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Research paper

Fortunella japonica extract as a reducing agent for green synthesis of silver nanoparticles

Nguyen Phung Anh [1], Truong Thi Ai Mi [1], Duong Huynh Thanh Linh [1], Nguyen Thi Thuy Van [1], Hoang Tien Cuong [1], Nguyen Van Minh [2], Nguyen Tri [1] *

[1] Institute of Chemical Technology - VAST, 01 Mac Dinh Chi Str., Ho Chi Minh City, Vietnam
[2] Open University Ho Chi Minh City, 97 Vo Van Tan Str., Ho Chi Minh City, Vietnam
**Corresponding author E-mail: ntri@ict.vast.vn*

Abstract

A rapid way of synthesizing silver nanoparticles (AgNPs) by treating Ag^+ ions with a green Fortunella Japonica (F.J.) extract as a combined reducing and stabilizing agent was investigated. The reaction solutions were monitored using UV-Vis spectroscopy, the size and shape of crystals were determined by scanning electron microscopy and transmission electron microscopy, the crystalline phases of AgNPs were presented by X–ray diffraction, and the relation of nanoparticles with Fortunella Japonica extract was confirmed using fourier transform infrared spectroscopy. The results indicated that no formation of AgNPs had taken place in the dark during 24 hours at room temperature and 40 ^oC. Meanwhile, it was found that the rate of AgNPs formation increased rapidly under the sunlight. The effects of the synthesis factors on the AgNPs formation were investigated. The suitable conditions for the synthesis of AgNPs using F.J. extract were determined as follows: F.J. extract was mixed with $AgNO_3$ 1.75 mM solution with the volume ratio of 3.5 $AgNO_3$ solution/1.5 F.J. Extract, stirred 300 rpm for 150 minutes at 40 ^oC under sunlight illumination. At these conditions, AgNPs showed high crystalline structure with the average size of 15.9 nm. The antibacterial activity of silver nanoparticles was determined by agar well diffusion method against *E. coli* and *B. subtilis* bacteria. The green synthesized AgNPs performed high antibacterial activity against both bacteria.

Keywords: *Fortunella Japonica Extract; Reducing Agent; Green Synthesis; Silver Nanoparticles.*

1. Introduction

Nanotechnology has been promising as a rapidly developing field with its application in science and technology. Noble metal nanoparticles such as silver, gold and platinum are broadly applied in medicinal applications. Among noble metals, silver nanoparticles (AgNPs) have received enormous attention in various fields such as biomedicine (medical biology) [1], drug delivery [2], water treating [3], agriculture [4], etc. Because of their extraordinary defence against wide range of microorganisms as well as the appearance of drug resistance against commonly used antibiotics [5], AgNPs were applied in biology, living organisms and medicine. Besides, due to their high conductivity [6], AgNPs were also applied in inks, adhesives, electronic devices, pastes, etc.

AgNPs had been synthesized by physio-chemical methods including chemical reduction [7], gamma ray radiation [8], micro emulsion [9], electrochemistry [10], laser ablation [11], hydrothermal method [12], microwave [13] and reduction of photochemical [14]. Although these methods had effective performance, they associated with the limitations like using toxic chemicals, high operational cost and energy needs. Therefore, the development of environmentally friendly processes of NPs synthesisusing no toxic chemicals with low cost has been a big challenge.

The exploit of green chemistry for the synthesis of AgNPs has obtained substantial achievements in the latest years. Considering the advantages, the effective cost and energy efficient, new substitutionfor AgNPs synthesis using microorganisms [15], plant extracts [16] and natural polymers [17] as reducing and capping agents has been emerging really fast. The association of nanotechnology and green chemistry has unfolded the range of AgNPs synthesis. The publications on green synthesis of AgNPs were investigated [13]. Most of these reviews focused on several plant and microbial sources for the synthesis. In which, plant parts like seeds [18], leaf [19], bark [20], stem [21] and fruit extracts [22] have been effectively used for synthesizing AgNPs.

Fortunella Japonica - a member of the Citrus genus has long been cultivated in Japan, China, and Southeast Asia. In addition to being used in the food industry, it has been used in folk medicine for treating sore throat and coughing. The extracts from Fortunella Japonica fruit and peel have previously been reported to contain various nutrients and components such as ascorbic acid, carotenoids, essential oils, and flavonoids [23]. The previous publications on Fortunella Japonica have provided evidences about abilities to promote health effects and pharmacological activities of Fortunella Japonica extract, including antioxidant activity [24], anti-metabolic disorder [25], and antimicrobial [26]. However, up to now no paper of AgNPs synthesis has been reported using Fortunella Japonica extract as a combined reducing and stabilizing agent.

In this paper, silver nanoparticles by the reduction of $AgNO_3$ solution were synthesized using Fortunella Japonica extract as a combined reducing and stabilizing agent. The effects of the synthesis time, the volume ratio of $AgNO_3$ solution/Fortunella Japonica extract, the stirring rate, the concentration of $AgNO_3$ solution and the forming temperature of AgNPs were assessed. The physic-chemical properties of the obtained AgNPs were investigated. The antibacterial of silver nanoparticles was evaluated against E. coli and B. subtilis bacteria by agar well diffusion method.

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2. Experimental

2.1. Materials

Fortunella Japonica was collected from Ben Tre, Vietnam. After washing and draining, it was squeezed to obtained solution. The solution was centrifuged at 4500 rpm for 30 minutes to remove the residues. After that, the solution was vacuum filtered through 0.22 μm filters to obtain Fortunella Japonica extract (F.J. Extract). The extract was preserved at 4 ℃ till further experiments. Silver nitrate ($AgNO_3$, > 99.8%) was purchased from Merck.

2.2. Synthesis of AgNPs

For testing the synthesis of AgNPs in the dark, 20 mL of Fortunella Japonica extract was mixed with 30 mL of 1.0 mM $AgNO_3$ solution and stirred at 300 rpm for 24 hours at 40 °C and room temperature (27 °C) in the dark. The synthesis process was conducted with 50 mL sample/batch.

For the experiments under sunlight, AgNPs were also synthesized according to above procedure and illuminated by sunlight. However, the effects of the factors such as $AgNO_3$ concentration, volume ratio of $AgNO_3$ solution/F.J. Extract, stirring rate, synthesis time and temperature on AgNPs synthesis were surveyed.

2.3. Characterization of synthesized AgNPs

The concentrations of silver nanoparticles in the solution were determined by UV-Vis spectrophotometer (UV–1800, Shimadzu, Japan) at a scanning speed of 200 to 800 nm with a resolution of 1 nm. The morphology of AgNPs was characterized by scanning electron microscopy (SEM) on FE–SEM JEOL 7401 instrument, and transmission electron microscopy (TEM) using JEOL JEM 1400 instrument. A drop of AgNPs solution was put on the carbon stub, dried and observed in TEM or SEM. Crystalline phases of prepared AgNPs powder dried at 60 °C were investigated by X–ray diffraction (XRD) using Bruker D2 Phaser powder diffractometer. The relation of nanoparticles with F.J. Extract was confirmed using Fourier transform infrared spectroscopy (FT-IR) carried out on a Tensor 27-Bruker spectrophotometer operating in the range of 400–4,000 cm^{-1} at a resolution of 2 cm^{-1}.

2.4. Antibacterial activity of AgNPs

The obtained AgNPs samples have been tested for antibacterial activity with E. coli and B. subtilis by zone of inhibition test [27]. Colonies were planted with the MHA method (Mueller-Hinton Agar), the bacterias then stored in the agar rods at 4 °C. Three colonies were added in the tube contained 5 mL pasteurized TSB (Trypticase Soy Broth) and statically cultured at 37 °C in 18 hours. The paper discs were wetted by the solutions and allowed to dry, these dried discs then got put onto the agar. Store all the samples in the refrigerator in 8 hours and finally incubated at 37 °C in 18 hours. Antibacterial activity was evaluated by measuring the diameter of the zone of inhibition around the agar.

3. Results and discussion

3.1. Effect of sunlight on the synthesis of AgNPs

UV-Vis spectral analysis of the samples synthesized in the dark (no light) was shown in Fig.1a. The result showed no remarkable difference in the absorbance patterns of the samples in the wavelength range of 400–450 nm. It indicated that no formation of AgNPs had taken place under completely no light during 24 hours at room temperature. Meanwhile, it was found that the rate of formation of AgNPs increased with the presence of direct sunlight after 30 minutes as shown in Fig.1b, the band indicating AgNPs in the solution in the range of 400–450 nm was observed. This can be explained that the presence of greater number of photons of certain wavelength in sunlight promoted the reducing action, thus, promoting the AgNPs formation. According to Cumar et al [28], AgNPs formation under sunlight was occurred with four main steps: i) The first step is the photo-activation including the photo-sensitization of polyphenolic compound (flavonoid) present in extract. As soon as the reaction mixture exposed to sunlight the flavonoid molecule absorbed the photons of energy and got excited. The second step involves the donation of the electrons by debonding of O-H group of the excited molecules for the reduction of Ag^+ to Ag°, which put substantial evidence after the photoinduced synthesis of AgNPs. The third step involves the nucleation of Ag° atoms to form nanoclusters, and the fourth step involves the simultaneous growth of the nanoparticles wherein; the nanoclusters nucleated to form the nanoparticles. Further, the protein molecule present in extract is believed to act as a capping agent and stabilized it. This prediction can be evident from the FT-IR spectra showing the involvement of –OH and $–NH_2$ groups in the synthesis and stabilization of AgNPs. The formation of nanoparticles under direct sunlight is described by equations as follows:

$$Ag^+ + H_2O \xrightarrow{h\nu} Ag° + H^+ + HO^*$$

$$Ag^+ + RCH_2OH \xrightarrow{h\nu} Ag° + H^+ + RC^*HOH$$

$$Ag^+ + RC^*HOH \xrightarrow{h\nu} Ag° + H^+ + RCHO$$

$$nAg° \longrightarrow AgNPs$$

So, the synthesis under direct sunlight was chosen to investigate the effects of other factors on AgNPs formation.

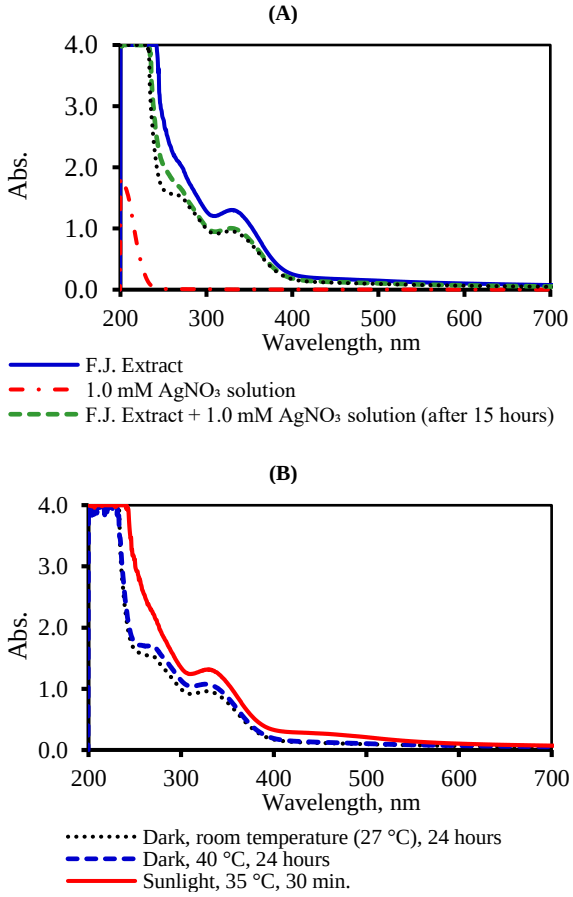


Fig. 1: UV-Vis Spectral Analysis of Different Suspension Samples.

3.2. Effects of reaction conditions on AgNPs synthesis

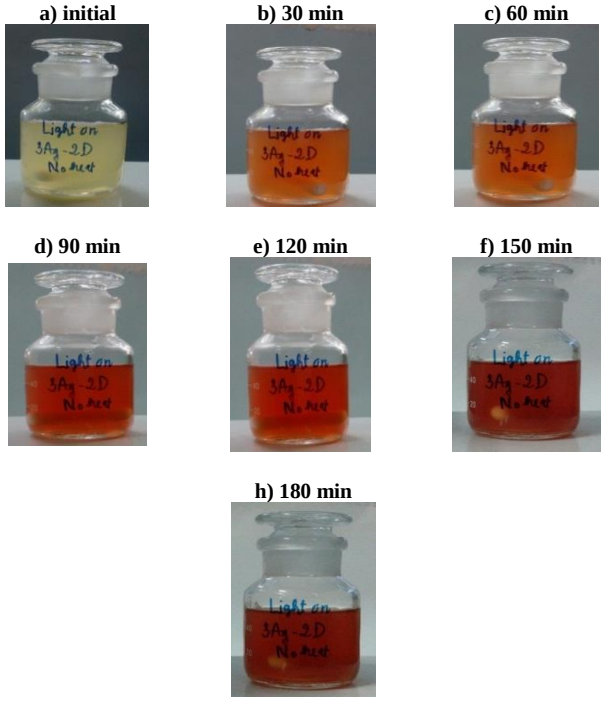
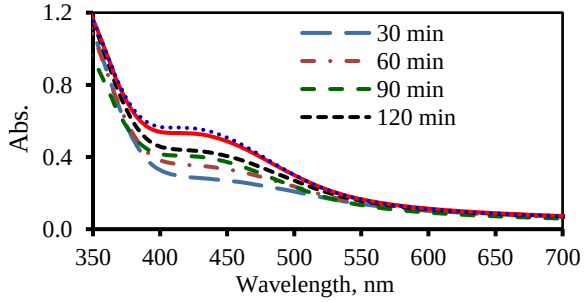
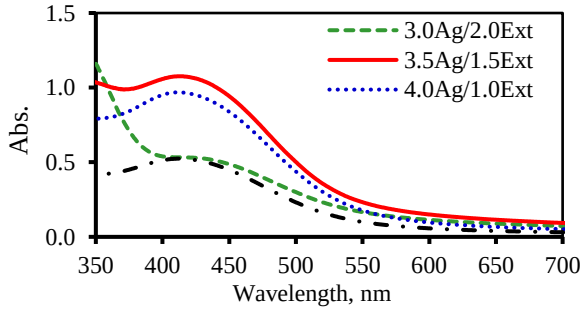


Fig. 2: By-Time Colour of AgNPs Solution (V = 50 mL; 3.0Ag/2.0Ext; T = 35 °C; Sunlight; V_{stir} = 300 Rpm; C_{ag+} = 1.0 mM).

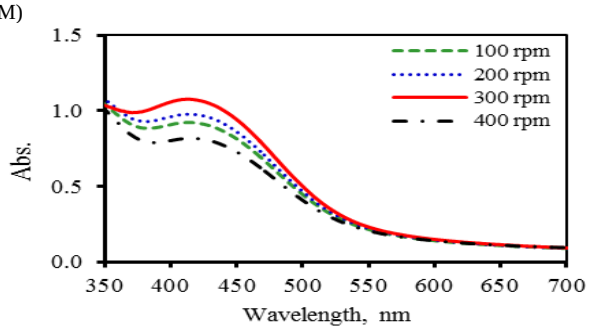
A) Effect of Synthesis Duration (3.0Ag/2.0Ext; T = 35 °C; V_{stir} = 300 Rpm; C_{ag+} = 1 mM)



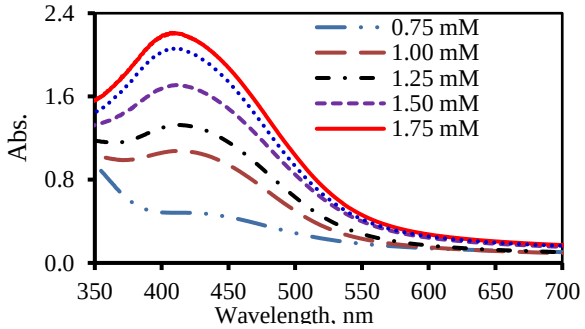
B) Effect of Volume Ratio of $AgNO_3$ Solution/F.J. Extract (T = 150 Min; T = 35 °C; V_{stir} = 300 Rpm; C_{ag+} = 1 mM)



C) Effect of Stirring Rate (T = 150 Min; 3.5Ag/1.5Ext; T = 35 °C; C_{ag+} = 1 mM)



D) Effect of $AgNO_3$ Concentration (T = 150 Min; 3.5Ag/1.5Ext; T = 35 °C; V_{stir} = 300 Rpm)



E) Effect of the Synthesis Temperature (T = 150 Min; 3.5Ag/1.5Ext; V_{stir} = 300 Rpm; C_{ag+} = 1.75 mM)

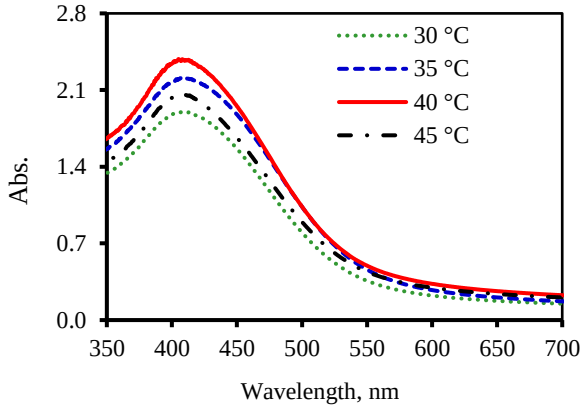


Fig. 3: UV-Vis Spectral Analysis of AgNPs Suspension Samples Synthesized Under Sunlight.

The absorbance peak was broaden indicating high conversion of silver ions to metallic silver nanoparticles at this duration at the early stage (after initial 30 minutes) as shown in Fig. 2 and 3a. When the synthesis time increased, the colour of the reaction mixture changed from yellow to dark brown (Fig.2). Prolonging the reaction time up to 150 minutes led to outstanding enhancement in the plasmon intensity, indicating that large amounts of silver ions were reduced and used for formation of AgNPs. In the reaction duration of up to 180 min, the formed silver nanoparticles just increased slightly, which could be attributed to some aggregation of formed AgNPs. Therefore, 150 minutes were chosen as the optimal reduction time for AgNPs synthesis using F.J. Extract as a combined reducing and stabilizing agent.

The formation of AgNPs reached highest performance with the volume ratio of $AgNO_3$ solution/F.J. Extract at 3.5/1.5 (seen in Fig.3b). With high extract concentrations, the components in the extract had effectively reduced the Ag^+ ions to Ag^o and provided enough capping agent for the stabilization of the synthesized nanoparticles through steric hindrance preventing their aggregation [29]. These results were good agreement with those obtained by Subramanian et al. [30].

Fig.3c showed when the stirring rate increased from 100 to 300 rpm, the formation of the AgNPs increased. However, while the stirring rate continuously rose up to 400 rpm, this formation decreased sharply. The strongly stirring power resulted in effective formation of nanoparticles because high rates of heat and mass transfer were essential in the process, especially on larger scale. Because of the increase in nanostructure concentration, stronger mixing was essential to provide uniform heat and mass transfer [31]. However, when the stirring rate was too high, it could break the AgNPs structure, leading to reducing the efficiency of the process. So, the stirring rate of 300 rpm was consistent for the synthesis process. The effect of $AgNO_3$ concentration on AgNPs formation was also investigated. In Fig.3d, the content of AgNPs increased as raising the initial Ag^+ concentrations from 0.75 to 1.75 mM. However, AgNPs formation decreased in the case of continuously increasing $AgNO_3$ concentration up to 2 mM. At low

concentration, nanoparticles have appeared no more, while nanoparticles have been formed at a higher concentration [32]. However, when silver concentrations were too high, silver nanoparticles agglomerated together reducing the efficiency of the process.

Synthesis of silver nanoparticles was performed at different temperatures in the range of 30 to 45 °C. The results in Figure 3e showed that the efficiency of silver nanoparticles synthesis was highest at 40 °C.

The suitable conditions for the synthesis of AgNPs using F.J. Extract were determined: the presence of sunlight illumination, $AgNO_3$ concentration of 1.75 mM, the volume ratio of $AgNO_3$ solution/F.J. Extract of 3.5/1.5, the stirring rate of 300 rpm, the synthesis time of 150 minutes and the temperature of 40 °C.

3.3. The characteristics of synthesized AgNPs

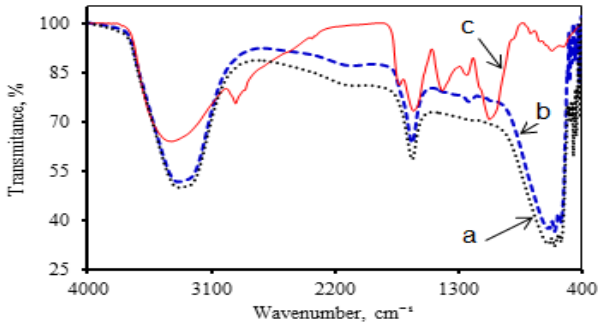


Fig. 4: FT-IR Spectra of F.J. Extract (A), AgNPs Solution (B) and AgNPs Powders (C) Synthesized at the Suitable Conditions.

FT-IR spectra of pure F.J. Extract, AgNPs solution synthesized using F.J. Extract and AgNPs powder dried at 60 °C were depicted in Fig.4. In all samples, three main bands could be observed. The broad band appearing at 3450 cm^{-1} was assigned for O−H stretching vibration indicating the presence of hydroxyl groups, suggesting the presence of carboxylic acids (citric-main component and ascorbic acids) in the extract [33, 34] that acted as both the reducing and stabilizing agents. Two peaks with high intensity at 1380 and 1630 cm^{-1} correspond to C−N stretch vibrations as well as to the amide bands of components in F.J. extract. The difference was not much on samples of pure F.J. Extract and AgNPs solution.

On the FT-IR spectrum of AgNPs powder, a band centered at 2950 cm^{-1} was related to the axial stretching of C-H bonds, a band centered at 1810 cm^{-1} was attributed to the axial stretching of C=O bonds of the acetamide groups, a band at 1420 cm^{-1} corresponded to the symmetric angular deformation of CH_3, and there was a broad band in the wavenumber range of 1153–897 cm^{-1} indicating the polysaccharide skeleton, including the vibrations of the glycoside bonds, C–O and C–O–C stretching. Compare to pure F.J. Extract, the FT-IR spectrum of AgNPs powder showed the presence of weaker signal in the range of 3000–3500 cm^{-1} in the synthesized nanoparticles. It indicated the decrease in the amount of –O–H groups of powder AgNPs sample. The decrease of –O–H group can be attributed to its reaction with Ag^+ ions added to the solution for nanoparticles synthesis. When Ag^+ ions came in contact with –O–H groups, the white colloidal particles of AgOH were formed and then turned into brown Ag nanoparticles after exposing the solution to bright sunlight due to surface plasmon resonance effect [35].

Fig.5 showed XRD diffraction pattern of AgNPs synthesized using F.J. Extract at the suitable conditions. It presented the feature crystal of AgNPs at 2θ = 28.5, 33.7, 38.1, 46.3, 64.4, and 76.8° with the strongest intensity at 2θ = 38.1° [36], indicating that the crystal structure of AgNPs was formed. The unassigned small peaks could be due to the crystallization of bio-organic phase occuring on the nanoparticle surface [36, 37]. Two small peaks observed at 55.3° and 57.6° are attributed to the presence of other organic substances in F.J. Extract. Based on XRD result, the average crystal size of AgNPs at 2θ = 38.1° was determined following the Scherrer's equation [38]:

$$d_{crys} = \frac{K\lambda}{\beta \cos(\theta)} \quad (1)$$

Where d_{crys} is the crystallite size; K is a shape factor of the particle (normally K = 0.94); λ is the wave length of X-ray radiation (λ = 1.5406 Å); β is also known as full-width at half the maximum intensity (FWHM) at peak 2θ = 38.1°; θ is Bragg angle. The average crystal size of silver nanoparticles synthesized using the F.J. Extract as a combined reducing and stabilizing agent was determined 15.9 nm.

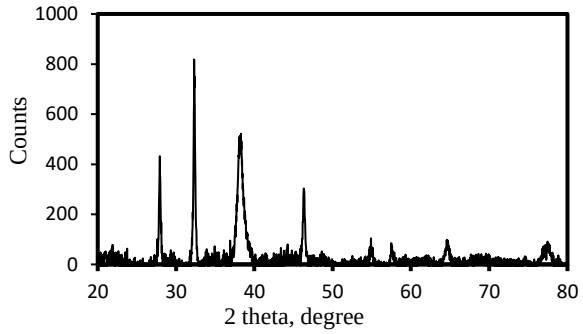


Fig. 5: XRD Diffraction of AgNPs Powder Synthesized at the Suitable Conditions and Dried at 60 °C.

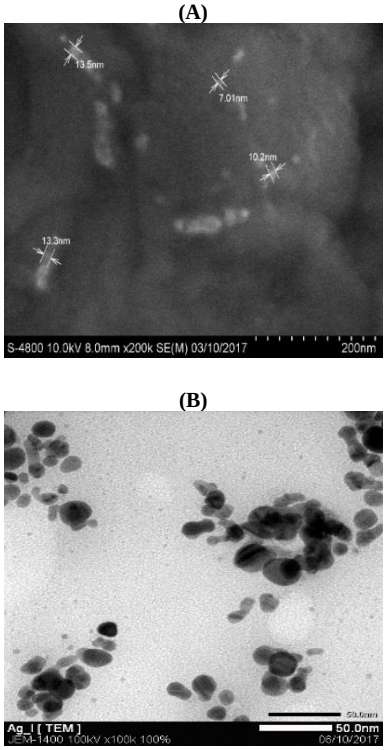


Fig. 6: SEM (A) and TEM (B) Images of AgNPs Synthesized at the Suitable Conditions.

The SEM and TEM images show that the synthesized AgNPs were nanoparticles with the size range of 4 – 25 nm (shown in Fig.6). This was consistent with the obtained XRD result.

3.4. Antibacterial activity of AgNPs

Fig.7 showed the inhibition zones of the synthesised AgNPs against the two bacterial strains. The zone of inhibition exhibited at each experiment was relatively small and similar. The zones of clearance observed against E. coli and B. subtilis were determined 23.0 and 16.3 mm, respectively. Synthesized AgNPs using of F.J. Extract as a reducing agent against E. coli was much higher than other studies such as Pomegranate fruit seeds (2.2 mm) [39], Nico-

tiana tobaccum leaf (4.0 mm) [40], lemon extract (3.0 mm) [41] and Neem leaves (6.0 mm) [42] as reducing and stabilizing agents. The potent antibacterial properties of AgNPs may be attributed to the released Ag ions, which could have interaction with microorganisms by means of their attaching to the surface of the cell membranes of bacteria and penetrating into the bacterial cells. In the bacterial cells, AgNPs could interact with sulfur- and phosphorus-containing compounds like DNA of bacterial to give rise to the deadly impairment of them [43].

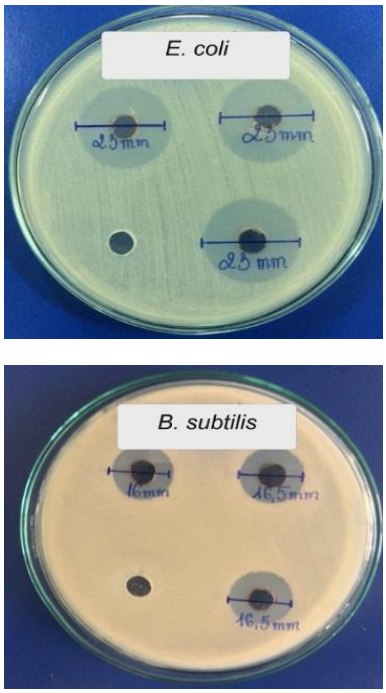


Fig. 7: The Diameter of the Zone Observed Against E. Coli. and B. Subtilis of AgNPs Sample Synthesized at the Suitable Conditions.

4. Conclusion

AgNPs were synthesized successfully using Fortunella Japonica extract combined with sunlight illumination. The results showed that the AgNPs formation was strongly dependent on the parameters of the synthesis process such as the time, the volume ratio of $AgNO_3$ solution/F.J. Extract, the stirring rate, the concentration of $AgNO_3$ solution and the temperature. The most suitable conditions for the AgNPs synthesis were proposed. The physico-chemical characteristics indicated that by this biosynthesis the obtained AgNPs were spherical in shape with an average size of 15.9 nm. The synthesized silver nanoparticles showed high antibacterial activity against E. coli and B. subtilis with the zones of clearance being 16.3 – 23.0 mm.

The reduction accomplished principally due to the combination of the different components of Fortunella Japonica extract and sunlight illumination played the pivotal role in AgNPs formation. The use of Fortunella Japonica extract as a combined reducing and stabilizing agent is one of the most efficient and promising methods in the preparation of AgNPs. It is a green, high yield, fast and low cost approach.

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