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Facile synthesis of sewage sludge-derived mesoporous material as an efficient and stable heterogeneous catalyst for photo-Fenton reaction

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ABSTRACT

The disposal of sewage sludge, which is produced numerously by wastewater treatment plants worldwide, is currently one of the most important environmental issues. Here we devised an alternative way of converting sewage sludge into mesoporous material (SS-Fe-350) through a facile synthesis method that resulted in an effective and stable heterogeneous catalyst for photo-Fenton reaction. X-ray diffraction, N_2 sorption isotherms and scanning electron microscope analysis indicated the existence of α-Fe_2O_3 within the pores of mesoporous SS-Fe-350 nanocomposite. The original dozens of mg/g of Fe content in the sewage sludge were also collectively identified as the catalytic site. A kinetic analysis showed that SS-Fe-350 exhibited rapid rhodamine B degradation and mineralization under UV light irradiation conditions and *p*-nitrophenol degradation and mineralization under both UV and visible ($\lambda > 400$ nm) light irradiation conditions. The possible reaction mechanism was investigated by the electron spin resonance technique. Moreover, SS-Fe-350 exhibited an excellent stability of catalytic activity and low Fe-ion leaching (<0.7 mg/L). This protocol provides an alternative environmentally friendly sewage sludge reuse method and a facile mesoporous material derived from sewage sludge that effectively degrades azo-dye and refractory organic pollutants.

1. Introduction

Sewage sludge, which consists of organic material, mainly dead bacterial cells, and inorganic component in the form of various oxides and salts, is defined as a pollutant by the US Environmental Protection Agency [1–4]. The annual amount of sewage sludge, which currently comprises about 30 million tons in China [5], 74 million tons in Japan [6], 5.6–7 million dry tons in the US [7] and 9.8 million dry tons in the EU [8], is estimated to increase continuously in the future. Thus, aggravated by their increasing numbers around the world, sewage sludge disposal is perhaps one of the most pressing problems related to water treatment plants currently. Traditional options for sludge disposal such as landfilling and ocean dumping are no longer acceptable, and alternatives such as thermal treatments also raise several concerns [9,10]. Therefore the initiative to reuse of sludge is certainly necessary from an environmental standpoint [11,12].

Heterogeneous photo-Fenton and photo-Fenton-like processes have the unique advantage of being able to completely mineralize organic pollutants by strongly oxidizing hydroxyl radical (OH•) generated, and can easily separate heterogeneous catalysts from treated wastewater while avoiding Fe leaching. They are among the most promising conversion processes for hazardous waste remediation and water disinfection [13–16]. Many studies have been performed and various supports have been used to prepare heterogeneous catalysts for the photo-Fenton process [16–18]. However, many heterogeneous catalysts encounter the leaching problem. The concentration of Fe ions is usually high due to a significant degree of leaching out from the heterogeneous catalysts during the photo-Fenton process, which not only causes the catalysts to lose their activity but also generates secondary metal ion pollution. In such cases, a cost-effective heterogeneous catalyst with high catalytic activity and long-term stability is essential to elevate catalytic efficiency and application.

Fe-based coagulants are among the most widely used coagulants in wastewater treatment plants worldwide, and the amount of Fe content in sewage sludge is significant, comprising dozens of mg/g of dried sludge [3,19,20]. Sewage sludge has been converted into mesoporous adsorbents and used to remove organics in the final stages of water cleaning, absorb acidic gases such as sulfur dioxide and hydrogen sulfide and remove chlorinated organics [11,20]. These are among the most efficient and environmentally friendly ways to use sewage sludge. It is expected that sewage

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sludge-derived material can be used as a heterogeneous catalyst for photo-Fenton reaction and to achieve high catalytic activity and long-term stability.

We developed a facile synthesis of sewage sludge-derived mesoporous material as an effective and stable heterogeneous catalyst for photo-Fenton reaction, and characterized and implemented it for the discoloration and mineralization of azo-dye under UV light irradiation conditions and organic pollutants under both UV and visible ($\lambda > 400$ nm) light irradiation conditions. For our target model pollutants, we chose the widely used Rhodamine B (RhB), which is harmful to humans on contact and toxic to aquatic organisms, and *p*-nitrophenol (*p*-NP), which the US Environmental Protection Agency considers a refractory, hazardous and priority toxic pollutant. We examined the stability of the as-synthesized catalyst and its possible photocatalytic mechanism by the electron spin resonance technique. Our study revealed alternative environmentally friendly ways to dispose of and reuse of sewage sludge, and provided a facile, stable and efficient heterogeneous catalyst for photo-Fenton reaction. To the best of our knowledge, this might be the first attempt of directly converting sewage sludge into a heterogeneous photo-Fenton catalyst under both UV and visible light irradiation conditions.

2. Experimental

2.1. Preparation of the catalysts

The dewatered sewage sludge sample used in this study was obtained from the Anting wastewater treatment plants located in Shanghai, China, which have a design capacity of 150,000 m^3/d [5]. The collected sludge was stored at 4 °C before use. All of the organic and inorganic reagents were of analytical grade unless otherwise stated. All of the solutions were prepared with water from a water purification system (Hitech Instrument Co., Shanghai, China).

The dewatered sewage sludge sample was heated to 350 °C in a muffle furnace in air for 3 h to obtain the catalyst known as SS-350. The sewage sludge-derived Fe-loading mesoporous material was prepared as follows: 10 g of dewatered sewage sludge was added to 20 ml 1 M $FeSO_4 \cdot 7H_2O$ solution and stirred for 3 h at room temperature. The Fe-loading sewage sludge was then recovered via centrifuging and dried in air at 105 °C overnight. Finally, the dried solid, which was designated SS-Fe-105, was calcined in air at 350 °C for 3 h, and the sewage sludge-derived Fe-loading nanocomposite was obtained and designated SS-Fe-350.

2.2. Characterization of the as-synthesized catalysts

Fourier transform infrared (FTIR) spectra were obtained on a KBr disk with a VERTEX 70 FT-IR (Bruker Co., Germany) to determine the functional groups of catalysts. The crystal structure of the as-synthesized catalysts was characterized via X-ray diffraction (XRD; X' Pert PRO, Philips Co., The Netherlands), and its morphology was observed using scanning electron microscopy (SEM; FEI Co., The Netherlands). The bulk chemical compositions of the catalysts were determined via an X-ray fluorescence spectrometer (XRF, PW2402, Philips Co., The Netherlands), and the Fe content was also measured via inductively coupled plasma spectrometry (ICP, Agilent 720ES, USA) after microwave digestion in a Teflon vessel using a mixture of HNO_3 + HCl + HF. The surface area was calculated according to the Brunauer–Emmett–Teller (BET) method.

2.3. Heterogeneous photo-Fenton degradation of RhB and p-NP

Azo-dye RhB and a typical persistent organic pollutant known as *p*-NP were chosen as the model pollutants to evaluate the photocatalytic activity of the as-synthesized catalysts. The photo-Fenton reactions were performed in a quartz glass cylinder measuring 8.5 cm high and 5.5 cm in diameter and filled with 150 ml of RhB (55.5 mg/L) or *p*-NP (65 mg/L) solution with constant magnetic stirring. A 30-W low-pressure mercury lamp was used as the UV light source and fixed next to the cylinder. For the experiments under visible light ($\lambda > 400$ nm) irradiation, an 11-W Philips GENIE cool daylight lamp was used with 2 M $NaNO_2$ acting as a cutoff filter [21]. The reaction temperatures were kept at 25 °C via an air conditioner. Outdoor experiments under solar light irradiation were also carried out.

During the degradation process, 0.05 g of as-synthesized catalyst was dispersed into the reactor, except for the control test in which no catalyst was added. The suspension was stirred in the dark for 30 min to disperse the catalyst, and then the pH of the reaction solution was adjusted to 4.00 for the sake of consistency. After the first sample was taken, the degradation reaction was initiated by adding 1 ml 3% H_2O_2 into the RhB solution or 1 ml 1.2% H_2O_2 into the *p*-NP solution, respectively, except for the control test in which no H_2O_2 was added. At given time intervals during the reaction, solution samples were taken and centrifuged at 4 °C to immediately remove any catalyst particles.

Electron spin resonance (ESR) signals of radicals trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were recorded at ambient

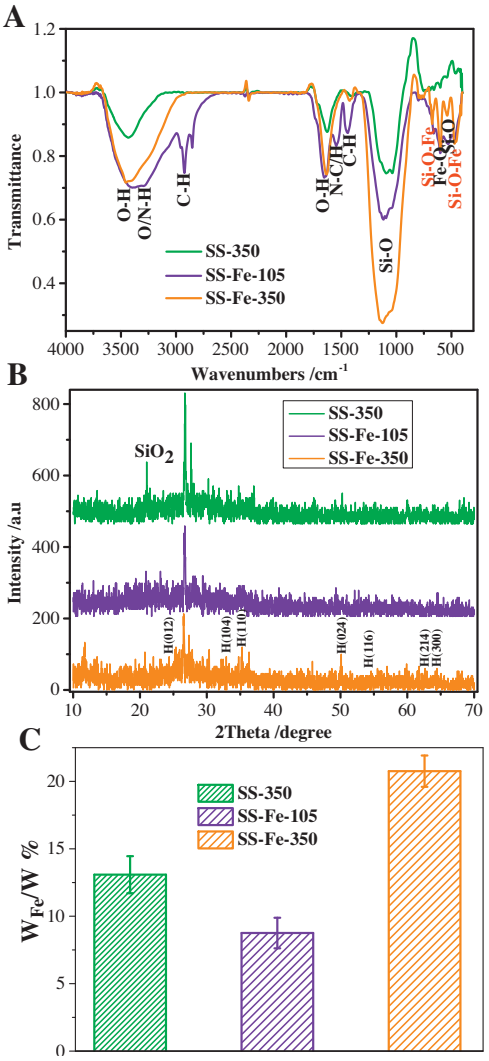

Fig. 1. Characterization of the as-synthesized sewage-sludge-derived catalysts. (A) FTIR spectra. (B) XRD spectrum (H represents hematite). (C) The respective Fe concentration (w/w%).