



Short communication

Facile synthesis of paper mill sludge-derived heterogeneous catalyst for the Fenton-like degradation of methylene blue



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ABSTRACT

Paper mill sludge-derived heterogeneous catalyst was synthesized through a facile method. X-ray diffraction (XRD) analysis confirmed the existence of α - Fe_2O_3 , and Fourier transformed infrared (FT-IR) spectroscopy proved the formation of chemical bonds (Fe–O–Si). The as-prepared catalyst exhibited effective methylene blue (MB) degradation and exhibited an excellent stability of catalytic activity. This study provides an alternative environmentally friendly reuse method for paper mill sludge and a low cost and effective heterogeneous catalyst.

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1. Introduction

The pulp and paper industry generates large quantities of sludge during the paper manufacturing process. Paper mill sludge is a byproduct from the wastewater treatment process. Each ton of paper produces about 45 kg of dry sludge [1]. The contaminated sludge can have direct toxic effects on aquatic ecosystem, and through the bioaccumulation of toxic contaminants in the food chain, which can cause an indirect risk to humans [2]. Traditionally, paper mill sludge has been disposed of by landfilling, composting, incorporation into cement, and incineration, but it may have potential environmental risks [3]. Therefore, from a long term perspective, it is necessary to explore novel and value-added methods to maximize recovery of useful materials and/or energy and minimize such residue from the paper industry [4].

Fenton is an effective process to degrade recalcitrant organic pollutants by the generation of strong, relatively non-selective hydroxyl radical ($\cdot\text{OH}$) [5,6]. However, there are some intrinsic drawbacks restricting the widespread application at the industrial scale of conventional homogeneous Fenton, such as strong acidic conditions, generation of huge iron sludge, and difficulty in recycling use [7,8]. These disadvantages promote the development of a heterogeneous catalyst for the Fenton system. Heterogeneous catalysts are noncorrosive and environmentally benign, which are also much easier to separate from treated wastewater [9]. Recently, many studies have been performed

and various supports have been used to prepare heterogeneous catalysts [10–12].

Paper mill sludge is difficult to handle and process, which contains 45–55% moisture, with 20% or more solids [3]. The sludge mainly consists of two components: fine cellulosic fibers (fibers too short to be retained on fiber screens and paper machines) and inorganic materials (such as kaolin, clay and calcium carbonate). Recently, paper mill sludge has been put to use by being converted into mesoporous adsorbents to remove organics from water or directly used as industrial raw material [13,14]. These methods are among the most efficient and environmentally friendly ways to use sewage sludge. It is expected that paper sludge can be converted into a heterogeneous catalyst for Fenton-like reaction and achieve high catalytic activity and long-term stability.

In our work, paper mill sludge-derived catalyst PMS-Fe-400 synthesized via a facile method, was used as an effective and stable heterogeneous catalyst for Fenton-like reaction and characterized and implemented it for the discoloration and mineralization of synthetic dye. As for our target model pollutant, widely used methylene blue (MB) was chosen as our target model pollutant, which presents in most textile industrial wastewaters, dissolution in water and easy spectrophotometric measurement and can cause nausea, hypertension, hemolysis and respiratory distress [15,16]. Degradation experiments were taken for several times to evaluate the stability of the as-synthesized material. We provided an alternative environmentally friendly ways to dispose of and reuse of paper mill sludge, and at the same time obtained a stable and efficient heterogeneous catalyst for the degradation of MB. To the best of our knowledge, this might be

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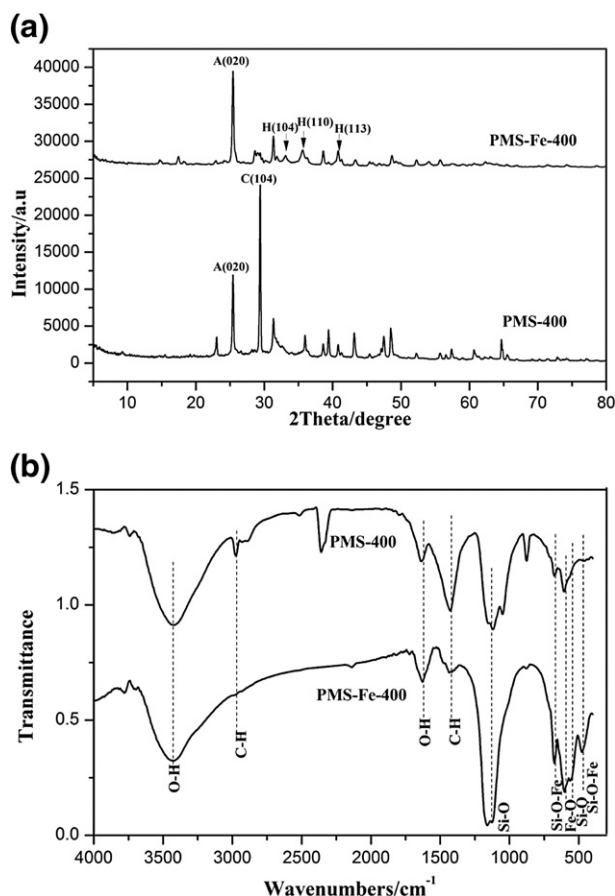


Fig. 1. (a) XRD spectrum (A represents Anhydrite, C represents Calcite, H represents hematite) and (b) FT-IR spectrum of paper mill sludge-derived catalyst.

the first attempt of directly converting paper mill sludge into a heterogeneous Fenton catalyst.

2. Experimental

2.1. Material

The sludge used in this study was collected from a paper mill effluent treatment plant located in Zhejiang, China, which has a design capacity of 20,000 m³/d. The sludge was stored at 4 °C before use. Hydrogen peroxide (H₂O₂, 30%, w/w), ferrous sulfate (FeSO₄·7H₂O), and methylene blue (MB) were of analytical reagent grade unless otherwise stated. All of the solutions were prepared with water from a water purification system (Merck Millipore Co., Shanghai, China).

2.2. Preparation of the catalyst

The hydrous sludge was dewatered naturally at room temperature in a ventilated place. The dewatered paper mill sludge sample was heated to 400 °C in a muffle furnace in air for 2 h to obtain the catalyst designated as PMS-400. The paper mill sludge-derived catalyst was prepared as follows: 10 g of dewatered sludge was added to 50 mL 0.5 M FeSO₄·7H₂O solution and stirred for 6 h at room temperature and then recovered via centrifuging and dried in air at 105 °C overnight. Finally, the Fe-loading sludge was calcined in air at 400 °C for 2 h, and the paper mill sludge-derived Fe-loading nanocomposite was designated as PMS-Fe-400.

2.3. Characterization

The functional groups of catalyst were detected by Fourier transform infrared (FT-IR) spectroscopy (Nexus, Thermo Nicolet Ltd., USA). The crystal structure of PMS-Fe-400 was analyzed by X-ray diffraction (XRD, Ultima IV, Rigaku Co., Japan).

2.4. Experimental procedures

Synthetic dye MB was chosen as the model pollutants to evaluate the catalytic activity of the as-synthesized catalyst. During the degradation process, 0.1 g of the catalyst was suspended in 100 mL of the MB (50 mg/L) aqueous solution. Before reaction, the suspension was sufficiently stirred for 10 min to disperse the catalyst. The initial pH of the reaction system was adjusted to 4 for the sake of consistency. 0.2 mL of the 3% H₂O₂ was added to initiate the degradation reaction. All experiments were carried out under constantly stirring to uniformly disperse the catalyst in the solution. About a 1-mL solution sample was withdrawn at given time intervals and centrifuged at 4 °C to immediately remove any catalyst particles. And then the solution samples were analyzed immediately by using a UV-Vis spectrophotometer (UV1750, Shimadzu Co., Japan). The content of total organic carbon (TOC) was determined by a TOC analyzer (TOC-V, CPH, Shimadzu Co., Japan). Moreover, to investigate the iron leaching behaviors from the catalyst, the iron ion concentration in solution versus time was measured by atomic absorption spectroscopy (AAS). PMS-Fe-400 was reused several times under the same conditions to evaluate the stability of the catalyst.

3. Results and discussion

3.1. Catalyst characterization

XRD was employed to investigate the structure and crystallinity of the as-prepared samples. As depicted in Fig. 1a, PMS-400 displayed two main diffraction peaks at $2\theta = 25.4^\circ$ and 29.4° , which corresponded to typical CaSO₄ (Anhydrite) and CaCO₃ (Calcite) crystallite structures respectively. However, the relative intensity of the Calcite (104) peak was remarkably weakened in the PMS-Fe-400 composite, which could be ascribed to the loading of Fe. Compared with PMS-400, the weak peak at $2\theta = 33.1^\circ$, 35.6° and 40.8° of PMS-Fe-400 can be assigned to the (104), (110) and (113) reflections of α -Fe₂O₃ (JCPDS, File No. 84-0306). Thus, the results suggested that PMS-Fe-400 mainly consisted of α -Fe₂O₃ (hematite) and CaSO₄ (Anhydrite) crystallites.

The functional groups and the chemical bonds on the catalyst surfaces were characterized by The FT-IR spectra. As showed in Fig. 1b, the peaks at 3451 and 1638 cm⁻¹ were assigned to O-H stretching

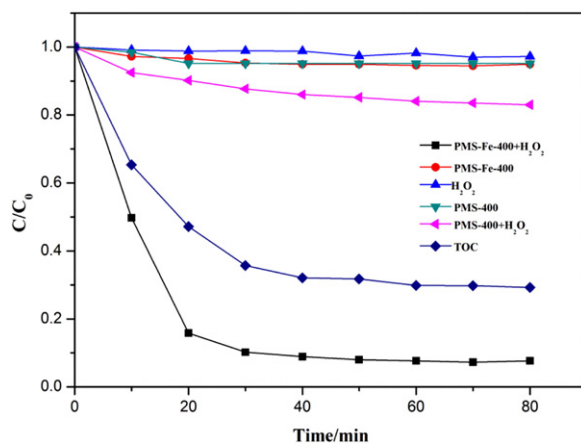


Fig. 2. Discoloration and TOC removal of MB under different systems (C_0 50 mg/L, H₂O₂ 1 g/L, Temp (25 ± 2) °C, pH = 4).

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