Indirect Electrochemical Oxidation of Dye Wastewater Containing Acid Orange 7 Using Ti/RuO$_2$-Pt Electrode

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Indirect electrochemical oxidation has been an alternative method for the decontamination of dye wastewater. In this study, the Ti/RuO$_2$-Pt anode was used to remove the Acid Orange 7 (AO7) from the synthetic dye wastewater. The influence of operating parameters, including NaCl dosage, current density, initial concentration and pH, on the removal of AO7 was studied. The performance of Ti/RuO$_2$-Pt anode for decomposition of dye and long time service was also investigated. The results show that, in the presence of chloride ion, the electrogenerated active chlorine played an important role in dye wastewater treatment. The pH of the solution had a significant effect on the existing form of active chlorine, and the optimum pH range was from weakly acidic to neutral. The changes of UV-Vis spectral, HPLC chromatogram and TOC during electrolysis indicated that, the dyestuff of AO7 could be decomposed and mineralized efficiently by electrolyzing with Ti/RuO$_2$-Pt anode. All AO7 and 79.48% of TOC were removed within 4 hours in the presence of 0.001 M NaCl at a current density of 10 mA/cm^2 and pH 6.8. The Ti/RuO$_2$-Pt electrode had a relative long service life for dye wastewater treatment, and no obvious passivation was observed from the repeated test and surface characterization.

1. INTRODUCTION

A large variety of dyes are widely used in many fields of up-to-date technology involving textile industry, leather tanning industry, paper production, food processing, and agricultural research

[1]. Among them, the aromatic azo dyes comprise about two-thirds of the total [2]. Because of their undesirable color, high toxicity and recalcitrance, dye wastewater has received particular environmental concern. Many conventional treatment methods, such as physical-chemical adsorption with activated carbon, chemical oxidation with ozone or other oxidants and biological methods are adopted to remove the dyes from the effluent [3, 4]. However, they have not been completely accepted for their own shortcomings [5, 6, 4]. Hence, in recent years, electrochemistry has been paid more attention as a new alternative treatment process for dye wastewater.

Electrochemical oxidation (EO) can effectively oxidize organics in solutions by direct or indirect oxidation [7, 8]. The indirect oxidation, which mainly relies on the electrogenerated oxidizing species (EOS) from water discharge at electrodes [1], is more efficient and extensively utilized to decontamination. According to Comninellis [8], the indirect oxidation could be summarized as two approaches: electrochemical conversion and combustion. The mechanism of indirect electrochemical oxidation has been suggested that, water is electrolyzed by anodic catalysis to produce physical-adsorbed (physisorbed) hydroxyl radicals.

$$MO_x + H_2O \rightarrow MO_x[\cdot OH] + H^+ + e^- \qquad (1)$$
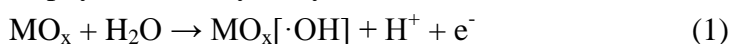
The physisorbed $\cdot OH$ may form chemisorbed active oxygen.

$$MO_x[\cdot OH] \rightarrow MO_xO + H^+ + e^- \qquad (2)$$
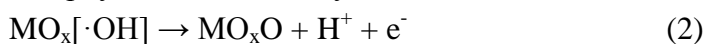
The hydroxyl radicals or the chemisorbed active oxygen will react with the organic matters (R).

$$\alpha MO_x[\cdot OH] + R \rightarrow \alpha MO_x + mCO_2 + nH_2O + xH^+ + ye^- \qquad (3)$$

$$MO_xO + R \rightarrow MO_x + RO \qquad (4)$$

Meanwhile, in the presence of chloride ion, another strong oxidant of hypochlorous acid may be produced on the anode during electrolysis and will react with organic matters [9, 10].

$$H_2O + Cl^- \rightarrow HClO + H^+ + 2e^- \qquad (5)$$

$$HClO + R \rightarrow product + Cl^- \qquad (6)$$
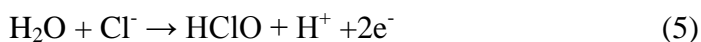
It is well known, hydroxyl radical is one of the strongest oxidant ($E^0 = 2.80$ V vs. SHE), however, has much shorter lifetime than HClO ($E^0 = 1.49$ V vs. SHE), and only acts while direct current is supplied to the anode [1]. Therefore, for decontamination of the dye wastewater which commonly contains amounts of inorganic salts, especially chloride, indirect oxidation by electrogenerated active chlorine is more cost-efficient and practical.

The oxidation behaviour of electrodes and the EOS produced in the EO process are influenced strongly by the nature of the anode material [11]. The so-called "non-active" anodes, such as boron doped diamond (BDD), PbO_2 and SnO_2, could form the physisorbed $\cdot OH$ more efficiently [2]. However, they are not useful for active chlorine production since they preferably generate $\cdot OH$ and other weaker oxidants species such as peroxodisulphate, peroxodicarbonate and peroxodiphosphate [12, 13]. Whereas, the "active" anodes such as dimensionally stable anodes (DSA) and Pt are found having much higher efficiency for oxidizing chloride ion than generating the physisorbed $\cdot OH$ [14, 15, 16]. Several researchers [17, 18] have demonstrated the effectiveness of Ti-based DSA electrodes for degradation of organic pollutants. Hence, the actual application of DSA electrodes is still limited for the short service life of the anode coating. In recent years, the doping of noble metals in the coating has been adopted to prolong the service life of anode, and an obvious effect was obtained. Through the comparison, Li et al. [19, 20] found the Ti/RuO$_2$ electrode doped with Pt (Ti/RuO$_2$-Pt) was an

relatively efficient and durable anode for indirect oxidation of the phenol wastewater, which has the very weak ability for direct oxidation and a high oxygen evolution potential (1.58 V vs. SHE).

In this study, based on the component characteristic of the dye wastewater, a typical active anode, Ti/RuO$_2$-Pt electrode, was selected for indirect electrochemical decontamination of the dye wastewater. The monoazo dye of Acid Orange 7 (AO7) was chosen as the model pollutant, because it is very useful as test and widely used in paperboard industries and wool textile dyeing [2]. The effects of the operating conditions (namely the dosage of chloride, current density, initial concentration and initial pH) on the AO7 removal were investigated. The ability for decomposition and mineralization of AO7 during electrolysis was examined systematically, and the passivation of the anode was also tested. The experimental results were expected to provide the reference information to apply Ti/RuO$_2$-Pt anode to treat the dye wastewater.

2. EXPERIMENTAL

2.1 Materials

All chemicals used in this study were analytical grade and used as received. All aqueous solutions were prepared with Milli-Q water (resistivity 18.2 MΩ·cm at 25 °C). Acid Orange 7 (C$_{16}$H$_{11}$N$_2$SO$_4$Na, CAS NO. 633-96-5, Fig. 1) was obtained from the Sinopharm Chemical Reagent Beijing Co. Ltd (China), and its purity is greater than 99%. A stock solution of 1000 mg AO7/L was prepared, being all the other solutions obtained by an appropriate dilution.
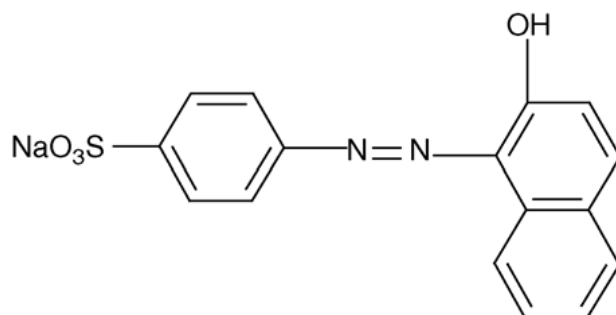
Figure 1. Molecular structure of Acid Orange 7

2.2 Experimental apparatus and methods

All experiments were carried out in an undivided electrochemical cell (15 cm × 6 cm × 15 cm) prepared with acryl plates. A Ti/RuO$_2$-Pt plate (TohoTech Company, Japan) was used as the anode, and a 304 stainless steel plate as the cathode. Both the area of anode and cathode were 67.5 cm^2 (15 cm × 4.5 cm). The distance between two electrodes was set at 10 mm. A DC potentiostat (JiZhan, China) was employed as the power supply for electrochemical degradation.

In each experiment, 1000-mL AO7 solution with different initial concentrations was prepared for electrolysis in galvanostatic mode. In order to maintain the necessary conductivity, 0.005 M sodium sulfate (Na_2SO_4) was added into the synthetic dye wastewater in all experiments. The influence of the operating parameters, including current density (*I*), sodium chloride (NaCl) dosage, initial pH and initial concentration, was investigated by varying one parameter and keeping the others constant. During each experiment, samples were taken from the electrochemical cell at a regular interval for analysis. Before analysis, all samples were filtered through a 0.2-μm syringe filter.

2.3 Analysis

The UV-Vis spectra of the samples were recorded from 200 to 600 nm using a DR5000 UV-Vis spectrophotometer (Hach, USA). The concentration of AO7 was determined with the absorbance at 484 nm, where the maximum absorbance in the scanning range is, according to Lambert-Beer law. A high performance liquid chromatograph (HPLC, Agilent 1100, USA) was used to monitor the changes of AO7 and its degradation intermediates. The HPLC system was equipped with an Ultimate XB-C18 column (ID=4.6 mm, length=150 mm, Welch Materials, USA) and a UV detector operating at 254 nm. The measurements were performed with a mobile phase of acetonitrile/water (0.025 M of ammonium acetate) = 35/65 (v/v) at a flow rate of 1.0 mL/min [21].

The total organic carbon (TOC) was measured by an Apollo 9000 TOC analyzer (Tekmar-Dohrmann, USA). The total chlorine concentrations of the samples were analyzed by a 7500 photometer (Palintest, UK) and Palintest AP268 tablet (limit of detection 0.01 mg/L). When total chlorine was to measure, enough sodium sulfite (Na_2SO_3) was firstly added into the samples and thereby all forms of chlorine were transferred into chloride ion. Surface morphology of the anode was characterized ex situ by a JSM6390 scanning electron microscope (JEOL, Japan).

3. RESULTS AND DISCUSSION

*3.1 Performance of Ti/RuO$_2$-Pt for AO7 removal with different electrolyte*

The performance of Ti/RuO$_2$-Pt anode for AO7 removal in the absence and presence of chloride are shown in Fig. 2a. It could be seen from that, in the absence of NaCl, the electrochemical removal of AO7 was very slow. Almost no promotion of AO7 degradation efficiency was observed with the increasing of Na_2SO_4 dosage from 0.005 M to 0.05 M. This agrees with previous studies, who found that the direct oxidation ability of Ti/RuO$_2$-Pt anode for some organic matters was relative low [20] and the hydroxyl radical productivity of the active anodes, e.g. RuO$_2$ and Pt, was poor [22, 8].

When NaCl was present in the synthetic solution, the performance of Ti/RuO$_2$-Pt anode for AO7 removal was improved significantly and the removal efficiency increased with the increasing of the NaCl dosage. In the presence of 0.001, 0.005 and 0.01 M NaCl, the required time for complete degradation of 50 mg/L AO7 was about 60, 30 and 25 min, respectively. The promotion of AO7 degradation with the addition of NaCl indicates that chloride played an important role in the indirect

electrochemical oxidation of dye wastewater using Ti/RuO$_2$-Pt anode. The dye could be degraded efficiently by the strong oxidant of hypochlorous acid formed during electrolysis. The possible process for the formation of HOCl, which had already been proposed by previous researchers [23, 9], is listed below:

$$2\,Cl^- \rightarrow Cl_2 + 2e^- \qquad\qquad (7)$$
$$Cl_2 + H_2O \rightarrow HClO + HCl \qquad\qquad (8)$$
$$HClO \leftrightarrows H^+ + ClO^- \qquad\qquad (9)$$

In this work, the electrochemical oxidation of AO7 followed the pseudo first-order reaction kinetics, and the process could be expressed with $-\ln(c_t/c_0) = k(t)$. The apparent reaction rate constants (k) and the correlation coefficients (R^2) of main reactions in present work are shown in Table 1.
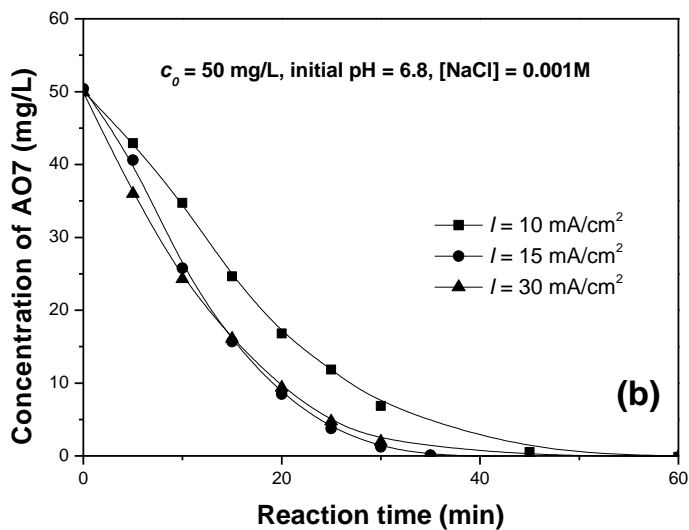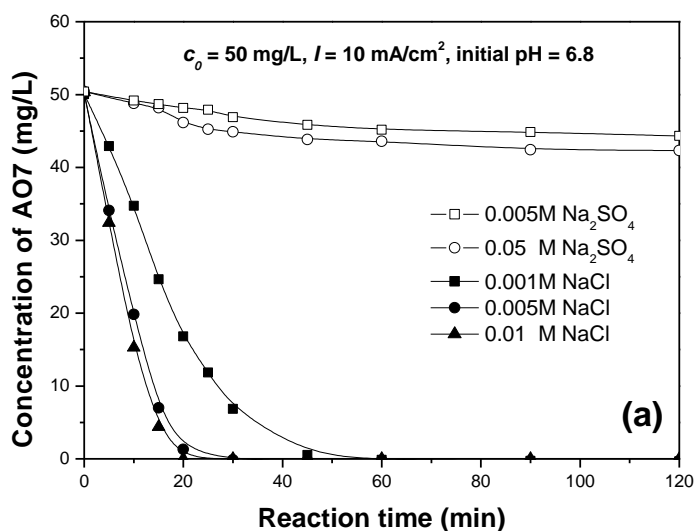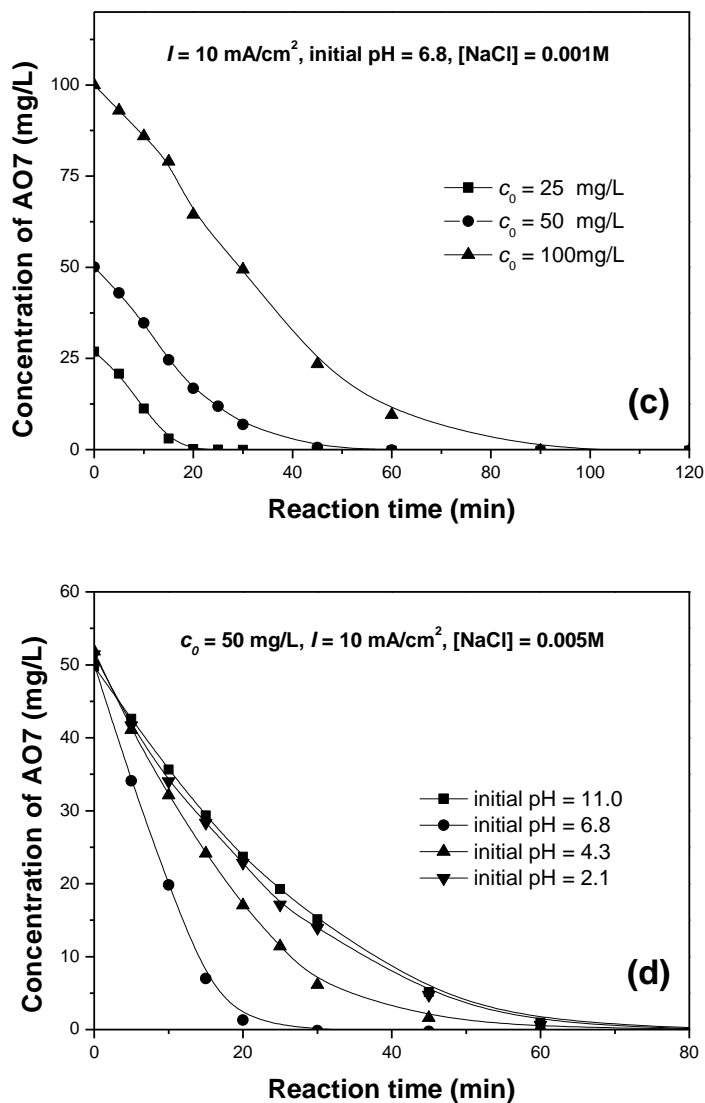
Figure 2. Effects of electrolyte (a), current density (b), initial concentration (c) and initial pH (d) on the removal of AO7.

Table 1. Apparent rate constants for electrochemical removal of AO7 under various conditions

Entry	c_0 mg/L	Supporting electrolyte	I mA/cm^2	Initial pH	k min^{-1}	R^2
1	50	0.005M Na$_2$SO$_4$	10	6.8	1.30×10^{-3}	0.9103
2	50	0.05M Na$_2$SO$_4$	10	6.8	1.99×10^{-3}	0.8978
3	50	0.001M NaCl	10	6.8	7.84×10^{-2}	0.9152
4	50	0.005M NaCl	10	6.8	1.52×10^{-1}	0.9337
5	50	0.01M NaCl	10	6.8	2.14×10^{-1}	0.9310
6	50	0.001M NaCl	15	6.8	1.28×10^{-1}	0.9165
7	50	0.001M NaCl	30	6.8	9.45×10^{-2}	0.9794
8	25	0.001M NaCl	10	6.8	2.03×10^{-1}	0.8948
9	100	0.001M NaCl	10	6.8	3.32×10^{-2}	0.9489
10	50	0.005M NaCl	10	2.1	5.92×10^{-2}	0.9453
11	50	0.005M NaCl	10	4.3	7.73×10^{-2}	0.9766
12	50	0.005M NaCl	10	11.0	5.40×10^{-2}	0.9466

3.2 Effects of current density and initial concentration

The electrochemical removal of AO7 was conducted at different current densities of 10, 15 and 30 mA/cm^2, and the results are presented in Fig. 2b. It is clear that the removal efficiency increased significantly with the increasing of the applied current density from 10 to 15 mA/cm^2. Since higher production of active chlorine could be achieved under higher current density [24], more AO7 was degraded during the same electrolysis time. However, when the current density continued increasing to 30 mA/cm^2, the degradation rate of AO7 did not increase as expected. The removal amount of AO7 was more than that achieved at 15 mA/cm^2 within the first 15 min of electrolysis, and then gradually less than that. Moreover, after 120 min electrolysis, the loss of total chlorine in the solution at 30 mA/cm^2 was 19.8% (from 35.5 to 28.47 mg/L), which was much higher than that at 15 mA/cm^2 (3.17%). It is implied that, because of the limitation for hydrolysis of Cl$_2$ (equation 8), more chlorine was escaped from aqueous solution as the form of Cl$_2$ under higher current density. The probable lower production of HClO, which caused by more loss of total chlorine in the chlorine circulation, should be the reason why the removal rate decreased slightly with the increasing of current density from 15 to 30 mA/cm^2. It is suggested that the selection of proper current density is important to electrochemical removal of AO7 with low chloride concentration.

To investigate the performance of Ti/RuO$_2$-Pt anode for electrochemical removal with different initial concentrations, the electrolysis of 25, 50 and 100 mg/L AO7 were carried out at a selecting current density and NaCl dosage. It could be seen from Fig. 2c, the complete removal could be achieved at both low and high initial concentrations. Through calculation, with the relative low chloride concentration of 0.001 M, the electricity power consumption for AO7 removal was about 71, 81, 89 kwh/kg AO7. Therefore, the Ti/RuO$_2$-Pt anode could perform well for electrochemical removal of AO7 with appropriate current density and NaCl dosage.

3.3 Effect of initial pH

Fig. 2d shows that the influence of initial pH on electrochemical removal of AO7 was significant. The order of reaction rates was pH6.8 > pH4.3 > pH2.1 > pH11.0 (data are shown in Tab. 1). The optimum pH range for AO7 removal with Ti/RuO$_2$-Pt anode is from neutral to weakly acidic, which is probably due to the effects of pH on the existing form of active chlorine in the solution.

Hypochlorous acid or hypochlorite was the major oxidant produced in the presence of chloride. There is an ionization equilibrium existing between them (equation 9), and the dissociation constant (pK$_a$) is 7.54 at 25 °C [25]. When pH was higher than the pK$_a$, hypochlorite (E^0 = 0.89 V vs. SHE), whose oxidative ability was weaker than that of hypochlorous acid [26], accounted for higher proportion in all the active substance. Hence, the indirect oxidative ability in alkaline range was lower than others. Additionally, the AO7 appeared negative electrical property in alkaline solutions [27]. They could compete with the chloride ions for the adsorption sites on the anode surface and thereby affected the production of active chlorine to some extent [28]. In present work, the reaction rates decreased gradually with the decreasing of pH from neutral to highly acidic range, though the proportion of HClO should increase theoretically in that changing trend of pH. The stronger inhibition

for the hydrolysis of Cl_2 (equation 2) in highly acidic environment should be the main reason for this decrease on reaction rate.

3.4 Decomposition and mineralization of AO7
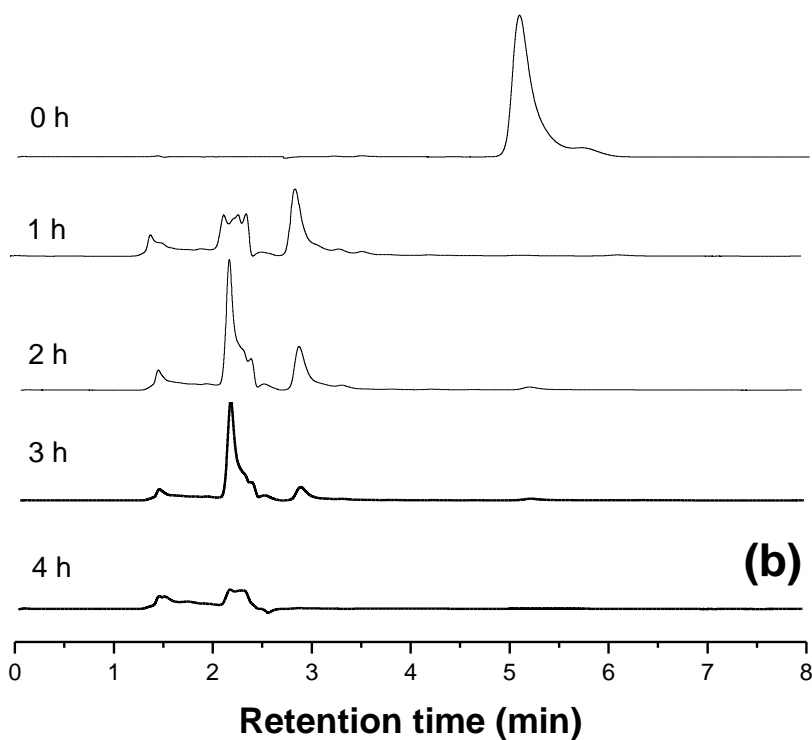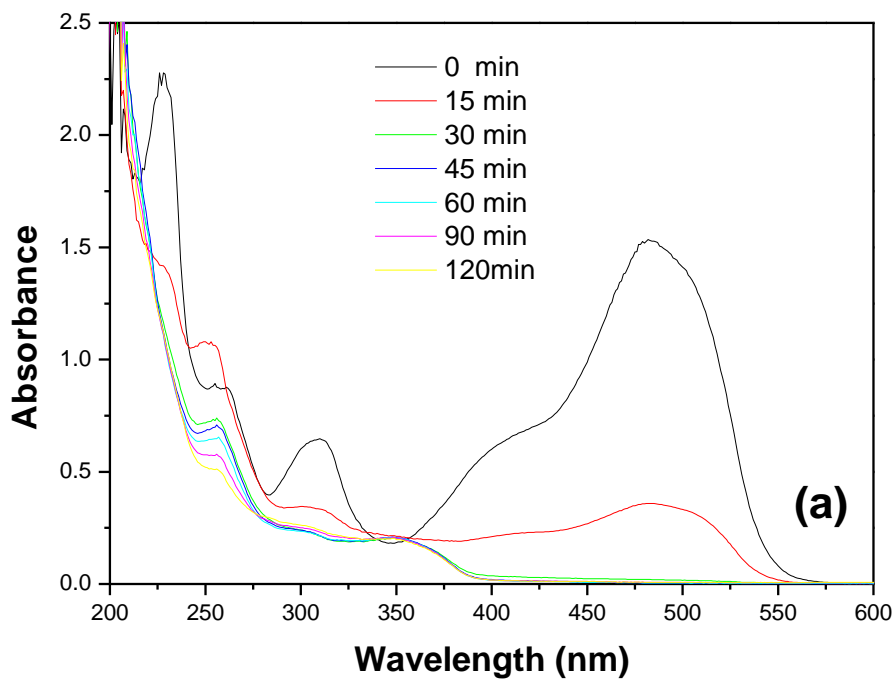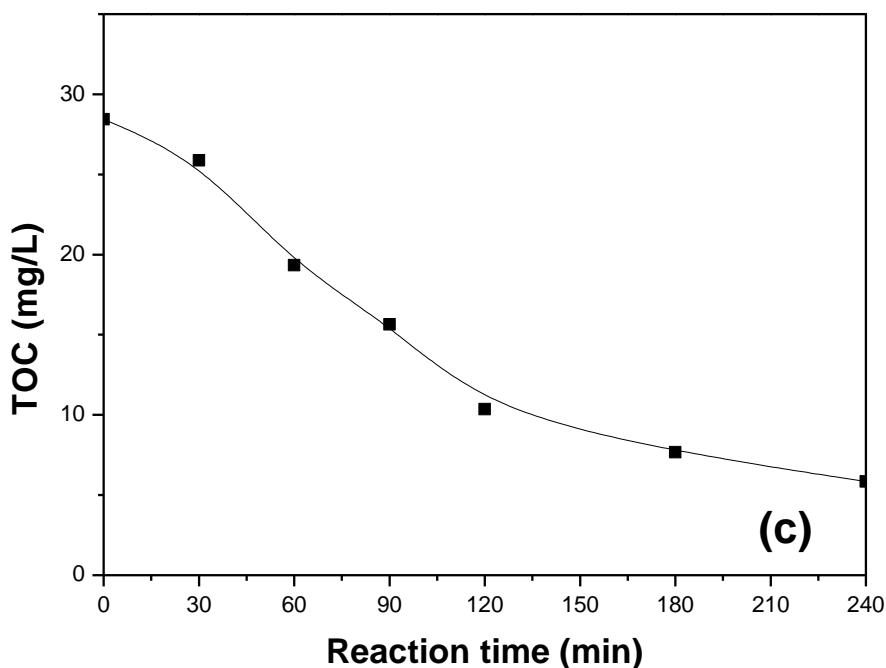
Figure 3. UV-Vis spectral (a), HPLC chromatogram (b) and TOC (c) changes as a function of reaction time during the electrochemical removal of AO7 with Ti/RuO$_2$-Pt anode. (c_0 = 50 mg/L, I = 10 mA/cm^2, initial pH = 6.8, [NaCl] = 0.001 M)

To the performance evaluation of a treatment process for dye wastewater, the degree of decomposition and mineralization is as important as the complete removal of parent compound. The UV-Vis spectral changes of AO7 solution during electrolysis are shown in Fig. 3a. AO7 has four characteristic absorption bands in the visible and ultraviolet region, which are a major absorption band at 484 nm, a shoulder absorption band at 430 nm and the ultraviolet absorption bands at 310 and 230 nm. They are due to the hydrazone, azo, naphthalene ring, benzene ring forms of AO7, respectively [21]. It is clear that, all four absorption bands diminished rapidly with the increasing of electrolysis time. This is implied that the active chlorine produced by Ti/RuO$_2$-Pt anode could destroy the chromophore group unselectively. In addition, in the early stage of electrolysis, a new absorption band appeared at 260 nm and reached maximum in the first 15 min. Subsequently, the new peak declined together with the other four. As found previously [29], the appearance of new absorption band should be due to the quinone intermediates produced by dye electrolyzed. The changes in solution color during electrolysis was observed with naked eyes that, the orange color of the solution faded rapidly, and kept the light yellow for long time, and then turned to colorless with continuous electrolysis. Through the comparison of the changes in color and the results of UV-Vis spectral, it could be inferred that the light yellow color just might be caused by the quinone intermediates.

In order to investigate the decomposition process using Ti/RuO$_2$-Pt anode deeply, the intermediates were monitored with HPLC system, and the evolution of HPLC chromatogram is shown in Fig. 3b. The peak at the retention time of 5.07 min responding to the parent compound AO7

diminished sharply and disappeared on the HPLC curve after 1 h electrolysis, which coincides with the result obtained by spectrophotometry. With the degradation of parent compound, several intermediates were detected on the HPLC curves. The intermediate with the retention time of 2.87 min appeared in the beginning of electrolysis; reached the peak value within 1 h and then diminished with the extending of reaction time; at last, it was complete removal after 4 h electrolysis. A group of intermediates at the retention time around 2.2 min was detected synchronously with the intermediate at 2.87 min. With the decreasing of the latter, the major peak at 2.17 in this group increased gradually within the first 2 h, and then decreased along with others. Additionally, another intermediate was monitored at the retention time of 1.45 min, which decreased slowly and even could be detected after 4 h electrolysis. It is likely that, this intermediate was transformed from other intermediates, and nearly was on the balance of formation and degradation during 4 h electrolysis. Overall, all kinds of the intermediates detected by HPLC could be removed efficiently with the Ti/RuO$_2$-Pt anode.

Fig 3c also shows that AO7 could be mineralized efficiently by the indirect oxidation with Ti/RuO$_2$-Pt anode, 79.48% of TOC (from 28.51 to 5.85 mg/L) was removed from the synthetic solution after 4 h electrolysis. Combining the results of UV-Vis spectral, HPCL and TOC analysis, the electrochemical degradation process of AO7 in the presence of chloride is clear. The AO7 was decomposed into several intermediates because of the cleavage of the molecular structure, and then further oxidized until to yield CO$_2$ and oxyanions such as nitrate and sulfate [21].

3.5 Passivation of electrode in long-term work
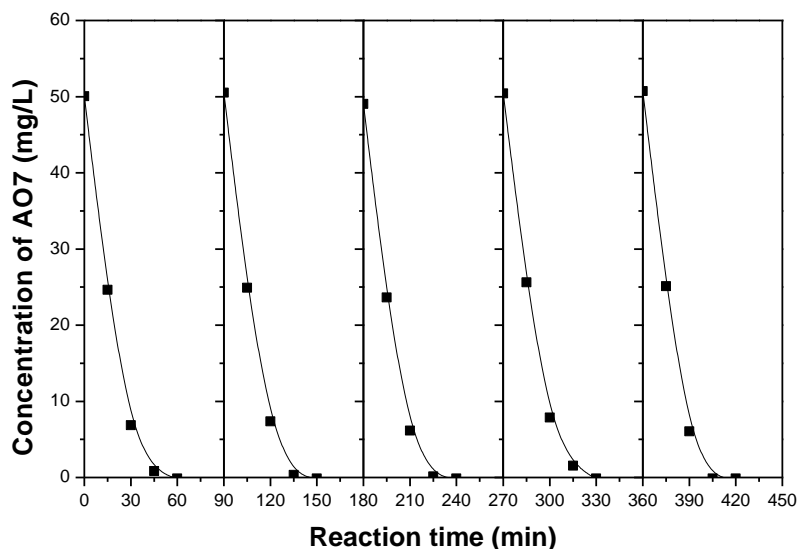
Figure 4. Performance of Ti/RuO$_2$-Pt anode for repeated removal of AO7 without washing ($c_0 = 50$ mg/L, $I = 10$ mA/cm^2, initial pH = 6.8, [NaCl] = 0.001 M)

In order to investigate the ability of Ti/RuO$_2$-Pt anode for long time work, the 90-min electrolysis of 50 mg/L AO7 was repeated five times without surface washing. It could be seen from

Fig. 4 that, the reproducibility of the experiments was very good, and the oxidation ability of Ti/RuO$_2$-Pt anode almost did not decrease after the continuous service of 450 min. After finishing all the experiments in this study (more than 100 h service in total), the surface morphology of the Ti/RuO$_2$-Pt anode was observed with SEM, and compared with that before used. From Fig. 5, no formation of polymeric film was observed on the surface of anode, which is mainly due to its poor direct oxidation ability [20]. Moreover, because of the doping of Pt [18], the coat of the anode showed good durability, which almost did not fall off after more than 100 h electrolysis. This demonstrates that Ti/RuO$_2$-Pt anode is suitable for the treatment of dye wastewater in long-term work.
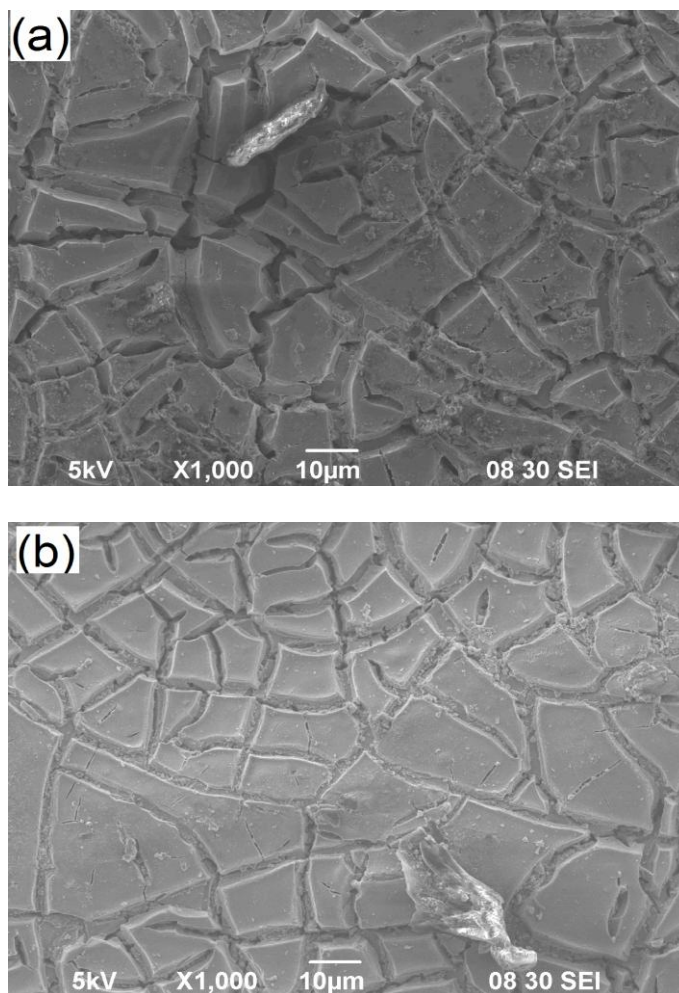
Figure 5. Surface morphology of Ti/RuO$_2$-Pt anode before (a) and after (b) use

4. CONCLUSIONS

In this work, the Ti/RuO$_2$-Pt electrode was employed successfully for indirect electrochemical decontamination of the wastewater containing AO7. The results suggest that, in the presence of chloride ion, the treatment of dye wastewater using the active anode which has poor hydroxyl radical productivity is feasible. The electrogenerated active chlorine could destroy the chromophore groups of

dye rapidly and oxidize the intermediates to CO_2 and other inorganic products efficiently. Through the repeated test and surface characterization, it is shown that the Ti/RuO_2-Pt electrode has broad prospect in actual application.

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