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# Preparation, characterization and application of nanosized copper ferrite photocatalysts for dye degradation under UV irradiation☆

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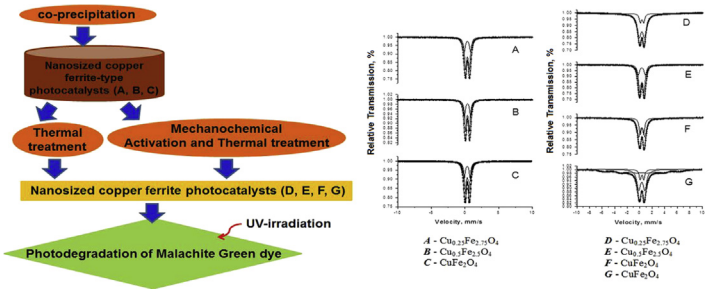
## HIGHLIGHTS

- Copper ferrites via co-precipitation, mechanochemical and/or thermal treatment.
- Nano ferrites show a super-paramagnetic and collective magnetic excitations nature.
- The co-precipitated $Cu_{0.25}Fe_{2.75}O_4$ posses the highest photocatalytic activity.
- The amount adsorbed Malachite Green by catalyst depends on the preparation method.
- The prepared copper ferrites can be applicable as cheap adsorbents and catalysts.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Nanosized copper ferrite-type materials ($Cu_xFe_{3-x}O_4$, $0 \leq x \leq 1$) have been prepared by combination of co-precipitation and mechanochemical activation and/or thermal treatment. The crystalline structure and morphology of the obtained ferrite nanopowders have been characterized by different instrumental methods, such as Powder X-ray diffraction (PXRD), Mössbauer and FT-IR spectroscopies, specific surface area and porosity measurements, thermal analyses (Differential Thermal Analysis and Thermogravimetric Analysis) and Temperature-Programmed Reduction. The average crystallite size of copper ferrites ranged between 7.8 and 14.7 nm and show a superparamagnetic and collective magnetic excitations nature. The photocatalytic decolorization of Malachite green oxalate under different UV illumination intervals was examined using these copper ferrites as photocatalysts. The results indicate that the prepared nanostructured copper ferrites showed enhanced photocatalytic activity and amount adsorbed Malachite Green dye. The co-precipitated nanosized copper ferrite powder with a low content of copper metal ions in a magnetite host structure ($Cu_{0.25}Fe_{2.75}O_4$) showed an apparent pseudo-first-order rate constant $15.4 \times 10^{-3}$ $min^{-1}$ and an amount adsorbed Malachite Green as model organic dye pollutant per 1 g catalyst of 33.4 ppm/g after the dark period. The results confirm that the copper ferrites can be suitable for photocatalytic treatment of wastewaters containing organic dyes. The new aspect of

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presented investigations is to study the influence of different degree of incorporation of copper ions into the magnetite host structure and preparation methods on the photocatalytic properties of nanosized copper ferrite materials and obtaining of potential photocatalyst ($Cu_{0.25}Fe_{2.75}O_4$) with higher photocatalytic activity ($15.4 \times 10^{-3}$ $min^{-1}$) than that of the standard referent Degussa P25 ($12 \times 10^{-3}$ $min^{-1}$) for degradation of organic dye Malachite green under UV irradiation.



## 1. Introduction

The Cu–Fe–O system is of long-standing interest in solid-state physics, mineralogy, ceramics and metallurgy [1,2]. Copper ferrite ($CuFe_2O_4$) is one of the most important spinel ferrites because it exhibits phase transitions, changing semiconducting properties, shows electrical switching and tetragonality variation when treated under different conditions in addition to interesting magnetic and electrical properties with chemical and thermal stabilities. It is used in a wide range of applications in gas sensing, catalytic applications, Li ion batteries, high density magneto-optic recording devices, color imaging, bioprocessing, magnetic refrigeration and ferrofluids [3–5].

A copper ferrite can be formulated as $(Cu^{2+})[Fe_2^{3+}]O_4$ where $Cu^{2+}$ and $Fe^{3+}$ occupy tetrahedral (A) and octahedral (B) positions of the FCC lattice formed by $O^{2-}$ ions. This ferrite is generally represented by the $(Cu^{2+})_{1-x}$ $(Fe^{3+})_x$ $[(Cu^{2+})_x$ $(Fe^{3+})_{2-x}]$ $O_4^{2-}$ formula where the ions within the brackets occupy the B sites and the ions outside the bracket occupy the A sites. Ideal copper ferrite adopts an inverse spinel structure ($x = 1$) with 8 $Cu^{2+}$ ions in B sites and 16 $Fe^{3+}$ ions equally distributed between A and B sites per unit cell (32 oxygen ions) [6].

The preparation method plays a very important role with regard to the chemical, structural and magnetic properties of the spinel ferrites [7,8]. Copper ferrite materials can be produced by various procedures, such as sonochemical method [9], ceramic method [2,10], hydrothermal route [3] or hydrothermal route coupled with a reverse micelle method [11], solid state reactions [12–15], co-precipitation [14–18], sol–gel [14], auto-combustion method [19], microwave-induced combustion process [20], electrospinning method [4], soft chemical methods – a complexation method and a self-propagating combustion [8], citric acid-aided process [15], etc.

In this study we report the synthesis of nanosized copper ferrite materials $Cu_xFe_{3-x}O_4$, $0 \leq x \leq 1$ with different stoichiometries, their physicochemical characterization and their application in photocatalytic reaction. The phase composition and structural properties of the prepared copper ferrites were established using different physicochemical methods. Application of these nanodimensional copper ferrite materials as potential photocatalysts for purification of water polluted by organic dyes is also reported; we used degradation of Malachite green oxalate dye in water under UV light as a test reaction. The relationships between synthesis conditions, structure, and photocatalytic properties are also discussed.

## 2. Experimental

### 2.1. Preparation of nanosized copper ferrite materials

Different series of copper ferrite materials were prepared using $FeCl_2 \cdot 4H_2O$ (Sigma Aldrich, p.a.), $FeCl_3 \cdot 6H_2O$ (P.P.H. "STANLAB" s.j) and $CuCl_2 \cdot 2H_2O$ (Valerus, p.a.) as the starting reagents, which were dissolved in distilled water to prepare 0.03 M solutions. These were mixed in 3:8:1, 1:4:1 and 0:2:1 volume ratios to produce samples ***A*** – $Cu_{0.25}Fe_{2.75}O_4$, ***B*** – $Cu_{0.5}Fe_{2.5}O_4$ and ***C*** – $CuFe_2O_4$, respectively. A 0.3 M solution of NaOH was used as precipitating agent, and slowly dropwise added to the solutions containing the metal salts, which were being vigorously stirred, until a constant pH value of 12.5 was reached. The suspensions were further stirred for 1 h at room temperature. The obtained dark brown precipitates were centrifuged and washed several times with distilled water until pH = 7. After drying at 40 °C for 24 h the three samples were thermally treated at 300 °C for 3 h in argon, nitrogen or air, respectively yielding samples ***D***, ***E***, and ***F***; the thermal treatment was performed in a furnace from Carbolite type MTF-12/38/400, England. An additional sample was prepared from sample C by milling 2.08 g of the solid using a milling container with volume 50 ml for 1 h at 200 rpm and a ***C***/balls mass ratio of 1/20 in a high energy planetary ball mill type PM 100, Retsch, Germany. After mechanochemical activation, the solid was thermally treated at 400 °C for 4 h in air, yielding sample ***G***.

### 2.2. Physicochemical characterization of synthesized nanodimensional copper ferrite materials

Powder X-ray diffraction (PXRD) diagrams of the prepared copper ferrite materials were recorded in a TUR M62 apparatus equipped with a HZG-4 goniometer, PC management and data accumulation, using CoKα radiation. JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used for the phase determination.

The average crystallite size, lattice microstrain parameter and unit cell parameter of synthesized copper ferrite phases was calculated by the Scherrer [21] and Williamson–Hall equations [22,23] using PowderCell program:

$$D = \frac{B\lambda}{\beta \cos \theta} \quad (1)$$

where $D$ is the average crystallite size of the phase under investigation, $B$ the Scherrer constant (0.89), λ the wavelength of X-ray beam used, $\beta$ the full-width half-maximum (FWHM) of diffraction, and $\theta$ the Bragg's angle [21].

$$\beta \cos \theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin \theta \quad (2)$$

where $\varepsilon$ is the value of internal strain [22,23], other variables having the same meaning as above.

Mössbauer spectra were taken at a constant acceleration mode on a Wissenschaftliche Elektronik GmbH apparatus, working with $^{57}$Co/Cr source and α-Fe standard. The parameters of hyperfine interactions of Mössbauer spectral components, isomer shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field in the site of iron nuclei ($H_{eff}$), line widths (FW) and component relative weights (G), were established by computer fitting.

The nitrogen adsorption–desorption isotherms for specific surface area and porosity assessment were recorded in a Gemini VII 2390T Surface Area Analyzer from Micromeritics; the samples had been previously degassed in a Flow Prep 060 degassing unit, also

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