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Combination of ultrasonic and Fenton processes in the presence of magnetite nanostructures prepared by high energy planetary ball mill

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ABSTRACT

High energy planetary ball milling process was used to prepare magnetite nanostructures from natural magnetite. The natural and ball-milled magnetite samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (HR-TEM), energy-dispersive X-ray spectroscopy (EDX), Brunauer-Emmett-Teller (BET) and Fourier transform infrared spectroscopy (FT-IR). The results of EDX indicated the presence of main elements including Fe and O in the structure of both unmodified and milled magnetite samples. The specific surface area of catalyst increased from 0.9116 m^2/g to 28.692 m^2/g after ball-milling process. The catalytic activity of prepared magnetite nanostructures was evaluated towards degradation of Acid Blue 185 (AB185) in ultrasonic assisted heterogeneous Fenton reaction. 6 h ball-milled catalyst exhibited the higher catalytic activity in degradation of AB185. The high degradation efficiency was obtained at initial pH of 3. Increasing the concentration of H_2O_2 from an optimum value of 15 mM led to decrease in degradation efficiency because of scavenging effect of H_2O_2 on hydroxyl radicals. The optimized catalyst concentration was obtained 1.5 g/L. Increasing initial dye concentration from 20 to 120 mg/L led to decrease in degradation efficiency from 99 to 88%. The prepared magnetite nanostructures exhibited good stability in repeated cycles. The produced intermediates of the degradation of AB185 in ultrasonic assisted heterogeneous Fenton process were monitored by GC–MS analysis.

1. Introduction

Azo dyes are a large group of synthetic dyes which make up 70% of commercial dyes. Azo dyes discharged in industrial wastewaters damage aquatic ecosystems and human health. Most of these dyes are chemically stable and difficult to remove by conventional treatment methods [1,2]. Advanced oxidation processes (AOPs) as green technologies, are a group of methods, which can use for the degradation of a wide range of organic compounds [3]. Among AOPs, Fenton reaction is a relatively inexpensive process is easy to operate and maintain. Fenton process is non-selective catalytic technique which based on generation of highly reactive hydroxyl radicals using acidic mixture of Fe^{2+} ions and H_2O_2 [4,5]. The reaction mechanisms are in Eqs. (1)–(6) [6,7]

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + {\cdot}OH \quad (1)$$

$$H_2O_2 + Fe^{+3} \rightarrow Fe - OOH^{+2} + H^+ \quad (2)$$

$$Fe - OOH^{+2} \rightarrow Fe^{2+} + HO_2^{\cdot} \quad (3)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad (4)$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \quad (5)$$

$${\cdot}OH + AB185 \rightarrow \text{Intermediates} \rightarrow H_2O + CO_2 \quad (6)$$

The use of ultrasonic irradiation for the direct degradation of organic contaminants has been gaining interest in the last years. Some investigations have indicated that the use of ultrasound process coupled with Fenton process (Fenton/US) could effectively destroy the organic pollutants [8,9]. By using ultrasonic irradiation in reaction medium, the thermal dissociation of water molecules allowing the generation of highly reactive ·OH radicals and enhances the oxidation power of Fenton process. High ultrasonic frequencies causes to formation of cavitation bubbles. The forma-

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tion, growth and collapse of bubbles generate high localized temperature and pressure named 'hot spot'. Collapsing of microbubbles leads to the thermal dissociation of water molecules consequently formation of reactive radical species such as ·OH as exhibited in Eqs. (7)–(11) [4,10–12].

$$H_2O+))) \rightarrow {}^{\cdot}OH + H^{\cdot} \quad (7)$$

$$O_2+))) \rightarrow 2O^{\cdot} \quad (8)$$

$$O^{\cdot} + H_2O \rightarrow 2{}^{\cdot}OH \quad (9)$$

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2 \quad (10)$$

$$H_2O_2+))) \rightarrow 2{}^{\cdot}OH \quad (11)$$

Ultrasound can promote the production of H_2O_2 (Eq. (10)) which can be used in the Fenton reaction. In the meantime hydrogen peroxide can be decomposed by ultrasonic waves to generate ·OH radicals as shown in Eq. (11). Consequently the degradation rate increases with generation of more hydroxyl radicals.

The major drawbacks of homogenous Fenton process is the pH control to prevent the $Fe(OH)_3$ precipitation. Furthermore, the catalyst needs to separate from treated wastewater. To overcome these problems Fenton process can be performed by using heterogeneous catalysts [4,12,13]. Magnetite [14–17], hematite [18] and pyrite [19] are used as efficient heterogeneous catalysts in Fenton process. Fe_3O_4 nanoparticles as a potential iron source catalyst has attracted increasing attention [12]. Using of nanostructured and well-dispersed catalyst particles reduces the mass transfer resistance and increasing the number of reaction sites [4,13]. Recently various chemical and hydrothermal methods have been used to produce nanostructured catalysts [20]. One way to produce magnetite nanostructures is to use mechanical ball milling (MBM) method. It was found that mechanical ball milling could efficiently generates fine and uniform nanostructures which could not made by more conventional chemical synthesis methods. Diverse nanomaterials such as ZrO_2 [21] and Cu_2O [22] were formed using the high energy MBM process.

The main objective of this study is to production of magnetite nanostructures with ball milling method for treatment of acid blue 185 by the heterogeneous sono-Fenton process. The prepared catalyst was characterized by XRD, SEM, HR-TEM, EDX, BET and FT-IR. The catalytic performance of prepared magnetite nanocatalyst was evaluated in removal of AB185 in ultrasound assisted heterogeneous Fenton process. The effects of operational parameters including the solution pH, the concentration of H_2O_2, milled catalyst dosage and initial AB185 concentration were investigated on the degradation efficiency of the dye. Finally, gas chromatography–mass spectrometry (GC–MS) was applied to identify the generated intermediates through the AB185 degradation.

2. Materials and methods

2.1. Materials

Magnetite was purchased from Karakaya Mineral Co. (Turkey). The azo dye, acid blue 185 was obtained from Haining Deer Chemical Co. (China) and its characteristics are reported in Table 1. Hydrogen peroxide (30%) was purchased from Merck (Germany). All other chemical reagents were supplied from Merck (Germany) and used without further purification. Distilled water was used throughout the experiments.

2.2. Preparation of magnetite nanostructures

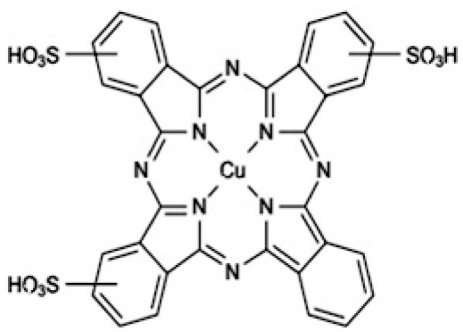
The magnetite sample (Karakaya Mineral Co, Turkey) was grounded using the jaw and cone crusher to the range of 0.5–2 cm. Then, the obtained sample was crushed further by rod and ball milling to reduce the size of magnetite sample to 0.425 μm. Finally, the interrupted milling in a high energy planetary ball mill (LB 200, Turkey) was performed for various times (2, 4 and 6 h) at a rotation speed of 900 rpm to obtain nanosized particles.

2.3. Characterization of catalysts

The X-ray diffractometer (XRD), Bruker D8 Advanced, Cu Kα (λ: 1.5404 Å), operating at 40 kV and 30 mA over a 2θ range of 20–80 was used for identification the magnetite phase before and after ball milling. The SEM equipped with an EDX microanalysis (Mira3 FEG-SEM Tescan, Czech) and high-resolution transmission electron microscope (HR-TEM) model (JEOL JEM-2100F (Japan)) were applied to recognize surface morphology, dimensions and chemical composition of samples. The FT-IR spectra of the samples were recorded in a wave number range of 4000–400 cm^{-1} by Tensor 27, Bruker spectrometer (Germany) using KBr pellet technique. Nitrogen sorption analysis was implemented using a Gemini series instrument (Nitrometrics, Japan). The surface area and pore volume were measured based on the BET model.

The point of zero charge of the magnetite nanostructures was determined according to the method explained by Taseidifar et al. [15]. Accordingly, 0.15 g of magnetite nanostructures was added to nine conical flask consisting 50 mL of NaCl (0.01 M), individually. The pH values of the solutions were adjusted to the range of 2–11 by adding of HCl and NaOH solutions using a pH meter

Table 1
Characteristic of Acid Blue 185.

Chemical structure	Molecular formula	Color index number	λ_{max} (nm)	M_W (g/mol)
	$C_{32}H_{12}CuN_8Na_3O_9S_3$	74200	618	822.25