Synthesis and sonocatalytic performance of a ternary magnetic MIL-101(Cr)/RGO/ZnFe2O4 nanocomposite for degradation of dye pollutants

Ladan Nirumand\textsuperscript{a}, Saeed Farhadi\textsuperscript{a,b}* , Abedin Zabardasti\textsuperscript{a}, Alireza Khataee\textsuperscript{b,c,v,*1}

\textsuperscript{a} Department of Chemistry, Lorestan University, Khoramabad 68135-465, Iran
\textsuperscript{b} Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran
\textsuperscript{c} Department of Materials Science and Nanotechnology Engineering, Near East University, 99138 Nicosia, North Cyprus, Mersin 10, Turkey

\begin{abstract}
In this study, new ternary magnetic MIL-101(Cr)/RGO/ZnFe2O4 catalyst (with 30\% wt of ZnFe2O4) was synthesized via a hydrothermal route for sonodegradation of organic dyes. The structural, optical and magnetic properties of the nanocomposite were detected by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV–visible spectroscopy (UV–visible), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) spectroscopy, vibrating sample magnetometer (VSM), atomic force microscopy (AFM), Raman spectroscopy and BET surface area analysis. To evaluate the sonocatalytic activity of the as-prepared MIL-101(Cr)/RGO/ZnFe2O4 nanocomposite, the H2O2-assisted degradation of organic dyes such as congo red (CR), methylene blue (MB), Rhodamine B (RhB) and methyl orange (MO) in aqueous solution was studied under ultrasound irradiation. The obtained results indicated that the ternary MIL-101(Cr)/RGO/ZnFe2O4 nanocomposite had better performance for sonodegradation of these dyes than MIL-101(Cr)/RGO, pure MIL-101(Cr) or ZnFe2O4. The enhanced sonocatalytic performance of the as-prepared ternary nanocomposite could be attributed to the fast generation and separation of charge carriers (electrons and holes) in ZnFe2O4 and MIL-101(Cr) and their transfer to the surface of graphene sheets. Moreover, the relatively high specific surface area of the MIL-101(Cr)/rGO and magnetic property of ZnFe2O4 improve the degradation efficiency of the dyes. The recovery of the ternary magnetic sonocatalyst from treated water could be easily achieved using an external magnetic field. The main influence factors on the sonocatalytic activity such as catalyst dosage and dye initial concentration were also investigated. The trapping experiments indicated that \textsuperscript{\textbullet}OH radicals are the prominent active species in dye degradation. In addition, the reusability test, was also carried out to ensure the stability of the employed sonocatalyst.
\end{abstract}

\section{1. Introduction}

In recent years, many researches have been made on solving the environmental issues including water treatment, especially on organic dyes. Textile, cosmetic, food and dye industries are serious sources of environmental pollution with dyes, which are not easily biodegradable and are toxic to human health and aquatic life [1]. So far, various techniques have been reported on the efficient elimination of hazardous and toxic organic dyes from aqueous solutions, such as biological treatment, oxidation, ozonation, photocatalytic or sonochemical degradation and adsorption [2,3]. Among them, sonolysis has been extensively used to degrade the organic pollutants. The chemical effect of ultrasound (US) comes from acoustic cavitation, which involves the formation, growth and collapse of bubbles in a liquid. The collapse of bubbles leads to production of spots with high local temperature and pressure. Under such extreme conditions, the highly reactive radical species such as \textsuperscript{\textbullet}OH, produce through dissociation of water molecules, which can oxidize organic dyes in water [4,5]. However, the application of ultrasound alone to complete degradation of organic pollutants requires long time and large amount of energy. To overcome these disadvantages, the combination of sonolysis with a suitable heterogeneous catalyst that is active under ultrasonic irradiation has been attracted in recent years. In the presence of a suitable catalyst, the generation of \textsuperscript{\textbullet}OH and sonocatalytic efficiency of the dye-pollutant degradation can obviously be enhanced, and this is likely due to a synergistic effect between the ultrasonic irradiation and the solid
semiconductor catalyst [6]. Furthermore, the sonocatalytic degradation is an environmentally friendly route. According to the literature, various semiconductors such as Fe3O4 [7], ZnO-biosilica [8], KNO3 [9], LuFeO3 [10], CdS/CN-TiO2 [11], La-doped ZnO [12], CoFe2O4/ZnS [13] and Fe3O4-graphene/ZnO@SiO2 [14] have been used as sonocatalysts. However, there is a need for developing new magnetic sonocatalysts with high catalytic activity.

In the past two decades, a class of newly-developed inorganic–organic hybrid porous materials, namely metal–organic frameworks (MOFs) has generated rapid development due to their versatile applications such as catalysis, storage and separation. Recent research has shown that these semiconducting materials, acting as catalysts, are quite effective in the photocatalytic degradation of organic pollutants [15]. Among various MOFs, MIL-101(Cr) is one of the most studied MOF materials [16,17]. MIL-101(Cr) is very fascinating material due to its mesoporous structure, large surface area and good hydrothermal stability, hence it has been widely investigated for adsorption of pollutants, catalysis, photocatalysis and drug delivery [18,19]. These properties make MIL-101(Cr) a good candidate for sonocatalytic activity. To further improve the catalytic performance of MOFs, some researchers focus on the introduction of graphene derivatives such as graphene oxide (GO), because GO can provide a dense array of carbon atoms to increase dispersive interactions and porosity of MOFs [20]. Moreover, coupling the MOF/GO systems with narrow band-gap magnetic semiconductors (e.g. ZnFe2O4) provides an effective way for improving catalytic activity and recycling using a suitable external magnet [21].

On the basis of the aforementioned considerations, in the present study, a novel ternary MOF-based nanocomposite, namely MIL-101(Cr)/RGO/ZnFe2O4 was prepared by a hydrothermal approach and its sonocatalytic activity was evaluated for the degradation of organic dyes (MB, RhB, Cr and MO) in water by using H2O2 as a hydroxyl radical (‘OH) source. The effects of parameters such as the catalyst dosage, H2O2 concentration, and the scavengers were investigated. Moreover, the sonocatalytic activity of pure ZnFe2O4, MIL-101(Cr) and MIL-101(Cr)/RGO were evaluated under the same conditions. To the best of the authors’ knowledge and based on the literature review, there is no report on the use of MOF-based nanocomposites as sonocatalyst for the degradation of organic dyes, especially in the presence of H2O2 as an environmental-friendly oxidizing agent.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used as received without further purification.

2.2. Preparation of graphene oxide (GO)

Graphene oxide was prepared through oxidation of graphite by the modified Hummers method [22]. Briefly, graphite powder (2 g) and sodium nitrate (1 g) were put into cold concentrated sulfuric acid (48 mL) in the ice-bath and stirred. Then, potassium permanganate (K2MnO4, 6 g) was added gradually to the suspension to prevent a rapid rise in temperature (less than 10 °C). The reaction mixture was continuously stirred for 30 min and then, re-stirred at room temperature for 2 h, after removal of the ice-bath. Distilled water (100 mL) was slowly added to the reaction vessel to keep the temperature under 100 °C. The diluted suspension was stirred for another 1 h at about 98 °C and then more diluted with distilled water (200 mL). To complete the reaction, hydrogen peroxide (H2O2, 30%, 20 mL) was added to the mixture. The mixture was centrifuged at 5000 rpm and washed with a 5% solution of HCl and deionized water until the pH of the filtrate was neutral and finally dried at room temperature. The obtained product was graphite oxide (GO). After the ultrasonic treatment, the as-synthesized graphite oxide could be further exfoliated to graphene oxide.

2.3. Preparation of the MIL-101(Cr)/GO composite

The MIL-101(Cr)/GO composite was synthesized by a hydrothermal method according to the following procedure: graphene oxide (0.1 g) was dispersed into 25 mL deionized water by sonication for 1 h at room temperature and then, Cr(NO3)3·9H2O (1.2 g) and terephthalic acid (H2BDC, 0.498 g) were added. The mixture was stirred at 40 °C for 30 min, transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 12 h. After cooling it down to room temperature, the green-colored solid were obtained. To obtain pure crystalline material with high porosity, a number of purifications e.g. washing with DMF and hot ethanol were used to remove the unreacted H2BDC and other molecules in the sample. Finally, the obtained MIL-101(Cr)/GO composite was dried at 423 K for 12 h. The amount of GO added in the preparation of the composite was 5 wt% of the initial materials weight.

2.4. Preparation of the MIL-101(Cr)/RGO/ZnFe2O4 nanocomposite

The ternary MIL-101(Cr)/RGO/ZnFe2O4 was fabricated by a hydrothermal method. In a typical synthesis, the binary MIL-101(Cr)/GO composite (0.46 g) synthesized in previous step was added to a water-glycerol solution (30 mL) of FeCl3·6H2O (1.08 g) and ZnCl2·2H2O (0.28 g). This mixture was stirred for 30 min and 1.6 g of acetic sodium was added to the suspension and restirred for 1 h. Then, it was placed in a Teflon-lined autoclave bomb and kept in an oven at 200 °C for 12 h. Finally, the black precipitate was magnetically collected and rinsed thoroughly with deionized water and absolute ethanol, followed by drying at 45 °C for 8 h. The as-prepared MIL-101(Cr)/RGO/ZnFe2O4 nanocomposite contained 30% wt ZnFe2O4 as confirmed by ICP-AES analysis.

2.5. Characterisation

The powder X-ray diffraction (XRD) patterns were obtained at room temperature on a Rigaku D/Max C III diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å). FT-IR spectra were recorded after grounding of the samples with KBr and compressing into pellets using FT-IR spectrometer (Model: Schimadzu FT-IR 8400S, Japan) over the wavenumber range from 4000 to 400 cm−1. Raman spectra were obtained using a Raman microscope (Model: Senterra (2009), Germany) with a laser at 785 nm. SEM images of nanocomposite particles were taken via field emission scanning electron microscope (FESEM) (Model: Mira3 TESCAN, Czech Republic) outfitted with energy dispersive X-ray analyzer (EDX) for the elemental analysis of the sample. A vibrating sample magnetometer (Model: MKDFD, Magnetic Daneshpajoh Kashan Co.,Iran,) with a maximum magnetic field of 10 kOe was applied for magnetic measurements. AFM images were recorded on a multi-mode atomic force microscopy (ARA-AFM, model Full Plus, ARA Research Co., Iran). In addition, UV–visible spectra were obtained on a Cary 100 Varian UV–Vis spectrophotometer in a wavelength range of 200–800 nm. The Brunauer-Emmett-Teller (BET) surface area was measured by N2 adsorption measurements at 77 K using Belsorp mini apparatus(made in Japan). The concentration of Zn and Cr in the filtrate was determined by inductively coupled plasma atomic emission spectroscopy (perkin elmer ICP-OES, USA).

2.6. Sonocatalytic tests

The sonocatalytic degradation of Cr, RhB, MO and MB was performed by a commercial ultrasonic machine (Sonic 6MX, England), operating at an ultrasonic frequency of 37 kHz. Experiments were