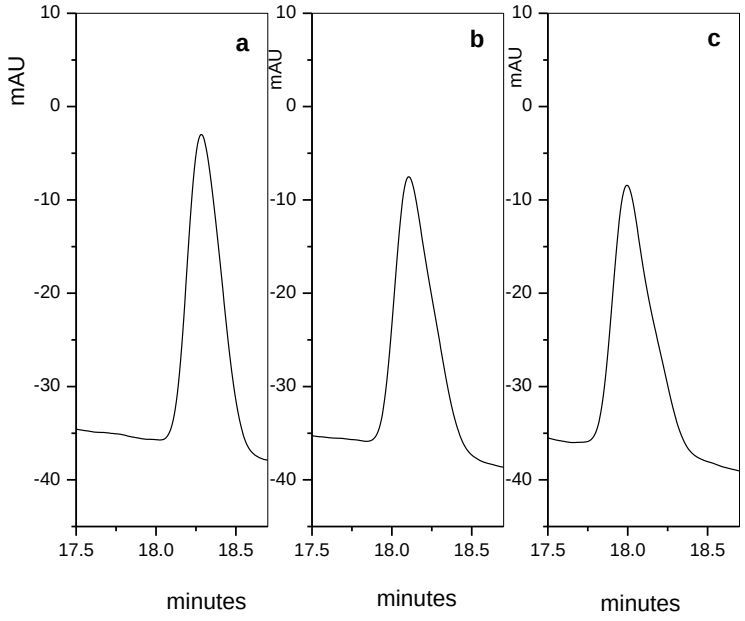

FIG. 4. (a) High performance liquid chromatogramsof unirradiated, (b) 20 minutes, (c) 80 minutes irradiated of DMP aqueous solutions (retention time 17.94 min), [DMP]: 25 mg L^{-1}, [H_2O_2]: 0.0 mM.

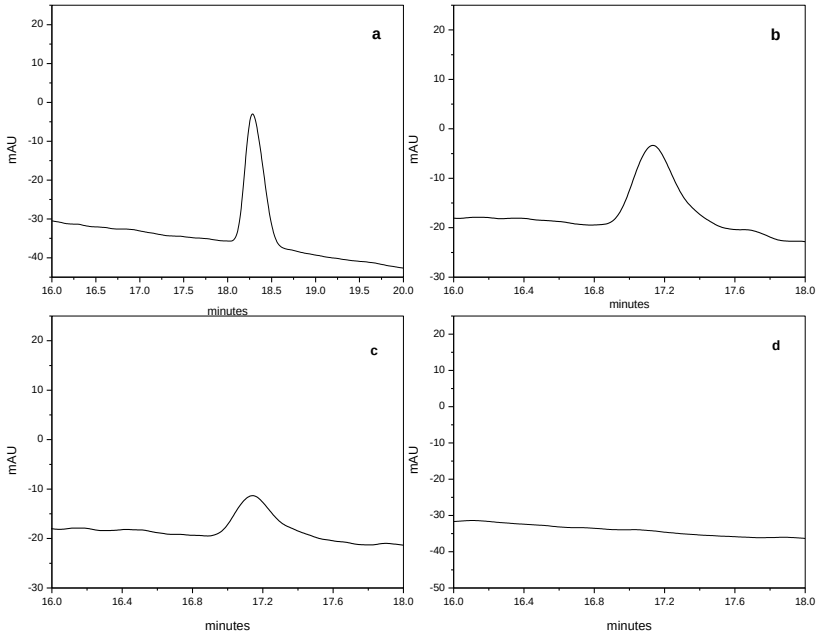

FIG. 5. (a) High performance liquid chromatograms of unirradiated, (b) 2 minutes, (c) 10 minutes, (d) 20 minutesUV irradiated of DMP aqueous solutions (retention time 17.94 min),[DMP]: 25 mg L^{-1}, [H_2O_2]: 4.8mM.

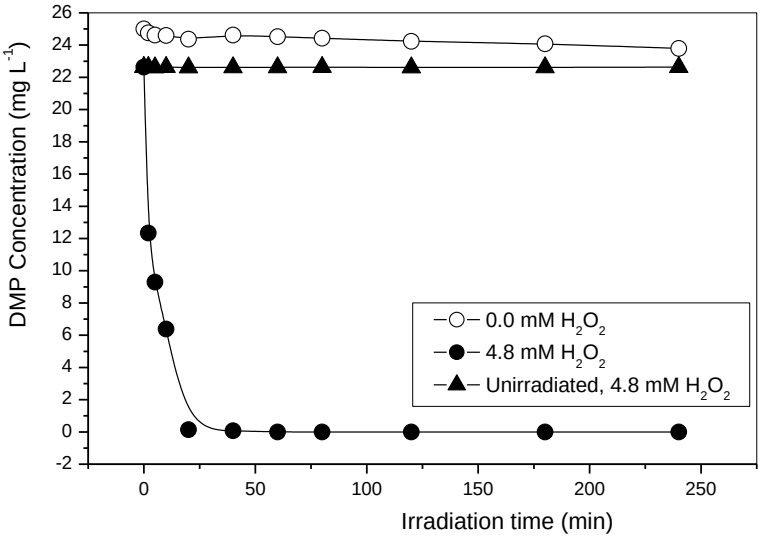

FIG. 6. Change in the amount of DMP concentration with the UV irradiation time in the absence and presence of hydrogen peroxide (4.80 mM) during irradiation of DMP aqueous solutions.

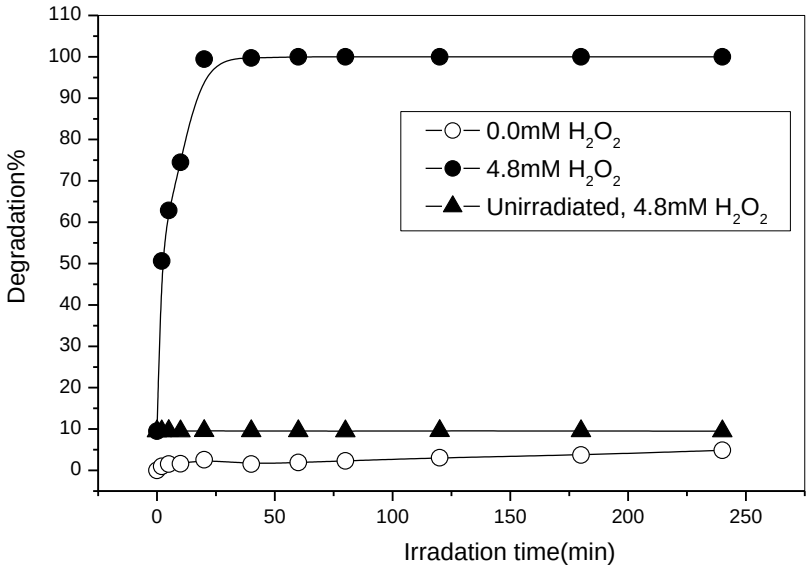

FIG. 7. Change in the amount of percent degradation with the UV irradiation time in the absence and presence of hydrogen peroxide (4.80 mM) during irradiation of DMPaqueous solutions.

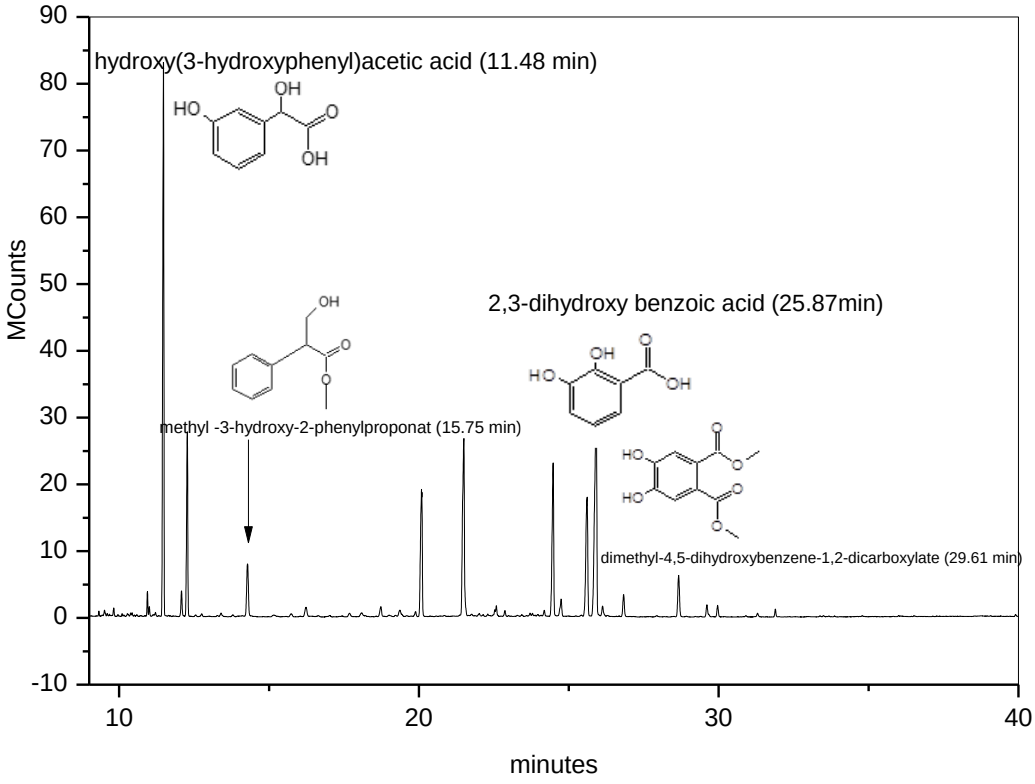

FIG. 8. GC chromatogram of DMP samples irradiated by UV-irradiation (20 min) and and retention times of intemediate species, hydroxy (3-hydroxyphenyl) acetic acid (11.48 min), methyl 3-hydroxy 2-phenyl propanoat (15.75 min), 2,3- dihydroxy benzoic acid (25.87 min), dimethyl 4,5-dihydroxybenzen-1,2-dicarboxylat (29.61 min). [DMP]: 25 mg L^{-1}, [H_2O_2]: 4.8 mM.

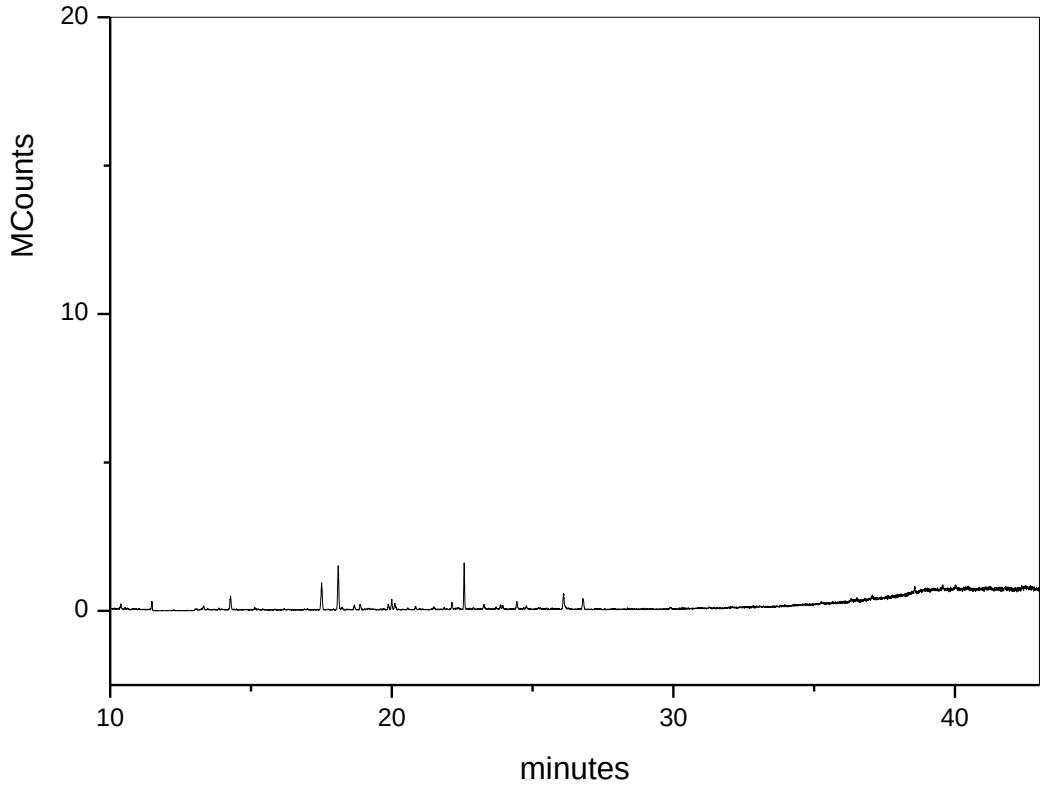

FIG. 9. GC chromatogram of DMP samples irradiated by UV-irradiation (60 min) after eluted from C18 cartridges in methyl alcohol, [H_2O_2]: 4.8 mM.

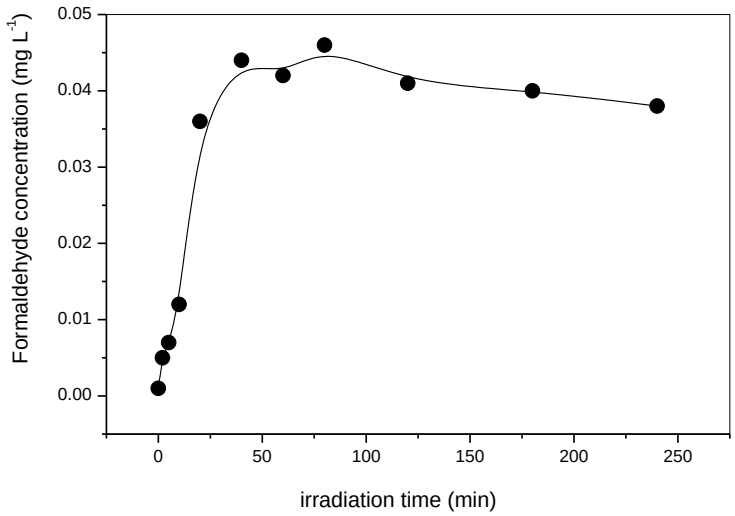

FIG. 10. Change in formaldehyde concentration with irradiation time. [DMP]: 25 mg L^{-1}, [H_2O_2]: 4.8 mM.

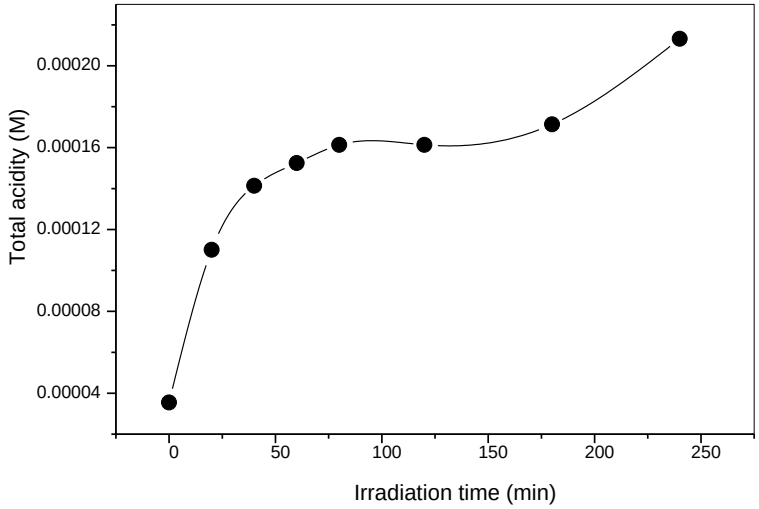

FIG. 11. The change in total acidity as a function of UV irradiation timein DMP aqueous solutions. [DMP]: 25 mg L^{-1}, [H_2O_2]: 4.8 mM.

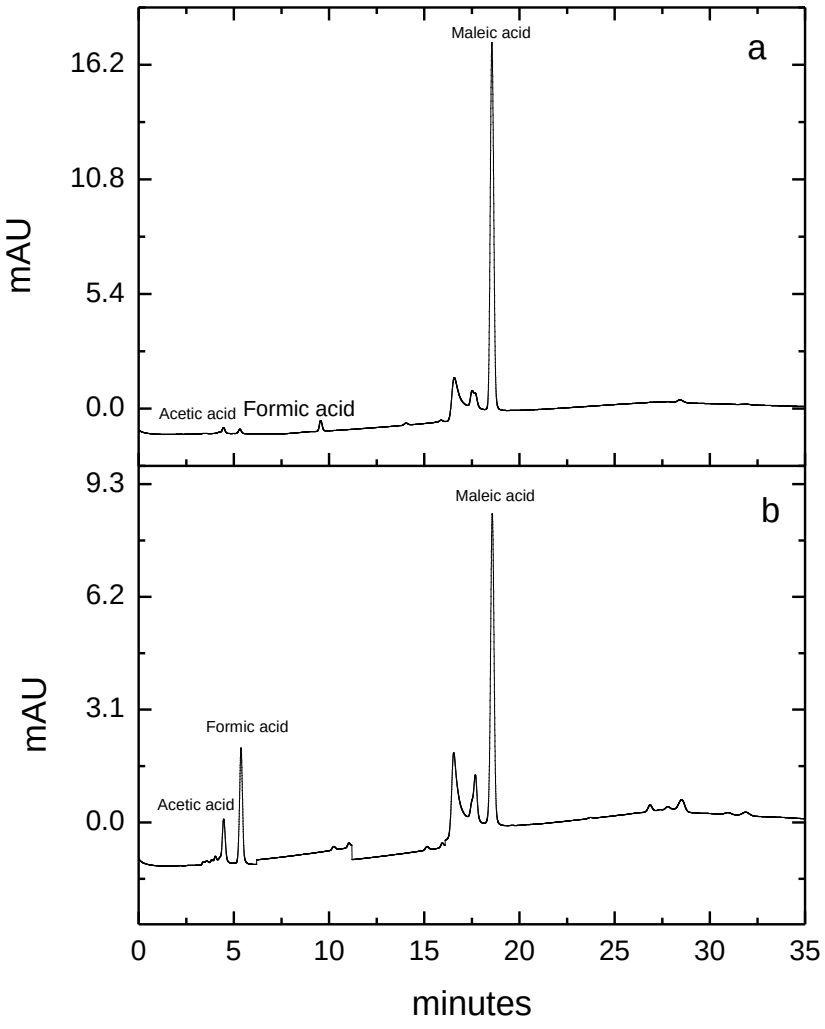

FİG. 12. Ion chromatogram of DMP solution irradiated with UV for (a) 240 minutes and (b) 2 minutes , Retention times are: for acetic acid (4.75), formic acid (5.58), maleic acid (18.50) [DMP]: 25 mg L^{-1}, [H_2O_2]: 4.8 mM.

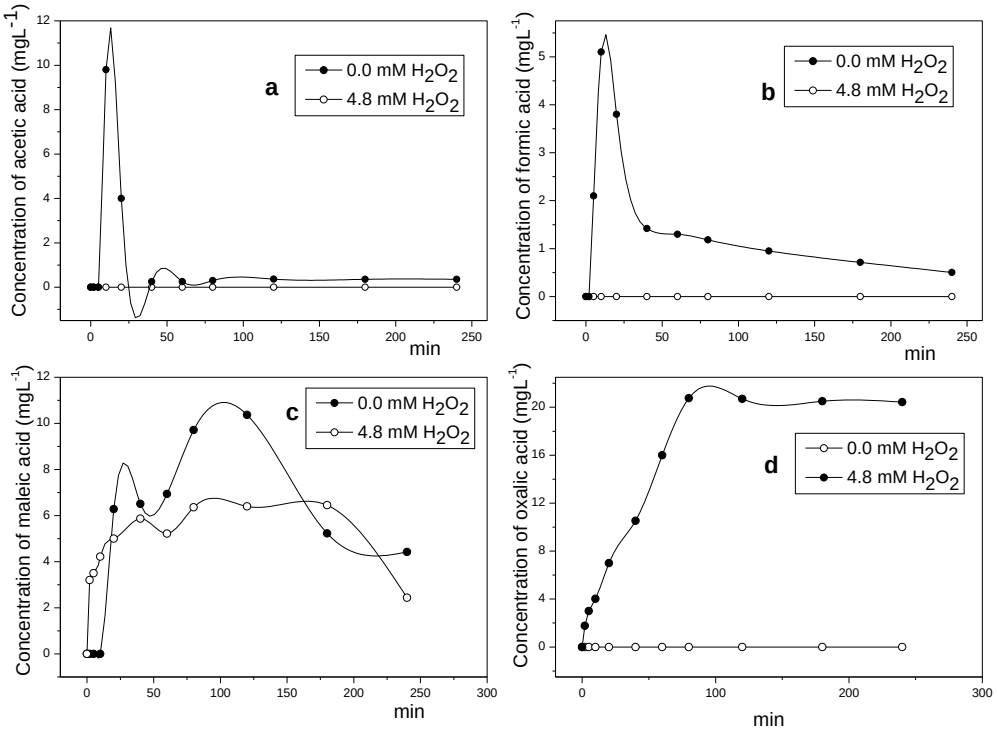

FIG. 13. Change in the amounts of (a) acetic acid (b) formic acid (c) maleic acid (d) oxalic acidconcentrations as a function of UV irradiation time in DMP solutions in the presence and absence of hydrogen peroxide. [DMP]: 25 mg L^{-1}, [H_2O_2]: 4.8 mM

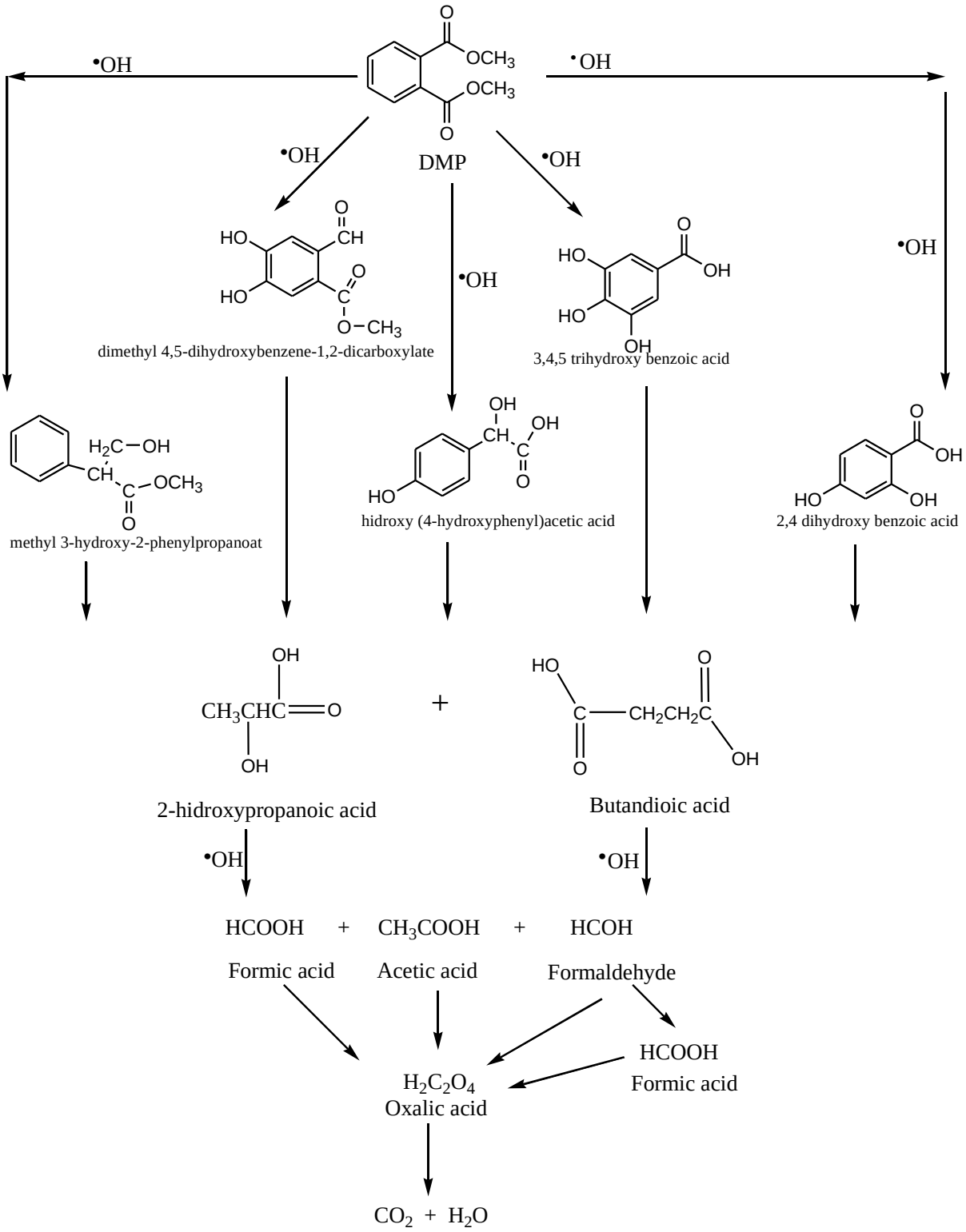

FIG. 14. Degradation mechanism of water-soluble DMP in UV / H_2O_2 process.

4. CONCLUSION

In this study, the degradation of DMP, which is widely used as a plasticizer in various conditions, has been studied. H_2O_2 which is hydroxyl radical sources, has been used in addition to water-photolysis products to increase UV-irradiation and degradation efficiency of toxic substances and intermediates for degradation of 25 mg L^{-1}DMP in aqueous solutions. In additi$_o$n, to investigate how these oxidants may form synergistic effects with irradiation, degradation of DMP by UV and UV/H_2O_2 processes were followed as a function of UV irradiation time and UV-Vis spectra were recorded. Since UV-irradiation is less effective in degradation of DMP UV-irradiation is performed at different concentrations of H_2O_2 (0.6-4.8 mM) in order to increase the degradation of DMP, the optimum H_2O_2 concentration is determined as 4.8 mM. To investigate the effect of only H_2O_2 on DMP degradation as a function of time, DMP aqueous solutions containing 4.8 mM H_2O_2 were kept at different UV irradiation times (0-240 min) and without any irradiation processes then the remaining DMP concentrations and degradation % were determined. As a function of H_2O_2 concentration In the presence of only 4.8 mM H_2O_2 and without any UV-irradiation processes, DMP degradation was determined to be 9.48 %. The degradation % of DMP in the absence of H_2O_2 in 25 mg L^{-1} DMP aqueous solutions after UV-irradiation (60 min) was 1.92% while in the presence of 4.8 mM H_2O_2 and for the same UV irradiation time the percent degradation of DMP was 100 %. The results showed that the synergistic effect of UV / H_2O_2 is more effective on DMP degradation. pH, total acidity, formaldehyde concentrations and dissolved oxygen (DO) values were recorded before and after irradiation processes. Due to degradation of DMP and spent of dissolved oxygen and formation of aliphatic acids at the same time, decrease in pH and DO values and increase in total acidity were observed in DMP solutions. Intermediates formed as a result of degradation of DMP were detected by using GC-MS and IC, and degradation mechanism of DMP was given by using of these intermediates.

5. ACKNOWLEDGEMENTS

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