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Article

Biosynthesis of copper nanoparticles supported on manganese dioxide nanoparticles using *Centella asiatica* L. leaf extract for the efficient catalytic reduction of organic dyes and nitroarenes

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ABSTRACT

In this study we designed a novel, cost-efficient and green method for the synthesis of copper nanoparticles (Cu NPs) supported on manganese dioxide (MnO₂) NPs, using *Centella asiatica* L. leaf extract as a naturally-sourced reducing agent, without stabilizers or surfactants. This synthetic process is environmentally-friendly and avoids the use of toxic reducing agents. Phenolic hydroxyl groups in the leaf extract are believed to reduce Cu²⁺ in solution to generate Cu NPs that are subsequently stabilized on the MnO₂ NP surfaces. The resulting Cu/MnO₂ nanocomposite was fully characterized using X-ray diffraction, transmission electron microscopy, field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy. This material was found to function as a highly active, efficient and recyclable heterogeneous catalyst for the reduction of Congo red, rhodamine B and methylene blue as well as nitro compounds such as 2,4-dinitrophenylhydrazine and 4-nitrophenol in the presence of NaBH₄ in aqueous media at ambient temperature. The high stability of the Cu/MnO₂ nanocomposite also allows the catalyst to be separated and reused several times without any significant loss of activity.

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1. Introduction

The presence of toxic organic dyes and nitroarenes in wastewaters is currently a significant concern because these compounds are chemically and biologically stable, and so are not removed by natural degradation processes [1–4]. Nevertheless, synthetic dyes and nitrophenols have potential applications in a wide range of industries, including the textile, plastic, leather, paper, food, cosmetic, printing and pharmaceutical industries [3]. Because of the potential toxicity of azo dyes in aquatic ecosystems, their mutagenic or carcinogenic properties and their capacity to discolor surface waters, the degradation of

organic dyes and nitroarenes has become an issue of considerable importance [5] and it is vital to develop efficient, eco-friendly processes to convert harmful organic waste effluent into valuable intermediate chemicals. A variety of treatments have been proposed, including physical and chemical process as well as combinations of these techniques. However, all involve certain limitations, such as the formation of waste sludge, harsh reaction conditions, poor efficiency, intensive energy requirements, high operational costs and incomplete mineralization [6].

Nanomaterials offer a solution to environmental and technological challenges associated with water treatment, catalysis

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and medicine [7,8]. As an example, the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) will proceed in the presence of metal nanoparticles (MNPs) [9,10]. There are several chemical and physical methods for the synthesis of these MNPs, although most suffer from drawbacks such as harsh reaction conditions, the use of toxic capping agents or hazardous stabilizers and the application of organic solvents or hazardous materials [11–14]. Thus, it would be helpful to explore highly efficient, greener methods for the synthesis of various MNPs that involve using gums, fungi, bacteria and plant extracts as biogenic agents under mild conditions without the use of toxic and corrosive materials or organic solvents [15,16].

A number of MNPs have been investigated as catalysts in various organic transformations because of their unique abilities, include high catalytic activity, superior efficiency, high thermal stability, strong electron transfer characteristics and large specific surface areas [17–20]. MNPs without supports are typically unstable and tend to undergo agglomeration [17–20], and so it is important to select the appropriate support material to obtain stable and uniformly distributed MNPs. Among the low cost, nontoxic metal oxides, MnO_2 [21,22] has significant applicability in energy storage [22,23] and sensors [24] and has also been extensively used in catalysis [25].

Centella asiatica L. (from the family *Apiaceae*) is a plant that is believed to offer a number of health benefits, including the ability to act as an antioxidant and anti-inflammatory, as well as to heal wounds and enhance memory (Fig. 1) [26,27]. The phytochemical screening of this plant has demonstrated a broad spectrum of phytochemicals, including alkaloids, flavonoids, saponines, terpenoids, tannins, phenols, glycosides, carbohydrates, quinines, resins and quamarines. Other phytoconstituents of this plant are asiaticoside, madecassoside, brahmoxide, bicycloclemene, centelloside, indocentelloside, oxyasiaticoside, thankuniside, asiatic acid, betulinic acid, centellic acid, madecassic acid, centellose, kaempferol, hydrocotyline, phellandrene, vitamin C, linamarase and triterpenoid trisaccharides [28–30]. Based on literature reports regarding the phytochemical content of this plant, leaf extracts were used during the present study for the biosynthesis of stable nanostructures.

The aim of this study was to apply *Centella asiatica* L. leaf extract to the green synthesis of a Cu/MnO_2 nanocomposite via the reduction of Cu^{2+} ions to Cu NPs followed by immobilization on the surfaces of MnO_2 NPs. The resulting Cu/MnO_2 nanocomposite, representing a recyclable heterogeneous catalyst, was applied to the catalytic reduction of 2,4-dinitrophenylhydrazine (2,4-DNPH), 4-NP, rhodamine B (RhB), methylene blue (MB) and Congo red (CR) in the presence of NaBH_4 in water at

Fig. 1. Photographic images of the *Centella asiatica* L. plant [31].

room temperature. To the best of our knowledge, this work is the first green synthesis of a Cu/MnO_2 nanocomposite using plant extracts.

2. Experimental

2.1. Instruments and reagents

Chemical reagents and solvents were purchased from the Merck and Sigma-Aldrich companies. All reagents were commercial reagent grade and were used as-received without further purification. Fourier transform infrared spectroscopy (FT-IR) data was acquired using a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) with the samples in the form of pressed KBr pellets. X-ray powder diffraction (XRD) patterns were obtained with a Philips PW 1373 goniometer ($\text{Cu } K\alpha = 1.5406 \text{ \AA}$) to assess the crystal structure of the Cu/MnO_2 nanocomposite. Diffraction patterns were recorded over the 2θ range from 10° to 80° at a scan rate of $2^\circ/\text{min}$. The formation of the Cu NPs was confirmed by UV-visible spectral analysis using a double-beam spectrophotometer (Hitachi, U-2900), and the morphology and particle dispersion of the Cu NPs were analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700). The shapes and sizes of the Cu/MnO_2 nanocomposite particles were identified via transmission electron microscopy (TEM) with a Philips EM208 microscope operating at an accelerating voltage of 90 kV. The chemical composition of the Cu/MnO_2 nanocomposite was determined using energy dispersive X-ray spectroscopy (EDS) in conjunction with FE-SEM.

2.2. Preparation of *Centella asiatica* L. leaf extract

The leaf extract was obtained by adding 50 g of dried, powdered leaf material to 250 mL of double distilled water in a 500 mL flask followed by vigorous mixing at 80°C for 30 min. The resulting mixture was centrifuged at 7000 r/min and filtered, after which the filtrate was stored in a refrigerator in preparation for use.

2.3. Biosynthesis of the Cu NPs using *Centella asiatica* L. leaf extract

A 10 mL portion of solution $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (5 mmol/L) was mixed with 100 mL of the aqueous plant extract with vigorous shaking over a 7 min time span. During this time, the mixture exhibited a gradual change to a dark color (as monitored by UV-Vis spectroscopy), indicating the formation of the Cu NPs. The mixture was subsequently filtered and centrifuged at 7000 r/min for 30 min and the resulting solid was washed with *n*-hexane and absolute ethanol to remove possible impurities.

2.4. Biosynthesis of the Cu/MnO_2 nanocomposite using *Centella asiatica* L. leaf extract

A mixture of 1.0 g MnO_2 and 50 mL of the aqueous extract was stirred for 20 min at room temperature. Following this, 30

mL of an aqueous CuCl_2 solution (0.08 mol/L) was added dropwise with vigorous stirring and the mixture was heated for 4 h at 80 °C. After the reaction, the Cu/MnO_2 nanocomposite was collected from the flask by filtration, then washed with distilled water to remove unreacted copper salts and dried at 110 °C for 5 h.

2.5. Reduction of 2,4-DNPH using the Cu/MnO_2 nanocomposite

In a typical trial, 25 mL of an aqueous solution 2,4-DNPH (10.076 mmol/L) was mixed with 10.0 mg of the Cu/MnO_2 nanocomposite and the mixture was stirred at room temperature for 2 min. Following this, 25 mL of a freshly prepared aqueous NaBH_4 solution (7.92 mmol/L) was added to the reaction mixture and the solution was stirred at ambient temperature until the deep yellow color disappeared, indicating the formation of 2,4-diaminophenylhydrazine (2,4-DAPH). The catalytic degradation of the 2,4-DNPH was tracked using a Hitachi U-2900 spectrophotometer to determine the absorption at 353 nm. Following the reaction, the Cu/MnO_2 nanocomposite was recaptured using centrifugation, washed with double distilled water and dried in preparation for reuse.

2.6. Reduction of 4-NP by the Cu/MnO_2 nanocomposite

To further assess the catalytic activity of the Cu/MnO_2 nanocomposite, 25 mL of aqueous 4-NP solution (2.5 mmol/L) was combined with 7.0 mg of the Cu/MnO_2 nanocomposite in a beaker. After stirring at room temperature for 1 min, 25 mL of a freshly prepared aqueous NaBH_4 solution (240 mmol/L) was added with further stirring and the absorption of the solution at 317 nm was recorded over time as the mixture transitioned to colorless due to the formation of 4-AP. After completion of the reaction, the used catalyst was recycled.

2.7. Reduction of organic dyes by the Cu/MnO_2 nanocomposite

In a typical trial, 25 mL of an aqueous CR solution (144 mmol/L) (or 310 and 209 mmol/L, respectively, in the case of MB and RhB) was added to 7.0 mg of the Cu/MnO_2 nanocomposite (in the case of MB and RhB, the catalyst amounts were 3.0 and 10.0 mg, respectively) in a beaker. After stirring at room temperature for 2 min, 25 mL of a fresh aqueous NaBH_4 solution (5.3 mmol/L) was added to the mixture with stirring and the reaction progress was monitored by UV-Vis spectroscopy. The concentrations of the CR, MB and RhB were determined using a Hitachi U-2900 spectrophotometer and tracking absorption at 493, 664 and 554 nm, respectively. At the end of the reaction, the used catalyst was separated by centrifugation, washed with water, dried and then reused.

3. Results and discussion

3.1. Preparation and characterization of the Cu/MnO_2 nanocomposite

This study grew out of our continuing interest in the syn-

Scheme 1. Proposed mechanism for green synthesis of the Cu NPs.

thesis of MNPs using the reducing and stabilizing properties of antioxidant phytochemicals in plant extracts, especially flavonoids and other polyphenolics, in aqueous media [5,32]. Compounds such as these in the *Centella asiatica* L. leaf extract were employed in the synthesis of the Cu NPs and Cu/MnO_2 nanocomposite, allowing the reduction of Cu^{2+} ions to Cu NPs without the addition of any other external reducing agent. It should be noted that the leaf extract also acted to immobilize the Cu NPs on the surfaces of the MnO_2 NPs to form the Cu/MnO_2 nanocomposite. In this process, which does not require the use of reductants, surfactants or hazardous chemicals, polyphenols are oxidized to their quinone form while Cu^{2+} ions are reduced to $\text{Cu}(0)$, as shown in Scheme 1.

The UV spectrum of the extract (Fig. 2) contains peaks at 335 nm (band I) and 240 nm (band II) assigned to cinnamoyl and benzoyl-type phenolic compounds, confirming the presence of phenolics in the extract, in agreement with previous reports [28–30]. The UV-Vis spectrum of the Cu NPs obtained using the plant extract (Fig. 2) exhibits significant changes in the absorbance maxima due to surface plasmon resonance. The color of the mixture was also observed to darken after 7 min in conjunction with increasing absorbance at 570 nm, indicating the formation of the Cu NPs. The NPs synthesized by this method were evidently quite stable as there were no significant variations in the shape, position or symmetry of this new absorption peak even after three weeks.

Furthermore, the FTIR spectra of the Cu NPs show an interaction between the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the phytochemicals. The peaks at 3500, 1718, 1475, 1300 and 1000 cm^{-1} represent hy-

Fig. 2. UV-Vis spectra of the original plant extract and the synthesized Cu NPs.

Fig. 3. FTIR spectrum of the biosynthesized Cu NPs.

droxyl (-OH), carbonyl (C=O), aromatic C=C and C-OH vibrations, respectively. Thus, the MNPs could possibly adsorb onto the surfaces of the phytochemicals via π -electron interactions, even in the absence of other strong ligating agents (Fig. 3).

Structural characterization of the Cu/MnO₂ nanocomposite was also performed using FTIR data, based on the spectrum shown in Fig. 4. This spectrum confirms that the functional group peaks were unaffected by immobilization of the Cu NPs on the surfaces of the MnO₂ NPs. The band at 3402 cm⁻¹ corresponds to the -OH stretching vibration of water in the sample, while the peak at 1621 cm⁻¹ represents the bending vibration of adsorbed water on the Mn NPs. The bands below 1000 cm⁻¹ comprise the fingerprint region associated with MNP hydroxides and oxides [33]. The peaks at 1403 and 1073 cm⁻¹ are assigned to O-Mn-O [34], while that at 515 cm⁻¹ is attributed to the vibration of Mn-O bonds.

The XRD pattern generated by the Cu NPs is shown in Fig. 5, and clearly indicates that crystalline Cu NPs were prepared using the *Centella asiatica* L. leaf extract. The peaks at 43.7°, 50.7° and 74.5° are assigned to the (111), (200) and (220) planes of the face centered cubic (fcc) structure, respectively.

The Cu/MnO₂ nanocomposite was characterized by FE-SEM, TEM and EDS analyses. FE-SEM and TEM were employed to assess the sizes and surface morphologies of the Cu/MnO₂ nanocomposite particles. The FE-SEM images of the nanocomposite in Fig. 6 demonstrate that the surfaces of the MnO₂ NPs were covered with Cu NPs, with the Cu NPs having a narrow size distribution.

The morphology and structure of the Cu/MnO₂ nanocompo-

Fig. 4. FTIR spectrum of the Cu/MnO₂ nanocomposite.

Fig. 5. XRD pattern of the synthesized Cu NPs.

Fig. 6. FE-SEM images of the Cu/MnO₂ nanocomposite.

site was also investigated by TEM at varying magnifications (Fig. 7). These images also confirmed that Cu NPs were formed on the MnO₂ NP surfaces and were small with a spherical morphology and did not undergo aggregation.

The EDS spectrum of the Cu/MnO₂ nanocomposite is presented in Fig. 8. This spectrum exhibits Cu, Mn and O peaks, providing further evidence for the successful synthesis of the Cu/MnO₂ nanocomposite.

3.2. Catalytic reduction of 2,4-DNPH, 4-NP, CR, RhB and MB

Fig. 7. TEM images of the Cu/MnO₂ nanocomposite.

Fig. 8. EDS spectrum of the Cu/MnO₂ nanocomposite.

using the Cu/MnO₂ nanocomposite in aqueous media

The catalytic performance of the Cu/MnO₂ nanocomposite was examined by assessing the reduction of several nitro compounds and organic dyes in the presence of sodium borohydride (NaBH₄) as a reducing agent. These reduction reactions were found to go to completion with very low amounts of the nanocatalyst during short time spans.

3.2.1. Catalytic reduction of 2,4-DNPH to 2,4-DAPH

The catalytic performance of the Cu/MnO₂ nanocomposite was evaluated during the reduction of 2,4-DNPH to 2,4-DAPH (Scheme 2), using UV-Vis spectroscopy to monitor the conversion by tracking the maximum absorbance peak of the 2,4-DNPH at 353 nm (Fig. 9). Following the addition of both the catalyst and the NaBH₄ to a solution of 2,4-DNPH, the solution transitioned from yellow to colorless and a new absorption

Scheme 2. The catalytic reduction of the 2,4-DNPH to 2,4-DAPH.

Fig. 9. UV-Vis spectra acquired during 2,4-DNPH reduction in the presence of NaBH₄ and the Cu/MnO₂ nanocomposite. Conditions: [2,4-DNPH] = 0.076 mmol/L; [NaBH₄] = 7.91 mmol/L; catalyst = 10.0 mg; temperature = 30 °C.

Table 1

Effects of NaBH₄ and catalyst concentrations on the reduction of 2,4-DNPH (0.076 mM) to 2,4-DAPH.

Entry	Catalyst (mg)	NaBH ₄ (equivalents)	Time (min)
1	—	104	120 ^a
2	MnO ₂ (10.0)	104	45 ^b
3	Cu/MnO ₂ nanocomposite (7.0)	75	5
4	Cu/MnO ₂ nanocomposite (10.0)	75	3
5	Cu/MnO ₂ nanocomposite (5.0)	104	4
6	Cu/MnO ₂ nanocomposite (7.0)	104	3
7	Cu/MnO ₂ nanocomposite (10.0)	104	2

^aNo reaction.

^bNot completed.

peak appeared at approximately 290 nm as a result of the formation of 2,4-DAPH. The data in Table 1 (Entry 1) indicate that there was no change in the solution up to 120 min when the Cu/MnO₂ nanocomposite was not included. As expected, when using solely the MnO₂ NPs (Entry 2), the reduction was not complete even after 45 min. The catalytic reduction of the 2,4-DNPH in the presence of the Cu/MnO₂ nanocomposite was substantially faster because of the synergic effect between the Cu and MnO₂ NPs. The reduction of the 2,4-DNPH was also examined in the presence of varying amounts of the Cu/MnO₂ nanocomposite and NaBH₄. It was determined that the catalytic reaction did not go to completion when using less than 5 mg of the catalyst, and the optimum result was obtained with 104 equivalents of NaBH₄ and 10.0 mg of the Cu/MnO₂ nanocomposite (Entry 7).

3.2.2. Catalytic reduction of 4-NP to 4-AP

The conversion of 4-NP to 4-AP (Scheme 3) is very important because of the environmental impact of the former compound. Herein, the progress of the 4-NP reduction reaction in aqueous media at room temperature was monitored by UV-Vis spectroscopy (Fig. 10), based on the maximum absorbance of the 4-NP at approximately 317 nm. The light-yellow color of the initial 4-NP solution was found to change to dark yellow upon adding NaBH₄ due to the formation of 4-nitrophenolate ions, in conjunction with the appearance of a new absorption band at 400 nm. In the absence of the catalyst, there were no obvious changes in the 400 nm peak under alkaline conditions even after 120 min, indicating that the reduction of the 4-nitrophenolate ion does not proceed solely in the presence of NaBH₄ (Entry 1). Following the addition of the Cu/MnO₂ nanocomposite to a solution containing 4-NP and NaBH₄, the absorbance at 400 nm decreased over time and a new peak appeared at approximately 300 nm due to the formation of 4-AP. The reaction was optimized by varying the

Scheme 3. The catalytic reduction of 4-NP to 4-AP in aqueous medium at room temperature.

Fig. 10. UV-Vis spectra acquired during the reduction of 4-NP in the presence of NaBH_4 and the Cu/MnO_2 nanocomposite. Conditions: [4-NP] = 2.5 mmol/L; $[\text{NaBH}_4]$ = 0.25 mol/L; nanocatalyst = 5.0 mg; temperature = 30 °C.

catalyst loading and the NaBH_4 concentration and the best results were obtained with 100 equivalents of NaBH_4 and 5.0 mg of the Cu/MnO_2 nanocomposite (Entry 8). The catalyst exhibited excellent performance and the reduction was complete within 4 min, as evidenced by the decolorization of the 4-nitrophenolate ion and the loss of the peak at 400 nm.

The catalytic activity of the MnO_2 NPs was also studied under the same conditions, and it was determined that the reduction reaction did not proceed. It was also found that the Cu NPs on their own exhibited higher catalytic activity than the MnO_2 NPs and were able to catalyze the reduction of 4-NP to 4-AP, but at a slower rate than the Cu/MnO_2 nanocomposite. As shown in Table 2, the reaction could be completed within 9 min in the presence of 5.0 mg of Cu NPs alone (Entry 9). Based on these results, the Cu/MnO_2 nanocomposite evidently produced the fastest reduction rate due to the synergic interaction between the Cu and MnO_2 NPs. In this method, the MnO_2 NPs (having a large surface area and excellent adsorption ability toward reactants based on π - π stacking interactions) act as an effective support to prevent the Cu NPs (having high catalytic activity) from agglomerating and also assist in recovering the Cu NPs.

In these reactions, the Cu NPs supported on the MnO_2 NPs acted as redox catalysts for the reduction of nitro compounds through an electron relay between the BH_4^- donor and the nitro

Table 2

Effects of NaBH_4 and catalyst concentrations on the reduction of 4-NP (2.5 mmol/L) to 4-AP.

Entry	Catalyst (mg)	NaBH_4 (equivalents)	Time (min)
1	—	100	100 ^a
2	MnO_2 (10.0)	100	45 ^a
3	Cu/MnO_2 nanocomposite (7.0)	0.0	100 ^b
4	Cu/MnO_2 nanocomposite (5.0)	50	31 ^b
5	Cu/MnO_2 nanocomposite (5.0)	79	18
6	Cu/MnO_2 nanocomposite (5.0)	100	4
7	Cu/MnO_2 nanocomposite (7.0)	79	15
8	Cu/MnO_2 nanocomposite (7.0)	100	4
9	Cu NPs (5.0)	100	9

^a No reaction.

^b Not completed.

Scheme 4. Proposed mechanism for the reduction of the 4-NP with Cu/MnO_2 nanocomposite.

group acceptor. Initially, the reactant molecules (NaBH_4 and 4-NP) were adsorbed on the Cu/MnO_2 nanocomposite surfaces via physical adsorption. After electron transfer from the nucleophilic BH_4^- ions to the electrophilic 4-nitrophenolate ions, hydrogen atoms from the hydride attack the 4-NP to reduce it (Scheme 4). Finally, the resulting 4-AP is desorbed from the surface of the catalyst and the catalytic cycle starts again.

3.2.3. Catalytic reduction of CR, MB and RhB

The reductions of RhB, CR, and MB were also examined using NaBH_4 in water at room temperature (Table 3) in conjunction with the new catalyst, following the maximum absorbance peaks at 554, 493 and 663 nm, respectively (Fig. 11). The catalyst loading was evidently vital to the decolorization of these dyes. No reduction was evident in the absence of the catalyst or the NaBH_4 . In contrast, the MB peak decreased rapidly (within 1 s) upon adding 3 mg of the catalyst. Additional experiments showed that there was no significant change in the reaction time when using larger amounts of the catalyst. The best results during the reductions of the CR and RhB were obtained with 7.0 and 10.0 mg of the nanocatalyst, respectively.

The efficiency of the Cu/MnO_2 nanocomposite during the reduction of 2,4-DNPH, 4-NP, MB, CR and RhB was compared with those of other reported catalytic systems. From Table 4, it can be concluded that the Cu/MnO_2 nanocomposite shows higher catalytic activity compared to other catalysts, based on

Table 3

Effects of catalyst loading on the reductions of CR, RhB and MB.

Entry	Dye (mmol/L)	NaBH_4 (mmol/L)	Catalyst (mg)	Time
1	CR (144)	5.3	5.0	87 s
2	CR (144)	5.3	7.0	35 s
3	CR (144)	5.3	3.0	191 s
4	RhB (209)	5.3	5.0	6 min
5	RhB (209)	5.3	7.0	4 min
6	RhB (209)	5.3	10.0	185 s
7	MB (310)	5.3	3.0	1 s
8	MB (310)	5.3	5.0	1 s
9	MB (310)	5.3	7.0	1 s

Fig. 11. UV-visible spectra of (a) CR, (b) RhB and (c) MB during reduction with NaBH_4 in the presence of the Cu/MnO_2 nanocomposite.

the reduced reaction time. In contrast to other reported catalysts, the Cu/MnO_2 nanocomposite is also recoverable, heterogeneous and can be easily prepared using *Centella asiatica* L. leaf extract without the use of dangerous, toxic and hazardous materials or surfactants, templates and capping agents.

3.3. Catalyst recyclability

One of the most important aspects of a catalyst from the perspective of green chemistry is recycling, and we therefore studied the recyclability of the Cu/MnO_2 nanocomposite fol-

lowing the reduction of 2,4-DNPH to 2,4-DAPH with NaBH_4 . After the completion of the reduction reaction, the nanocatalyst could be separated from the reaction mixture and was subsequently washed with deionized water, dried and reused for the next cycle without any significant decrease in catalytic activity. Therefore, the catalyst was stable during the reduction reactions. According to TEM, FE-SEM and EDS analyses of the recycled catalyst after five replicate reactions, the particles shapes and sizes were unchanged, with no obvious variations in the chemical composition of the Cu/MnO_2 nanocomposite (Figs. 12–14). According to the UV-Vis spectra, the time required for the catalytic reduction of nitroarenes with NaBH_4 in the presence of the catalyst was nearly the same up to the fifth reuse.

Table 4

Catalytic activities of various catalysts during the reductions of 4-NP, 2,4-DNPH, MB, CR and RhB by NaBH_4 .

Substrate	Catalyst	Time	Ref.
4-NP	HMMS- NH_2 -Pd	60 min	[35]
	TiO_2 -G1%	60 min	[36]
	GA-Pt NPs	8 h	[37]
	Polymer-anchored Pd(II) complex	5.5 h	[38]
	Cu NPs	2 h	[18]
	Au-GO	30 min	[39]
	p(AMPS)-Co composite	28 min	[40]
	Ag/KCC-1	510 s	[19]
	Resin-Au NPs	20 min	[41]
	KCC-1/Au	12 min	[42]
	PdCu/graphene	1.5 h	[43]
	Pd-FG	12 min	[44]
2,4-DNPH	Cu/MnO_2 nanocomposite	4 min	This work
	Ag@AgCl NPs	60 min	[45]
MB	Cu/MnO_2 nanocomposite	2 min	This work
	$\text{Fe}_3\text{O}_4/\text{Ag}$	15 min	[46]
	PS/Ag	10 min	[47]
	Au/ Fe_3O_4 @C	10 min	[48]
	Au-PANI nanocomposite	15 min	[49]
	SiNWAs-Cu	14 min	[50]
	Ag/HLaNb $_2\text{O}_7$	47 min	[51]
	Fe_3O_4 @PANI@Au	18 min	[52]
	Ag NPs/seashell	2.5 min s	[53]
	Cu/eggshell nanocomposite	10 s	[54]
CR	Cu/MnO_2 nanocomposite	1 s	This work
	Cu@SBA-15	7 min	[20]
	copper nanocrystals	500 s	[55]
RhB	Cu/MnO_2 nanocomposite	35 s	This work
	Ag/HLaNb $_2\text{O}_7$	47 min	[51]
	Fe_3O_4 @PANI@Au	18 min	[52]
	$\text{Fe}_3\text{O}_4/\text{Ag}$	15 min	[46]
	Cu/MnO_2 nanocomposite	185 s	This work

Fig. 12. FE-SEM images of the recovered Cu/MnO_2 nanocomposite.

Fig. 13. EDS spectrum of the recovered Cu/MnO_2 nanocomposite.

Fig. 14. TEM images of the recovered Cu/MnO₂ nanocomposite.

4. Conclusions

The present study demonstrates a green and facile method for the preparation of a Cu/MnO₂ nanocomposite through the reduction of Cu²⁺ ions to Cu(0) in the presence of *Centella asiatica* L. leaf extract, acting as a reducing and stabilizing agent, under organic solvent-free conditions. In this synthetic process, we employed a simple, natural, environmentally-friendly and non-hazardous material without the need for expensive or harmful chemical reagents and organic solvents. The FTIR spectrum of Cu NPs with the *Centella asiatica* L. leaf extract indicated that polyphenols or flavonoids present in the extract played a vital role in the bioreduction of the Cu²⁺ ions. The Cu/MnO₂ nanocomposite exhibited excellent catalytic activity as an efficient heterogeneous catalyst for the reduction of nitro compounds and organic dyes in conjunction with NaBH₄ in water at room temperature under mild conditions. According to the obtained results, the performance of the Cu/MnO₂ nanocomposite is somewhat better than those of previously reported catalysts in the literature. The notable advantages offered by this method include an efficient, facile and safe protocol for the synthesis of the Cu/MnO₂ nanocomposite, including the use of *Centella asiatica* L. leaf extract as a stabilizing and reducing agent, the elimination of toxic and harmful chemicals, short reaction times and recyclability of the catalyst. Moreover, the

catalyst can be readily separated and reused several time without any significant loss in its catalytic activity.

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References

- [1] A. Bianco-Prevot, C. Baiocchi, M. C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marci, L. Palmisano, *Environ. Sci. Technol.*, **2001**, 35, 971–976.
- [2] B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, *Chemosphere*, **2002**, 46, 1173–1181.
- [3] R. J. Dai, J. Chen, J. Lin, S. Y. Xiao, S. Chen, Y. L. Deng, *J. Hazard. Mater.*, **2009**, 170, 141–143.
- [4] J. C. Spain, *Annu. Rev. Microbiol.*, **1995**, 49, 523–555.
- [5] W. B. Zhang, X. M. Xiao, T. C. An, Z. G. Song, J. M. Fu, G. Y. Sheng, M. C. Cui, *J. Chem. Technol. Biotechnol.*, **2003**, 78, 788–794.
- [6] B. Manu, S. Chaudhari, *Bioresour. Technol.*, **2002**, 82, 225–231.
- [7] J. A. Dahl, B. L. S. Maddux, J. E. Hutchison, *Chem. Rev.*, **2007**, 107, 2228–2269.
- [8] J. E. Hutchison, *ACS Nano*, **2008**, 2, 395–402.
- [9] L. H. Ai, H. T. Yue, J. Jiang, *J. Mater. Chem.*, **2012**, 22, 23447–23453.
- [10] B. Baruah, G. J. Gabriel, M. J. Akbashev, M. E. Booher, *Langmuir*, **2013**, 29, 4225–4234.
- [11] C. Noguez, *J. Phys. Chem. C*, **2007**, 111, 3806–3819.
- [12] X. Z. Zhou, X. Huang, X. Y. Qi, S. X. Wu, C. Xue, F. Y. C. Boey, Q. Y. Yan, P. Chen, H. Zhang, *J. Phys. Chem. C*, **2009**, 113, 10842–10846.
- [13] A. B. Lowe, B. S. Sumerlin, M. S. Donovan, C. L. McCormick, *J. Am. Chem. Soc.*, **2002**, 124, 11562–11563.
- [14] J. H. He, T. Kunitake, A. Nakao, *Chem. Mater.*, **2003**, 15, 4401–4406.
- [15] C. M. Cirtiu, A. F. Dunlop-Briere, A. Moores, *Green Chem.*, **2011**, 13, 288–291.
- [16] X. B. Lin, M. Wu, D. Y. Wu, S. Kuga, T. Endo, Y. Huang, *Green Chem.*, **2011**, 13, 283–287.
- [17] J. R. Chiou, B. H. Lai, K. C. Hsu, D. H. Chen, *J. Hazard. Mater.*, **2013**, 248–249, 394–400.

Graphical Abstract

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Biosynthesis of copper nanoparticles supported on manganese dioxide nanoparticles using *Centella asiatica* L. leaf extract for the efficient catalytic reduction of organic dyes and nitroarenes

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A Cu/MnO₂ nanocomposite was prepared through reduction of Cu²⁺ ions to Cu NPs using *Centella asiatica* L. leaf extract and applied to the reduction of organic dyes and nitro compounds in aqueous media.

- [18] Z. Y. Duan, G. L. Ma, W. J. Zhang, *Bull. Korean Chem. Soc.*, **2012**, 33, 4003–4006.
- [19] Z. P. Dong, X. D. Le, X. L. Li, W. Zhang, C. X. Dong, J. T. Ma, *Appl. Catal. B*, **2014**, 158–159, 129–135.
- [20] B. K. Ghosh, S. Hazra, B. Nak, N. N. Ghosh, *Powder Technol.*, **2015**, 269, 371–378.
- [21] S. B. Ma, K. W. Nam, W. S. Yoon, X. Q. Yang, K. Y. Ahn, K. H. Oh, K. B. Kim, *J. Power Sources*, **2008**, 178, 483–489.
- [22] S. Komaba, A. Ogata, T. Tsuchikawa, *Electrochem. Commun.*, **2008**, 10, 1435–1437.
- [23] X. M. Feng, Z. Z. Yan, N. N. Chen, Y. Zhang, Y. W. Ma, X. F. Liu, Q. L. Fan, L. H. Wang, W. Huang, *J. Mater. Chem. A*, **2013**, 1, 12818–12825.
- [24] X. M. Feng, Y. Zhang, J. Song, N. N. Chen, J. H. Zhou, Z. D. Huang, Y. W. Ma, L. Zhang, L. H. Wang, *Electroanalysis*, **2015**, 27, 353–359.
- [25] X. M. Feng, Y. Zhang, Z. Z. Yan, N. N. Chen, Y. W. Ma, X. F. Liu, X. Y. Yang, W. H. Hou, *J. Mater. Chem. A*, **2013**, 1, 9775–9780.
- [26] B. M. Hausen, *Contact Dermatitis*, **1993**, 29, 175–179.
- [27] M. Z. Borhan, R. Ahmad, M. Rusop, S. Abdullah, *J. Appl. Chem.*, **2013**, 1–7.
- [28] F. X. Maquart, G. Bellon, P. Gillery, Y. Wegrowski, J. P. Borel, *Connect. Tissue Res.*, **1990**, 24, 107–120.
- [29] S. O. Ngele, O. T. J. O. Wilberforce, *Global J. Pharmacol.*, **2016**, 10, 101–107.
- [30] S. Singh, D. R. Singh, V. S. Banu, N. Avinash, *Ind. Crops Prod.*, **2014**, 61, 115–119.
- [31] Available at: <http://urbol.com/centella-asiatica-gotu-kola/>.
- [32] F. Han, V. S. R. Kambala, M. Srinivasan, D. Rajarathnam, R. Naidu, *Appl. Catal. A*, **2009**, 359, 25–40.
- [33] H. Kumar, R. Rani, *Int. Lett. Chem. Phys. Astron.*, **2013**, 19, 26–36.
- [34] M. Jayandran, M. M. Haneefa, V. Balasubramanian, *J. Appl. Pharm. Sci.*, **2015**, 5, 105–110.
- [35] P. Wang, F. W. Zhang, Y. Long, M. Xie, R. Li, J. T. Ma, *Catal. Sci. Technol.*, **2013**, 3, 1618–1624.
- [36] C. Xu, Y. Yuan, R. S. Yuan, X. Z. Fu, *RSC Adv.*, **2013**, 3, 18002–18008.
- [37] B. Sreedhar, D. K. Devi, D. Yada, *Catal. Commun.*, **2011**, 12, 1009–1014.
- [38] M. Islam, P. Mondal, A. S. Roy, K. Tuhina, *Transition Met. Chem.*, **2010**, 35, 427–435.
- [39] Y. Choi, H. S. Bae, E. Seo, S. Jang, K. H. Park, B. S. Kim, *J. Mater. Chem.*, **2011**, 21, 15431–15436.
- [40] N. Sahiner, *Progr. Polym. Sci.*, **2013**, 38, 1329–1356.
- [41] D. Shah, H. Kaur, *J. Mol. Catal. A*, **2014**, 381, 70–76.
- [42] H. L. Yang, S. W. Li, X. Y. Zhang, X. Y. Wang, J. T. Ma, *J. Mater. Chem. A*, **2014**, 2, 12060–12067.
- [43] A. K. Shil, D. Sharma, N. R. Guha, P. Das, *Tetrahedron Lett.*, **2012**, 53, 4858–4861.
- [44] Z. M. Wang, C. L. Xu, G. Q. Gao, X. Li, *RSC Adv.*, **2014**, 4, 13644–13651.
- [45] Th. B. Devi, Md. Ahmaruzzaman, S. Begum, *New J. Chem.*, **2016**, 40, 1497–1506.
- [46] L. H. Ai, C. M. Zeng, Q. M. Wang, *Catal. Commun.*, **2011**, 14, 68–73.
- [47] Z. W. Deng, H. B. Zhu, B. Peng, H. Chen, Y. F. Sun, X. D. Gang, P. J. Jin, J. L. Wang, *ACS Appl. Mater. Interf.*, **2012**, 4, 5625–5632.
- [48] Z. B. Gan, A. W. Zhao, M. F. Zhang, W. Y. Tao, H. Y. Guo, Q. Gao, R. R. Mao, E. H. Liu, *Dalton Trans.*, **2013**, 42, 8597–8605.
- [49] B. Zhang, B. T. Zhao, S. H. Huang, R. Y. Zhang, P. Xu, H. L. Wang, *CrystEngComm*, **2012**, 14, 1542–1544.
- [50] X. L. Yang, H. Zhong, Y. H. Zhu, H. L. Jiang, J. H. Shen, J. F. Huang, C. Z. Li, *J. Mater. Chem. A*, **2014**, 2, 9040–9047.
- [51] Z. J. Jiang, C. Y. Liu, L. W. Sun, *J. Phys. Chem. B*, **2005**, 109, 1730–1735.
- [52] S. H. Xuan, Y. X. J. Wang, J. C. Yu, K. C. F. Leung, *Langmuir*, **2009**, 25, 11835–11843.
- [53] A. Rostami-Vartooni, M. Nasrollahzadeh, M. Alizadeh, *J. Colloid Interf. Sci.*, **2016**, 470, 268–275.
- [54] M. Nasrollahzadeh, S. M. Sajadi, A. Hatamifard, *Appl. Catal. B*, **2016**, 19, 209–227.
- [55] P. H. Zhang, Y. M. Sui, C. Wang, Y. N. Wang, G. L. Cui, C. Z. Wang, B. B. Liu, B. Zou, *Nanoscale*, **2014**, 6, 5343–5350.

采用积雪草树叶提取物生物合成二氧化镁纳米粒子负载的铜纳米颗粒用于高效催化还原有机染料和芳香硝基化合物

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摘要: 本文设计了一个经济、绿色的新型方法, 采用积雪草树叶提取物作为自然的还原剂, 在不使用稳定剂或表面活性剂的情况下合成了MnO₂纳米粒子负载的Cu纳米颗粒(Cu NPs)。该合成过程环境友好, 且避免使用有毒的还原剂。树叶提取物中的酚羟基将溶液中的Cu²⁺还原为Cu NPs, 后者再稳定在MnO₂ NPs表面。采用X射线衍射、透射电镜、场发射扫描电镜、能量散射谱和红外光谱对所得Cu/MnO₂纳米复合物进行了表征。结果表明, 该材料可用作高活性、高效可重复使用的多相催化剂, 用于室温水溶液NaBH₄存在下刚果红、罗丹明B和亚甲基蓝, 以及硝基化合物, 如2, 4-二硝基苯酚和4-硝基苯酚的催化还原。Cu/MnO₂纳米复合物的高稳定性可使其被分离出来, 重复使用数次而活性无明显下降。

关键词: 生物合成; 积雪草; Cu/MnO₂纳米复合物; 还原; 芳香硝基化合物; 有机染料

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