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Fenton-like catalytic activity of wet-spun chitosan hollow fibers loaded with Fe_3O_4 nanoparticles: Batch and continuous flow investigations

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ABSTRACT

Fenton-like catalysts based on nanosized Fe_3O_4 impregnated on dry–wet spun chitosan hollow fibers (CS HFs) were prepared according to the dipping-drying method. The prepared catalysts were characterized using XRD, SEM and TEM. The Fenton-like catalytic activity of prepared Fe_3O_4-chitosan hollow fibers was evaluated by the degradation of reactive blue 19 as model dye. Effects of pH and H_2O_2 concentration on improving the catalytic activity were investigated. It was found that heterogeneous Fenton-like degradation of the dye follows an apparent pseudo first order kinetic model. The reusability of prepared catalysts was also investigated after three successive runs. The catalytic performance of Fe_3O_4–CS HFs was finally studied in a continuous system, for which with a tailored module was designed.

1. Introduction

The exponential growth of industries and population has put considerable attention on the earth's natural resources. Likewise, pollution related to human activities has increased greatly over the past few decades [1]. Nowadays, a great development has been achieved for destructing persistent organic pollutants in wastewaters by advanced oxidation processes (AOPs) [2]. These AOPs, although making use of different reacting systems, are all characterized by the same chemical feature: the production of hydroxyl radicals, a very reactive species that attacks most of the organic molecules with little or no selectivity [3].

The Fenton reaction is one of the most used AOPs to generate hydroxyl radicals, which consists in the use of a combination of hydrogen peroxide and a soluble ferrous salt [4]. Fenton reactions have become of great interest due to the two facts: (i) hydrogen peroxide is inexpensive, easy to handle and relatively safe (ii) iron is comparatively inexpensive, safe and environmentally friendly with respect to any other transition metal [5].

However, several drawbacks of the current Fenton process limit the scale-up of its application, including the narrow pH range for reaction (pH 2.5–3.5) and the accumulation of iron-containing sludges, which are regarded as a secondary pollution involving the loss of catalyst [6].

Heterogeneous catalysts with low Fe dissolution, such as iron oxides and mixed oxides (Fe_3O_4/CeO_2), Fe^0 nanoparticles are increasingly replacing homogeneous Fe^{2+}/Fe^{3+} solutions to prevent the accumulation and precipitation of iron from Fenton reacting systems [7].

In addition, chelate based-Fenton reactions, in which chelating agents can minimize loss of iron by avoiding its precipitation, have

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been reported to significantly enhance the degradation of organic contaminants even at neutral pH [5,8,9].

Chitosan (CS), a linear natural polysaccharide prepared by partial deacetylation of chitin extracted from crustacean shells, is environmentally friendly, biocompatible and excellent biosorbent for metal ions owing to its functional groups and structural features [10].

Recently, CS has attracted researchers' attention as a natural chelating agent of catalytic metal ions [9,11–14]. One of the most interesting advantages of chitosan is its processability into different physical forms and morphologies, such as powder, nanoparticles, gel beads, membranes, sponge, fibers or hollow fibers (HFs) [15].

However, to the best of our knowledge, most studies on the heterogeneous Fenton reactions based on CS as a bio-chelating agent report the use of CS in the form of powders, flakes or gel beads that are difficult to be used for practical application.

This is the first study on the Fenton-like catalytic properties of nanoscale Fe_3O_4 impregnated on dry–wet spun CS HFs. Herein, we report the development of Fenton-like catalysts based on nanosized Fe_3O_4 impregnated on the CS hollow fibers prepared according to the dipping-drying method. The influence of operational parameters on the catalytic properties of the prepared materials was evaluated during the oxidation of reactive blue 19 (RB 19) as a model pollutant.

2. Experimental

2.1. Materials

All reagents were of analytical grade and were used without further purification. The experiments described in this work employed reactive blue 19 (RB19) also known as Remazol Brilliant Blue R (Color index number: 61200, chemical formula: $C_{22}H_{16}N_2Na_2O_{11}S_3$, M_W: 626.54 g mol^{-1}, λ_{max}: 598 nm) as a model pollutant. The solutions were prepared with distilled water.

2.2. Preparation of catalysts

Chitosan hollow fibers were prepared according to the procedures reported in our previous works [16,17]. The preparation of Fe_3O_4–CS HFs was carried out as follows. First, the as-spun CS hollow fibers were crosslinked by immersing in glutaraldehyde bath (5 g l^{-1}) for 1 h. The reason for choosing high concentration of glutaraldehyde was to prevent dissolving of CS HFs in solutions containing of iron ions. After removal from the glutaraldehyde solution, the crosslinked CS HFs were rinsed with distilled water. Then, the crosslinked CS HFs were soaked in the $FeCl_3{\cdot}9H_2O$ solution (0.1 M) for 30 min. The chitosan HFs were washed with deionized water, and soaked in the $FeSO_4{\cdot}7H_2O$ (0.05 M) solution for 30 min. After that, the CS HFs with iron ions were washed with deionized water. This cycle was repeated three times and Fe (II and III)–CS HFs complex was obtained. Finally, the HFs were soaked in the NaOH (3 M) solution for 12 h at 60 °C to achieve Fe_3O_4–CS nanocomposite hollow fibers. Then the Fe_3O_4–CS HFs were washed with deionized water and dried. Removing water directly from a wet hollow fiber in the air may cause changes of its morphology. Therefore, solvent exchange drying in a two-step procedure was used as an effective method to minimize changes of HFs morphology according to previously published procedures [16,17]. Although the crosslinking reaction of CS with glutaraldehyde determines a worsening of mechanical properties, nevertheless the prepared CS hollow fibers loaded with Fe_3O_4 nanoparticles have acceptable mechanical properties.

2.3. Characterization

The morphology of synthesized catalysts was studied by SEM (QUANTA 200 FEI ESEM). Hollow fibers were freeze fractured, using liquid N_2 to produce a clean brittle fracture. Further characterization of the morphology of Fe (III)–CS and Fe_3O_4–CS HFs was carried out using TEM (ZEISS EM 10) to show the presence of iron oxyhydroxide and magnetite nanocrystals in CS HF matrix. XRD analysis was performed on a diffractometer (Siemens D5000) with Cu Kα radiation (λ = 1.5418 Å). Measurements were conducted in the 2θ range from 10° to 80°.

2.4. Evaluation of catalytic activity

The performance of the prepared catalysts was evaluated by degrading RB19 as a model pollutant. The removal of RB19 in the presence of H_2O_2 was carried out with a total volume of 100 ml, using appropriate dosage of catalyst. All chemical reactions were performed under magnetic stirring. The reactions were monitored by a UV–vis spectrophotometer (UV-160A Shimadzu) at a wavelength corresponding to the maximum absorbance.

The dye removal efficiency (η) of synthesized catalysts was calculated using the following equation:

$$\eta = \left(\frac{C_o - C}{C_o}\right) \times 100 \quad (1)$$

where, C_o is the initial concentration of dye and C is its concentration at time t.

3. Results and discussion

3.1. Characterization of the catalysts

X-ray diffraction patterns of pure chitosan and Fe_3O_4–CS HFs are shown in Fig. 1. It is known that chitosan has a large number of —NH_2 and —OH groups, which form a number of hydrogen bonds in chitosan. The broad peak around 20.18 (Fig. 1a) belongs to the hydrogen bonds of chitosan.

The XRD pattern of prepared Fe_3O_4–CS HFs (Fig. 1b) could be indexed as Fe_3O_4 according to the standard ICPDS (card no. 0315-88). It can be noticed that the peak at 2θ = 20.18° assigned to chitosan is obvious in the pattern of Fe_3O_4–CS nanocomposite HFs, indicating that the alkali treatment might weaken or destroy the interaction between iron ions and chitosan, which induce the reconstruction of hydrogen bonds in chitosan.

Fig. 2 shows the SEM images illustrating the cross-section, inner and outer surface morphologies of CS–Fe_3O_4 HFs. HFs have external diameter of about 850 μm and a thickness of about 110 μm. An almost dense morphology can be seen from cross-section image of hollow fibers. The difference between inner and outer surface morphology can be attributed to the effect of the different NaOH concentration of the inner (20%wt.) and outer (10%wt.) coagulant

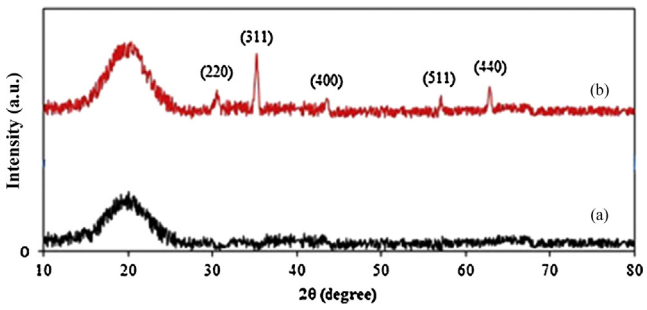

Fig. 1. X-ray diffraction patterns of (a) CS and (b) Fe_3O_4–CS HFs.