



Activated carbon fiber as heterogeneous catalyst of peroxymonosulfate activation for efficient degradation of Acid Orange 7 in aqueous solution



Shiyang Yang*, Tuo Xiao, Jun Zhang, Youyuan Chen, Lei Li

Key Laboratory of Marine Environment and Ecology, Ministry of Education, Qingdao 266100, China
College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

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ABSTRACT

Increasing attention has been paid to environmental friendly activation method of peroxymonosulfate (PMS) in the field of advanced oxidation processes (AOPs). In this work, activated carbon fiber (ACF) was utilized as an effective and green catalyst to activate peroxymonosulfate (PMS) for degradation of aqueous organic pollutant. As results indicated, a very low dosage of ACF (0.3 g L^{-1}) could efficiently activate PMS to eliminate Acid Orange 7 (AO7), a probe compound, and the degradation of AO7 followed first order kinetics. Surface chemistry analyses of ACF samples, including BET specific surface area, pH at the point of zero charge, Boehm titration and FTIR spectroscopy, suggested that the basic sites on ACF surface were likely to be the active sites inducing the decomposition of PMS and the generation of radicals. Quenching studies confirmed that sulfate radicals ($\text{SO}_4^{\cdot-}$) and hydroxyl radicals (HO^{\cdot}), which formed on the surface of ACF, were the primary oxidizing species. A possible pathway for AO7 degradation was proposed by monitoring the temporal evolution of intermediates in the solution, with the use of GC–MS and ionic chromatography (IC). It is suggested that the degradation process of AO7 was initiated by cleavage of azo linkage and further undergoes ring-opening reactions.

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1. Introduction

Advanced oxidation processes (AOPs) are considered as one of the most effective methods to degrade organic contaminants due to the generation of powerful oxidizing species. AOPs based on the hydroxyl radical (HO^{\cdot}), which has a redox potential of 1.8–2.7 V vs. NHE (normal hydrogen electrode) [1], have been widely studied and used in water or wastewater treatment [2–4]. In recent years, increasing attention has been paid to the sulfate radical ($\text{SO}_4^{\cdot-}$). Compared to HO^{\cdot} , $\text{SO}_4^{\cdot-}$ demonstrated the same or even a higher redox potential of 2.5–3.1 V vs. NHE [5] and has a great ability to oxidize organic pollutants. Persulfate (PS) and peroxymonosulfate (PMS) is an oxidant which has been widely studied to generate $\text{SO}_4^{\cdot-}$ with activators including UV [6], heat [7], base [8] and transition metals [9,10].

Porous carbon materials are excellent adsorbents and have been used since many years ago. Nowadays, the catalytic ability of activated carbon (AC) has attracted much scientific interests in the field of wastewater treatment. AC has many oxygen-containing functional groups on the surface, which may act as active sites of

the electron-transfer mediator, resulting in decomposition of hydrogen peroxide (H_2O_2) [11] and PS [12]. Researchers have found that contaminants can be successfully degraded in the AC/ H_2O_2 system [13–16] or in the AC/PS system [17]. Our group previously confirmed that granular activated carbon (GAC) can also catalyze PMS to produce radicals for degradation of azo dye Acid Orange 7 (AO7) [18].

In the current work, we explore the application of activated carbon fiber (ACF), which has higher adsorption rates in the gas or liquid phase [19]. For a long time, ACF was exclusively used in waste water treatment based on its function as adsorption materials [20,21], and in recent years it was also studied as catalyst supports [22,23]. However, to the best of our knowledge, there are no previous studies on the application of ACF for directly catalytic PMS oxidation, although catalytic ozonation or Fenton oxidation with ACF has been studied [4,24].

The objectives of this present study are, (a) to demonstrate the feasibility of ACF as a catalyst to activate PMS for degradation an azo dye Acid Orange 7 (AO7), which has commonly been used as a model compound for HO^{\cdot} or $\text{SO}_4^{\cdot-}$ based AOPs [2,4,17]; (b) to investigate the reaction kinetics involving the influence of the concentration of PMS and the dosage of ACF; (c) to find the active sites on ACF surface which are responsible for the decomposition of PMS; (d) to identify the dominating oxidizing species generating

* Corresponding author at: College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China. Tel.: +86 532 66782780.

E-mail address: shiningpup@hotmail.com (S. Yang).

from PMS decomposition and resulting in AO7 decay; and (e) to give the possible pathway of AO7 degradation.

2. Material and methods

2.1. Materials

Peroxymonosulfate (PMS), which is available as a triple salt of sulfate commercially known as oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), was purchased from Shanghai Ansin Chemical Company, China. AO7 and other chemicals were purchased from Shanghai Chemical Reagent Company and used without purification. Commercial activated carbons (granular, about 2 mm in diameter and 4 mm in length, $S_{\text{BET}} = 1050 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{total}} = 0.49 \text{ cm}^3 \text{ g}^{-1}$ and $V_{\text{micro}} = 0.26 \text{ cm}^3 \text{ g}^{-1}$) were supplied by Shanxi Xinhua Chemical Plant. Commercially viscose-based activated carbon fibers (felted, 10–20 μm in diameter and 3–4 mm in thickness, $S_{\text{BET}} = 1080 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{total}} = 0.52 \text{ cm}^3 \text{ g}^{-1}$ and $V_{\text{micro}} = 0.50 \text{ cm}^3 \text{ g}^{-1}$) were obtained from Sutong Carbon Fiber Company, China. Before use they were both washed with distilled water and subsequently dried at 105 °C for 24 h. The dried GAC and ACF samples were then kept in a desiccator for later use and labelled as GAC0 and ACF0.

2.2. Reactor and procedure

The experiments of AO7 removal by GAC or ACF adsorption, PMS oxidation, and GAC or ACF catalytic PMS oxidation were all carried out in 500 mL flasks containing 250 mL of AO7 solution with an initial concentration of 100 mg L^{-1} . The flasks were partially immersed in a water bath fitted with a temperature controller. The reaction mixture was stirred constantly at 25 ± 1 °C. Unless otherwise specified, the dosage of GAC or ACF was 0.3 g L^{-1} , and the mole ratio of PMS to AO7 was 20/1. The initial pH was adjusted to 5 by using 1 M NaOH or 1 M H_2SO_4 . At a fixed interval, samples were withdrawn and filtered before to be analyzed.

In the special experiments involving ACF pretreatment by PMS, 0.3 g L^{-1} ACF was immersed in 250 mL PMS solution of which the initial concentration is 5.71 mM. The concentration was as same as general oxidation experiments, and the reaction mixture was stirred constantly at 25 ± 1 °C. After specific time, ACF samples were filtered out and washed with distilled water alternately for several times, thereafter were dried at 105 °C for 3 h. After that these PMS-oxidized ACF samples were also stored in a desiccator. It should be noted that the experimental results labelled as ACF15, ACF30 and ACF60 were the products of ACF pretreated with a PMS solution (5.71 mM) for 15 min, 30 min and 60 min, respectively.

2.3. Analytical methods

The decolorization of AO7 was monitored by measuring the absorbance of samples at 484 nm (UNICO 2100 spectrophotometer, UNICO (Shanghai) Instruments Co., Ltd., China) as a function of reaction time.

The concentration of PMS was analyzed via an iodometric titration method [25]. The point of zero charge (pH_{pzc}) for ACF was determined according to a mass titration method [26]. The Boehm titration method was used to determine the acidity and the basicity of ACF [27].

Specific surface area was determined by a ST-08A Specific Surface Area Analyzer. Fourier transform infrared (FTIR) spectroscopy analysis of the ACF was performed on a BRUKER TENSOR 27 spectrometer.

GC–MS was used to detect the organic intermediate products of AO7 degradation. The sample at 120 min was extracted with CH_2Cl_2 (3 times, 20 mL each time). The extraction liquid was then

concentrated to 1.0 mL on a rotatory evaporator, and was kept at 4 °C prior to GC analysis. The concentrated sample in CH_2Cl_2 (1 μL) was injected into a 6890 N/5975 GC/MS system for analysis. DB-5MS capillary column with an inner diameter of 0.250 mm and a length of 30 m was adopted in the separation system. The GC column was operated in a temperature programmed mode by maintaining the temperature at 40 °C for 5 min, then increasing to 290 °C with an increment of 3 °C min^{-1} and finally holding at 290 °C for 10 min. Electron impact (EI) mode at 70 eV was used and the mass range scanned was 0–500 m/z . The substance analysis was undertaken with reference to the software of NIST MS search 2.0.

The concentration of NH_4^+ , NO_2^- , CH_3COO^- and HCOO^- was performed with ionic chromatography (ICS-3000) and equipped with cation exchange column of IonPac CS11-HC and anion exchange column of IonPac AS12A.

3. Results and discussion

3.1. Catalytic activity of ACF

Fig. 1a shows AO7 removal by PMS oxidation, GAC or ACF adsorption, and GAC or ACF catalytic PMS oxidation. In 120 min, the decolorization ratios of AO7 were 6%, 56% and 100% in the system of PMS, ACF0 and the ACF0/PMS combined system, respectively. Activation is necessary for application since PMS has a low reactivity. Obviously, there existed a synergistic effect in the ACF0 and PMS combined system. That is to say, ACF has a great catalytic activity of PMS activation for AO7 degradation.

Besides, it should also be noticed that the AO7 elimination rate in the ACF0/PMS system is much higher than that in the GAC0/PMS system, in which only about 11% AO7 was removed in 120 min. This phenomenon may be attributed to the fact that ACF had a higher adsorption rate for AO7 (Fig. 1a). It is due to pore volume and uniform microporosity [28] and a higher catalytic activity of

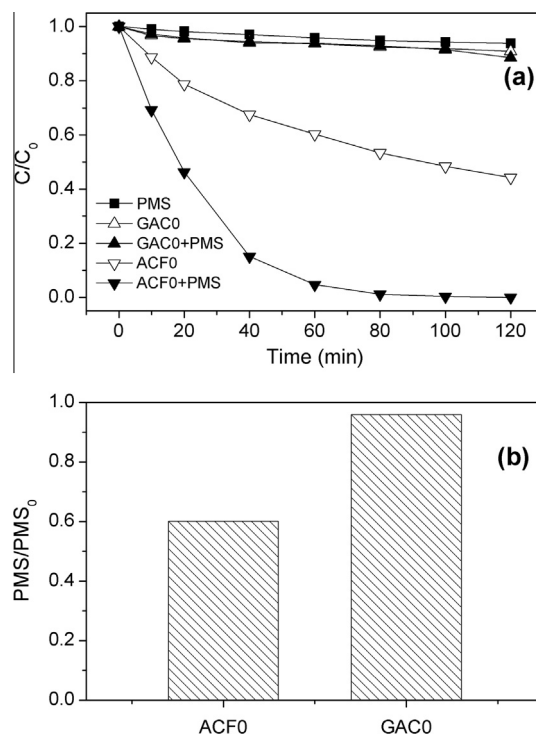


Fig. 1. (a) The degradation of AO7 in different systems. (b) The comparison of PMS decomposition ratios in the presence of ACF0 and GAC0.

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