ABSTRACT

The discovery of various advanced materials that are applicable in remediation of environment pollutants was rapidly advancing because of their applications in wide range. Green synthesized Nano particles (NPs) were currently gaining attention in photodegradation of dyes and metals due to its ecofriendly, cost effective and simple production. Hence this study intended to synthesize and characterize the nano sized copper particles using aqueous root extract of *Schrebera swietenioides* Roxb., as green reducing agent. The synthesized NPs were characterized and proved that the NPs were aggregates with spherical shape to undefined shapes with an average particle size of 32±4 nm and contain 82.5 % of copper metal in the particles. Further, the synthesized NPs were applied for the removal of Sudan red (III) dye, Azure A dye and Lead metal. The findings proved that the NPs had potential degradation efficacy on the degradation of Sudan dye, Azure A dye and Lead metal. The NPs were durable and could be reusable with high degradation efficacy after three cycles of study for both dyes and metal in the study. Therefore, the green synthesized Cu NPs are potential candidates for photocatalytic applications.

Keywords: Copper nano particles, Photo catalytic activity, Azure A dye, Lead metal degradation.

INTRODUCTION

Now a day, nanotechnology has emerging as new research era that dealt with production, structural identification, amendment, and utilization of nanoparticles (NPs) in various tremendous applications in the various fields such as cosmetics, pharmaceutics, food industry, medicine, optics, electronics, and textile industry.[1,2] Nanomaterials are the extremely small size materials with 1-100 nm size with very high volume to surface area ratio and due to this these materials have enhanced applications than the bulk materials of similar category.[1,3,4] In particular, metal nanoparticles have received very high interest due to its electromagnetic and optical properties.[5] Among different types of metal nanoparticles, copper nanoparticles (CuNPs) have drawn incredible interest due to their significant optical, catalytic, physicochemical and heat transfer properties.[6] Moreover, CuNPs have been reported its remarkable significance in various fields such as chemical manufacturing[7], medicinal application[8], energy storage[9], solar cells[10] and dye degradation[11].

The NPs synthesis using chemical-mediated process involves the utilization of various chemicals which may be toxic and may pollute the environment.[12] The NPs synthesized using Physico chemical methods may have less stability and are expensive, involvement of toxic chemicals and complicate synthesis process. To overcome these drawbacks, the biological method of NPs synthesis gained a great attention. The NPs synthesis using biological method involving non-toxic chemicals, environmentally friendly in nature, economic and involving simple procedure with rapid synthesis.[13] Various researchers have published green synthesis methodologies for NPs synthesis using biological compounds such as microbes[14], mushrooms[15], plant extracts[16] etc.

In general, various metals were available in oxide form, but some of them only having wide applications in technical aspects. The oxides of transition metals like copper, iron, zinc etc., have potential significance due to its ability to adapt as nano fluid coolant in several heat transfer applications. The narrow band gap copper oxide (CuO) causes semiconducting properties and were used in various photoconductive applications.[17]

Copper was utilized as a starting material for synthesizing CuO NPs and copper is abundant in nature and is economically low price. They are proved to be having wide range of applications in various files such as ink-jet-printed electronics[18], li-ion battery[19], Gas sensing[20], anticancer activity[21], antimicrobial activity[22],...
photocatalytic activity\textsuperscript{[23]}, larvicidal activity\textsuperscript{[24]}, wound healing activity\textsuperscript{[25]} etc. Hence, the present work has been intended to synthesize CuO NPs using aqueous root extract of \textit{Schrebera swietenoides} Roxb., as biological reducing agent by following green synthesis approach. The NPs synthesized were characterized using various techniques such as UV-visible spectrophotometry, FT-IR (Fourier transmission infrared spectroscopy), SEM (scanning electron microscopy), TEM (transmission electron microscopy), XRD (X-ray powder diffraction) and EDX (Energy-dispersive X-ray spectroscopy). Further the applicability of the synthesized NPs for reduction of carcinogenic dyes such as Sudan red (III) dye and Azure A, pollutant Lead (Pb) metal in aqueous solution

**MATERIALS AND METHODS**

**Chemicals and Reagents**

The chemicals used during the synthesis of NPs and its application study such as copper sulphate, sodium hydroxide, Sudan red (III) dye, Azure A dye, Lead acetate etc., were of analytical reagent grade and were purchased from Merck chemicals, Mumbai.

**Root sample collection**

The fresh roots of \textit{S. swietenoides} were collected in Tirumala hills, Tirupati. The plant material was identified by Dr. Ch. Srinivasa Reddy, Assistant Professor, Department of Botany, SRR & CVR Government Degree College (A) Vijayawada and a dried specimen was stored in the department with specimen number SRR-CVR/2019-20/Bot/31. The fresh roots of the plant were collected, the debris and related dust was removed by washing with double distilled water. Then the roots were cut into very small pieces and shade dried till the fixed weight was obtained in two successive measurements. Then the dried roots were powdered, and the powdered root material was used for copper NPs synthesis.

**Aqueous root extract preparation**

An accurately weighed root powder (10 g) was immersed in a beaker containing 100 mL distilled water. The root extract was prepared by incubating the root powder solution at 40 °C for 80 min. Furthermore, the root extract was kept at room temperature for cooling, and filtered using Whatman filter paper \textsuperscript{[26]} and the filtrate was utilized for NPs synthesis.

**Synthesis of copper nanoparticles**

The aqueous root extract of \textit{S. swietenoides} mediated copper nanoparticles were synthesized as per the procedure described by Suresh et al., 2020\textsuperscript{[27]} with slight modifications briefly, 50 mL of aqueous root extract was added to a 500 mL volumetric flask containing 400 mL copper sulphate (5 mM) solution. The pH was adjusted to 7 using sodium hydroxide (1 N) solution. The colour change was indicated for the formation of Cu NPs. Then it was centrifuged and the obtained pellet was washed with water to remove unreacted reactants as well as plant extract. The pure pellet was dried in an air oven at 60 °C for 2 h. the dark brown pellet of Cu NPs was collected and stored for further use.

**Characterization of copper nanoparticles**

The crystalline, functional and characterization of synthesized Cu NPs was evaluated using various techniques such as UV-visible spectrophotometer, FE-SEM (Field emission scanning electron microscope), TEM (Transmission Electron Microscope) EDX (Energy-dispersive X-ray spectroscopy) and X-ray diffraction (XRD) studies. The optical absorption characteristics of the Cu NPs were evaluated using UV-visible spectrophotometer (JASCO, Japan) and measurement was made by scanning the NPs in aqueous solution 800 to 400 nm range. The shape, size, surface morphology and topography of the NPs were determined using FE-SEM (NOVA NANOSEM 450, FEI, USA) and TEM (Jeol/JEM 2100, Japan) analysis. The elemental composition of the NPs was confirmed by EDX (Rontec Xflash 3001, Japan) analysis. The crystal structure of the NPs was determined by XRD (Rigaku Corporation, Japan) studies which were performed at a scan speed of 2° /min in 20° to 80° diffraction angles \textsuperscript{(20)}.\textsuperscript{[28,29]}

**Photo catalytic Experiment**

Photo catalytic efficiency of Cu NPs was illustrated by performing photo catalytic activity in visible light region.\textsuperscript{[30]} The pollutant and carcinogenic dyes such as Sudan red (II) and azure A dyes and lead metal were used for determining photo catalytic efficiency of the Cu NPs. The catalyst at selected fixed weight was dispersed in 50 mL of the aqueous dye solution at a concentration of 75 ppm of Sudan red dye, 25 ppm of azure A dye and 50 µg/mL concentration of lead metal solution separately. The content was exposed to visible light irradiation for 2 h with continuous stirring. An aliquot was withdrawn at every 15 min time interval, centrifuged the solution and the dye/metal content measured using UV spectrophotometer. The absorbance values observed in each time interval were compared with corresponding standard calibration curves drawn at 513 nm for Sudan red (III) dye\textsuperscript{(31)}, 600 nm for azure A\textsuperscript{(32)} and 500 nm\textsuperscript{(33)} for Lead metal. The results observed were used for the evaluation of the photo catalytic efficiency of the Cu NPs.

**Durability of Cu NPs**

In the durability test of the catalyst for the photo degradation of dyes and metal under visible light, five consecutive cycles were tested. The samples were washed thoroughly with water and dried using vacuum at 40 °C for 6 hours after each cycle. The dried samples in each cycle were studied for its photo catalytic activity as per the procedure described above for each dye and metal in the study. The results observed in each cycle was used for the evaluation of its durability for the reduction of metal and dyes in the study.\textsuperscript{[34]}

**RESULTS AND DISCUSSION**

The unique optical properties of the nanosized particles have great interest in exploring the various nanosized particles with
different activities. Hence in this study, copper NPs were synthesized by adopting a green synthesis approach. The aqueous root extract of roots *S. swietenioides* was selected as green reducing agent for copper NPs synthesis. In the process of synthesis of NPs, the reaction mixture exhibits a different array of colours and the colour change was the primary indication for the formation of NPs. The colour change observed from blue colour to dark brown within 1 h confirms that formation of copper NPs will complete with in a less time of 1 h.

The root extract of *S. swietenioides* contains various chemical constituents that have the ability to convert reduction of Cu\(^+\) to Cu\(^0\) and hence NPs were formed \[35\].

The UV-visible absorption spectra of Cu NPs show characteristic absorption maxima at 340 nm (Figure 1) confirms the formation of nanosized copper particles and the results observed were in good argument with the literature\[26, 36\].

![Figure 1: UV-visible scanning spectra of Cu NPs.](image)

The FE-SEM analysis was performed to evaluate the morphology of Cu NPs and analysis results were given in figure 2a. The SEM analysis confirmed that the Cu NPs were particles size was distributed nearly monodispersed with an average particle size of around 35 nm. The particles were observed to be aggregates with spherical shape and some of them were undefined shape nanoparticles. The constituents present in the synthesized Cu NPs were examined using EDX analysis and results shown in figure 2b. The EDX spectra produce major peak at 0.93 and 8.02 keV corresponds to elemental copper. The peaks corresponding to carbon and oxygen were detected in the EDX spectra may be due to the biomolecules that were used for the capping of the Cu NPs. The % copper content in the synthesized Cu NPs was 82.5 %. Similar type size distribution and shape was reported along with the elemental composition of Cu NPs in previous findings \[26\] that supports the results achieved in the present study.

![Figure 2: SEM (a) and EDX (b) analysis results of Cu NPs](image)

TEM analysis is utilized in the conviction of the appearance, morphological structure, size distribution and orientation of physical and biological samples including NPs. The TEM analysis of synthesized NPs was shown in figure 3a and results confirm that the NPs were spherical to irregular in shape with broad size distribution \[37\]. The NPs were widely dispersed in 15-45 nm range size with an average particle size of 35 nm. XRD study was performed to evaluate the crystalline phase of the synthesized Cu NPs. XRD spectra show five characteristic peaks identified at 20 angles of 16.38°, 32.15°, 39.81°, 49.87° and 53.20°. These diffraction peaks correspond to the h,k,l values of the reflections from (110), (111), (220), (800) and (713) and the diffractions were corroborating with standard values of the JCPDS card 89-5899.\[38\]. The Scherrer formula (D = 0.9 λ/β cos θ, where β = full width at half maximum at the θ angle and λ = wavelength) was adopted in calculating the average crystalline size of the CuNPs and results obtained as 32±4 nm on the (111) plane.

![Figure 3: TEM (a) and XRD (b) analysis results of Cu NPs](image)
Sudan dyes are the azo compounds which are generally utilized to confer colour to different materials like food, textiles, oils, gasoline, inks and solvents etc\(^1\). These are very low price and produce red colour and hence were used to intensify the colour of various food products such as chili, paprika powders, curry, palm oil etc\(^2\). However, due to its mutagenic and carcinogenic properties, these compounds were classified as class 3 carcinogens by IARC (International Agency for Research on Cancer). Hence it is significantly imperative to reduce or elimination of these azo dye compounds. The degradation of Sudan red using synthesised Cu NPs can be conveniently monitored by using UV-visible absorption spectrophotometer. Figure 4 shows the UV-visible absorption spectra of Sudan dye solution containing the Cu NPs at 0 h and 2 h treatment and the spectrum clearly shows the characteristic maximum absorption at 513 nm for Sudan red (III) dye which in drastically decreased after 2 h of treatment of Cu NPs.

**Figure 4:** Comparative UV-visible absorption spectra of Sudan dye with no treatment and treated with Cu NPs after 2 hours

The photocatalytic reduction of Sudan dye was studied at various strengths of nano catalyst at 75 ppm concentration of dye and results were given in figure 5. The % reduction of Sudan dye was observed to be increased with increase in time. The % degradation of 20.50±0.036, 38.13±0.028, 54.28±0.153 and 61.23±0.060 was observed with in contact time of 45 min at a catalyst dose of 0.25, 0.5, 0.75 and 1.0 g/L respectively confirms the dose dependent activity of the NPs (Figure 5a). The dye reduction activity was significantly high in the initial time of reduction study and more than 50 % reduction activity was observed in 45 min of treatment at 0.75 g/L and 1.0 g/L strength of Cu NPs. The reaction order of the photocatalytic degradation of Sudan red dye was confirmed by plotting graph by considering ln \(A_0/A\) on y- axis and time on x-axis where \(A_0\) is the initial concentration of dye solution and \(A\) is the concentration of dye solution after NPs treatment at selected time interval. The results were given in figure 5b and the degradation reaction follows a pseudo first order reaction kinetics with respect to Sudan red dye. The rate constant (k) was calculated as 3.77×10\(^{-3}\), 5.85×10\(^{-3}\), 1.27×10\(^{-2}\) and 1.37×10\(^{-2}\) respectively for the Sudan red dye reduction study conducted at Cu nano catalyst dosage of 0.25, 0.5, 0.75 and 1.0 g/L respectively.

**Figure 5:** Photo catalytic degradation of Sudan red (III) dye using Cu NPs synthesized using *S. swietenoides* root extract

a) The photodegradation time profile with different strengths of Cu NPs on the reduction of Sudan red (III) dye at a concentration of 75 ppm;

b) The photo degradation time profile of \(A/A_0\) for 75 ppm Sudan red (III) dye concentration treated with various strengths of photo catalyst (Cu NPs).

Azure A is a small planar cationic dye which is rapidly used in colouring, textile, paper and biological industries. The acute

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exposer to this dye is harmful to humans and may cause jaundice, vomiting, and increased heart rate.\textsuperscript{[12]} Hence the green synthesized Cu NPs were utilized for the reduction of Azure A dye in aqueous solutions. The reduction study was monitored, and reduction efficiency was estimated using UV-visible absorption spectrophotometer at 600 nm wavelength. The UV-visible absorption spectra of untreated Azure A dye solution and the NPs treated Azure A solution were depicted in figure 6 which clearly confirms the significant reduction of Azure A concentration after treating with synthesized NPs.

Figure 6: Comparative UV-visible absorption spectra of Azure A with no treatment and treated with Cu NPs after 2 h

In the reduction study, the Azure A dye solution at 25 ppm concentration was utilized with various strengths of nano catalyst at different time intervals. As depicted in table 7a, reduction of dye was increased with increase in time in all the strengths of NPs studied. The reduction efficiency was observed to be very high in the initial time of adsorption due to the vacant surface-active groups of the NPs that facilitate the easy adsorption of dye particles. The % degradation of 29.32±0.050, 34.24±0.026, 46.71±0.020 and 64.00±0.566 was observed within contact time of 45 min at a catalyst dose of 0.25, 0.5, 0.75 and 1.0 g/L respectively confirms the dose dependent activity of the NPs (Figure 5a).

Figure 7: Photocatalytic degradation of Azure A dye using Cu NPs synthesized using \textit{S swietenioides} root extract

(a)

(b)

a) The photodegradation time profile with different strengths of Cu NPs on the reduction of Azure A dye at a concentration of 25 ppm;

b) The photodegradation time profile of $A_0/A$ for 25 ppm Azure A dye concentration treated with various strengths of photocatalyst (Cu NPs).

The results confirm that with in a very less time of 30 min, approximately 50 % dye (49.76±0.451) reduction was observed at nano catalyst dose of 1 g/L. The photocatalytic degradation study follows pseudo first order reaction kinetics with respect to Sudan red dye and $\ln A/A_0$ vs time of adscription graph was represented in figure 7b. The rate constant (k) was calculated as 3.96×10$^{-3}$, 8.69×10$^{-3}$, 1.53×10$^{-2}$ and 1.28×10$^{-2}$ respectively for the Sudan red dye reduction study conducted at Cu nano catalyst dosage of 0.25, 0.5, 0.75 and 1.0 g/L respectively.
Lead metal have significant adverse effect on environment as well as human health. Lead accumulates in the human body over many years and can cause damage to the red blood cells, kidneys and brain. Young children’s and pregnant women face high risk towards the lead pollution.\cite{41} Hence the synthesized Cu NPs were applied for the reduction of Lead in aqueous solutions and dithizone visible spectrophotometer method\cite{33} at 500 nm wavelength was adopted for the estimation of Lead in the NPs treated and untreated solutions. The Lead-dithizone complex formed due to the Lead present in the NPs treated and untreated solution confirms that the NPs treatment significantly decreases the Lead content in the aqueous solution (Figure 8).

**Figure 8:** Comparative UV-visible absorption spectra of Lead metal solution with no treatment and treated with Cu NPs after 2 h

The absorbance observed in each treatment was used for calculating the Lead content in the aqueous solution and then the % lead reduced in each treatment was calculated. The % metal reduction was observed as 61.23±0.060 % within 45 min at NPs dose of 1.0 g/L whereas at the same time the % reduction was observed to be 20.50±0.036, 38.13±0.028 and 54.28±0.153 proved the dose dependent metal reduction activity of the NPs (Figure 9a). At a contact time of 1 h, the % Lead reduction was observed as 82.45±0.059 % for NPs at 1.0 g/L dose that metal reduction activity was almost completed within 1 h of contact time at 1.0 g/L dose of nano catalyst. The rate constant (k) was determined from the linear plot of ln(A0/A) versus reduction time in minutes (Figure 9b).

**Figure 9:** Photo catalytic degradation of Lead metal using Cu NPs synthesized using S. swietenioides root extract

The degradation reaction follows a pseudo first order reaction kinetics. The rate constant (k) was calculated as 4.38×10^{-3}, 9.80×10^{-3}, 1.47×10^{-2} and 2.04×10^{-2} respectively for the Lead metal reduction study conducted at a nano catalyst dosage of 0.25, 0.5, 0.75 and 1.0 g/L respectively.

The adsorption of Lead metal using the synthesized Cu NPs was further confirmed by EDX analysis. The Lead treated NPs were subjected to EDX analysis shows characteristic peak corresponding to lead was identified along with Cu. The % Lead content in the NPs after treatment was observed to be 37.5 % (Figure 10). This confirms that in the photocatalytic degradation study, Lead was adsorbed on
the surface of the NPs and hence the same was detected in the EDX spectra.

Figure 10: EDX spectra of Cu NPs after Lead reduction activity study showing the characteristic peak corresponding to Lead metal confirms the adsorption of Lead metal on the surface of the NPs.

The reusability of the photocatalyst is the cardinal parameter in photocatalysis process as it effects significantly on the treatment process cost. The % degradation of both dyes and metal was observed to be very high in all the five cycles studied. The degradation efficiency of Sudan dye was observed to be more than 98% for three cycles and on the fifth cycle the degradation efficiency was 94% (Figure 9). The Azure A degradation efficiency was observed to be 87% on the fifth cycle and more than 98% in second cycle, whereas the Lead metal degradation efficiency was 91 % in fifth cycle of experiment. The downturn of photo catalytic degradation rate could be a result of blockage of active sites due to intense adsorption and catalytic degradation on the heterogeneous catalyst surface. This confirms that the Cu NPs were having high durability and reusability.

CONCLUSIONS
Collectively, the present study investigates the green route of synthesis of nanosized copper particles using S. svietenioides roo extract as green reducing agent for the capping of NPs. The NPs were characterized and confirmed that the NPs were observed to be aggregates with spherical shape and undefined shape with an average size of 32±4 nm with metal content was 82.5 %. Further the Cu NPs were applied for its photocatalytic degradation of Sudan red dye, Azure A dye and Lead metal in aqueous solution. Based on our findings, it can be confirmed that the NPs were having high degradation efficiency with less contact time was observed on the studied dyes and metal studied. Thus, the synthesized catalyst proved as promising material in photocatalytic domain for environmental depollution of aquatic dye/metal pollutants.

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REFERENCE