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ULTRASOUND-ASSISTED IN THE SYNTHESIS OF SILVER NANOPARTICLES USING SODIUM ALGINATE MEDIATED BY GREEN METHOD

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Silver nanoparticles (Ag-NPs) have been successfully synthesized using ultrasound irradiation in the sodium alginate media. $AgNO_3$ and ultrasound irradiation have been used as silver precursor and physical reducing agent to accelerate the synthesis of Ag-NPs. The presence of Ag-NPs can be detected from the changing color of the suspensions. The silver ion reduction was confirmed through the surface plasmon resonance absorption at around 446 nm. The spherical shape and an average diameter of 24.59 nm were observed by using Transmission Electron Microscopy. The XRD pattern was assigned that the sodium alginate/Ag-NPs is crystalline in nature with fcc planes. The FT-IR spectra shows that the Ag-NPs do not appear many different with sodium alginate due to van der Waal forces. Therefore, this Ag-NPs using sodium alginate can be an alternative in the metal nanoparticles synthesis due to green and speedy method. Moreover, these nanoparticles can apply in many applications such as anti-microbial and sensor devices.

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1. Introduction

Silver nanoparticles (Ag-NPs) have been received high attention because of their different properties than other metals [1, 2]. Indeed, the Ag-NPs have been researched and applied to many products especially for antimicrobial activity, biomedical science [3-5] and sensitive sensor devices [6]. The applications of Ag-NPs grown year by year therefore the productions also will be raised on the future.

The synthesis of Ag-NPs can be conducted by physicochemical [7], lots of the materials used in these synthesis have potentially hazardous. In consequence, the eco-friendly and safe method is needed in the synthesis of Ag-NPs. Green method by using plant-mediated can be an alternative method due to natural sources. In addition, plant-mediated usually needs more time like our team research using marine seaweed until 720 min [8]; in other conditions it can be until 36 hours [9, 10] for the synthesis of Ag-NPs. This reason is due to the weak chemical reaction rate from the plant-mediated stabilizer. Therefore, not only plant-mediated is the important media but also time synthesis is another part which is important as well. The plant-mediated media and short time synthesis are better combination in the synthesis of Ag-NPs.

Ultrasonic radiation is one of the famous irradiation method for accelerating various organic reaction [11-13] producing nanoparticles such as Ag-NPs due to nontoxic, environmental friendly and simple. One of the rapid techniques for the synthesis of metal nanoparticles is ultrasound irradiation due to high effect in temperature and pressure. This extreme condition from

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ultrasound irradiation can produce reactive free radical species and it will be followed in producing of metal nanoparticle in short time [14].

Sodium alginate is a terrestrial plant from marine algae which is abundant in tropical climate like India, Malaysia and Indonesia [15]. This marine algae is a natural polymer that composed as an anionic copolymer containing of α-L-guluronate and β-D-mannuronate [16]. Sodium alginate usually uses for bioengineering and pharmaceutical industries due to low toxicity [17], therefore this material can be used also as an alternative media in the synthesis of Ag-NPs. Yang and Pan have been successfully synthesized Ag-NPs using sodium alginate as a reducing and stabilizing agent however it needed much time around 6-12 hours [18]. This condition has made a motivation to produce a green and speedy method to synthesis of Ag-NPs using natural stabilizer and ultrasound irradiation.

In this paper, the synthesis of sodium alginate/Ag-NPs was successfully synthesized under ultrasound irradiation. This green method has been produced Ag-NPs in short time with good distribution. Sodium alginate/Ag-NPs has been characterized to study the silver reduction, morphology, crystallinity and biomolecules.

2. Materials and Methods

2.1 Chemicals

Silver nitrate ($AgNO_3$) was used as the source of Ag ions that obtained from Bendosen 99.89% (C0721-2284551). Sodium alginate is a marine algae as the natural stabilizer was purchased from Acros Organics Chemicals, UK. Deionized water was used in all experiments. All chemicals were used as received without further purification.

2.2 Synthesis of silver nanoparticles

10 mM silver nitrate solution was mixed with 0.3 w% of sodium alginate in 400 mL, it was stirred until the solution dissolved. The solution of sodium alginate/$AgNO_3$ was irradiated until 240 min under ultrasound equipment that was carried out with the Ti-probe of ultrasonic liquid processor (Hielscer UP-200S-RN, Germany). This solution was exposed at amplitude of 70% and cycle of 0.5 Hz in the room temperature. A control reaction was also held without ultrasound irradiation.

2.3 Characterization of silver nanoparticles

The suspension was characterized after irradiation 240 min with UV-visible (UV-Vis) spectrophotometer (UV-1800 Shimadzu) at wavelength of 300-800 nm. Transmission Electron Microscope (TEM) (Tecnai G2 F20 series) was applied to study the morphology of sodium alginate/Ag-NPs. X-ray Diffraction (XRD) patterns were recorded on a powder X-ray diffractometer in the 2-θ range of $5\text{-}80^0$. Fourier transform infrared (FT-IR) spectroscopy was recorded on spectrometer by ATR method and the spectra were scanned in the range of 600-4000 cm^{-1}.

3. Results and Discussion

The reduction of $AgNO_3$ was seen from color change (clear to the brown color) of the solution after 240 min irradiation. Color intensity of the solution increased directly after time to time irradiation which is shown in Fig. 1. Ultrasound irradiation as the main reduction agent in this reaction has given strong collapse solution of high temperature and pressure.

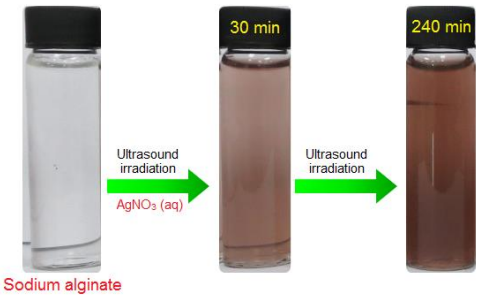

Fig. 1. Photographs of sodium alginate before irradiation and sodium alginate/Ag-NPs after irradiation (30 and 240 min).

3.1 UV-visible Spectroscopy Study

The high temperature and pressure have effected in the chemical structure of the silver nitrate and sodium alginate. Thus, the formation of free radical had been produced after irradiation and grew as Ag^0 and finally it changed to Ag-NPs [8]. The control ($AgNO_3$ and sodium alginate) without ultrasound irradiation showed no color change; therefore the presence of ultrasound irradiation has given important effect in the producing of Ag-NPs.

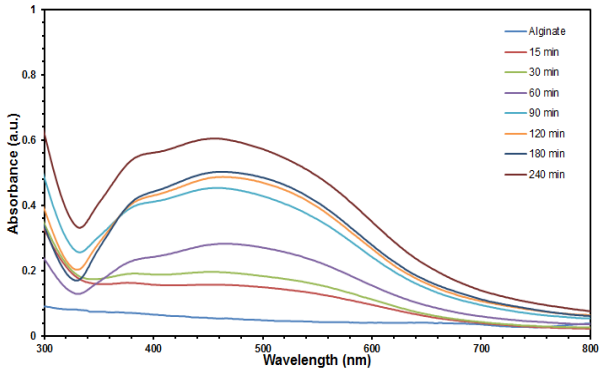

Fig. 2.The UV-Vis absorption spectra of synthesizing Ag-NPs on sodium alginate under varying times of ultrasound irradiation.

Absorbance band of all suspensions in Fig. 2 showed the peak around 446-468 nm which is corresponded of Ag-NPs. These peaks are in the range of 400-500 nm which is relevant to coherent oscillation surface plasmon resonance (SPR) of the Ag-NPs after ultrasound irradiation [19]. In addition, this condition is also similar to the SPR vibrations of sodium alginate/Ag-NPs which prepared by Microwave irradiation [20]. The absorption band of suspension increased to a higher wavelength and the peak shifted to the left implying the formation of more and smaller Ag-NPs (blue-shift). Ag^+ ions were reduced to Ag^0 by ultrasound irradiation as the main reducing agent [14]. With higher rate and time reaction from ultrasound irradiation, more of Ag-NPs produced with the darker color of these suspensions.

3.2 Transmission Electron Microscopy Study

The morphology of the green synthesis of sodium alginate/Ag-NPs using ultrasound irradiation was further confirmed by the TEM images which shown in Fig. 3 and Fig. 4. The images depict that the sodium alginate/Ag-NPs (Fig. 4) are spherical in shape, with the particle distribution between 3 to 57 nm and an average diameter of 24.59 nm. This size is almost same with Balavandy *et al.* research which they had been prepared Ag-NPs using sodium alginate also however by adding NaOH [21]. On the contrary, in the Fig. 3 shows the surface of sodium alginate

as the media in this synthesis. Therefore, these TEM images indicate of the good distribution of Ag-NPs and this green synthesis can be a new alternative in the synthesis of Ag-NPs [22].

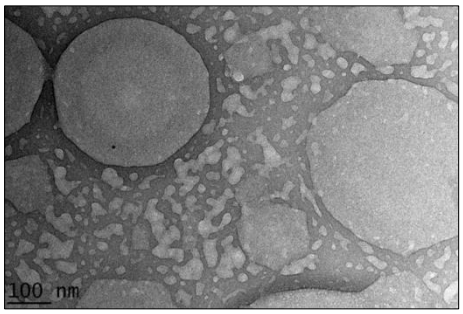

Fig. 3. TEM image of sodium alginate before ultrasound irradiation.

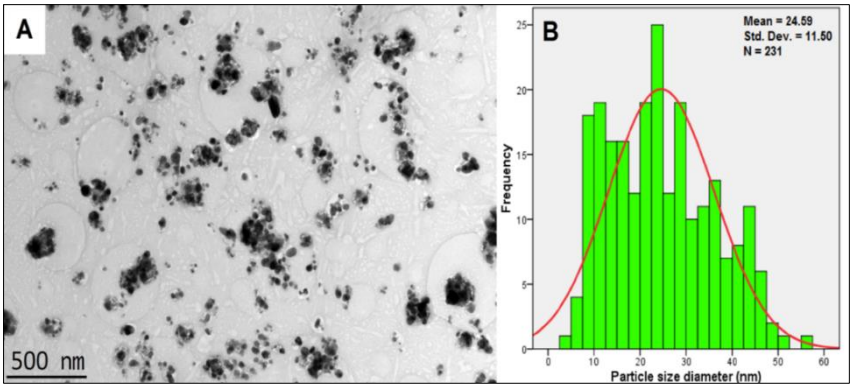

Fig. 4. TEM image of sodium alginate/Ag-NPs after irradiation (A) and its histogram (B).

3.3 X-ray Diffraction Analysis

The XRD pattern analysis in Fig. 5 indicates that the synthesis of Ag-NPs on sodium alginate using ultrasound irradiation are crystalline and the four distinct diffraction peaks on (111), (200), (220) and (311) could be assigned at 38.26º, 44.47º, 64.71º and 77.74º, respectively. These Ag-NPs crystalline planes are face-centered cubic (ffc) and in agreement with the database of ICDD/ICSD from X'Pert HighScore Plus (ICSD Silver 01-087-0719). However, the crystallinity of sodium alginate has been given in broad reflection at around 14.11º [20, 23]. This XRD pattern clearly illustrates that the sodium alginate/Ag-NPs formed in this synthesis are crystalline in nature [24].

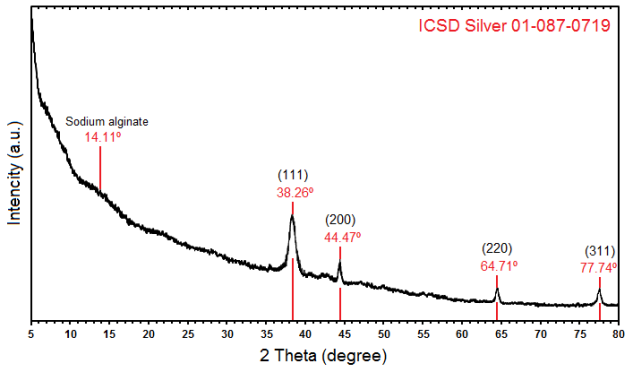

Fig. 5.XRD pattern of synthesized sodium alginate/Ag-NPs after 240 min irradiation.

3.4 Fourier Transform Infrared Study

Infrared spectroscopy was carried out to confirm the chemical structure of the sodium alginate and after 240 min ultrasound irradiation which shown in Fig. 6. The Fig. 6a shows the characteristic absorption bands of the sodium alginate as the media, the peak at 1025.72 cm^{-1} assigned to the stretching vibration of C-O-C group. The absorption band at 1296.98 cm^{-1} noticed for C-O stretch [25]. A peak at 1593.68 cm^{-1} attributed to the asymmetric stretching modes of carboxylate anion; and the band at 3251.99 cm^{-1} corresponded to the stretching of O-H [26]. On the other hand, in Fig. 6b shows that the FT-IR after 240 min ultrasound irradiation. The peak at 1024.81, 1589.05 and 3256.46 cm^{-1} represented for the stretching of C-O-C group, carboxylate anion and O-H group, respectively from the sodium alginate/Ag-NPs. However, no bonding interaction between silver and sodium alginate was observed clearly from this spectra. This phenomenon related with Lin *et al.* who have been reported that the silver may interact with the sodium alginate matrix mainly by van der Waals interaction therefore it cannot show the peak in good intensity [27].

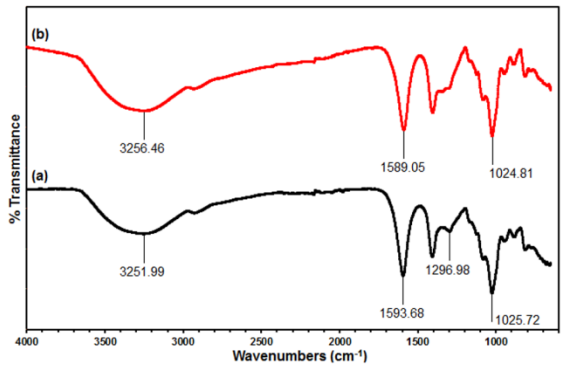

Fig. 6.FT-IR spectra of sodium alginate media (a) and sodium alginate/Ag-NPs 240 min ultrasound irradiation (b)

4. Conclusions

The green and speedy of the synthesized sodium alginate/Ag-NPs under ultrasound irradiation were successfully prepared using ultrasound irradiation method. The UV-visible spectra was characterized that these suspensions have absorption at 446-468 nm which means that it was formed of the Ag-NPs. The TEM images show that the particles shape is in spherical with an average diameter of 24.59 nm. The XRD pattern shows the crystalline of the Ag-NPs with fcc planes and the FT-IR has been shown that the Ag-NPs and sodium alginate have interaction by the van der Waals forces. In addition, this sodium alginate/Ag-NPs have also good stability and it can use in many applications. Moreover, this method is easy to scale up in the production of Ag-NPs.

Acknowledgments

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