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Enhanced Degradation of Aspirin by Electrochemical oxidation with Modified PbO_2 Electrode and Hydrogen Peroxide

Qizhou Dai, Yijing Xia, Liying Jiang, Wenlong Li, Jiade Wang, Jianmeng Chen[*]

College of Biological & Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, China
[*]E-mail: jchen@zjut.edu.cn

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The degradation of aspirin was performed by electrochemical oxidation with a novel modified PbO_2 electrode assisted by H_2O_2. The effects of electrolyte concentration, current density, initial aspirin concentration and H_2O_2 concentration on the aspirin degradation were examined in this study. Under an optimized condition, the removal of aspirin concentration, COD and TOC after 150 minutes treatment reached 94%, 81% and 61%, respectively. It was found that H_2O_2 was effective to accelerate the organic pollutants degradation. Based on the degradation intermediates detected by IC and GC-MS, a possible degradation mechanism of aspirin was proposed.

Keywords: Electrochemical oxidation; Aspirin; PbO_2 electrode; hydrogen peroxide

1. INTRODUCTION

Since first synthesized in 1887 by Felix Hoffmann, aspirin (acetylsalicylic acid) has been one of the most frequently used drugs with its analgesic, anti-inflammatory, antipyretic and anti-platelet actions [1]. It was reported that the risk of a first myocardial infarction (MI) reduced 44% under aspirin treatment among middle aged men [2, 3]. However, as it is widely used, this kind of pharmaceutical wastewater would be potential a pollution source without suitable way of treatment.

In recent years, electrochemical oxidation as one of the advanced oxidation processes (AOPs) for the removal of wastewater containing toxic or biorefractory organic substance, has attracted considerable attentions for its strong oxidation performance, mild condition, and environmental compatibility [4-6]. The characteristic of the anode is one of the most important factors influencing the effect of electrochemical oxidation technology [7-9]. And PbO_2 anode showed the advantages in electrochemical oxidation for organic wastewater treatment, the mechanism of hydroxyl radical on the PbO_2 anode was mainly formed as following equation [10]:

$$PbO_2(h^+) + H_2O_{ads} \longrightarrow PbO_2(\cdot OH)_{ads} + H^+ \qquad (1)$$

The hydroxyl radicals can efficiently decompose organic pollutants. In addition, the research showed that H_2O_2 could react with organic compounds [11, 12]. In electrochemical oxidation, if the addition of H_2O_2 could accelerate the organic radical reactions and thus greatly enhance the degradation of organic pollutants, it would be quite useful for the application of electrochemical oxidation in pharmaceutical wastewater pollution control.

The purpose of the present work was to investigate the feasibility of electrochemical degradation process assisted by H_2O_2 for the degradation of aspirin. The effects of electrolyte concentration, current density, initial aspirin concentration and H_2O_2 concentration on the degradation of aspirin were studied systematically. Furthermore, the degradation intermediates were identified and the degradation mechanism of aspirin was discussed.

2. EXPERIMENTAL

2.1 Materials and chemicals

Aspirin (CAS No. 50-78-2) was provided by J&K Chemical. Other chemicals used as received were of analytical reagent grade or higher grade. And the water in all experiments was ultra pure water.

2.2 Electrode preparation

The anode used in the experiments was a novel β-PbO_2 anode modified with fluorine resin and rare earth. The preparation procedures include thermal decomposition, α-PbO_2 preliminary deposition and β-PbO_2 deposition. More details of the anode preparation and its electrochemical characteristics were presented in previous work [10, 13]. In the end, Ti/SnO_2- Sb_2O_3 /PTFE-La-Gd-β-PbO_2 electrode was prepared.

2.3 Analysis method

The samples were selected depending on the time of 0, 10, 30, 60, 90, 120 and 150 min. The concentration of aspirin in aqueous solution was detected by a High performance liquid chromatography system (1200, Agilent Technologies, USA), equipped with a C18 column (4.6mm×150mm). The chemical oxygen demand (COD) was determined by the dichromate method (DRB200, Hach, USA), and the detection wavelength was 440nm (U-2910, Hitachi, Japan). The total oxygen demand (TOC) was analyzed using a TOC Analyzer (TOC-V CPN, Shimadzu, Japan) based on the combustion-infrared method. Ion Chromatograph (ICS-200, Dionex, USA) and Gas chromatography-Mass spectrometry (GC7890/MS5975, Agilent Technologies, USA) were also used to analyze intermediate products during reaction. The pH value of each solution was measured by pH meter (pHs-3E, Leici, China).

The average current efficiency (ACE) was calculated by the following equation [14]:

$$ACE = \frac{(COD_0 - COD_t)FV}{8It} \times 100\% \qquad (2)$$

Where COD_0 and COD_t are the chemical oxygen demand at initial time and the given time t (g/L), respectively. F is the Faraday constant ($96487 C \cdot mol^{-1}$), V is the volume of the solution (dm^3), I is the current (A), and t is the reaction time (s).

3. RESULTS AND DISCUSSION

3.1 Effect of electrolyte concentration

It is important to investigate the effect of elecrtrolyte concentration since its conductivity and actual wastewater usually contains considerable amount of salts. Na_2SO_4 was selected as the supporting electrolyte to avoid the generation of toxic and carcinogenic chlorinated species [15]. Different concentrations of $NaSO_4$, varying from 0.05 mol/L to 0.5 mol/L, were applied to study the influence on the removal of aspirin, as was shown in Figure 1. On the condition of initial aspirin concentration 500 mg/L, current density 50 mA/cm^2, it was found that an increase of Na_2SO_4 concentration up to 0.1 mol/L leading to the enhancement of the removal of aspirin. Further increase of the electrolyte concentration showed negatively on the degradation of aspirin removal.

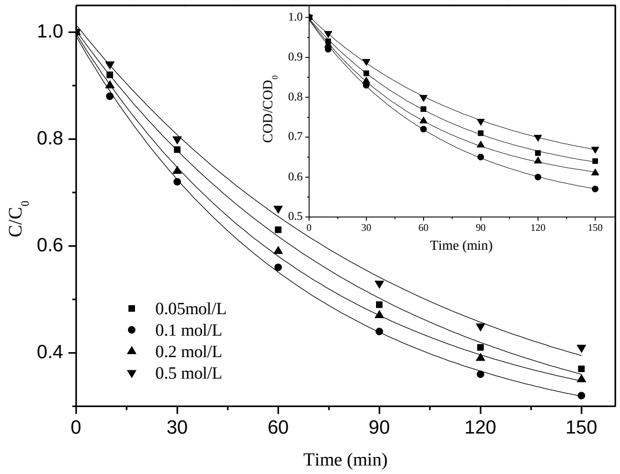

Figure 1. The aspirin degradation on different electrolyte concentration

Under the condition of electrolyte concentration 0.1 mol/L, the relatively optimized removal of aspirin and COD attained 68% and 43%, respectively. When the electrolyte concentration got 0.5 mol/L, the aspirin degradation and COD removal decreased to 58% and 33%. Thus, an increasing of the electrolyte concentration could enhance the conductivity in solution and accelerate the electron transformation in reactions, and it was limited in a certain rage. The reason might be explained that a layer of salt film was formed on the electrode surface under a high concentration of electrolyte, which would impede the migration of aspirin to the electrode surface and decrease the probability of effective contact between the organic pollutants and •OH free radicals or other active groups generated on the electrode surface [16]. Thus, 0.1 mol/L Na_2SO_4 was chosen as the supporting electrolyte for the rest of the present study.

3.2 Effect of current density

Current density is an important parameter on pollutant removal in electrochemical process. Some research indicated that high current density could cause an increase of electrode material decomposition while it could also lead to side reactions including oxygen evolution at the same time [17]. Thus, on condition of initial aspirin concentration 500mg/L, Na_2SO_4 0.1mol/L, to investigate the relatively optimal current density, comparative experiments were conducted under five variables, such as 10 mA/cm^2, 30 mA/cm^2, 50 mA/cm^2, 70 mA/cm^2, 90 mA/cm^2. As shown in Figure 2, aspirin degradation and COD removal rate were improved with the increasing applied current density, which was similar with those reported in literatures [18, 19].

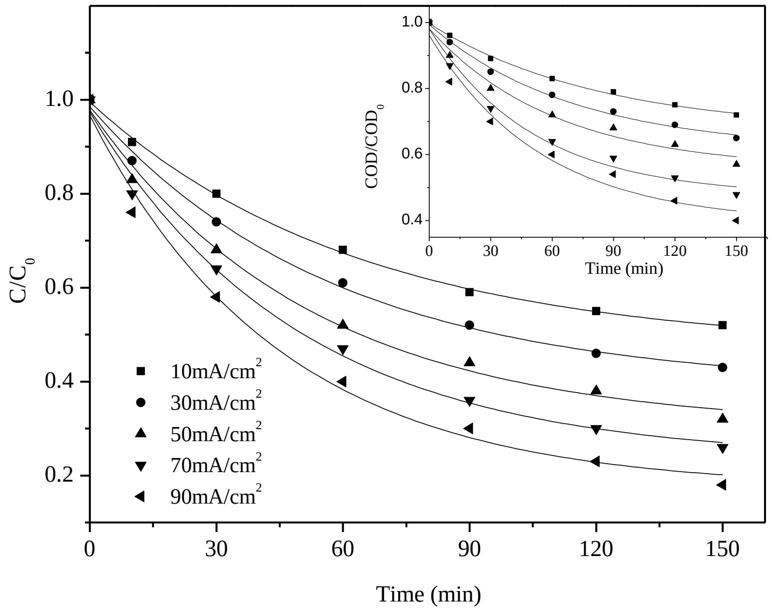

Figure 2. The aspirin degradation on different current density

This phenomenon could be ascribed to the production of hydroxyl radicals increased [20], which eventually made for the decomposition of aspirin. At current density 10 mA/cm^2, the aspirin degradation rate was only 46%, while at current density 90 mA/cm^2, 82% aspirin decomposed in the process. Simultaneously, the COD removal rate increased from 24% to 60%. It was obvious that the increase of current density had a positive effect on aspirin decomposition and COD removal. However, as was shown in Figure 3, the current efficiency was 64%, 38%, 31%, 22% and 18% at 10, 30, 50, 70 and 90mA/cm^2 after 120 min electrolysis time, respectively. It could be deducted that the current efficiency decreased with the increasing of current density. Moreover, the current efficiency also decreased with the increasing of electrolysis time. For example, when current density was at 50 mA/cm^2, the current efficiency reached 65%, 45%, 38% and 31% at 30 min, 60 min, 90 min and 120 min, respectively. Such a decrease in the current efficiency could be explained that more side reactions came up and more electrical energy was converted into heat energy [21]. The results supported that the performance would be cost-effective at a low current density but need long treatment time, while at a high current density it was much more efficient but costly. These outcomes were in accord with previous study [22]. Thus, according to the removal rate and current efficiency, the current density of 50 mA/cm^2 would be a good choice, where aspirin degradation, COD removal and current efficiency were relatively high.

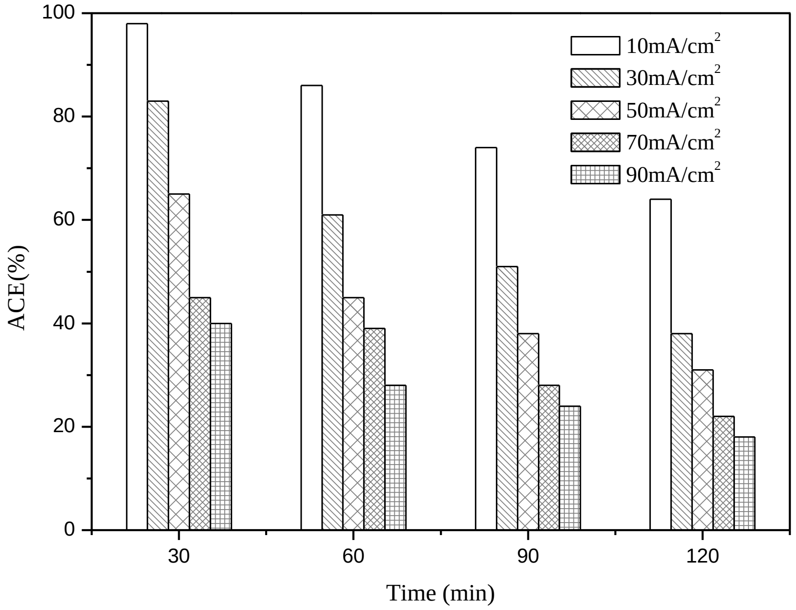

Figure 3. The average current efficiency on different current density

3.3 Effect of initial aspirin concentration

From an application angle, it is important to study the degradation rate of initial concentration of aspirin. Hence, on condition of Na_2SO_4 0.1mol/L, current density 50mA/cm^2, the effect of initial concentration of aspirin, ranging from 100 mg/L to 900 mg/L, on aspirin degradation and COD removal was investigated. As was shown in Figure 4, the removal of aspirin and COD attained 93% and 65% respectively under the initial concentration of 100 mg/L after 150 min. But when initial aspirin concentration enhanced to 900 mg/L, the removal rate of aspirin and COD declined to 51% and 31%, respectively. It was observed that aspirin degradation and COD removal rate declined with an increase in initial concentration of aspirin.

Assuming a constant rate of hydroxyl radicals produced in electrochemical process, the ratio of hydroxyl radical to aspirin concentration would decrease with the increasing of initial concentration. Thus aspirin degradation and COD removal decreased as a function of the shortage of reactive oxygen species. Moreover, an increasing of initial aspirin concentration would lead to more intermediate species formed, which were easily absorbed on the surface of anode and prevented the contact between pollutant and active sites [23, 24]. As a result, the intermediate products would limit the degradation of aspirin through competing with organic species for the reaction with hydroxyl radicals. Thus an appropriate initial aspirin concentration of 500 mg/L was chosen in the study.

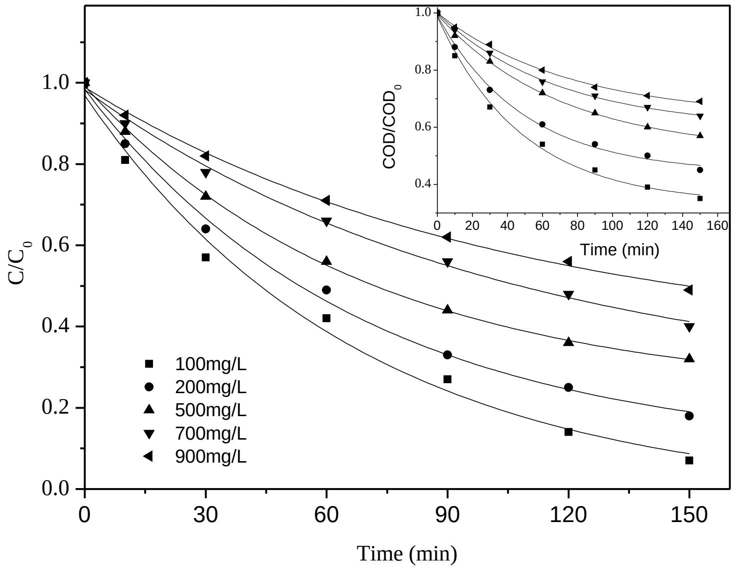

Figure 4. The aspirin degradation on different initial aspirin concentration

3.4 Effect of H_2O_2 concentration

It is well known that the dose of H_2O_2 is a key parameter in the electrochemical process, depending on its nature of reductant and oxidizability. Hydrogen peroxide is one of the most important electrochemical intermediate products [25], thus the effect of its concentration worth studying. Hydrogen peroxide produces the form of hydroxyl radicals in two ways [26]. Firstly, Hydrogen peroxide loses an electron and changes into active $HO_2\cdot$ radicals. Secondly, it also can achieve a electron and oxidize into active •OH radicals.

$$H_2O_2 - e \xrightarrow{\cdot OH} HO_2 \cdot + H^+ \qquad (3)$$

$$H_2O_2 + e \xrightarrow{\cdot OH} \cdot\mathrm{OH} + OH^- \qquad (4)$$

On the condition of initial aspirin concentration 500mg/L, Na_2SO_4 0.1mol/L, current density 50mA/cm^2, electrochemical degradation of aspirin was conducted in the presence and absence of H_2O_2. Figure 5 showed the effect of different H_2O_2 dose on the degradation of aspirin. The removal rate of aspirin concentration was 68%, 75%, 86%, 89%, 94%, 92% with 0 mg/L H_2O_2, 100 mg/L H_2O_2, 200 mg/L H_2O_2, 500 mg/L H_2O_2, 1000 mg/L H_2O_2, 1200 mg/L H_2O_2, respectively. While the COD removal efficiency ranged from 43% to 81% with different concentrations of H_2O_2. It was noticed that aspirin degradation and COD removal were significantly improved by the addition of H_2O_2. The increase in the removal of aspirin and COD could be explained by the fact that the generation of high active groups such as •OH, HO_2·and H· radicals [27]. Figure 5 also illustrated that there was an optimum dosage of H_2O_2 during the electrochemical degradation of aspirin. The maximum removal rate of aspirin concentration and COD were 94% and 81% respectively when H_2O_2 concentration reached 1000 mg/L. However, higher concentration of H_2O_2 at 1200 mol/L, aspirin decomposition and COD removal decreased to 92% and 78%, respectively. The fact might be explained that H_2O_2 also could become a scavenger of hydroxyl radicals resulting in less aspirin to be decomposed. Thus moderate dose of H_2O_2 needs to be considered for the decomposition of aspirin.

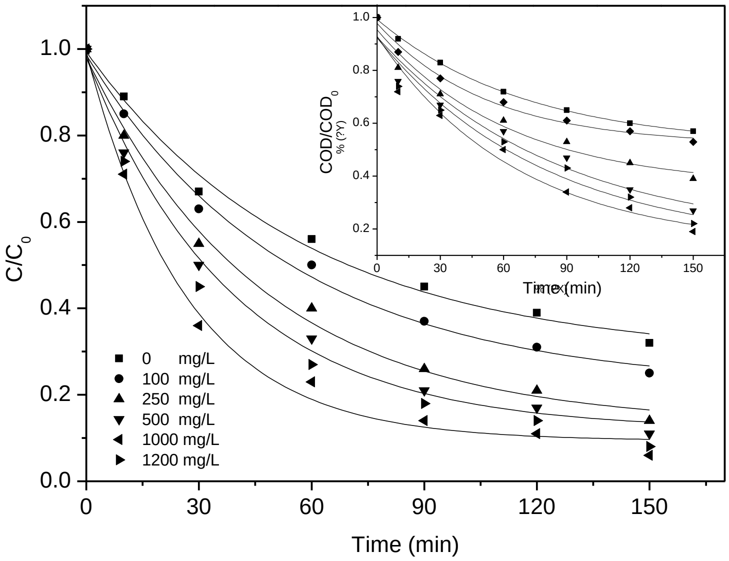

Figure 5. The aspirin degradation and COD removal of different H_2O_2 concentration

3.5 Kinetic studies

Some studies indicated that electrochemical degradation of organic substance fitted appropriately by pseudo-first-order kinetics [28, 29].

The related pseudo-first-order kinetic model is shown as

$$\ln\frac{C}{C_0} = -kt \qquad (5)$$

Where C_0 and C represent initial aspirin concentration and aspirin concentration at given time t (min), respectively, t is reaction time (min) and k is the rate constant (min^{-1}).

Kinetic study for H_2O_2 assisted electrochemical degradation was undertaken on the condition of initial aspirin concentration 500mg/L, current density $50mA/cm^2$ and Na_2SO_4 0.1mol/L. Results showed the degradation of aspirin on modified PbO_2 anode assisted by H_2O_2 was well fitted with first-order kinetic. As was illustrated in Figure 6, a typical plot of linear regression ($ln(C/C_0)$) versus time t for the decomposition of aspirin assisted by H_2O_2 gave straight line. The regression coefficient R^2 values were shown in Table 1 ranging from 0.983 to 0.994, confirming that the decomposition process followed the first order reaction. And the corresponding rate constant (k) calculated from slopes were 0.007 min^{-1}, 0.009 min^{-1}, 0.013 min^{-1}, 0.014 min^{-1}, 0.018 min^{-1}, 0.016 min^{-1} with different H_2O_2 dose varying from 0 mg/L H_2O_2 to 1200 mg/L H_2O_2. Apparently, the electrochemical degradation of aspirin with 1000 mg/L H_2O_2 had the relatively best performance. The results were in good agreement with above study.

Table 1. Rate coefficients for electrochemical degradation of aspirin assisted by H_2O_2

H_2O_2 concentration (mg/L)	κ (min^{-1})	R^2
0	0.007	0.994
100	0.009	0.990
250	0.013	0.987
500	0.014	0.983
1000	0.018	0.989
1200	0.016	0.990

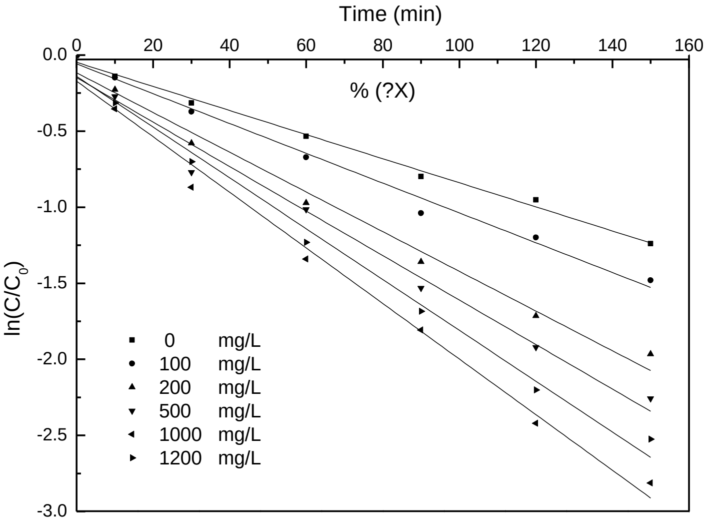

Figure 6. First order kinetic plot of aspirin degradation with different H_2O_2 concentration

3.6 Aspirin degradation mechanism analysis through TOC and IC method

The results of initial aspirin concentration 500mg/L, current density 50mA/cm^2, Na_2SO_4 0.1mol/L, degradation analysis of aspirin obtained through total organic carbon (TOC) analysis were shown in Figure 7. It was observed that single electrochemical process gave a TOC removal rate of aspirin about 37% after 150 min. While the application of 1000 mg/L H_2O_2 assisted electrochemical degradation resulted in 61% reduction in TOC. The enhancement in the mineralization of aspirin by the effect of H_2O_2 could be explained by the additional generation of hydroxyl radicals and the increased electron transfer between the solution and electrode surface [30]. Therefore, it was observed that a combination of electrochemical method and H_2O_2 was effective to decompose aspirin in aqueous solution. However, further analysis was required to propose the degradation mechanism.

As shown in Figure 7, the concentrations of low molecule acid including oxalic acid, acetic acid, formic acid, maleic acid and salicylic were detected in aqueous solution of aspirin electrochemical degradation through IC method. It was noticeable that the changes in the concentration of small molecule intermediate products as a function of electrolysis time assisted with 0 mg/L H_2O_2 or 1000 mg/L had a big difference. The formation of salicylic acid increased to peak at 30 min without H_2O_2 and 20 min with 1000 mg/L H_2O_2, while other smaller molecule acid increased continuously in the process. For example, acetic acid and formic acid reached maximum at 60 min and 120 min without H_2O_2, respectively. With the assist of 1000 mg/L H_2O_2, acetic acid and formic acid reached peak at 30 min and 90 min. The results suggested that H_2O_2 to some extent accelerated the formation of low molecule acid. Combined with other studies [13, 31], it could be deduced that the tendency of aspirin decomposition went toward short carbon chain under electrolysis, indicating that low molecule acid eventually converted to CO_2. This conclusion was in good agreement with the TOC analysis.

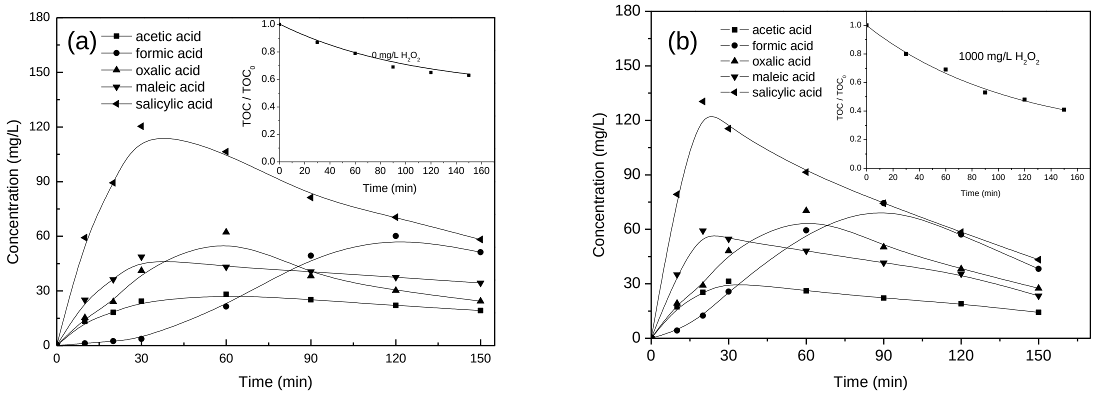

Figure 7. The changes on TOC and small molecule intermediate assisted with 0 mg/L and 1000 mg/L H_2O_2

3.7 Possible reaction pathway of aspirin degradation

To further explore the possible degradation mechanism, GC-MS method was employed to identify the intermediate products of aspirin degradation. Some aromatic compounds such as salicylic acid, phenol and 2,3-dihydroxybenzoic acid were detected through this method. Based on the observed results and previous studies [32-34], a possible degradation mechanism including hydrolysis, electrophilic addition, electro transfer, decarboxylation, radical reaction, ring open and mineralization was proposed in Figure 8. Through hydrolysis reaction, aspirin firstly decomposed to salicylic acid and acetic acid. Following that, the salicylic acid went on further degradation. Partial salicylic acid changed into phenol through decarboxylation, while the others turned into 2,3- dihydroxybenzoic acid or 2,4- dihydroxybenzoic acid via electrophilic addition and the attack of hydroxyl radicals. Afterwards, phenol was further oxidized to catechol which would convert into 3,4-dioxo-1,5-cyclohexadiene-1-carboxylic and hydroquinone which would change into p-benzoquinone. Then, maleic acid and fumaric acid came into being following the benzene ring open of 3,4-dioxo-1,5-cyclohexadiene-1-carboxylic, p-benzoquinone, 2,3- dihydroxybenzoic acid and 2,4- dihydroxybenzoic acid, as were reported by the former researchs [35, 36]. In addition, maleic acid and fumaric acid would transform into smaller molecule acid such as succinic acid, malonic acid, oxalic acid, acetic acid and formic acid. The last step was the mineralization of the different small molecule compounds, which ultimately converted to CO_2 and H_2O.

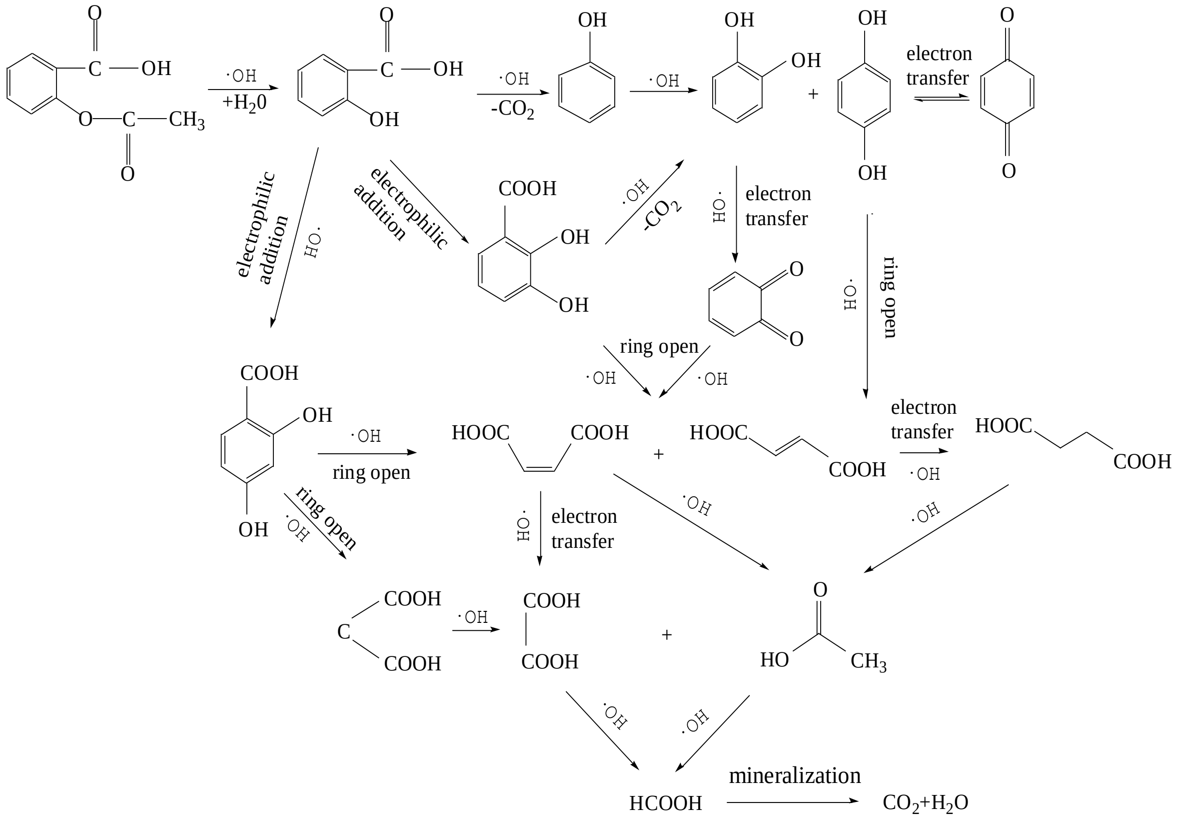

Figure 8. A possible degradation pathway for aspirin by electrochemical oxidation

4. CONCLUSION

In conclusion, the combination of electrochemical method and H_2O_2 has a positive effect on the degradation of aspirin in aqueous solution. The effects of electrolyte concentration, current density, initial aspirin concentration and the dosage of H_2O_2 on the degradation of aspirin and COD removal were analyzed. It was found that the addition of H_2O_2 strongly enhanced the degradation of aspirin. The oxidative degradation of aspirin affected by H_2O_2 concentration was well fitted with pseudo-first-order kinetic model and the optimized electrochemical degradation efficiency was observed to occur in the presence of 1000 mg/L H_2O_2. The removal of aspirin, COD and TOC reached 94%, 81% and 61% after 150 minutes reaction time, respectively, under a given condition as: 500mg/L aspirin concentration, 50mA/cm^2 current density, 0.1 mol/L electrolyte concentration (Na_2SO_4) and 1000mg/L H_2O_2. Based on the degradation intermediates detected by IC and GC-MS method, a possible degradation mechanism of aspirin including hydrolysis, electrophilic addition, electro transfer, decarboxylation, radical reaction, ring open and mineralization was proposed.

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