Biosynthesis of monodispersed stable copper nanoparticles using _Syzygium cumini_: characterization and potential applications

Muhammad Imran Din[a,*], Rida Akbar[a], Zaib Hussain[a], Rida Khalid[a], Muhammad Arshad[b], Tajamal Hussain[a], Safyan A. Khan[c]

[a]_School of Chemistry, University of the Punjab, New Campus Lahore 54590, Pakistan, Cell: +92-33-19743520;_
Fax: +92-42-99231269; emails: imrandin2007@gmail.com (M.I. Din), ridaakbar56@gmail.com (R. Akbar),
drzh1972@hotmail.com (Z. Hussain), ridakhalid42@gmail.com (R. Khalid), tajamalhussain.chem@pu.edu.pk (T. Hussain)
[b]_Institute of Chemistry, The Islamia University of Bahawalpur, Baghdad-ul-Jadeed Campus, Bahawalpur-63100, Pakistan,_
email: muhammad.arshad@iub.edu.pk
[c]_Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31261,_
Saudi Arabia, email: safyan@kfupm.edu.sa

ABSTRACT

This study reports a novel, facile and eco-friendly approach for the reduction of $CuSO_4 \cdot 5H_2O$ into stable and well-dispersed copper nanoparticles (Cu NPs) using aqueous leaf extract of _Syzygium cumini_. The reduction was affirmed by UV-Visible spectrophotometer maximum absorbance at 535 nm. The effect of various parameters including temperature, pH, precursor salt concentration and incubation time on particle size of Cu NPs has been evaluated. Fourier-transform infrared spectroscopy showed a strong band at $3,307 \text{ cm}^{-1}$ indicating the O–H groups of alcohols and phenols. Scanning electron microscopy analysis showed spherical morphology of Cu NPs with particle size of 19 nm. The prepared nanoparticles showed excellent catalytic performance for the removal of methylene blue (MB) from the aqueous medium using sodium borohydride ($NaBH_4$) as a reducing agent. The kinetic studies showed that Cu NPs followed pseudo-first-order for catalytic reduction of MB.

Keywords: Green synthesis; Nanomaterials; Methylene blue; Nanoparticles; Catalytic reduction

1. Introduction

Nanotechnology has gained appreciable attention in the various domains of science and technology [1,2]. Nanoparticles are the building blocks of nanotechnology. Nanoparticles have become center of attention due to their fascinating catalytic, optical, and magnetic properties [3–5]. These fascinating novel properties make them different and often superior to the related bulk material and atoms/molecules. Nanoparticles are extensively used in catalysis, communication, computing chips, nano-mechanical part, photosensors, drug delivery, cosmetics and anti-aging drugs [6–9]. Among several metal nanoparticles, copper nanoparticles (Cu NPs) have attained considerable heed due to their ubiquitous catalytic, optical, electrical, antifungal and antibacterial properties [10–12]. Several conventional methods such as chemical reduction method, sono-electrochemical and physical methods are mostly employed for the synthesis of Cu NPs [13,14] but the involvement of hazardous chemicals and disposal of these chemicals pose a disadvantage to chemical methods. Physical methods are not so adequate due to the expensive equipment required to prepare nanoparticles [15]. Recently, green synthetic approach has been considered

* Corresponding author.

more convenient and advanced as compared to traditional chemical and physical methods due to large availability of feedstock, facile synthesis procedure, eco-friendly and cost-effective properties [16]. Among all the feedstock, plants have been mainly used for industrial application of NPs because of facile synthetic approach and more stable nanoparticles [17,18]. Plants are nature's factories of biomolecules such as polysaccharides, carbohydrates, proteins, tannins, alkaloids and alcoholic compounds [19]. The reduction of metal ions to metal nanoparticles and stability of synthesized nanoparticles is most probably due to these biomolecules [20]. Cherian et al. [21] adopted novel biogenic route for the preparation of stable Cu NPs using *Cymbopogon citratus* stabilizing agent. However, Nasrollahzadeh et al. [22] also used biogenic route for the preparation of CuO NPs in the presence of *Gundelia tournefortii* leaves extract and studied its application for catalytic degradation of 4-nitrophenol. Raina et al. [23] biogenically prepared Cu NPs and Ag NPs in the presence of *Centella asiatica* extract and studied their applications for the catalytic reduction of different dyes. They found that biogenically synthesized Cu NPs showed excellent results as compared to Ag NPs. To the best of our knowledge the catalytic reduction of methylene blue (MB) dye using Cu NPs stabilized by *Syzygium cumini* plant extract has not been reported in the literature. Recently, due to rapid industrialization water pollution has been increasing day by day which directly or indirectly affects aquatic and human life. Among organic pollutants, MB dye has become the centre of attention due to its high solubility and huge stability in aquatic medium [24,25]. Additionally, MB dye has a serious deleterious impact on both human and aquatic life hence, it is necessary to reduce MB dye into non-toxic products [26]. Various methods have been reported to degrade MB dye but the catalytic reduction of MB dye in the presence of a biogenically synthesized catalyst would be more suitable [27–32]. Therefore, to investigate the catalytic efficiency of biogenically synthesized catalyst MB dye is used as a model contaminant.

In this study, *Syzygium cumini* (Family Myrtaceae) plant extract was employed for the reduction of copper ions to synthesize Cu NPs. However, *Syzygium cumini* plants are highly known for medicinal purposes and used as anti-diarrheal, anti-bacterial and hypoglycemic agents [33,34]. *Syzygium cumini* plant possesses various phytochemicals such as phenols, alkaloids, tannins, flavonoids and glycosides which help in the reduction of metal salt [35]. Plant extract is rich in metabolites such as proteins, flavonoids and polyphenols which not only act as reducing agents but also as capping agent and prevent accumulation of nanoparticles [36]. However, the effect of different parameters was studied to obtain excellent yield of Cu NPs. Different characterization techniques such as UV-Visible, Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were studied to confirm the morphology and successful synthesis of Cu NPs. After the successful formation of Cu NPs, the model reaction of catalytic reduction MB was performed to investigate its catalytic potential.

2. Materials and methods

2.1. Materials

Sodium hydroxide (NaOH), methylene blue ($C_{16}H_{18}N_3SCl$), copper sulfate ($CuSO_4 \cdot 5H_2O$), hydrochloric acid (HCl), sodium borohydride ($NaBH_4$) and distilled water. All chemicals were of analytical grade and were used without any further purification. *Syzygium cumini* leaves were collected from the local market, Lahore, washed with normal water followed by the distilled water and then dried overnight.

2.2. Synthesis of Cu NPs

For the preparation of plant extract, 10 g of *Syzygium cumini* leaves were taken and soaked in deionized water overnight. The leaves were then ground in a pestle and mortar into a fine paste and the mixture was boiled for 30 min. The mixture was then filtered and stored in refrigerator at 4°C for further use. After this, 10 mL of 1 M $CuSO_4 \cdot 5H_2O$ aqueous solution was added along with 20 mL of prepared *Syzygium cumini* extract. The mixture was stirred on a hot plate for 30 min at 80°C and pH was maintained at 12 using NaOH and HCl solutions. After 30 min, a color change was observed indicating the formation of NPs. The mixture was centrifuged and the resultant precipitates were washed with deionized water and finally dried at 80°C.

2.3. Optimization parameters

To define the optimum conditions for biogenic synthesis of Cu NPs in the presence of *Syzygium cumini* leaf extract effect of different parameters such as effect of temperature, pH, initial concentration of precursor salt and incubation time was evaluated by synthesizing the nanoparticles at varying temperatures (room temperature, 50°C and 80°C), pH values (5, 9, 11 and 12), incubation time (30, 60 and 90 min) and different precursor salt concentrations (0.001, 0.1 and 1 M).

2.4. Catalytic degradation of pollutants

1 mL of 10 ppm MB and 0.2 g of Cu NPs were taken along with 1 mL of distilled water and 1 mL of 0.1 M $NaBH_4$ at ambient temperature. The catalytic activity was assessed by observing the change in absorption at characteristic maximum wavelength (λ_{max} = 665 nm) of MB with UV-Vis absorption spectrophotometer.

2.5. Characterization

UV-Vis (UVD-3500 Lambda, Inc., USA) spectrophotometer was used for confirmation of biogenic preparation of Cu NPs. Catalytic reduction of MB dye was also observed through UV-Vis analysis. Fourier transform infrared spectroscopy (Model Cary-630) was recorded for solid Cu NPs in the wavelength range 400–4,000 cm^{-1} at a resolution of 4 cm^{-1} to evaluate the possible reducing metabolites which could be responsible for the stabilization of NPs from the *Syzygium cumini* extract. Scanning electron microscopy

(SEM; Hitachi S-4700) operating at 25 kV was also used to investigate the morphological characteristics of biogenically synthesized Cu NPs. The Cu NPs samples were equilibrated in distilled water (25°C) and then freeze-dried (Lyotrap freeze dryer) for 48 hrs before carrying out SEM analysis.

3. Results and discussions

3.1. UV-Visible analysis

UV-Visible spectroscopy is an efficient characterization technique for the determination of synthesis and stabilization of nanoparticles. Herein, Cu NPs were synthesized which showed maximum absorbance peak at 535 nm due to surface Plasmon absorption of nanoparticles as shown in Fig. 1. However, no additional peak was observed in UV-Visible spectrum of Cu NPs which indicates the formation of pure NPs. Additionally, peak intensity was high, confirming the enhanced yield of Cu NPs. Similarly, Yallappa et al. [37] prepared Cu NPs by using *Terminilia arjuna* bark extract under microwave irradiation showing SPR peak at 535 nm. Optical properties of Cu NPs also have been studied by changing different reaction parameters such as temperature, pH, incubation time and precursor salt concentration using double beam spectrophotometer. Herein, the reaction mixture was incubated at room temperature, 50°C and 80°C. It was observed that higher temperatures lead to high temperature broadening of peaks due to thermal volume expansion and electron-phonon scattering of nanoparticles, respectively [38]. The optimum temperature was found to be 80°C. Temperatures higher than 80°C may lead to agglomerated particles due to accelerated growth and nucleation rate. Caroling et al. [39] reported the synthesis of Cu NPs in the presence of aqueous gooseberry extract and observed optimum yield at 80°C. Samari et al. [40] successfully synthesized Cu NPs in the presence of *Manilkara zapota* L. and found optimum yield at 60°C. Fig. 2b shows the effect of pH on synthesis of Cu NPs. pH is an important factor which directly affects the size and shape of NPs. It was observed that at different pH values (5, 9, 11 and 12), pH 12 showed a favorable increase in the formation of Cu
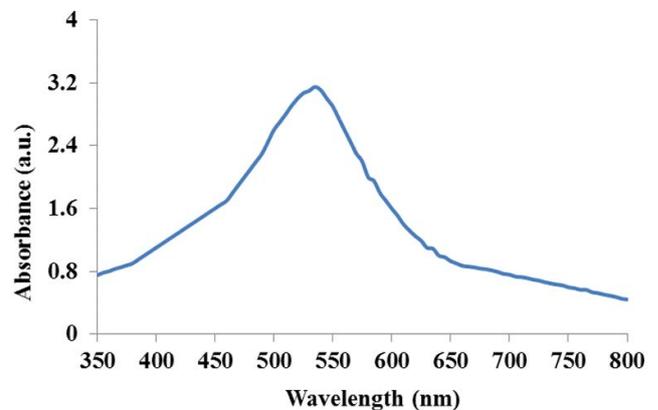
Fig. 1. Absorption spectrum of Cu NPs.
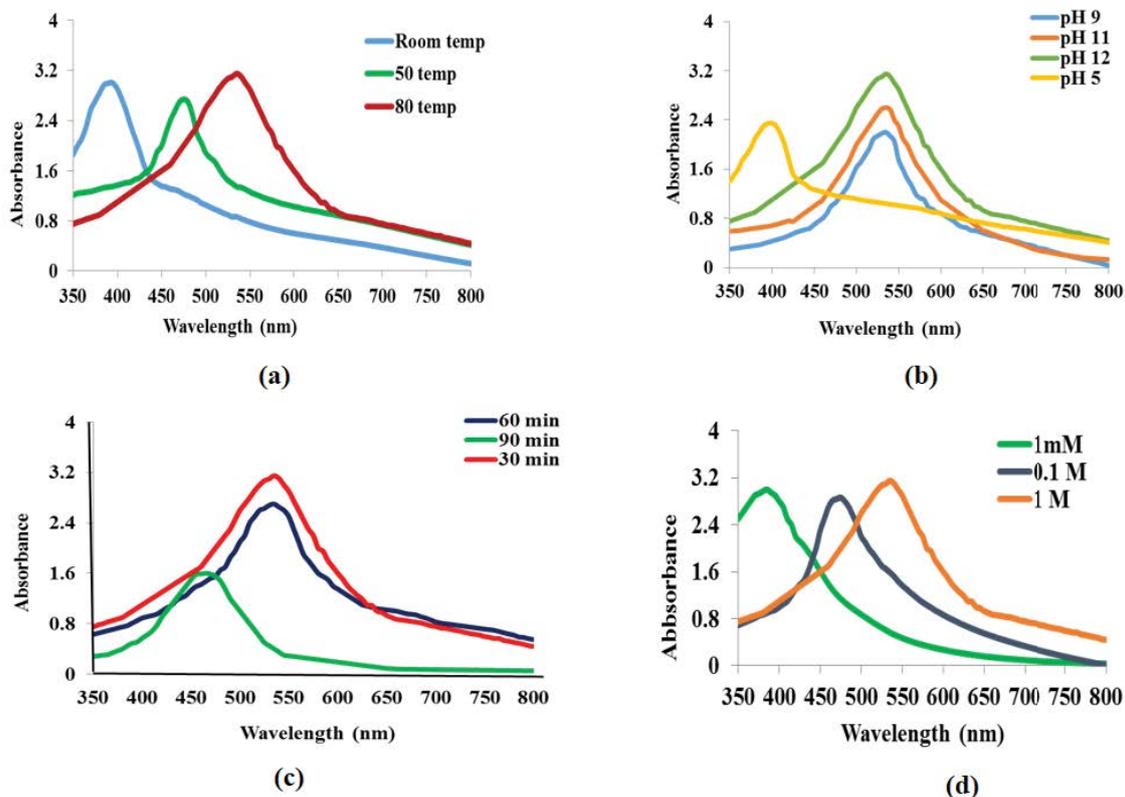
Fig. 2. Absorption spectra of Cu NPs at different (a) temperatures, (b) pH, (c) incubation time and (d) precursor salt concentration.

NPs. The acidic pH phytochemicals in the plant extract are protonated and do not favor the complexation with metal ions. Hence, at lower pH the extract is not considered a good stabilizing and reducing agent [41,42]. At basic pH the phyto-active compounds present in *Syzygium cumini* extract become deprotonated and facilitate the chelation of metal salt [42]. Steady increase in the absorbance was observed from pH 9 to 12 without any shift in maximum absorption (λ_{max} 535 nm). Suresh et al. [43] reported synthesis of Cu NPs by employing hydrazine as reducing agent, L. ascorbic acid as antioxidant agent and found optimum yield at pH 12. Samari et al. [40] found similar results for biogenic synthesis of Cu NPs and reported pH 11 as optimum pH for the synthesis of Cu NPs.

Incubation time is also an important parameter affecting the morphology of NPs. The reaction was observed at different incubation times, that is, 30, 60 and 90 min by maintaining other factors at fixed composition (Fig. 2c). Maximum absorption peak was observed at incubation time of 30 min. Hence, the complete reduction of copper ions and formation of stable Cu NPs was achieved within 30 min of reaction. Ghany et al. [44] reported the synthesis of Cu NPs using corn cob wastes and reported optimum yield at 30 min.

To evaluate the effect of concentration of precursor salt the synthesis of Cu NPs was conducted at 80°C temperature, pH 12 and incubation time of 30 min in the presence of 0.001, 0.1 and 1 M precursor salt concentration as shown in Fig. 2d. A high concentration of precursor salt leads to more collision of very small nanoparticles leading to particle growth. Moreover, the reaction rate is slow at a lower concentration. Hence, a 1 M concentration of precursor salt is most appropriate for the synthesis of stable and monodispersed nanoparticles.

3.2. FTIR analysis

FTIR spectroscopy is used to investigate the functional groups moieties of synthesized nanomaterials. Fig. 3 shows the FTIR spectra of biogenically synthesized Cu NPs. Various characteristic bands of Cu NPs were observed at 3,307; 2,916.5; 2,849.5; 1,582.90; 1,340.05; 1,104.2; 875.0 and 718.4 cm^{-1}, respectively. The broad peak observed at 3,307 cm^{-1} corresponds to the O–H functional group of alcohols or phenols [45]. However, the sharp peaks at 2,916.5 and 2,849.5 cm^{-1} corresponds to OCH$_3$ stretching and –CH stretching which indicates the presence of aromatic C–H bond. The band at 1,582.90 cm^{-1} can be assigned to C=C bending vibrations and the band at 1,582 cm^{-1} can also be linked to the aromatic ring. The intense peak at 1,340.05 cm^{-1} shows the –CH$_3$ bending of alkane functional group. However, a sharp band at 1,104.2 cm^{-1} corresponds to the C–O stretching vibrations [46]. Results indicated that alcohols, phenols, aromatics and alkanes are the most probable biomolecules involved in the synthesis and capping of Cu NPs.

3.3. SEM analysis

The morphological studies of Cu NPs were investigated using SEM analysis which shows that Cu NPs were spherical in shape and well segregated without any agglomeration as shown in Fig. 4. Homogenous and spherical nanoparticles with average particle size of 19 nm were observed in SEM analysis. The obtained results are comparable to the biogenically synthesized Cu NPs in the presence of *Eclipta prostrata* leaves extract [47].

3.4. Catalytic reduction of MB

MB, a highly carcinogenic contaminant, has been widely utilized in various industrial applications such as coloring paper, dyeing fabrics and as a hair coloring agent [48]. MB causes serious threats to human health, for example, diarrhea, gastritis infections, eye problems, vomiting and asthma. Hence, it is necessary to eradicate such pollutants from aqueous environment. In this work, biogenically synthesized Cu NPs have been employed for the catalytic reduction of MB dye in the presence of NaBH$_4$.
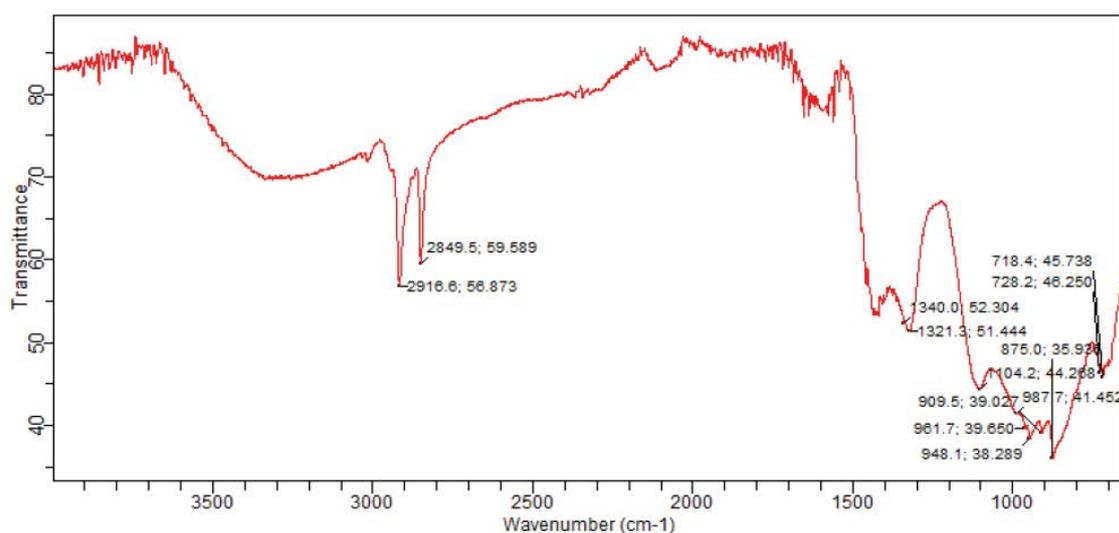
Fig. 3. FTIR spectra of Cu NPs.

The degradation was observed by measuring the absorbance at λ_{max} = 665 nm. A gradual decrease in absorbance was observed. As the absorbance is directly related to the concentration of the sample, the percentage degradation was calculated by the following formula.

$$\%\text{Degradation} = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

where C_o and C_t are the initial concentration of sample and concentration at time t, respectively. The plot of percentage degradation vs. time indicates that within the 60 min of reaction, complete degradation of MB dye was observed (Fig. 5a). The rate of degradation of MB is only the function of C_o of dye and thus the pseudo-first-order kinetics is followed (Fig. 5b). The rate constant can be calculated from the plot of $\ln(C_o/C_t)$ vs. time.

$$\ln\left(\frac{C_0}{C_t}\right) = k_{app}t \qquad (2)$$

The slope of the plot will give the value of apparent rate constant (k). The apparent rate constant was found to be 0.0461 min^{-1} and the R^2 value was close to 1 (0.997), respectively. Fig. 6 shows the action spectra that confirms the successful and complete degradation of MB dye in 60 min.

In order to evaluate the catalytic efficiency for industrial or large scale applications catalyst are recycled. Herein, the catalyst showed slight decrease in the degradation of MB dye even after four cycles as shown in Fig. 7. Hence, Cu NPs were found to be an excellent and cost-effective catalyst for wastewater treatment.
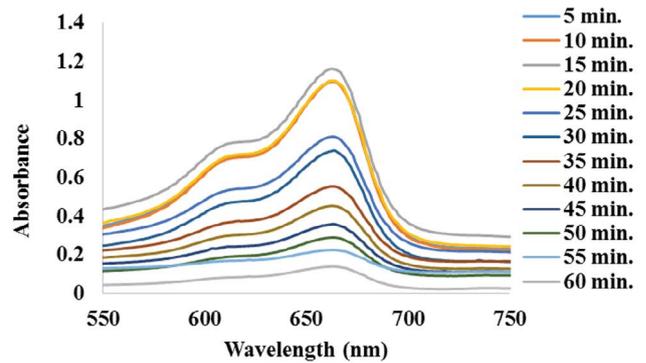
Fig. 6. Action spectra for degradation of MB dye in the presence of Cu NPs.
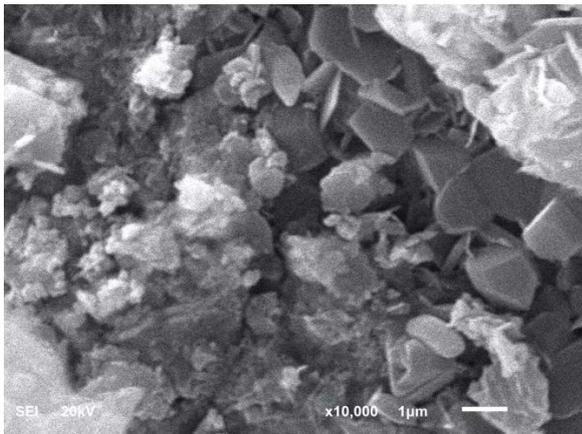
Fig. 4. SEM analysis of Cu NPs.
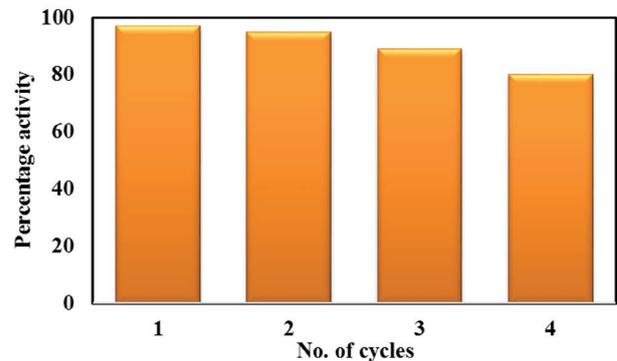
Fig. 7. Recyclability of biogenically synthesized Cu NPs for degradation of MB dye up to 4 cycles.
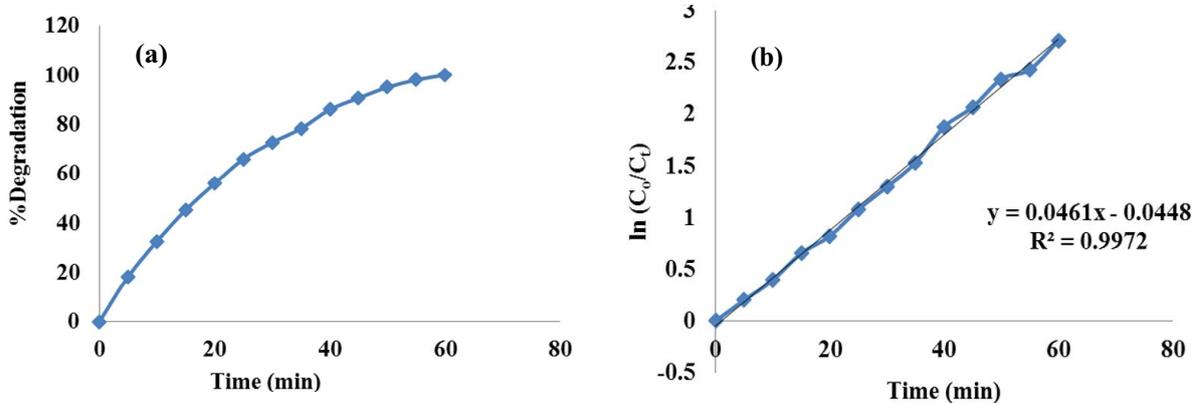
Fig. 5. Graph of % degradation of MB vs. time (b) graph of $\ln(C_o/C_t)$ vs. time.

4. Conclusion

Copper nanoparticles were biogenically synthesized in the presence of leaf extract of *Syzygium cumini* which acts as an excellent stabilizing and reducing agent. This green synthetic route is simple, cost-effective, efficient, facile and eco-friendly for the successful synthesis of NPs that prevent agglomeration of nanomaterials. The influence of various factors on the formation of NPs was determined and the optimum conditions were studied for scale up synthesis. The optimized yield was obtained at 80°C, 12 pH, 60 min and 1 M salt concentration. UV-visible spectroscopy confirmed the successful synthesis of Cu NPs by showing single peak at 535 nm. FTIR confirmed the bio-fabrication of various metabolites on the Cu NPs. SEM analysis showed the homogenous and spherical shaped Cu NPs with average size of 19 nm. The synthesized nanoparticles showed excellent catalytic activity for the removal of MB from aqueous solution. The results showed that catalytic reduction of MB followed pseudo-first-order kinetics with a maximum degradation efficiency of 100% within 60 min. Cu NPs showed excellent performance in terms of catalytic reduction of MB dye. However, the use of Cu NPs as electrodes and in electronic applications could be studied in the future. It is anticipated that these eco-friendly materials could enhance the conductivity of different electrodes.

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