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Zinc ferrite nanoparticle as a magnetic catalyst: Synthesis and dye degradation

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ABSTRACT

In this paper, magnetic zinc ferrite ($ZnFe_2O_4$) nanoparticle was synthesized and its photocatalytic dye degradation ability from colored wastewater was studied. Reactive Red 198 (RR198) and Reactive Red 120 (RR120) were used as model dyes. The characteristics of $ZnFe_2O_4$ were investigated using Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). Photocatalytic dye degradation by $ZnFe_2O_4$ was studied by UV–vis spectrophotometer and ion chromatography (IC). The effects of $ZnFe_2O_4$ dosage, initial dye concentration and salt on dye degradation were evaluated. Formate, acetate and oxalate anions were detected as dominant aliphatic intermediate. Inorganic anions (nitrate and sulfate anions) were detected as dye mineralization products. The results indicated that $ZnFe_2O_4$ could be used as a magnetic photocatalyst to degrade dyes from colored wastewater.

1. Introduction

The presence of dye in water and wastewater is one of the main problems of developing countries. Some of dyes due to their complex aromatic structure and synthetic origin are difficult to degrade. In addition they produce toxic or carcinogenic byproducts by several reactions such as hydrolysis and oxidation in aqueous media. Thus they should be degraded suitably from a point of view of public health and safety [1–9].

Advanced oxidation processes (AOPs) are used to degrade pollutants in aqueous media by strong oxidants such as hydroxyl radicals ($HO^{\bullet}$). Homogeneous (e.g. Fenton reaction) or heterogeneous catalysts (supported metal catalysts, metal oxides, graphite, etc.) can be used to produce hydroxyl radicals from H_2O_2 [10,11].

An emerging field in AOPs is the application of magnetic catalysts to degrade pollutants [12–15]. The properties of magnetic catalysts have opened a new field in engineering separations applications. They could be separated based on their nanostructures since the ease of direction of magnetization would vary depending on the ordering of atoms in the magnetic structure [16,17]. The application of iron based nanoparticles has been extensively studied. The iron nanoparticles are very effective to remove a wide variety of organic and inorganic contaminants [16]. The application of a magnetic field of low intensity induces the magnetization of the material and thus makes the use of a magnetic force possible, but when the magnetic field is cut of, the magnetization immediately decreases to zero [18,19]. This last point is important for the release of particles after degradation of pollutants from aqueous media.

A literature review showed that the photocatalytic dye mineralization using magnetic zinc ferrite ($ZnFe_2O_4$) nanoparticle was not studied in details. In this paper, $ZnFe_2O_4$ nanoparticle was synthesized and characterized. The photocatalytic dye degradation and mineralization ability of $ZnFe_2O_4$ from colored wastewater in the presence of hydrogen peroxide (H_2O_2) was investigated in details. Reactive Red 198 (RR198) and Reactive Red 120 (RR120) were used as model dyes. The characteristics of $ZnFe_2O_4$ were investigated using Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). Photocatalytic dye degradation was studied by UV–vis spectrophotometer and ion chromatography (IC). The effects of $ZnFe_2O_4$ dosage, initial dye concentration and salt on dye degradation were evaluated.

2. Experimental

2.1. Chemicals

Reactive Red 198 (RR198) and Reactive Red 120 (RR120) were obtained from Ciba and used without further purification. The chemical structure of dyes was shown in Fig. 1. All other chemicals were of analytical grade and purchased from Merck.

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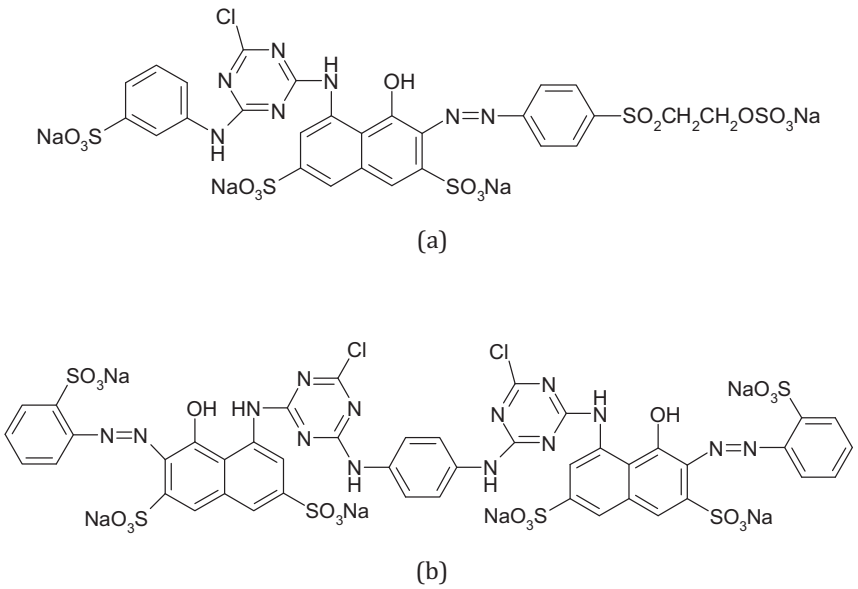

Fig. 1. The chemical structure of dyes (a) RR198 and (b) RR120.

2.2. Synthesize of $ZnFe_2O_4$ nanoparticle

Zinc ferrite nanoparticle was synthesized in our laboratory. 4.90 g zinc nitrate and 13.4 g iron nitrate was dissolved in 50 mL distilled water and added to aqueous mixed solution 4.2 g NaOH in 70 mL distilled water and 3 mL ethylene diamine. This solution was heated at 90 °C for 1 h to achieve complete chelation. The powder was calcined on alumina crucible at 600 °C for 1 h, with a heating rate of 10 °C/min.

2.3. Characterization

The functional groups of the material were studied using Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer Spectrophotometer Spectrum One) in the range of 4000–450 cm^{-1}. Crystallization behavior was identified by XRD model Siemens D-5000 diffractometer with Cu Kα radiation (λ = 1.5406 Å) at room temperature. The morphological structure of the material was examined by scanning electron microscopy (SEM) using a LEO 1455VP scanning microscope.

2.4. Photocatalytic reactor

Experiments were carried out in a batch mode photoreactor. The irradiation source was a UV-C lamp (200–280 nm, 9 W, Philips), which was placed in the inner quartz tube of the reactor.

2.5. Photocatalytic dye degradation

The photocatalytic dye degradation experiments were conducted by mixing various amounts of $ZnFe_2O_4$ (0–0.20 g) in photoreactor containing 800 mL of a dye solution (100 mg/L) and H_2O_2 (1.2 mM) at 25 °C. The solution samples were withdrawn from the reaction medium at regular time intervals. The $ZnFe_2O_4$ was separated from solution using magnetic force and the change on the absorbance at maximum wavelength (λ_{max}) of dyes (520 nm for RR198 and 514 nm for RR120) was monitored by UV–vis spectrophotometer (Perkin-Elmer Lambda 25).

The effect of $ZnFe_2O_4$ dosage on the photocatalytic dye degradation was investigated by contacting 800 mL of dye solution (100 mg/L) and H_2O_2 (1.2 mM) at room temperature (25 °C) for 60 min. Different amounts of $ZnFe_2O_4$ (0, 0.05, 0.10, 0.15 and 0.20 g) were applied.

The effect of initial dye concentration on the photocatalytic dye degradation was studied. The $ZnFe_2O_4$ (0.20 g) was added to 800 mL of different dye concentrations (100, 150, 200 and 250 mg/L) and H_2O_2 (1.2 mM).

The effect of salt on the photocatalytic dye degradation was studied. Different salts (Na_2SO_4, NaCl and $NaHCO_3$) (0.02 mol) were added to 800 mL of dye solution (100 mg/L) containing H_2O_2 (1.2 mM) and $ZnFe_2O_4$ (0.20 g) at room temperature (25 °C).

Ion chromatograph (METROHM 761 Compact IC) was used to assay the appearance of carboxylic acids, nitrate and sulfate ions formed during the degradation and mineralization of dyes (solution: 800 mL, dye: 100 mg/L, $ZnFe_2O_4$ (0.20 g) at room temperature (25 °C)) using a METROSEP anion dual 2, flow 0.8 mL/min, 2 mM $NaHCO_3$/1.3 mM Na_2CO_3 as an eluent, temperature 20 °C, pressure 3.4 MPa and conductivity detector.

3. Results and discussion

3.1. Characterization

The FT-IR spectrum of $ZnFe_2O_4$ nanoparticle was shown in Fig. 2. It has two peaks at 3450 cm^{-1} and 600–500 cm^{-1} which indicate O–H stretching vibration and metal-oxygen vibration, respectively [20]. The peak at 1625 cm^{-1} was attributed to OH bending of molecular water [21].

Fig. 3 illustrates the XRD pattern of the $ZnFe_2O_4$ nanoparticle. The results showed that spinel was formed as the most intense (3 1 1) peak and Miller indices (2 2 0), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) matched well with the reflections of the zinc ferrite reported in the previous published paper [21].

SEM has been a primary tool for characterizing the surface morphology and fundamental physical properties of material surface. It is used to determine the particle shape and appropriate size distribution of the material. The SEM micrograph of the $ZnFe_2O_4$ (Fig. 4) shows a relatively homogeneous particle size distribution of $ZnFe_2O_4$.