www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2015.5792 Published online by the VBRI press in 2015

Noval approach for synthesis sulfur (S-NPs) nanoparticles using *Albizia julibrissin* fruits extract

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Received: 05 January 2015 Revised: 02 March 2015 and Accepted: 03 March 2015

ABSTRACT

Sulfur nanoparticles have been successfully prepared from sodium thiosulfate in the presence of *Albizia julibrissin* fruits extract at room temperature. The resulting sulfur nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). XRD characterizes the final product as highly crystalline sulfur, exhibited high purity, spherical shape with average particle size of about 20 nm, and particle size distribution in range 10 nm to 100 nm. The particle size of nanoparticles could be controlled by tuning the amount of *Albizia julibrissin* fruits extract. FT-IR analysis of S-NPs indicated a new chemistry linkage on the surface of sulfur nanoparticles. This suggests that *Albizia julibrissin* fruits extract can bind to sulfur nanoparticles through carbonyl of the amino acid residues in the protein of the extracts, therefore acting as stabilizer and dispersing agent for synthesized sulfur nanoparticles. This research provides a greener and more environment-friendly synthetic method for the production of sulfur nanoparticles for antibacterial and antifungal activities. Copyright © 2015 VBRI Press.

Keywords: Green synthesis; sulfur nanoparticles; *Albizia julibrissin* fruits extract; characterization.

Akl M. Awwad is professor and senior scientist at Royal Scientific Society, Jordan. He received his Ph.D. degree in Physical Chemistry from University of Strathclyde, Glasgow, U.K. He has published over 100 peer reviewed articles, 7 books and holds 5 patents. His current researchinterests include the green synthesis of the advanced Nano materials, chemical thermodynamics and water treatment.

Introduction

Nanosize sulfur particles have many important applications like in pharmaceuticals, synthesis of nano composites for lithium batteries; modification of carbon nano tubes, fertilizers, phosphate fertilizers, antimicrobial agents, In agricultural field, sulfur is used as a fungicide against the apple scab disease, in conventional culture of grapes, strawberry, many vegetables, and several other crops. Sulfur is one of the oldest pesticides used in agriculture and it has a good efficiency against a wide range of powdery mildew diseases as well as black spot. Few researchers reported different methods for synthesis sulfur nanoparticles such as electrochemical method [**1**], water-in-oil microemulsion [**2, 3**], eggshell membrane template [**4**], heating sublimed sulfur and Polyethylene glycol-200 [**5**], chemical precipitation **[6]**, supersaturated solvent method **[7]**, surfactant assisted route **[8, 9]**, liquid phase precipitation method [**10**], H_2S reduction by iron chelates in W/O microemulsion [**11**], and ultrasonic treatment of sulfur-cystine solution [**12**]. These methods have many disadvantages due to the difficulty of scale up of the process, separation and purification of nanoparticles from the microemulsion (oil, surfactant, co-surfactant and aqueous phase, and consuming huge amount of surfactant.

Alibizia julibrissin is a small deciduous tree growing to 5–16 m tall, with a broad crown of level or arching branches. The bark is dark greenish grey in color and striped vertically as it gets older. The leaves are bipinnate, 20–45 cm long and 12–25 cm broad, divided into 6–12 pairs of pinnae, each with 20–30 pairs of leaflets; the leaflets are oblong, 1–1.5 cm long and 2–4 cm broad. The flowers are produced throughout the summer in dense inflorescences, the individual flowers with small calyx and corolla and a tight cluster of stamens 2–3 cm long, white or pink with a white base, looking like silky threads. The fruits are a flat brown pod 10–20 cm long and 2–2.5 cm broad, containing several seeds inside.

Realizing the importance of sulfur nanoparticles in different applications, the development of an easy and green method is highly essential for nanosize sulfur particles. To the best of our knowledge, biological approach using fruits aqueous extract of *Albizia julibrissin* has been used for the first time as capping and stabilizing agent for the synthesis of sulfur nanoparticles.

Experimental

Materials

Sodium thiosulfate, $Na_2S_2O_3$ (99%, Alfa Aesar, Germany) and hydrochloric acid, HCl (37%, Merck, Darmstadt, Germany) were used as received without any further purification. Sterile distilled water was used with conductivity 1 µS/cm.

Preparation of plant leaf extract

Albizia julibrissin fruits were washed several times with distilled water to remove the dust particles and then dried to remove the residual moisture. The dried fruits were grounded to a fine powder in a grinding mill (Retsch RM 100, Thermo Fisher Scientific, NH, USA) and sieved to get size fraction < 44 µm. 20 gram of *Albizia julibrissin* fruits boiled in 500 ml glass beaker along with 400 ml of sterile distilled water for 10 minutes. After boiling, yellow color solution is formed and allowed to cool at room temperature. The aqueous extract of fruits was separated by filtration with Whatman No.1 filter paper and then centrifuged at 1200 rpm for 5 minutes to remove heavy biomaterials. The aqueous extract was stored at room temperature to be used for green synthesis of sulfur nanoparticles. **(Fig. 1)** shows a photograph of *Albizia julibrissin* fruits and their aqueous extract.

Synthesis of sulfur nanoparticles

In a typical reaction synthesis, sulfur nanoparticles (SNPs) synthesized as follows: an appropriate amount of sodium thiosulfate, $Na_2S_2O_3$ dissolved in 50 ml of *Albizia julibrissin* fruits extract under stirring for 5 minutes at room temperature and then diluted to 100 ml by sterile distilled water. Afterwards hydrochloric acid was added drop by drop with mild stirring for allowing the sulfur precipitations uniformly.

In *Albizia julibrissin* fruits extract and acidic solution, sodium thiosulfate ($Na_2S_2O_3$) undergoes through a disproportionation reaction to sulfur and sulfonic acid according to:

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + S + SO_2 + H_2O$$

The suspended sulfur particles obtained were separated by centrifugation at 1000 rpm for 5 minutes and then repeatedly washed with sterile distilled water to remove any biological materials. The sulfur nanoparticles after purification were dried in a vacuum at 80^{o}C for 2 h. The product was light yellow powder used for SEM, XRD, and FTIR analysis.

Fig. 1. Photograph of *Albizia julibrissin* fruits and their aqueous extract

Characterization techniques

Scanning electron microscopy (SEM) analysis of synthesized sulfur nanoparticles was done using a Quanta FEI 450 SEM machine. Powder X-ray diffraction was performed using a X-ray diffractometer, Shimadzu, XRD-6000 with CuKα radiation λ = 1.5405 Å over a wide range of Bragg angles ($3^o \leq 2\theta \leq 80^o$). Fourier transform infrared spectroscopic measurements were done using Shimadzu, IR-Prestige-21 spectrophotometer.

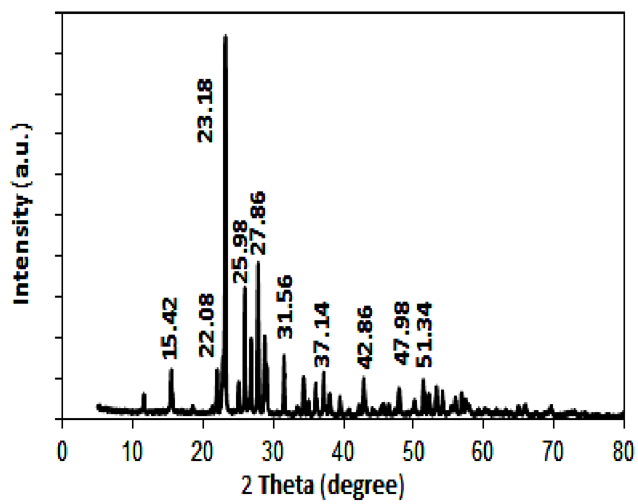

Fig.2. XRD pattern of the synthesized sulfur nanoparticles.

Results and discussion

The XRD analysis of sulfur nanoparticles synthesized is illustrated in Fig. 2. The 2θ peaks at 15.42^o, 22.08^o, 23.18^o, 25.98^o, 27.86^o, 31.56^o, 37.14^o, 42.86^o, 47.98^o, and 51.34^o are attributed to the crystal planes of sulfur at 113, 220, 222, 040, 313, 044, 422, 319, 515, and 266 respectively. Synthesized sulfur nanoparticles are well-crystalline, the position and the relative intensity of the diffraction peaks match well with the standard monoclinic phase sulfur diffraction pattern (JCPDS 4: 8-0247). There is no other phase found, which means that phase pure monoclinic sulfur was prepared under these experimental conditions.

The average particle sizes of the synthesized SNPs were calculated using Debye-Scherrer formula [**13, 14**]:

$D = K \lambda / \beta \cos \theta$

Where, D is the mean diameter of nanoparticles, β is the full width at half-maximum value of XRD diffraction lines, λ is the wavelength of X-ray radiation source 0.15405 nm, θ is the half diffraction angle–Bragg angle and K is the Scherrer constant with value from 0.9 to 1. The average crystallite size of the synthesized sulfur nanoparticles was of about 40 nm. The unassigned peaks in XRD pattern, (**Fig. 2)** are thought to be related to crystalline and amorphous organic phases of extracts. Different samples of SNPs were prepared using different amounts of *Albizia julibrissin* fruits extract and sodium thiosulfate. The obtained results showed that the average particle size of the synthesized sulfur nanoparticles decreased with increasing *Albizia julibrissin* fruits extract in the reaction mixture.

It was observed that the sulfur nanoparticles synthesized are extremely stable for nearly two weeks with very little aggregation of sulfur particles in the solution by this method. The surface-modified sulfur nanoparticles coated with biomaterials of *Albizia julibrissin* fruits showed good long-term stability compared to the bare sulfur particles in aqueous solution.

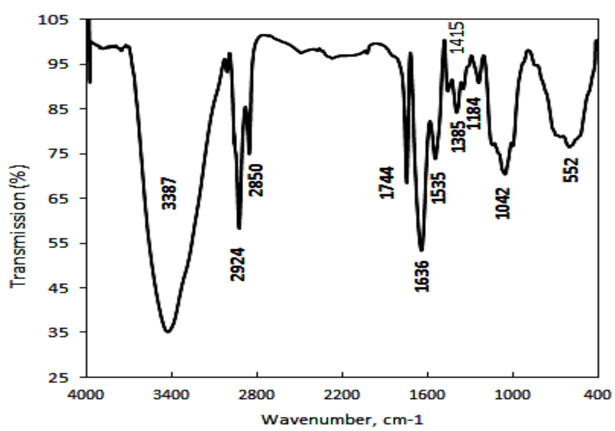

Fig. 3. FT-IR of *Albizia julibrissin* fruits extract.

FT-IR analysis was carried out to identify the possible biomolecules responsible for the capping and stabilization of sulfur nanoparticles synthesized by *Albizia julibrissin* fruits extract. The powder extract display a number of absorption peaks, reflecting their complex nature. FT-IR spectra of *Albizia julibrissin* fruits extract is shown in **(Fig. 3).** A strong absorption band at 3387 cm^{-1} could be ascribed to the stretching absorption band of amino (-NH) and hydroxyl (–OH) stretching H-bonded alcohols and phenols. The strong absorption peaks at 2924 $cm^{-1}$and 2850 cm^{-1}could be assigned to the asymmetric and symmetric stretching of –CH, $–CH_2$ and $-CH_3$ functional groups of aliphatic. The peak appears at 1744 cm^{-1} is due the presence of carbonyl stretching vibration of the acid groups of fatty acids present in extracts. The band at 1636 cm^{-1} is characteristic of amide carbonyl group in amide I and amide II. The amide band I is assigned to the stretch mode of the carbonyl group coupled to the amide linkage while the amide II band arises as a result of the N-H stretching modes of vibration in the amide linkage. The peak at 1535 cm^{-1} could be attributed to N-O stretching in nitro compounds. The peak at 1415 cm^{-1} corresponds to stretching of carboxyl group. C-N stretch of aromatic amines and carboxylic acids give rise to band at 1385 cm^{-1}. The peak at 1184 cm^{-1} can be due to C-O vibrations of alcohols, phenols and C-N stretching vibrations of amine. The band at 1042 cm^{-1} assigned to the C-O stretching vibrations of alcohols C-N stretching vibrations of amine. Additional peaks at 552 cm^{-1} can be assigned to bending modes of aromatic compounds.

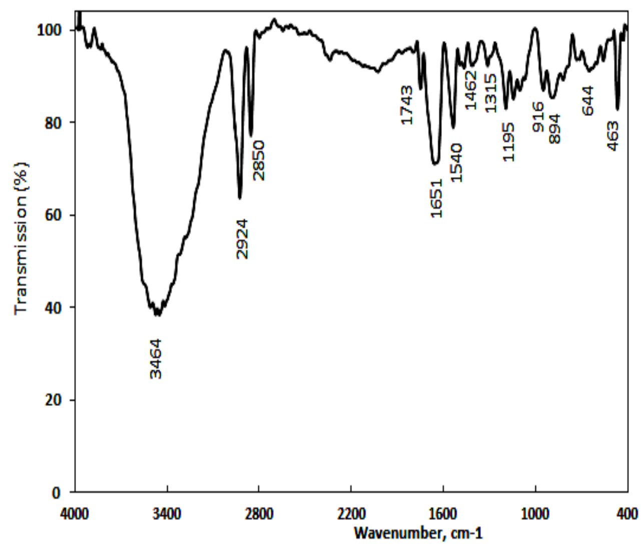

Fig. 4. FT-IR of synthesized sulfur nanoparticles using *Albizia julibrissin* fruits extract.

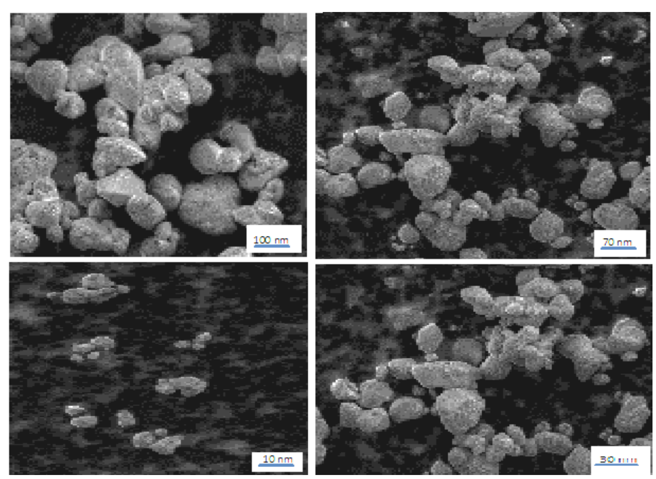

Fig. 5. SEM images of biosynthesized sulfur nanoparticles.

The FT-IR spectrum of the synthesized sulfur nanoparticles is shown in **(Fig. 4).** The FT-IR spectrum of sulfur nanoparticles indicated presence of all characteristic peaks of monoclinic sulfur compared with standard sulfur. All observed characteristic peaks of *Albizia julibrissin fruits* extract observed in FT-IR of sulfur nanoparticles, with shifting in the wavenumber, **(Fig. 4)**. The FT-IR spectrum of the synthesized sulfur nanoparticles shows all characteristic peaks of α-sulfur at 463 cm^{-1}, 644 cm^{-1}, 894 cm^{-1}, 916 cm^{-1}, when compared with standard α-sulfur. FT-

IR spectra of SNPs indicate a new chemistry linkage on the surface of sulfur nanoparticles. This suggests that *Albizia julibrissin* fruits extract can bind to sulfur nanoparticles through carbonyl of the amino acid residues in the protein of the extracts, therefore acting as stabilizer and dispersing agent for synthesized sulfur nanoparticles and prevent agglomeration of sulfur nanoparticles.

The SEM images of the sulfur nanoparticles synthesized in *Albizia julibrissin* fruits extract is shown in **(Fig. 5)**. These images indicate that nanoparticles prepared via suggested method are almost spherical in shape and uniform size. The agglomeration of sulfur crystals was avoided during preparation as evidenced by the SEM data.

Conclusion

In this study, a novel green synthesis method for the preparation of sulfur nanoparticles from thiosulfate ion in the presence *Albizia julibrissin* fruits extract was developed. The particle size of sulfur nanoparticles can be controlled from 10 nm to 100 nm by adjusting the reaction parameters including the initial sodium thiosulfate concentration and the quantity of fruits extract. The synthesized sulfur nanoparticles were characterized by XRD, FT-IR, and SEM techniques. The obtained results showed that as-prepared monoclinic sulfur nanoparticles with average crystallite size about 20 nm had spherical shape. The explored ecofriendly, high efficient sulfur nanoparticles synthesized using *Albizia julibrissin* fruits extract are expected to have more extensive applications in biomedical and agricultural fields as well as for large scale up production.

Acknowledgements

This work was supported by Funding Program No. 47/2014 Abdul Hameed Shoman Fund for Support of Scientific Research, Jordan Authors thank the Royal Scuientific Society and the University of Jordan for providing all facilities to carry out this research work.

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