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Fenton-like degradation of Methylene Blue using paper mill sludge-derived magnetically separable heterogeneous catalyst: Characterization and mechanism

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ABSTRACT

For the paper industry, the disposal and management of the yielded sludge are a considerable challenge. In our work, the paper mill sludge-derived magnetically separable heterogeneous catalyst (PMS-Fe-380) was prepared easily through a facile synthesis method. The morphology and structure of PMS-Fe-380 were fully characterized by means of X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and Brunauer–Emmet–Teller analysis. The catalytic activity of PMS-Fe-380 was evaluated by degradation of Methylene Blue (MB). The reusability and stability of PMS-Fe-380 were evaluated in five repeated runs, which suggested that PMS-Fe-380 manifested excellent stability of catalytic activity. Moreover, leaching tests indicated that the leached iron is negligible (<0.5 mg/L). This study provides an alternative environmentally friendly reuse method for paper mill sludge and a novel catalyst PMS-Fe-380 that can be considered as a promising heterogeneous Fenton-like catalyst.

Introduction

Huge quantity of excess sludge is yielded by the pulp and paper industry during the paper manufacturing process. Paper mill sludge is generated as a byproduct by the paper wastewater treatment process in the paper mill. Under present pulp and paper technology, each ton of paper generates approximately 45 kg of dry excess sludge (Son et al., 2004). The contaminated sludge can have direct toxic effects on aquatic ecosystems, and through the bioaccumulation of toxic contaminants in the food chain, which can cause an indirect risk to humans (Nzihou and Stanmore, 2013). The disposal of paper mill sludge is quite dependable on the legislation applied in each country. Traditionally, paper mill sludge has been mainly disposed of by energy recovery, composting, incorporation into cement, and incineration, but these may cause potential environmental risks (Hamzeh et al., 2011). Taking into account that some of those traditional disposal options are being progressively restricted, it is essential to develop economically and environmentally acceptable methods to maximize recovery of useful materials and/or energy and minimize such residue from the paper industry (Stoica et al., 2009).

Fenton process is often employed to degrade non-biodegradable organic pollutants by the generation of relatively non-selective, strong oxidative hydroxyl radicals ($HO^{\cdot}$) (Garcia-Segura et al., 2012; Lucas et al., 2007). However, conventional homogeneous Fenton has some intrinsic drawbacks restricting the widespread application of, such as narrow pH range (pH 2–3), generation of huge amounts of iron sludge, deactivation by the iron complexation reagents and difficulty in recycling catalysts (Pignatello et al., 2006; Wang and Xu, 2012). These disadvantages have promoted the development of heterogeneous catalysts for the Fenton process. Heterogeneous Fenton

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catalysts are noncorrosive and environmentally benign, and are also more convenient to separate from treated wastewater (Soon and Hameed, 2011). Recently, many researches have been conducted and various catalyst supports have been employed to synthesize heterogeneous catalysts.

Paper mill sludge, which contains 20% or more solids, with 45%–55% moisture, is difficult to manage and dispose (Hamzeh et al., 2011). This kind of sludge contains two major components: fine cellulosic fibers that are 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 utilized by conversion into mesoporous adsorbents to remove organic pollutant from water or reclaimed as industrial raw material (Calisto et al., 2014; Devi and Saroha, 2014; Hamzeh et al., 2011). These methods are among the most efficient and environmentally friendly ways to make use of paper mill sludge. It was expected that paper mill sludge can be converted into a heterogeneous catalyst for Fenton-like reactions and achieve high catalytic activity and long-term stability.

In our work, the paper mill sludge-derived catalyst PMS-Fe-380, prepared *via* a facile method, was employed as an effective and stable heterogeneous catalyst for the Fenton-like reaction, and was characterized and implemented for the decolorization and mineralization of synthetic dye. The widely used dye Methylene Blue (MB) was chosen as our target model pollutant. It is present in most textile industrial wastewaters, soluble in water and easily measured by spectrophotometric techniques, and can cause nausea, hypertension, hemolysis and respiratory distress (Naraginti et al., 2015; Silva et al., 2011). Degradation experiments were carried out repeatedly to evaluate the stability and activity of the as-synthesized heterogeneous catalyst. Thus, we developed an alternative environmentally friendly method to dispose of and reclaim paper mill sludge, and meanwhile obtained an efficient and stable heterogeneous Fenton catalyst for the degradation of MB. To the best of our knowledge, this may be the first attempt to directly convert paper mill sludge into a heterogeneous Fenton catalyst.

1. Experimental

1.1. Material

The paper mill sludge used in this study was sampled from a paper mill effluent treatment plant located in Zhejiang, China, with a designed capacity of 20,000 m^3/day. The moisture content of the wet sludge is 87.7% ± 0.4%. The sludge was stored at 4°C before use. Hydrogen peroxide (H_2O_2, 30%, *w*/*w*), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), and 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).

1.2. Preparation of the catalysts

The moist sludge was dried naturally at room temperature. The dewatered sludge sample was heated to 380°C in a muffle furnace in air for 2 hr to obtain the material designated as PMS-380. The paper mill sludge-derived catalyst was prepared followed the below process: 10 g of dewatered sludge was added to 50 mL 0.5 mol/L $FeSO_4{\cdot}7H_2O$ solution and stirred for 6 hr at room temperature, and then recovered *via* centrifuging and dried in air at 105°C overnight. Finally, the Fe-loaded sludge was calcined in air at 380°C for 2 hr, and the paper mill sludge-derived Fe-loaded nanocomposite was designated as PMS-Fe-380.

1.3. Characterization

The crystal structure of PMS-Fe-380 was analyzed by X-ray diffraction (XRD; Ultima IV, Rigaku Co., Japan). The functional groups of the as-synthesized material were detected by Fourier transform infrared (FT-IR) spectroscopy (Nexus, Thermo Nicolet Lt., USA). The surface morphology was observed by scanning electron microscopy (SEM, FEI Co., The Netherlands). The surface area was determined by the Brunauer-Emmett-Teller (BET) method (ASIC-2, PE Co., USA). The bulk chemical composition of each element present were analyzed *via* an energy dispersive X-ray detector (EDX) attached to the SEM.

1.4. Experimental procedures

During the experiment, 0.1 g of the catalyst was suspended in 100 mL of MB (50 mg/L) aqueous solution. Before the reaction, the suspension was stirred for 10 min to sufficiently disperse the catalyst. For the sake of consistency, the initial pH of the reaction system was adjusted to 4. Then, 3% H_2O_2 was added to initiate the degradation reaction. All experiments were conducted under constant stirring to guarantee good dispersion of the catalyst. A 1-mL solution sample was withdrawn at given time intervals and centrifuged at 4°C to immediately remove any catalyst particles. Then the solution simples were analyzed immediately 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). The degradation process followed a pseudo first-order equation, and the kinetics was expressed as $\text{In}(C_0/C) = kt$, where, k (min^{-1}) represents the observed rate constant, and C_0 (mg/L) and C (mg/L) are the concentrations before and after reaction for t min, respectively. 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, AA-6300C, Shimadzu Co., Japan). To evaluate the stability of the catalyst, PMS-Fe-380 was recycled and reused several times under the same conditions.

2. Results and discussion

2.1. Catalyst characterization

Fig. 1 shows that the XRD pattern of PMS-380 exhibited two major diffraction peaks at $2\theta = 25.4°$ and 29.4°, which corresponded to typical $CaSO_4$ (anhydrite) and $CaCO_3$ (calcite) crystalline structures respectively. The results means that $CaSO_4$ and $CaCO_3$ were present in PMS-380, which agreed well with the EDS results (Table 1). However, as Fig. 1 depicted, the relative intensity of the calcite (104) peak was obviously weakened in the PMS-Fe-380 material, which may be due to the loading of iron. Compared with PMS-380, the weak peaks