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BIOSYNTHESIS OF SILVER NANOPARTICLES BY *Plectranthus amboinicus* LEAF EXTRACT AND THEIR CATALYTIC ACTIVITY TOWARDS METHYLENE BLUE DEGRADATION

BIOSÍNTESIS DE NANOPARTÍCULAS DE PLATA POR EXTRACTOS DE HOJA DE *Plectranthus amboinicus* Y SU ACTIVIDAD CATALÍTICA HACIA LA DEGRADACIÓN DE AZUL DE METILENO

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Abstract
Synthesis of nano-material with the controlled size and shape is the prime concern of research in nanotechnology. In this study, the synthesis of silver nanoparticles (Ag NPs) were carried out using *Plectranthus amboinicus* leaf extract as reducing agent. The synthesized Ag NPs was characterized by using X-ray diffraction, scanning electron microscope, Fourier transform infrared spectroscopy and UV-vis spectroscopy. We further investigated the catalytic property of the biosynthesized Ag NPs by degradation of methylene blue (MB) in the presence of sodium borohydride. Compared with commercial Ag NPs, the proposed *Plectranthus amboinicus* leaf extract-deduced Ag NPs exhibited a much higher catalytic performance due to the well dispersibility caused by the attachment of biomolecules on the Ag NPs surface.
Keywords: biosynthesis, *Plectranthus amboinicus*, silver nanoparticle, catalyst.

Resumen
La síntesis de nano-materiales con el tamaño controlado y la forma es el interés principal de investigación en la nanotecnología. En este estudio, la síntesis de nanopartículas de plata (Ag NPs) fue realizada usando *Plectranthus amboinicus* el extracto de hoja como agene reductor. Las NPs de Ag sintetizadas fueron caracterizadas usando la difracción de rayos X, escaneo con microscopio electrónico, transformada de Fourier de espectroscopía infrarroja y la espectroscopia de UV-vis. Además investigamos la propiedad catalítica de las NPs de Ag biosintetizadas por la degradación de azul de metileno en la presencia de borohidrato de sodio. Comparado con NPs comerciales de Ag, las NPs de Ag de extracto de hoja de *Plectranthus amboinicus* expusieron un desempeño catalítico mucho más alto debido a la buena dispersión causada por la adición de biomoléculas sobre la superficie de NPs de Ag.
Palabras clave: biosíntesis, *Plectranthus amboinicus*; nanopartículas de plata, catalizador.

1 Introduction

Synthesis of nanomaterials and control of their characteristics and properties have been explored for diverse applications. Nanoparticles (NPs) can be synthesized using various chemical, physical and biological methods. Among these methods, chemical synthesis method is found to be easy and cost effective but some of them use toxic raw materials. It has been reported by many researchers that, as biosynthesis of NPs is free from toxic chemicals it is more suitable for the biological application of NPs.

Microorganisms, plant extracts, fungi and other natural bio-materials have been used for synthesizing metal NPs. For example, Patel *et al*. (Patel *et al*., 2016) recently synthesized Cu NPs with simple and green technique by using *Ocimum sanctum* plant leaf extract as reducer as well as stabilizer. Vágó and co-workers report a one-step and green method for the synthesis of gold nanoparticles by randomly selected

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21 types of microscopic fungi (Vágó *et al*., 2016). There are many reports on the synthesis of metal, semiconductor, and nanomaterial using aloe vera plant extracts (Dinesh *et al*., 2015; Kumar *et al*., 2015; Medda *et al*., 2015). Among them, synthesis of inorganic nanomaterials using plant mediate reducing agent has been found more favorable due to the low cost and high yield.

Ag NPs with different size and shape have been applied in various fields due to their superior electrical, optical and catalytic properties. However, current synthesis methods for Ag NPs often require toxic chemical reduction reagent and expensive equipment. To overcome these problems, development of an environmentally friendly method for Ag NPs synthesizing is in high demand. Biosynthesis of Ag NPs have been reported by several research groups. For example, Meng and co-workers used the extract of *Gynostemma pentaphyllum* Makino as reducing as well as stabilizing agent to obtain Ag NPs (Meng *et al*., 2016). Gopinath and co-workers used a Tribulus terrestris plant dried leaf extract for Ag NPs synthesis (Gopinath *et al*., 2015).

Our previous study showed the leaf extract of *Plectranthus amboinicus* can be successfully used for synthesizing ZnO nanoparticles (Fu and Fu, 2015). In this work, we further explored the potential of the *Plectranthus amboinicus*, which proposed a simple room temperature synthesis of Ag NPs using *Plectranthus amboinicus* leaf extract. *Plectranthus amboinicus* is a tender fleshy perennial plant in the family Lamiaceae with an oregano-like flavor and odor. The synthesized Ag NPs was then subjected to a series of characterizations. In addition, the catalytic activity of the biosynthesized Ag NPs was investigated by degradation of methylene blue in the presence of sodium borohydride. The performance comparison of the biosynthesized Ag NPs with commercial Ag NPs was carried out.

2 Experimental

2.1 Materials

The preparation of *Plectranthus amboinicus* leaf extract was according to our previous report (Fu and Fu, 2015). *Plectranthus amboinicus* plants were purchased from a local nursery of Jiangsu province, China. The plant leaves were cleaned with double distilled water and ethanol. Then, 10 g of *Plectranthus amboinicus* leaves were washed with water and crushed by a shredder. The slurry was then sonicated in 30 mL of water for half hour. The leaf extract was filtered through Whatman No. 1 filter paper and stored in refrigerator for further experiments. $AgNO_3$, methylene blue (MB) and $NaBH_4$ were purchased from Sigma-Aldrich.

2.2 Biosynthesis of Ag NPs

Ag NPs were synthesized using wet chemical route. Typically, 5 mL of *Plectranthus amboinicus* leaf extract was added to 95 ml of 1 mM aqueous $AgNO_3$ solution. The mixture was stirred at 25 °C for 3 days. The result solution was centrifuged and washed copiously with water for several times and then dried in a vacuum desiccator.

2.3 Characterization

The morphology of the prepared samples was characterized using a field emission scanning electron microscope (FeSEM, ZEISS SUPRA 40VP, Germany). The crystal phase information of sample was characterized from 10° to 80° in 2θ by a XRD with Cu Kα (λ = 0.1546 nm).radiation (D8-Advanced, Bruker). The optical analysis was obtained by UV-vis spectrophotometer (Perkin Elmer Lambda 950). The surface functional groups present on the samples were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet iS5, Thermo Scientific).

2.4 Catalytic degradation of methylene blue

The catalytic activity of the biosynthesized Ag NPs was investigated as follows: the reduction of MB by $NaBH_4$ has been chosen as a model reaction. For a typical reaction, 0.1 mL of $NaBH_4$ (0.5 M) was mixed with 2 mL MB (10 mg/L) solution. After addition of 5 μL of catalyst (0.5 mg/mL), the catalytic reduction process was monitored by a UV-vis spectroscopy at regular intervals of time.

3 Result and discussion

The reduction of $AgNO_3$ by *Plectranthus amboinicus* leaf extract can be visually observed. The solution changed color from pale green to light brown, and going darker with increasing time at room temperature. UV-visible spectroscopy was used for confirming the successful formation of the Ag

NPs. It was known that spherical Ag NPs show a surface Plasmon resonance band at wavelength around 420-480 nm. As shown in the Figure 1A, the spectrum of biosynthesized Ag NPs (after 3 days reaction) displays a strong surface Plasmon resonance band centered at 432 nm, suggesting the successful formation of Ag NPs (Shameli *et al*., 2012). The comparison of different reaction periods synthesized Ag NPs spectra showed the surface Plasmon resonance peak increased along with the reaction time, indicating the continued reduction process conducted by *Plectranthus amboinicus* leaf extract. After 3 days reaction, the intensity of the surface Plasmon resonance peak showed no further increasing, suggesting all the Ag ions were reduced by *Plectranthus amboinicus* leaf extract. The formation of Ag NPs at the beginning showed a narrow size distribution, which can be proven by the narrow surface Plasmon resonance band. However, the surface Plasmon resonance band showed a growth when prolong the reaction, suggesting the size distribution of the biosynthesized Ag NPs become larger. After 3 days reactions, the center of the surface Plasmon resonance band red shifted from 445 nm to 432 nm.

Figure 1B shows the XRD pattern of biosynthesized Ag NPs. It can be seen that the XRD pattern showed five peaks at 2θ, which corresponded to (111), (220), (202) and (311) planes of standard cubic crystalline silver crystals. No crystallized impurity was recorded by the XRD analysis, suggesting the proposed biosynthesis method could result a high purity Ag NPs.

The possible reduction component from the *Plectranthus amboinicus* leaf extract were identified using FTIR spectroscopy. Figure 2 A shows the FTIR spectra of *Plectranthus amboinicus* leaf extract and biosynthesized Ag NPs. It can be seen that the spectrum of the *Plectranthus amboinicus* leaf extract showed a series absorbance bands at range from 700 to 2000 cm^{-1}. The peak at 1620 cm^{-1} was mainly attributed due to the carboxyl group of C-C stretching vibration present in the plant leaf extract (Gajbhiye *et al*., 2009). The absorbance bands at 1332 and 1226 cm^{-1} are associated with the C-O belong to polysaccharides and C-O belong to polyols, respectively (Philip, 2011). The reducibility of polysaccharide and polyols can be used for nanomaterials reduction (Begum *et al*., 2009; Huang *et al*., 2007). On the other hand, the FTIR spectrum of biosynthesized Ag NPs showed the similar distinct peak with minor absorption bands shift. Therefore, the attachment of biomolecules on the biosynthesized Ag NPs surface was confirmed. The surface absorption of biomolecules on Ag NPs could prevent the particle aggregation due to their surface charges. The morphology of biosynthesized Ag NPs was observed using SEM. As shown in Figure 2B, the image confirm the formation of nanoparticles with spherical shape. The measurement (based on 100 individual Ag NP measurement) revealed that the average size of the biosynthesized Ag NPs was 35 nm. The size distribution was further illustrated in Figure 2C.

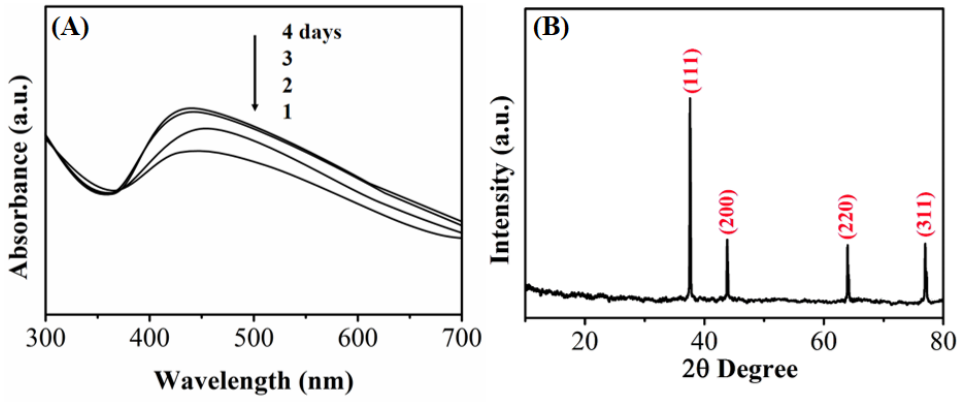

Fig. 1. (A) UV-vis spectra of Ag NPs formed at different reaction periods by *Plectranthus amboinicus* leaf extract. (B) XRD pattern of biosynthesized Ag NPs.

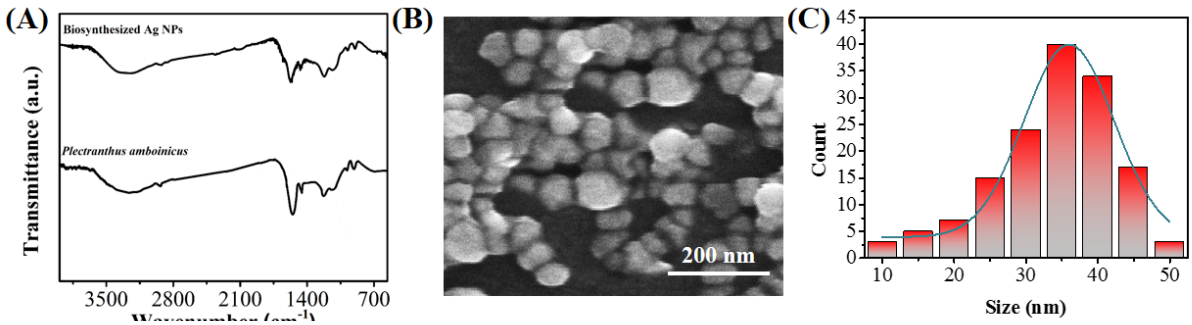

Fig. 2. (A) FTIR spectra of *Plectranthus amboinicus* leaf extract and biosynthesized Ag NPs. (B) SEM image of the biosynthesized Ag NPs. (C) Size distribution of the biosynthesized Ag NPs.

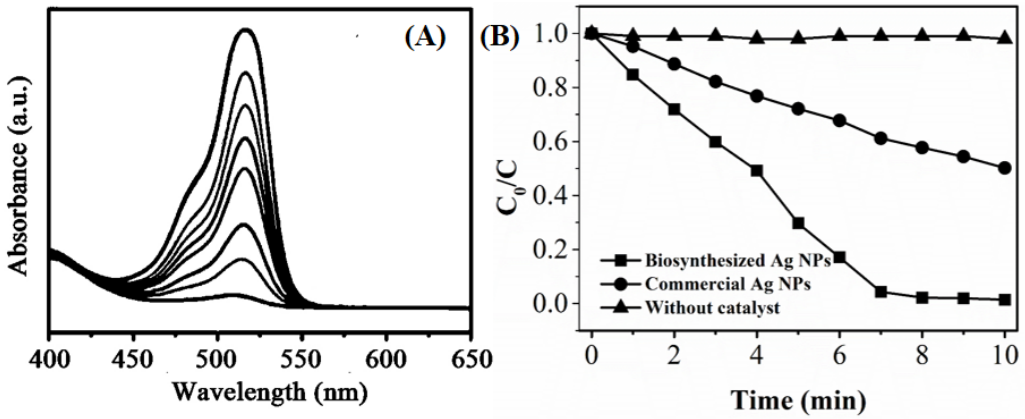

Fig. 3. (A) UV-vis spectra of MB during the degradation process. (B) Degradation profiles of $NaBH_4$, biosynthesized Ag NPs and commercial purchased Ag NPs.

The catalytic property of the biosynthesized Ag NPs was investigated by the degradation of methylene blue (MB), a heterocyclic aromatic dye wildly used in the textile industrial. The absorption peak at 665 nm, corresponding to the n-π* transition, was used for determining the concentration change during the degradation process. The degradation of MB using $NaBH_4$ without any catalyst showed a very slow progress. After 1 h reaction, only 2% of MB molecules were degraded by the $NaBH_4$. On the other hand, the degradation process cannot be triggered when the absence of the $NaBH_4$. Increased degradation of MB has been achieved through the inclusion of biosynthesized Ag NPs, which is shown by a strong decrease in the absorption intensity. Figure 3A shows the UV-vis spectra of MB after addition of biosynthesized Ag NPs for 7 min. It can be seen that the complete degradation of MB can be achieved within 10 min. In order to comparison of the catalytic performance of the biosynthesized Ag NPs, commercial purchased Ag NPs were used as a control group. Figure 3B shows the MB degradation profiles using different catalyst. It can be seen that the biosynthesized Ag NPs exhibited a much higher degradation process compared with that of the commercial Ag NPs. The first order rate constants obtained for MB using biosynthesized Ag NPs and commercial Ag NPs are 1.201/min and 0.457/min, respectively.

As well known, catalysis process happens on the catalysts surface. Therefore, increasing the available surface area of the catalyst is the key factor for enhancing the effectiveness of the catalyst.

A critical problem of metal nanoparticles is the aggregation due to the lack of the surface charge, which consequently decrease in active surface area. The biomolecules present on the synthesized Ag NPs could play as the stabilizer for preventing the aggregation of the Ag NPs under aqueous condition, which remains the catalytic performance of the catalyst. During the degradation process, Ag NPs act as a platform for electron transfer reaction.

Conclusion

In this contribution, we demonstrated the synthesis of Ag NPs by a green biosynthesis method using *Plectranthus amboinicus* leaf extract as reducing agent and stabilizer. The biosynthesized Ag NPs showed a well dispersibility due to the surface attachment of biomolecules. The average size of the biosynthesized Ag NPs was 35 nm. Moreover, the biosynthesized Ag NPs showed better catalytic performance for the degradation of MB than the commercial Ag NPs. This novel biosynthesized Ag NPs presented here enriches the nanoscale community with new basic materials and enabling greater potential applications.

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