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RESEARCH ARTICLE

Copper oxide nanoparticles: Synthesis, characterization, optical property and its application for the removal of methyl green dye

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ABSTRACT

In this paper, nanoparticles of copper oxide (CuO) were synthesized using solid-state thermal decomposition of the new copper precursor at 600 ºC for 3 h. The copper precursor was prepared from the mixture of CuCl2.6H2O and benzoic acid in H2O in the presence of KOH. Nanoparticles of copper oxide were characterized by Fourier transform infer-red (FT-IR), UV-Vis and photoluminescence (PL) spectroscopy X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). All results confirmed the preparation of pure phase of CuO nanoparticles. In addition, adsorption of methyl green in aqueous solution of copper oxide nanoparticles as adsorbent was studied at various parameters such as adsorbent dosage and agitation time. It was found that methyl green dye removal increased by adsorbent dosage (0-30 mg) and contact time (0-120 min). This research revealed that the copper oxide nanoparticles could be used as a suitable adsorbent for removal of various organic dyes from aqueous solutions.

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INTRODUCTION

Organic dyes such as bromophenol blue [1], direct red 31 (DR-31) [2], direct green 6 (DG-6) [3], ,ethyl orange [4], reactive orange 13 [5], crystal violet [6], reactive red 198 (RR-198) [7] and sunset yellow [8] are the most commonly used materials in numerous industrial fields. These organic dyes are toxic and harmful for the environment and they can cause irreversible cellular carcinogenesis. Thus, it is necessary to control and remove organic pollutants in an environment samples. Until now, various separation technologies are used in the removal of organic dyes from wastewaters [1-8]. The organic pollutant removal using magnetic nanoparticle such as NiO [1], $ZnFe_2O_4$ [3,7], $NiFe_2O_4$ [4-6,8], as adsorbent is an attractive field because of little toxicity, low cost, and good chemical stability [1-8]. From various techniques for dye removal, the adsorption route is one of the easiest and most effective methods due to simple and easy design, preparation of small amounts of harmful byproducts and finally for the availability of the wide range of absorbent [1-8]. Copper oxide as a p-type semiconductor nanoparticles with band gap in the range 1.8-2.5 eV, have been great attention in recent years due to their wide fields of application, such as antibacterial activities [9, 10], adsorption of dyes [11-13], H_2S and acetaldehyde sensor [14,15]. Fterich et al. studied the effect of concentration of hexamethylenetetramine in optical properties of CuO nanoparticles prepared by hydrothermal technique and shown a remarquable influence of the amine concentration in the optical properties of CuO nanoparticles [16].

The present study focused on the preparation of copper oxide nanoparticles by simple, low-cost and environmental-friendly and removal studies of methyl green from aqueous solution. Also, optical property of CuO nanoparticles has been studied.

EXPERIMENTAL

Materials and measurement

All solvents and compound were purchased

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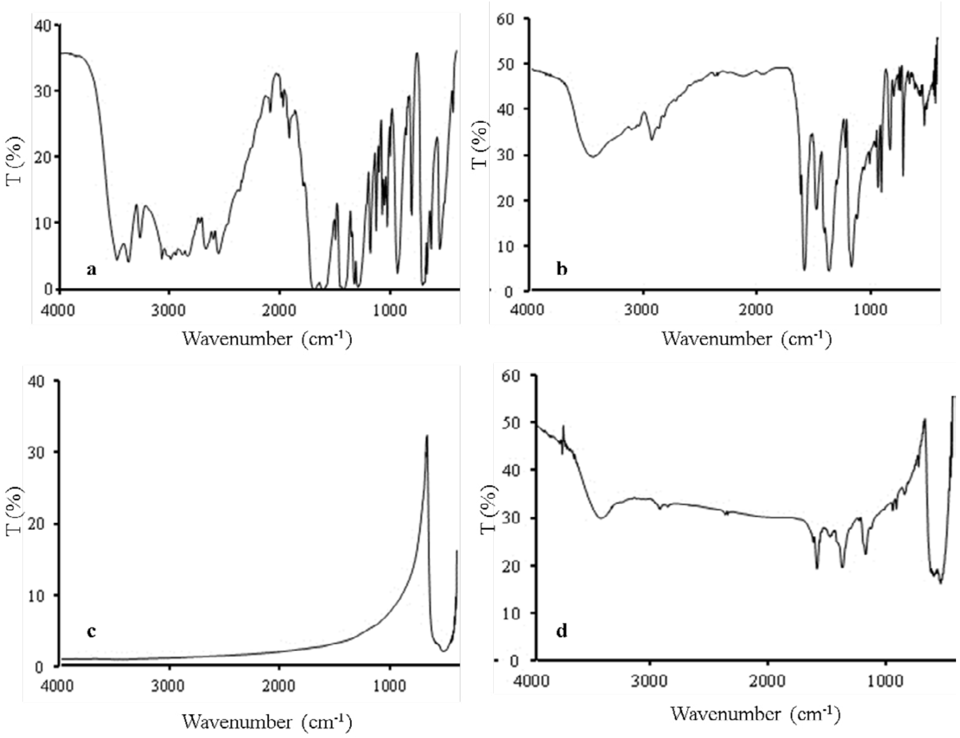

Fig. 1. FT-IR spectra of a) Cu precursor, b) methyl green, c) CuO nanoparticles and d) CuO-methyl green

from Merck and Aldrich Company and used without any further purification. Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on an FT-IR Perkin–Elmer spectrophotometer. Optical absorption measurements were done using a UV-Vis spectrophotometer in the wavelength ranges of 200-800 nm at room temperature. The photoluminescent (PL) emission spectra were performed using Hitachi F4500 spectrofluorimeter. X-ray powder diffraction was done with a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation in the range 2θ = 10°–80°. Transmission electron microscopy image (TEM) was obtained Philips CM120 with a LaB_6 cathode operating at 120 kV.

Synthesis of CuO nanoparticles

For synthesis of CuO NPs, 1 gr $CuCl_2·6H_2O$ was added to a 10 mL water solution of 1 g benzoic acid dissolved in 10 mL water and the mixture was stirred for about 20 min. Then, the mixture was transferred to an oven with temperature of 80°C. After about 24 h, the precipitates as copper precursor were heated at 600 °C for 3h. The black precipitates were collected and washed with cold methanol and dried at room temperature. Then the product was characterized by FT-IR, UV-Vis, PL, XRD and TEM.

Adsorption procedures

First, a 1000 mL of methyl green with 10 ppm was prepared. The dye removal studies were investigated in beakers containing 100 mL of dye solution and at room temperature (25 °C). Then, the effect of different quantities of adsorbent (2, 5, 10 and 20 mg) was studied for 15 min and agitated time (15, 30, 45, 60, and 120 min) was studied at the presence of 5 mg of CuO. After each time, the samples were centrifuged and absorption spectrum of solution was determined using UV-Vis spectrophotometer

RESULTS AND DISCUSSION

FT-IR spectra

FT-IR spectra of copper precursor, methyl green, CuO nanoparticles and CuO-MG are shown in Fig. 1a-d, respectively. There are several sharp peaks in the FT-IR spectrum of the copper precursor and methyl green assigned to the functional groups such as OH, C=O, C-H, C-C, C=C and C=N (Figs. 1a and 1b). While in the FT-IR spectrum of the as-prepared CuO nanoparticles, there is a broad peaks between

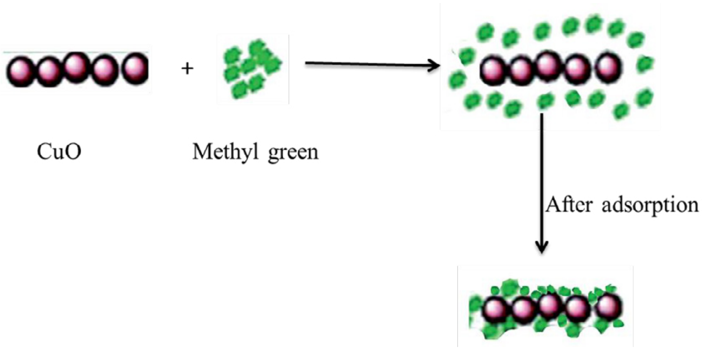

Fig. 2. Mechanism of methyl green adsorption on the surface of CuO nanoparticlews

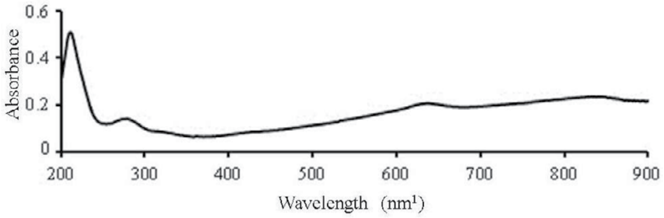

Fig. 3. UV-Vis spectrum of the as-prepared CuO nanoparticles.

447 – 586 cm^{-1} with the maximum at 512 cm^{-1}, assigned to the Cu-O stretching [16-18]. There is no any peak at about 610 cm^{-1} correspond to Cu_2O (Fig. 1c). Then, FT-IR spectrum indicates the formation of CuO [16]. After adsorption of MG on the surface of CuO nanoparticles after 120 min, centrifuged the solution and the precipitate was filtered off and dried at room temperature. FT-IR spectrum of CuO-MG is displayed in Fig. 1d. A broad peak at 3418 cm^{-1} assigned to the O-H vibration of the water molecules adsorbed on the surface of CuO nanoparticles. Three sharp peaks at 1685, 1364 and 1171 cm^{-1} assigned to the various vibrations of MG and confirmed the adsorption if MG on the surface of CuO nanoparticles. This adsorption is physical, because there is no shift in the characteristic peaks in pure MG and MG adsorbed on the surface of CuO nanoparticles. The mechanism of this physical adsorption is depicting in Fig. 2 [19].

UV-Vis and PL spectrum

UV-Vis spectrum of the as-prepared CuO nanoparticles is shown in Fig. 3. A strong absorption appeared at 211 nm assigned to the direct transition of electrons [20]. Also a peak appeared at 280 nm is correspond to the surface plasmon absorption of metal oxide [10, 21]. These peaks confirmed the formation of CuO nanoparticles [22].

To investigate the optical property of the as-prepared CuO nanoparticles, PL spectrum is gathered (Fig. 4). In the PL spectrum, there are three emission peaks were observed at 323 nm, 430 nm and 639 nm (Fig. 4). The first one corresponds to the recombination electrons and holes band-edge between conduction and valence bands, the second one is due to defects in oxygen vacancies or copper interstitials and the third one is attributed to native defect of copper and oxygen [20].

XRD pattern

XRD patterns of CuO show in Fig 5. The intensities of peaks at various 2θ positions are in good agreement with the pure CuO nanoparticles with JCPDS card No. 05-0661 [23]. The broadening peaks show that the particle size of the product falls in nano range. Also, there are no any impurity peaks in the XRD pattern of CuO nanoparticles confirms it's almost purity of the product. According to the Scherer formula, the average size of the particles is estimated about 15 nm.

TEM image

Fig. 6 shows the TEM image of the CuO nanoparticles and presents that the CuO are spherical shapes with a narrow size distribution.

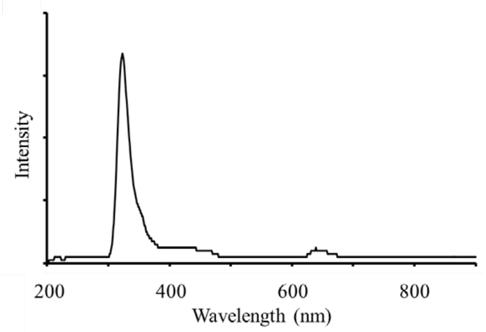

Fig. 4. PL spectrum of the as-prepared CuO nanoparticles.

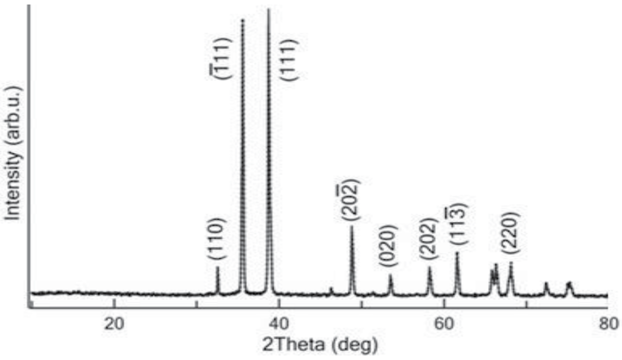

Fig. 5. XRD pattern of as-prepared CuO nanoparticle

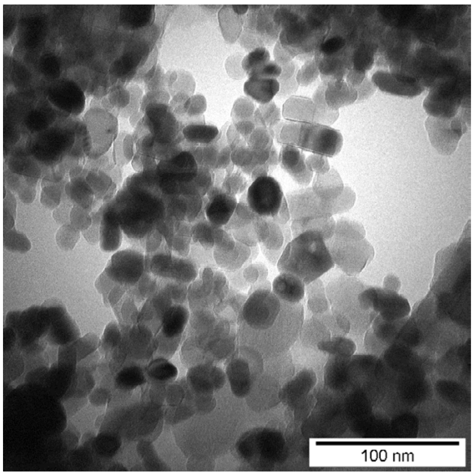

Fig. 6. TEM image of as-prepared CuO nanoparticles

Methyl green removal studies

Fig. 7 illustrated the UV-Vis spectra of methyl green solutions at different adsorbent content of CuO nanoparticles like 5, 10, 20 and 30 mg at constant stirring speed for 15 min. According to the Fig 6, the methyl green removal (adsorbed onto the surface of CuO nanoparticles) increase on increasing the content of CuO nanoparticles due to increase in surface area and the number of adsorbent sites [24,25]. Increase adsorption of methyl green onto the surface of CuO nanoparticles observed when the content of CuO is raised from 0 mg (A = 0.677) to 10 mg (A = 0.207) and after that the adsorption quantity is almost constant (A = 0.155 for 20 mg and 0.157 for 30 mg).

The effect of agitation time (15, 30, 45, 60 and 120

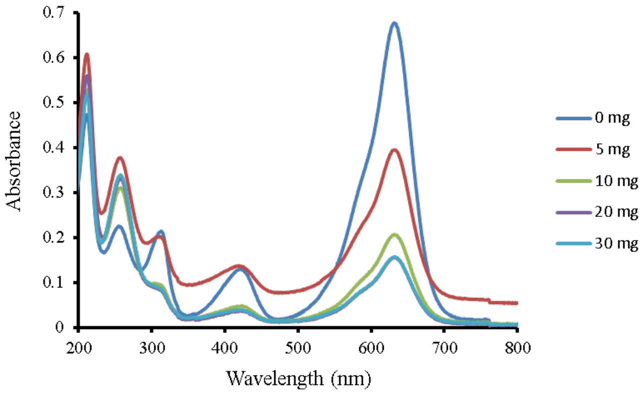

Fig. 7. UV-Vis spectra of methyl green solution at various content of CuO nanoparticles (for 15 min).

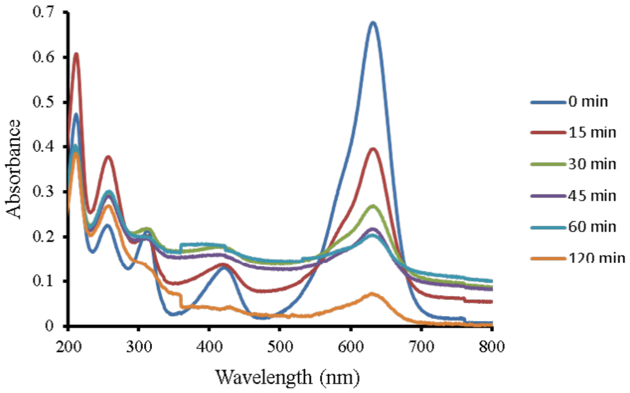

Fig. 8. UV-Vis spectra of methyl green solution at different agitation time (at the presence of 5 mg CuO).

min) at constant stirring speed on the methyl green removal at the presence of 5 mg CuO nanoparticles as adsorbent was studied. Fig. 8 illustrated the UV-Vis spectra of methyl green solutions at different times. According to the Fig 8, the methyl green removal increase on increasing the time agitation from 0 min to 120 min due to the completed of adsorption of methyl green onto the surface of CuO nanoparticles. However, the content of methyl green remove for 45 and 60 min is almost constant. After 120 min, about 90% of methyl green removed.

CONCLUSION

Spherical CuO nanoparticles with uniform size distribution has been prepared by simple and low-cost method and characterized by FT-IR, XRD, UV-Vis, PL and TEM. As prepared CuO nanoparticles used as adsorbent of methyl green dye. The effect of amount of adsorbent and agitation time was studied. The adsorption experiment results show that the maximum contact time was 120 min and usage of 30 mg adsorbent is the best condition for removal of methyl green.

CONFLICT OF INTEREST

All authors declare that no conflicts of interest exist for the publication of this manuscript.

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