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Melissa Officinalis L. leaf extract assisted green synthesis of CuO/ZnO nanocomposite for the reduction of 4-nitrophenol and Rhodamine B

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ABSTRACT

CuO/ZnO nanocomposite has been synthesized using *Melissa Officinalis* L. leaf extract as a mild, renewable and non-toxic reducing agent and efficient stabilizer in the absence of hazardous and toxic materials. SEM, EDS, elemental mapping, TEM and XRD have been used for the characterization of CuO/ZnO nanocomposite. CuO nanoparticles (NPs) with sizes in the 10–20 nm range have been formed, as shown by TEM micrograph. Furthermore, excellent catalytic activity in the degradation of 4-nitrophenol (4-NP) and Rhodamine B (RhB) in water at ambient temperature has been shown by CuO/ZnO nanocomposite.

1. Introduction

Toxic dyes and nitroarene compounds are highly hazardous in the environment and are potentially toxic toward humans, animals and plants. Thus, the degradation of organic dyes is of great environmental and industrial importance. Environmentally acceptable processes in the catalytic reduction of colorless organic pollutants are becoming increasingly necessary [1]. A well-known example of such organic pollutants is 4-nitrophenol (4-NP), which is a toxic and bio-refractory compound, damaging the central nervous system, liver, kidney and blood of humans and animals and causing various diseases [2]. The high stability and low solubility of 4-NP in water makes its degradation to non-dangerous products difficult. 4-Aminophenol (4-AP), the reduction product of 4-NP, is widely applied in the preparation of analgesic and antipyretic drugs as a photographic developer and corrosion inhibition [3], making the reduction of 4-NP to 4-AP greatly important both environmentally and industrially. Metal nanoparticles (MNPs) catalyze the reduction of 4-NP to 4-AP by facilitating electron relay from the donor BH_4 to the acceptor 4-NP to overcome the kinetic barrier [4].

CuO NPs are MNPs catalysts, which play an important part in the overall catalytic performance [5]. Nevertheless, there are disadvantages associated with CuO NPs such as difficulty of quantitative separation from the reaction mixture, impossibility to recycle, excess use of Cu reagents and agglomeration [5]. To overcome these problems, CuO NPs have recently been supported on solid supports such as zeolites to form composite catalysts [6]. ZnO NPs are inorganic compounds widely applied as efficient supports for the immobilization of the MNPs given their exceptional opto-electronic properties, low synthesis cost, environmentally friendliness and highly versatile device fabrication [7–10]. Thus, the development of a simple method for the synthesis of well dispersed, stable CuO NPs and their immobilization on an effective support is highly desirable.

Bio-derived materials are alternative environmentally benign supports in this regard. The advantages of biological methods compared with other methods are: (i) no costly and poisonous capping agents or stabilizers are required, (ii) high temperature calcinations are not necessary for the preparation of the final product, (iii) no poisonous organic solvent or hazardous materials are required and (iv) the methods can be easily scaled up. A metal NP preparation method using various plant extracts or tree gums has recently been reported [4,5,11–14]. However, the agglomeration of metal NPs during catalytic reactions is unavoidable [4,15,16].

Hence, in our experiment, *Melissa Officinalis* L. (lemon balm) leaf extract has been used to synthesize CuO/ZnO nanocatalyst. *Melissa Officinalis* L. is a well-known medicinal plant from the family of lamiaceae. The many pharmacological actions of *Melissa Officinalis* L. include purgation, antibacterial, antitumor, antimutagenicity curing mental and renal disorders. The bioactive components of *Melissa officinalis* L. leaf are anthraquinones, dianthrones, stilbenes, anthocyanins, flavonoids, polyphenols, organic acids, and chromones. *Melissa Officinalis* L. is a well-known medicinal plant from the family of lamiaceae. The plant is high inflavonoid. Flavonoids of lemon balm such as rosmarinic acid and anthocyanin have an antiviral and antioxidant effect [17–19]. Thus, the plant can be used as an important source for bioreduction of metallic ions and production of nanoparticles considering the potent antioxidants contained in it.

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We report an environmentally friendly approach for the preparation of the CuO/ZnO nanocomposite using *Melissa Officinalis* L. leaf extract as a reducing and stabilizing agent. Furthermore, the catalytic activity and recyclability of CuO/ZnO nanocomposite in the reduction of 4-NP and RhB in aqueous medium at ambient temperature using $NaBH_4$ as the hydrogen source have been investigated. The catalyst can be easily recycled following the reaction completion. *Melissa Officinalis* L., however, has never been applied in the green synthesis of CuO/ZnO nanocomposite despite its natural abundance, non-toxicity and biological relevance.

2. Experimental

2.1. Instruments and reagents

Reagents were all obtained from Merck and Aldrich Chemical Companies and used without further purification. A Varian model 640 spectrophotometer was used to record IR (KBr) spectra. A Philips model X'PertPro diffractometer X-ray diffraction equipped with a graphite monochromator crystal was used to perform X-ray diffraction (XRD) measurements. The X-ray wavelength was 1.5405 A° and the diffraction patterns were recorded in the 2θ range (10–80) with scanning speed of 2°/min. Scanning electron microscopy (SEM) (Cam scan MV2300) was used to investigate the morphology and particle dispersion. EDS (Energy Dispersive X-ray Spectroscopy) performed in SEM was used to measure the chemical composition of the prepared nanostructures. The chemical analysis of prepared nanostructures was carried out by EDS (S3700N). A double beam Perkin Elmer Lambda 25 UV–Vis spectrophotometer was used to record UV–Visible spectral analysis. Transmission electron microscope (TEM) was used to identify the CuO/ZnO nanocomposite shape and size using aPhilips-EM-2085 transmission electron microscope with an accelerating voltage of 100.0 kV.

2.2. Preparation of Melissa Officinalis L. leaf extract

10 g of *Melissa Officinalis* L. powdered dried leaves were added to 60 mL of double distilled water in a 250 mL flask and well stirred using a magnetic heater stirrer at 100 °C for 440 min to obtain the extract. The extract was then centrifuged at 6000 rpm and filtered. The filtrate was kept in a refrigerator for further use.

2.3. Preparation of the CuO NPs using the aqueous extract of the leaves of Melissa Officinalis L

30 mL of aqueous extract of the plant was added to 10 mL of 5 mM $CuCl_2 \cdot 2H_2O$ solution at 70 °C and vigorously shaken. The mixture became dark after 1 min.; showing the formation of CuO NPs (as monitored by UV and FT-IR techniques). The nanoparticle colloidal dispersion was then filtered and centrifuged at 7000 rpm for 30 min. The obtained precipitate was finally washed with absolute ethanol to remove possible impurities and kept in Ar atmosphere to protect it from deformation and decomposition.

2.4. Preparation of the CuO/ZnO nanocomposite using the aqueous extract of the leaves of Melissa Officinalis L

CuO/ZnO nanocomposite was prepared by the green method. 1.0 g of ZnO NPs was mixed with 0.3 g of $CuCl_2 \cdot 2H_2O$ and 50 mL of the aqueous plant extract in a 100 mL conical flask and then heated at 75 °C under vigorous stirring. The solid product was collected by centrifugation approximately 2 h later and then washed several times with water and ethanol.

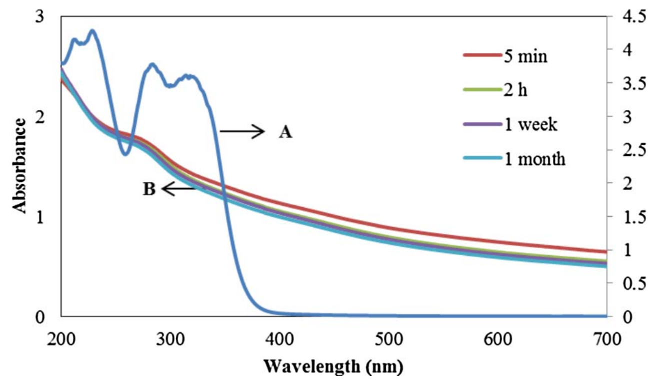


Fig. 1. UV–Vis spectra of the aqueous extract of the leaves of *Melissa Officinalis* L. (A) and biosynthesized CuO NPs using aqueous extract of the leaves of *Melissa Officinalis* L. between 5 minand1 month (B).

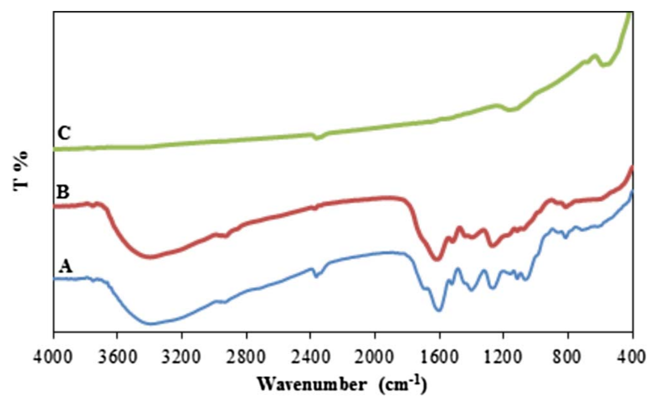
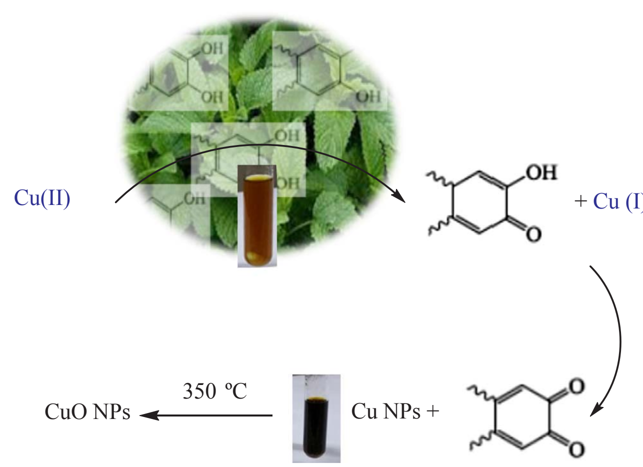


Fig. 2. FT-IR spectra of the aqueous extract of the leaves of *Melissa Officinalis* L. (A), Cu NPs (B) and CuO NPs (C) synthesized using aqueous extract of the leaves of *Melissa Officinalis* L.



Scheme 1. Possible mechanism of the reduction of Cu^{2+} and formation of the CuO NPs.

2.5. RhB catalytic degradation in the presence of the CuO/ZnO nanocomposite

5.0 mg of the CuO/ZnO nanocomposite were added to an aqueous solution containing RhB (2.0×10^{-5} M, 25 mL) and freshly prepared aqueous $NaBH_4$ solution (2.6×10^{-3} M, 25 mL) in a typical experiment and stirred for 1 s at room temperature. The absorption peak change at the maximum wavelength (λ_{max} = 551 nm) was recorded to monitor the reduction of RhB. The catalyst was separated from the reaction mixture by centrifugation following reaction completion, washed with double distilled water and then dried for the next cycle.