



# Catalytic wet peroxide oxidation of a reactive dye by magnetic copper ferrite nanoparticles



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## ABSTRACT

The aim of this work was to study copper ferrite nanoparticles (CFNs) as a catalyst in catalytic wet peroxide oxidation of C.I. Reactive Red 120 (RR120) as a model organic pollutant in aqueous solutions. CFNs were synthesized by polymeric precursor method and characterized with various techniques (e.g. XRD, FTIR, SEM, and TEM and VSM). The prepared nanoparticles had the nanocrystalline pure single-phase structure. Values of saturation magnetization, remanent magnetization and coersivity were found to be 6.5 emu/g, 2.1 emu/g and 380 Oe, respectively. The degradation of RR120 was investigated in the presence of hydrogen peroxide and CFNs at various temperatures and pHs. The most effective RR120 degradation was achieved at pH 3 and 75 °C. The catalyst was recovered and reused 6 times without noticeable loss of activity.

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## 1. Introduction

Textile industries produce large volume of wastewater that contains various pollutants such as dyes, surface active materials and textile auxiliaries [1,2]. Textile wastewater treatment may require a complete dye removal. Therefore, the research on decolorization of colored wastewater is very important [3]. While most organic compounds in wastewater can be degraded by conventional biological and physical–chemical treatments, many synthetic organic compounds in textile wastewater such as dyes and surfactants are recalcitrant and resistant to biodegradation. Thus, these methods are not usually adequate for complete dye removal from textile wastewater [1,4].

Chemical oxidation is an alternative solution for treating wastewater containing organic pollutants by converting these compounds to biodegradable products [5]. The wastewater can be treated using different oxidizing agents such as chlorine, hydrogen peroxide, ozone, UV irradiation and etc. This is an attractive method for wastewater decolorization since it is normally efficient and fast [6].

Advanced oxidation processes (AOPs) have also been proposed for wastewater treatment. AOPs are based on the formation of very active hydroxyl radicals, which react quickly with the organic

materials. Among AOPs, catalytic wet peroxide oxidation is an attractive oxidation treatment for decolorization and degradation of dyes due to their efficiency, moderate cost, low waste and sludge, the lack of toxicity of the reagents, and the simplicity of the technology [7,8]. The combined addition of H<sub>2</sub>O<sub>2</sub> and a catalyst containing a bivalent metal (i.e. Fe, Cu, Co or Mn) enhance the degradation rate of organic compounds in wastewater [9–12]. Various oxidation catalysts (e.g., Cu–Al, Al–Fe pillared clays, Cu (NO<sub>3</sub>)<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, . . . ) have been studied for the removal of different organic compounds [13–20]. There is always a great interest toward synthesis of new catalysts with higher efficiency and performance which can be separated easily from the wastewater after treatment. Magnetic separation is considered as a fast and effective technique for separating magnetic particles [21].

Ferrite magnetic nanoparticles belong to a family of magnetic materials that can be used in many areas such as high-density information storage, ferrofluid technology, magnetic drug delivery, magnetic refrigeration, medical diagnostics, catalysts, MRI enhancement and gas sensors [22–27]. Ferrite magnetic nanoparticles are recyclable, environmentally friendly, economical and efficient catalysts for organic reactions. Nano-sized magnetic particles possess high performance in the separation process due to the high specific surface area and the absence of internal diffusion resistance [27,28].

In homogeneous catalytic oxidation such as Fenton process, the recovery or separation of catalyst (i.e. Fe<sup>2+</sup>) is technically and

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economically unfeasible. Therefore, in this work we report a heterogeneous catalytic oxidation of an azo reactive dye (RR120) by air-stable, magnetically separable, recyclable CFNs in the presence of hydrogen peroxide. Based on the literature review, there is only one paper dealing with photocatalytic degradation of a dye in the presence of CFNs as a catalyst [29]. This study sheds more light on the performance and factors controlling catalytic wet peroxide oxidation of RR120 in aqueous solutions.

## 2. Experimental

### 2.1. Materials

Iron(III) nitrate 9-hydrate, copper nitrate 6-hydrate, hydrogen peroxide (30%), sulfuric acid, sodium hydroxide, citric acid and ethylene glycol were of analytical grade from Merck Chemicals, Germany. Commercially available C.I. Reactive Red 120 (RR120) with  $\lambda_{\text{max}} = 516 \text{ nm}$  was used as a model pollutant in this study. The structure of this dye can be found in other references [30,31].

### 2.2. Preparation and characterization of copper ferrite nanoparticles

$\text{CuFe}_2\text{O}_4$  nanoparticles (CFNs) were prepared by polymeric precursor method. Stoichiometric amounts (molar ratio of Fe/Cu = 2) of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solutions were mixed with aqueous solutions of citric acid and ethylene glycol. 10 mmol of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 5 mmol of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (molar ratio of Fe/Cu = 2) were dissolved in 20 mL of deionized water. 45 mmol of citric acid and 93 mmol of ethylene glycol were dissolved in 20 mL deionized water. These two solutions were mixed and the molar ratio of total metal ions to citric acid was kept as 1:3. A mass proportion of 60:40 was used for citric acid: ethylene glycol. The temperature of the solution was raised to 85 °C and maintained at this temperature for 2 h up to the gel formation. The resulting gel was heated at 300 °C for 1 h, leading to the expansion of its original volume to three times and formation of the porous semi-carbonized powder precursor. The powder precursor was then calcined at 500 °C for 2 h, with a heating rate of 10 °C/min at ambient atmosphere.

X-ray diffraction (XRD) was performed on a Philips PNA-analytical diffractometer using  $\text{CuK}\alpha$  radiation. SEM micrographs were obtained on a LEO 1455VP scanning electron microscope. TEM images were recorded on a Philips CM 200 FEG transmission electron microscope. FT-IR spectrum (500–4000  $\text{cm}^{-1}$ ) was recorded on a Perkin Elmer spectrophotometer. A vibrating sample magnetometer (VSM) was used for magnetic measurement at room temperature. BET surface area was determined by Quantachrome Quantasorb surface analyzer and  $\text{N}_2$  as the adsorbate.

### 2.3. Decolorization studies

The initial dye concentration of RR120 solution was set to 50 ppm. The solution pH was adjusted using 0.5 M HCl and/or 0.5 M NaOH. The solution temperature was set at the desired value and maintained under magnetic stirring with apparent speed of 1000 rpm.

For monitoring the decolorization, the dry catalyst was added to the dye solution and once the desired temperature was reached, hydrogen peroxide was introduced to the reactor. This point was considered as “zero time” in all the experiments. At different time intervals, 1–2 mL samples were extracted and cooled to the room temperature in order to stop the reaction. At each sampling time, the catalyst was separated either by centrifugation or collected by an external magnetic field and the solution was immediately used for analysis. The absorption spectra of the dye solutions were recorded with a Cecil 2021 spectrophotometer. At the end of the

reaction, the catalyst was separated magnetically and washed with distilled water and ethanol for further reuse.

The chemical oxygen demand (COD), which is a measure of the concentration of all compounds that can be oxidized by the  $\text{Cr}_2\text{O}_7^{2-}$  anion in acidic media, gives a measure of degradation of pollutants and intermediates produced during the dye degradation. Complete removal of the RR120 is expected to represent the most effective reduction in COD. The COD determination was carried out using oxidation with potassium dichromate in sulfuric acid and heating for 2 h at 150 °C according to Hach method no. 8000. Due to interferences of  $\text{H}_2\text{O}_2$  with the COD measurements,  $\text{MnO}_2$  powder was added to destroy residual  $\text{H}_2\text{O}_2$  in the treated solution [32].

## 3. Results and discussion

### 3.1. Characteristics of nanoparticles

The XRD pattern of the catalyst is shown in Fig. 1. The XRD pattern of this material matched very well with the  $\text{CuFe}_2\text{O}_4$  standard (JCPDS file number 00-025-0283). All of the diffraction peaks confirmed the formation of the pure single-phase copper ferrite with face-centered cubic spinel phase and  $Fd3m$  (227) space group. The presence of single phase  $\text{CuFe}_2\text{O}_4$  has been further confirmed by the absence of  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$  peaks. No diffraction peaks of other impurities are observed in the pattern.

The crystallite size of the catalyst estimated from XRD peak broadening using Scherrer's formula [33].

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where  $t$  is the crystallite size,  $\lambda$  the wavelength of X-ray radiation ( $\text{CuK}\alpha$ ),  $\theta$  the Bragg angle, and  $\beta$  the full width at half maximum (FWHM) of the most intense diffraction peak. The crystallite size of the catalyst was found to be 29 nm.

BET surface area analysis showed that the  $\text{CuFe}_2\text{O}_4$  powder has a surface area of 19.02  $\text{m}^2/\text{g}$ . Scanning electron micrographs were used to show the morphological features of the powder (Fig. 2). The SEM micrograph of the catalyst showed that the particles have almost spherical morphology, regular in shape and dispersed uniformly but agglomerated to some extent due to the interaction between magnetic nanoparticles.

The TEM images of the copper ferrite nanoparticles are shown in Fig. 3. The figure indicates that the particles are almost spherical with an average diameter of about 21 nm. This is in a good agreement with the crystalline size of the catalyst that obtained from the XRD method.

FT-IR spectrum of the copper ferrite nanoparticles has been provided in the supporting information (Fig. S3). The absence of some organic bands such as peaks at about 1732  $\text{cm}^{-1}$  of uncoordinated carbonyl groups and peaks at around 1610 and 1373  $\text{cm}^{-1}$  related to the asymmetric  $\nu_{\text{as}}(\text{COO})$  and symmetric  $\nu_{\text{s}}(\text{COO})$  stretching vibration of COO groups, respectively, can be ascribed to the decomposition of organic ligands in the gel after calcination. The broad band at 3446  $\text{cm}^{-1}$  is ascribed to the stretching mode of the free or absorbed water. The FT-IR spectrum confirms the formation of the organic free CFNs. Two vibrating bands at around 547 and 480  $\text{cm}^{-1}$  are attributed to the metal–oxide  $\nu(\text{M–O})$  stretching vibration, characteristic of copper ferrites.

Magnetic properties of CFNs were measured by Vibrating Sample Magnetometer (VSM) at room temperature. Fig. S2 shows the ferromagnetic hysteresis loop of the nanoparticles. The saturation magnetization, remanent magnetization and coercivity values were 6.5 emu/g, 2.1 emu/g and 380 Oe, respectively. From the hysteresis loops, the ratio  $R$  of the remanent to the saturation

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