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Research Article

Fusarium Antifungal Activities of Copper Nanoparticles Synthesized by a Chemical Reduction Method

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We report on the process of synthesizing copper nanoparticles (Cu Nps) for a short reactive time by chemical reduction method with a support of CTAB reductive agent. Their properties were determined by ultraviolet-visible (UV-Vis) absorption spectrum, the X-ray (XRD) analysis, Fourier transform infrared spectroscopy (FT-IR), and Transmission Electron Microscopy (TEM) images. The antifungal activity of Cu Nps was evaluated by testing against *Fusarium* sp. The Cu Nps were obtained with the average size in the range of 20–50 nm having spherical shape. The survey shows that when Cu Nps were used at 450 ppm concentration in 9-day incubation, 93.98% of fungal growth was inhibited.

1. Introduction

Transition metals and their oxides are widely used in materials because of their specific electrical, structural, catalytic, optical, and magnetic properties [1–3]. Among transition metal materials, copper is the most important material. The unique catalytic and optical properties show that copper nanoparticles (Cu Nps) are potential candidates for the reaction of H_2O dissociation [4], used in ultrafast catalytic activity for the degradation of some organic dyes such as methylene blue (MB) and rose bengal (RB) [5], and applied in a wide variety of conductive inks for printing in electronics [6–8] as well as antifungal/antibacterial applications [9–15]. In particular, the fungus inhibition efficiency of Cu Nps is better than other metal nanoparticles, such as Al, Fe, Mn, Ni, Zn, and products of bigger size Cu particles [16].

Fusarium species (sp.) is the largest expansion in "Tuberculariaceae" family and it exists in host plants and is the major cause which wilts host plants [17]. Because the colonies spread across the tissue and fill xylem vessels, water transport process is hindered, making the plants wilt [16, 18, 19]. Furthermore, *Fusarium* sp. also produces a number of toxic substances in the host vascular tree which can also cause wilting [20]. *Fusarium* sp. is a common fungal disease on many crops and it is one of the most devastating diseases spotted on tomato, potato, dragon fruit, watermelon plants and other cucurbits, and so forth [18, 21, 22].

Currently, the antagonistic organisms, such as *Bacillus coagulans* [23] or a wide variety of chemicals to eliminate harmful microorganisms are often used. In particular, the use of generic drugs with a large amount of copper leads to copper residues in produce as well as higher soil and water pollution. Plant microelements as Cu Nps are known to play critical roles in plant disease resistance through enzyme activation for defense barrier production [16]. Furthermore, the use of Cu Nps helps to reduce the amount of chemicals in the prevention against *Fusarium* sp. fungal diseases. According to Durán et al. [24] and Prabhu et al. [25], like silver nanoparticles, Cu Nps also demonstrated the size-dependent antibacterial activity. Therefore, to achieve the maximum antibacterial activity, it is necessary to develop various methods for the synthesis of monodisperse copper nanoparticles with small size; that is, the ratio of surface area to volume is large [26, 27].

There are many methods for synthesis of Cu Nps such as hydrothermal [28], photoreduction [29–31], thermal decomposition [11], and polyol and microwave-assisted polyol method [9, 32, 33]. However, the production of Cu Nps is much more challenging in comparison to noble metals because Cu Nps are placed in the open air leading to the aggregation immediately due to surface oxidation. To avoid this problem, an inert environment, such as argon or nitrogen, inorganic solvents, protective polymers, or surfactants, was used [34]. In the chemical reduction techniques, a copper salt is reduced by a reducing agent such as sodium borohydride ($NaBH_4$), hydrazine (N_2H_4), ascorbate, polyol, isopropyl alcohol with cetyltrimethylammonium bromide (CTAB), and glucose [34]. Besides, a literature review of Xiong et al. has reported that a simple, environmentally friendly, and cost-effective method for preparing highly stable dispersions of Cu Nps was used from green chemicals, such as Vitamin C (ascorbic acid, AsA) [35]. However, the ascorbic acid is a weak reducing agent; the reaction rate in the water solvent is slow; therefore, it takes more time to form Cu Nps (approximately 14 hours) [36–38]. In addition, the higher reaction temperature or longer reaction time favors the growth rate of pure metallic Cu [39, 40]. Therefore, reductive chemicals such as ascorbic acid and CTAB were combined in aqueous solution at 80°C to improve reaction rate in this study. Moreover, we study the surface plasmon resonance effect of Cu Nps via UV-Vis spectrum and investigation of the *Fusarium* sp. antifungal properties at various Cu Nps concentrations. The purpose of this investigation shows that Cu Nps are a significant potential as bactericidal agents.

2. Experimental

2.1. Materials. Cu Nps solutions were prepared by chemical reduction method from chemicals and materials including copper (II) chloride dehydrate ($CuCl_2{\cdot}2H_2O$, Merck, Germany, 99.99%), cetyltrimethylammonium bromide [$(C_{16}H_{33})N(CH_3)_3Br$, CTAB, India, 99.99%], deionized (DI) water from Thermo Scientific Equipment, ascorbic acid ($C_6H_8O_6$, India, 99.99%), D-glucose ($C_6H_{12}O_6$, Sigma-Aldrich, 99.5%), chloramphenicol ($C_{11}H_{12}Cl_2N_2O_5$), double-distilled water (Vietnam), and the TCBS agar (Difco, USA). The potatoes and dragons were made in Vietnam.

2.2. Synthesis of Cu Nps by a Chemical Reduction Method. In a typical synthesis, 0.1712 gram $CuCl_2{\cdot}2H_2O$ was stirred with 50 mL DI water in 15 minutes to form $CuCl_2$ solution having blue color. Next, 10 mL ascorbic acid (0.1 M) was slowly dropped into the above solution and the mixture solution achieved a pH of around 5. To survey the effect of CTAB, 10 mL CTAB (0.025 M) solution was slowly dropped into the mixture of $CuCl_2$ solution and ascorbic acid. These mixtures were kept at 80°C until a red-brown solution was obtained. During the course of the reaction, the solution turned into red-brown color indicating the formation of Cu NPs.

2.3. Characterization of Cu Nps. To examine the existence of Cu Nps in the synthesized solution, we determined the surface plasmon resonance properties throughout the absorption spectra in the UV-Vis band taken by using UV-visible spectrophotometer (U2910, Hitachi, Japan). The Fourier transform infrared spectroscopy (FT-IR) spectrum was recorded on a FT-IR spectrometer (Vertex 80, Bruker, Germany) with the range of 400 to 4000 cm^{-1} in transmission mode at room temperature to identify the functional group present on the samples and responsible for the stability of nanoparticles. Morphologies include the sizes and shapes of the samples which were recorded by Transmission Electronic Microscope (TEM) on a JEM 1400 instrument. The X-ray diffraction (XRD) analysis was carried out (Bruker D8 Advance 5005) at a voltage of 45 kV with Cu Kα radiation (λ = 1.5406 Å) to examine the crystalline phase of synthesized nanoparticles.

2.4. The Test of the Fusarium sp. Antifungal Activity of Cu Nps. Firstly, *Fusarium* sp. fungal samples were taken from tomato and dragon fruit plants. After that, *Fusarium* sp. fungal samples were isolated in agar water media. This media was chosen for the fungal isolation media including 1000 mL distilled water, 20 g/L agar, and 0.25 g/L chloramphenicol. Secondly, the fungal samples were isolated and incubated in potato D-glucose agar (PDA) media including 1000 mL of distilled water, 20 g/L agar, 200 g potatoes, 20 g D-glucose, and 0.25 g/L chloramphenicol. Thirdly, we recorded the temperature, date, and time of incubated samples at survey times and observed the growth of fungus. Finally, we measured diameter of fungal colonies and estimated the inhibition efficiency of Cu Nps at various concentrations. The inhibition percentage of fungal plant pathogens was calculated by using formula as suggested by Vincent [41]:

$$\text{Inhibition Efficency } (I, \%) = \frac{C - T}{C} \times 100. \quad (1)$$

Hence, I is inhibition percentage; C is growth of fungal plant pathogens in control (mm), and T is growth of fungal plant pathogens in dual culture plate (mm).

3. Results and Discussion

3.1. Preparation of Cu Nps. Figure 1(a) shows the absorption spectra of the prepared samples and these samples after being stirred for 15 minutes. The absorption spectrum of the prepared samples shows two peaks at 420 nm and 560 nm wavelengths. Nevertheless, the absorption spectrum of the samples which were stirred for 15 minutes shows only a peak at 560 nm wavelength and its intensity has significantly increased. The peak at 560 nm relates to existence of the Cu Nps [31] and peaks from 400 nm to 420 nm of wavelength relate to the copper oxide nanoparticles [32]. According to [42–45], the peak at 550–600 nm of the wavelength can be assigned to the absorption of Cu Nps. This result indicated the rapid formation of the Cu Nps for 15-minute reaction. However, if the synthesized sample with a reductive chemical as ascorbic acid is used, Cu Nps will be not formed for 2-hour reaction but for 14-hour reaction. The statement mentioned above was demonstrated by the absorption spectrum of the synthesized sample at only ascorbic acid condition for 2-hour

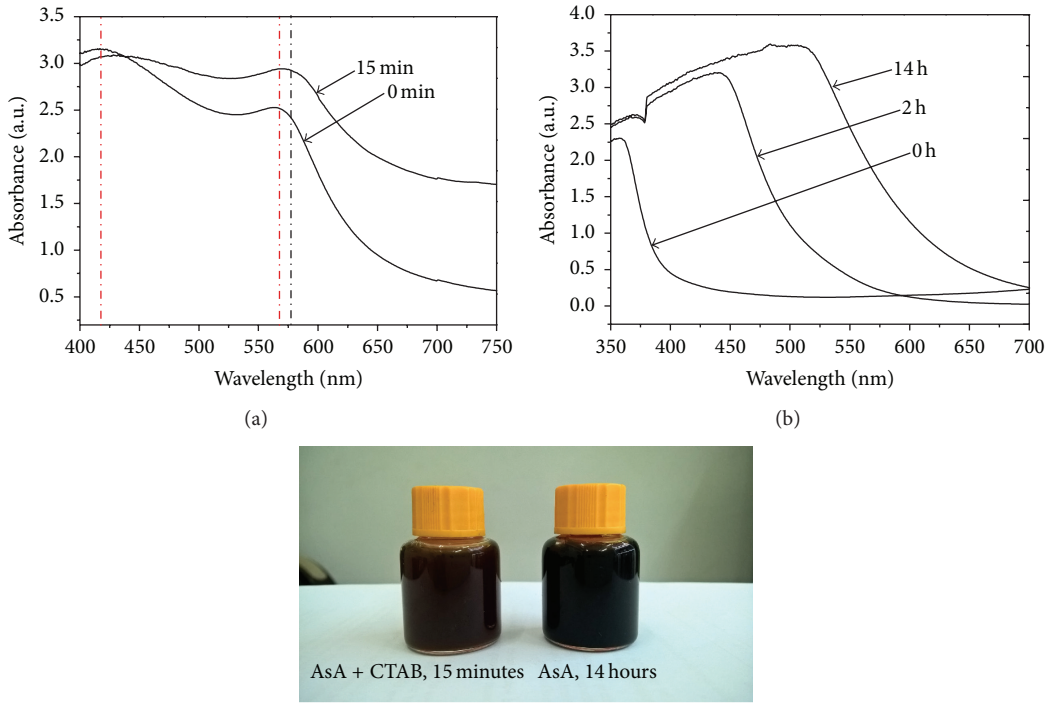


Figure 1: Absorption spectra of the samples (a) supported CTAB and (b) nonsupported CTAB at different reaction periods and (c) the color of the synthesized samples.

and 14-hour reactions (Figure 1(b)). This result agrees with Xiong et al.' research [35].

Figure 1(c) shows the color of the synthesized sample with ascorbic acid and CTAB reduction chemicals for a 15-minute period and the other one synthesized only with ascorbic acid for 14-hour period of time. This result exhibited that the synthesized sample with only ascorbic acid was brown while the synthesized sample with the support of CTAB was red-brown.

Furthermore, the Cu Nps solution synthesized by the support of CTAB was evaporated at 150°C for 2 hours at atmosphere. After that, the Cu Nps powder was characterized by XRD pattern. Figure 2 exhibits the XRD pattern of Cu Nps powder. The peaks observed at 2θ values of 43.39°, 50.49°, and 74.18° correspond to (111), (200), and (220) planes of metallic Cu [11, 30, 46]. Apart from the metallic Cu peaks, several other diffraction peaks appeared at 36.54° and 61.6° representing the formation of cubic copper (I) oxide nanocrystals [37, 47, 48]. The result was explained that Cu Nps might be formed by oxidation when the solution was evaporated at 150°C for 2 hours at atmosphere.

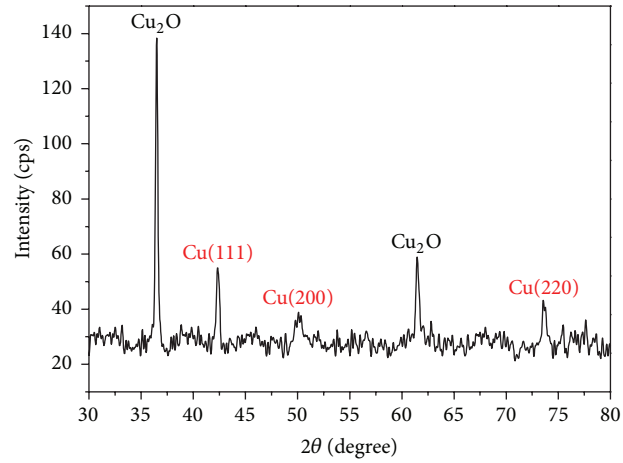


Figure 2: XRD pattern of the Cu Nps powder.

3.1.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis. Figure 3 represents the appearance of some different peaks, such as peaks at 3400 cm^{-1}, 1630–1761 cm^{-1}, 1142–1345 cm^{-1}, and 724–928 cm^{-1} bands of the wavenumber. According to Xiong et al. [35], the peaks were observed at 3481 cm^{-1}, 1718 cm^{-1}, and 1681 cm^{-1} corresponding to the -OH stretch of the H_2O molecules, oxidized ester carbonyl groups, and conjugated carbonyl groups, respectively. Besides, according to Viana et al., peaks at broadband of the 900–1000 cm^{-1} were presented for N-CH_3 stretching vibration [49]. The appearance of these peaks was caused by the residual CTAB after reactions creating Cu Nps completely.

3.1.2. Transmission Electron Microscopy (TEM) Analysis. The sizes and shapes of Cu Nps were characterized by TEM images. Figure 4 shows that the shapes of Cu NPs are spherical with uniform sizes. The particles size of Cu Nps is in the range from 20 nm to 50 nm. Besides, the shapes of Cu Nps are mainly spherical, which relates to copper phase [50].

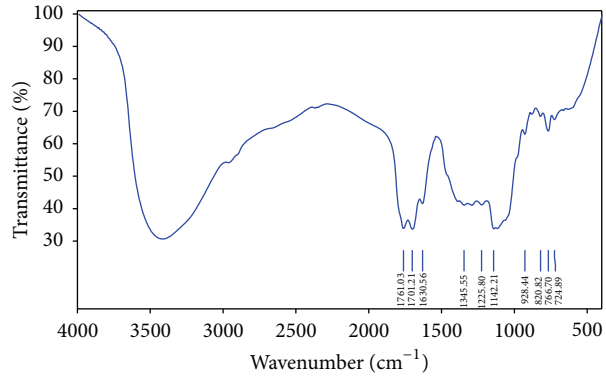
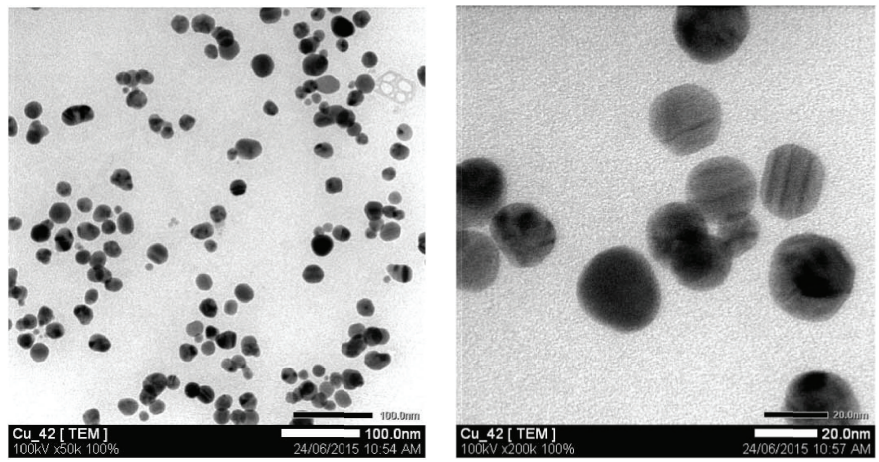


Figure 3: FTIR spectrum of the Cu Nps solution.



(a) (b)

Figure 4: TEM images of Cu Nps solution for different scales: (a) 100 nm and (b) 20 nm.

3.2. The Fusarium sp. Antifungal Properties of Cu Nps Solutions. We survey the effect of Cu Nps solutions on the development of *Fusarium* sp. by determining the diameter of the fungal colonies on the samples including the non-Cu Nps solution sample and other samples with Cu Nps solution with the concentrations of 300 ppm, 380 ppm, and 450 ppm, respectively. The diameter of the fungal colonies was determined after the incubation periods of 3 days, 6 days, and 9 days, respectively. The images of colonies according to incubation period at various Cu Nps concentrations are exhibited in Figure 5. These results show that Cu Nps inhibited the development of *Fusarium* sp. It demonstrated that the diameter of colonies in all samples was supplemented with Cu Nps being smaller than the reference sample. In 3-day incubation, the diameters of fungal colonies for additional formulations of 300 ppm and 380 ppm of Cu Nps were measured about 8.67 mm, while the reference sample developed rapidly with the diameter of the fungal colony being about 15.33 mm. The fungal colony of the sample at the Cu Nps concentration of 300 ppm is still developing in 9-day incubation, while the diameter of the fungal colony of the samples at the Cu Nps concentration of 380 ppm was approximately 44 mm after they were incubated for 6 days and it almost unchanged the next 3 days. Meanwhile, the diameter of *Fusarium* sp. colony was 5 mm. It remains after being incubated for 9 days. In addition, Figure 6 shows the change of the diameter of fungal colonies at various incubation periods for various concentrations of Cu Nps solutions. These diagrams show that the more the Cu Nps concentration increases, the more the diameter of fungal colonies decreases. Remarkably, the diagram of the diameter of the colonies with the Cu Nps concentration of 450 ppm was a straight line. This result demonstrated that the diameter of the fungal colony almost does not increase in the samples at the Cu Nps concentration of 450 ppm.

From these above results, we determined the *Fusarium* sp. inhibition efficiency of Cu Nps solution and it was represented in Figure 7. These results show that the inhibition efficiency of Cu Nps was good in the *in vitro* condition. However, the inhibition efficiency of Cu Nps increases according to the concentration used. In a 3-day incubation, Cu Nps solutions inhibited 43% of growth of fungi of the samples at the concentration of 300 ppm and 380 ppm. Meanwhile, Cu Nps solution could inhibit 67.38% of the fungal growth at 450 ppm concentration after being incubated for 3 days and reaches 93.98% if incubated for 9 days. At this time the

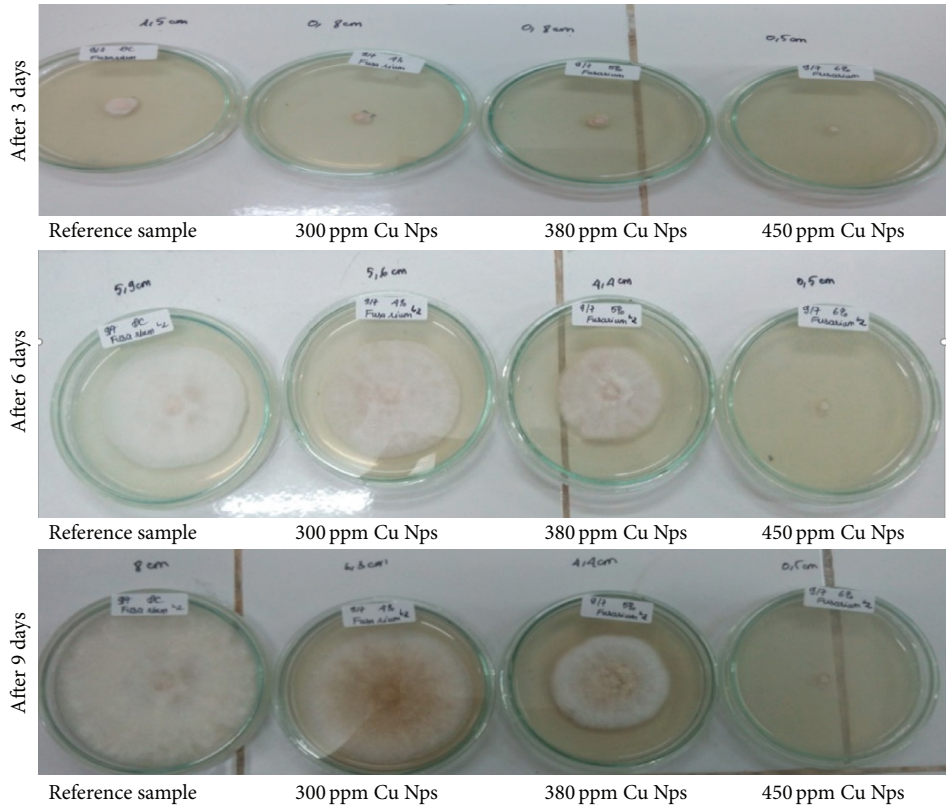


Figure 5: The diameter of *Fusarium* sp. colonies according to incubation period at various Cu Nps solution concentrations.

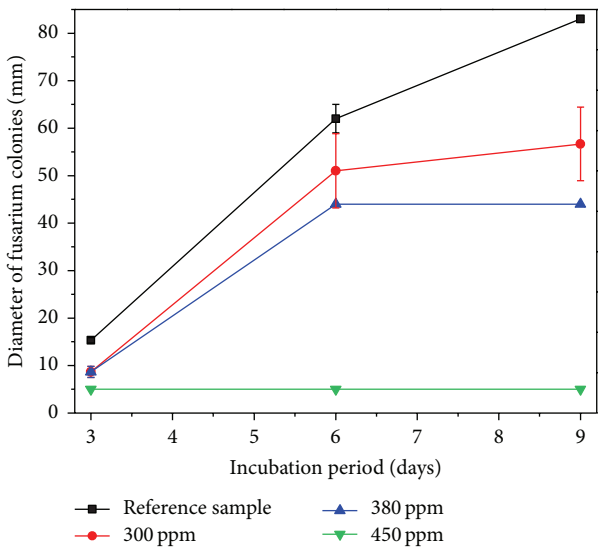


Figure 6: The diagram of the formation of the diameter of *Fusarium* sp. colonies according to incubation period at various Cu Nps solution concentrations.

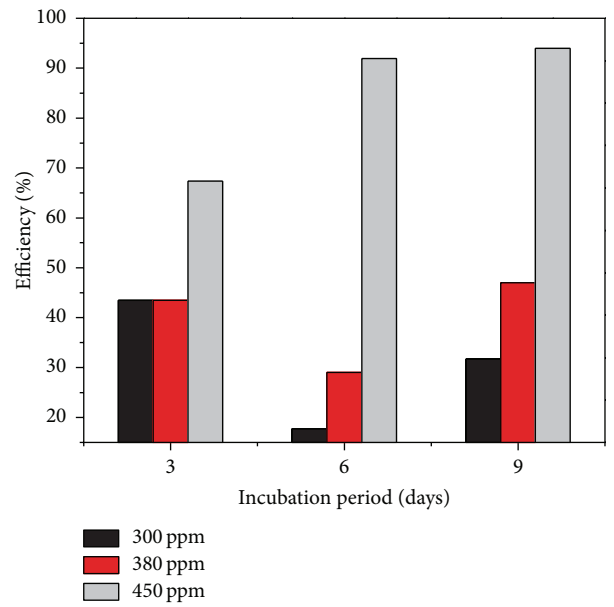


Figure 7: The *Fusarium* sp. inhibition efficiency of Cu Nps solutions.

results show that inhibition efficiency of Cu Nps solution went up significantly due to 450 ppm concentration dish; the fungi were inhibited intensively and no longer grew in a 3-day incubation. In contrast, the fungi in the reference sample still grew normally and their diameter increased constantly.

4. Conclusion

We successfully prepared Cu Nps for a short reaction time (about 15-minute reaction) by chemical reduction method with a support of CTAB reductive agent. The absorption

spectrum of Cu Nps solutions prepared after a 15-minute reaction shows an absorption peak at 560 nm wavelength, a typical peak for the existence of Cu Nps. The size of Cu Nps is in the range from 20 nm to 50 nm and their shapes are mainly spherical. The more the Cu Nps concentration increases, the more the inhibition efficiency increases. Moreover, the diameter of the fungal colony almost does not increase and could inhibit 93.98% of the fungal growth at the 450 ppm Cu Nps concentration after a 9-day incubation.

Competing Interests

The authors declare that they have no competing interests.

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