Enhanced Fenton-like degradation of methylene blue by magnetically activated carbon/hydrogen peroxide with hydroxylamine as Fenton enhancer

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ABSTRACT

Magnetically activated carbon/γ-Fe$_2$O$_3$ (AC/γ-Fe$_2$O$_3$) nanocomposite was evaluated as a potential catalyst for degradation of methylene blue (MB) in the presence of hydrogen peroxide (H$_2$O$_2$) and hydroxylamine (NH$_2$OH). The morphology, magnetic, structure and porous properties of the AC/γ-Fe$_2$O$_3$ catalyst were characterized by using field emission scanning electron microscopy (FE-SEM), vibration sample magnetometer (VSM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and N$_2$ adsorption–desorption isotherms. The effect of various parameters such as H$_2$O$_2$ and NH$_2$OH dosages, initial pH value and amount of catalyst on the degradation of MB were investigated. Optimum conditions were determined to be 2.0 g L^{-1} AC/γ-Fe$_2$O$_3$, pH 5.0, 12.0 mmol L^{-1} H$_2$O$_2$ and 4.0 mmol L^{-1} NH$_2$OH. Under these conditions, complete degradation of 100 mg L^{-1} MB was achieved in 15 min. After seven successive catalytic cycles, the magnetic nanocomposite remained its original catalytic activity. Meanwhile, the high saturation magnetization value (30.3 emu g^{-1}) of the AC/γ-Fe$_2$O$_3$ nanocomposite was favorable for the separation and recycling of the catalyst from the reaction media after the catalytic reactions.

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1. Introduction

Various pollutants such as dyes and heavy metal ions following the arrival to ecosystems lead to the serious global environmental pollution [1–6]. Large amounts of dyes are used in textile, leather, paper, rubber, cosmetics and synthetic detergents industries. Dye effluents discharged from mentioned industries possess serious environmental and health problems [7–9]. Colored substances like dyes usually have a synthetic origin and complex aromatic molecular structure which makes them highly resistant to biodegradation with conventional physical and biological oxidation treatment processes [10–14]. Methylene blue (3,7-Bis(dimethylamino)phenothiazin-5-ium chloride, MB) is a water-soluble organic dye, widely used in textile industries. However, MB can cause eye burns which may be responsible for permanent injury to the eyes of human and animals [15]. It can result in nausea, diarrhea, vomiting, breathlessness and mental confusion. Accordingly, effective mineralization of MB in the environmental area has attracted considerable attention [16,17]. A variety of chemical, physical, and biological techniques are currently available for treatment of municipal and industrial wastewaters. Biological treatment is a proven technology with

some distinct advantages (e.g. complete mineralization, in-situ and cost-effective treatment) and disadvantages (e.g. treatment is complex and time-consuming). Physical methods such as adsorption, ion-exchange, liquid–liquid extraction, etc. are also ineffective on contaminants which are not readily volatile or adsorbable. Furthermore, these treatment methods simply transfer the pollutants to another phase rather than destroying them, which make their large-scale adaptation nonfeasible from the practical point of view. In contrast, chemical oxidation technologies have been considered a promising method due to their ability for complete mineralization in a wider range of organic pollutants [18,19]. In this context, advanced oxidation processes (AOPs) provide alternative approaches to remove organic contaminants from industrial wastewater using biological processes [20]. Among the various AOPs, Fenton process based on the generation of reactive hydroxyl radical ($^\bullet$OH) have been widely implemented to detoxify recalcitrant pollutants [21–23]. However, homogeneous Fenton processes usually have different treatment requirements [24], resulting in increased overall costs [25]. To overcome these limitations, heterogeneous Fenton-like systems using Fe-containing catalyst have been fabricated and used in wet hydrogen peroxide catalytic oxidation [26,27]. Recently, some studies [28,29] investigated the use of magnetic iron oxides (γ-Fe$_2$O$_3$ and Fe$_3$O$_4$) particles to degrade organic contaminants such as dyes in effluents. However, utilization of these materials in nanosized form is

difficult because of the natural tendency of aggregation during the reaction [28,30]. So, there are some challenges to increasing the catalytic activity and long-term stability of iron oxides nanoparticles due to ease oxidation of ferrous atoms [31–33]. Recently, supported metal oxide catalysts have been widely employed in the oxidation of organic pollutants [34]. Carbon-based nanomaterials such as graphene (Gr) [35,36], carbon nanotube (CNT) [37–39], and activated carbon (AC) [40–42] have attracted considerable attention due to their high adsorption capability, good chemical stability, and excellent heat resistance [20,43,44].

Herein, we reported the use of magnetically activated carbon/γ-Fe_2O_3 (AC/γ-Fe_2O_3) nanocomposite as a catalyst for the decolorization of MB dye as a substrate using hydrogen peroxide (H_2O_2) as an environmentally beginning oxidant and hydroxylamine (NH_2OH) as reducing agents. The proposed AC/γ-Fe_2O_3 nanocomposite prepared without toxic organic and expensive equipment under mild conditions. It's performance for the first time as a novel Fenton-like catalyst in the treatment of an aqueous solution containing MB was investigated. Due to the participation of NH_2OH, the generation of hydroxyl radical was much faster in the proposed Fenton-Hydroxylamine system. The main experimental factors, such as initial pH, H_2O_2 and NH_2OH concentration and dosage of the catalyst on the heterogeneous Fenton process were also evaluated. Additionally, the stability and reusability of the AC/γ-Fe_2O_3 catalyst were studied. Composite structures of AC/γ-Fe_2O_3 catalyst have a large surface area with more reactive sites than pure γ-Fe_2O_3, and it can improve electron transfer from electron-donor to electron-acceptor, leading to enhanced catalytic degradation activity.

2. Experimental

2.1. Reagents

All chemicals and reagents used in this study were of analytical grade. Hydrogen peroxide (H_2O_2. 30% w/v), ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), ferric chloride hexahydrate ($FeCl_3.6H_2O$), and AC (gas chromatographic grade, 40–60 mesh) were purchased from Merck (Darmstadt, Germany). MB and hydroxylamine hydrochloride ($NH_2OH.HCl$) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Stock solution (500 mg L^{-1}) of MB was prepared by dissolving the appropriate portion of their solid material in deionized water. Dye test solutions were obtained by diluting the stock solution to the desired concentrations.

2.2. Instruments

A Cary 50 single detector double beam in–time spectrophotometer (Varian, Australia) was used for determining the amount of analyte (MB) retained by the catalyst and recording the spectra as required. An incubator shaker model AR.81 (Pars Azma, Tehran, Iran) was used for mixing the solutions. The morphology and composition of the synthesized composites were analyzed with field emission scanning electron microscope (FE-SEM, CARL ZEISS- AURIGA 60 microscope, Jena, Germany), which was equipped with an energy-dispersive X-ray analyzer (EDX). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker tensor 27 spectrometer (Madison, WI, USA) using the standard KBr disk method (sample/KBr = 1/100). All transmittance spectra were taken at the spectral resolution of 4 cm^{-1} for 64 scans over the wave number region 4000–400 cm^{-1}. A vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Co., Kashan, Iran) was applied to determine the magnetic property of the resultant composite. To determine the specific surface area of samples, Brunauer–Emmett–Teller (BET) specific surface area and pore volume were measured by N_2 adsorption at 77 K using a Belsorp-mini II (BEL Japan, Inc.). The pore volume and pore diameter distribution were derived from the adsorption branches of isotherms using the Barrett–Joyner–Halenda (BJH) model. X-ray powder diffraction (XRD) analysis of the AC and AC/γ-Fe_2O_3 samples was performed on PANalytical X'Pert PRO MPD instrument (PANalytical B.V., Almelo, The Netherlands) equipped with a back monochromator
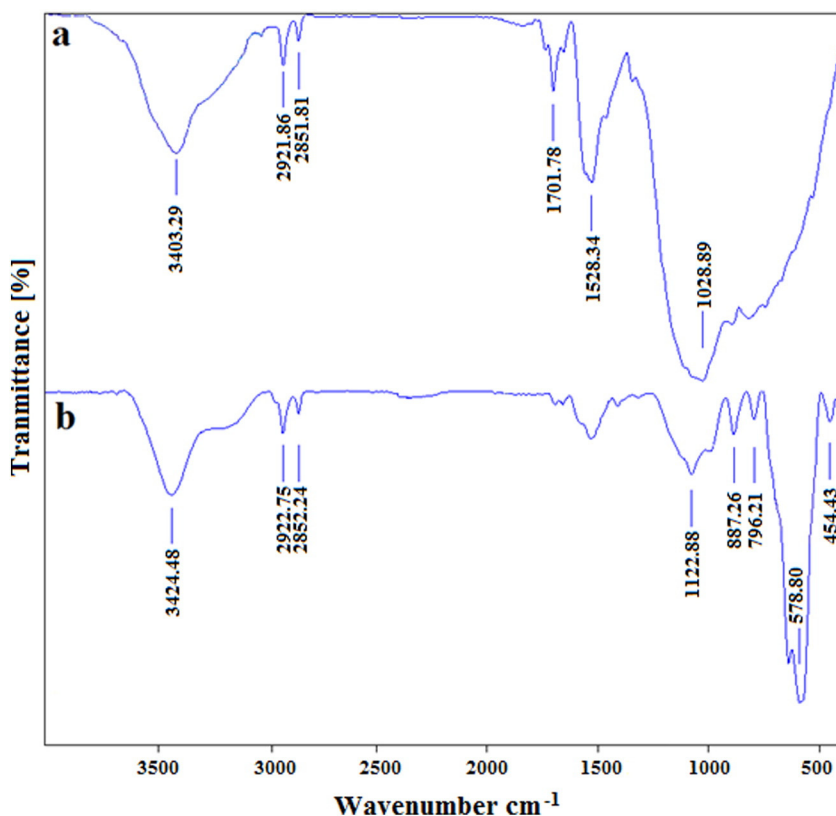

Fig. 1. FT-IR spectra of (a) AC and (b) AC/γ-Fe_2O_3 nanocomposite.