



An effective heterogeneous iron-based catalyst to activate peroxymonosulfate for organic contaminants removal



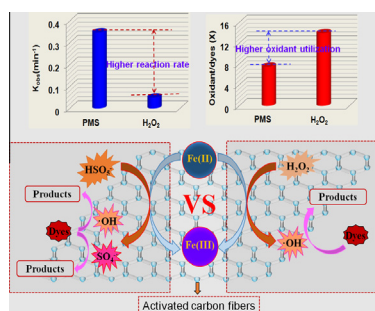
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HIGHLIGHTS

- Radicals ($\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$) acted as active species in the Fe@ACFs/PMS system.
- The system displayed high oxidant utilization efficiency and low activation energy.
- The negative effect of NaCl in H_2O_2 activation was turned into a positive effect.

GRAPHICAL ABSTRACT



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ABSTRACT

Peroxymonosulfate (PMS) activation has received increasing attention owing to the generation of powerful radicals for the removal of organic pollutants in the environmental catalysis field, although the development of highly efficient and environmentally benign oxidation processes has proven to be a significant challenge. In this work, an effective and stable catalyst (Fe@ACFs) has been tested for the first time for the heterogeneous activation of PMS for the removal of organic pollutants. The experimental results revealed that Fe@ACFs displayed sustained catalytic ability, and compared with the most commonly used oxidant, H_2O_2 , the introduction of PMS contributed specifically to the activity enhancement of the catalytic system. Meanwhile, electron paramagnetic resonance (EPR) combined with two kinds of radical scavengers (methanol and *tert*-butyl alcohol) has been employed to confirm that hydroxyl radicals ($\cdot\text{OH}$) and sulfate radicals ($\text{SO}_4^{\cdot-}$) serve as the active species in the reaction process. Importantly, the negative effect of NaCl normally observed in hydrogen peroxide activation was turned into a positive effect at high NaCl concentrations. Furthermore, the catalyst also displayed excellent stability and reusability in these experiments, avoiding secondary contamination and being conducive to green catalysis. This work provides a new process to solve the dichotomy between efficiency and environmental benignity in PMS activation, which may find practical application for the treatment of organic pollutants in water.

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1. Introduction

In recent years, advanced oxidation processes (AOPs) have received considerable and increasing attention as promising technologies to treat wastewater containing toxic and non-biodegradable pollutants due to the generation of highly reactive radicals [1–

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6]. Among these various AOPs, activated peroxymonosulfate (PMS) oxidation has been regarded as an interesting treatment method because PMS is more easily activated compared with hydrogen peroxide, which is one of the most commonly used oxidants in AOPs [7,8]. Although some research has demonstrated that heat and UV irradiation can be used to activate PMS to generate powerful radicals, these techniques are restricted in practical application owing to their high energy input [9,10]. Recently, many studies related to the activation of PMS have focused on transition metals. Among the various transition metal catalysts, cobalt stands out as one of the most efficient elements [11,12]. However, cobalt has been identified as a pollutant associated with certain health problems, such as pneumonia and asthma, which is clearly a significant disadvantage regarding the use of cobalt-based catalysts [13,14]. Therefore, there is an urgent need to develop novel technologies for activating PMS in an efficient and environmentally friendly manner.

Iron is one of the most commonly used metallic elements, and has been widely used for developing various catalysts due to its non-toxicity, low cost, and effectiveness [15,16]. Recently, some studies have reported the use of iron ions for homogeneous activation of PMS for the generation of highly reactive radicals [17,18]. However, the iron ions/PMS system has to be operated within an acid pH range due to the hydrolysis and precipitation of iron ions, and the removal of the iron ions from the solution after the reaction incurs additional operational costs [19,20]. These non-ignorable disadvantages limit the widespread application of the homogeneous iron/PMS process in wastewater treatment engineering.

The development of supports for heterogeneous iron-based catalysts could offer an alternative method that avoids the above disadvantages. Various supports, such as clay [21], resin [22], zeolite [23], and activated carbon [24], have been used to prepare heterogeneous iron-based catalysts. Compared with these supports, activated carbon fibers (ACFs) represent a highly microporous carbon material with an extremely high adsorption capacity and a large surface area. In addition, ACFs in the form of felt or cloth of various shapes are preferable for handling compared to granular or powder supports [25,26]. By virtue of their remarkable properties, ACFs have great potential as an excellent support material for the construction of heterogeneous iron-based catalysts [27,28]. Hence, in this work, ACFs have been selected to support iron ions to obtain a Fe@ACFs catalyst, which has been tested for the heterogeneous activation of PMS. The aim has been to obtain an iron-based catalyst as an alternative to toxic cobalt-based catalysts for effective activation of PMS for the removal of organic pollutants. Moreover, the use of Fe@ACFs could also avoid leaching of iron ions from the homogeneous iron/PMS system, thereby reducing secondary contamination. To the best of our knowledge, the removal of organic pollutants by the combination of Fe@ACFs and PMS has not hitherto been reported.

For the current work, the common azo dyes Reactive Red M-3BE (RR M-3BE) was selected as a probe compound. The factors that may influence the removal of azo dyes, such as the dosages of catalyst and oxidant, initial pH, reaction temperature, and the presence of several common anions (especially chloride ions), were investigated. More importantly, various radical scavengers, monitored by electron paramagnetic resonance (EPR), have been employed to investigate the mechanism of PMS activation by Fe@ACFs. Differences between the Fe@ACFs/PMS and Fe@ACFs/H₂O₂ systems, such as catalytic oxidation activity, oxidant utilization efficiency, and activation energy, have also been investigated. It is anticipated that this study may open a new perspective in the development of environmentally benign and highly efficient approaches for the activation of PMS, and thus has potential value in environmental engineering.

2. Experimental

2.1. Materials and reagents

Activated carbon fibers were obtained from Jiangsu Sutong Carbon Fiber Co., Ltd. (Jiangsu, China) (see the [Supplementary information](#) for more details of the ACFs). Ferric chloride hexahydrate (FeCl₃·6H₂O) and potassium peroxymonosulfate (PMS, 2KHSO₅·KHSO₄·K₂SO₄) were analytical grade reagents. The spin trapping agent 5,5-dimethyl-pyrroline-N-oxide (DMPO) was purchased from Hangzhou Mike Chemical Instrument Co., Ltd. The dyes used in the experiments was Reactive Red M-3BE (RR M-3BE), which was obtained commercially and used without further purification. All other chemical reagents used in this study were provided by Hangzhou Mike Chemical Instrument Co., Ltd. (Hangzhou, China). Doubly-distilled water was used throughout this study.

2.2. Catalyst preparation

The activated carbon fibers were treated with acid, washed with water, and dried according to the methods described by Yao et al. [27]. Fe@ACFs was prepared by immersing acidified ACFs in aqueous ferric chloride solution (see the [Supplementary information](#) for details of this process).

2.3. Experimental procedures and analysis

2.3.1. Experimental procedures

Batch experiments on the catalytic oxidation of the dyes were carried out in 100 mL glass beakers by shaking in a thermostated water bath (SHA-B, Guowang Laboratorial Equipment Factory, China) that was adjusted to 50 °C or other temperatures as required. In all experiments, a reaction volume of 50 mL was used. RR M-3BE solution (50 μm), Fe@ACFs (2 g/L), and PMS or H₂O₂ (0.5 mm) were added simultaneously at the beginning of each experiment. At predetermined intervals (2 min), samples were withdrawn from the flask for analysis using an ultraviolet/visible (UV/Vis) spectrophotometer (Hitachi U-3010). For all of the reported experiments, the initial pH of the solution was adjusted with 0.1 m NaOH or 0.1 m HClO₄ prior to the addition of Fe@ACFs and PMS.

2.3.2. Analytical methods

The decoloration efficiency of the dyes was determined using the UV/Vis spectrophotometer. The kinetics of decoloration of the dyes may be described by a pseudo-first-order equation (Eqs. (1) and (2)):

$$dC/dt = -k_{\text{obs}}C \quad (1)$$

$$C_t = C_0 \exp(-k_{\text{obs}}t) \quad (2)$$

where C_t is the actual concentration of the dyes solution at time t , C_0 is the initial concentration of the dyes, and k_{obs} is the pseudo-first-order rate constant (min^{-1}). The k_{obs} values were obtained from the slopes of the regression lines for plots of $-\ln(C_t/C_0)$ versus time (t).

Electron paramagnetic resonance (EPR) spectra of radicals trapped by DMPO were examined by using a Bruker A300 spectrometer at ambient temperature. The settings for the EPR spectrometer were as follows: center field, 3520 G; sweep width, 100 G; microwave frequency, 9.77 GHz; modulation frequency, 100 kHz; power, 20.00 mW. The leaching of iron ions was monitored by spectrophotometric detection of phenanthroline and the absorbance was immediately read at a wavelength of 510 nm [29]. In order to determine the PMS concentration, samples were prepared by placing 1 mL of reaction solution in a 4 mL cuvette.

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