Catalytic degradation of Acid Orange 7 in water by persulfate activated with CuFe$_2$O$_4$@RSDBC

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Abstract
In this study, a novel series of rectorite/sludge derived biochar (RSDBC) supporting CuFe$_2$O$_4$ (CuFe$_2$O$_4$@RSDBC) composites were prepared as an effective catalyst to active persulfate (PS) for the removal of Acid Orange 7 (AO7) in water. The character of catalyst was analyzed by scanning electron microscope (SEM), transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FTIR) and x-ray diffraction (XRD). Various influencing factors including initial pH, PS concentration, catalyst dosage, initial dye concentration and reaction temperature were investigated. The optimal reaction conditions were found to be: PS concentration 2 mM; catalyst dosage 0.6 g l$^{-1}$; initial pH value 7.0 and 25 $^\circ$C of reaction temperature. Further radical quenching tests were performed by using ethanol, tert-butanol (TBA) and benzoquinone (BQ), which confirmed that sulfate radicals (SO$_4$·) and hydroxyl radicals (HO·) were the reactive species in the degradation process. The Gas chromatography-mass spectrometry (GC-MS) analysis was employed to determine the intermediate products and a plausible degradation pathway is proposed. In addition, the CuFe$_2$O$_4$@RSDBC sample exhibited high color removal ability (95%) and stable performance after three successive runs. At last, the catalyst proved a good removal effect for actual dye wastewater. These results indicate that CuFe$_2$O$_4$@RSDBC hybrids could be as effective catalysts for PS activation on dye pollutants elimination.

List of abbreviations
Acronyms

RSDBC: rectorite/sludge derived biochar
AO7: acid orange 7
AOP: advanced oxidation process
SEM: scanning electron microscope
TEM: transmission electron microscope
FTIR: fourier transform infrared spectroscopy
GC-MS: gas chromatography-mass spectrometer
PS: persulfate
XRD: x-ray diffraction
GAC: granular activated carbon
REC: rectorite
SS: sewage sludge
BET: Brunauer–Emmett–Teller

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1. Introduction

In recent decades, water contamination caused by organic pollutants such as azo dyes have received increasing attention in the word [1–3]. AO7 is a common azo dye widely utilized in many manufacturing industries such as pulp, textile, printing, leather, cosmetic, paper, agricultural and food [4–7]. AO7 may cause serious environmental problems because of their toxic or carcinogenic effects. Conventional chemical and microbial treatment processes have limited ability to degrade AO7 [6, 8]. Therefore, it is urgent to develop powerful methods for degradation of AO7 to minimize its ecological risk.

Advanced oxidation processes (AOP) based on the formation of highly reactive oxygen species such as SO4− and HO− which are capable of degrading almost all toxic and persistent pollutants quickly without selectivity [1, 3, 5, 9, 10]. In comparison with HO−, SO4− demonstrated high stability, and equal or even higher standard redox potential (2.5–3.1 V). PS and peroxymonosulfate (PMS) are strong oxidizer which can generate SO4− with activation methods including UV, heat, base, carbon materials and metals [11–14]. Metals or metal-based materials are the common catalysts to activate PS for oxidizing organic pollutants [12, 15]. However, the disadvantage of high cost, high toxicity and the reuse problem limit practical applications of metal catalysts [16–18].

Spinel ferrite particles with formula MFe2O4 (M = Mn, Co, Ni, and Cu, etc.), have been suggested as powerful catalysts for organic pollutants treatment processes [17, 19–21]. Among these catalysts, copper ferrite (CuFe2O4) has achieved more attention because it shows chemical and thermal stabilities, magnetically separable properties and high capability of producing active radicals [22–24]. CuFe2O4 and its derivative composites were prepared and utilized as the catalyst in fuel cell, PS and PMS activation, hydrogen peroxide (H2O2) activation and ozone oxidation [20, 23–28]. In these works, various organic contaminants were efficiently removed.

In our previous study, rectorite/sludge derived biochar (RSDBC) was synthesized as an economical and environmental friendly frame material, which showed good adsorptive properties of pollutants [29]. RSDBC can also be recognized as a supporting carrier with metal oxide because of its porous structure [11, 29–32]. In addition, the oxygen-containing functional groups on RSDBC surface may act as active sites of the electron-transfer mediator, which can be a catalyst to activate H2O2 and PS for degradation of wastewater containing dyes or other organic pollutants [29, 33–37].

Hence, in consideration with the low-cost and multifunction of RSDBC and the high efficiency of CuFe2O4 for PS activation, the objective of this study is to fabricate a new catalyst of RSDBC supporting CuFe2O4 (CuFe2O4@RSDBC) and evaluate its catalytic performance to active PS for the degradation of AO7. The key parameters such as initial pH, PS concentration, catalyst dosage, initial dye concentration, and solution temperature on the degradation of Acid Orange 7 were investigated. Furthermore, radical quenching tests were performed and kinetics of degradation was explored. Gas chromatography–mass spectrometry (GC–MS) was also applied to identify the intermediates and the degradation pathway of AO7 was proposed accordingly. Also, the application of catalyst in actual dye wastewater treatment was performed.

2. Materials and methods

2.1. Materials

Rectorite (REC) was obtained from Hubei Mingliu Inc., Ltd, China. The sewage sludge (SS) was collected from Yuelu Wastewater Treatment Plant, Hunan, China. The SS was dried for 48 h at 60 °C and then passed through 60 mesh sieve (0.3 mm). AO7 (4-(2-hydroxynaphthylazo) benzene-sulfonic acid sodium salt) was purchased from Shanghai No. 3 Reagent Factory (China). Actual dye wastewater was collected form Wuhan Baiyun printing and dyeing mill (China). All other reagents were of analytical grade and purchased from Sigma-Aldrich. All aqueous solutions were diluted with ultrapure water.

2.2. Synthesis of CuFe2O4@RSDBC

RSDBC precursor was prepared according to a reported process [29]. In a typical CuFe2O4@RSDBC synthesis procedure, Cu(NO3)2·3H2O (0.025 M) and Fe(NO3)3·9H2O (0.05 M) were dissolved in 100 ml ultrapure water through an ultrasonic method. Then, an appropriate amount of RSDBC was added into above solution. After stirring for 2 h, 75 ml NaOH (4 M) was slowly dropped into the suspension and heated at 90 °C for 2 h. Afterwards, the solid materials were filtered and washed with ultrapure water. Finally, the sample was put in an

BQ benzoquinone
TBA tert-butanol
oven at 80 °C overnight. To obtain the optimal performance, CuFe₂O₄@RSDBC catalysts with different mass ratios (1:1, 1:3, 1:5, 3:1 and 5:1) of CuFe₂O₄ and RSDBC were prepared and thus named as CuFe₂O₄@RSDBC (1:1), CuFe₂O₄@RSDBC (1:3), CuFe₂O₄@RSDBC (1:5), CuFe₂O₄@RSDBC (3:1) and CuFe₂O₄@RSDBC (5:1), respectively.

2.3. CuFe₂O₄@RSDBC characterization
The crystal phases of the as-prepared samples were studied by using x-ray diffraction with Cu Kα radiation (XRD, D8 ADVANCE, Bruker AXS). The morphology of the samples was characterized by scanning electron microscopy (SEM) (Zeiss SIGMA, Germany) and transmission electron microscopy (TEM) (JEOL, Japan). The surface elemental mapping of samples was determined by energy dispersive x-ray spectroscopy (EDX) (EDAX, Genesis). Fourier transform infrared spectroscopy (FTIR, Nicolet 5700) was performed to analyze the surface functional groups of the samples. The surface areas and nitrogen adsorption-desorption isotherms of the samples were determined by a BELSORP-Mini II analyzer and calculated by Brunauer–Emmett–Teller (BET) method.

2.4. Experimental section
Before each run, a stock solution of AO7 was prepared with deionized water and the initial pH was adjusted to 7 by using 0.05 mol l⁻¹ Na₂HPO₄ and KH₂PO₄. Then catalyst and PS were added into 250 ml flasks containing 100 ml of AO7 solution with an initial concentration of 20 mg. All experiments were conducted at constant temperature (25 ± 1 °C). At selected time intervals, samples were taken and filtered before analysis. The absorbance of AO7 was monitored at λmax = 485 nm and the absorbance of actual dye wastewater was monitored at λmax = 350 nm, by using a UV-2204PC spectrophotometer (XIPU Co., China). Decolorization rate was calculated according to the following equation:

$$\text{Decolorization rate} (\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%$$

where C₀ and Cₜ is AO7 concentration before and after process at each batch, respectively. The detection limit of AO7 range from 0.25 mg l⁻¹ to 60 mg l⁻¹ (R² > 0.99).

The intermediate products during the degradation process were detected by gas chromatography-mass spectrometry (GC-MS) (Shimadzu QP2010 Plus). Before analysis, 100 ml of sample solution was extracted with 10 ml of dichloromethane for 10 times, and then the extracts were concentrated by rotary evaporator at 40 °C to about 1 ml. A DB-5 MS capillary column (30 m length × 0.25 mm ID × 0.25 µm film thickness) was employed for GC separation. The GC equipments were operated in a temperature programmed mode with an initial temperature of 40 °C held for 2 min and ramped first to 100 °C with a 15 °C/min⁻¹ rate, then ramped to 200 °C with a 5 °C/min⁻¹ rate and held for 2 min, finally ramped to 280 °C with a 20 °C/min⁻¹ rate and held at that temperature for 10 min. Helium was used as the carrier gas. Electron impact (EI) mass spectra were scanned from 30 to 550 m/z.

3. Results and discussion

3.1. Characterization of the catalyst
The microstructure properties of RSDBC and CuFe₂O₄@RSDBC are listed in table 1. The specific surface areas of RSDBC and CuFe₂O₄@RSDBC calculated by the BET model were 18.233 and 22.948 m² g⁻¹, respectively. Also, the CuFe₂O₄@RSDBC displayed higher total pore volume and average pore diameter than that of RSDBC which was beneficial to contact pollutants and increase the catalytic ability.

SEM images and TEM images were shown in figure 1 to indicate the morphology and microstructure of RSDBC and CuFe₂O₄@RSDBC. From SEM image of figure 1(A) (RSDBC), it was observed that RSDBC had rough and porous surface. SEM image of figure 1(B) (CuFe₂O₄@RSDBC) clearly showed some fine particles well loaded on CuFe₂O₄@RSDBC surfaces, which were not found on the RSDBC surfaces. As shown in TEM image of figure 3(C) (RSDBC) and 3D CuFe₂O₄@RSDBC, CuFe₂O₄ nano-particle exhibited significant crystal lattice planes while the RSDBC around was amorphous. The elemental mapping of CuFe₂O₄@RSDBC was further confirmed by the EDX analysis. Figure 2 showed obvious elements of cooper, iron, oxygen, silicon and
aluminum, all of which are typical elemental composition of CuFe₂O₄@RSDBC. This may indicate that the CuFe₂O₄ was successfully loaded on RSDBC.

The XRD patterns of RSDBC and CuFe₂O₄@RSDBC are shown in figure 3. The diffraction peak at 2θ = 20.8° and 26.58° were characterized peaks of RSDBC [29], which were observed at 2θ = 20.88° and 26.78° in CuFe₂O₄@RSDBC. In addition, the characteristic peaks at 2θ of 18.3°, 30.18°, 35.5°, 43.32°, 50.46°, 53.62°, 57.08° and 62.72° were found in the XRD pattern of CuFe₂O₄@RSDBC. The peaks were very close to the (101), (112), (311), (004), (220), (312), (321) and (440) crystal planes of CuFe₂O₄ JCPD standard (PDF No.34-0425).

Figure 1. SEM image of (A) RSDBC, and (B) CuFe₂O₄@RSDBC hybrids, TEM images of (C) RSDBC, and (D) CuFe₂O₄@RSDBC hybrids.

Figure 2. EDX elemental mapping of CuFe₂O₄@RSDBC.
The observed strong XRD peaks indicate that the CuFe$_2$O$_4$@RSDBC was successfully synthesized. In addition, the diameter of the nanoparticle can be determined by the Scherrer equation $(D = \frac{0.89}{\lambda} \beta \cos \theta)$, where $D$ is the nanoparticle size, $\lambda$ is the incident x-rays wavelength (0.15405 nm), $\beta$ is the diffraction peak width in the half-maximum and $\theta$ is the diffraction angle [40, 41]. The average particle size of the samples is found to be 27 nm.

The figure 4 compares the FTIR spectra of RSDBC and CuFe$_2$O$_4$@RSDBC to qualitatively determine characteristic functional groups. In the case of RSDBC, the peak at 1035 cm$^{-1}$ was corresponding to the Si–O stretching vibration while the peaks at 470–541 cm$^{-1}$ were assigned to the Si–O bending vibration [29, 42]. For the CuFe$_2$O$_4$@RSDBC, the peak observed at 572 cm$^{-1}$ were corresponding to the symmetrical stretching of the Fe–O band in the tetrahedral FeO$_6$ groups of spinel-type compounds [25, 38, 43, 44]. The peaks at 3420–3440 cm$^{-1}$ were associated with hydroxyl stretching vibration, which were found to be 3432 cm$^{-1}$ in RSDBC and 3440 cm$^{-1}$ in CuFe$_2$O$_4$@RSDBC [45]. The FTIR spectra revealed that the main characteristic peaks of CuFe$_2$O$_4$ and RSDBC were observed in the CuFe$_2$O$_4$@RSDBC hybrids.

3.2. AO7 degradation by PS activated with CuFe$_2$O$_4$@RSDBC

3.2.1. Degradation of AO7 under different systems

To comprehensively evaluate the degradation performances of the samples for removal of AO7 in different systems, a series of experiments were performed in this work. As shown in figure 5, the adsorption efficiency of AO7 by RSDBC, CuFe$_2$O$_4$, and CuFe$_2$O$_4$@RSDBC was measured as 25.9%, 10.9% and 21.3%, respectively. The high adsorption efficiency of RSDBC and CuFe$_2$O$_4$@RSDBC may contribute its porous structure. 27.2% degradation efficiency was achieved by CuFe$_2$O$_4$@RSDBC under visible light illumination ($P = 100$ w) indicated that CuFe$_2$O$_4$@RSDBC had limited photodegradation ability because of the narrow band gap of CuFe$_2$O$_4$ (1.4 eV) [15]. In addition, minor degradation efficiency was achieved when AO7 was with PS alone (6.7%) because of the limited oxidation ability of PS ($E_0 = 2.01$ V versus NHE) [10]. With CuFe$_2$O$_4$ and RSDBC in the absence of PS, the degradation efficiency increased to 76.4% and 36.2%, suggesting that both CuFe$_2$O$_4$ and RSDBC shows PS activation ability [12, 20, 24, 46]. Meanwhile, CuFe$_2$O$_4$@RSDBC/PS process exhibited higher degradation efficiency than any other process. Apparently, CuFe$_2$O$_4$@RSDBC (3:1) had the highest catalytic potential (94.8%) among these ratios. The enhanced catalytic performance may attribute to the increase adsorption efficiency of CuFe$_2$O$_4$@RSDBC which result in more frequent contact between pollutants and catalyst. Unless otherwise stated, CuFe$_2$O$_4$@RSDBC (3:1) was selected for characterization and catalytic performance evaluation in the following experiments.
3.2.2. Effect of catalyst doses

As shown in figure 6, the degradation efficiency of AO7 increased obviously from 59.3% to 95.9% when the catalyst dosage added from 0.2 to 0.8 g l⁻¹. The increase of catalyst dosage would lead to an incremental total surface area and more reactive radicals which would enhance the degradation of AO7 [5, 44, 46, 47]. Nevertheless, a tiny improvement (1.7%) was observed when catalyst dosage increased from 0.6 to 0.8 g l⁻¹ and the degradation efficiency even decreased when the catalyst was added to 1.6 g l⁻¹. This may attribute to agglomeration of excessive CuFe₂O₄@RSDBC which resulting in lower catalytic activity [20, 44, 48]. Also, high concentration of catalyst would release Fe³⁺ which generated Fe²⁺ by electron transfer, the side reaction between Fe²⁺ and sulfate radicals would lead to PS consumption, as described by the following equation (1) [49].
Hence, catalyst dosage of 0.6 g l\(^{-1}\) was selected in the following experiments.

\[
\text{Fe}^{2+} + \text{SO}_4^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-}
\]  

### 3.2.3. Effect of PS concentrations

The effect of PS concentration was studied by ranging the concentration of PS from 0.5 to 4 mM. As presented in Figure 7, when PS concentration increased from 0.5 to 4 mM, the degradation efficiency increased significantly from 44.9 to 94.8%. The increase of PS concentration would generate more reactive radicals to accelerate degradation of AO7 \[8, 50\]. However, the degradation efficiency of AO7 increased slightly when PS concentration increased from 2 to 4 mM. This may have been because the radical self-consumption and side reactions between radical and PS would be prior to radical-organic reactions at a relatively higher PS concentration \[6, 20, 51\]. Therefore, 2 mM was selected as the optimal PS concentration in this work.

### 3.2.4. Effect of initial solution pH

The impact of different initial solution pH on the degradation of AO7 was examined at different initial pH values ranging from 3 to 11. As shown in Figure 8, neutral and acidic solutions exerted positive effects on AO7 degradation while alkaline conditions exhibited negative effects. This may attribute to the short lifetime of active radicals in alkaline solution, which resulting in active radicals are not sufficiently long-lived to attack organic pollutants \[9, 52\]. As the nature pH of AO7 is closed to 7, pH 7 was selected in following studies.

### 3.2.5. Effect of temperature

To investigate the effect of different temperatures on AO7 removal, the degradation experiments were performed at 15, 25 and 35 °C. Figure 9 presented that increasing temperature exerted a positive effect on AO7 degradation. This is because an increase in temperature would accelerate the reactant molecule movements between reactive radicals and pollutants \[25, 53\]. Also, higher reaction temperature would generate more reactive radicals to degrade pollutants \[54\]. As 93.2% of AO7 could be removed at 25 °C and high reaction temperature would consume more energy and cost, 25 °C was selected as the optimal temperature in following experiments.

### 3.2.6. Effect of common inorganic anion on AO7 degradation

Figure 10 shows the effect of inorganic anion on AO7 degradation. It revealed that AO7 degradation efficiency enhanced with the addition of Cl\(^{-}\). This could be ascribed to may attribute to the active chlorine species generated through reaction between Cl\(^{-}\) and reactive radicals which accelerated AO7 degradation, as shown in equations (2)–(4) \[44\]. Furthermore, it can be seen that the addition of HCO\(_3\)\(^{-}\) obviously inhibited AO7
degradation. The reduction of AO7 degradation efficiency may attribute to the generation of less active radical (e.g., CO$_3^{2-}$) by reaction between HCO$_3^-$ and active radicals, as described in equations (5) and (6) [55].

\[
\begin{align*}
\text{Cl}^- + \text{SO}_4^{2-} & \rightarrow \text{Cl}^- + \text{SO}_4^{2-} \\
\text{Cl}^- + \text{HO}^- & \rightarrow \text{HOCl}^- \\
\text{Cl}^- + \text{Cl}^- & \rightarrow \text{Cl}_2^- \\
\text{SO}_4^{2-} + \text{HCO}_3^- & \rightarrow \text{CO}_3^{2-} + \text{HSO}_4^- 
\end{align*}
\]
To further identify the reactive species involved in the CuFe$_2$O$_4$@RSDBC/PS process, radical quenching tests were employed by ethanol, TBA and phenol. Ethanol is believed to scavenge both $\cdot$SO$_4$ and HO$^-$ while TBA is mainly used to quench HO$^-$ \cite{15, 56}. Figure 9 illustrated that the degradation efficiency was 30.8% and 39.7% with the addition of Ethanol and TBA, respectively. It is indicated that the removal rate of AO7 is obviously inhibited in the presence of scavengers and the inhibition performance follows the trend: ethanol $>$ TBA.

\[
\text{HO}^- + \text{HCO}_3^- \rightarrow \text{CO}_3^- + \text{H}_2\text{O}
\]  \hspace{1cm} (6)

### 3.2.7. Radical identification

To further identify the reactive species involved in the CuFe$_2$O$_4$@RSDBC/PS process, radical quenching tests were employed by ethanol, TBA and phenol. Ethanol is believed to scavenge both SO$_4^-$ and HO$^-$ while TBA is mainly used to quench HO$^-$ \cite{15, 56}. Figure 9 illustrated that the degradation efficiency was 30.8% and 39.7% with the addition of Ethanol and TBA, respectively. It is indicated that the removal rate of AO7 is obviously inhibited in the presence of scavengers and the inhibition performance follows the trend: ethanol $>$ TBA.
However, TBA and ethanol are hydrophilic which could only quench reactive radicals in the solution. Phenol is hydrophobic and can scavenge $\cdot \text{SO}_4$ and $\cdot \text{HO}$ on the surface of catalyst [47]. As shown in figure 11, the degradation efficiency decreased significantly with the presence of phenol. Theses results indicated that reactive radicals including $\cdot \text{SO}_4$ and $\cdot \text{HO}$ were responsible in the process of AO7 degradation and the radicals were mainly produced near or on the surface of CuFe$_2$O$_4$@RSDBC.

### 3.2.8. The degradation pathway of AO7

To identify the intermediate products formed during CuFe$_2$O$_4$@RSDBC/PS process, GC-MS was employed and the main intermediate products detected were shown in table 2 and a possible degradation pathway was proposed (figure 12) based on the results and previous studies [5–8, 11, 57]. Through the cleavage of N=N, AO7 was firstly decomposed to aromatic intermediates such as Sodium sulfanilamide and 1-amino-2-naphthol [8, 15]. These two intermediates were not detected because that 1-amino-2-naphthol is oxygen sensitive and might be easily oxidized under aerobic circumstances and sodium sulfanilamide is thermally stable and highly soluble in aqueous solution [5, 8]. After that, sodium sulfanilamide was subsequently decomposed to 1,4-benzoquinone (A) [7, 57]. Meanwhile, 1-amino-2-naphthol was firstly oxidized to phthalic anhydride (B) and phthalimide (C) [6, 11]. These compounds were further degraded into benzene derivatives such as phthalic acid (D) methyl hydrogen phthalate (E) and acetoephonine (F) [8, 57]. Further oxidation reactions resulted in aromatic ring cleavage and generation of smaller molecule compounds and finally converted to carbon dioxide and water.

#### Figure 11. Effect of radical scavengers on the degradation of AO7 ($\text{[AO7]} = 20 \, \text{mg l}^{-1}$, [Catalyst] = 0.6 g l$^{-1}$, [PS] = 2 mM, $T = 25 \pm 1 \, ^\circ \text{C}$, $\text{pH} = 7$, [EtOH] = [TBA] = [Phenol] = 0.2 M).

#### Table 2. GCMS identified reaction intermediates during AO7 degradation.

| Compound | Retention time (min) | Chemical name          |
|----------|----------------------|------------------------|
| A        | 9.05                 | 1,4-benzoquinone       |
| B        | 14.975               | Phthalic anhydride     |
| C        | 22.325               | Phthalimide            |
| D        | 14.95                | Phthalic acid          |
| E        | 14.925               | Methylhydrogen phthalate |
| F        | 10.65                | Acetoephonine          |

However, TBA and ethanol are hydrophilic which could only quench reactive radicals in the solution. Phenol is hydrophobic and can scavenge $\cdot \text{SO}_4$ and $\cdot \text{HO}$ on the surface of catalyst [47]. As shown in figure 11, the degradation efficiency decreased significantly with the presence of phenol. Theses results indicated that reactive radicals including $\cdot \text{SO}_4$ and $\cdot \text{HO}$ were responsible in the process of AO7 degradation and the radicals were mainly produced near or on the surface of CuFe$_2$O$_4$@RSDBC.
3.2.9. Degradation kinetics

The degradation kinetics of AO7 were investigated by pseudo first order reaction model, which was calculated by the following equation [26, 43]:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt$$  \hspace{1cm} (7)

Where $C_0$ is the initial pollutant concentration (mg l$^{-1}$), $t$ is reaction time (min), $C_t$ is the pollutant concentration (mg l$^{-1}$) at time $t$, $k$ is the apparent rate constant (min$^{-1}$).

As shown in figure 13, the $R^2$ (correlation coefficient) values of 0–20 min and 20–60 min were 0.951 and 0.989 respectively which indicated that the degradation efficiency of AO7 fitted the pseudo first order model ($R^2 > 0.95$) at 0–20 min and 20–60 min. As being calculated, the rate constant $k$ between 0–20 min and 20–60 min was 0.081 min$^{-1}$ and 0.031 min$^{-1}$. This result showed that the degradation rate was significantly reduced after 20 min. With the increase of time, the consumption of reactive radicals may slow down the degradation of AO7. The degradation rate is relatively fast at the beginning, and the rate is significantly reduced after 20 min, probably because the number of active sites on the catalyst surface decreases with the progress of the degradation experiment, and the intermediate products produced during the degradation process further

Figure 12. Proposed pathway for the degradation of AO7.
consume minerals and also consume free radicals. The degradation kinetics rate of Acid Orange 7 is slowed down.

3.2.10. Reusability of the catalyst
Table 3 shows the reusability of the catalyst over three cycles. It was found that the degradation ratio declined gradually during repeated uses and remained at 82.3% after three cycling runs, corresponding to a mass of loss of 15.8%. The results indicated a promising stability and recyclability of CuFe₂O₄@RSDBC.

3.2.11. Application of catalyst in actual dye wastewater treatment
Figure 14 presented that removal effect of CuFe₂O₄@RSDBC for actual dye wastewater at three different chrominance (125, 250, 500). As presented in figure 14, when the chrominance of actual dye wastewater increased from 125 to 500, the degradation efficiency decreased slightly from 97.9 to 90.8%. The high degradation efficiency (>90%) indicated that CuFe₂O₄@RSDBC would have a good application in dye wastewater treatment.

4. Conclusions
A novel series of CuFe₂O₄@RSDBC were successfully synthesized as the catalyst for PS activation, exhibiting excellent performance for AO7 degradation after 60 min treatment. The as-prepared CuFe₂O₄@RSDBC (3:1) hybrids exhibited better PS catalytic activity than other ratios. Nearly 95% color removal was readily obtained under the optimal conditions (2 mM of PS concentration, 0.6 g l⁻¹ of catalyst dosage, initial pH of 7.0 and 25 °C of reaction temperature). In addition, radicals quenching tests were explored and sulfate radical was identified as the main reactive radicals for AO7 degradation. The main intermediates were identified by GC–MS technique and a possible degradation pathway of AO7 was proposed. Furthermore, CuFe₂O₄@RSDBC remained high activity after three cycling runs. At last, the catalyst presented good removal effect for practical dye wastewater.

**Figure 13.** Kinetic curve of AO7 degradation.

**Table 3.** Reusability of the catalyst.

| Cycle | 1   | 2   | 3   |
|-------|-----|-----|-----|
| Degradation ratio (%) | 92.8 | 88.5 | 82.3 |
| Mass recovery (%)      | 93.7 | 89.3 | 84.2 |
The results show that CuFe$_2$O$_4$@RSDBC hybrids could be as effective catalysts for PS activation on dye pollutants removal.

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