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Research Article

Microwave-Assisted Synthesis of CuO Nanoparticles Using *Cordia africana* Lam. Leaf Extract for 4-Nitrophenol Reduction

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Copper-oxide-based nanomaterials play an important role as a low-cost alternative to nanoparticles of precious metals for the catalytic reduction of 4-nitrophenols. In this study, CuO nanoparticles were synthesized by a microwave-assisted method using *Cordia africana Lam.* leaf extract for reduction or stabilization processes. The synthesized CuO nanoparticles (NPs) were characterized using X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS). The analysis indicated that nanocrystals of the monoclinic CuO phase having a cluster of agglomerated morphology with a crystallite size of about 9 nm were synthesized. We also evaluated the catalytic performance of CuO NPs against 4-nitrophenol (4-NP) reduction. The catalyst has shown excellent performance completing the reaction within 12 min. Furthermore, the performance of CuO NPs synthesized at different pH values was investigated, and results indicated that the one synthesized at pH 7 reduced 4-NP effectively in shorter minutes compared to those obtained at higher pH values. The CuO NPs synthesized using *Cordia africana Lam.* leaf extract exhibited a better reducing capacity with an activity parameter constant of 75.8 $min^{-1} \cdot g^{-1}$. Thus, CuO synthesized using *Cordia africana Lam.* holds a potential application for the catalytic conversion of nitroarene compounds into aminoarene.

1. Introduction

Water is an essential component responsible for the survival of life on Earth [1]. These days, pollution of water has become one of the challenges people are facing because of the continuous rise in the organic, inorganic, and biological pollutants which have industrial and domestic sources [2, 3]. Organic pollutants such as pesticides, synthetic dyes, phenols, and aromatic hydrocarbons are among the major causes of water pollution [4–8]. Among organic water pollutants, 4-nitrophenol (4-NP) and its derivatives have been listed as toxic pollutants by the US Environmental Protection Agency (EPA) [9]. It is known that 4-NP has versatile applications in pesticides, fungicidal agents, dyes, drugs, and leather manufacturing industries as raw materials [10]. 4-NP and its derivatives possess high solubility and stability in aqueous media [9] and pose serious human health complications [2, 3, 11]. Therefore, it is of crucial significance to remove effectively or transform these pollutants into chemicals with low toxicity level.

Over the past decades, a considerable amount of methods have been utilized for the removal of 4-NP pollutant from water including adsorption [12], emulsion liquid membrane [13], bioremediation [14], micellar-enhanced ultrafiltration [15], reverse osmosis [16], photocatalysis [17], catalytic reduction [18], and others [19, 20]. However, the method that is ecofriendly, cost-effective, and efficient is still the biggest challenge that researchers are trying to achieve. While 4-NP is a toxic nitroaromatic compound, its reduced form 4-aminophenol has a low toxicity level and has application in a variety of industries for the synthesis of drugs, dyes, and others. Therefore, the use of catalysts to transform

nitroaromatic compounds into economically valuable and less toxic chemicals is highly desirable, and it is a growing area of investigation for environmental remediation.

Owing to their distinctive properties, nanostructured catalysts of metals (Pd, Pt, Ag, and Au) provide a sustainable way in the transformation of organic compounds in an environmentally benign manner in an aqueous medium [21–23]. However, the high cost and high chance of agglomeration of the bare metallic nanoparticles during reactions are serious problems that limited their large-scale application as a catalyst. Coupling metallic NPs with suitable support material is one of the mechanisms employed to overcome limitations due to agglomeration. Several reports pointed out that the dispersibility and stability of metallic nanostructured materials could be improved by coupling metallic NPs with support materials such as graphene [24], bentonite [25], sodium borosilicate [11], graphene oxide/manganese dioxide nanocomposite [26], and magnetic biodegradable microcapsules [27]. Recently, there are increasing interest in using nonnoble metal oxide semiconductor catalysts as a low-cost alternative to the precious-metal-based catalysts for the reduction of 4-NP [28]. Among metal oxides, CuO NPs catalysts have attracted significant attention in the field of catalysis due to the advantages of low cost, versatility, distinct acid-base properties, and redox properties. CuO NPs have applications in photocatalysis [29], as an antimicrobial [30], in biomedical industry [31], as a gas sensor [32], as solar cells [33], and as batteries [34]. Reports have shown that CuO NPs have the capacity of catalyzing the reduction of 4-NP [35–38].

CuO nanostructure materials can be synthesized using physical, chemical, and biological methods including flame spray pyrolysis and spin-coating processing [39], hydrothermal [34], microwave-assisted [40], solution combustion [41], precipitation [42], biosynthesis [43], and others. Microwave- (MW-) based techniques as a heating source have advantages of faster rate of reaction, higher reproducibility, better product purity, higher yields, and scalability compared to conventional heating processes [44, 45]. Varieties of CuO nanostructures such as nanosheet [32], nanodiscs [46], nanoflower [32], colloidal [29], and others [40, 47] have been synthesized using MW-assisted methods. In addition to simple and scalable techniques of synthesizing nanostructures, it is desirable to comply with the principles of green chemistry, which requires the use of methods that promote minimum energy consumption, use of low-cost and ecofriendly reagents, and none or minimum waste generation [48]. In this regard, plant extracts are promising alternatives to the harsh chemicals for reduction and stabilization processes [49]. The resulting nanostructured materials are usually ecofriendly, less expensive, and less susceptible to chemical contaminants [31, 50]. Among the various types of nanostructured materials synthesized using plant extracts are metallic [51, 52], metallic-based composites [8, 11, 53–56], metal oxides [57, 58], and metal oxide nanocomposites [59]. CuO NPs have been synthesized using biomolecules of various plants such as *Gloriosa superba L.* [47], *Sapindus mukorossi* [60], *Murayya koeniggi* [37], *Sambucus nigra L.* [43], *Aloe Vera* [61], *Cynodon dactylon and Cyperus rotundus* [62], *Catha edulis Forsk* [30], *Moringa oleifera* and *Punica grantum* [63], *Anthemis nobilis* [57], and *Tamarix gallica* [58]. However, synthesis of CuO NPs with the support of *Cordia africana Lam.* for 4-NP has not been reported elsewhere to the best of our knowledge. According to the literature data, the aqueous extract of *Cordia africana Lam.* leaf contains phytochemicals with strong reducing power like polyphenols and tannins [64].

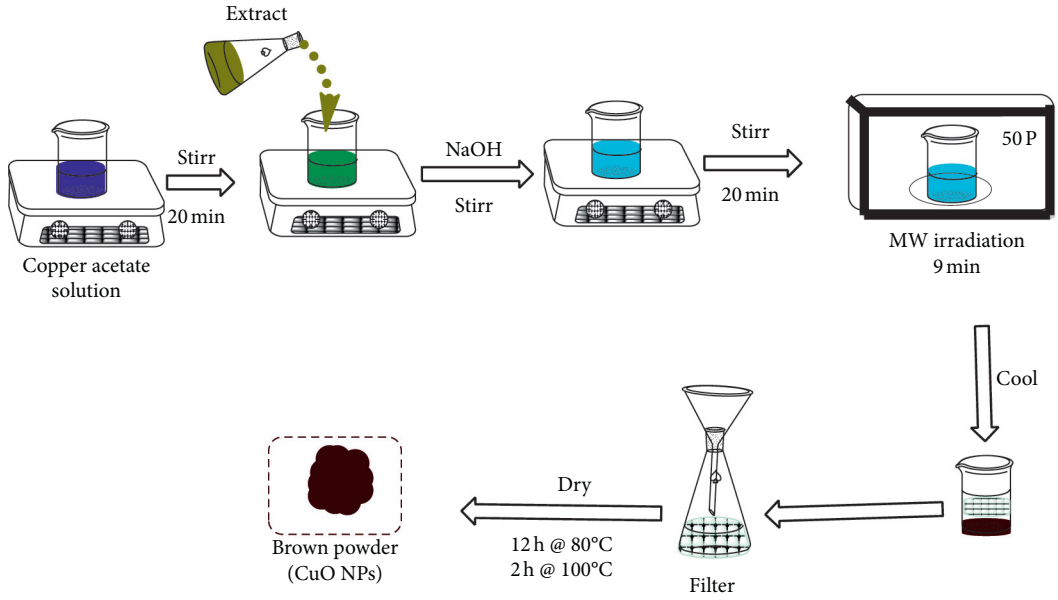
Herein, we report the synthesis of CuO NPs employing an effective, low-cost, facile, and fast MW-assisted method using an aqueous extract of *Cordia africana Lam.* leaf, NaOH, and copper (II) acetate for catalytic reduction of 4-NP. The resulting catalyst was characterized by XRD, FTIR, and SEM techniques. The catalytic performance of CuO NPs was also evaluated against 4-nitrophenol reduction in the presence of $NaBH_4$ in aqueous media. Besides, the performance of the catalyst synthesized at different pH values was demonstrated.

2. Experimental

2.1. Materials. All of the chemical reagents were of analytic grade: cupric acetate ($Cu(CH_3COO)_2.H_2O$) (UNI-CHEM, 99%) and sodium hydroxide (NaOH) (Loba, 98%). The leaves of *Cordia africana Lam.* were collected from the Adama Science and Technology University campus and its surroundings, Adama, Ethiopia. Deionized water (DW) was used throughout the experiment.

2.2. Extract Preparation. The leaves of *Cordia africana Lam.* were washed thoroughly several times with tap water and DW sequentially to remove dust particles attached to the surface of the plant and then allowed to air dry. Then, the dried leaves were powdered using a grinder. 20 g leaf powder and 200 mL DW were mixed in a 1000 mL conical flask and stirred for 20 min. Then, the mixture was heated up to the boiling point and allowed to boil for 10 min under stirring. After cooling to room temperature, it was stirring continued for 20 min and then filtered to obtain an extract using Whatman filter paper. The resulting extract was stored at about 4°C for further use.

2.3. CuO Synthesis. CuO NPs were prepared by the MW-assisted modified method using $Cu(CH_3COO)_2.H_2O$ and *Cordia africana Lam.* leaf extract [40]. In a typical procedure, 6.2 g $Cu(CH_3COO)_2.H_2O$ was added to a 1000 mL beaker containing 100 mL DW and then stirred for 20 min. Then, 10 mL of the extract was added to the $Cu(CH_3COO)_2.H_2O$ solution under stirring. To adjust the pH, NaOH aqueous solution was added drop wise while stirring. After 20 min of stirring, the mixture was placed into a domestic microwave (MW) oven with a maximum power of 1000 W, and only 50% power output was used for 9 min. The brown precipitates were collected and washed with DW and ethanol sequentially. Finally, the residue was dried at 80°C for 12 h and then at 100°C for 2 h. The dried powder was powdered using a mortar and pestle. The flow chart of the synthesis of the CuO NPs is shown in Scheme 1.



Scheme 1: Flow chart for CuO NPs synthesis by the MW method.

2.4. Characterization. The crystal structure characterization and phase analysis studies of the as-prepared samples were realized by XRD (Shimadzu XRD-7000) with Cu Kα radiation ($\lambda = 1.5406$ Å) sources. FTIR spectra of the samples were recorded on a Spectrum 65 FT-IR (PerkinElmer) with a spectral resolution of 4 cm^{-1} in the range 4000–400 cm^{-1} using KBr pellets. The surface morphology and composition of the synthesized sample were characterized by SEM-EDX (COXIEM-30).

2.5. Performance Tests. In order to evaluate the catalytic performance of the CuO NPs, a 4-NP reduction reaction was conducted. Typically, 20 mg $NaBH_4$ and 100 mL 4-NP (20 ppm) aqueous solutions were transferred to a conical flask. After 2 min shaking, 5 mg of the catalyst was added to the $NaBH_4$ and 4-NP mixture. The progress of the 4-NP reduction was monitored by using a UV-vis spectrophotometer (SM-1600) at a wavelength around 400 nm at room temperature. From the resulting mixture, 3 mL was taken out every 3 min and transferred to the cuvette for the absorbance measurement. The kinetic analysis was conducted using equations (1) and (2).

For C_o and C_t corresponding to the concentration of 4-NP at time 0 and t, respectively,

$$\ln\left(\frac{C_t}{C_0}\right) = \ln\left(\frac{A_t}{A_0}\right) = -k_{app}t\,, \tag{1}$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_{app}t\,, \tag{2}$$

where A_o and A_t corresponds to the absorbance of C_o and C_t.

3. Results and Discussion

3.1. XRD Analysis of CuO Nanoparticles. To investigate the crystallinity and phase of the synthesized material, the XRD technique was used. The XRD pattern of the CuO NPs obtained using *Cordia africana Lam.* leaf extract is displayed in Figure 1. The noticeable peaks positioned at 2θ values of 32.44°, 35.46°, 38.68°,48.7°, 53.50°, 58.0°, 61.49°, 66.14°, 67.86°, 72.38°, and 74.89° correspond to (110), (002), (111), (20–2), (020), (202), (11–3), (31–1), (113), (311), and (004) crystal planes, respectively. These values agree with the monoclinic CuO phase (JCPDS Card number 48–1548, *C*2/*c* space group). The absence of peaks matching to $Cu(OH)_2$ and Cu_2O in the pattern with the appearance of all peaks corresponding to the monoclinic CuO phase signifies the formation of pure crystalline CuO by MW-assisted synthesis method. The crystallite size of the sample was calculated using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos\theta}, \tag{3}$$

where D = crystallite size, λ = the wavelength of the X-ray source applied, β = the width of the peak at half of its height (FWHM), θ = the Bragg angle, and k = the shape constant ≈ 0.9. The average crystallite size of the CuO NPs calculated for the highest peaks at 35.46° and 38.68° was around 9 nm. The resolved sharp peaks with the crystallite size of about 9 nm suggest the formation of the nanocrystalline CuO [65].

3.2. FTIR Analysis. The FTIR spectra of the aqueous extract of *Cordia africana Lam.* leaf and the CuO NPs synthesized using *Cordia africana Lam.* leaf extract are shown in Figure 2. Several characteristic bands were shown in the spectra of both the *Cordia africana Lam.* leaf extract (Figure 2(a)) and CuO NPs synthesized using the extract (Figure 2(b)). In both spectra (Figures 2(a) and 2(b)), the bands at 3400 and 2920 cm^{-1} correspond to the O–H and C-H functional groups stretching vibrational frequencies, respectively. Similarly, the

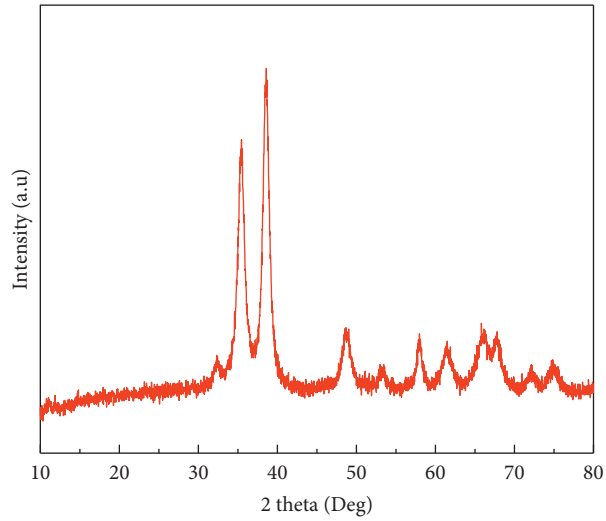


Figure 1: XRD pattern of the as-synthesized CuO NPs using *Cordia africana Lam.* leaf extract.

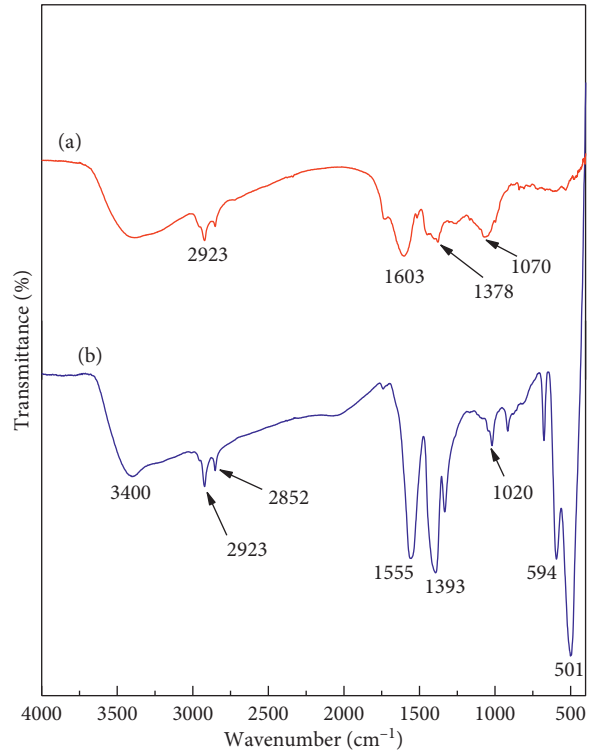


Figure 2: FTIR spectrum of (a) leaf extract of *Cordia africana Lam.* of and (b) as-synthesized CuO NPs.

bands at 1603 and 1300 to 1000 cm^{-1} (Figure 2(a)) belong to the stretching vibrations of the C=C aromatic ring and C–OH [58]. The sharp peaks that appeared at 1555 and 1393 cm^{-1} (Figure 2(b)) could be attributed to the carboxylate C-O stretching vibrations (asymmetric and symmetric). The bands arising due to the vibrational frequencies of the metal-oxygen (M–O) bond generally appear in the region below 1000 cm^{-1}. Hence, the peaks positioned at 497 and 591 cm^{-1} belong to characteristic vibrations of Cu–O bond, revealing CuO NPs formation [66]. No infrared active modes from Cu_2O were detected, indicating that, under the conditions stated in the synthesis method, only the CuO phase was selectively produced. A comparison of the extract spectrum with that of CuO NPs shows that the molecules of the extract are found adsorbed on the surface of the CuO NPs. Furthermore, the FTIR results indicate the formation of the CuO phase supporting the XRD result.

3.3. Morphology Analysis. Figures 3(a) and 3(b) show the surface analysis of the SEM image of the sample with different magnifications. The SEM image reveals that the CuO

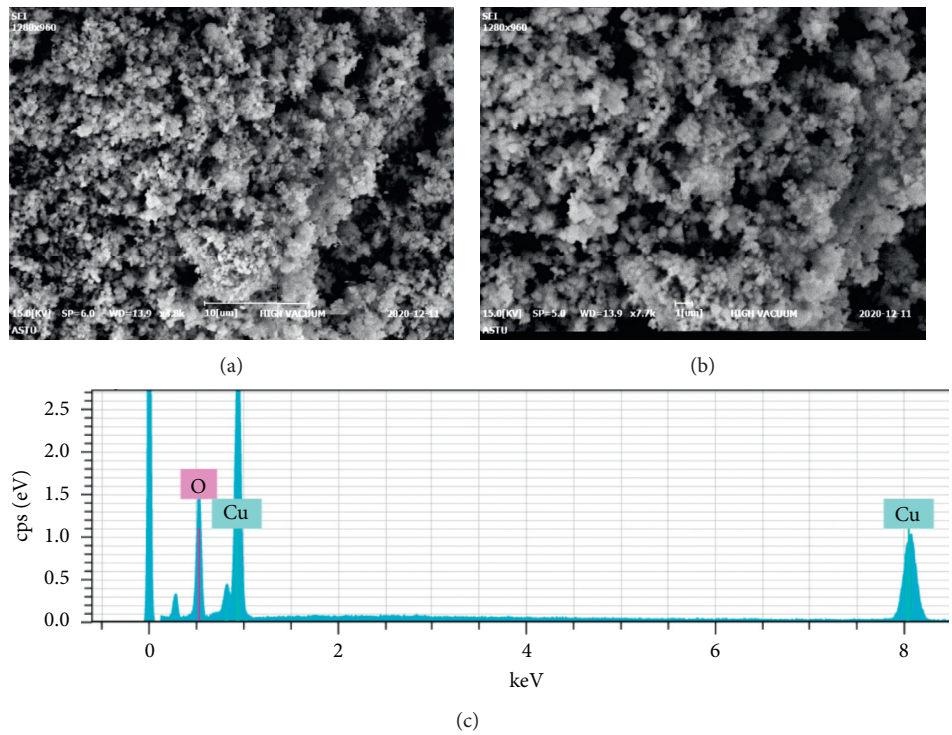


Figure 3: SEM images and of CuO NPs synthesized with *Cordia africana Lam.* leaf extract with low magnification (a) and high magnification (b); (c) EDS spectrum.

nanostructure synthesized using *Cordia africana Lam.* leaf extract by the MW-assisted method exhibits a uniformly distributed cluster of agglomerated morphology. The image taken at high magnification (1 μm) shows that some particles having spherical-shaped morphology are found separated from the agglomerated clusters. Figure 3(c) demonstrates the energy-dispersive spectroscopy (EDS) analysis of the sample obtained at 20.0 kV HV accelerating voltage. The EDS spectrum of the sample confirmed that the sample is composed of Cu and O elements. Thus, the biomolecules of the extract have taken part in the formation of CuO NPs.

3.4. Catalytic Reduction Reaction. The performance of the as-synthesized CuO NPs as a catalyst was evaluated against 4-NP reduction in the presence of $NaBH_4$ as a reducing agent. Figure 4 shows the reduction of 4-NP into 4-aminophenol. The UV-vis absorbance of p-NP in the absence of $NaBH_4$ displayed a peak at around 320 nm. However, the peak at 320 nm disappeared, and a new intense peak at around 400 nm appeared when $NaBH_4$ was added to the p-NP solution. In alkaline media, a light yellowish p-NP solution changes to an intense yellowish-orange p-nitrophenolate ion with absorbance at around 400 nm (Figure 4(a)). The intense initial spectrum was the UV-vis absorbance of the mixture of p-NP and $NaBH_4$ without catalysts.

After catalyst addition, the peak at 405 nm was gradually decreasing while the new peak at around 300 nm started growing, representing the conversion of the p-nitrophenolate ion into p-aminophenol, as indicated in Scheme 2 and Figure 4(d). The time taken for the complete conversion of 4-NP was measured based on the disappearance of the absorbance peak at around 400 nm in the presence of the CuO catalyst. It took less than 12 min for the complete conversion of 4-NP into aminophenols when the CuO catalyst was used, while no change was observed in the absence of the catalyst (Figure 4(e)). The pH at which the CuO NPs were synthesized has a significant influence on the reducing capability of the resulting CuO catalysts. As depicted in Figure 5, CuO NPs synthesized at pH 7 performed better than those synthesized at higher pH values. The difference in performance could be due to the variation in morphology of the resulting CuO nanostructures, which significantly affects the rate of the 4-NP catalytic reduction reaction [35].

The kinetics of the 4-NP reduction reaction in the presence of the CuO catalyst synthesized at different pH values is shown in Figure 5(e). Since the concentration of $NaBH_4$ is much higher than that of 4-NP, the analysis was conducted using the concentration of 4-NP alone [67]. The kinetic analysis results indicated that the data best fit with pseudo-first-order equation (equation (1)). The apparent rate constant (k_{app}) of the reaction can be obtained from the slop of a plot $\ln(C_t/C_o)$ vs t. Figure 5(e) shows that the rate of catalytic reduction reaction of 4-NP is the highest for the CuO catalyst synthesized at pH 7 using *Cordia africana Lam.* leaf extract.

There are different catalytic mechanisms proposed for the reduction reaction of nitroarene compounds into aminoarene. Generally, the mechanism of 4-NP reduction by $NaBH_4$ using metal-oxide-based catalysts involves transfer

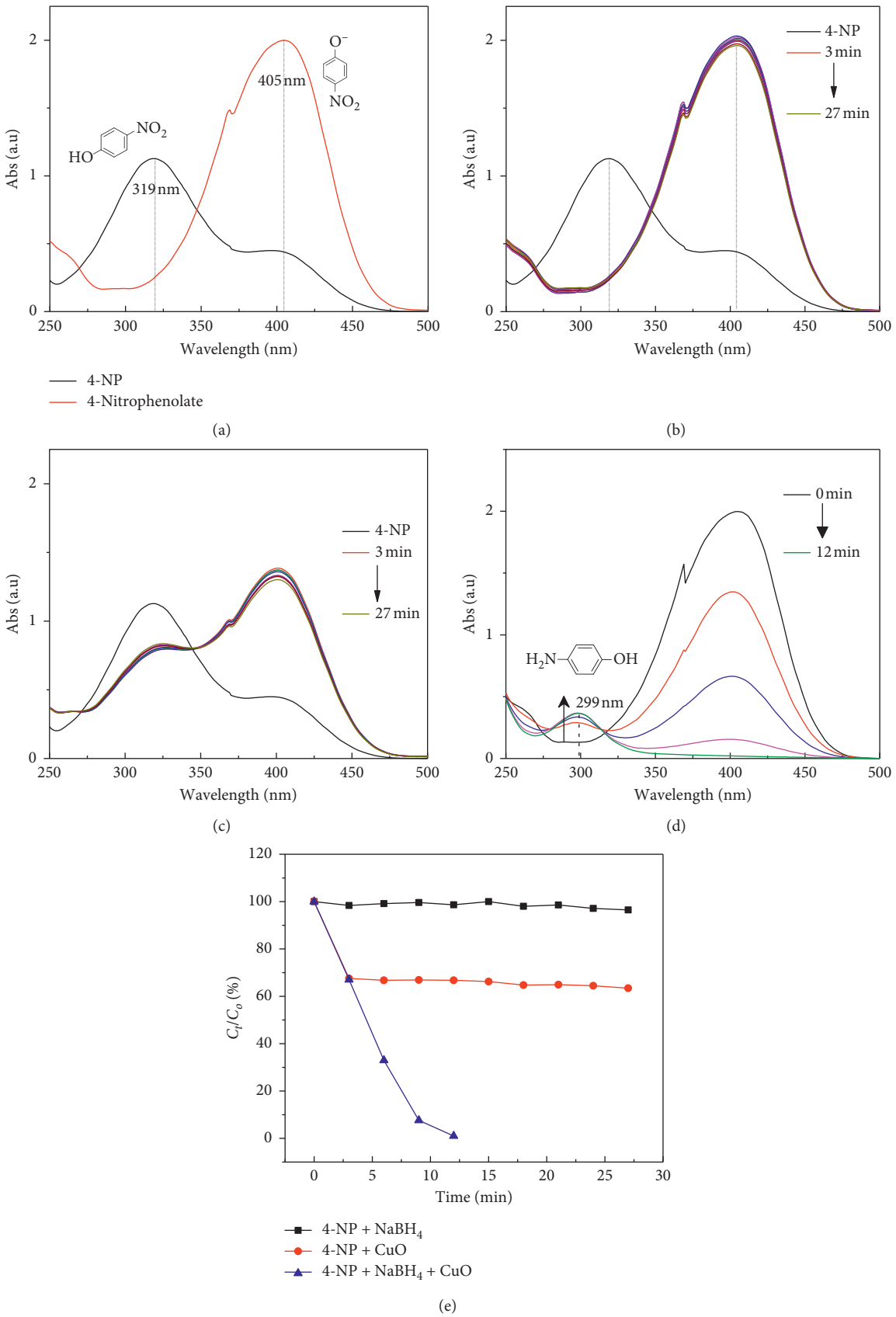
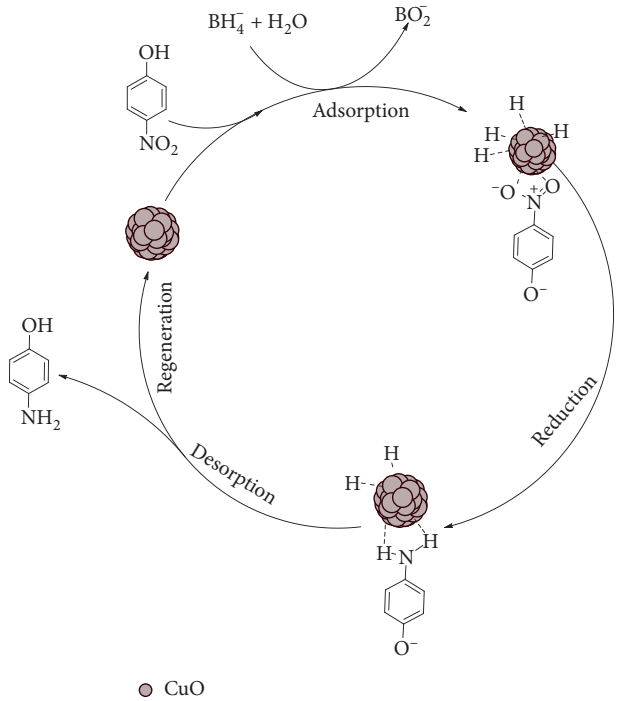


FIGURE 4: (a) Absorption spectra of 4-NP before and after the addition of aqueous $NaBH_4$ solution, (b) reduction of 4-NP with $NaBH_4$ but without a catalyst, (c) reduction of 4-NP with CuO but without $NaBH_4$, (d) reduction of 4-NP with $NaBH_4$ in the presence of a CuO catalyst, and (e) plots of C_t/C_0) *versus* reaction time (min) for the reduction of 4-NP with and without a CuO catalyst and NBH_4.



Scheme 2: Catalytic reduction reaction of 4-NP into 4-aminophenol using CuO NPs [18].

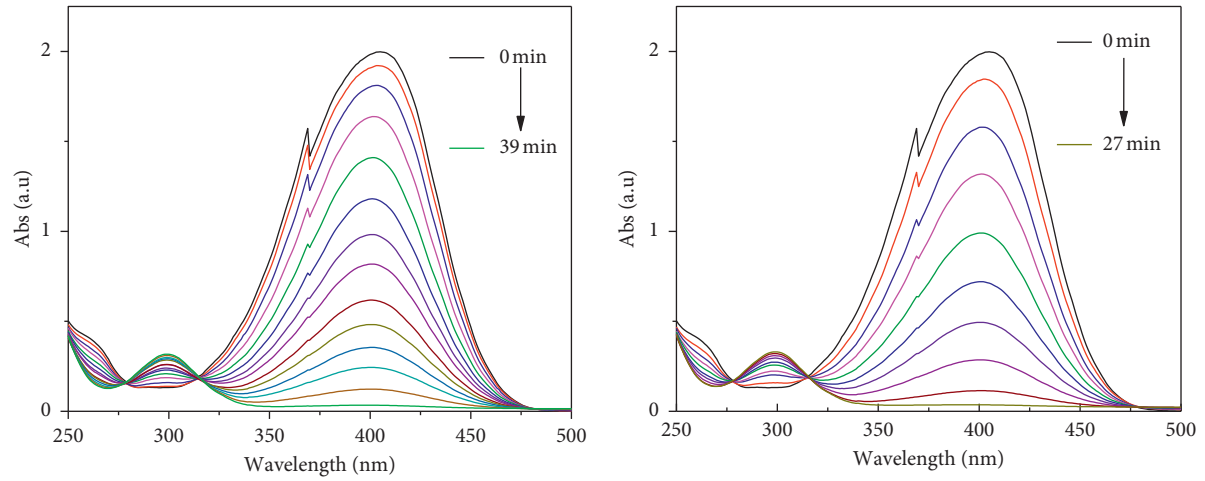


Figure 5: Continued.

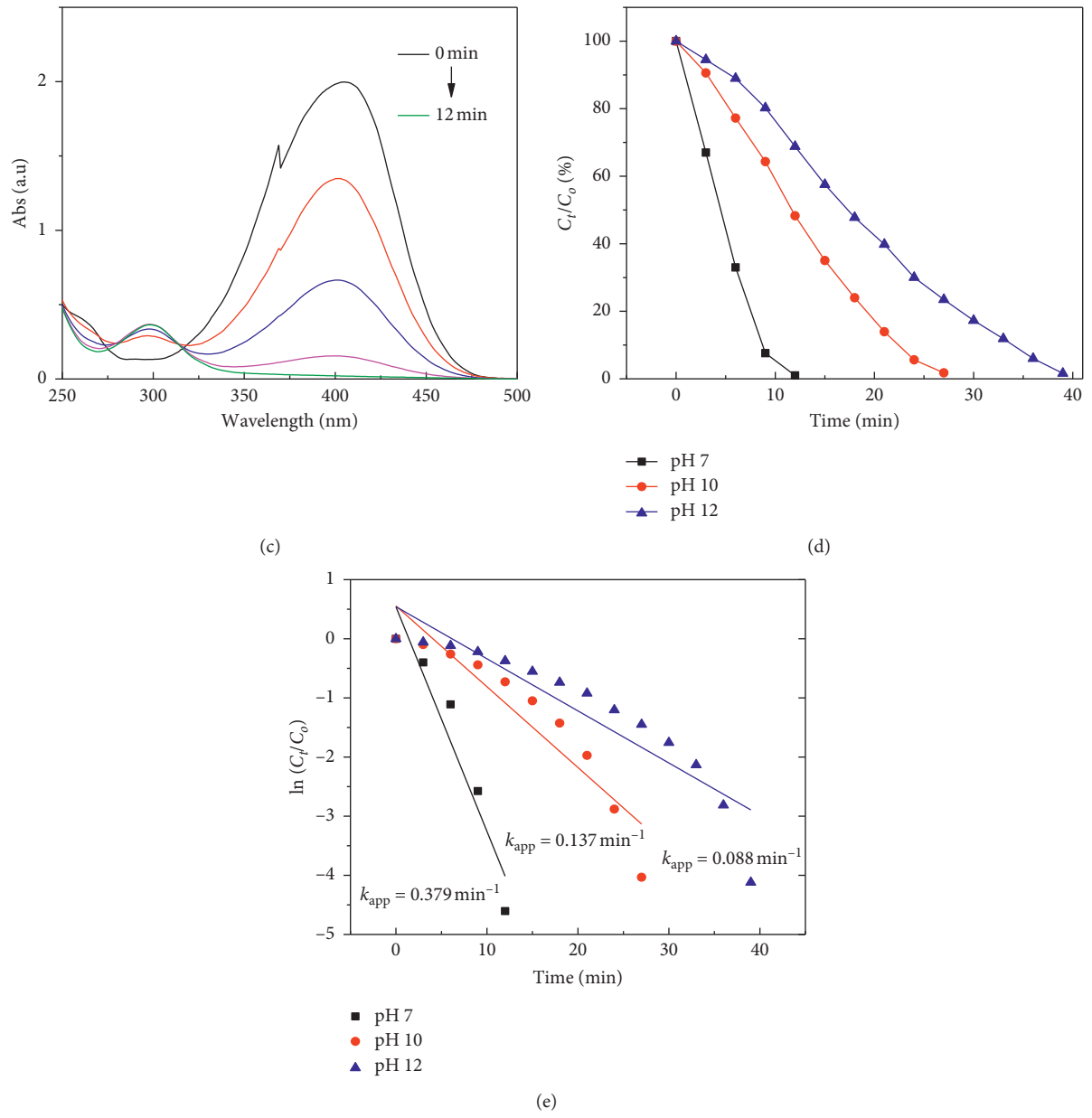


FIGURE 5: Reduction of 4-NP using CuO nanostructures synthesized at different pH values: (a) pH = 12, (b) pH = 10, (c) pH = 7, (d) plots of C_t/C_0 versus reaction time (min), and (e) plots of $\ln(C_t/C_0)$ versus reaction time (min).

TABLE 1: Comparison of the catalytic activity of CuO NPs with the previously reported CuO-based catalysts for the reduction of 4-NP.

Catalyst	4-NP (x10^{-3} mmol)	$NaBH_4$ (x10^{-3} mmol)	Catalyst amount (mg)	Time (min)	Rate constant, k_{app} (min^{-1})	Ratio constant K, (min^{-1}·g^{-1})	Ref
CuO nanoleaves	0.36	30	1	15	0.022	22	[71]
CuO flowers	0.25	50	2	4	0.565	282.5	[72]
Pd/CuO NPs	62.5	6250	7	1	3.3	471	[73]
CuO@C	100	2250	50	18	0.36	7.2	[74]
CuO/ZnO/ Eggshell	2	1320	20	30	0.2037	6.79	[75]
CuO/Cu_2O nanowires	0.25	50	0.1	4	0.5014	125.35	[76]
CuO NPs	14.38	528	5	12	0.379	75.8	Present work

of electrons and hydrogen, adsorption and desorption steps [68, 69]. The mixture of $NaBH_4$ and 4-NP in an aqueous medium produces 4-nitrophenolate and BH_4^- ions. BH_4^- provides both hydrogen and electrons [70]. Besides, in an aqueous environment, water serves as an additional source of hydrogen. Both BH_4^- and 4-nitrophenolate ions adsorb onto the surface of the catalyst. Then, the catalysts assist the transfer of electrons/hydrogen from the BH_4^- ions to the NO_2 group of the 4-nitrophenolate to produce 4-aminophenolate ions. Finally, the 4-nitrophenolate ions desorb from the catalyst surface. The major steps in the catalytic reduction of 4-NP using CuO nanoparticles are shown in Scheme 2.

The catalytic performance of the present nanocatalyst is compared with previously reported CuO-based nanocatalysts for the 4-NP reduction under different the reaction conditions (Table 1). The results indicated that the CuO NPs synthesized using *Cordia africana Lam*. leaf extract exhibited a better reducing capacity with an activity parameters constant of $75.8\,min^{-1}\cdot g^{-1}$. This value is higher than that reported for CuO nanoleaves, CuO@C, and CuO/ZnO/Eggshell nanocomposites [71, 74, 75].

4. Conclusions

CuO Nps were successfully synthesized using the aqueous extract of *Cordia africana Lam.* leaf following the MW-assisted method. The XRD result revealed the formation of a monoclinic CuO phase with an average crystallite size of 9 nm. The FTIR spectra confirmed the formation of CuO, NPs supporting the XRD result. Similarly, the EDS spectrum revealed that the synthesized material is composed of Cu and O elements. The SEM micrograph indicated that the obtained CuO NPs were found as agglomerated clusters of spherical-shaped morphology. The resulting NPs showed high catalytic efficiency with a catalyst loading of 5 mg in 12 min towards the reduction of 4-NP. CuO NPs synthesized at pH 7 showed strong catalytic activities compared to those synthesized at pH values 10 and 12. Thus, the CuO NPs synthesized using *Cordia africana Lam.* leaf extract showed great promise as a potential candidate for the reduction of other nitroarenes and dyes.

Data Availability

The [Excel] data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Aklilu Guale Bekru conducted the study and wrote the first draft, and the supervision and editing were carried out by Prof. Rajalakshmanan Eswaramoorthy. The co-authors Osman Ahmed Zelekew, Dinsefa Mensur Andoshe, and Fedlu Kedir Sabir participated in analyzing the results and drafting the manuscript.

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