



Synthesis of magnetically separable MnO₂/Fe₃O₄/silica nanofiber composite with enhanced Fenton-like catalytic activity for degradation of Acid Red 73

Xuekun Tang^{a,b,1}, Jing Huang^{a,b,1}, Kun Liu^{a,b,*}, Qiming Feng^a, Zishun Li^{a,b}, Minlin Ao^{a,b}

^a School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

^b Hunan Key Laboratory of Mineral Materials and Application, Central South University, Changsha 410083, China

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ABSTRACT

For the first time, the hierarchical MnO₂/Fe₃O₄/silica nanofiber (MnO₂/Fe₃O₄/SNF) composite was successfully fabricated by immobilization of highly dispersed Fe₃O₄ nanoparticles and MnO₂ nanosheets on the surface of chrysotile-based silica nanofiber through layer-by-layer assembly. In the composite, the silica nanofiber was served as backbone to inhibit the self-aggregation of nano-sized catalysts and maintain the stability of the overall structure. The as-synthesized composite was employed to catalyze the degradation process of Acid red 73 (AR-73) with the assistance of peroxymonosulfate (PMS). It was found that the composite exhibited an obvious enhancement in catalytic performance in comparison to the unsupported MnO₂ and Fe₃O₄/MnO₂ nanoparticles. Besides, the composite exhibited other advantages of easy separation and good recyclability. It was proposed that the excellent catalytic activity could be attributed to the high dispersion structure of the nano-catalyst in the composite. This research also exhibited the great potential of chrysotile-derived silica nanofiber as support material for the efficient assembly of nano-sized catalyst to apply in environmental remediation.

1. Introduction

Synthetic dyes, as the indispensable chemicals, are widely used in many industrial activities (e.g. textiles, paints and leather) [1]. However, dye-containing wastewater has been over discharged into ecosystem over the last decades and become one of the most widespread pollutant [1–3]. These organic chemicals are resistant to natural degradation and highly toxic even at low concentrations, which pose long-term risk and destruction to the ecosystem [1,4]. Thus, researches on the degradation of dyes in aqueous solutions are of practical significance.

To date, many environmental management technologies, such as biological treatment [5], ozonation [6], adsorption [7,8] and advanced oxidation process (AOP) [9], etc. have been applied for removal of dyes from effluent. Among these methods, AOP has been identified as a cost-effective option for treatment of dye-containing wastewater due to its high efficient [9,10]. As the most popular AOP, Fenton reaction using homogeneous or heterogeneous Fe(II)/H₂O₂ catalytic systems can generate hydroxyl radicals with high oxidative potential to degrade organic pollutants [9]. However, the demanding of low pH value (3–4) and generation of by-product (iron sludge) limit its broader application [11].

Sulfate radical (SO₄^{•-}), which can be generated from peroxymonosulfate (PMS) in neutral condition, has been considered as a promising alternative to hydroxyl radical (•OH). Besides, the SO₄^{•-} has higher redox potential (E₀ = 2.5–3.1 V) than that of •OH (E₀ = 1.9–2.7 V) [12]. For the generation of sulfate radicals from PMS, using transition metal oxides as catalyst is much more suitable than heating or UV light irradiation [10]. Among the various transition metal catalysts, MnO₂ stands out as one of the most appropriate catalyst for practical application [13,14]. Because, on the one hand, MnO₂ processes a high catalytic activity due to its unique Mn²⁺/Mn⁴⁺ redox loop [10,13]. On the other hand, MnO₂ has much higher cost performance and lower toxicity than the other transition metal oxides (e.g. CuO, CeO₂, Co₃O₄) [10]. It's known that the nano-sized MnO₂ exhibits much higher catalytic activity due to its larger exposed active surface [15]. However, similar to the other nano-catalysts, the fabrication and application processes of nano-sized MnO₂ suffer from several drawbacks, such as agglomeration, difficult separation and recovery of fine catalyst particles, which limit its practical application [10,16].

To overcome the drawbacks, we rationally designed a trilaminar core-shell structured MnO₂/Fe₃O₄/silica nanofiber composite (hereinafter referred to as MnO₂/Fe₃O₄/SNF) to enhance the catalytic activity and cyclicity of nano-sized MnO₂. In the composite, silica nanofiber

* Corresponding author at: School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China.

E-mail address: kliu@csu.edu.cn (K. Liu).

¹ These authors contributed equally to this work.

(SNF) prepared from natural mineral chrysotile is selected as the core material and serves as backbone of the composite to inhibit the self-aggregation of nano-sized catalyst and maintain the stability of the overall structure [17,18]. Because, for one thing, the SNF is composed of nearly 100% amorphous structured SiO_2 with a mass of surface hydroxyl groups [19]. Based on this property, it can effectively hinder the growth of nano-catalyst from agglomeration during thermal treatment and reaction [20–22]. For another, SNF has special 1D nano-structure with a diameter of 20–60 nm and a length of several microns [18,19]. In comparison to the micron-sized supports (such as diatomite [23], silica gel [24], active carbon [25] and allophane [26]), the nano-sized diameter enables SNF to provide much more surface area for immobilization of nano-sized catalysts to obtain a better dispersity [21]. Besides, the micron-length allows SNF to be easily recovered like the other micron-sized materials. On the surface of SNF, a layer of highly dispersed Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4\text{NP}$) is covered as the interlayer of the composite. Firstly, the incorporation of $\text{Fe}_3\text{O}_4\text{NP}$ enables the composite to be easily separated from solution via convenient and cost-effective magnetic separation method. Secondly, the $\text{Fe}_3\text{O}_4\text{NP}$ not only has the ability to catalyze PMS to generate sulfate radicals, but also can serve as co-catalyst for MnO_2 to enhance its catalytic performance [27,28]. The outer shell of the composite is composed of nano-sized MnO_2 catalyst due to its high catalytic activity [14]. Basing on the support of SNF, the MnO_2 in the outer shell will be highly dispersed, leading to enhanced catalytic performance.

Based on the above summary, it is therefore of considerable interest to develop the $\text{MnO}_2\text{-Fe}_3\text{O}_4\text{-SNF}$ combination system to realize a higher catalytic performance since no similar report has been published so far. Herein, in the current research, we synthesized this kind of $\text{MnO}_2/\text{Fe}_3\text{O}_4/\text{SNF}$ composite via thermal decomposition process and hydrothermal method. Acid Red 73 (AR-73), a typical azo dye, was selected as model degradation target to test the catalytic performance of $\text{MnO}_2/\text{Fe}_3\text{O}_4/\text{SNF}$ [29]. As expected, the as-prepared $\text{MnO}_2/\text{Fe}_3\text{O}_4/\text{SNF}$ has much higher catalytic performance towards AR-73 degradation than that of single MnO_2 or Fe_3O_4 . This work may inspire the future development of various catalyst by employing mineral-derived silica nanofiber as support.

2. Experimental

2.1. Materials preparation

All the reagents in the experiments were of analytical grade and commercial available. They were used as received without further purification. Deionized water was used throughout this study. Chrysotile collected from Xiaobabao asbestos mine, Qilian, Qinghai Province, China, was used as the raw material to prepare the silica nanofibers through physicochemical dispersion and acid leaching process according to our previous route [19].

The $\text{MnO}_2/\text{Fe}_3\text{O}_4/\text{SNF}$ was synthesized through a two-step approach. Firstly, highly dispersed Fe_3O_4 nanoparticles were immobilized on the surface of SNF through a thermal decomposition method. Briefly, 300 mg of as-prepared SNF and 900 mg of Iron (III) acetylacetonate were completely dispersed in 100 mL triethylene glycol under vigorous stirring to form a uniform suspension. After continual stirring for 30 min, the suspension was heated from room temperature to 278 °C at a heating rate of 3 °C/min in argon atmosphere and kept at reflux for 30 min. After natural cooling to room temperature, the solid content in the mixture was magnetically separated by a magnet and successively washed by ethanol and de-ionized water for 6 times. The collected solid was dried under 60 °C for 5 h in a vacuum oven to obtain the final product (named as $\text{Fe}_3\text{O}_4/\text{SNF}$).

Secondly, the MnO_2 nano-catalysts were coated on the surface of $\text{Fe}_3\text{O}_4/\text{SNF}$ through a hydrothermal method by using KMnO_4 as Mn source. Briefly, 300 mg of as-prepared $\text{Fe}_3\text{O}_4/\text{SNF}$ and 350 mg of KMnO_4 were homogeneously stirred in 70 mL de-ionized water for

10 min. After that, the mixture was transferred into a Teflon-lined autoclave with 100 mL capacity. The autoclave was sealed and heated to 160 °C for 16 h, then naturally cooled to room temperature. The resulting solid content in the autoclave was magnetically separated, then washed with deionized water for several times, and lastly dried at 60 °C in a vacuum oven for 5 h to obtain the final $\text{MnO}_2/\text{Fe}_3\text{O}_4/\text{SNF}$. For comparative purpose, the naked MnO_2 , Fe_3O_4 and $\text{MnO}_2/\text{Fe}_3\text{O}_4$ were also prepared according to the similar methods mentioned above without the addition of $\text{SNF}/\text{Fe}_3\text{O}_4$ or SNF.

Calculated from weight change data, the $\text{Fe}_3\text{O}_4/\text{SNF}$ was estimated to be composed of 39 wt% Fe_3O_4 and 61 wt% SNF, the $\text{MnO}_2/\text{Fe}_3\text{O}_4/\text{SNF}$ was estimated to be composed of 37 wt% MnO_2 , 25 wt% Fe_3O_4 and 38 wt% SNF.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer (Empyrean, Panalytical, Holland) using $\text{Cu K}\alpha$ source ($\lambda = 0.15418$ nm) at a scanning rate of 3°/min between 5° and 80°. The X-ray photoelectron spectroscopy (XPS) was performed on an ultrahigh vacuum electron spectrometer (K-Alpha 1063, Thermo Fisher, UK). Spectra were collected using a monochromatic Al $\text{K}\alpha$ source (1486.7 eV) and a $300 \times 500 \mu\text{m}$ spot size. Survey scans were performed at a pass energy of 100 eV and a step size of 1 eV, while a pass energy of 30 eV and a step size of 0.05 eV were adopted for the high-resolution scans. All binding energies were calibrated using contaminant carbon ($\text{C}1\text{s} = 284.6$ eV). The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on an infrared spectrometer (UV-2350, Shimadzu, Japan) from 4000 cm^{-1} to 400 cm^{-1} . Sixteen scans were accumulated with a resolution of 4 cm^{-1} for each spectrum. The morphological images of the as-prepared samples were acquired on a scanning electron microscope (SEM) (MIRA3 XMU/XMH, TESCAN, Czech) operated at an accelerating voltage at 200 kV and a transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan) at an accelerating voltage of 200 kV. The surface area, pore volume and pore size distribution were determined by nitrogen adsorption-desorption at 77 K on a Quantachrome Autosorb-1 system. Based on the nitrogen adsorption-desorption isotherm, the pore size distribution and the surface area were calculated by the BJH method and the BET equation. The magnetic properties of the samples were investigated on a vibrating sample magnetometer (7404, Lake Shore, USA).

2.3. Evaluation of catalytic performance

The evaluation of the Fenton-like catalytic activity was carried out at room temperature by degradation of AR-73 under the assistance of PMS. The chemical structure of AR-73 is illustrated in Fig. 1. In a typical degradation test, 10 mg as-prepared catalyst was dispersed in 100 mL AR-73 solution (30 mg/L) to form a suspension. Then, the suspension was continuously stirred for 30 min to establish adsorption-desorption equilibrium. After that, the catalytic reaction was initiated by adding PMS (2 mM) into the suspension. At predetermined intervals, about 3 mL of suspension was sampled and separated by a $0.45 \mu\text{m}$ syringe filters to produce clear solution. The concentration of AR-73 in the

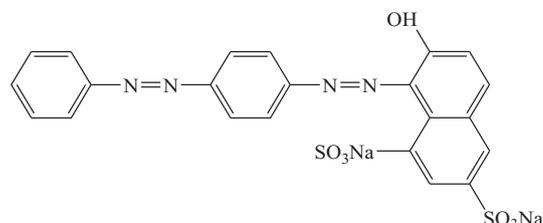


Fig. 1. Chemical structure of AR-73.

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