Sonocatalytic performance of magnetically separable CuS/CoFe$_2$O$_4$ nanohybrid for efficient degradation of organic dyes

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**Abstract**

The sonocatalytic activity of the magnetic CuS/CoFe$_2$O$_4$ (CuS/CFO) nanohybrid was studied through the H$_2$O$_2$-assisted system for degradation of watersoluble organic pollutants such as methylene blue (MB), rhodamine B (RhB) and methyl orange (MO). The CuS/CFO nanohybrid was fabricated at 200°C by hydrothermal method. X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) equipped with energy dispersive X-ray microanalysis (EDX); Fourier-transform infrared spectroscopy (FT-IR), UV–Vis spectroscopy, magnetic measurements, and Brunauer-Emmett-Teller (BET) were employed for the characterizing the structure and morphology of the so-synthesized nanohybrid. Compared with sonolysis/H$_2$O$_2$, the higher degradation of MB (25 mg/L) was achieved via sonocatalytic process. The degradation efficiency of sonolysis/H$_2$O$_2$, sonocatalysis using CuS/H$_2$O$_2$, CFO/H$_2$O$_2$ and CuS/CFO/H$_2$O$_2$ systems was 6%, 62%, 23% and 100% within reaction time of 30 min for MB, respectively. The integration of H$_2$O$_2$ and catalyst dosage intensified the sonocatalytic degradation of MB. On the other hand, adding a hydroxyl radical (•OH) scavenger (tert-butyl alcohol) and a hole scavenger (diiodide ethylenediaminetetraacetahte) decreased the degradation efficiency from 100% to 35% and 72% within 30 min, indicating the •OH radicals as prominent oxidizing agent of this process. Furthermore, the magnetic property of the sample helped for easier separation of the nanohybrid, made it recyclable with a negligible decline in the performance even after four consecutive runs.

**Keywords:** CuS/CoFe$_2$O$_4$
Magnetic sonocatalysis
Nanohybrid
Ultrasound-assisted degradation

1. Introduction

Many industries are widely using organic dyes that are among new chemicals. Huge amount of production and vast applications of organic dyes result in production of toxic industrial wastewaters resistant to biological degradation. Therefore, degradation and mineralization of organic dyes are not easily feasible using conventional treatment methods [1,2]. In recent years, great attention has been paid to the application of ultrasound as an advanced oxidation process (AOP) for water and wastewater treatment due to its high efficiency and simple operation [3,4].

However, degradation by only sonication has a low rate for removing organic contaminants using a lot of energy and time for an incomplete removal process [5], unless using sonocatalysts which are active under ultrasonic irradiation leading to accelerate •OH generating [6]. Various catalysts such as TiO$_2$, ZnO, Cu$_2$S, GdS, ZnS, ZnO-NRs-AC, Cu: ZnS-NPs-AC, MIL-101(Cr)/RGO/ZnFe$_2$O$_4$ and CoFe$_2$O$_4$@ZnS have shown good sonocatalytic activities [7–13]. However, there is a need for developing new magnetic sonocatalysts with high catalytic activity.

Photocatalytic and sonocatalytic reactions have the same mechanisms for pollutants degradation based on creating electron–hole pairs on the surface of catalyst [14]. Copper sulfide (CuS) is regarded as one of the major p-type semiconductors due to its versatility, availability and low-toxicity nature. In addition, it has excellent optical, electronic and other physical and chemical properties [15]. Due to its good photosensitivity, excellent physical and chemical stability, CuS is an important semiconductor nanomaterial having direct band gap with various potential applications. These applications include catalysis, solar cell, photothermal conversion, gas sensing, lithium ion batteries and nanometer-scale switches [16]. Recent studies have mainly focused on the photocatalytic activity of CuS for degradation of dyes as major ecological contaminants [17]. However, the high rate of recombination of electron–hole pairs is the main disadvantage of pure CuS nanoparticles [18]. In addition, difficult separation, recovery and recycling as well as high cost of large scale produc-
tion are among the limitations of application of these types of photocatalysts [19].

Recently, coupling the catalysts with magnetic materials has been applied as a new approach for improving catalytic activity, magnetic and antiphotocorrosion characteristics for effective recovery and reuse [20–22].

In the present study, the results of an efficient H₂O₂-assisted sonodegradation of three organic dyes in aqueous solutions over magnetic CuS/CoFe₂O₄ (CuS/CFO) as a new sonocatalyst were reported. This sonocatalyst was synthesized via loading CoFe₂O₄ (CFO) on the hydrothermally prepared CuS from copper (II) diethanolithiocarbamate (Cu(DEDTC)₂) complex. Moreover, the as-prepared sonocatalyst was characterized by FE-SEM, EDX, XRD, FT-IR and UV–visible spectroscopy. Methylene blue (MB), methyl orange (MO) and rhodamine B (RhB) were used as organic dye models for evaluating sonocatalytic activity of pure CuS, CFO and CuS/CFO nanohybrid. The effects of the main operational parameters such as amounts of dye, catalyst and H₂O₂, as well as the enhancers and radical scavengers were investigated. Furthermore, the sonocatalytic activity of CuS/CFO nanohybrid, pure CuS and CFO was compared under the similar conditions.

2. Experimental

2.1. Materials

Analytical grade of all chemicals for synthesis of reported nanocomposite was used without further purifications. Copper chloride (CuCl₂, 99%), diethanolamine (C₆H₁₂NO₇, 98%), carbon disulfide (CS₂, 98%), iron nitrate (Fe(NO₃)₃·9H₂O, 99%), cobalt nitrate (Co(NO₃)₂·6H₂O, 99%), hydrogen peroxide (H₂O₂, 30%), methylene blue (MB, C₁₆H₁₂ClN₃S), methyl orange (MO, C₁₄H₈N₄Na₂O₄S) and rhodamine B (RhB, C₂₃H₃₅ClN₂O₃) purchased from Merck company (Germany).

2.2. Preparation of the CuS and CFO nanoparticles

The reported method was used for synthesizing Cu(II) diethanolithiocarbamate (DEDTC) complex [23] wherein 30 mL of deionized water was added to 0.5 g of Cu(II) diethanolithiocarbamate for 24 h at 200 °C, then allowed to room temperature cooling and finally, the contents were filtered. The precipitate was washed using distilled water and ethanol separately for 2 times to eliminate the unreacted single-source precursor as well as by-products.

The preparation of CFO nanoparticles was carried out as follows: 0.62 g of Co(NO₃)₂·6H₂O as well as 1.71 g of Fe(NO₃)₃·9H₂O were solved in 25 mL of deionized water and stirred for 1 h at room temperature. Before hydrothermal treatment at 180 °C for 12 h, its pH was adjusted to 11 with NaOH solution (6 M) and stirred for 1 h. At the end, the black product was washed for 3 times with deionized water and ethanol and dried at 60 °C for 6 h in the oven.

2.3. Preparation of the CuS/CFO nanohybrid

For synthesizing the magnetic CuS/CFO nanohybrid with uniform dispersion, 0.113 g of CuS nanoparticles was applied into 25 mL deionized water and sonicated for 1 h. Then, 0.43 g of Fe(NO₃)₃·9H₂O and 0.15 g of Co(NO₃)₂·6H₂O were added into the suspension and stirred for 1 h. After that, the mixture with pH of 11 obtained by adding NaOH solution (6 M) was re-stirred for 1 h and left in a 50 mL Teflon-lined stainless steel autoclave for 24 h under auto-generated pressure at 200 °C. Finally, it was cooled down to the room temperature and the final yield was filtered after washing with water.

2.4. Characterization of the synthesized materials

The as-prepared samples in crystalline phase were introduced into an X-ray diffraction (XRD) apparatus equipped with a Siemens X-ray Diffractometer (XpertPro, analytical, Holland), Cu Kα radiation (λ = 0.15406nm), 40 kV accelerating voltage and 30 mA emission current. FT-IR spectra were recorded in the range of 4000–400 cm⁻¹ using KBr pellets. The characteristic functional groups were analyzed utilizing a Shimadzu FTIR 8400S spectrophotometer. Elemental analysis was performed utilizing a Perkin Elmer 2400 CHN elemental analyzer. X-ray photoelectron spectroscopy (XPS) was performed using a K-α 1486.6 eV line and a pass energy of 16.3 eV. The XPS spectra were deconvoluted using the CasaXPS software. X-ray photoelectron spectroscopy (XPS) was used for characterization of surface and interface properties. The XPS spectra were analyzed using CasaXPS software. The Ultrasonic cleaning of the samples was conducted using an ultrasonic cleaner for 10 min. The BET surface area of the samples was measured using a Micromeritics ASAP 2020 instrument. The amino groups of the samples were also analyzed by the Kjeldahl method. The TEM images were recorded using a JEOL JEM-1010 microscope. The degradation efficiency of the samples was calculated using the following equation:

\[ \text{Degradation efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \]

where \( C_0 \) is the initial concentration of the dye, and \( C_t \) is the concentration of the dye at time \( t \).

3. Results and discussion

3.1. Characterization of the CuS/CFO nanocomposite

The XRD diffraction patterns of CuS, CFO and CuS/CFO nanostructures are presented in Fig. 1. Based on the diffraction peaks in Fig. 1(a), body-centered Hexagonal phase (JCPDS No. 79–2321) of the CuS nanoparticles can be approved and broadening of these peaks is related to their nanocrystalline feature. Fig. 1(b) obviously shows that all the diffraction peaks are matched very well with standard data of the spinel cubic structure of CFO (JCPDS No. 01–1121), and no additional peaks were observed. Fig. 1(c) shows that the CuS/CFO nanohybrid has been successfully prepared as the XRD pattern exhibits diffraction peaks of both CuS and CFO. The absence of any other peaks indicated that the sample was composed of only CuS and CFO. The average size of the CuS/CFO nanohybrid crystallite was estimated about 17 nm calculated by Debye–Scherzer equation [24].