Electrochemical Oxidation of Rhodamine B: Optimization and Degradation Mechanism

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Titanium based lead dioxide electrodes were successfully prepared by the method of electrodeposition in nitrate solution, including titanium base, Sn-SbO$_X$ interlayer, α-PbO$_2$ middle layer and β-PbO$_2$ active layer. Rhodamine B (RhB) was selected as the model pollutant to optimize the effects of operational factors in the electrochemical oxidation process. The removal of RhB and chemical oxygen demand (COD) were detected at different reaction time and the relative optimized results were achieved on condition of the concentration of supporting electrolyte, initial RhB concentration, pH value and applied current density at 0.1 mol/L, 200 mg/L, 4.4, and 20 mA/cm^2, respectively. The kinetics results on RhB removal indicated that RhB degradation by electrochemical oxidation followed the pseudo-first-order reaction. Besides, UV-vis spectra revealed that the conjugated structure of RhB was easier and prior to be degraded. The intermediates generated in the solution were identified by GC/MS and a possible degradation pathway of RhB was proposed.

1. INTRODUCTION

In recent years, kinds of refractory organic chemicals were produced with huge production and these chemical would cause a serious health risk problem without efficient treatment[1]. The organic dyes is one of the representative chemical and there are lots of industries, such as textile, cosmetic, paper, leather, agricultural research, light-harvesting arrays, which could produce wastewater containing dyes with high concentration[2]. Most wastewater containing dissolved dyes are biorefractory and toxic. It has been found that a small amount of dye pollutants could still be harmful to human health and ecosystem. Therefore, it is meaningful and necessary to treat the dye wastewater [3,4,5].

Rhodamine B (RhB) is a kind of synthetic dye, and it is widely used in colored glass, cell fluorescent stain, fireworks and other industries. RhB was used as food additives previous, and then it was forbidden in foods production after it was proved to be is carcinogenic. In order to eliminate the harm of RhB, varieties of technologies had been applied to removal the RhB, including activated sludge process[6], ion exchange[7], photocatalysis[8], chemical flocculation[9], adsorption[10], and so on. Advanced oxidation processes (AOPs) are usually thought as a kind of green technologies for the high removal efficiency on biorefractory organic pollutants at environmental friendly condition [11]. Electrochemical oxidation is a typical advanced oxidation process with well performance in the treatment of kinds of different wastewater, including pharmaceutical wastewater[12], pesticide wastewater[13] and printing and dyeing wastewater[14]. One of the important part of the electrochemical oxidation process is anode material and several common materials have reached relatively satisfied results, such as BDD, PbO_2, SnO_2, and so on[15-17]. PbO_2 electrode is an effective treatment in organic wastewater treatment process due to its good conductivity, chemical stability, high oxygen evolution potential and relatively low cost[18].

In this work, titanium based lead dioxide electrodes were prepared. In order to study the effect of electrode, Rhodamine B (RhB) was selected as the target pollutant because its universality and perniciousness. Experiments were taken to study and optimize the effects of operating parameters, including supporting electrolyte concentration, initial RhB concentration, applied current density and the initial pH value. Kinetics based on RhB concentration was analyzed to study the electrochemical oxidation performance of the electrode. The UV-vis spectra of RhB solution and intermediates identified by GC/MS were performed to study the degradation mechanism of RhB.

2. EXPERIMENTAL

2.1. Chemicals and reagents

The RhB was analytical reagent and purchased from the Aladdin Industrial Corporation (Shanghai, China). All other chemicals and reagents were analytical grade.

2.2. Preparation of electrodes

2.2.1. Titanium base pretreatment

Titanium substrates were cut with a dimension of 20mm×115mm (reaction area is 14cm^2, 20mm×70mm), and polished by 200-grit and 600-grit sandpaper, then cleaned by ultrasound to remove the residual sands. After polish, the titanium substrates were steeped in a 14.5% (by mass) sodium hydroxide solution for 30 min. Next, titanium substrates were disposed with a 16.7% sulfuric acid solution at a bath temperature of 60 ℃ for 20 min. Finally, titanium substrates were etched with a 15% oxalic acid solution at a bath temperature of 80 ℃ for 3h. After all pretreatments were done, titanium substrates were kept in 1% oxalic acid solution.

2.2.2. Preparation of Sn-SbO$_X$ interlayer

Sn-SbO$_X$ interlayer was prepared by thermal decomposition, the solution used for thermal decomposition contains 7.53g SbCl$_3$, 104.16g SnCl$_4$.5H$_2$O, 192.14g citric acid and 251ml ethylene glycol. Titanium substrates were smeared evenly with the solution and putted in tube type electric furnace at 515 ºC, the process was repeated 10 times. Especially, the last bake time is 66min, which is 50 minutes longer than the 9 times previous.

2.2.3. Preparation of α-PbO$_2$ middle layer

The layer of α-PbO$_2$ was prepared by DC electrodeposition at a current density of 5mA/cm^2 for 1h in an alkaline electrolyte which consisted of 0.08 mol/L yellow lead oxide and 3.5 mol/L sodium hydroxide. During the whole process, the solution was putted in the water bath at the temperature of 60 ºC, and a pure titanium plate as the cathode, the titanium substrate covered with Sn-SbO$_x$ as the anode.

2.2.4. Preparation of β-PbO$_2$ active layer

The β-PbO$_2$ layer is the main reaction layer of the electrode, which is prepared in a acidic electrolyte at a current density of 50mA/cm^2. The composition of the electrolyte contains 0.3mol/L Pb(NO$_3$)$_2$, 0.01mol/L NaF, 6ml/L PTFE(60%, wt%), and use HNO$_3$ to adjust the pH value to 1.8. Before the electrodeposition, ultrasonic was utilized to mix the electrolyte. Also, the solution was kept at temperature 80°C, a pure titanium plate as the cathode, and use the electrode coated with α-PbO$_2$ as the anode.After 2 hours electrodeposition, the PbO$_2$ electrode was completed.

2.3. Electrochemical oxidation degradation

The RhB degradation experiment was carried on in a reactor with volume of 250mL RhB solution, PbO$_2$ electrode was used as anode and a parallel pure titanium slice selected as cathode. During the reaction, a magnetic stirrer was taken. In this study, we considered four parameters include the supporting electrolyte concentration (0.05-0.4 mol/L), initial RhB concentration (50-500mg/L), initial pH (1.5-11.0), and current density(5-50mA/cm^2). Samples were taken at a certain time and detected the removal of RhB and COD.

2.4. Analytical methods

The concentration of RhB was detected by ultraviolet-visible spectrophotometer (DR6000, Hach, USA) at wavelength of 554 nm. The fast degestion-spectrophotometer method was used to determine the COD, and a digester (DRB200, Hach, USA) was applied. UV-vis adsorption of the solution at different reaction time was acquired by ultraviolet-visible spectrophotometer (DR6000, Hach, USA). Gas Chromatography-Mass spectrometry (GC7890/MS5975, Agilent Technologies, USA) was used to identify the intermediate products generated during the oxidation of RhB. The

sample was extracted with methylene choloride and blown by nitrogen to concentrate the macromolecular substances and derivatized with BSTFA, then 1μL of the sample was injected in splitless mode at 290 ℃ of the injection port with helium as carrier gas. The temperature-rising program is listed as follows. Firstly, keep the column temperature at 60 ℃ for 3 min, then heat to 300 ℃ with a rate of 8 ℃/min and hold at 300 ℃ for 5min. The ionization energy was 70ev and the ion source is EI source.

At the different reaction time, we computed the instantaneous current efficiency (ICE) which depended on the change of COD with the following equation[19]：

$$ICE = \frac{(COD_0 - COD_t)}{8It} FV \times 100\% \tag{1}$$

where COD_0 and COD_t represent the COD concentration at reaction time of 0 min and the left COD after reaction for t min (g/L) respectively. F is the Faraday constant (96487 C/mol), V is the volume of solution (dm^3), t is the reaction time (s), and I is the current (A).

3. RESULTS AND DISCUSSION

3.1. Electrochemical degradation of RhB

3.1.1. Effect of electrolyte concentration
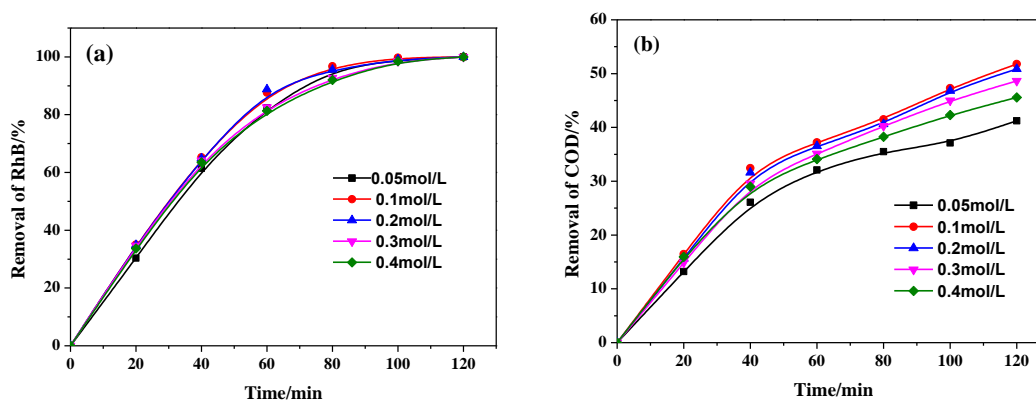
Figure 1. The effect of the electrolyte concentration (a) RhB removal; (b) COD removal

As the conductivity of RhB solution is too weak, electrolyte should be added to the solution to provide the conductivity. Due to the excellent stability and good conductivity, Na_2SO_4 was chosen as the supporting electrolyte at different concentrations of 0.05 mol/L, 0.1 mol/L, 0.2 mol/L, 0.3 mol/L, and 0.4 mol/L. With a current density of 30 mA/cm^2 and initial RhB concentration of 100 mg/L, we discussed the effect on the degradation of RhB and COD.

As show in Fig.1, the change of Na_2SO_4 concentration had hardly great impact on the removal on RhB. However, when the supporting electrolyte changed, the change of COD removal was clearly to be observed. When the Na_2SO_4 concentration increased from 0.05 mol/L to 0.1 mol/L, the removal of COD also had an obvious improvement. It could be explained that more electrolyte enhanced the

conductivity of solution and the COD removal efficiency was increased[20]. However, when the concentration of Na_2SO_4 increased further after 0.1 mol/L, the COD removal efficiency decreased instead. It could be attributed to that more Na_2SO_4 concentration would lead more anions around the anode, which may compete with the active sites of the electrode, and finally lead to the decline of COD removal[21]. The other phenomenon we should note is that higher electrolyte lead to lower cell voltage, which means less energy consumption. But low cell voltage may not activated electron transfer efficiently according to the energy-band theory[22]. By the above part of the analysis and discussion, we chose 0.1 mol/L Na_2SO_4 to do our following experiments.

### 3.1.2. Effect of initial concentration of RhB
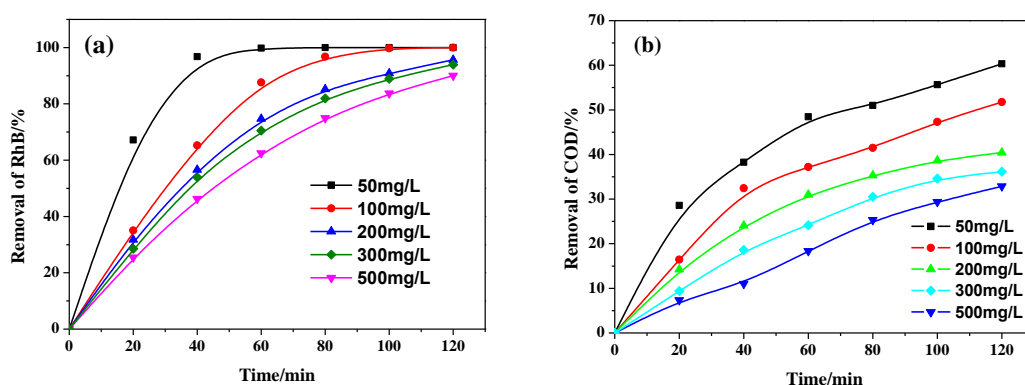
Figure 2. The effect of the initial RhB concentration (a) RhB removal, (b) COD removal

The ingredient of actual wastewater usually affected by many factors, and it is necessary to study the impact of initial concentration on RhB and COD removal efficiency. Different RhB concentration from 50 mg/L to 500 mg/L was tested with the electrolyte concentration of 0.1 mol/L and the current density of 30 mA/cm^2.

Fig.2 showed the removal of RhB and COD with different initial RhB concentration. Obviously, as the RhB concentration increased, both the RhB and COD removal showed significant decrease tendency. The actual RhB removal amount increased with the increasing initial RhB concentration, this phenomenon is similar to the oxidation reported by Azzam[23]. The possible reason is that at higher RhB concentration, more intermediates would be produced, which would occupy some active sites and influence the degradation of RhB. During the reaction, these intermediates gathered around the electrode, and would result in the electrode contaminated[24]. Compared the COD removal efficiency with RhB removal efficiency, it would be found that RhB removal were higher than the former, which indicate that the mineralization are incomplete as some intermediates were produced[25].

3.1.3. Effect of initial pH value

The pH value would make a great impact on the electrochemical oxidation of pollutants, some people thought that a better effect would happen if the oxidation process happened in acidic condition. However, some people hold the converse opinions[28-30]. In this study, H_2SO_4 and NaOH were used to adjust the pH ranging from 1.6 to 11.0, containing both acidic and alkaline media. The applied current density is 30mA/cm^2, the electrolyte concentration is 0.1 mol/L, and the RhB concentration is 200 mg/L.
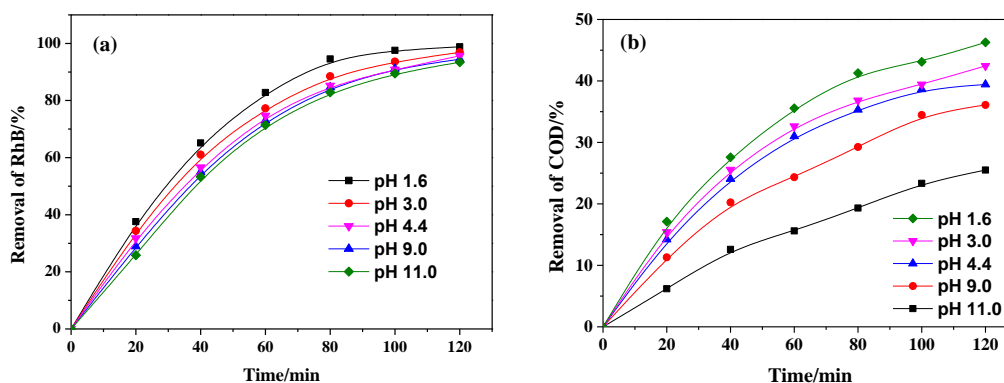
Figure 3. The effect of the initial pH (a) RhB removal, (b) COD removal

As show in Fig. 3(a), the change of pH could not have outstanding influence on the removal of RhB, they all had showed high removal efficiency at the end of reaction. Things changed when come to the removal of COD, from Fig. 3(b), we can clearly to see that the removal COD showed opposite tendency with the change of pH value, when pH risen, COD removal efficiency decreased. It can be explained that the process of hydroxyl radicals act on the removal of COD may independent[31]. Besides, oxygenation reaction would be more intense in the alkaline solution, as shown in equation (2) and (3)[32]. Although an acidic media would have better excellent removal efficiency, adjust the pH would raise the cost, so we selected the neutral pH as the optimum parameter to do the following experiments.

$$2 \cdot OH \rightarrow O_2 + 2H^+ + 2e^- \tag{2}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{3}$$

3.1.4. Effect of current density

An important problem of electrochemical oxidation technology is the energy consumption, which is closely related to the current density. In order to clarify the effect of current density, the current density ranging from 5mA/cm^2 to 50mA/cm^2 were tested, other parameters are 200mg/L of the RhB concentration and 0.1 mol/L Na_2SO_4.

As show in Fig. 4(a) and Fig. 4(b), a significant improvement of RhB and COD removal happened as the current density increased. When the current density increased from 5mA/cm^2 to

10mA/cm^2, the removal of RhB just increased by 4.12% but 19.10% when it changed from 10 mA/cm^2 to 20 mA/cm^2. Meanwhile, the kinetic constant almost doubled. High current density may promote the electrode produce more active sites, such as hydroxyl radicals, which lead to the improvement of RhB and COD removal. The instantaneous current efficiency (ICE) of different current density was calculated by equation (1) and show in Fig. 4(c). On the contrary, the high current density showed a lower ICE. It can be explained that high current density generated more hydroxyl radicals, but it would be consumed by intermediates at the same time[26]. Furthermore, high current density may be conducive to the secondary reaction like oxygen evolution[27].
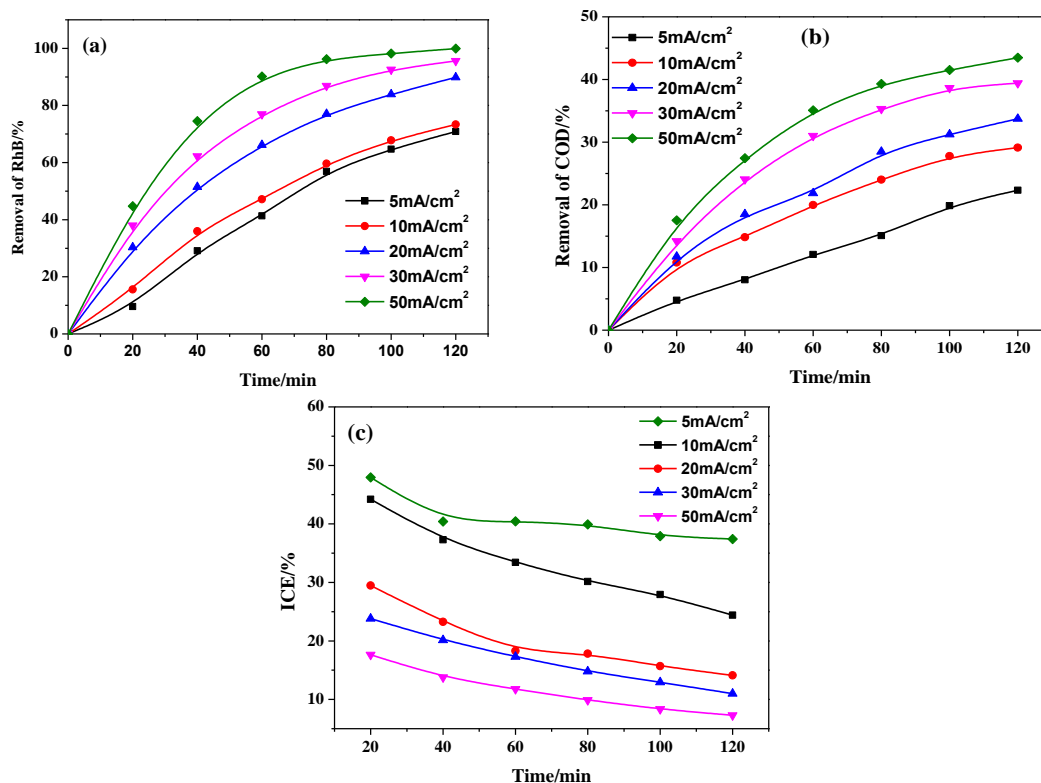
Figure 4. The effect of the current density (a) RhB removal, (b) COD removal, (c) ICE

3.2 RhB electrochemical degradation kinetics

In order to study the mechanism of the PbO$_2$ electrode in the electrochemical oxidation progress, kinetics on the strength of RhB concentration were analyzed. The results indicated that the degradation of RhB followed the pseudo-first-order kinetics, which could be showed in the following equation:

$$Ln\frac{C_0}{C_t} = kt \tag{4}$$

Besides, half-lives times were calculated by following equation:

$$t_{1/2} = \frac{Ln2}{k} \tag{5}$$

where C_0 is the initial RhB concentration (mg/L), C_t is the RhB concentration at reaction time t (s), k is the reaction rate constant (s^{-1}), and $t_{1/2}$ is the half-lives (s). The specific kinetics data were showed in the following table.

Table 1. The kinetics data for the RhB degradation at different parameters

| Parameters		Rate constants ($k \times 10^{-2}$, s^{-1})	Half-lives ($t_{1/2}$, min)	R^2
Electrolyte concentration (mol/L)	0.05	0.0321	21.59	0.963
	0.1	0.0373	18.58	0.962
	0.2	0.0347	19.97	0.973
R_c=100,pH=4.4,C_d=30	0.3	0.0304	22.80	0.987
	0.4	0.0293	23.65	0.989
Initial RhB concentration (mg/L)	50	0.0876	7.91	0.985
	100	0.0373	18.58	0.962
	200	0.0256	27.07	0.999
E_c=0.1,pH=4.4,C_d=30	300	0.0221	31.36	0.996
	500	0.0181	38.29	0.995
pH	1.6	0.0356	19.47	0.990
	3.0	0.0275	25.2	0.995
	4.4	0.0245	28.26	0.996
E_c=0.1,R_c=200,C_d=30	9.0	0.0236	29.36	0.997
	11.0	0.0221	31.36	0.997
Current density (mA/cm^2)	5	0.0101	68.61	0.993
	10	0.0111	62.43	0.998
	20	0.0186	37.26	0.996
E_c=0.1,R_c=200,pH=4.4	30	0.0257	27.07	0.997
	50	0.0395	17.54	0.992

*E_c=Electrolyte concentration (mg/L);R_c=Initial RhB concentration (mg/L); pH=pH value; C_d=Current density(mA/cm^2)

From the table 1 we found that the electrolyte concentration and the pH did not show significant impact on the rate constants. When the electrolyte concentration increased from 0.05 mol/L to 0.4 mol/L, and the solution pH changed acidic to alkaline, there were no obvious change happened to the rate constants and the half-lives. On the other hand, the rate constants decreased from 8.76×10^{-4} s^{-1} to 1.81×10^{-4} s^{-1} when the initial RhB concentration increased from 50mg/L to 500 mg/L, and the half-lives almost increased four times meanwhile, which was 7.91 min at first. Current density also showed great impact on the rate constants and half-lives, which changed from 1.01×10^{-4} s^{-1} to 3.95 $\times 10^{-4}$ s^{-1} and 68.61 min to 17.54 min respectively as the applied current density increased from 5 mA/cm^2 to 50 mA/cm^2. In summary, the initial RhB concentration and the current density will show more influence on the electrochemical oxidation of RhB.

3.3. Degradation mechanisms of RhB
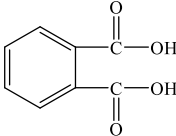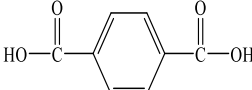
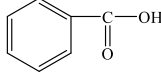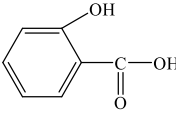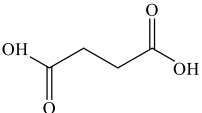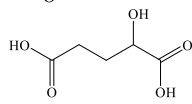*3.3.1. The UV-vis absorption spectra analysis*
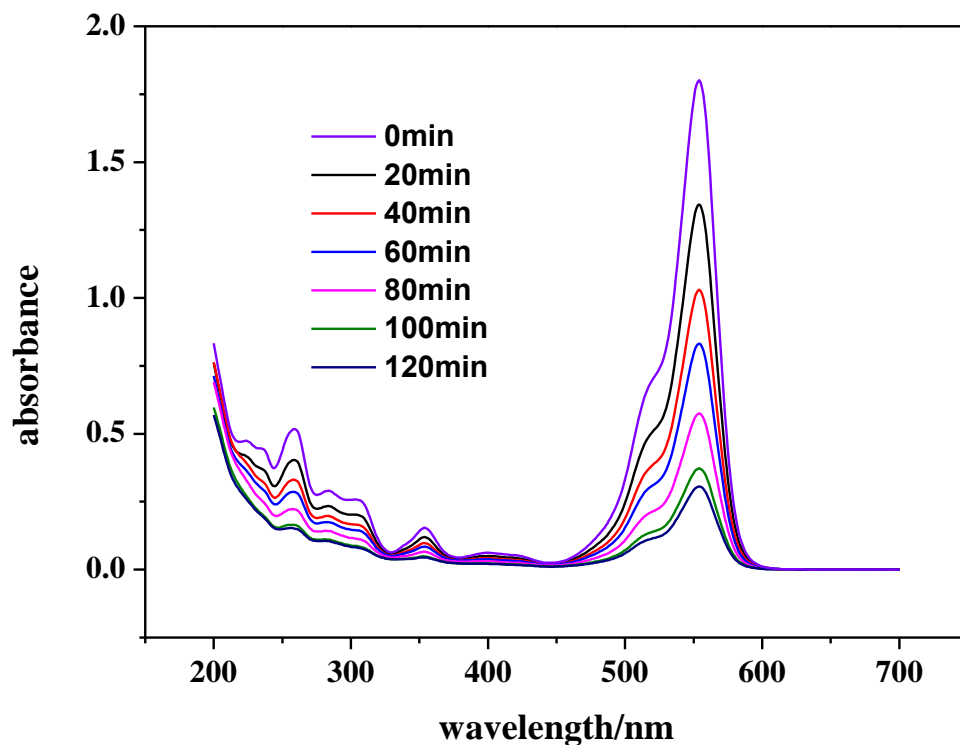
**Figure 5.** The RhB absorption spectra change with the reaction time.

In order to study the mechanism of electrochemical oxidation with PbO_2 electrode, we collected the data of UV-vis spectra of RhB at different reaction time, as showed in Fig. 5. It is clearly to see three peaks in the original UV-vis absorption curve of initial RhB solution, the absorption wavelength are 554 nm, 259 nm, and 354 nm respectively. Among those absorbance peaks, the peak at 554 nm could be explained the effect of the chromosphere structure of RhB, and benzene rings in the RhB molecular made contribution to the appearance of the other two peaks.

The degradation of RhB could be divided into two processes, N-demethylation and destruction of the conjugated structure[33]. If the conjugated structure of RhB is destroyed, the absorption at 554 nm would decrease. Besides, if N-demethylation happened during the reaction, the absorption peak would move to the blue region[34]. In this case, there is no distinct blue-shift of absorption, so we proposed that the destruction of the conjugated structure was the main attribution to the degradation of the RhB. Besides, the absorbance peaks at 354 nm and 259 nm decreased in the consequence of benzene ring cracking. Compared the variation tendency of three peaks, the absorbance at 554 nm was declined much faster than the others, indicating that the conjugated structure of RhB was easier and prior to be degraded.

3.3.2. Degradation pathway of RhB

Table 2. intermediate products identified by GC/MS

Code	Molecular formula	Name	Structure
M1	$C_8H_6O_4$	1,2-Benzenedicarboxylic acid	
M2	$C_8H_6O_4$	1,4-Benzenedicarboxylic acid	
M3	$C_7H_6O_2$	benzoic acid	
M4	$C_7H_6O_3$	Salicylic acid	
M5	$C_4H_6O_4$	Succinic Acid	
M6	$C_7H_6O_3$	2-hydroxyglutaric acid	
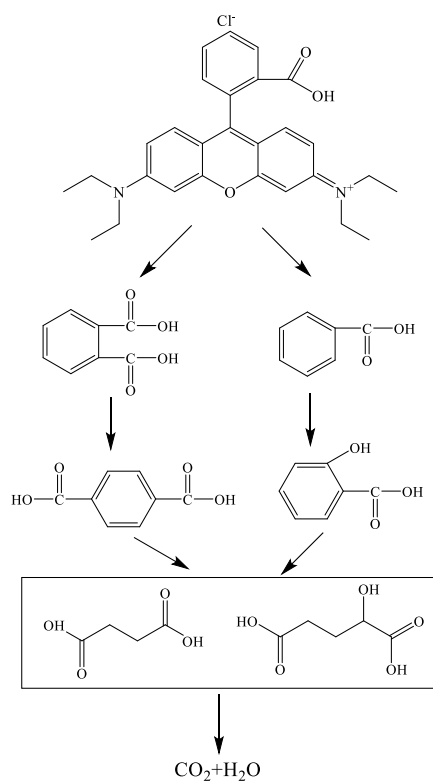
Figure 6. Possible degradation pathway of RhB in electrochemical oxidation

To explore the possible degradation pathway of RhB, we detected the macromolecular intermediate products by GC/MS and the results were shown in table 2. According to the intermediate products ,we speculated the possible degradation pathway ,as shown in Fig. 6. It had been reported that during the electrochemical oxidation process, hydroxyl radicals were generated at the surface of electrode at first[35], then RhB diffused to the electrode surface, hydroxyl radicals would attack the chromophore structure and decolorize the RhB[36]. In the process, it would generate someintermediate products as 1,2-Benzenedicarboxylic acid and benzoic acid. With the effect of hydroxyl radicals, 1,2-Benzenedicarboxylic acid and benzoic acid transfer to 1,4-Benzenedicarboxylic acid and Salicylic acid. Then benzene rings were opened and produced some acids as Succinic Acid and 2-hydroxyglutaric acid, finally, they were mineralized into CO_2 and H_2O.

4. CONCLUSIONS

The effect of operational parameters on the electrochemical degradation of RhB was studied. After 120 min electrolysis, removal of RhB and chemical oxygen demand reached 95.58% and 33.73% at the optimal condition of supporting electrolyte concentration 0.1 mol/L, initial RhB concentration 200 mg/L, applied current density 20 mA/cm^2 and pH value 4.4. Besides, the kinetic analysis proved that the degradation of RhB followed the pseudo-first-order kinetics. The UV-vis spectra implied that conjugated structure in the RhB molecule was easy to be destructed, and made the most contribution to the degradation of RhB. Based on the intermediate products identified by GC/MS, we speculated the possible degradation pathway of RhB during the electrochemical oxidation process.

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