



Fe-Ag/GAC catalytic persulfate to degrade Acid Red 73



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ABSTRACT

The present study reported a novel Fe-Ag/GAC catalyst and investigated its catalytic activity for the degradation of Acid Red 73 by persulfate. The results of characterization of Fe-Ag/GAC showed that Nano-Ag was supported uniformly on GAC with high degree of crystallinity and Fe distributed mostly in the forms of noncrystalline FeO/Fe₃O₄ or FeOOH. The presence of catalyst greatly enhanced the removal rate of AR 73, and it was found that 99% of decolorization efficiency and 84.1% of total organic carbon removal (TOC) of AR 73 could be obtained at the neutral pH within 60 min, respectively. The optimized experiments found that either higher temperature or higher dosage of Fe-Ag/GAC or Na₂S₂O₈ was favored for the degradation of Acid Red 73. Lowering solution pH could improve the degradation rate of AR 73. The recycling test indicated that the catalyst was relatively stable, showing a promising application.

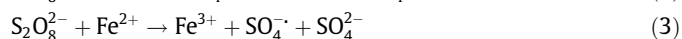
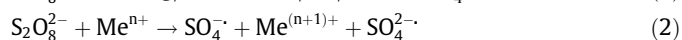
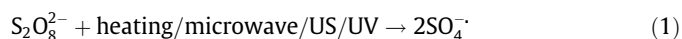
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1. Introduction

The textile industry is one of the biggest sources of water pollution, and dyeing process of textile results in most of wastewater [1]. Azo dyes, the maximum amount of dye usage [2], are difficult to remove through traditional treatment methods because of their complex structure and high stability and chromaticity [3]. Therefore, it is necessary to put forward more practical and economical technologies to treat azo dyes.

Advanced oxidation processes (AOPs), which involve generation of strong radicals, such as sulfate radical (SO₄^{•-}) with a higher standard potential of 2.6–3.1 V and a longer half-life compared to HO[•], have been demonstrated to be effective for wastewater remediation [4–6]. As a source of SO₄^{•-}, sodium persulfate (Na₂S₂O₈) presents high solubility, high stability and wide operative pH range in aqueous solution [7,8]. However, reactions of persulfate with organic substance in water are generally slow at ambient temperature, therefore it is necessary to activate persulfate to accelerate the degradation rate of organic compound. Generally, persulfate can be activated by heating [9], ultraviolet [10], microwave [11,12], ultrasound irradiation [13] or transition metal ions [14,15] by reactions (1) and (2). Although previous works have suggested that these activation methods could effectively activate persulfate to degrade pollutants. However, each of them has its own disadvantage. For example, thermal activation of persulfate is found to be strongly pH-dependent [16]. UV activation needs

high requirement for the equipment, which will increase cost and limit its application [17]. Transition metal ions (like Fe²⁺, Fe³⁺, Co²⁺, Ag⁺) are commonly used as activators for activation of persulfate or peroxymonosulfate [17,18]. Among these metals, Fe²⁺ as an efficient, inexpensive and non-toxic catalyst, has been the most widely used to activate S₂O₈²⁻ via reaction (3) [18]. However, if we increase the total dose of ion, a lot of iron sludge will be produced in the process of after-treatment, and also excessive Fe²⁺ will react with SO₄^{•-} to lower the oxidative efficiency via reaction (4) [19]. So similar to conventional Fenton process, there exist some drawbacks in Fe²⁺/S₂O₈²⁻ process, such as consumption of Fe²⁺, too fast reaction rate, low efficiency of free radical and large amount of Fe³⁺ sludge [17,18]. Therefore, it is significant to explore a catalyst which can somewhat overcome above shortages to active S₂O₈²⁻.



It is beneficial for practical application to apply heterogeneous transition-metal catalyst for persulfate activation to generate sulfate radical [20–22]. Many researchers are enthusiastic about looking for efficient heterogeneous catalysts for catalytic oxidation in AOPs. Granular activated carbon (GAC) is one of the most versatile materials, which has been widely used as an adsorbent, catalyst

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and catalyst support [22]. It is suggested that supported metal on GAC will be conducive to aqueous reactions, which results in the occurrence of catalytic oxidation reaction on the surface of GAC. Thereby GAC could facilitate the reaction of organic radicals to sulfate radicals, thus improving the oxidative efficiency. Ferrous ion has been widely used for the catalyst which can effectively activate $\text{Na}_2\text{S}_2\text{O}_8$ [23]. Some reports have shown that Fe-based catalyst is good for activation of $\text{Na}_2\text{S}_2\text{O}_8$ and the total iron leaching ratio was low at neutral pH [23,24]. However, the catalytic efficiency of Fe-based catalyst is still unsatisfied at present. As reported by Cai et al., the combination of ultrasound with Fe-Co/GAC could activate $\text{Na}_2\text{S}_2\text{O}_8$ to degrade reluctant organic compounds, where the degradation efficiency approached 98.3% within 60 min. However, the efficiency of Fe-Co/GAC/ $\text{Na}_2\text{S}_2\text{O}_8$ for degradation of Acid Orange 7 decreased to 77.7% without the help of ultrasound [13]. Also, Co is considered as the priority pollutant in water and can lead to several health problems, and the requirement of further treatment would cause the additional cost [16]. In order to effectively regenerate Fe^{2+} , some other reducing metal ions were introduced to provide electrons for the reduction of Fe^{3+} . The electrocatalysis of Nano-silver materials has attracted much attention for promoting speed of electron transfer in recent years [25]. It was deduced that such Ag-containing complex substances could accelerate electron transfer and promote the redox cycle of $\text{Fe}^{2+}/\text{Fe}^{3+}$. Additionally, Ag (I) also showed best the efficiency for activation of $\text{Na}_2\text{S}_2\text{O}_8$ according to the reaction (7) [3]. Therefore, Ag doping might be a breaking point in enhancing the catalytic efficiency of Fe/GAC. Besides, to the best of our knowledge, GAC supported nano-silver doped with Fe has not been explored to activate $\text{Na}_2\text{S}_2\text{O}_8$ for degradation of the reluctant pollutants.

In this study, a new Fe-Ag/GAC catalyst was prepared through impregnation method, and its activity for decolorization of Acid Red 73 (AR 73) was investigated. The stability of the catalyst was also tested through the recycling test.

2. Materials and methods

2.1. Chemicals and materials

Silver nitrate (AgNO_3 , 99.8%), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 99%), Acid Red 73 (AR 73), nitric acid (HNO_3), sulfuric acid (H_2SO_4 , 95%), sodium hydroxide (NaOH), potassium iodide (KI), acetic acid (HAc), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), ammonium iron(II) sulfate hexahydrate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), hydrochloric acid (HCl, 36–38 wt%), hydroxylammonium chloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$), ammonium acetate, and 1,10-phenanthroline, starch, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and tert-butyl alcohol (TBA), were all purchased from Aladdin industrial Corporation, China. Granular activated carbon (GAC) was obtained from Kun-Shan Da xi yang Chemical industry Co. Ltd. (China). All chemicals were of analytical grade and used without further purification. All the solutions were prepared by deionized water. Nitrogen (N_2 , 99.99%) was purchased from Hangzhou Dongzheng industry Co., Ltd. (China).

2.2. Preparation of catalyst

In the typical procedure, granular active carbon (GAC) was pretreated by being dipped in a mixed acid solution ($V_{10\% \text{ nitric acid}} : V_{20\% \text{ sulphuric acid}} = 1 : 1$) for 12 h, then washed and dried in vacuum. The pretreated GAC was immersed in 50 mL of AgNO_3 solution at room temperature for 4 h. After being filtrated and dried, the obtained solid was calcined in N_2 atmosphere at 500°C for 2 h. The product was labeled as Ag/GAC. Ag/GAC was immersed in 50 mL of 0.6 mol L^{-1} FeSO_4 solution at room

temperature for 6 h. The obtained composite was calcined in N_2 atmosphere at 500°C for 4 h. In all steps, the samples were dried in vacuum oven at 110°C before being calcined at a tube furnace in N_2 atmosphere.

2.3. Characterization of catalyst

Scanning Electron Microscopy (SEM) analysis was used to characterize the surface structure and morphology of the catalyst by a Hitachi S-570 (Japan) model instrument. The elemental composition was determined through energy dispersive X-ray spectroscopy (EDS). Surface area and pore size distribution were measured through Nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics 3flex. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation. The pore diameter distribution was determined by the Barrett–Joyner–Halenda (BJH) method based on the Kelvin equation. X-ray powder diffraction (XRD) patterns were detected with a $\text{Cu K}\alpha$ radiation in the 2θ ranges of $10\text{--}80^\circ$ on a PANalytical X'Pert Pro X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was collected on a K-alpha X-ray photoelectron spectrometer with a monochromatic $\text{Al K}\alpha$ source for the determination of the chemical species of iron and Ag. The points of zero charge (pH_{PZC} values) of the catalyst were determined by the pH drift method [26]. The pH_{PZC} value of Fe-Ag/GAC catalyst was 7.4.

2.4. Catalytic oxidation procedure

The catalytic performance of catalyst was carried out in 500 ml glasses beakers to which 200 ml AR 73 solution was added, and then stirred with a magnetic bar at a speed of 300 rpm. At suitable intervals, 2 ml of solution sample was taken out and immediately filtered through a $0.45 \mu\text{m}$ membrane to measure the absorbance at 508.5 nm [27]. Effects of different operating parameters were also investigated, such as initial pH, dosages of catalyst and $\text{Na}_2\text{S}_2\text{O}_8$, initial concentration of AR 73, and reaction temperature.

In a typical experiment of AR 73 degradation, the catalyst was added after $\text{Na}_2\text{S}_2\text{O}_8$ to start the reaction. For the experiment of effect of temperature, the dye solution was heated to the set temperature before adding $\text{Na}_2\text{S}_2\text{O}_8$ and the catalyst. The effect of initial pH of solution was conducted at the pH range of 3.0–11.0.

2.5. Analytical procedure

The absorbency of AR 73 was measured at 508.5 nm by an UV-visible spectrophotometer. Each experiment was repeated three times, and the result in figure was the average of duplicate experiments of three times. In all experiments, the range of error for each result was always less than 5%. Decolorization efficiency was calculated using Eq. (6).

$$\text{Decolorization efficiency (\%)} = (A_0 - A_t)/A_0 \times 100\% \quad (6)$$

where the A_0 and A_t were the absorbency of the sample at times of 0 and t , respectively. The temperature of solution was controlled by a collective heating thermostatic magnetic stirrer (DF-101S, Hui Chong Instrument Co., Ltd Shanghai, China). The pH value of the solution was recorded by a pH analyzer (PHS-3C, General Instrument Co., Ltd., Shanghai, China), and was controlled by adding H_2SO_4 or NaOH solution. The concentration of $\text{Na}_2\text{S}_2\text{O}_8$ was analyzed using the iodometric titration method [28]. A PerkinElmer ELAN DRC-e ICP-MS was used to detect the leaching iron and silver in solution. Total Fe ion in solution also was determined by means of 1,10-phenanthroline spectrophotometry. Total Organic Carbon (TOC) was determined by a Liqui TOC analyzer (Liqui TOC, Elementar, Germany).

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