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Efficient degradation of Orange G with persulfate activated by recyclable $FeMoO_4$

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HIGHLIGHTS

- $FeMoO_4$ can strongly catalyze persulfate for OG degradation.
- $FeMoO_4$ exhibited excellent sustained catalytic ability and reusability.
- The contribution of $SO_4^{\cdot-}$ was higher than that of $HO^{\cdot}$ to OG degradation.
- The possible mechanism of persulfate activation by $FeMoO_4$ was elucidated.

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ABSTRACT

In this study, $FeMoO_4$ was applied to activate persulfate (PS, $S_2O_8^{2-}$) for azo dye Orange G (OG) degradation. The catalyst was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption-desorption isotherms. $FeMoO_4$ showed excellent efficiency in activating PS for OG removal. More than 95% could be removed after 40 min under reaction conditions of 4 mM PS, 0.3 g L^{-1} $FeMoO_4$ and 0.2 mM OG. The effect of different parameters (PS doses, $FeMoO_4$ doses and pH) were evaluated. The results showed that acid condition provided higher efficiency and overdosing $FeMoO_4$ and PS presented a scavenging effect. Major intermediates were identified and possible degradation pathway was proposed. Recycle tests presented that $FeMoO_4$ had excellent recyclable stability in activating PS for OG removal. Sulfate radicals and hydroxyl radicals all occurred in the oxidation reactions and the former came first. The oxidation reaction was involved in the translation of Fe^{2+}/Fe^{3+} occurred on the surface layer. This study revealed that the $FeMoO_4$/PS system is a very promising method for degrading organic contaminants in the environment.

1. Introduction

Azo dyes are characterized by the existence of several benzene cycles and one or more azo bonds (-N=N-), which are often used in various industries, including textile, paper, leather, cosmetics and plastics industries. Many azo dyes are toxic, mutagenic, carcinogenic and non-biodegradable, which pose long-term risks to the ecosystem and cause human health problems (Gan et al., 2017; Aveiro et al., 2018). Orange G is one typical kind of azo dyes, whose structure was shown in Fig. S1. Since conventional treatment technology cannot effectively degrade and mineralize azo dyes in wastewater, advanced oxidation processes (AOPs) including Fenton, ozonation, photolysis and so on were applied to decompose toxic and non-biodegradable azo dyes (Li et al., 2016; Baena-Nogueras et al., 2017; Larouk et al., 2017). However, these processes always needed additional energy or the oxidants such as H_2O_2 is not easily to be stored. Sodium peroxydisulfate used as persulfate is more easily to be stored. In addition, compared to $^{\cdot}OH$, $SO_4^{\cdot-}$ have similar high oxidation potential of 2.8 V but longer life span of 30–40 μs (Yang et al., 2014; Lutze et al., 2015; Jawad et al., 2018). Thus, AOPs based on sulfate radicals ($SO_4^{\cdot-}$) are drawing more and more attentions. $SO_4^{\cdot-}$ can be produced by different method

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such as ultraviolet, pyrolysis or chemical activation of persulfate (PS, $S_2O_8^{2-}$) or peroxymonosulfate (PMS, SO_5^{2-}) (Lin et al., 2017; Xia et al., 2017; Yan et al., 2017).

In recent years, it has become a hot area to generate sulfate radical for pollutant degradation in heterogeneous PS activation (Lin et al., 2015; Oh et al., 2016; Jawad et al., 2018), which also falls into the scope of this journal. Iron elements was regarded as one of the most effective elements for PS activation (Anipsitakis and Dionysiou, 2004). Thus, different Fe-based materials thus as Fe^0 (Zou et al., 2014),Fe/S modified carbon nanotubes (Cheng et al., 2016) and Fe–C (Li et al., 2018) were developed for PS activation. For heterogeneous PS activation, deactivation is an important issue for practical use of catalysts. Developing recyclable persulfate activators is one of challenges for current and future research. Herein, $FeMoO_4$ could be synthesized in acid aqueous solution and keep stable in acid or alkaline water. Furthermore, the produced Fe(III)-materials $Fe_2(MoO_4)_3$ after initial PS activation could also keep the ability for PS activation (Tian et al., 2013; Lu et al., 2015) for pollutant degradation. Thus, $FeMoO_4$ may be a good recyclable material to activate persulfate activator for organic pollutants degradation. This study therefore aims to investigate $FeMoO_4$ to activate PS for pollutant removal. To the best of our knowledge, it is the first time to study recyclable $FeMoO_4$ material to activate PS for pollutant removal in aqueous solutions. Herein, we provided a recyclable material $FeMoO_4$ to activate persulfate for pollutant removal. Material characterization methods and classis quenching tests were used to uncover the mechanism. It is expected that this study would provide an environmental and efficient technology for wastewater treatment.

2. Materials and methods

2.1. Chemicals

Ultrapure water was produced by a Millipore milli-Q system. $FeSO_4 \cdot 7\ H_2O$, CH_2Cl_2, $Na_2MoO_4 \cdot 2H_2O$ and HCl were obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). 5, 5-dimethyl-1-pyrrolidine N-oxide (DMPO), persulfate (PS) and Orange G (OG) were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). All reagents were analytical grade at least and used without any further purification.

2.2. Preparation of $FeMoO_4$

$FeMoO_4$ used in this report was synthesized by a solvothermal method according to the literature (Zhang et al., 2011) with certain modification to improve the production of $FeMoO_4$ by one time. Briefly, 3 mmol of $FeSO_4 \cdot 7\ H_2O$ and 3 mmol of $Na_2MoO_4 \cdot 2H_2O$ were dissolved in 51 mL HCl solution whose pH was 2.00. Then, the solution was put into a Teflon-lined autoclave of 100 mL capacity. The autoclave was soon transferred into an oven of 180 °C. After heating for 4 h, the product $FeMoO_4$ was washed by deionized water and ethanol several times.

2.3. Characterization

Technologies such as X-ray diffraction (XRD) (Bruker, German), scanning electron microscopy (SEM) (Quanta 200, Holland), Brunauer–Emmett–Teller (BET) (ASAP 2020; USA), Transmission Electron Microscope (TEM) (FEI Tecnai G2 f20 s-twin 200Kv, USA) and X-ray photoelectron spectroscopy spectrometer (XPS) (Thermo Scientific ESCALAB 250, USA) were used to characterize the materials.

2.4. Experiment procedure and analysis

Batch tests were carried out in glass conical flask with 100 mL aqueous solution and shaken in a rotary shaker (ZHWY-20102C, Shanghai, China) at 180 rpm and 25 ± 0.5 °C. Orange G (OG) and persulfate (PS) stock solution were added to DI water, then catalysts were added to initiate the reaction. The initial pH could be adjusted by NaOH (0.1 mM) or H_2SO_4 (0.1 mM) solution if necessary. A certain amount of solution sample was withdrawn at specified time intervals, then immediately an equal amount of ethanol was added for detection at a maximum absorption wavelength of 478 nm by UV–Vis spectrophotometry method (Thermo Fisher, Evolution 201, USA). PS concentration was analysis by a rapid spectrophotometric method provided by Liang et al. (2008). In addition, details of GC-MS and Electron Paramagnetic Resonance (EPR) tests could be found in Supporting information.

3. Results and discussion

3.1. Characterization of $FeMoO_4$

The XRD patterns of $FeMoO_4$ activators are presented in Fig. 1 (A). Almost all peaks could be related to β- $FeMoO_4$ (JCPDS 22–0628) and two weak peaks (marked with clover symbol) could be related to α- $FeMoO_4$ (JCPDS 22–1115). The XRD presented that the samples mainly comprised β- $FeMoO_4$ phase with a little α-$FeMoO_4$ impurity. The SEM morphology of $FeMoO_4$ is shown in Fig. 1 (B). Based on the SEM images, the catalyst has a fine and uniform rodlike shape. The rods possessed a length of 300–600 nm and a diameter of 50–200 nm. TEM images of fresh samples are shown in Fig. 1(C) and (D). Fig. 1 (C) and the inset presented that the surface of fresh samples was similar to the inner part. Fig. 1 (D) presents the high-resolution TEM (HRTEM) image gotten from the same rod and the corresponding fast Fourier transform (FFT) image in the inset. About 0.33 nm of d-spacing could be known with the help of Digital Micrograph, which agreed with the result of similar literature (Zhang et al., 2015). Brunauer–Emmet–Teller (BET) measurement shown in Fig. 1(E) presented that the samples possessed a BET surface area of about 12.1 $m^2\ g^{-1}$. The inset shows a mesoporous size distribution of about 35.78 nm in diameter which was calculated by Barrett-Joyner-Halenda method (BJH).

XPS technology was applied to tell the surface element species and their oxidation states. The survey spectrum in Fig. 2 (A) confirms that the samples comprised Fe, Mo, and O. The Fe2p, Mo2p and O1s XPS spectra are shown in Fig. 2(B)–(D) respectively to present the oxidant states of the main elements. The peak Fe2p3/2 at about 711.0 eV and Fe2p1/3 at about 724.2 eV indicated the existence of Fe^{2+} oxidation state, which confirmed that $FeMoO_4$ containing Fe^{2+} was synthetized successfully (Zhang et al., 2015). Mo 3d5/2 peak at binding energies of about 232.5 eV and Mo 3d3/2 peak 235.6 eV suggest the present of Mo^{6+} oxidation state. Fig. 2 (D) shows that the O1s spectrum contains two child components. The primary one at peaks at 530.4 eV corresponded to the lattice oxygen, and the minor one at 532.1 eV may be due to the chemisorbed oxygen. The XPS results confirm the successful synthesis of $FeMoO_4$, which agreed with the XRD results.

3.2. Catalytic activity of $FeMoO_4$

Tests based on different systems as comparison for degradation of OG were carried out to tell the catalytic activity of $FeMoO_4$. As shown in Fig. 3 (A), it can be observed that $FeMoO_4$ showed excellent efficiency in activating PS for OG removal. More than 95% could be removed after 40 min when the initial concentration of OG, PS and catalyst were 0.2 mM, 4 mM and 0.3 g L^{-1} respectively.