



Preparation and catalytic activity of Fe alginate gel beads for oxidative degradation of azo dyes under visible light irradiation

Yongchun Dong*, Wenjing Dong, Yanan Cao, Zhenbang Han, Zhizhong Ding

Division of Textile Chemistry and Ecology, School of Textiles, Tianjin Polytechnic University, 63 Chenglin Road, Hedong District, Tianjin 300160, China

ARTICLE INFO

Article history:

Received 14 October 2010

Received in revised form 20 February 2011

Accepted 14 March 2011

Available online 9 April 2011

Keywords:

Ferric ion

Alginate

Gel bead

Fenton catalyst

Dye degradation

ABSTRACT

Fe alginate gel beads were prepared by adding sodium alginate aqueous solution drop-wise into the FeCl_3 gelling solution using a syringe needle at room temperature, and measured in terms of size, mass and Fe content, then characterized using SEM, XRD, FT-IR, XPS and TGA, respectively. The gel beads were evaluated as the heterogeneous Fenton catalysts for oxidative degradation of two typical azo dyes, Reactive Blue 222 and Acid Black 234 in the presence of H_2O_2 under visible light irradiation. Some important factors affecting the preparation of the beads and their catalytic function such as FeCl_3 concentration, irradiation intensity and pH value were examined. The results indicated that Fe^{3+} ions coordinated with oxygen atoms in carboxyl groups from glucose chains of alginates to form the Fe alginate gel beads. And Fe^{3+} ion was a central cation that has a coordination number of 6 in the complex. Higher concentration of FeCl_3 solution caused the significant increase in the Fe content of the gel bead during preparation. Fe alginate gel beads showed a great catalytic role in the degradation of the azo dyes in a wide pH range of 3.0–8.0. Moreover, higher Fe content and increasing irradiation intensity could promote the catalytic performance of Fe alginate gel beads.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Photoassisted Fenton technologies have been widely used in the degradation of water-soluble organic dyes in the industrial wastewater. Ferrous salts react with H_2O_2 to produce hydroxyl free radicals during the Fenton reaction, which attack the unsaturated dye molecules, thus decolorizing the wastewater [1]. However, it should be noticed that Fenton reactions are limited to the acidic $\text{pH} < 4$. Moreover, the Fe ion sludge with a large volume after Fenton reaction is a considerable drawback because the removal of the Fe ions at the end of treatment by precipitation is rather a costly process. To avoid these limitations, some attempts have been made to develop the heterogeneous photocatalysts for the Fenton reactions by immobilizing Fe ions on the polymer substrates. For example, a Nafion membrane [2–4] or pellet [5] was used for immobilizing Fe ions to form a Fe/Nafion catalyst for the decoloration of azo dye in water. But, it is known that Nafion membrane or pellet is too expensive to be used as a catalyst support in an industrial scale [6]. Hence, it is necessary to explore new heterogeneous catalysts for the photoassisted Fenton reactions by using lower cost polymer materials as the support substrates. The fibrous heterogeneous Fenton catalysts were produced by ligating reaction between modified

polyacrylonitrile fibers and ferric ions. And it was found that the dyeing wastewater was decolorized with H_2O_2 in the presence of fibrous catalysts [7,8].

Alginate acid is a naturally occurring linear polysaccharide composed of (1–4)-linked-D-mannuronic acid (M units) and -L-guluronic acid (G units) monomers, which vary in amount and sequential distribution along the polymer chain depending on the source of the alginate [9]. Moreover, because of the unique gelling properties, alginates can react with metal ions to form stable organic–inorganic hybrid composite materials, which may be found promising applications in the environmental purification and remedy areas [10–13]. In addition, it has been reported that complex of Fe ions with alginate was active during the Fenton-enhanced degradation of Orange II [12]. However, the information regarding preparation and catalytic function of Fe alginate gel beads as the heterogeneous Fenton catalysts for the degradation of the organic pollutants is still scarce. In the present study, we aim to prepare and characterize the Fe alginate gel beads and evaluate their catalytic property in the oxidative degradation of two azo dyes in the presence of H_2O_2 . The influence of some important variables on the preparation and catalytic performance of the beads was also investigated. In addition, we are more concerned about whether Fe alginate gel beads have better catalytic performance for the dye degradation at or over $\text{pH} 5.0$ to avoid the costly initial pH adjustment of many effluents to attain acidic conditions before applying the oxidative treatment.

* Corresponding author. Tel.: +86 22 24528430; fax: +86 22 24528054.
E-mail addresses: dye@tjpu.edu.cn, dyefib@yahoo.com.cn (Y. Dong).

2. Experimental

2.1. Materials and reagents

Sodium alginate and $\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$ were of agent grade and obtained from Shanghai Medical Co. (Shanghai, China). Two azo dyes including Reactive Blue 222 (Abbr. RB 222) and Acid Black 234 (Abbr. AB 234) were commercially available, and purified by reprecipitation method in this experiment, the molecular structures of which are presented in Scheme 1. Double distilled and deionized water was used throughout the study.

2.2. Preparation of Fe alginate gel beads

A given concentration of sodium alginate aqueous solution was prepared by dissolving the appropriate weight of solid sodium alginate in distilled water. Five milliliters of sodium alginate solution was added drop-wise into a 250 ml FeCl_3 gelling solution using a 1.0-mm syringe needle at a dropping rate of approximate 1.0 ml min^{-1} at room temperature to produce the Fe alginate gel beads. These brown beads were cured for 6 h in the gelling solution with mild stirring (60 rpm) using magnetic mixer at room temperature, and then filtered off and washed repeatedly with distilled water, and stored in distilled water for the dye degradation study.

2.3. Determination of coordination number for Fe alginate complex

To determine the coordination number for Fe alginate complex, an electric conductivity method reported by Cheng et al. [14] was used in this work. Different concentrations ($0.25\text{--}12.0 \text{ mmol L}^{-1}$) of FeCl_3 aqueous solution were prepared and mixed with 3.00 mmol L^{-1} sodium alginate aqueous solution at the same volume (25 ml) in order to obtain a series of reaction systems with different molar ratios of the concentration of FeCl_3 to the concentration of sodium alginate in solution. The coordination reactions in these systems were conducted at 25°C until the reaction equilibrium was reached. And the electric conductivities for different concentrations of FeCl_3 solutions before and after coordination reaction were determined using a DDSJ-308A conductivity meter (Shanghai Jingmi Instrumental Co., China). Then the difference in the electric conductivity between FeCl_3 solutions before and after coordination reaction for each concentration was calculated and used to determine the coordination number for the resulting complex of Fe^{3+} ion with alginate. It is noticed that the electric conductivities of distilled water and 3.00 mmol L^{-1} sodium alginate aqueous solution were also measured to be $1.12 \times 10^{-2} \text{ ms cm}^{-1}$ and 1.29 ms cm^{-1} at 25°C , and took out from the calculation for the electric conductivities of FeCl_3 solutions and reaction systems, respectively.

2.4. Characterization for Fe alginate gel beads

2.4.1. Diameter and mass

The diameter and mass of Fe alginate gel beads in wet or dry state were measured using digital vernier calipers and balance, respectively, and then mean diameter and mean mass of each gel bead were obtained by the measurement of 20 beads out of approximately 200.

2.4.2. Fe content ($C_{\text{Fe-bead}}$)

In order to determine the Fe content immobilized on the surface of Fe alginate gel beads, they were selected randomly and treated with 50 ml of 2.0 mol L^{-1} H_2SO_4 aqueous solution at room temperature for 24 h. Fe^{3+} ions were released from Fe alginate gel beads and dissolved in acidic solution. And then the concentration of Fe^{3+} ions

in the solution was determined by using a WXF120 atomic absorption spectrometer (Beijing Rayleigh Analytical Instrument Co.), for calculating total Fe content of the beads. Average Fe content for single bead was obtained by the measurement of 20 beads out of approximately 200.

2.4.3. Composition and structure

The composition of Fe alginate gel bead was verified by using a Nicolet Magna-560 Fourier transform spectrometer (Nicolet Instrument Co., USA) with 4 cm^{-1} resolution. The powder X-ray diffraction measurement of the bead was conducted on a Rigaku Xd/Max-2500 X-ray diffractometer (Rigaku Co., Japan) operating with Cu K α radiation at 40 kV and 20 mA, 2θ ranges from 5° to 80° , and the scan rate used was $0.025^\circ/\text{min}$. The binding energy analyses were performed on a PHI 5600 X-ray photoelectron spectrometer (Pekin Elmer Co., USA), and binding energy of C1s was shifted to 284.8 eV as the reference. The surface morphology of Fe alginate gel beads was examined by FEI Quanta 200 scanning electron microscope (FEI Co., USA). TGA (Thermal Gravimetric Analysis) of the samples was carried out with a STA 409 PC thermal analyzer (NET-ZSCH Co., Germany). TGA of the samples was performed up to a temperature of 700°C , with a starting point at room temperature in an atmosphere of nitrogen. The heating rate was uniform in all cases at $10^\circ\text{C min}^{-1}$.

2.5. Activity towards H_2O_2 decomposition

100 Fe alginate gel beads as the catalysts were placed into the reactor containing 150 ml of 0.10 mol L^{-1} H_2O_2 aqueous solution. Air was delivered to the H_2O_2 solution from the bottom of the reactor in order to ensure thorough mixing of the beads with the solution. The reaction temperature was 25°C , and air supply was 100 ml min^{-1} . To examine the H_2O_2 decomposition in the presence of the beads, 1–2 ml of samples were withdrawn for analysis of the residual H_2O_2 concentration at intervals of time and analyzed by titration with 0.02 mol L^{-1} concentration of KMnO_4 solution [7]. The analysis of the residual concentration of H_2O_2 was repeated three times for each sample and the results were averaged.

2.6. Photocatalytic reaction setup

The photoreaction system was specially designed in this experiment and consisted mainly of chamber, lamp, electromagnetic valve, relay, and water bath. A 400 W high pressure mercury lamp (Foshan Osram Illumination Co., China) was used as illuminating source for photocatalytic reaction. A cut-off filter was used to ensure irradiation only by visible light ($\lambda > 420 \text{ nm}$). The chamber was made of polished aluminum because it is highly reflective in the visible light range. Ten open Pyrex vessels of 150 ml capacity were used as reaction receivers in water bath. An electromagnetic valve was operated by relay and used to control temperature in water bath. The intensity of visible light irradiation over the surface of test solution was controlled by adjusting the distance between lamp and surface of test solution, and was measured using FZ-A radiometer (Beijing BNU Light and Electronic Instrumental Co., China). The schematic diagram of photoreaction system was described in Fig. 1.

2.7. Photocatalytic procedure and analysis

Stock dye solutions were prepared by dissolving 5.0 g of each dye in 1000 ml of boiling deionized water. Test solutions (100 ml) were made by diluting the stock to typical effluent dye concentration of 0.05 mmol L^{-1} and followed by addition of 3.0 mmol L^{-1} H_2O_2 and 50 Fe alginate gel beads (unless otherwise stated). And NaOH (0.10 mol L^{-1}) and HNO_3 (0.10 mol L^{-1}) solutions were used to adjust pH values. Test solutions were then placed into reaction

Download English Version:

<https://daneshyari.com/en/article/55761>

Download Persian Version:

<https://daneshyari.com/article/55761>

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