

# Copper-spent activated carbon as a heterogeneous peroxydisulfate catalyst for the degradation of Acid Orange 7 in an electrochemical reactor

Jing Li, Heng Lin, Lin Yang and Hui Zhang

## ABSTRACT

The exhausted activated carbon generated from the adsorption of heavy metal wastewater needs further treatment/disposal. In this study, a new application of copper-spent activated carbon (Cu-AC) was proposed. Cu-AC was used to activate peroxydisulfate (PDS) for the decolorization of Acid Orange 7 (AO7) and electrical current was introduced to enhance the process. The decolorization followed a pseudo-first-order kinetic pattern well ( $R^2 > 0.95$ ). 92.4% of color removal at 60 min and 38.3% of total organic carbon removal at 180 min were achieved when initial pH value was 9.0, current density was 16 mA/cm<sup>2</sup>, PDS concentration was 5 mM and Cu-AC dosage was 0.25 g/L. The radical scavengers including methanol, *tert*-butanol and phenol, as well as electron paramagnetic resonance test, were employed to investigate the oxidizing species responsible for AO7 decolorization. The stability of Cu-AC was confirmed by three recycle experiments.

**Key words** | Acid Orange 7, copper, electrochemical, peroxydisulfate, spent activated carbon

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## INTRODUCTION

The dye wastewater is considered as bio-refractory and can hardly be degraded by conventional wastewater treatment processes (Yang *et al.* 2011). The activated persulfate process has been proved to degrade azo dyes effectively using highly reactive species such as sulfate radicals (Zhou *et al.* 2015). Among various activation methods, homogeneous activated persulfate using transition metals has attracted great attention (Lei *et al.* 2015b). However, the transition metal activated process is only effective under acid conditions and high metal sludge is generated during the neutralization stage before the effluent is discharged (Wu *et al.* 2012). To overcome these drawbacks, heterogeneous metal catalysts were synthesized to activate persulfate under a wide pH range (Cai *et al.* 2015b). Activated carbon (AC) is considered as a good catalyst support and AC supported metal catalysts have been used to activate persulfate (Cai *et al.* 2014a, 2015a).

As a good adsorbent, AC has also been widely applied to the adsorptive removal of heavy metal from wastewater (Demirbas *et al.* 2009). Nevertheless, heavy metal exhausted AC will cause secondary pollution and needs further treatment/disposal. In this study, a new application of copper-spent activated carbon (Cu-AC) was proposed in which Cu-AC was employed as a catalyst to activate persulfate

and electrical current was introduced to enhance the heterogeneous activation process (Cai *et al.* 2014b; Lin *et al.* 2014b). The activity and stability of Cu-AC was evaluated, the reactive radicals generated in this process were identified, and the effect of important parameters on color removal was investigated.

## METHODS AND MATERIALS

Acid Orange 7 (AO7, C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>NaO<sub>4</sub>S) with reagent purity grade was obtained from Sinopharm Chemical Reagent Co., Ltd (China). AC was purchased from Aladdin Industrial Corporation (Shanghai, China). Before utilization, AC was washed with abundant deionized water to wash off the impurity on the surface and subsequently dried at 120 °C for 24 h before being sealed in hermetic bags.

Copper adsorption experiments were conducted in a series of 500 mL beakers. At the designated time, 5 mL solutions were taken to determine the residual copper concentration. After 24 h adsorption, the saturated AC (Cu-AC) was filtered and dried at 120 °C for 24 h.

The experimental set up of decolorization was similar to our previous study (Lin et al. 2013b). In each run, a fresh stock solution of AO7 was prepared in deionized water with the initial concentration ( $C_0$ ) of 100 mg/L. The initial pH ( $\text{pH}_0$ ) was adjusted by 1 mol/L sulfuric acid or 1 mol/L sodium hydroxide after peroxydisulfate (PDS) and supporting electrolyte  $\text{Na}_2\text{SO}_4$  (50 mM) were applied. The decolorization of AO7 was conducted in a 250 mL glass beaker at constant current using a plate anode (Ti/RuO<sub>2</sub>-IrO<sub>2</sub>) and a plate cathode (stainless steel). Both anode and cathode have the same dimensions (5.0 × 11.9 cm) and the electrode gap is 4.0 cm. A magnetic stirrer with a water bath was used to mix the solution and to keep the temperature at 25 °C. The reaction was initiated when the direct current power was turned on and the Cu-AC was added. At pre-selected time intervals, 2 mL aliquot was withdrawn and filtered through 0.45 μm membranes before analysis.

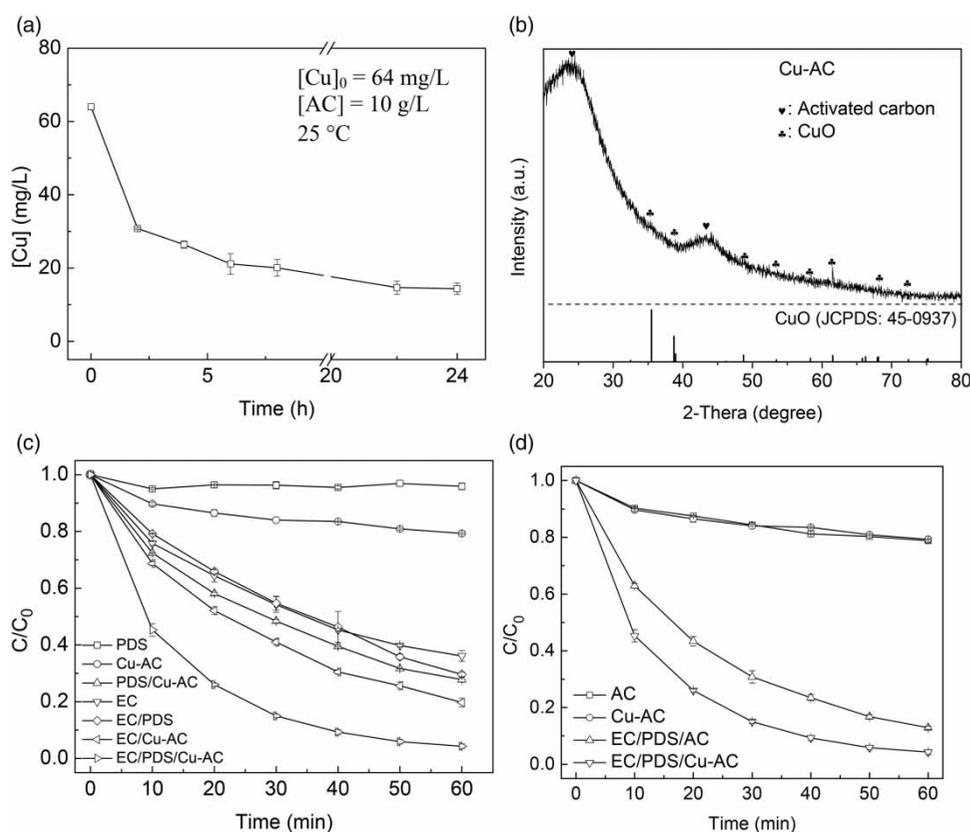
The absorbency of AO7 was monitored at  $\lambda = 485$  nm using a Rayleigh UV-9100 spectrophotometer (China). The concentration of residual PDS was measured by iodometric titration with thiosulfate. The concentration of copper ion was determined by atomic absorption spectrometer. Total

organic carbon (TOC) was measured by a Jena multi N/C 3100 TOC analyzer. The reactive radicals were examined with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent by electron paramagnetic resonance (EPR) using a JEOL FA 200 spectrometer.

## RESULTS AND DISCUSSION

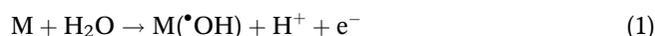
### AO7 decolorization under different systems

Figure 1(a) illustrates the adsorption of copper by AC. As can be seen, 77.6% of copper was removed after 24 h adsorption, indicating the amount of copper adsorbed was 4.97 mg g<sup>-1</sup>. The X-ray diffraction (XRD) pattern of spent AC was detected on a X'Pert Pro X-ray powder diffractometer (PANalytical, The Netherlands). It can be seen from Figure 1(b) that AC peaks were detected appearing at  $2\theta = 23.8^\circ$  and  $43.2^\circ$  (Yu et al. 2012) and the peaks at  $2\theta = 35.5, 38.9$  and  $61.5$  indicating the formation of CuO (Lei et al. 2015a). The produced copper-saturated AC (Cu-AC) would be used as catalyst in the subsequent experiments.

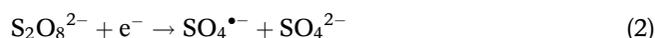


**Figure 1** | (a) Adsorption of copper by AC, (b) XRD pattern of Cu-AC, (c) decolorization of AO7 under different systems, (d) comparative performance between AC and Cu-AC. Conditions (c), (d): [PDS] = 10 mM, [Cu-AC] = 0.5 g/L, [AC] = 0.5 g/L, current density  $j = 16$  mA/cm<sup>2</sup>,  $\text{pH}_0$  5.0.

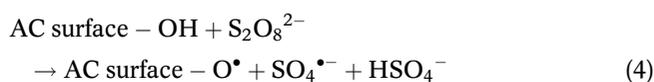
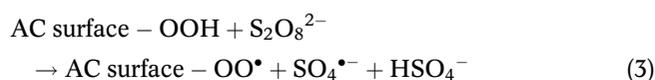
The result of AO7 decolorization under different systems is illustrated in Figure 1(c). It can be seen that PDS alone had little effect on color removal because PDS exhibits a low oxidation potential ( $E^0 = 2.01$  V) for the degradation of AO7 without activation. Although AC was saturated with copper ion, it can still adsorb 20.7% of AO7. The decolorization was increased to 63.9% when anode oxidation was employed and hydroxyl radicals ( $M^{\bullet}OH$ ) were generated at the dimensionally stable anode (DSA) (M:  $RuO_2-IrO_2$ ) (Lin *et al.* 2013b):



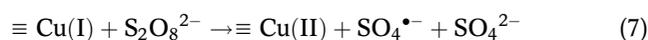
Moreover, the combination between electrochemical oxidation (EC), PDS and Cu-AC would improve color removal to some extent. After 60 min reaction, the decolorization efficiencies achieved in EC/PDS, PDS/Cu-AC and EC/Cu-AC systems were 70.4%, 72.2% and 80.3%, respectively. In EC/PDS process, sulfate radicals would be produced via the following reaction (Lin *et al.* 2014b):



When Cu-AC instead of PDS was applied to the electrolytic reactor (EC/Cu-AC), it would perform as particle electrodes (Xiong *et al.* 2001) and, thereby, have increased mass transfer coefficient (Lin *et al.* 2013a). The coupling of PDS with Cu-AC in the absence of current (PDS/Cu-AC) would lead to the generation of sulfate radicals via the activation of PDS by AC as well as copper (Liang *et al.* 2009, 2013):



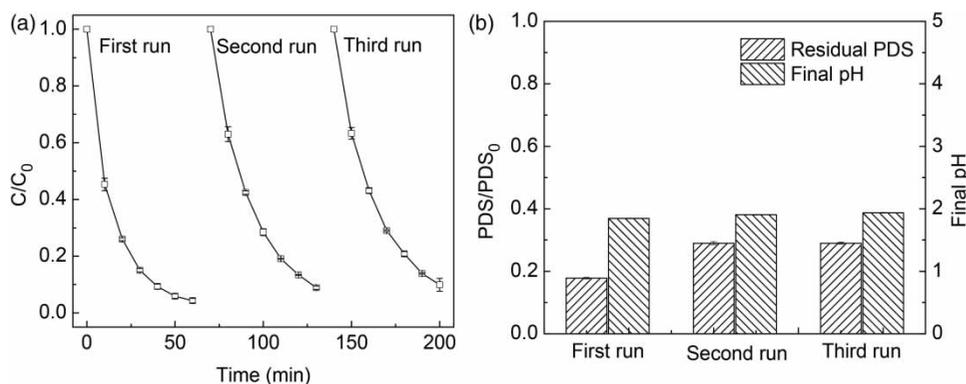
Nevertheless, reaction (5) occurs at a lower reaction rate since a higher energy barrier needs to be overcome (Liu *et al.* 2012). The introduction of current into the PDS/Cu-AC system would result in the reduction of  $\equiv Cu(II)$  into  $\equiv Cu(I)$ , which can efficiently activate PDS to generate sulfate radicals (Ding *et al.* 2013):



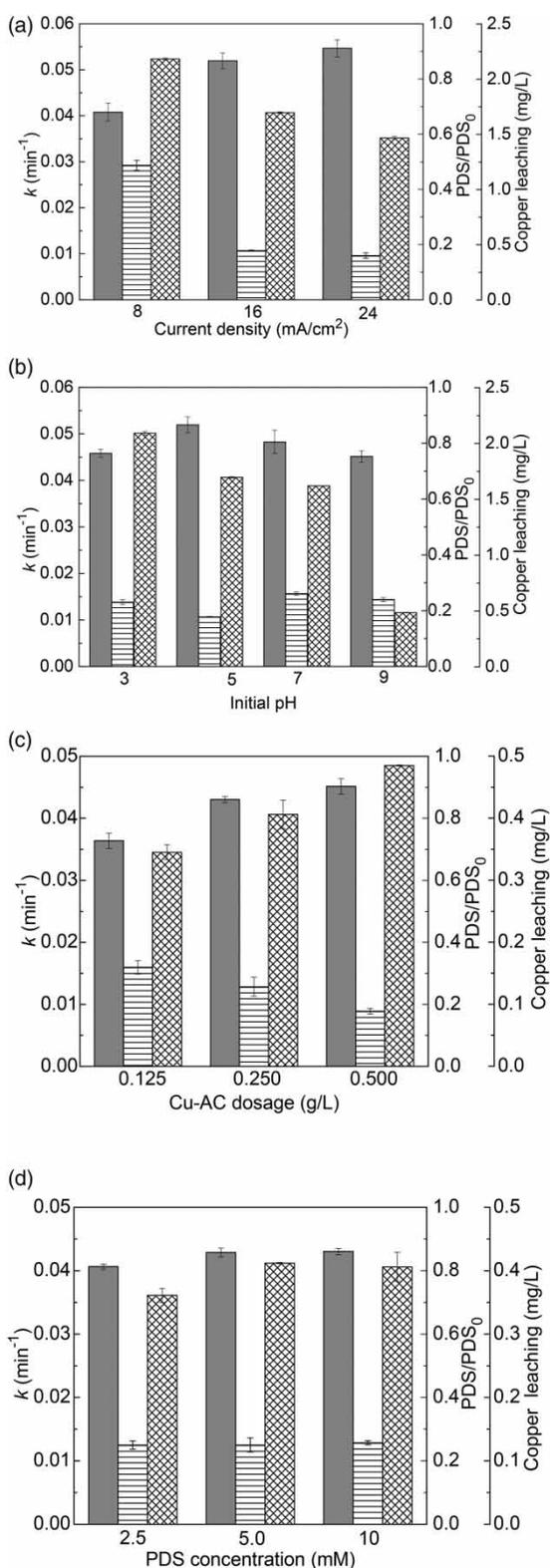
Therefore, the highest color removal (95.7%) was achieved in the EC/PDS/Cu-AC system.

The results of kinetic analysis indicated that the decolorization of AO7 followed a pseudo-first-order model with correlation coefficients  $R^2 > 0.95$ . Moreover, the rate constant achieved in the EC/PDS/Cu-AC system ( $0.052 \text{ min}^{-1}$ ) was higher than the sum of rate constants when AO7 was individually removed in the EC ( $0.017 \text{ min}^{-1}$ ) and PDS/Cu-AC systems ( $0.021 \text{ min}^{-1}$ ). It indicated that there existed a synergistic effect in terms of decolorization rate between electrochemical and the heterogeneous activation of PDS by Cu-AC (Zhang *et al.* 2013; Wang *et al.* 2014; Lin *et al.* 2014a).

In order to verify the contribution of copper activation, a comparative experiment was performed using fresh AC and spent AC (Cu-AC) as catalyst in the EC/heterogeneous activation process. As shown in Figure 1(d), the decolorization



**Figure 2** | (a) Recycling study of the decolorization of AO7, (b) remaining percentage of PDS and final pH at the end of each run. Conditions: [PDS] = 10 mM, [Cu-AC] = 0.5 g/L,  $j = 16 \text{ mA/cm}^2$ ,  $pH_0 = 5.0$ .

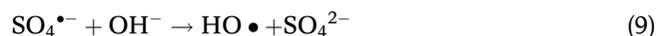
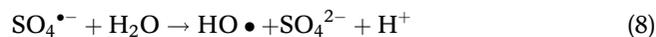


**Figure 3** | The effect of (a) current density ([PDS] = 10 mM, [Cu-AC] = 0.5 g/L, pH<sub>0</sub> 5.0), (b) initial pH ([PDS] = 10 mM, [Cu-AC] = 0.5 g/L,  $j$  = 16 mA/cm<sup>2</sup>), (c) Cu-AC dosage ([PDS] = 10 mM,  $j$  = 16 mA/cm<sup>2</sup>, pH<sub>0</sub> 9.0) and (d) PDS concentration ([Cu-AC] = 0.25 g/L,  $j$  = 16 mA/cm<sup>2</sup>, pH<sub>0</sub> 9.0) (■)  $k$ , (▨) PDS/PDS<sub>0</sub>, (▩) Copper leaching.

rate in the EC/PDS/Cu-AC system was higher than that in the EC/PDS/AC system, and the corresponding rate constant was 0.052 versus 0.034 min<sup>-1</sup>. As a result, the EC/PDS/Cu-AC process could achieve higher decolorization efficiency (95.7%) than the EC/PDS/AC process (87.1%). Considering Cu-AC exhibited nearly the same adsorption capacity as AC, it can be concluded that the spent AC was superior to the fresh one to activate PDS.

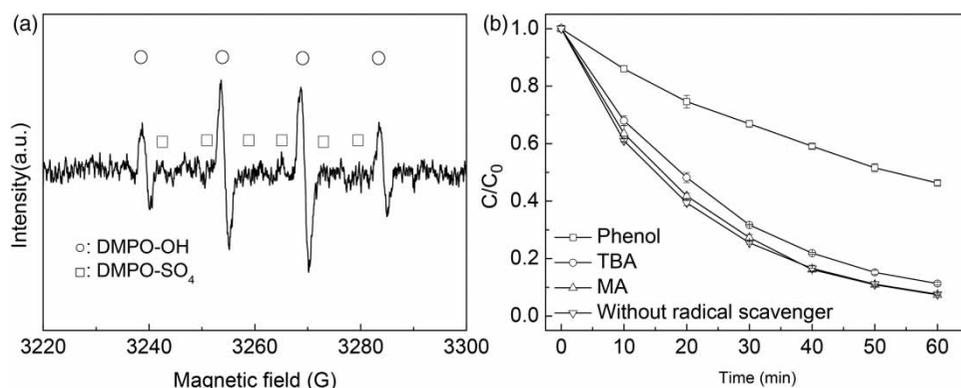
### Reusability of Cu-AC catalyst

Figure 2(a) illustrates the decolorization efficiency varied insignificantly in the first two cycles, i.e. 95.7% in the first cycle versus 91.1% in the second cycle. Afterwards, the decolorization efficiency changed little in the third cycle (90.1%). This can be indirectly verified by nearly the same decomposition ratio of PDS in the last two cycles, as shown in Figure 2(b). After each cycle, pH dropped from 5.0 to below 2.0. It is due to the production of carboxyl acids (Zhong *et al.* 2011). In addition, SO<sub>4</sub><sup>•-</sup> could react with H<sub>2</sub>O to produce H<sup>+</sup> (Equation (8)) and consume OH<sup>-</sup> (Equation (9)) resulting in the reduction of solution pH (Lin *et al.* 2014b):



### Effect of operating conditions

Figure 3(a) illustrates that the rate constant increased from 0.041 to 0.052 min<sup>-1</sup> as the current density rose from 8 to 16 mA/cm<sup>2</sup>. With the increase of current density, the generation of HO• and SO<sub>4</sub><sup>•-</sup> via Equations (1) and (2), respectively, was promoted (Lin *et al.* 2013b). Moreover, the increasing current density favored the cathodic reduction of ≡Cu(II) via Equation (6) and, consequently, more sulfate radicals would be produced via Equation (7). This can be verified by the fact that the decomposition percentage of PDS was only 51.3% at  $j$  = 8 mA/cm<sup>2</sup> while it increased to 82.2% when the current density reached to 16 mA/cm<sup>2</sup>. However, with the further increase in current density, the side reactions such as evolution of hydrogen and oxygen would become significant. This would hinder the cathodic reduction reaction (6) and influence the generation of reactive radicals via Equations (1), (2) and (7). Therefore, the decomposition percentage of PDS only increased by 1.8% when the current



**Figure 4** | EPR spectra (a) and decolorization of AO7 with the presence of different radical scavengers (b) in EC/PDS/Cu-AC process ([radical scavenger]/[AO7] = 1,000:1, [DMPO] = 10 mM, [PDS] = 5 mM, [Cu-AC] = 0.25 g/L,  $j = 16 \text{ mA/cm}^2$ ).

density rose from 16 to 24  $\text{mA/cm}^2$ , and the corresponding rate constant increased by  $0.003 \text{ min}^{-1}$  (only a 5.2% increase).

As depicted in Figure 3(b), initial pH ( $\text{pH}_0$ ) had insignificant effect on the rate constant. Despite this, the highest rate constant was obtained at  $\text{pH}_0$  5.0, which was in agreement with the largest decomposition of PDS achieved at this pH value. Unfortunately, at  $\text{pH}_0$  5.0 or even 7.0, the leached copper was higher than 0.5 mg/L, the discharge standard of China (GB 8978-1996). The leached copper decreased to below 0.5 mg/L when  $\text{pH}_0$  rose to 9.0.

With Cu-AC dosage increasing from 0.125 to 0.250 g/L, the decomposition percentage of PDS increased from 68.0 to 74.3% and, consequently, the rate constant increased from 0.036 to 0.043  $\text{min}^{-1}$  (Figure 3(c)). More  $\equiv\text{Cu(I)}$  would be produced through Equation (6) at higher Cu-AC dosage, and then more sulfate radicals would be generated via Equation (7). A slight increase was observed with a further increase of Cu-AC dosage.

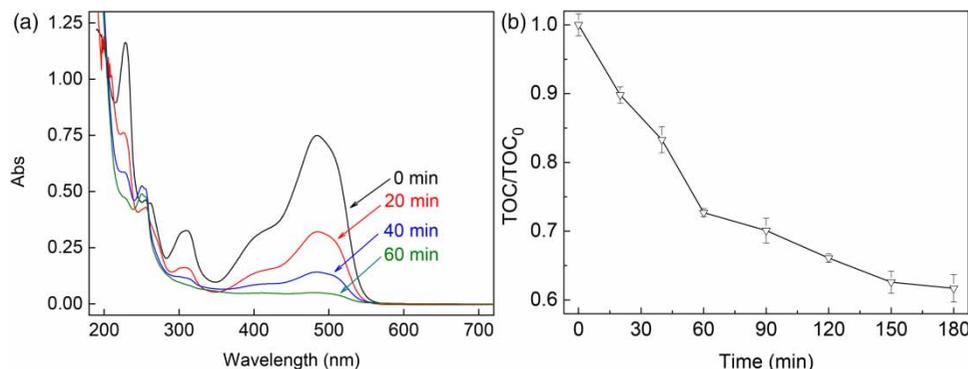
As illustrated in Figure 4(d), the rate constant increased from 0.041 to 0.043  $\text{min}^{-1}$  as PDS concentration increased from 2.5 to 5.0 mM. PDS is the source of reactive radicals,

and more radicals would be generated at higher PDS dose (Cai *et al.* 2014b). But when the PDS concentration further increased to 10.0 mM, a little increase in rate constant was achieved. This is because the overdosed PDS would scavenge sulfate radicals via Equation (10):



### Reaction mechanism in the EC/PDS/Cu-AC system

In the activated PDS process, hydroxyl radicals would also be generated via Equations (8) and (9). To identify the oxidizing species responsible for AO7 decolorization in the EC/PDS/Cu-AC system, EPR test coupled with DMPO as the spin-trapping agent was conducted to detect any radicals produced in the EC/PDS/Cu-AC system. DMPO reacted with  $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$  to form the typical DMPO-OH and DMPO- $\text{SO}_4$  signals. The  $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$  could be detected by measuring the signals of DMPO-OH and DMPO- $\text{SO}_4$  adducts, respectively (Fang *et al.* 2014). Figure 4(a) clearly indicates



**Figure 5** | UV spectral changes of AO7 (a) and mineralization of AO7 (b) in EC/PDS/Cu-AC process. Conditions: [PDS] = 5 mM, [Cu-AC] = 0.25 g/L,  $\text{pH}_0$  9.0,  $j = 16 \text{ mA/cm}^2$ .

the existence of both HO• and SO<sub>4</sub><sup>-</sup> radicals. Moreover, radical scavenging experiments were performed using methanol (MA) and *tert*-butyl alcohol (TBA). MA can scavenge both HO• and SO<sub>4</sub><sup>-</sup> since the rate constants of MA and these two radicals are very high, i.e.,  $1.6 \sim 7.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  and  $1.2 \sim 2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , respectively. TBA is an effective quenching agent for HO• because it reacts with HO• much faster than SO<sub>4</sub><sup>-</sup> with rate constant being  $3.8 \sim 7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  and  $4.0 \sim 9.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ , respectively. As depicted in Figure 4(b), neither MA nor TBA inhibited the decolorization significantly at the scavenger/AO7 molar ratio of 1,000/1. MA and TBA are assumed to quench the radicals present in the bulk liquid due to their hydrophilic characteristics (Yang et al. 2011). Phenol is another strong quencher of HO• and SO<sub>4</sub><sup>-</sup> as their rate constants are  $6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  and  $8.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , respectively. Due to its hydrophobic properties, phenol could approach the carbon surface to react with radicals generated at the Cu-AC surface. Therefore, the decolorization was significantly slowed down and the decolorization efficiency decreased from 92.4 to 53.7% at a phenol/AO7 molar ratio of 1,000:1. The results indicated that the adsorbed radicals accounted for AO7 decolorization (Yang et al. 2011; Fang et al. 2014).

### The variation of UV-vis spectra and TOC

Figure 5(a) illustrates that the absorption spectrum of AO7 has three main adsorption bands at 225, 310 and 485 nm. All the bands decreased as the reaction proceeded, indicating the azo bond and benzene-like structures in the AO7 molecule were destroyed (Cai et al. 2015a).

Figure 5(b) shows that although 92.4% decolorization efficiency was obtained after a 60 min reaction, only 27.3% of TOC was removed. When the time was extended to 180 min, TOC removal rose to 38.3%. To achieve high mineralization efficiency, a very high PDS to AO7 mole ratio and very long reaction time are needed (Zhou et al. 2015).

### CONCLUSION

The exhausted Cu-AC was applied as catalyst in a novel EC/PDS/Cu-AC process to efficiently oxidize AO7 in aqueous solution. A radical quenching study revealed that the oxidation of AO7 occurred on the surface of Cu-AC and both SO<sub>4</sub><sup>-</sup> and HO• were responsible for AO7 degradation. Recycle experiments showed Cu-AC catalyst was stable and could be reused. It showed the spent AC saturated

with metals such as copper could be used as an efficient catalyst in SO<sub>4</sub><sup>-</sup>-based AOPs, which may provide a new application of metal exhausted AC.

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