

# Biosynthesis of Copper Oxide nanoparticles from *Drypetes sepiaria* Leaf extract and their catalytic activity to dye degradation

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**Abstract.** The synthesis of metal nanoparticles through a green method is a rapid biogenic and offers few advantages over the common chemical and physical procedures, as it is an easy and fast, eco-friendly and does not involve any costly chemicals as well as hazardous chemicals. In this study, we report synthesis of CuO NPs by using *Drypetes sepiaria* Leaf extract (DSLE). The synthesized CuO NPs was characterization using different technique such as UV, IR, XRD, and TEM. The formation of CuO NPs was confirmed by Surface Plasmon Resonance (SRP) at 298 nm using UV-Vis spectroscopy. Crystallinity of CuO NPs was confirmed by powder XRD and the characteristic functional groups of synthesised CuO NPs were identified by FTIR spectroscopy. The size and shape of the synthesized CuO NPs was determined by transmission electron microscopy (TEM). In addition, we performed photocatalytic activity to examine the photocatalytic degradation efficiency of CuO NPs to Congo Red. The colloidal solutions of CuO NPs showed good catalytic activity.

## 1. Introduction

Generally, nanoparticles can be defined as a particle existing between 1 nm and 100 nm in size i.e. it acts as a link between macroscopic world and microscopic atomic world. Nanostructured materials synthesized by various gas phase or vacuum methods came in forefront in the 1980's period [1-5]. In addition, other methods such as pyrolysis, attrition and hydrothermal were used in parallel. Also some physical and chemical methods are widely used to synthesis nanoparticles. But biosynthesis process have a lot of advantages in the synthesis of nanoparticles due to cost-effective, eco-friendly and better alternative to physical and chemical methods [6, 7]. Also, other chemical methods employ toxic chemical, additives, or capping agents. Chemical synthesis routes use surface controlling agents in liquid phases during growing stages of nanoparticles to avoid coalescence, nucleation followed by agglomeration in controlling size [8]. Evaporation and condensation are some important physical approaches in synthesising nanoparticles. Green chemistry as a new method provides clean, reliable, biocompatible, and eco-friendly approach for the preparation of the nanoparticles [9]. Out of different bioagents plant extract is an emerging area of research and it has potentially advantageous over chemical and physical methods [10]. Among these methods the green methods are more popular because of non-usage of toxic chemicals, only using plant extract, Plant extracts containing phytochemicals act as both reducing agent and stabilizing agent in the synthesis of metal nanoparticles. In compare to different chemicals involved, the bioreduction process is relatively complex in nature.



Nanoparticles are used or being evaluated for use in many fields. Among different nanoparticles, transition metal nanoparticles have wide application including chemistry, physics, biotechnology, environmental chemistry, etc. [11, 12]. It has so many applications in antimicrobials, ie, silver compounds have been used to treat burns, wound infections [13]. Various salts of silver and their derivatives are used as antimicrobial agents [14,15]. Also Ag nanoparticles show antibiotic activity, used in synthesising its composites for development of disinfecting filters and coating materials [16-18].

Catalytic properties of CuO nanoparticles were investigated against degradation of Congo red dye. The synthesized CuO nanoparticles were found highly active for the degradation of Congo red dye in a relatively short interval of time. This investigation indicates that CuO nanoparticles prepared by green synthesis can be used efficiently for the degradation of Congo red.

## 2. Material and methods

### 2.1. Materials

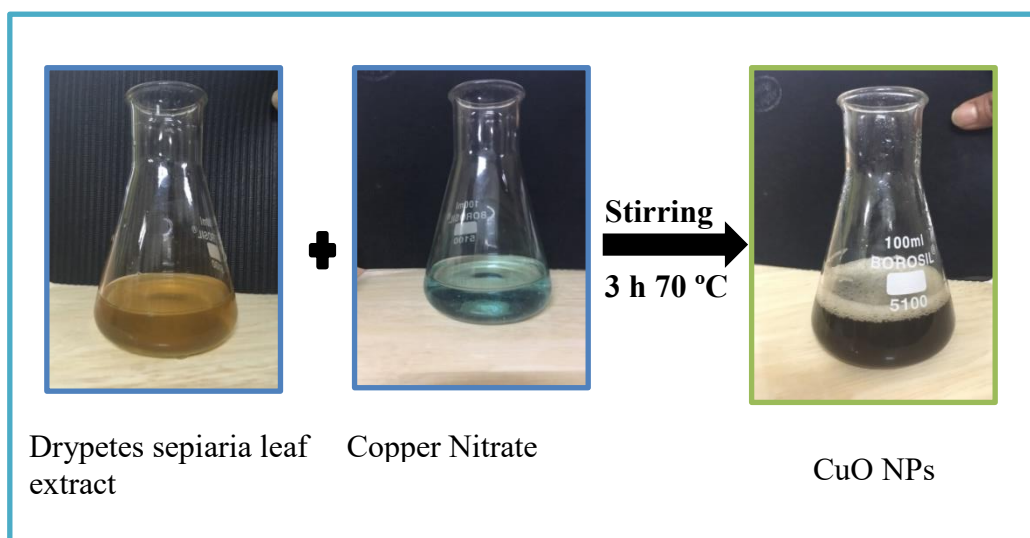
Copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), sodium borohydride ( $\text{NaBH}_4$ ), organic dyes such as Congo red dye (CR), was purchased from Sigma-Aldrich, India while other reagents were of analytical grade. Milli-Q water was used throughout the study.

### 2.2. Preparation of *drypetes sepiaria* leaf extract

*Drypetes sepiaria* leaves are collected, dried and grinded and washed with tap water followed by distilled water, after thorough washing about 3 gm of the grinded leaves along with 100mL of double distilled water is heated in a hot plate at  $70^\circ\text{C}$  for 30 minutes. After the formation of the plant extract, it is filtered using whatmann filter paper. And then freshly prepared extract was used for the synthesis of CuO NPs.

### 2.3. Preparation of CuO NPs using *drypetes sepiaria* leaf extract

Aqueous  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (40 mL of 0.1 M) solution was added to freshly prepared 20 mL of the plant extract and it's stirred using a magnetic stirrer at 600 rpm for 3 hours at  $70^\circ\text{C}$ . The deep blue colour of the copper nitrate solution changes to dark brown on the addition of plant extract. After 5 hours, a brownish-black coloured nanoparticle is formed which indicates the formation of CuO NPs. The solution is then carefully transferred and centrifuged for 30 minutes at 2000 rpm. The centrifugate is then washed with absolute alcohol and evaporated which is then followed by double distilled water twice, and then evaporate and collected crushed into powder for further analysis Figure 1.



**Fig 1.** Experimental procedure for the synthesis of CuO NPs

#### 2.4. Characterization of synthesized CuO NPs

##### 2.4.1. UV-Visible spectroscopy (UV-Vis) analysis

The initial characterization was carried out by a UV-visible spectroscopy (Jasco V-670 UV-visible double beam spectrophotometer), the synthesized colloidal CuO NPs solution with deionised water. The spectra were recorded in between wavelength range 200 nm to 800 nm, and the obtained data was re-plotted using Origin 8.5 software.

##### 2.4.2. Fourier Transform Infra Red (FTIR) analysis

The functional groups in phytochemicals was characterized by FTIR study of purified dried CuO NPs using shimadzu IR AFFINITY-1 against DSPE powder as control using JASCO FT-IR 4100 in the diffuse reflectance mode at a resolution of 4 cm in KBr pellets against pure untreated dry DSPE powder as control under the same instrumental conditions.

##### 2.4.3. X-ray diffraction (XRD) analysis

After complete reduction CuO NPs were separated by centrifugation at 3500 rpm for 20 min and pellet obtained was washed thoroughly with de-ionized water for 4 times, dried and used for XRD and FT-IR analysis. The XRD analysis of purified CuO NPs was carried out by a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.54^{\circ}$ ). The diffractogram was recorded in the scanning range ( $2\theta$  value) of  $10^{\circ}$  to  $90^{\circ}$  with a scanning rate of  $4^{\circ}/\text{min}$  and a step size of  $0.02^{\circ}$ .

##### 2.4.4. Transmission electron microscopy analysis

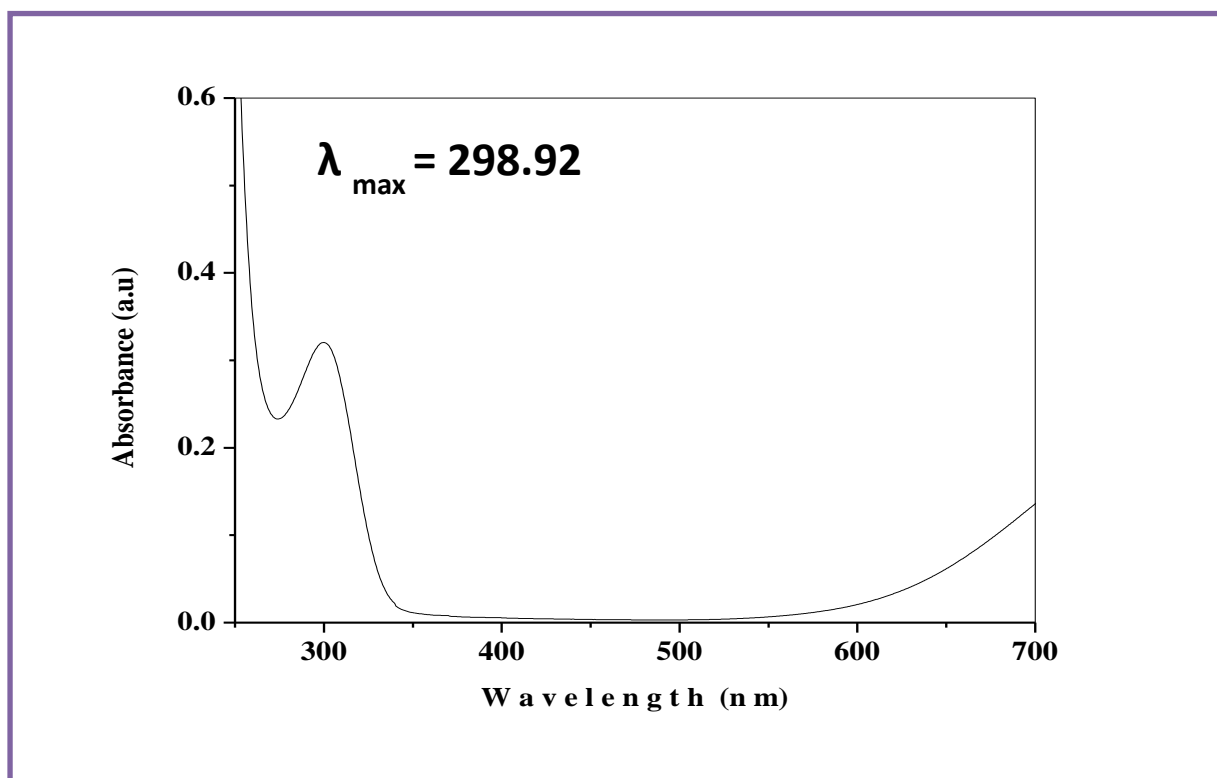
JEOL-JEM 2100 transmission electron microscope with an acceleration voltage of 200 kV was used to get high resolution TEM images and selected area electron diffraction (SAED) pattern. To resolve the morphology of CuO NPs, 400  $\mu\text{L}$  of the CuO NPs colloidal solution was diluted with 1 mL de-ionized water using ultrasonic bath. The TEM samples of CuO NPs were prepared by placing drops of solution on carbon coated grids and drying at ambient conditions.

### 2.4.5. Determination of Catalytic activity

The catalytic activity of synthesized CuO NPs was studied by dyes degradation of organic dyes such as Congo red dye [19, 20]. The optimised Catalytic activities of the biosynthesised copper oxide nanoparticles were determined using Congo red dye. In brief, about 0.1 mL of  $10^{-4}$  M Congo red dye is made up to 10 mL. About 3 mL each from this is transferred to a test tube. 18 g of  $\text{NaBH}_4$  is made up to 10 mL and kept aside. Different concentrations of  $\text{NaBH}_4$  and catalyst are tested on the Congo red dye. The catalytic degradation of organic dyes was observed by measuring UV-Visible spectra at regular time intervals [21, 22].

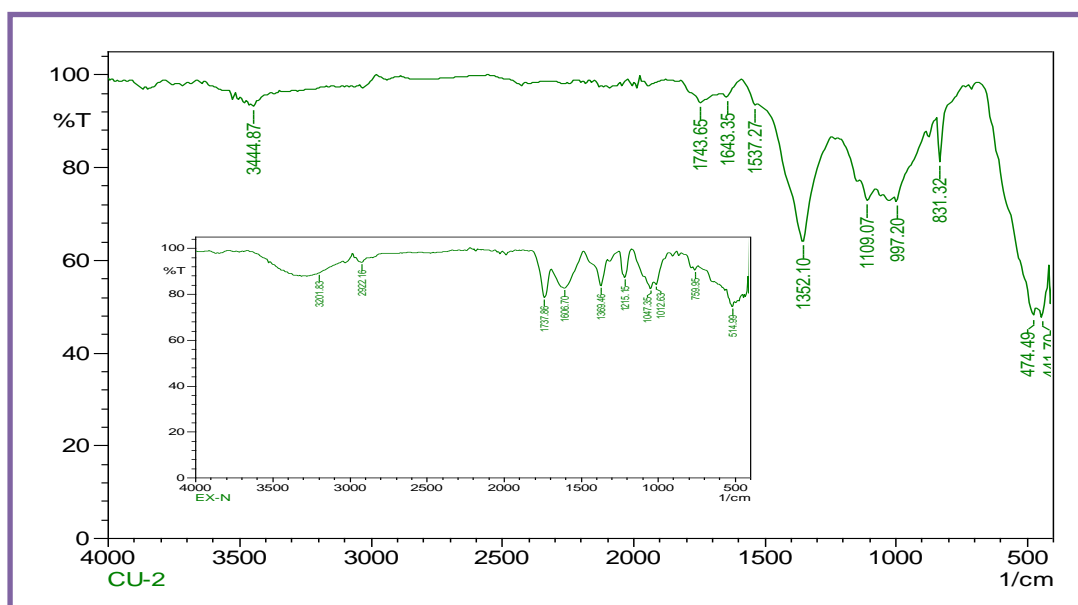
## 3. Result and discussion

From Figure 2 formation of CuO NPs was initially observed by visual colour change and then confirmed by UV-visible spectroscopy. When the extract was added to copper nitrate solution there was an immediate colour change within a short period from light blue colour to dark black indicating the formation of CuO NPs. Fig. 2 displays the UV-Vis absorption of CuO NPs with a distinct characteristic maximum absorption peak at 298 nm. The Formation of CuO NPs was also confirmed by UV- Visible spectroscopy, it is one of the important techniques to establish the formation and stability of NPs in solution. The progress of CuO NPs formation was checked by UV-Visible spectroscopy at 298 nm which is the significant band for CuO NPs. Also, SPR band depends on nature, size and shape of the synthesized particles. The single Plasmonic band indicates spherical CuO NPs while two or more bands because of quadrupole and multiple Plasmon excitations indicate its anisotropic nature. The single fine band at 298 nm represents the formation of CuO NPs.



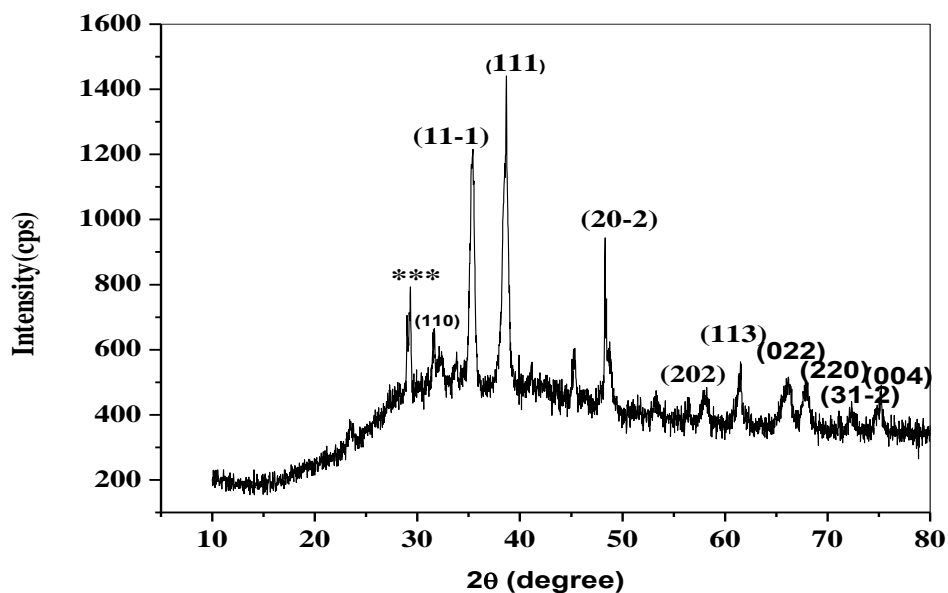
**Figure 2.** UV-Vis spectra of synthesised CuO NPs

Figure 3. The FTIR spectra were recorded in the solid phase at a range of 4000 – 400  $\text{cm}^{-1}$ . Multifunctional groups present in the green synthesised CuO NPs and the drypetes sepiaria leaf extract is studied using FTIR analysis. The peak at 1109.7  $\text{cm}^{-1}$  is due to the formation of green synthesised CuO NPs. The peak at 3444.87  $\text{cm}^{-1}$  is due to the –O–H bond stretching and the peaks at 1643.35  $\text{cm}^{-1}$  and 1743.65  $\text{cm}^{-1}$  are due to –C=O stretching of ester and amide groups. The peak at 1537  $\text{cm}^{-1}$  indicates the presence of aromaticity in the synthesised particles.



**Figure 3.** FTIR Spectra of synthesised CuO NPs

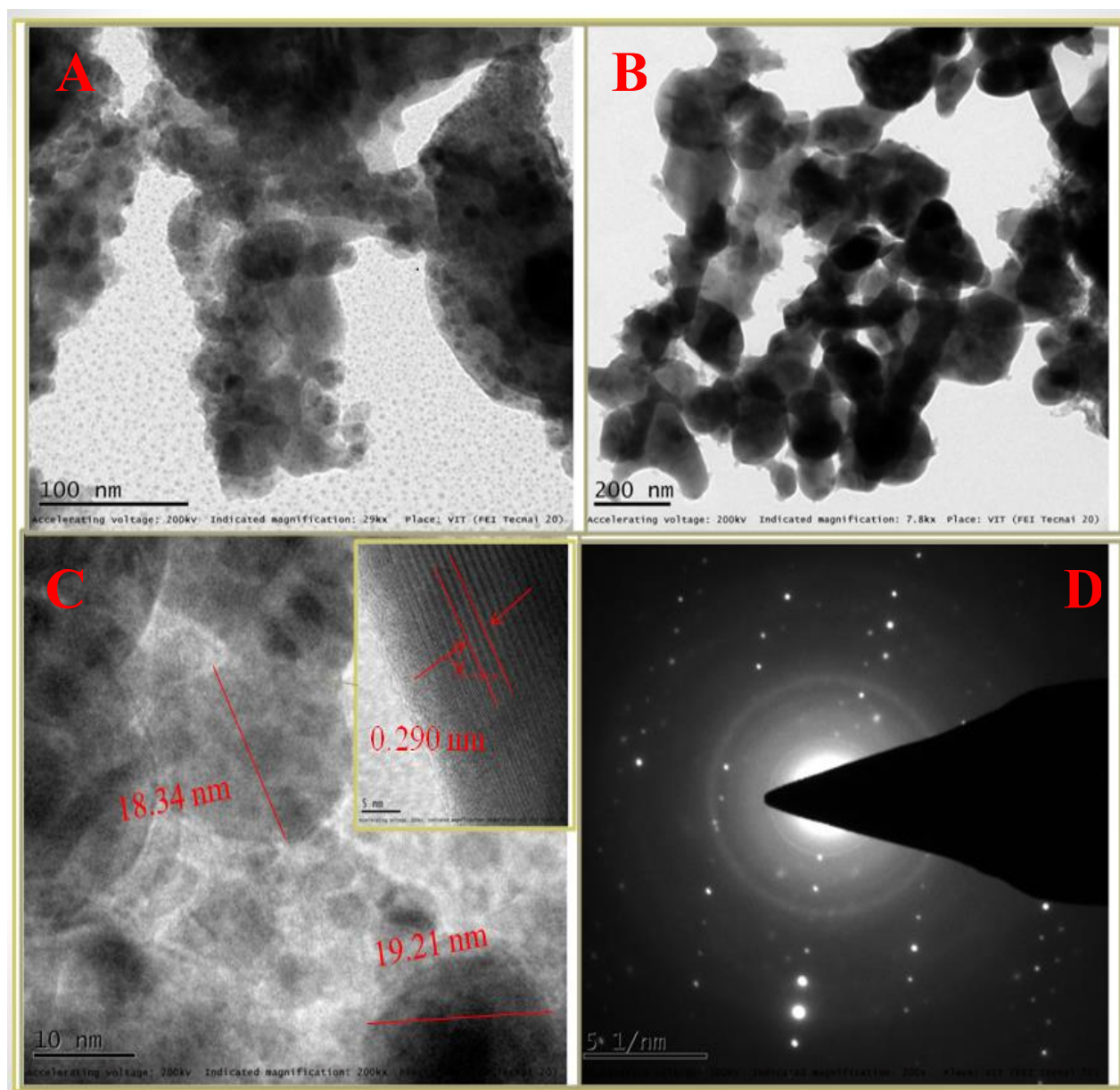
Figure 4. Shows the XRD technique which is used for the phase determination of crystal structures of the nanoparticles. The XRD analysis of the synthesised particles show characteristic diffraction peaks at  $2\theta$  of 32.37, 35.19, 38.49, 48.14, 58.01, 61.31, 66.01, 67.66, 72.37 and 75.19, which were assigned to (110), (11-1), (111), (20-2), (202), (113), (022), (220), (31-2) and (004) planes respectively. From the analysis by XRD, the monoclinic structure of CuO NPs prepared from drypetes sepiaria leaf extract was suggested. The monoclinic structure of CuO, so obtained, is then confirmed by comparison with the data provided in MATCH! Software [card no. 96-901-5925] and the cell parameter of the synthesised particle is 4.6832 Å. All the diffraction peaks corresponds to typical monoclinic structure and no other phase was observed. The average crystallite size of CuO nanoparticles was calculated using the Scherrer formula,  $D = 0.9 \lambda / \beta \cos \theta$ , where  $\lambda$  is the wavelength of X-ray radiation,  $\beta$  is the full width at half maximum (FWHM) of the peaks at the diffracting angle  $\theta$ . It was found to be 25 nm indicating its crystalline nature.



**Figure 4.** X-ray diffraction of synthesised CuO NPs

Figure 5. Morphology, size and shape of synthesised CuO NPs were determined by TEM analysis; Fig 5 (A-C) the present visualised images of the synthesis CuO NPs. The images expose the formation of spherical CuO NPs which in clear agreement with UV-Visible data. The average size of the CuO NPs was found as 18.77 nm. Biomolecular capping onto the surface of the CuO NPs were evidenced by TEM analysis (Fig. 5A and 5B). The crystalline nature of CuO NPs was further confirmed by SAED pattern. Fig. 4 (D) which exposes the diffraction rings with bright spots and is indexed to crystalline nature of synthesized CuO NPs. The fringe spacing is  $2.90 \text{ \AA}$  (JCPDS card NO. 96-901-5925) Fig. 5(C), which is authentic to CuO NPs.

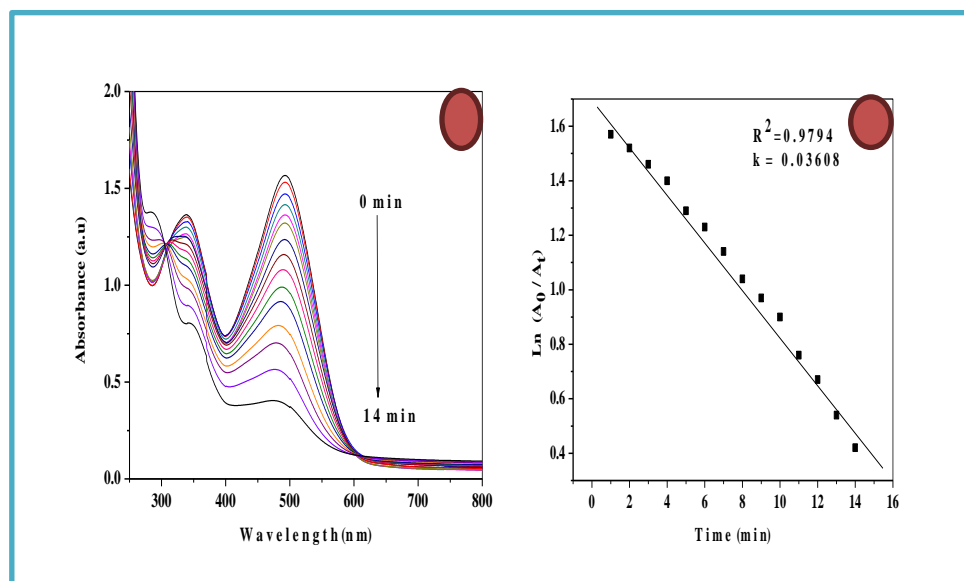




**Figure 5.** TEM images of CuO NPs different magnifications 100 nm (A), 200 nm (B), 10 nm (C) and SAED pattern (D).

### 3. 1. Catalytic activity of CuO NPs for degradation of Congo Red (CR)

Figure 6(a, b). The catalytic activity of the synthesized CuO NPs has been studied on the degradation of Congo red dye. During the degradation process, about 3mL of Congo red dye ( $10^{-4}$ M) was taken and 300  $\mu$ L of NaBH<sub>4</sub> solution(0.05M) followed by 150  $\mu$ L (1 mg/mL) of the prepared catalyst is added. The colour of the dye rapidly decreased and completely disappeared in 14 mins. It represents the formation of Lueco Congo red. The degradation of Congo red dye with CuO NPs yields Lueco Congo red without the formation of any by-product. Compare to high concentration of NaBH<sub>4</sub> the degradation rate was understood to be self-sufficient of the NaBH<sub>4</sub> concentration and catalytic rate followed pseudo first order kinetic equation and rate constant  $k$  was calculated as  $0.03608 \text{ min}^{-1}$ .



**Figure 6.** UV-Visible spectra for the degradation of Congo red by  $\text{NaBH}_4$  in the presence of CuO NPs (A) and kinetic of catalytic activity (B).

#### 4. Conclusion

In this study, a cost-effective and simple way to synthesise stable CuO NPs using drypetes sepiaria leaf extract has been introduced. The synthesised CuO NPs were initially confirmed by using UV-Vis spectroscopy and the crystalline nature of CuO NPs was evidenced through XRD studies. Different multifunctional groups of plant extract was confirmed by FTIR. The synthesised CuO NPs showed good catalytic activity in the degradation of organic dyes such as Congo red using  $\text{NaBH}_4$  as the reducing agent. The significant catalytic performance of CuO NPs is due to their high surface to volume ratio providing more active sites of the reactant molecules to interact. The colloidal solution is stable, suggesting that extract can be used as both reducing and stabilising agent for the preparation of CuO NPs.

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