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Synthesis of nickel–zinc ferrite magnetic nanoparticle and dye degradation using photocatalytic ozonation

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ABSTRACT

In this paper, nickel–zinc ferrite magnetic nanoparticle (NZFMN) was synthesized and its dye degradation ability using photocatalytic ozonation was investigated. The NZFMN was characterized by X-ray diffraction (XRD), scanning electron microscopic (SEM), Fourier transforms infrared (FTIR) and alternative gradient force magnetometer (AGFM). Reactive Red 198 (RR198) and Direct Green 6 (DG6) were used as dye models. UV–vis and ion chromatography (IC) analyses were employed to study dye degradation. The effects of operational parameters on decolorization such as NZFMN dosage, dye concentration, salt and pH were studied. RR198 and DG6 were completely decolorized (100%) by photocatalytic ozonation using NZFMN. Formate, acetate and oxalate anions were detected as dominant aliphatic intermediates. Nitrate, sulfate and chloride ions were detected as mineralization products of dyes. Results showed that the photocatalytic ozonation using NZFMN was a very effective method for dye degradation.

1. Introduction

The discharge of colored wastewater into natural streams poses severe problems because of toxicity of some dyes to the aquatic life and damaging to the aesthetic nature of the environment [1–4]. Thus, there is an urgent need for colored wastewater to develop effective methods of treatment.

Several methods such as adsorption and photocatalysis were used to remove dyes from wastewater [5–9]. Ozone is an effective oxidant to degrade pollutants [10–12]. Organic compounds are degraded by molecular ozone and/or hydroxyl radicals ($OH^{\bullet}$) generated by ozone decomposition. Aldehydes and carboxylic acids are produced by ozonation of organic compounds, both of which do not react with ozone. This is an important limitation of ozonation to mineralize the organics. In addition, oxidation of compounds by ozone is relatively slow and selective. Thus, radical processes have to be implemented. Reaction of radical with organics is a nonselective and fast reaction. Photocatalytic ozonation allows the effective formation of hydroxyl radicals [10].

The decomposition of ozone and hydroxyl radical formation during the photocatalytic ozonation is controlled by catalyst. It provides fast and more effective mineralization of organics. Several catalysts have been proven to be effective to degrade pollutants by photocatalytic ozonation [10–30].

A literature review showed that the photocatalytic ozonation of nickel–zinc ferrite magnetic nanoparticle (NZFMN) was not investigated. In this paper, NZFMN was synthesized and its dye degradation ability using photocatalytic ozonation was investigated. For water-catalyst separation purposes, NZFMN was used. The NZFMN was characterized by X-ray diffraction (XRD), scanning electron microscopic (SEM), Fourier transforms infrared (FTIR) and alternative gradient force magnetometer (AGFM). Reactive Red 198 (RR198) and Direct Green 6 (DG6) were used as dye models. UV–vis and ion chromatography (IC) analyses were employed to study dye degradation. The effect of operational parameters on decolorization such as NZFMN dosage, dye concentration, salt and pH was studied.

2. Experimental

2.1. Reagents

Reactive Red 198 (RR198) and Direct Green 6 (DG6) were obtained from CIBA. The chemical structure of dyes was shown in Fig. 1. Other chemicals were analytical grade and obtained from Merck and used as received.

2.2. Synthesis of NZFMN

4.85 g nickel nitrate, 4.96 g zinc nitrate and 26.93 g iron nitrate were dissolved in 300 mL water and added to aqueous mixed solution (57.64 g citric acid (CA) in 100 mL water and 34.62 mL

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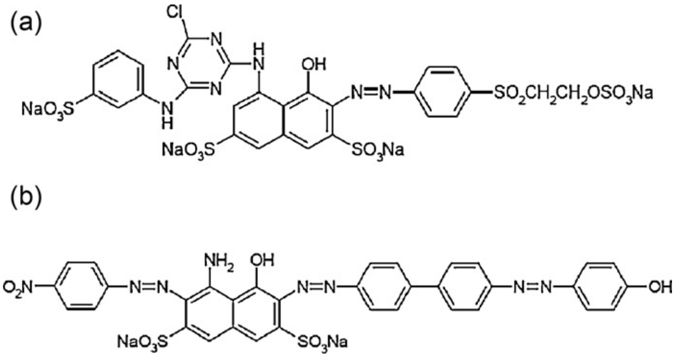

Fig. 1. The chemical structure of dyes (a) RR198 and (b) DG6.

ethylene glycol (EG)). This solution was heated at 80 °C for 2 h to achieve complete chelation. Then temperature was raised to 90–110 °C to promote polyesterification. The heating process accelerated esterifications between CA and EG and led to achieve a clear and viscous brown resin. The resin was heated at 300 °C for 1 h to decompose of organic constituents. The powder precursor was milled in planetary mono mill (model pulversette 6 Fritsch Gmbh) with zirconium mortar and passed through a 170 mesh sieve. The powder precursor was calcined on alumina crucible at 600 °C for 1 h, with a heating rate of 10 °C/min [31].

2.3. Characterization of NZFMN

Crystallization behavior of *NZFMN* was identified by XRD model Siemens D-5000 diffractometer with Cu Kα radiation (λ = 1.5406 Å) at room temperature. The microstructure of *NZFM* was investigated by a LEO 1455VP SEM model LEO 1455 VP. Fourier transforms infrared spectrum of ferrite sample was recorded by PerkinElmer spectrum FTIR spectrophotometer in the range of 4000–400 cm^{-1}. Variation magnetization with respect to applied field was studied by AGFM mode 155 at room temperature.

2.4. Photocatalytic reactor

Experiments were carried out in a batch water-jacketed photoreactor with total capacity of 2 L. The ozone source was an Ozonica Series generator from Ozoneab Co. The irradiation source was a UV-C lamp (9 W, Philips), which was placed in the inner quartz tube of the reactor.

Ozone was produced from oxygen (99.99%) in an ozone generator (Green Technology Co., Iran). The oxygen flow rate was controlled at 0.08 L/min using a flow controller (Besta model LZB-3WB, Taiwan). The ozone was introduced from the reactor bottom. The ozone gas concentration was measured in the reactor inlet with an ozone analyzer (Orbisphere model 3600, Switzerland). The inlet ozone concentration was 55 g/m^3.

2.5. Photocatalytic ozonation of dyes

Experiments were performed using a 1 L solution containing specified concentration of dye with 5 mg/L of NZFMN. The solution pH was adjusted using HCl or NaOH. Samples were withdrawn from sample point at certain time intervals and analyzed for decolorization and degradation.

Decolorization of dye solution was checked and controlled by measuring the absorbance at maximum wavelength (λ_{max}) of dyes (520 nm for RR198 and 634 nm for DG6) at different time intervals by UV–vis spectrophotometer (Perkin-Elmer Lambda 25 spectrophotometer).

The effect of NZFMN dosage on dye oxidation was investigated by contacting 1 L of dye solution (150 mg/L) at room temperature (25 °C) and pH 3. Different amounts of NZFMN (0, 2.5, 5, 10 and 20 mg/L for RR198 and 0, 2.5, 5, and 10 mg/L for DG6) were applied.

The effect of initial dye concentration on the percentage of dye oxidation was studied. The optimum amount of NZFMN (5 mg/L) was added to 1 L of different dye concentrations (50, 100, 150 and 200 mg/L). These experiments were performed at pH 3.

The effect of salt on the percentage of dye oxidation was studied. 0.02 M of different salts (Na_2SO_4, Na_2CO_3 and $NaHCO_3$) was added to 1 L of dye solution (150 mg/L) at room temperature (25 °C) with optimum amount of NZFMN (5 mg/L).

The effect of pH on dye oxidation was investigated by contacting 1 L of dye solution (150 mg/L) at room temperature (25 °C) and optimum amount of NZFMN (5 mg/L).

Ion chromatograph (METROHM 761 Compact IC) was used to assay the appearance of carboxylic acids and inorganic ions formed during the degradation and mineralization of dyes (solution: 1 L, dye: 150 mg/L, NZFMN: 5 mg/L, pH: 3 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 discussions

3.1. Characterization of NZFMN

Fig. 2 illustrates the X-ray diffraction (XRD) patterns of the calcined sample at 600 °C. It is clear that all peaks matching with the standard pattern of *NZFMN* (JCPDF 08-0234), which was prepared by polymeric precursor method [31]. The average calculated crystallite size from Scherrer's formula [32] using the intensive peak (3 1 1) revealed 31 nm.

The SEM micrograph of the *NZFMN* (Fig. 3) shows a relatively homogeneous grain distribution, which was made up of particles with the size in the nanosized range. This result is in agreement with the results of XRD analysis.

The FTIR of sample in the wavelength ranges from 4000–400 cm^{-1} is shown in Fig. 4. A broad absorption band around 3400 cm^{-1} and less intensive band at 1620 cm^{-1} are attributed to the stretching vibration of the hydrogen-bonded O–H groups [33,34]. In all spinel and ferrite in particular, two main broad metal–oxygen bands are seen. The strongest one, is appeared in the

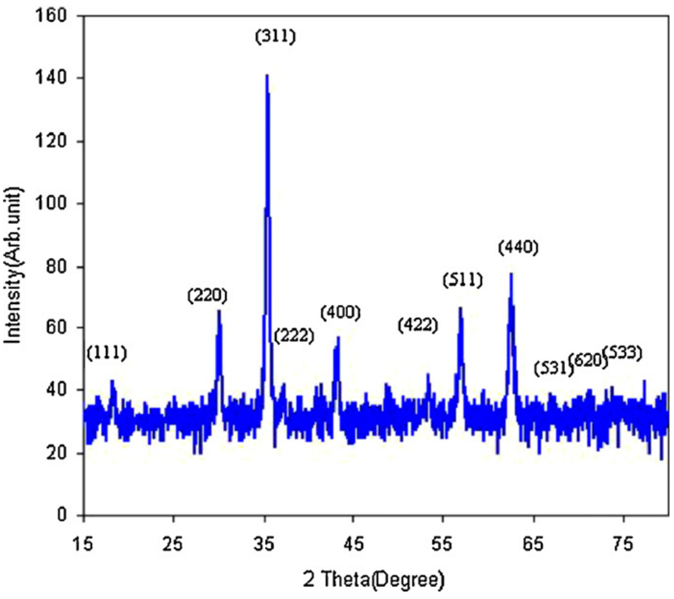

Fig. 2. XRD pattern of *NZFM*.