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Original Research Article

Green Synthesis of Copper Nanoparticles Designed from *Ocimum sanctum* for Purification of Waste Water

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ABSTRACT

Green nanotechnology and its utility in synthesis of nanoparticles is an area of significant research intertest. For this project, synthesis of copper nanoparticles was done using *Ocimum sanctum* extract. Copper nanoparticles are gaining more attention in the field of agriculture, sensor, organic reactions, water purification etc. The prepared nanoparticles were characterized by XRD and UV–Vis spectroscopy. Method used for the synthesis of stable copper nanoparticles is rapid and ecofriendly. As we know, our river water is getting polluted mostly by waste coming out from our industries. Copper nanoparticles prepared by leaf extract are not hazardous to our environment. We have conducted our study by using Methylene blue dye (MB) and Rhodamine B (Rh B) dye. We have also studied the dye degradation reactions by using UV visible spectrophotometer.

Keywords: Copper nanoparticles, UV-Vis spectroscopy, *Ocimum sanctum* (Tulsi).

1. INTRODUCTION

Nanotechnology mainly deals with synthesis of nanoparticles of various sizes, different shapes, differing in chemical composition and in controlled conditions with their potential use for human benefits (Elumalai *et al*., 2010; Hagens *et al.*, 2007). It deals with manufacturing, studying and handling of matter at nano scale in the range of 1-100 nm (Rajan, 2006). Nanotechnology is being used in every sector for completing human needs and for future technologies. Materials can be prepared by different approaches such as Top down and Bottom up approach in nanotechnology (Albrecht *et al.*, 2006). So nanoparticles designed by these approaches lead to increase in the surface of the particles which leads to their different chemical, mechanical, magnetic and optical properties, as compared to bulk materials (Mazur, 2004). Synthesis of nanoparticles (NPs) by Physical and chemical methods are costly, time consuming, laborious and also requires lots of energy. These methods release hazardous chemical in our atmosphere and are also harmful to human beings due to the use of toxic chemicals (Mittal *et al.*, 2013).

Environment pollution is increasing due to the fast industrialization, urbanization and various activities of human beings. Air and water pollution have increased in the last 20 years due to the heavy use of different harmful chemicals and toxic dyes in industries. Dyes are used in many areas such as paint, textiles, food, plastic, paper, printing ink etc. But every human invention has disadvantages too. Most dyes are non-biodegradable and are a threat to the environment because after dying clothes, they are discharged into river bodies where they pollute the water, resulting in an increase in oxygen demand by the bacteria to break the organic waste from water or increase the biological oxygen demand (BOD). So dyes show significant toxicity to the environment, animals and are also one of the causes of eutrophication (Safavi & Momeni, 2012). Therefore, there is a need to remove these dyes from water for minimizing the water pollution. This is a very difficult task due to their complex structure and stability. Scientists have synthesized different molecules for the above said problem (Wang *et al*., 2010). The conventional method used for the preparation of Cu NPs involve the use of expensive, toxic and harsh chemicals, flocculation, activated carbon-sorption, redox treatment and electrocoagulation whereas the biological method involves the use of plant extract for preparation of copper nanoparticles which is an eco-friendly and greener method. So, this is the reason we have used biological method (Padma *et al*., 2018). Cu NPs have a small radius which increases its surface to volume ratio associated with a large number of active sites due to which they have easy interactions with other particles. They have antimicrobial properties and are highly reactive as compared to other nanoparticles. They are cheap, easily synthesized and can be stored for a longer time (Kulkarni *et al.*, 2015). We preferred copper nanoparticles over silver and gold nanoparticles due to its exceptional properties. We have characterized our Cu NPs using UV-Vis spectroscopy and XRD. So this is a greener method for removal of harmful dyes from river bodies instead of using UV light (Musa *et al.*, 2016; Sinha & Ahmaruzzaman, 2015).

2. MATERIALS AND METHODS

2.1 Materials:

Copper Sulphate pentahydrate (99%) was purchased from TCI Chemicals. Rhodamine blue (Rh B, 99%), Methylene blue (MB, 99%) were procured from Merck, India.
Solvents were purchased from a local vendor. *Ocimum sanctum* (Tulsi) leaves were taken from Maitreyi College.

2.2 Synthesis:

In the typical procedure, *Ocimum sanctum* (Tulsi) leaf extract was prepared by the procedure mentioned in the literature (Usha *et al.,* 2017). 20 mL of Tulsi extract was added to the 100ml of 0.01 M of copper sulphate pentahydrate ($CuSO_4.5H_2O$) solution and stirred on the magnetic stirrer for 24 hours. The colour change was observed from dark green to sea green. The solution was centrifuged at 6000 rpm for 15 min and copper nanoparticles were obtained. These nanoparticles were washed by water 4-5 times and then dried. Copper nanoparticles were characterized by the UV and XRD.

2.3 Characterization:

Powder X-Ray Diffraction (XRD) patterns of the Nanoparticles were collected at room temperature using a Bruker D8 Advance diffractometer system employing monochromatized Cu Kα radiation (λ=1.54056 Å) source. Perkin Elmer Lamda 35 UV-Visible spectrophotometer was used for Optical studies.

2.4 Photocatalytic test:

All the photocatalytic experiments were performed under 250 W mercury lamp for visible light irradiation. The distance measured between the reaction mixture and the light source was 12 cm and then the reaction mixture was ultra-sonicated for 10 to 15 sec for complete dispersion catalyst in reactants solution. We have studied the photocatalytic activity of copper nanoparticles for the degradation of methylene blue and Rhodamine B dye. For the degradation of Rhodamine B dye, 10 mg of synthesized copper nanoparticles was dispersed in 25 ml of 10^{-4} M solution of dye and 2 mL of 0.01 M sodium borohydride solution was also added (Musa *et al.,* 2016). We have stirred the solution for 30 min to attain the adsorption–desorption equilibrium of dye solution on the surface of the NPs, the suspended solution was allowed to stand for 30 minutes in the dark before visible irradiation, then dye was exposed to visible light in catalytic chamber. At regular intervals of time, 2 ml of suspension was withdrawn and immediately centrifuged. The concentrations of various reaction mixtures were monitored in supernatant solution by recording absorption spectra for various dyes (the gradual decrease absorption peak at 655 nm for Methylene Blue (MB), 550 nm for rhodamine B (Rh B). We have followed the same procedure for both the dyes.

2.5 Catalyst recyclability and stability:

Reproducibility of catalyst was analyzed by performing various reactions using the same catalyst by washing it several times with water and drying and reusing for further photocatalytic activity of sample. Reproducibility tests were performed for 6 cycles for degradation of MB and Rh B respectively. Catalyst stability was checked by again measuring the UV visible spectra and then by XRD.

3. RESULTS AND DISCUSSION

3.1. UV/Visible Spectrum:

UV studies show that there was a broad band due to the collective oscillation of conduction electrons which interact with electromagnetic radiation; this process is known as surface plasmon resonance. We get various parameters such as particle size, adsorbed species on the surface and chemical surrounding due to the shifting of this band. Cu NPs exhibit a sea green colour in aqueous solution due to excitation of surface plasmon vibrations and reduction of copper ions to Cu NPs. We had noticed the Colour change from dark green to sea green during the formation of copper nanoparticles. Kumar *et al*. (2013) have reported ultra violet band in the range of 550–600 nm. The UV/Vis spectrum of CuNPs showed a surface plasmon absorption band with maximum absorbance at 600 nm (Figure 1) indicating the presence of stable and well dispersed CuNPs.

3.2. X-Ray Diffraction:

XRD pattern of Cu nanoparticles synthesized by using a leaf extract of Tulsi (*Ocimum sanctum*) is monitored at a high angle of 2θ range (0°-55°) as shown in Figure 2. The XRD pattern shows a high crystallinity of Cu sample level with various diffraction angles as given in literature (Djangang *et al.,* 2015). The diffraction angle observed at 21.1° is related to the Tulsi leaf extract medium. There are peaks in the range of 20° - 40° confirming the formation of Copper nanoparticles (Saranyaadevi *et al*., 2014).

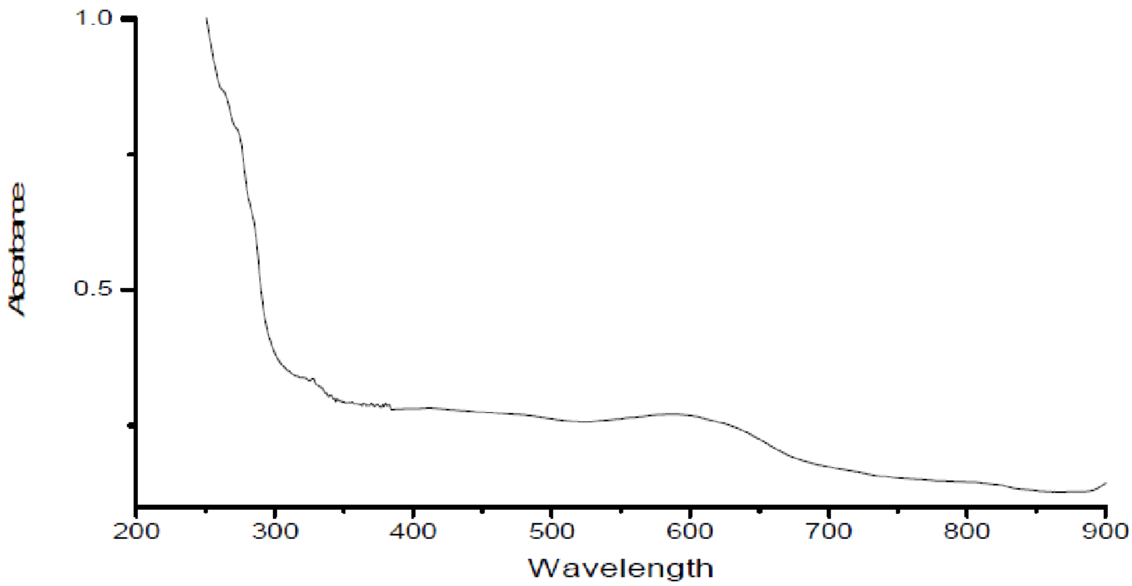


Figure 1: UV/Vis spectrum of as-synthesized CuNPs (a surface plasmon absorption band with maximum absorbance at 600 nm)

3.3. Photocatalytic Degradation of Rhodamine B and Methylene Blue:

We had carried out a few controlled reactions by varying the amount of the catalyst (5 mg, 10 mg and so on) with time, keeping the substrate concentration constant. In the photochemical reactor vessel (as shown in Figure 3), 25 mL of 0.01 mM Rh B was taken and a dye degradation reaction was carried out by using 5.0 mg of Cu NPs (standard reaction).

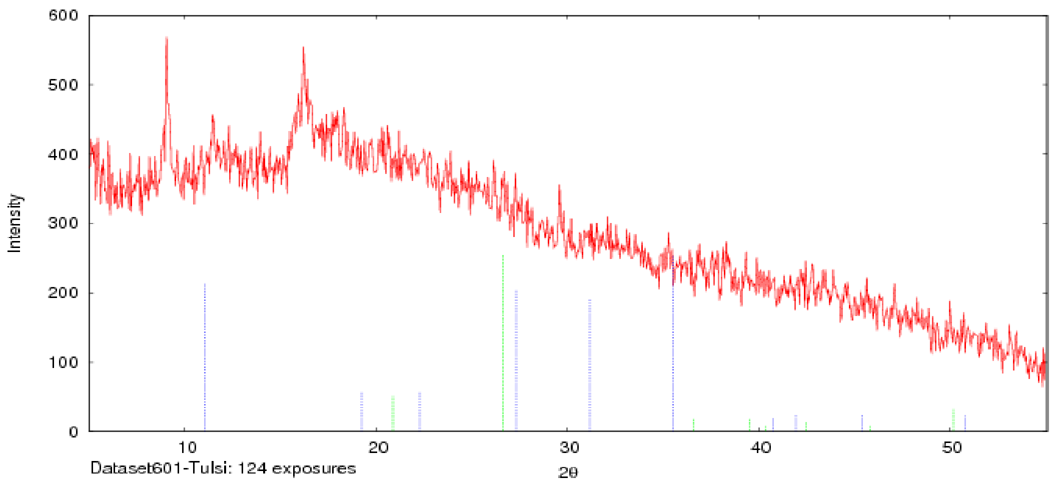
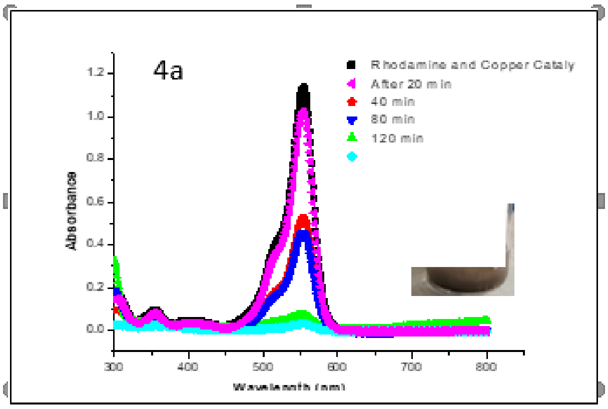


Figure 2: XRD spectra of synthesized CuNPs using Tulsi extract

Figure 3: Photocatalytic Reactor

Complete degradation (99.9%) of 0.01 mM Rh B dye takes place in 2.5 hours in the presence of the Cu Np photocatalyst, where the intensity of the peak at λmax = 550 nm decreased gradually without shifting the peak position to the baseline, indicating complete degradation as shown in Figure 4(a). Similarly Complete degradation (99.9%) of 0.01 mM Methylene blue dye takes place in 2 hours in the presence of the Cu Np photocatalyst, where the intensity of the peak at λmax = 655 nm decreased gradually without shifting the peak position to the baseline, indicating complete degradation of the Methylene blue dye as shown in Figure 4(b). The peak was observed at 550nm with absorbance 1.1 before degradation (shown with black line in Figure 4a).Later after 150 minutes the peak was observed at 550nm with absorbance 0.05 (shown with light blue line). Similarly, we observed for methylene blue as shown in Figure 4b.



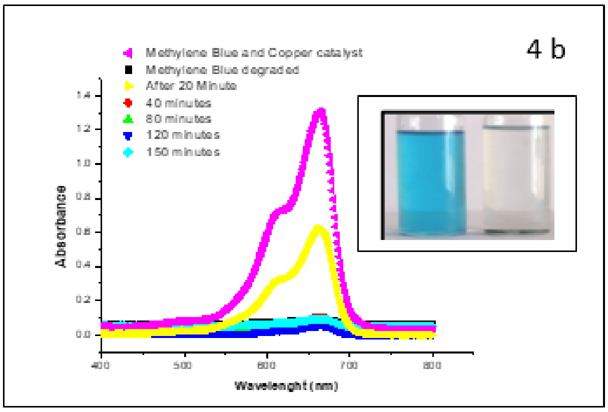
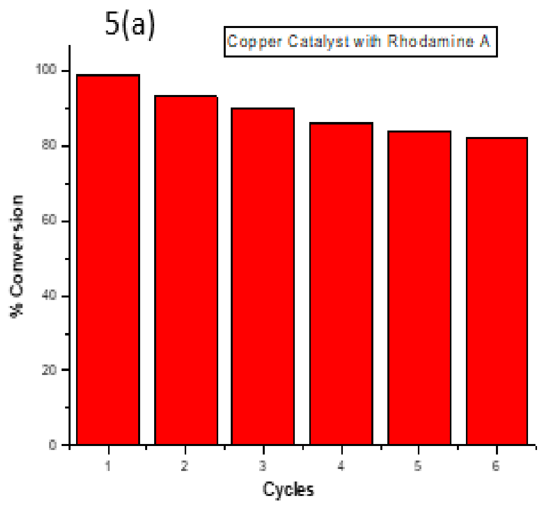


Figure 4a: UV-Visible spectrum of Rhodamine B dye degradation (Inset: complete degradation of Rhodamine Dye).

Figure 4b: UV-Visible spectrum of Methylene Blue dye degradation (Inset: complete degradation of Methylene Blue Dye)



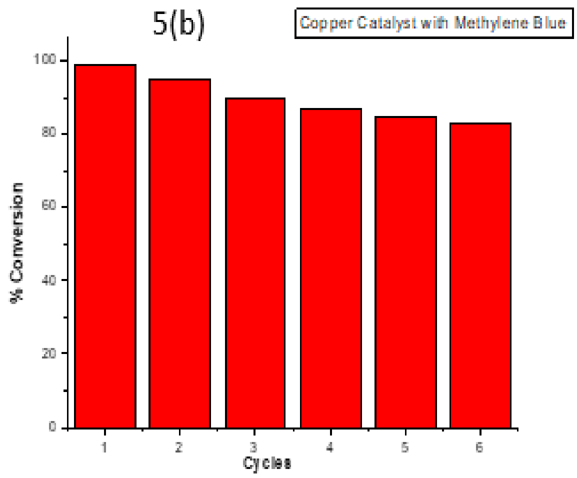


Figure 5a: Recyclability study of Cu NPs for Rhodamine B dye.

Figure 5b: Recyclability study of Cu NPs for Methylene Dye

The reusability of the photocatalysts was studied over 6 continuous cycles, and the photocatalytic activities versus the number of cycles are shown in Figure 5. There was only 10 to 15% loss of catalyst after 6 cycles.

4. CONCLUSION

Copper nanoparticles were synthesized by a simple, economic, greener approach. It is emphasized that Copper nanoparticles exhibited photocatalytic activity under visible light for the degradations of various dyes and purification of water. The conversion of both the dyes was >99.9%.

5. CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest.

6. SOURCE OF FUNDING

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