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Photocatalytic degradation of an azo textile dye (C.I. Reactive Red 195 (3BF)) in aqueous solution over copper cobaltite nanocomposite coated on glass by Doctor Blade method

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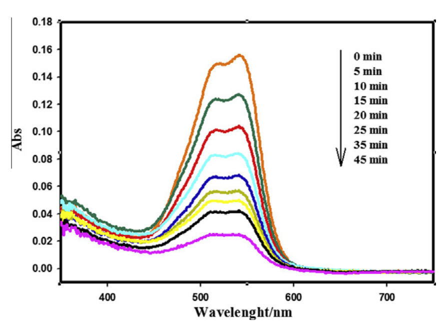
HIGHLIGHTS

- Photocatalytic degradation of reactive brilliant red X-3B was studied.
- Copper cobaltite nanocomposite was coated on glass by Doctor Blade method.
- UV-DRS, XRD and FESEM measurements were performed for structural and optical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

The degradation of C.I. Reactive Red 195 (3BF) in aqueous solution using copper cobaltite nanocomposite coated on glass by Doctor Blade method was studied. Structural, optical and morphological properties of nanocomposite coatings were characterized by X-ray powder diffractometry (XRD), diffuse reflectance spectroscopy (DRS) and field emission scanning electron microscopy (FESEM). The nanoparticles exhibit a particle size of 31 nm, showing a good nanoscale crystalline morphology. The photocatalytic activity of copper cobaltite nanocomposite coated on glass was studied by performing the photocatalytic degradation of 3BF at different irradiation time. The effect of irradiation time on the degradation of 3BF was studied and the results showed that more than 85% of the 3BF was degraded in 45 min of irradiation. The pseudo-first-order kinetic models were used and the rate constants were evaluated with pseudo first order rate constants of 4.10×10^{-2} min^{-1}. The main advantage of the photocatalyst coated on glass overcomes the difficulties in separation and recycle of photocatalyst suspensions.

Introduction

Worldwide industries have used different kind of dyes and large amounts of dyes are released into the water environment which causes severe health problems [1–4,5]. Industrial waste water must be treated prior to discharging them into the water environment. Advanced oxidation processes are the most useful methods for mineralizing pollutants rather than non-destructive methods which transfer pollutants from water to sludge. Semiconductor photocatalysts are the most favorite choice for mineralizing pollutants. The photocatalysts must be stable, low-cost, and non-toxic with good photo-catalytic activity [6–9]. Spinel cobaltites have narrow band gap with promising photocatalytic activity. For scale up purposes there are needs to synthesize copper cobaltites at moderate condition such as co-precipitation. Co-precipitation process is favored for its reduced temperature of processing [10–12]. When the suspension of photocatalyst is used for photodegradation of pollutants, the suspended photocatalyst must be separated after each reaction. Coating and immobilization of photocatalyst

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overcomes the difficulties in separation and recycle of photocatalyst. Photocatalyst coating films can be prepared by various techniques [13,14]. Some spinel-type oxides [15] are semiconductor materials with narrow band gap and could be used in the degradation of environmental pollutants. Copper cobaltite, ($CuCo_2O_4$) is a typical spinel material and it has also attracted growing interest in diverse applications such as catalyst, refractory material, microwave dielectric and ceramic capacitor, and humidity sensors and a candidate for anode materials of lithium battery [16–18]. Most of the methods for preparation of copper cobaltite are either difficult, needs high temperature or costly which diminishes preparation of the nano-sized materials in a large scale as compared to the co-precipitation synthesis. We had conducted deposition of new copper cobaltite nanocomposite on commercial borosilicate glass substrates using spin-coating and Doctor Blade method. Our study revealed that copper cobaltite nanocomposite coatings exhibited favorable optical properties as photocatalyst. To the best our knowledge, Doctor Blade coated copper cobaltite on glass and photocatalytic performance of nanocomposite in 3BF aqueous solution is not reported. The objectives of the study were to optimize the photocatalytic performance of nanocomposite oxides coating. The film surface was characterized using diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM).

In this research copper cobaltite nanocomposite was synthesized via a co-precipitation method using copper nitrate, cobalt nitrate and sodium carbonate as precursors. Structural, optical and morphological properties of nanocomposite coatings were characterized by X-ray powder diffractometry (XRD), diffuse reflectance spectroscopy (DRS) and field emission scanning electron microscopy (FESEM). The effect of irradiation time on the degradation of 3BF has been studied and the results showed that more than 85% of the 3BF (Fig. 1) was degraded in 45 min. The degradation mechanism of 3BF was also discussed with the change of UV–vis spectra of 3BF at different degradation time.

Materials and methods

Chemicals

The 3BF used for photocatalytic degradation was obtained from local textile dye industries and was utilized without further purification. Copper nitrate and cobalt nitrate was obtained from Merck Company (Germany). Sodium carbonate was supplied by Sigma Chemicals Company. Other reagents were all analytical grade.

Preparation of nanostructure copper cobaltite

The nanostructure copper cobaltite was synthesized following the procedure: a solution (0.7 M) of $Cu(NO_3)_2{\cdot}3H_2O$ was mixed with a solution (2.3 M) of $Co(NO_3)_2{\cdot}6H_2O$. To this mixture was added a saturated solution of Na_2CO_3 dropwise, stirred for 1 h at 60 °C. The precipitate was filtered, washed thoroughly with distilled water, dried at 120 °C for 24 h and annealed at 350 °C for 4 h (Fig. 2).

Coating of nanostructure copper cobaltite on glass by Doctor Blade method

Preparation of copper cobaltite paste and coating the paste on glass by Doctor Blade were performed by our previous reports [19–22].

Photocatalytic degradation of C.I. Reactive Red 195 (3BF) by copper cobaltite coated on glass by Doctor Blade method

The paste of copper cobalt oxide coated on a glass slide (6 cm × 2 cm and 2 mm thickness) by Doctor-Blade method and the thin film annealed at 400 °C for 1 h. The B3F solution as dye with a concentration of 10 mg/L (ppm) prepared as an initial solution. This solution exposed at O_2 gas for 30 min. The copper cobalt oxide thin film immersed into a petri dish with 25 ml of the initial B3F solution (Fig. 1) and maintained at dark conditions for 1 h. The concentration of this solution determined by measuring the absorbance by UV–vis spectrophotometer was 9.57 mg/L (ppm) after remaining at dark condition (calculated from standard curve). The reaction system illuminated by a 230 W Hg (g) lamp at different times and the concentration of the B3F solution determined by measuring the absorbance by a Cary 500 UV–vis spectrophotometer for photocatalytic activity examination.

Apparatus

Copper cobaltite was characterized by UV-DRS, XRD and FESEM analysis. Diffuse reflectance spectra (DRS) were collected with a V-670, JASCO spectrophotometer and transformed to the absorption spectra according to the Kebelka relationship. The structure and crystal phase composition of the composites were determined by XRD patterns with a X-ray diffractometer (D8 Advance, BRUKER) in the diffraction angle range 2θ = 20–60°, using Cu Kα radiation. The crystallite size D of the sample was estimated using the Scherer's equation, $(0.9\lambda)/(\beta\cos\theta)$, by measuring the line broadening of main intensity peak, where λ is the wavelength of Cu Kα radiation, β is the full width at half-maximum, and θ is the Brag's angle. Morphology was measured by using a FE-SEM, Hitachi, and model S-4160. The borosilicate glass substrates coated using spin coating method (Spin Coater, Modern Technology Development Institute, Iran).

Results and discussion

Characterization

The crystal phase structures of prepared copper cobaltite nanocomposite was characterized by XRD measurements (Fig. 3) and

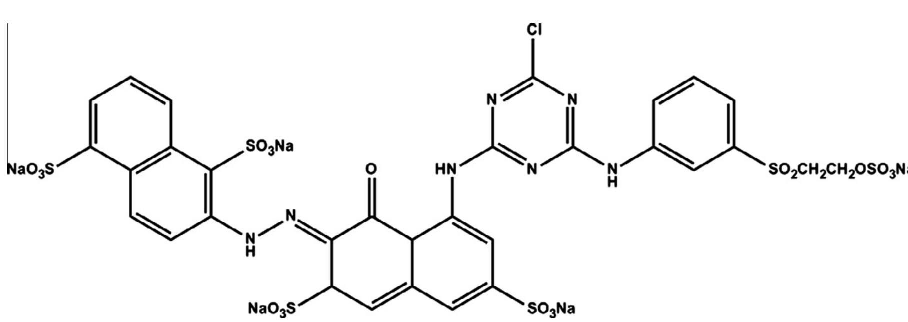

Fig. 1. Chemical structure of 3BF.