



# Degradation of Acid Orange 7 using peroxymonosulfate catalyzed by granulated activated carbon and enhanced by electrolysis



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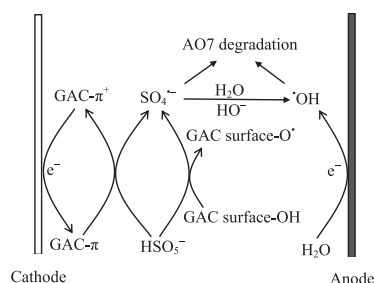
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## HIGHLIGHTS

- GAC as metal-free catalyst was combined with electrochemistry to catalyze PMS.
- The  $\pi$ -electron density and hydroxyl group content of GAC favors the activation of PMS.
- The generation of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  was verified by EPR and radical scavenging experiments
- The stability of GAC was significantly improved with the assistance of electrolysis.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Electrochemistry coupled with granulated activated carbon catalysis of peroxymonosulfate (electro/GAC/PMS) as a novel wastewater treatment process was performed for the degradation of Acid Orange 7 (AO7) in aqueous solution. The decolorization of AO7 was compared under different permutations and combinations of electro-oxidation, GAC and PMS. It showed that the electro/GAC/PMS process was the most effective and the decolorization of AO7 followed pseudo-first order kinetics. The surface chemistry of GAC samples was analyzed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Compared with the fresh samples,  $\pi$ -electron density and hydroxyl group content decreased under the GAC/PMS system, but kept the similar values under the electro/GAC/PMS system. Electron paramagnetic resonance and radical scavenger studies were used to verify the formation of sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) and hydroxyl radicals ( $\cdot\text{OH}$ ). The optimized conditions were found to be: current density  $8 \text{ mA cm}^{-2}$ ; PMS concentration  $5 \text{ mM}$ ; GAC dosage  $0.5 \text{ g L}^{-1}$ ; and initial pH value 5.0. GAC recycling experiments over 4 runs showed some decrease in reactivity. Overall, the results indicate that 100% color removal was readily achieved and 50.4% of TOC was removed which shows high efficiency of the electro/GAC/PMS process.

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## 1. Introduction

Azo dyes are widely utilized in many manufacturing industries such as paper, pulp, leather, printing and textiles. The disposal of dye wastewater from these industries is problematical as the waste-water is highly colored and some dyes may have

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carcinogenic and/or mutagenic effects (Brillas and Martínez-Huitle, 2015; Cai et al., 2015). Azo dyes have the  $-N=N-$  chromophoric group and may be monoazo, diazo or polyazo dyes. Unfortunately, the properties of dye wastewater, such as visible color even at low concentrations, chemical structure and resistance to light and chemical attack, make them highly recalcitrant to microbial degradation (Brillas and Martínez-Huitle, 2015; Li et al., 2015), so biological treatment processes such as activated sludge are ineffective for removal of these dyes from wastewater (Zhang et al., 2005). Consequently, more powerful technologies are needed for the remediation of dye-contaminated wastewater.

In recent years, advanced oxidation processes (AOPs) have found an increasingly wide utilization in environmental pollution control, especially for the treatment of biorefractory wastewater (Martínez-Huitle and Brillas, 2009; Brillas and Martínez-Huitle, 2015). Traditional AOPs are based on the formation of hydroxyl radicals ( $\cdot OH$ ) which are capable of oxidizing almost all organic pollutants quickly without selectivity, and the oxidants commonly used are hydrogen peroxide and ozone. In recent years, other types of strong oxidizing agents, peroxydisulfate (PDS) and peroxymonosulfate (PMS), which can be catalyzed to produce sulfate radicals ( $SO_4^{\cdot -}$ ), have attracted considerable attention (Saputra et al., 2013; Chen and Huang, 2015; Lei et al., 2015; Matzek and Carter, 2016). PMS alone has a limited ability to degrade organics but can be catalyzed by UV, transition metal ions, anions (such as  $HCO_3^-$ ,  $HPO_4^{2-}$ , and  $CO_3^{2-}$ ) and even halide ions in water (Yang et al., 2010).

Along with the homogeneous Fenton reaction, the homogeneous metal ion activated PMS process has a number of drawbacks. Firstly, the lower-valent metal ion is difficult to regenerate after conversion to the higher-valent one; therefore large amounts of metal ions are required to activate PMS (Wu et al., 2012b). Secondly, the metal such as  $Co^{2+}$ , introduced as catalyst, may be toxic and this can give rise to additional problems such as increased expense (Anipsitakis and Dionysiou, 2003) and the catalyst may be difficult to recover from water for reuse. In order to overcome these disadvantages, heterogeneous catalysts have become the focus in wastewater treatment technology and various heterogeneous metal oxide catalysts for PMS have been reported (Yang et al., 2008; Shukla et al., 2010; Xu et al., 2016). Since the leaching of metal ions is a major consideration in wastewater treatment, alternative catalysts have been sought. It has been reported that metal-free granulated activated carbon (GAC) could decompose PMS (Zhang et al., 2013) to generate sulfate radicals via electron transfer between GAC and oxidant (Saputra et al., 2013):



Electrochemical process has been demonstrated to be efficient methods for the degradation of organic pollutants and has such advantages as environmental compatibility, versatility, high energy efficiency, ease of operation, amenability to automation and safe operation (Martínez-Huitle and Brillas, 2009). However, in electrochemical process alone, satisfactory degradation efficiency usually requires a long reaction time or high current density (Wu et al., 2012a). Previously, we have shown that an electrochemical process combined with metal catalysts (Cai et al., 2014, 2016; Lin et al., 2014, 2016) to catalyze PDS could efficiently decolorize AO7 but to the best of our knowledge no work has been reported on the use of electrochemical process combined with GAC to catalyze PMS (GAC/PMS). Therefore, in this study, electrochemistry coupled with GAC/PMS process was proposed for the degradation of AO7, and the effects of various reaction parameters such as current density, PMS concentration, GAC dosage and initial pH are reported. Furthermore, electron paramagnetic resonance technique (EPR) and radical scavenging experiments using methanol, *tert*-butanol and

phenol have been performed to investigate the radicals generated in the reaction system. In order to obtain an insight into the electro/GAC/PMS reaction, Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were applied to investigate the change of oxygen surface groups on GAC before and after use. Under optimum conditions, the decolorization and mineralization of AO7, and the release of nitrogen were investigated. UV–vis spectroscopy was used to examine the change in adsorption bands over time. The stability and reusability of GAC were also estimated.

## 2. Materials and methods

### 2.1. Materials

Reagent purity grade AO7 (4-(2-hydroxynaphthylazo)benzenesulfonic acid sodium salt) was obtained from Sinopharm Chemical Reagent Co., Ltd. (China) and used without further purification. GAC used in this study was purchased from the Aladdin Industrial Corporation (Shanghai, China) and before use it was repeatedly washed with deionized water to remove any surface impurities and was subsequently dried at 120 °C for 12 h. PMS ( $2KH_2SO_5 \cdot KH_2SO_4 \cdot K_2SO_4$ , 99%) was obtained from China Langchem Inc. (Shanghai) and all other reagents used were of analytical grade if not otherwise noted and all sample solutions were prepared using deionized water.

### 2.2. Experimental section

The experimental set-up was similar to our previous study (Lin et al., 2014). The electrolytic treatment of AO7 was conducted in an undivided 250 mL glass beaker, fitted with a magnetic stirrer, and immersed in a water bath to maintain a constant temperature of 25 °C. The mixed metal oxide plate anode (DSA, Ti/RuO<sub>2</sub>-IrO<sub>2</sub>) and the stainless steel (SS) cathode having the same dimensions (5.0 cm × 11.9 cm) were arranged with a 4.0 cm gap between them. A model LW-3030KD direct current (DC) power supply from Shanghai Wenkai Power Equipment Co., Ltd (China) was used to provide the constant current. Before each run, a fresh stock solution of AO7 was prepared in deionized water with an initial concentration ( $C_0$ ) of 100 mg L<sup>-1</sup>. Sodium sulfate (50 mM), which acts as the background electrolyte, and the appropriate amount of PMS were added to an AO7 solution (200 mL) in the beaker and the solution was stirred with a magnetic stirrer to ensure complete dissolution. The initial pH ( $pH_0$ ) was measured with a Mettler-Toledo FE20 pH-meter and was adjusted as appropriate with sulfuric acid or sodium hydroxide. Then an appropriate amount of GAC was added and the DC power supply was turned on with constant current. At selected time intervals, aliquots (2 mL) were removed using a 5 mL syringe and filtered through a 0.45 μm membrane (Millipore) prior to analysis. Control GAC samples for FTIR and XPS analysis were produced by adding all reactants except for AO7 and were filtered through 0.45 μm membranes, dried at 120 °C for 12 h and retained for analysis.

### 2.3. Analytical methodologies

The absorbance of AO7 was monitored at  $\lambda = 485$  nm using a Rayleigh UV-9100 spectrophotometer. The concentration of AO7 was determined by use of a standard line of absorbance versus concentration. Residual PMS was measured by iodometric titration with thiosulfate (Wahba et al., 1959). The TOC of the samples was quantified using an Analytik Jena Multi N/C 3100 analyzer fitted with a non-dispersive infrared absorption detector with a flow rate of 150 mL min<sup>-1</sup> of oxygen. Ammonia-nitrogen ( $NH_4^+-N$ ) (HJ 535-

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