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REVIEW ARTICLE

GREEN SYNTHESIS OF COPPER NANOPARTICLES USING ALOE VERA AND ITS CHARACTERIZATION

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ABSTRACT

This study presents the green synthesis of copper nanoparticles using leaf extract of Aloe vera (Aloe Barbadensis Miller) as reducing and sabilizing agents. The main objective of this work is to develop economically and environmentally friendly method for the synthesis of copper nanoparticles. The precursor used was the aquesous solution of CuSO4.5H2O. The sample prepared were characterized by UV-visible spectroscopy, Energy dispersive spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FTIR).UV-vis spectroscopy revealed formation of copper nanoparticles showing maximum absorption peak at 596 nm. The EDX analysis indicated the presence of 38.747% of elemental copper and FTIR showed presence of phenolic and carbonyl group.

INTRODUCTION

In the context of developing advanced materials, nanotechnology play crucial role providing cost effective and convenient route. Large number of literatures related to nanomaterial published each year has just proved that it is topic of choice for the researchers worldwide. No doubt, the scope of nanotechnology is broad as it encompasses wide range of fields such as physics, chemistry, biology, computer science, engineering, medicine, biotechnology, environment, textile, automobile *etc* (Ramsden, 2009; Porter and Youtie, 2009; Saxton, 2007; Bhattacharyya *et al.,* 2009). In simple words, synthesis, design, characterization and application of materials controlling shape and size of nanoscale refers the nanotechnology. It is found to be important from the academic as well as from industrial point of view (Porter and Youtie, 2009; Sozer and Kokini, 2009; Duncan, 2011 and Wong *et al.,* 2006). Nanomaterials are of various kinds depending upon the type of nanoparticles included such as organic, inorganic or metallic nanoparticles (Hussain *et al.,* 2006). Among various types of nanoparticles, metal and metal oxide nanoparticles are found to be of great significance because of their characteristic optical, electronic, magnetic, catalytic, chemical and medical properties. Consequently, they have been extensively used for developing highly efficient nanodevices employed in various fields such as electronics, pharmaceutical, textile, solar cell, cosmetics, water treatment, food packaging, health care, gas sensor, energy science, drug and gene delivery *etc.* (Swathy, 2014; Blackman, 2009; Mody *et al.,* 2010; Conde *et al.,* 2012; Hashemipour *et al.,* 2011). Among various metallic nanoparticles, copper and its oxide nanoparticles are reported to be of great significance for its high conducting, anti-bactericidal, catalytic properties. It has been applied since the ancient times…from the literatures, its anti-bactericidal properties have been found higher compared to that of highly expensive noble metals gold and silver hence, it provides good substitutes over Au and Ag in various chemical and metallurgical processes. Besides above mentioned applications, copper nanoparticles are being highly toxic to microorganism but non-toxic to animal cells, due to this phenomena it has been extremely used as an effective bactericidal agent compared to other metal nanoparticles (Karthik and Kannappan, 2015; Umer *et al.,* 2014). In recent years, copper nanoparticles (CuNPs) have been synthesized *via* clean and green method avoiding various physical and chemical methods. Main reason behind the necessity of using green method is the toxic chemicals and byproducts produced in the conventional methods which drastically degrade the environment. Obviously, the green synthesis is reliable, biocompatible, cost-effective, environmentally friendly, and sustainable procedures for synthesis of metallic nanoparticles (Honary *et al.,* 2012; Devasenan *et al.,* 2016 and Saranyaadevi *et al.,* 2014). In the green method, biological resources available in nature like parts of plants, algae, fungi, yeast, bacteria *etc*. have been used for synthesis. Green synthesis of nanoparticles is also considered to be a bottom up technique, where the oxidation or reduction is the main reaction that occurs during the production

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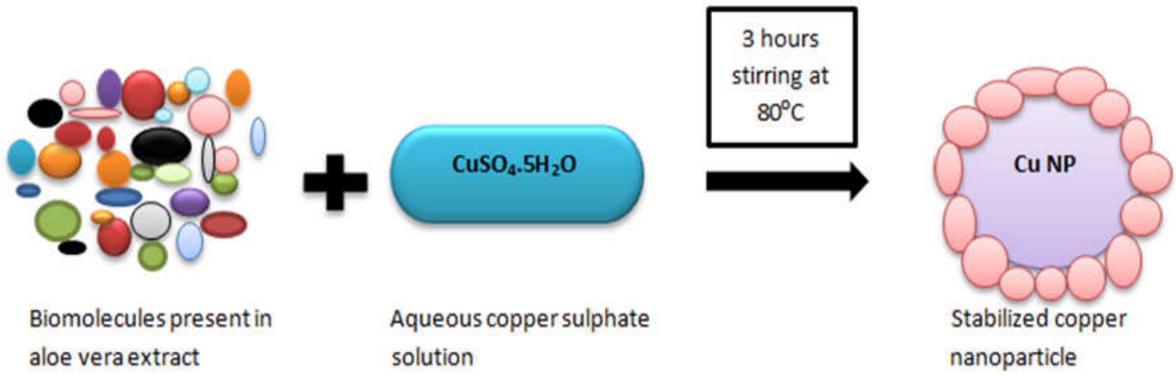

Figure 1. Schematic diagram of bioreduction of aqueous copper sulphate solution by biomolecules present in aloe vera extract to from stabilized copper nanoparticles

of nanoparticles (Caroling *et al.,* 2015). In this method the biomolecules present in plant parts or microorganisms itself act as reluctant and capping agents for synthesizing metal nanoparticles (Umer *et al.,* 2014; Honary *et al.,* 2012, Makarov *et al.,* 2014; Bashir *et al.,* 2011and Arya, 2010). Aloe vera *(Aloe barbadensis* Miller) is a plant (Bashir *et al.,* 2011; Arya, 2010; Sahu *et al.,* 2013) belonging to the family of *Liliaceae* which is mostly succulent with a whorl of elongated, pointed leaves (Bashir *et al.,* 2011; Lopez *et al.,* 2013). The word Aloe vera appears to be derived from Arabic word "Alloeh", which means shining bitter substance while "vera" in Latin means true (Sahu *et al.,* 2013; Lopez *et al.,* 2013). The plant leaves contains numerous amino acids, anthraquinones, vitamins, minerals, enzymes, saponins, sterol, natural sugars and other bioactive compounds (Sahu *et al.,* 2013; Lopez *et al.,* 2013; Saeed *et al.,* 2004) and the main active constituent of the aloe vera plant extract is aloineand anthraquinone. This plant has anti-microbial, anti-inflammatory, anti-oxidant, aphrodisiac, anti-helmenthic, antifungal and antiseptic values (Lopez *et al.,* 2013 and Saeed *et al.,* 2004). From the Literatures review, only a very little work has been done for the synthesis of copper nanoparticles using plant leaf constituents. Hence, the present research is mainly focused on green synthesis of copper nanoparticles using easily available aloe vera leaf extract and its characterization.

Experimental Methods

Chemicals: A.R grade copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) as chemical precursor, MW = 249.68 gm/mol, Sodium hydroxide, Hydrochloric acid (12N) was used in the synthesis.

Preparation of plant leaves extrac

Firstly, 60 gm of fresh aloe vera leaves were washed with running tap water and then by distilled water. The leaves were crushed with mortar and pestle. After that mashed fresh leaves was mixed with 200 mL of distilled water in a 250 mL of Round bottom flask and kept in water bath at 80°C for 45 min. Then it was filtered off using normal filter paper and then again filtered using Whatmann No.1 filter paper. The resulting leaf extract was stored at refrigerator for further use.

Green synthesis of copper nanoparticles

Here, the Cu NPs were prepared using protocol of (Egziabher and Michael, 2012) with slight modification.

In a typical synthesis of copper nanoparticles, 30 mL of fresh leaf extract was added to 270 mL of 0.01 M $CuSO_4.5H_2O$ aqueous solution and the mixture was kept at 80°C with constant stirring on a magnetic stirrer for about 3 hr. The suspension produced was centrifuged at 3000 rpm for 30 min and the supernatant liquid was decanted off and residue was washed with 10 mL of distilled water. Centrifugation-decantation-washing processes were repeatedly done three times to remove impurities. The obtained precipitate was dried in an oven at 70°C for 30 min. The as synthesized copper nanoparticles were then subjected for further characterization. The scheme of bio-reduction of copper sulphate solution is shown in Figure 1.

Characterization Techniques

Preliminary Test: In preliminary test, the bio reduction of the copper sulphate using aqueous aloe vera extract was monitored by observing the color change after mixing the copper sulphate solution and aloe vera extract in every 1 hr interval and the appearance of brown color indicates the formation of copper nanoparticles. Photograph of the copper nanoparticles are shown in Figure 2.

UV-Visible Spectroscopic Studies: The green synthesis of copper nanoparticles was monitored by using UV-Visible single beam spectrophotometer (UV-2510 TS) in the range 300-700 nm at resolution of 1nm. The measurements were recorded in every 1 hour interval by taking a small aliquot of the sample in cuvette and it was also diluted according to its requirement. All the absorption peaks were corrected against the background spectrum of water as reference.

Energy Dispersive X-ray (EDX) Spectroscopic Studies*:* The EDX observation was carried out by using instrument EDX-8000. For EDX analysis, the residue obtained after repeated washing was mixed with 3 mL distilled water and that liquid sample was used to observe the pattern of as synthesized copper nanoparticles.

Fourier Transform Infrared (FTIR) Spectroscopic Studies: Fourier Transform Infrared Spectra were recorded in using FTIR spectroscopy (Affinity-1s) in Attenuated Total Reflectance (ATR) mode in the wavelength range of 4000 to 750 cm^{-1} at the resolution of 8 cm^{-1}.

RESULTS AND DISCUSSION

Results of green synthesis of copper nanoparticles by reduction of aqueous copper ions using leaf extract of aloe vera (*Aloe barbadensis* Miller) and the progress of formation of copper nanoparticles was monitored by color inspection and UV-Vis spectroscopy.

copper nanoparticle (Figure 3). It is being only preliminary result; it is further confirmed by UV-Vis spectroscopic studies.

UV-Visible Absorption Spectroscopic Studies: The results of UV-Visible spectra of aqueous $CuSO_4.5H_2O$ mediated with aloe vera leaf extract as a function of reaction time is shown in Table 4. From Table 1 it is clear that bio-reduction of Cu^{2+}

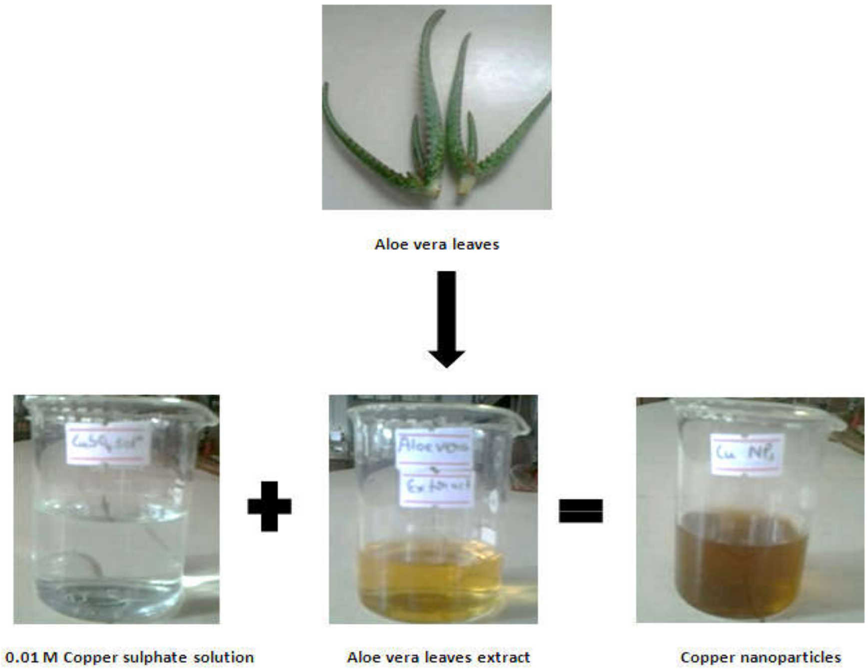

Figure 2. Photographs of copper sulpate solution, aloe vera leaves extract and solution developing Cu NPs in order

Figure 3. Reaction mixture showing variation of color with increase in reaction time

Preliminary Test: When copper nanoparticles were synthesized using materials from leaf extract of aloe vera (*Aloe barbadensis* Miller) as reducing and stabilizing agent, the blue color aqueous copper sulphate pentahydrate solution was turned to brown color indicating the formation of Cu NPs (27) which is shown in Figure 2. When copper sulphate was added to the yellowish aloe vera extract the color of mixture was immediately appeared to be light green color which indicates that the plant extract began to reduce the copper sulphate solution. Thus, it is clear that aloe vera extract act as reducing agent. Then color of reaction solution gradually started to change with increase in time of stirring and finally brown color solution was obtained. Therefore, aloe vera extract completely reduced the 0.01 M copper sulphate within 3 hour to form a ions to Cu nanoparticles using leaf extract was in dicated by the change of color from light green to brown. It may be due to the excitation of Surface Plasmon Resonance (SPR) effect and reduction of copper ions. The absorption peak of copper sulphate immediately after adding plant extract was found to be 343 nm. Then the characteristic absorption peak gradually shifted with time which and absorption peaks at 386 nm and 450 nm were observed within the time interval of 2 hr. The maximum absorption peak of copper nanoparticles appeared at 596 nm (Figure 4) after 3 hr which indicating the formation of copper nanoparticles which is nearly equal to the maximum absorption peak at 580 nm as reported in the literature (Joseph *al.,* 2016). The synthesis of stabilized copper nanoparticles is further confirmed by EDX analysis.

Table 1. Maximum absorption peak of reaction mixture at different time and color

Color	Time	λmax(nm)
Light green	Immediately after mixing	343
Slightly dark green	1 hr	386
Dark green	2 hr	450
Brown	3hr	596

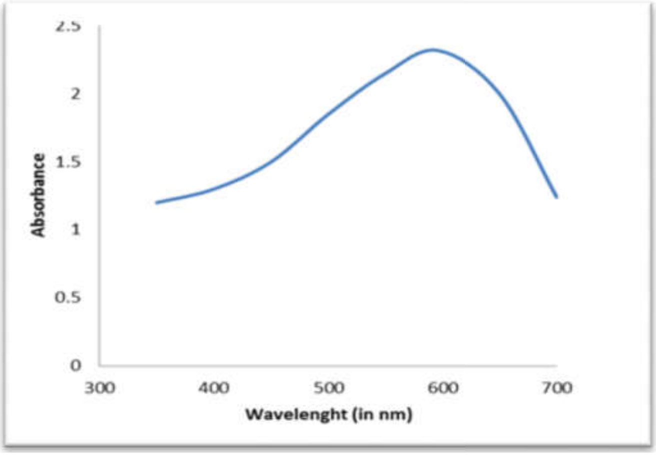

Figure 4. UV-Visible spectra of green synthesized copper nanoparticles after 3 hr

Energy Dispersive X-ray (EDX) Spectroscopic Study: Energy Dispersive X-ray spectrum of as synthesized copper nanoparticles are shown in Figure 5. From the figure, the optical absorption peak was observed at 8 keV, typical for the absorption of metallic copper nanoparticles (19). Strong signals from the copper atoms were observed, while other signals for Si, S, P, K, Fe, Bi, Ca and Ti atoms were also recorded which is shown in the spectrum.

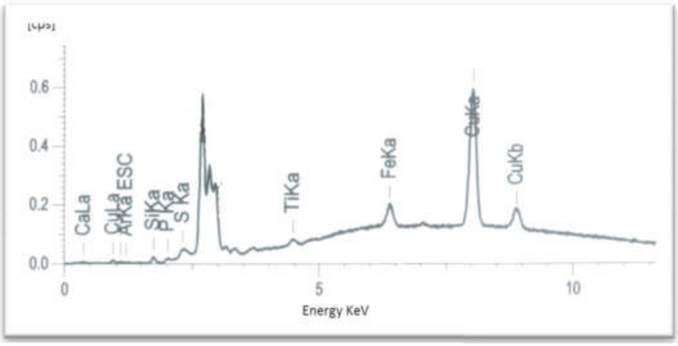

Figure 5. EDX of green synthesized copper nanoparticles

From the EDX signals, it is clear that copper nanoparticles synthesized from aloe vera extract have shown the highest weight percentage of elemental copper, along with different metal. The amount in weight percentage of different elements present in the sample are presented in Table 2 in descending order. From Table 2, it is clear that the weight percentage of elemental copper is 38.747% so formation of copper nanoparticles was found to be confirmed by EDX since the weight percentage of copper is equivalent with the purity of copper nanoparticles formed (Caroling *et al.,* 2015). It can be concluded that the as synthesized Cu NPs were found to be about 38% pure and other were present as impurities.

Fourier Transform Infrared Spectroscopic Study: The FTIR spectra of synthesized Cu NPs through green synthesis is shown in Figure 6. The synthesized Cu NPs displays a number of absorption peaks at 1510 cm^{-1}, 1645 cm^{-1}, 1750 $cm^{-1}$and 3325 cm^{-1}.

Table 2. Elements present in colloidal solution and their weight percentage

Elements	Weight (in %)
Cu	38.747
Si	26.163
S	11.270
P	8.094
K	4.646
Fe	3.506
Bi	3.221
Ca	2.740
Ti	1.613

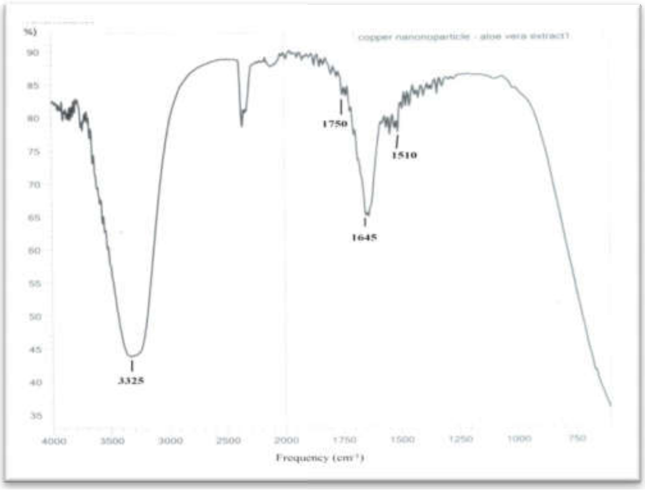

Figure 6. FTIR spectra of green synthesized copper nanoparticles

The peak at 1510 cm^{-1} and 1645 cm^{-1} are characteristic of alkenyl C=C stretch and amide C=O stretch respectively. The peak at 1750 cm^{-1} is due to presence of carbonyl functional group C=O. The absorption peaks at 3325 cm^{-1} corresponding to phenolic group OH. The FTIR analysis of CuNPs suggested that they are surrounded by carbonyl groups and phenolic group which are abundantly present in biomolecules of aloe vera that help in the stabilization of the nanoparticles. The chemical constituents present in aloe leaf extract such as tannin, saponin, flavonoids, steroids, terpenoids, and aloineare responsible for the reduction of copper ions to copper nanoparticles due to their capping and reducing capacity (Sahu *et al.,* 2013) which suggests that the biomolecules could possibly perform dual functions of formation and stabilization of copper nanoparticles in the aqueous medium.

Conclusion

The present study illustrates simple, convenient and eco-friendly method for the synthesis of copper nanoparticles by using leaf extract of aloe vera (*Aloe barbadensis* Miller). The reductions of the metal ions through the leaf extract leading to the formation of copper nanoparticles. Characterizations of the synthesized copper nanoparticles have been successfully done using UV-Vis, EDX and FTIR techniques. UV- V is spectroscopy study confirmed the formation of Cu NPs. Energy dispersive X-ray (EDX) analysis confirmed the presence of elemental copper and its weight percentage. FTIR results show that reduction and stabilization of copper nanoparticles are carried by biomolecules metabolites present in the leaf extract such as alkaloids, protein, and tannins *etc*. which contain phenolic, carbonyl groups. Therefore, this greener approach toward the synthesis of copper nanoparticles, using plant leaf material as reducing and capping agent, has many advantages such as ease with which the process can be scaled up, economic viability, environmentally benign and renewable, where no need to use high pressure, energy, temperature and toxic chemicals.

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