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GREEN SYNTHESIS OF SILVER NANOPARTICLES USING POLYSACCHARIDE EXTRACTED FROM *LAURENCIA OBTUSA* ALGAE

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ABSTRACT

The aim of this work was to synthesis of silver nanoparticles (AgNPs) using water soluble Polysaccharide extracted from marine algae (*L. obtusa*) as reducing agents for silver ions as well as stabilizing agents for the synthesized AgNPs. The formation of silver nanoparticles was confirmed by Surface Plasmon Resonance (SPR) at 350 to 550 mm, by using fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The maximum absorption peaks are in the range of 400-420 nm. The particles were spherical in shape in the range of 4-10 nm.

1. INTRODUCTION

Many researchers have widely used noble nanoparticles in various technological applications because of their unique properties. The noble metal nanoparticles, in general, and silver nanoparticles (AgNPs), in particular, are known for their versatile applications in medical **[Becker, 1999]**, food processing **[Tankhiwale and Bajpai, 2010]** and textile industries **[Duran *et al.*, 2010]** as well as in consumer goods **[Jiang *et al.*, 2004; Rai *et al.*, 2009].**

A large number of physical, chemical, biological, and hybrid methods are available to synthesize different types of nanoparticles **[Liu *et al.*, 2001].** The nanoparticles formed using each method show specific properties. However, biosynthesis of metal nanoparticles by plant extracts is a green modern alternative for their production **[Shameli *et al.*, 2012].** Green synthesis of nanoparticles makes use of environmentally friendly, non-toxic and safe reagents **[Salam *et al.*, 2012].**

The main objectives of the present study are: (i) to synthesize AgNPs using polysaccharide of *L. obtusa* algae (ii) to characterize AgNPs using UV–Vis spectroscopy, FT-IR, XRD and TEM**.**

2. EXPERIMENTAL

2.1. Material

The red algal used throughout the present work were collected from the beach of Red Sea, Alexandria, Egypt. These were found attached to

the rocky belt existed about 15 meters from the sea-shore and at about two meters depth and were Freshly collected algal species were repeatedly washed with sea-water followed by tap-water to remove sand, salt and any extraneous matters. The cleaned samples were shade dried and homogenized to fine powder and kept for further treatments.

2.2. Extraction of polysaccharide

The defatted algae powder was successively percolated with hot water till complete exhaustion. The extract was concentrated to about 50 ml under reduced pressure using rotary evaporator device. Polysaccharide were precipitated using Absolute ethanol (250 ml) which added drop-wise with stirring till complete precipitation occurred. The residue obtained was washed with absolute ethanol then weighed and saved for further study.

2.3. Synthesis of silver nanoparticles (AgNPs)

AgNPs were synthesized from silver nitrate using polysaccharide of *L. obtusa* as reducing and stabilizing agent. 30 mg of the extract residue dissolve 95 ml of distilled water and adjust pH =12 using sodium Hydroxide and complete volume to 99 ml with distilled water then put it on magnetic stirrer hot plate at temperature 90 °C and added 1ml of (0.1M) $AgNO_3$ solution were added to the reaction mixture then the reaction mixture was kept at different durations (15, 30, 45, and 60min).

2.3.1. Ultraviolet-visible (UV-vis) spectroscopy analysis

Change in color was visually observed in the silver nitrate solution incubated with polysaccharide of *L. obtusa*. The reduction of silver ions was monitored from 300 to 800 nm by Jasco V-670 UV-V after 5-fold diluting the sample with distilled water against distilled extract as blank at a resolution of 1 nm.

2.3.2. Fourier transform infrared (FTIR) spectroscopy analysis

For FTIR spectroscopy measurements, the bio-synthesized AgNPs were purified, dried and palleted with potassium bromide in the ratio of 1:100. FTIR spectrum of samples was recorded on (JASCO FT-IR 4100 instrument, Japan). All measurements were carried out in the range of 400– 4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.3.3. Transmission electron microscopy (TEM).

The size and morphology of the synthesized AgNPs were determined by high resolution transmission electron microscopy (TEM, JEOL JEM 2100, Japan). The sample for TEM studies was prepared as follows: 1 ml of the reaction mixture containing AgNPs was diluted to 5 ml, sonicated using ultrasonic bath and a

drop of it was placed on a Cu grid with ultrathin Cu on holey C-film and it was allowed to dry in a vacuum. The instrument was operated with an acceleration voltage of 200 kV.

2.3.4. X-ray diffraction (XRD)

The synthesized nanoparticles were examined by XRD (6000 - shimadzu - Japan). The powdered AgNPs was stacked in the cubes of XRD and the result was taken in the XRD equipment at this condition: X-ray tube target, copper potassium alpha radiation; voltage, 40.0 (kV); current, 30.0 (mA). Divergence slit, 1.00000 (deg); scatter slit, 0.00000 (deg); receiving slit, 0.30000(mm). Scanning drive axis, Theta-2Theta, scan range, 4.0000 - 90.0000 (deg); scan mode, continuous scan; scan speed, 8.0000 (deg/min); sampling pitch, 0.0200 (deg).

3. RESULTS AND DISCUSSION

3.1. Visible observation

The Colour of *L. obtusa* Polysaccharide before addition of $AgNO_3$ solution is yellow, after its treatment with $AgNO_3$ solution, the colour changes to reddish-brown which indicated the formation of AgNPs (**Fig. 1**). This colour change is due to surface Plasmon excitation of the formed nanoparticles which affects the optical property.

Figure 1: Colour change before and after addition of $AgNO_3$ solution. Where (A) the polysaccharide of *L. obtusa* algae (B) the biosynthesized AgNPs

3.2. UV-vis spectra analysis

UV-Vis absorption spectroscopy is an important technique to determine the formation and stabilization of biosynthesized AgNPs in aqueous solution. AgNPs were synthesized at optimized

conditions of temperature 90°C and pH=12 meanwhile the time was varied (15, 30, 45 and 60 min), the formation of silver nanoparticles was monitored by UV spectrophotometer. The maximum absorption peaks are in the range of 400-420 nm which is a typical plasmon band of silver metal **[Durán *et al.*, 2005; Ahmad *et al.*, 2003]**, suggesting the formation of silver nanoparticles (**Fig. 2**).

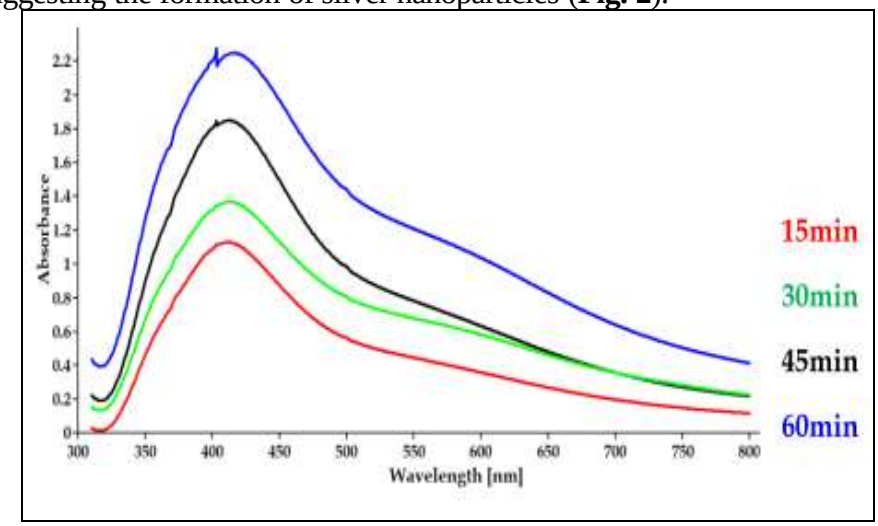

Figure 2: UV-Visible absorption spectra of biosynthesized silver nanoparticles from polysaccharide extract of *L. obtusa* at different times interval, constant pH and temperature.

3.3. FTIR spectroscopy

FTIR study reveals the multi-functionality of *L. obtusa* polysaccharide by identifying the possible functional groups in the biomolecules of this poly saccharides. A FT-IR spectrum of the synthesized AgNPs and polysaccharide by this green method is shown in **Figure 3**. Data of this figure indicate that the polysaccharide manifest absorption peaks at about 3441 were assigned to OH stretching vibration, the peak at 2932 cm-1 corresponds to C-H alkane ,1480 represent –C=C– group. The peak at 1141 cm^{-1} corresponds to C-O stretching vibration. These results were previously proved by Parida et al., 2014; Namvar *et al.*, 2014. As is evident (**Fig. 3**), both FTIR spectra of the Polysaccharide extract and the Polysaccharide extract containing AgNPs have the same trend but the intensity of functional groups present in nanoparticlrs sample is small, and this proves that the different functional groups in the bioactive compounds polyphenols, protein and polysaccharide are consumed for reduction of Ag^{+} to Ag^{0} and stabilization of the biosynthesized AgNPs.

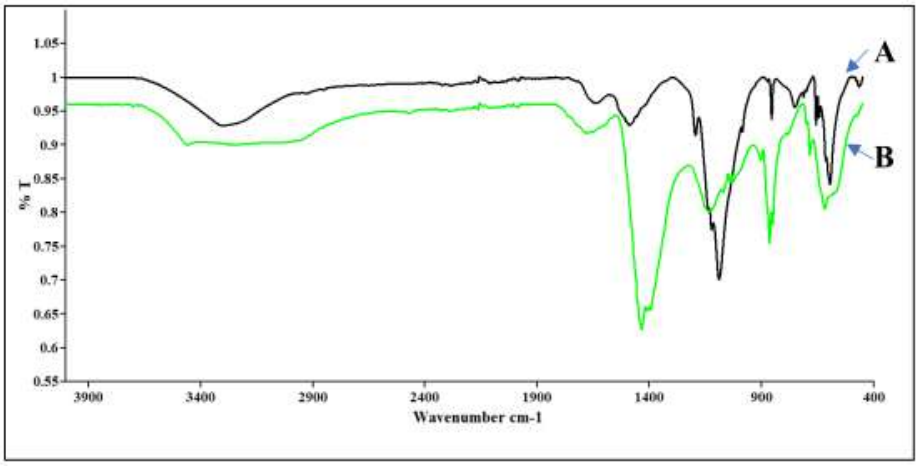

Figure 3. FTIR spectra of (A) Polysaccharide extract of *L. obtusa* algae and (B) biosynthesized AgNPs

3.4. Transmission Electron Microscope (TEM)

TEM provides further insight into the morphology and particle size distribution profile of the AgNPs and revealed a pattern similar to that of the biosynthesized AgNPs characterized by TEM [Bindhu and Umadevi, 2013; Das *et al.,* 2013]. The data obtained from transmission electron-micrograph (Fig. 4) showed distinct shape and size of AgNPs. The particles were spherical in shape in the range of 5-10 nm.

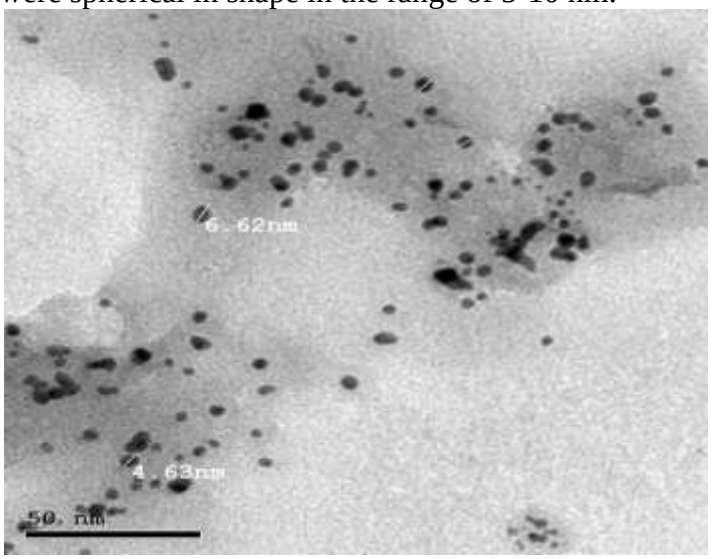

Figure 4. TEM of AgNPs from polysaccharide of *L. obtusa* algae.

3.5. XRD analysis

Analysis through X-ray diffraction was carried out to confirm the crystalline nature of the particles, and the XRD pattern showed numbers of Braggs reflections that may be indexed on the basis of the face centered cubic (fcc) structure of silver. A comparison of our XRD spectrum with the standard confirmed that the silver particles formed in our experiments were in the form of nanocrystals, as evidenced by the peaks at 2θ values of 38, 44.7, and 65, and 77.7 θ, corresponding to (111), (200), (220) and (311), respectively Bragg reflections of silver. The XRD results clearly show that the silver nanoparticles formed by the reduction of Ag^+ ions by the *L. obtusa* polysaccharide are crystalline in nature **[Umoren *et al.*, 2014]**.

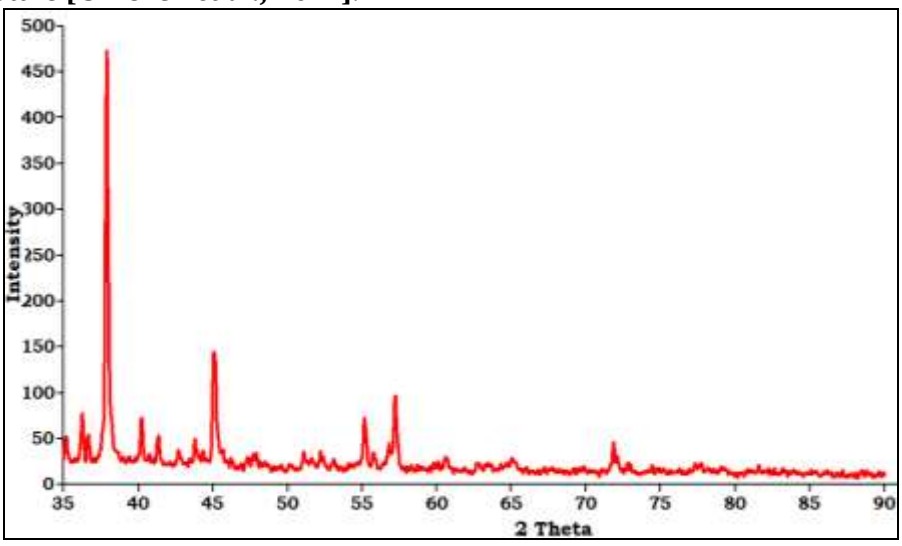

Figure 5 . XRD pattern of AgNPs from Polysaccharide of *L. obtusa* algae .

4. CONCLUSION

Green chemistry approach towards the synthesis of nanoparticles has many advantages such as, ease with which the process can be scaled up and economic viability. We have developed a fast, eco-friendly and convenient method for the synthesis of silver nanoparticles using *L. obtusa* polysaccharide with a diameter range of size 5-10 nm. These particles and spherical. No chemical reagent or surfactant template was required in this method, which consequently enables the bioprocess with the advantage of being environmentally friendly. Color change occurs due to surface plasmon resonance (SPR) during the reaction with the ingredients present in the polysaccharide extract results in the formation of silver nanoparticles which is confirmed by UV–Vis, FT-IR, TEM and XRD.

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التحضير الآخضر لجسيمات الفضة النانو مترية باستخدام السكريات العديدة المستخلصة من طحلب لورانسيا اوبتيوزا

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تهدف هذه الدراسة الي تحضير جسيمات فضة نانومتريه وذلك باستخدام السكريات العديدة المستخلصة من الطحالب البحرية كعوامل مختزله لأيون الفضة كما استخدمت في نفس الوقت ايضا كعوامل مثبته لجسيمات الفضة النانوية التي تم تحضيرها. وقد تم التأكد من تكوين جزيئات الفضة النانو مترية عن طريق بعض التحاليل الطيفية باستخدام مطياف الأشعة فوق البنفسجية–المرئية (UV–vis.) عند طول موجي من ٣٠٠–٨٠٠ نانومتر، مطياف الاشعة تحت الحمراء (FTIR) وطاقة التشتت لطيف الاشعة السينية(XRD) والميكروسكوب الالكتروني النافذ (TEM) – وقد أظهرت هذه الجسيمات أقصى قمة امتصاص عند ٤٠٠–٤٢٠ نانومتر وكانت دائرية الشكل ويتراوح حجمها من٤– ١٠ نانومتر.