Iron oxide nanofibers: A new magnetic catalyst for azo dyes degradation in aqueous solution

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HIGHLIGHTS

- A simple and novel magnetic α-Fe$_2$O$_3$ nanofibers were successfully synthesized.
- The nanofibers were used as a catalyst for the pretreatment of hardly degradable azo dye in wastewater.
- The effect of variables on the decolorization efficiency was studied by chemometric design.
- Under optimum condition, the decolorization efficiency of MO by α-Fe$_2$O$_3$ nanofibers was >99%.
- The method proved to be a simple, effective with high reusability and negligible leaching of Fe ions.

GRAPHICAL ABSTRACT
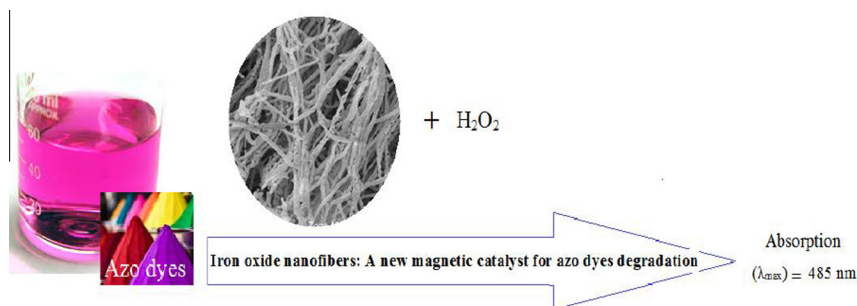
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ABSTRACT

In this study, a simple and novel magnetic α-Fe$_2$O$_3$ nanofibers were successfully synthesized by electrospinning of a solution of polyvinyl alcohol (PVA) and Fe(NO$_3$)$_3$·9H$_2$O composite nanofibers followed by calcinations. These nanostructures were used as heterogeneous iron Fenton catalyst for the effective degradation and decolorization of methyl orange (MO) in aqueous solution. The initial and final concentrations of MO were determined using a UV–visible spectrophotometer. The morphologies and structures of the nanofibers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The average diameter of magnetic α-Fe$_2$O$_3$ nanofibers was between 50 and 90 nm. The effect of different variables on the decolorization efficiency was studied simultaneously using an experimental design. The variables of interest were as concentration of methyl orange, and H$_2$O$_2$, amount of catalyst, pH, temperature and time of decolorization. A Plackett–Burman design was performed for screening in order to determine the significant variables affecting the decolorization efficiency. Then, the significant factors were optimized by a Box–Behnken design (BBD) and the response surface equations were derived. Under the optimum conditions, the decolorization efficiency of methyl orange using α-Fe$_2$O$_3$ nanofibers was >99% in a short period time of 10 min. Finally, the developed process was successfully applied for degradation and decolorization of MO using magnetic α-Fe$_2$O$_3$ nanofibers as a catalyst in waste water samples.

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1. Introduction

Many industries, such as dyestuffs textile, paper and plastics, generate a considerable amount of dye containing wastewater effluents as a result of using dye to color their products. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms [1–3]. The decolorization and degradation of dyes in textile wastewater continues to be a problematic issue. Methyl orange (MO) is a common water soluble azo dye with N=N groups [4,5]. These aromatic amines are suspected to be carcinogenic and mutagenic to humans and harmful to aquatic life as well as these azo dyes cannot easily be degraded and are relatively resistant to conventional biological treatment methods [6]. A number of alternative methods such as coagulation, flocculation, ion-exchange, irradiation, precipitation, biological treatment, ozonation treatment, adsorption on activated carbon membrane filtration and advanced oxidation methods have been developed for dye degradation [7–15].

Advanced oxidation processes (AOPs) play an important role in waste water treatment. In situ generation of highly potent chemical oxidants such as hydroxyl radicals ($\cdot$OH) and per hydroxyl radicals ($\cdot$OOH) oxidize the organic species present in the wastewater into harmless, stable and inorganic compound such as carbon dioxide and water [16]. Among AOPs, powerful oxidants such as H_2O_2, O_3, $KMnO_4$ have been used for in situ chemical oxidation of dye and organic pollutants from wastewater and polluted oils in presence of transition metal salt or oxides as catalyst [17–19]. Fe(III) ion were applied in dye degradation as a fenton catalyst such as H_2O_2/Fe^{2+} or Fe^{3+} and H_2O_2/Fe^{2+} or Fe^{3+}/UV radiation systems. However, homogeneity, difficulty in stabilization and separation process of these catalysts is the main challenges [20]. Compared with salts, iron oxides are magnetically separable, environmental friendly with low toxicity and inexpensive that makes them a good candidate for the practical application in wastewater treatment [21,22]. Up to today a variety of iron oxide such as Fe_3O_4 [23–27], palladium/hydroxyapatite/Fe_3O_4 nanocatalyst [28], zerovalent iron particles [29], Fe_2O_3 composite [30], Fe_2O_3–CeO_2–TiO_2/γ-Al_2O_3 catalyst [31], Fe–Fe_2O_3 nanostructures [32] and Fe_2O_3/SiO_2 composites [33] have been prepared and used in AOPs. However, to the best knowledge of authors, no study has been conducted on the catalytic activities of magnetic Fe_2O_3 nanofibers in dye degradation such as methyl orange decolorization. One-dimensional (1D) magnetic nanostructures such as nanofibers have novel properties such as enhanced magnetic moments [34–36]. Recently, the design and controllable synthesis of one-dimensional (1D) Fe_2O_3 nanostructure is of great interest to scientists. For example Jiang's group have synthesized magnetic α-Fe_2O_3 nanofibers by electrospinning of poly (vinyl alcohol) (PVA)/$Fe(NO_3)_3\cdot 9H_2O$ composite nanofibers followed by calcination [37]. Also, α-Fe_2O_3 nanofibers have shown good activity as sensor to C_2H_5OH vapor [38].

Therefore, in this paper, we herein report the use of magnetic α-Fe_2O_3 nanofibers as a catalyst for the decolorization of methyl orange using hydrogen peroxide as an environmentally beginning oxidant. A chemometric method was used for the screening and optimization of the effective factor on the decolorization efficiency of MO using Fenton-like α-Fe_2O_3 nanofibers catalyst. At first, Plackett–Burman design was used for determination of the main effective factors followed by applying Box–Behnken design and response surface methodology (RSM) to achieve the optimum levels of the main effective factors, by employing STATGRAPHICS, statistical and graphical analysis software.

2. Experimental

2.1. Reagents and materials

All chemicals used here were of reagent grade and used without further purification. Methyl orange (MO) was purchased from Sigma–Aldrich (Milwaukee, WI, USA). Reagent grade water was collected from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Ferric nitrate $Fe(NO_3)_3\cdot 9H_2O$ and polyvinyl alcohol were purchased from Merck, Germany. The pH of the solution was adjusted to desired value using dilute solutions of HNO_3 or NaOH. The required concentration of the MO solution was made using deionized water.

2.2. Instrumentation

The electrospinning process was carried out using Electroris (FNM Ltd., Iran, www.fnm.ir) as an electrospinner device. This device can control the electrospinning parameters such as high voltage (1–35 kV), syringe pump (0.1–100 mL h^{-1}), injection rate, drum rotating speed, working distance, needle scanning rate, and temperature of the electrospinning media. Calcinations was carried out using Exciton furnace (Exciton Co. Ltd., Iran, www.exciton.ir) that provides heating rate controlling up to 1800 °C. The obtained nanofibers were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy and Vibrating Sample Magnetometer (VSM). SEM image was observed using SEM (Philips XL 30 and S-4160) with gold coating. Powder XRD spectrum was recorded at room temperature by a Philips X'pert 1710 diffractometer using Cu Kα (α = 1.54056 Å) in Bragg–Brentano geometry ($\theta - 2\theta$). FT-IR spectra were obtained over the region 400–4000 cm^{-1} with NICOLET IR100 FT-IR with spectroscopic grade KBr. Magnetic properties of catalyst were obtained by Vibrating Sample Magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, MDK Co., Iran, www.mdk-magnetics.com). A Perkin Elmer model 503 atomic absorption spectrometer (Waltham, GA, USA) with deuterium lamp background correction equipped with HGA-2100 furnace controller was used throughout this work.

2.3. Preparation of magnetic α-Fe_2O_3 nanofibers

The magnetic α-Fe_2O_3 ceramic nanofibers were prepared according to the reported method with some modification [37]. Briefly, 0.8 g of PVA powder was dissolved completely in 10 ml deionized hot water (8 wt.%). Then 0.4 g ferric nitrate $(Fe(NO_3)_3\cdot 9H_2O)$ was added to the PVA aqueous solution with stirring. After 6 h stirrings, the solution was loaded into a plastic syringe which inner diameter of pinhead was 0.8 mm. The pinhead was connected to Electroris and aluminum foil served as the counter electrode. The voltage of electrospinning, the rate of flow and the distance between the capillary and the substrate electrode were 15 kV, 1 ml/h and 12 cm, respectively. The electrospun PVA/$Fe(NO_3)_3\cdot 9H_2O$ composite nanofibers were placed in a vacuum oven for 12 h at room temperature in order to remove the solvent residuals, then the α-Fe_2O_3 ceramic nanofibers were obtained via calcinations of polymer nanofibers at 800 °C with 20 °C min^{-1} heating rate for 6 h in air to completely eliminate the organics.

2.4. Decolorization procedure of MO

Decolorization of MO in aqueous solutions was investigated in batch experiments. Stock standard solution of MO was prepared