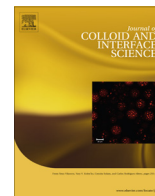




Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



Regular Article

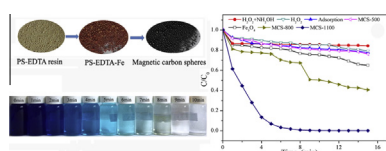
Novel magnetic porous carbon spheres derived from chelating resin as a heterogeneous Fenton catalyst for the removal of methylene blue from aqueous solution



Junjun Ma, Lincheng Zhou*, Wenfeng Dan, He Zhang, Yanming Shao, Chao Bao, Lingyun Jing

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Institute of Biochemical Engineering & Environmental Technology, Lanzhou University, Lanzhou 730000, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 October 2014

Accepted 14 January 2015

Available online 24 January 2015

This paper is dedicated to the memory of Professor Yanfeng Li

Keywords:

Magnetic carbon spheres
 Ion-exchange
 Methylene blue
 Fenton-like catalytic
 Degradation

ABSTRACT

Porous magnetic carbon spheres (MCS) were prepared from carbonized chelating resin composites derived from ethylenediaminetetraacetic acid-modified macroporous polystyrene (PS-EDTA) resin, and then loaded with iron composites via ion exchange. The resulting composites were characterized for this study using X-ray diffraction, Mössbauer spectroscopy, and Raman spectroscopy, X-ray photoelectron spectroscopy, Brunauer–Emmett–Teller surface area method, scanning electron microscopy, and vibrating sample magnetometry. The porous magnetic carbon spheres were then used, in the existence of H_2O_2 and NH_2OH , with a view to remove methylene blue from the aqueous solution by catalyze a heterogeneous Fenton reaction. Results indicated excellent removal rates and removal efficiency for this catalytic system. Optimal degradation was achieved (nearly 100% within 10 min) using initial concentrations of $5 \text{ mmol H}_2\text{O}_2 \text{ L}^{-1}$, $2.5 \text{ mmol L}^{-1} \text{ NH}_2\text{OH}$ and 40 mg L^{-1} methylene blue. The catalyst retained its activity after six reuses, indicating strong stability and reusability. Porosity of the catalyst contributed to its high activity, suggesting its potential application for the industrial treatment of wastewater.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Advanced oxidation processes (AOPs) are becoming increasingly important technologies due to their potential effectiveness for treating organic pollutants, especially contaminants resistant to biodegradation [1]. AOPs involve various chemical, photocatalytic, electrocatalytic, and Fenton oxidation methods [2–4]. The environmentally benign and inexpensive Fenton process has its own unique advantages as an oxidizing method, including high degradation efficiency, simple operation, and mild reaction conditions [5,6].

This process involves the reaction between hydrogen peroxide as an oxidant, and iron ions as a catalyst, to produce highly active, mainly non-selective $\cdot\text{OH}$ radicals with oxidation potentials of 2.8 V [7]. A Fenton reaction using iron salts as catalysts is defined as a homogeneous Fenton process [8]. However, there are some drawbacks associated with this method, including mass transfer limitations, pH dependence of the system (2.5–4.0) [9], and difficult recovery. Heterogeneous Fenton catalysts, which employ porous supporters as the iron composite carriers in Fenton reactions, represent a possible solution to overcoming the problems associated with homogeneous catalysis. Porous carbon is inexpensive, non-toxic and harmless to the environment. Porous carbon spheres possess high specific surface area, which make them ideal heterogeneous Fenton

* Corresponding author.

E-mail address: zhoulc@lzu.edu.cn (L. Zhou).

catalyst supports. Due to these important qualities, significant research efforts have been directed towards loading iron composites onto the porous carbon spheres, for applications involving degradation of organic pollutants [10–12].

Several studies have reported the application of porous magnetic carbon spheres synthesized by carbonizing polymer spheres, which were then loaded with iron precursors. Polymer microspheres were frequently used as the carbon sources, as they possess many advantages, including their small size, ease of handling, and reduced diffusion limits [13–15]. However, this preparation technology is complex, and costly. Conversely, chelating resins are inexpensive and environmentally friendly, and can be modified by attaching a variety of chemical functional groups exhibiting extremely high chelating capacity for metal ions [16]. At present, we are aware of only one study reporting the preparation of a porous magnetic carbon ball carbide, synthesized via carbonized ion exchange of a resin sphere in a $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ solution, and its subsequent application for the adsorption of organic matter [17]. Although these magnetic carbon spheres are characterized by high surface areas, increased absorption capacity, and reusability, they have not been shown to thoroughly remove all organic pollutants. Additionally, to the best of our knowledge, this current study is the first to report the use of a chelating resin as a carbon source to synthesize a heterogeneous Fenton catalyst for the degradation of methylene blue (MB).

In this study, porous magnetic carbon microspheres (MCS) with catalytic properties were prepared using an ethylenediaminetetraacetic acid-modified macroporous polystyrene (PS-EDTA) resin that had been loaded with Fe^{3+} by ion exchange. This industrial resin is a relatively inexpensive carbon source that can be prepared using simple methods. The MCSs were then characterized using X-ray diffraction (XRD), Raman spectroscopy, Mössbauer spectroscopy (MS), the Brunauer-Emmett-Teller (BET) analyses, scanning electron microscopy (SEM), and vibrating sample magnetometry (VSM). The ability of the MCSs to catalyze the heterogeneous Fenton oxidation of MB was tested under different conditions of initial pH, catalyst dosage, H_2O_2 concentration, and NH_2OH concentration. The stability and reusability of MCS was also assessed. Their removal mechanism was investigated by LC-MS. Its excellent performance and low simple cost preparation gives the composite great utility practical value.

2. Experimental

2.1. Preparation of the MCSs

The PS-EDTA resins were synthesized according to the method described by Yang et al. [18]. Approximately 2 g of PS-EDTA were soaked in 50 mL of FeCl_3 (0.02 mol/L) solution in an Erlenmeyer flask, and rotated for 12 h at 45 °C and pH 2.0. The PS-EDTA was separated from the mixture by filtration and the excess iron ions were removed by washing thoroughly with distilled water. The PS-EDTA-Fe was appended in a column, followed by addition of an aqueous solution containing NaCl and NaOH (5% w/v), which immediately turned reddish brown. The assembled beads were thoroughly washed with distilled water to neutral pH. After drying for 12 h at 60 °C, the samples were carbonized by heating the samples from 500 to 1100 °C at a rate of 5 °C/min, under an N_2 atmosphere. The resulting magnetic carbon sphere composites were named as MCS - t (where t was the carbonization temperature).

2.2. Characterization of the materials

The crystal structures of MCSs catalysts were monitored by X-ray diffraction (XRD, model D-MAX-RB, Riau, Japan). The param-

eters of the XRD were Cu $K\alpha$ and $l = 0.154$ nm. Raman spectra were recorded on a Dilor LABRAM-1B multichannel confocal micro spectrometer. Mössbauer spectra were obtained with a $^{57}\text{Co}/\text{Rh}$ source, at liquid N_2 temperatures, calibrated with $\alpha\text{-Fe}$. X-ray photoemission spectroscopy (XPS) was recorded on a Kratos ASIS-HS X-ray photoelectron spectroscope equipped with a standard and monochromatic source (Al $K\alpha$) operated at 150 W (15 kV, 10 mA). The N_2 adsorption-desorption isotherm was measured at liquid N_2 temperature (76 K) using a Micromeritics ASAP 2010M instrument. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The morphologies of the MCSs composites were characterized by scanning electron microscopy (SEM JSM-6701F). Magnetic properties were characterized by a vibrating sample magnetometer (VSM, LAKESHORE-7304) at room temperature. UV-vis detection was carried on a TU-1810PC UV-vis spectrophotometer (Purkinje General, Beijing, China). All fluorescence spectra were recorded using an F97Pro spectrofluorophotometer (Leng Guang Industrial Co., Ltd., Shanghai, China). The reactions were also monitored by LC-MS Trap mass spectroscopy (AB 3200-QTRAP), ESI conditions were as follows: dry gas temperature, 553 K; dry gas (N_2) flow rate, 5 L min^{-1} ; nebulizer pressure, 10 psi; capillary voltage, 4.5 kV; skimmer voltage, 30 V; capillary exit, 70 V; the target mass set to 300.

2.3. Testing catalytic activity

The degradation experiment was conducted by adding carbon spheres to 20 mL of a 40 mg L^{-1} MB solution in the presence of H_2O_2 and NH_2OH , and the suspension was shaken at 30 °C. The pH of the solution was without any adjustment during the catalytic reaction. After the reaction, the carbon spheres were separated using an external magnetic field, and the reaction mixture was filtered through a micro filtration membrane (0.45 μm) to separate the powder MCS catalyst. The concentration of MB was then determined using an UV-vis spectrometer, with a maximum absorbance wavelength for MB at 614 and 664 nm. After the reaction, the catalyst was separated by an external magnetic field, and then the same amount of fresh methylene blue, H_2O_2 , and NH_2OH solution were added into the reaction flask after each recycled. The recycle ability of the MCS catalyst was evaluated by successive tests of MB decolorization and TOC removal efficiency.

To evaluate the mineralization of the MB, total organic carbon (TOC) was measured, equipped with an automatic sample injector as described previously. Reported TOC values represent the average of at least three measurements.

The solutions containing leached iron ions were obtained and tested by inductively coupled plasma emission spectroscopy (ICP). The values represent the average of three measurements.

2.4. The degradation mechanism

The organic compounds where in the reaction solution during the decolonization were measured using liquid chromatography and mass spectrometry (LC-MS).

3. Results and discussion

3.1. Characterization of MCSs

The method to fabricate MCSs spheres for ultrafast oxidative decomposition of MB dye is illustrated in Fig. 1. In the first step, the carboxyl group on the surface of PS-EDTA forms a complex with Fe^{3+} at pH 2.0. This process results in binding of numerous iron ions by an electrostatic force. The Fe^{3+} is subsequently desorbed and simultaneously precipitates as Fe^{3+} hydroxides during

Download English Version:

<https://daneshyari.com/en/article/6997081>

Download Persian Version:

<https://daneshyari.com/article/6997081>

[Daneshyari.com](https://daneshyari.com)