Journal of Hazardous Materials 263 (2013) 600–609

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Could microwave induced catalytic oxidation (MICO) process over $CoFe_2O_4$ effectively eliminate brilliant green in aqueous solution?

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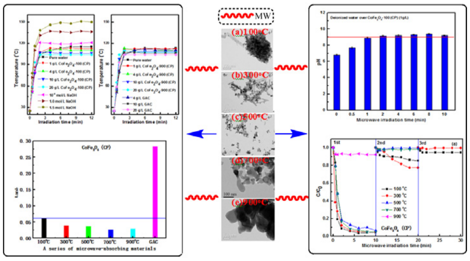
HIGHLIGHTS

- The elimination of BG over $CoFe_2O_4$(CP) was mainly due to the residue of NaOH.
- Salicylic acid failed to capture hydroxyl radicals within MICO process.
- This study indicated dim prospects for the MICO-based elimination of contaminants.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 August 2013
Received in revised form 7 October 2013
Accepted 9 October 2013
Available online 18 October 2013

Keywords:
$CoFe_2O_4$
Brilliant green
Microwave induced catalytic oxidation (MICO)
Dielectric loss tangent
Wastewater treatment

ABSTRACT

In this study, we adopted the chemical co-precipitation (CP) method and sol–gel method followed by calcination at temperatures of 100–900 °C for 12 h to synthesize $CoFe_2O_4$ materials, which were further characterized by TEM, XRD and XPS techniques. The properties of $CoFe_2O_4$ materials were evaluated in a microwave (MW) induced catalytic oxidation (MICO) process for the elimination of brilliant green (BG). The results showed that: (1) the removal rates of BG gradually decreased over a series of $CoFe_2O_4$ materials prepared by CP method and calcinated with 100–700 °C (except 900 °C) for 12 h within three reuse cycles; for comparison, no removal of BG was obtained over $CoFe_2O_4$ synthesized by sol–gel method and $CoFe_2O_4$-900 (CP); (2) no hydroxyl radicals were captured with salicylic acid used as molecular probe in the MICO process; (3) MW irradiation enhanced the release of residual NaOH within the microstructure of $CoFe_2O_4$ and further discolored BG, because BG is sensitive to pH; (4) granular activated carbon (GAC), an excellent MW-absorbing material possessing higher dielectric loss tangent compared to that of a series of $CoFe_2O_4$ materials, could not remove BG in suspensions at a higher efficiency, even if the loading amount was 20 g L^{-1}. Accordingly, MICO process over $CoFe_2O_4$ materials and GAC could not effectively eliminate BG in suspensions.

1. Introduction

Recently, microwave (MW) irradiation has emerged as a potentially powerful tool in environmental applications, including soil remediation [1], purification of hazardous wastewater (WW) [2], and treatment of sewage sludge [3,4]. The main advantages are attributed to shorter reaction time, and higher reaction speed [5,6]. Thus, a series of stand-alone or coupled processes associated with

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http://dx.doi.org/10.1016/j.jhazmat.2013.10.022

MW irradiation have been developed, including the following: (1) MW alone [7,8], (2) MW combined with oxidants [9–13], (3) MW integrated with photochemical process [14,15], (4) MW coupled with Fenton process [16], and (5) MW induced catalytic oxidation (MICO) process over MW-absorbing materials. In recent years, MICO process has been widely adopted [5] owing to its simple reaction conditions and no need for photoirradiation and addition of oxidants.

Several recent studies have evaluated the MICO process for the treatment of a number of contaminants. For example, Lai et al. [17,18] revealed the high degradation efficiency of phenols by microwave-enhanced catalytic process over nickel oxides and Co_3O_4. Similarly, He et al. [19] reported that ~97% of crystal violet ($100\,mg\,L^{-1}$) was rapidly eliminated in nano-nickel dioxide suspensions after MW irradiation (800 W, 5 min) with ~81% of total organic carbon (TOC) removal. Moreover, Bi et al. [20] reported that ~94% of color removal was obtained with MW irradiation (400 W, 1.5 min) over CuO_n–La_2O_3/γ-Al_2O_3 under the optimal condition (with catalyst dosage as $70\,g\,L^{-1}$, pH 7, concentration of ClO_2 as $80\,mg\,L^{-1}$), corresponding to ~67.9% of TOC removal. Zhang et al. [21] found that ~100% decolorization rate of Brilliant Green (BG; 50 mL, $20\,mg\,L^{-1}$) was obtained by MICO process (600 W, 2 min) over $CoFe_2O_4$ (0.3 g). Furthermore, up to 97% of BG, corresponding to 91% of TOC, was removed under MW irradiation (2.0 min) due to the synergistic effects of MW and $NiFe_2O_4$ [22], suggesting this is a promising application in treatment of various dyestuff in wastewater on a large scale. Similarly, ~99.8% degradation percentage of acid fuchsin, corresponding to 91.2% of TOC removal, was obtained using MW irradiation (1.5 min) over $MgFe_2O_4$ with the advantages of low cost and rapid processing [23]. For comparison, the main advantages of $CoFe_2O_4$-based MICO process include simple materials synthesis method without addition of sodium hypochlorite, and no need for oxidants in the MICO process, indicating the potential for pilot-scale application. However, BG was sensitive to pH [24,25], implying that the NaOH residue within $CoFe_2O_4$ materials prepared by co-precipitation method [21] might affect or enhance the MICO-based elimination of BG through a secondary pathway. Moreover, the MICO process over $CoFe_2O_4$ materials prepared by sol–gel process or other methods has not been reported, still. Notably, the above literature studies have not fully examined the relationship between MICO process and MW-absorbing properties of different materials. Accordingly, it was considered necessary to further assess the MICO process in this study.

For this purpose, we attempted to conduct this study from two aspects as follows: (1) to characterize the $CoFe_2O_4$ materials synthesized by chemical co-precipitation method and sol–gel method followed by their calcination at different temperatures (100–900 °C) and examine the role of residue NaOH within the microstructure of $CoFe_2O_4$ on the pH variation of aqueous solution and on the MICO-based removal of BG; and (2) to assess the feasibility of the MICO-based elimination of BG over a series of MW-absorbing materials, including granular activated carbon (GAC) in suspensions.

2. Experimental

2.1. Materials and reagents

Typical cationic triphenylmethane dye BG (CAS 630-03-4, $C_{27}H_{34}N_2O_4S$, MW = 482.64) was purchased from Acros Organics Company. HPLC grade ammonium acetate, acetic acid and acetonitrile were obtained from Tedia Company. Milli-Q water (with a resistivity of 18.2 MΩ cm at 25 °C) was used throughout this study. Commercial fly ash-originated GAC (analytical grade, $400\,m^2/g$ of BET area, 4% of ash content) was bought from Guangzhou Chemical Reagent Co. (China) with a particle size of 1–3 mm. Prior to adsorption, GAC was immersed in a 10% HCl solution for 4 h, then washed with distilled water, and eventually dried at 105 °C for 12 h. Additionally, salicylic acid (SA, 99.5% of purity), a commonly used radical scavenger, was obtained from Shanghai Chemical Reagent Company (China).

2.2. Synthesis of a series of $CoFe_2O_4$ materials

In this study, the materials were synthesized by chemical co-precipitation method [21] and sol–gel method [26] and further denoted as $CoFe_2O_4$ (CP) and $CoFe_2O_4$ (sol–gel). In a typical CP procedure, $FeCl_3{\cdot}6H_2O$ (54.06 g) and $CoCl_2{\cdot}6H_2O$ (23.8 g) were dissolved in distilled water (1 L) with the stoichiometric proportion of Co^{2+}/Fe^{3+} as 1:2, and further stirred at room temperature for 1 h. Then, NaOH solution ($4\,mol\,L^{-1}$, 250 mL) was added dropwisely, until colloid was obtained. The precipitate was washed by doubly distilled water, and dried at 80 °C for 12 h. Then, the precipitate was grinded, further boiled with doubly distilled water under reflux condensation condition until the neutral effluent pH was obtained, and eventually dried at 100 °C for 12 h. For comparison, $Fe(NO_3)_3{\cdot}9H_2O$ (40.4 g) and $Co(CH_3CO_2)_2{\cdot}4H_2O$ (12.45 g) were also added into ethylene glycol (200 mL) in the sol–gel procedure, and distilled water (30 mL) was added dropwisely. Then, the mixed solutions were maintained at 70 °C for 10 h under reflux condensation condition, further irradiated by MW irradiation (0.9 kW) for 15 min, and subsequently dried at 100 °C. Eventually, the above-obtained powers were calcinated at 100–900 °C for 12 h. The oven ramp rate during heating process was $10\,°C\,min^{-1}$; after heat treatment, the samples were finally cooled down under natural cooling conditions.

2.3. Sample characterization

A series of $CoFe_2O_4$ powers were analyzed by X-ray diffraction (XRD) using Cu KR radiation over the scan range within 25–65° and a 2θ scan rate of $2°\,min^{-1}$ (Bruker D8 Advance), high-resolution transmission electron microscopy (HRTEM, JEM 1010 electron microscopy instrument), scanning electron microscopy (SEM, Hitachi S-3400N II, Japan), and energy dispersive spectroscopy (EDS, EX-250, Horiba, Japan). Moreover, X-ray photoelectron spectra (XPS) were recorded on a KRATOS AXIS Ultra DLD spectrometer equipped with a hemispherical electron analyzer and an Al anode (Al Ka = 1486.6 eV) powered at 150 W, a pass energy of 20 eV, and a hybrid lens mode. Reflection loss was measured using a HP8510 network vector analyzer working at 2–18 GHz hand. The samples were mixed with epoxide-resin glue at a ratio of 85:15, then pressed full circle for disclosing the complex relative permittivity ($\varepsilon = \varepsilon' - i\varepsilon''$). With the assistance of microwave network vector analyzer (VNA, Agilent, E8363C), the complex magnetic permeability and the duplicate coefficient of dielectrical loss could be determined with the sweep frequency scope as 2–18 GHz. The VNA specimens were fabricated by pressing a mixture of samples and phenolic resin into a steel mode.

2.4. Elimination of BG over MICO process

Prior to MW irradiation, suspensions containing BG (50 mL, $20\,mg\,L^{-1}$) and $CoFe_2O_4$ (0.05 g) were mixed by ultrasonic wave (SB-5200DT, 200 W, 40 KHz, Ningbo Scientz Biotechnology Co., LTD.) in the dark for 30 min to establish adsorption/desorption equilibrium. Then, the suspensions were irradiated with MW energy (2.45 GHz, 0.9 kW, in Fig. 1S) in a 250-mL flat bottom Pyrex flask, which was connected with a water reflux condenser (60 cm, length) through a communication pipe. After certain intervals, small aliquots of suspension were withdrawn and centrifuged