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Green synthesis, characterization of silver sulfide nanoparticles and antibacterial activity evaluation

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ABSTRACT

This research work presents a facile and green route for synthesis silver sulfide (Ag_2SNPs) nanoparticles from silver nitrate ($AgNO_3$) and sodium sulfide nonahydrate ($Na_2S.9H_2O$) in the presence of *rosemary* leaves aqueous extract at ambient temperature (27 °C). Structural and morphological properties of Ag_2SNPs nanoparticles were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The surface Plasmon resonance for Ag_2SNPs was obtained around 355 nm. Ag_2SNPs was spherical in shape with an effective diameter size of 14 nm. Our novel approach represents a promising and effective method to large scale synthesis of eco-friendly antibacterial activity silver sulfide nanoparticles.

Capsule Summary: A green and fast-route for the synthesis of silver sulfide nanoparticles using rosemary leaves at room temperature was reported and NPs showed promising antimicrobial activity.

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INTRODUCTION

Silver sulfide (Ag_2S) nanomaterial is an important material used in solar cell batteries, thermoelectric sensors, infrared detectors, photovoltaic cells, conductors and antimicrobial activity (Bruhwiler et al., 2002; Fakhri et al., 2015; Kumari et al., 2014). Several methods have been reported for synthesis silver sulfide nanoparticles (Ag_2SNPs) such a template-based method at room temperature and ambient pressure (Xiao et al., 2002), water-in-CO_2 microemulsions (Liu et al., 2004), a microwave-assisted template-free method (Su et al., 2016), modified homogenus precipitation route (Xaba et al., 2017), sonochemical synthesis (Du et al., 2007), hydrothermal method (Yu et al., 2012), by multi-solvent thermal decomposition method (Sahib et al., 2017), *via* a one-pot method in ethylene glycol with 3-mercaptopropionic acid (Kubie et al., 2011), modified chemical bath deposition technique (Jadhav et al., 2013), synthesis of silver sulfide nanoparticles capped with either chitosan, green tea, *Combtretum molle* or black wattle extracts (Sibiya and Moloto, 2018), conversion of silver thiolate polymers with sodium sulfide in a dual-phase solution preparation (Schaaff and Rodinone, 2003), metal-reducing bacterium *Shewanella oneidensis* MR-1 (Debabova et al., 2013), chemical method (Zhao and Song, 2014), multi-solvent thermal decomposition method (Khaleelullah et al., 2017), sonochemistry method (Kang et al., 2018) hydrochemical bath deposition from aqueous solutions (Sadovnikov et al., 2016) and nucleation process (León-Velázquez et al., 2010). These methods and routes for synthesis silver sulfide nanoparticles have many disadvantages due to toxic chemicals used and waste products, which create a problem to environment, also high energy consumption, difficulty of large-scale of processes and wasteful purifications (Cárdenas Riojas et al., 2019; Deshmukh et al., 2019; Fletcher et al., 2019; Huang et al., 2019; Maharubin et al., 2019; Sadovnikov, 2019). Recently, green approach in synthesis of nanomaterials has given significant attention to protect environment from hazardous wastes. Herein, the objective of the present research work was to synthesize silver sulfide nanoparticles by green route using *rosemary* (*Rosmarinus officinalis*) leaves aqueous extract at room temperature and studying antibacterial activity.

MATERIAL AND METHODS

Fig. 1: Rosemary leaves and their aqueous extract

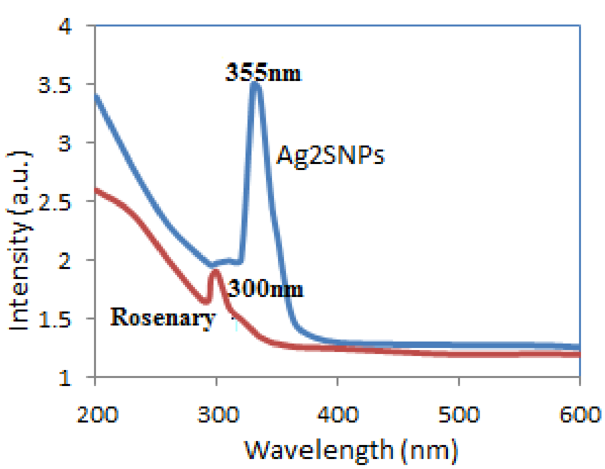

Fig. 2: UV-vis absorption spectra of silver sulfide

Reagents and chemicals

Silver nitrate ($AgNO_3$, 99%), sodium sulfide nonahydrate ($Na_2S.9H_2O$, 99.99%) were purchased from Sigma-Aldrich. Ethanol was purchased from Merck (Darmstadt-Germany). Ultrapure water from with a resistivity of 18.2 MΩ/cm was used for the preparation of solutions. *Rosemary* plant leaves were collected from different gardens at the Royal Scientific Society, Amman City, Jordan.

Rosemary leaves aqueous extract

Rosemary leaves were dried in our laboratory for one week at room temperature and then crushed to small pieces. 20g of rosemary was mixed with 400 ml deionized-water and boiled for 10m. Afterwards, the aqueous extract was obtained by filtration on Whitman filter paper No. 1 and kept in a stoppered bottle for further experimental work (Fig. 1).

Green synthesis of silver sulfide (Ag_2SNPs)

Silver sulfide nanoparticles were synthesized by mixing silver nitrate with *rosemary* aqueous extract and sodium sulfide at ambient temperature. In a typical synthesis, 1g of silver nitrate was dissolved in100ml of rosemary aqueous extract under magnetic stirring at room temperature (27^{o}C) for ~ 10min. Afterwards, the sodium sulfide solution (1g/100ml de-ionized water) was added dropwise to the solution of $AgNO_3$/rosemary aqueous extract under continuous magnetic stirring. A yellow color of $AgNO_3$/rosemary leaves aqueous extract started changing to a suspended gray-black color indicating the formation of silver sulfide nanoparticles.

Characterization techniques

Ultraviolet-visible (UV-vis) spectra from 200 to 700 nm were measured on a Shimadzu UV-vis spectrophotometer (UV-3600, Japan). The morphology of Ag_2SNPs was observed using transmission electron microscopy (TEM, a Hitachi H7500 at 80 kV and transmission electron microscopy (SEM, a Quanta FEI 450 SEM machine). The elemental mapping of imaged objects was characterized using an energy-dispersive X-ray (EDX) detector. Powder X-ray diffraction was performed using a X-ray diffractometer (Shimadzu) XRD-6000 with CuKa 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-Prestig-21 spectrophotometer.

Antibacterial activity and minimum inhibitory concentration (MIC)

The antibacterial activity of Ag_2SNPs was investigated using the disc diffusion method. About 20 mL of sterile molten Mueller Hinton agar was poured into sterile petri dishes.

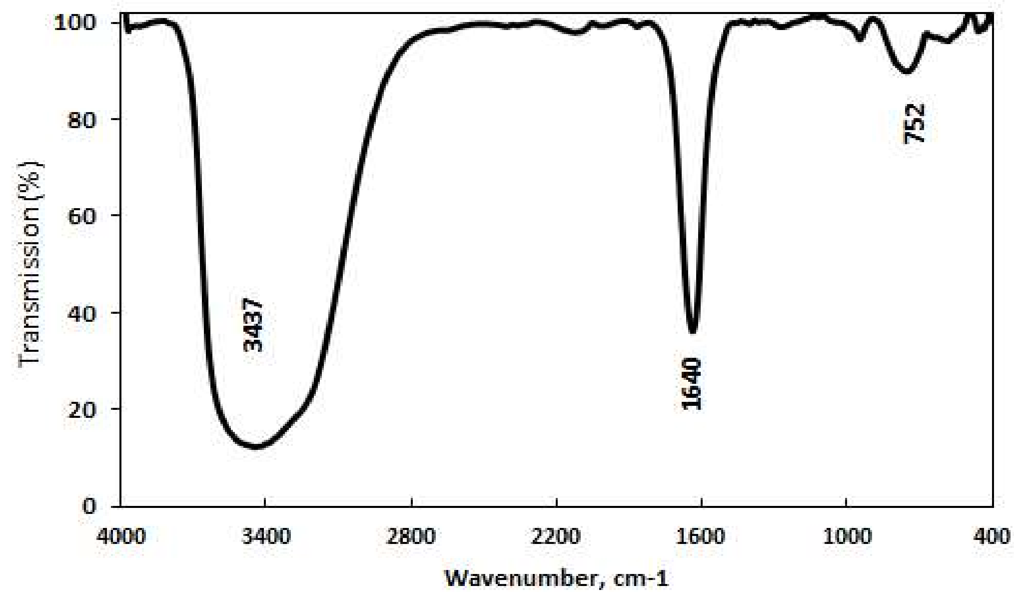

Fig. 3: FT-IR of *rosemary* leaves aqueous extract

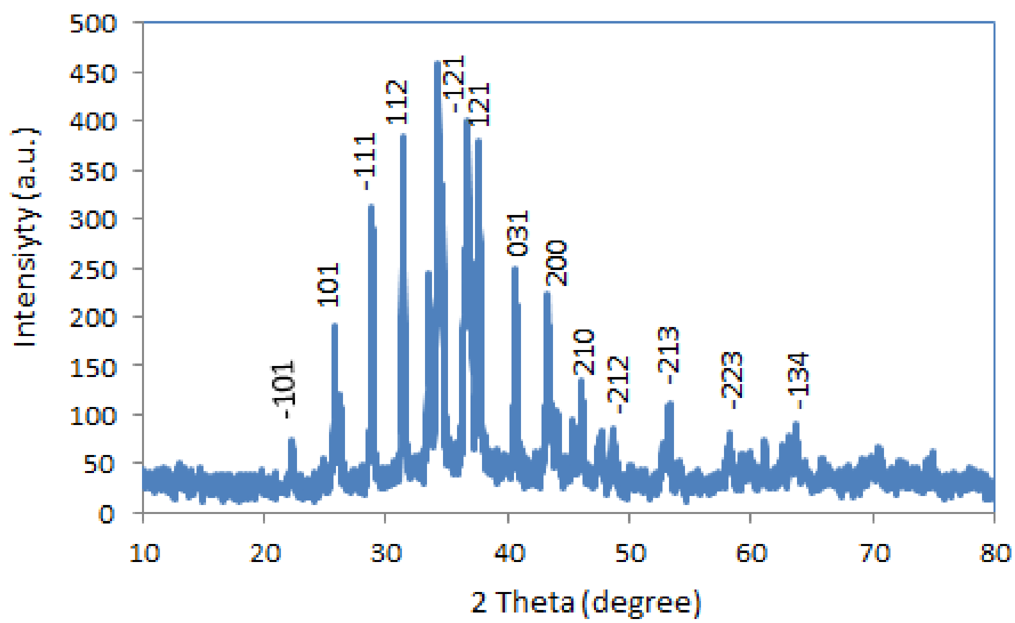

Fig. 4: XRD pattern of synthesized silver sulfide nanoparticles (Ag_2SNPs)

Triplicate plates were swabbed with the overnight culture (105 cells/mL) of Escherichia coli and Staphylococcus aureus bacteria. 5mg/mL of Ag_2S nanoparticle samples capped with rosemary leaves extract was added into the discs, placed in the petri dishes and incubated for 24 hours at a temperature of 37 ± 2°C. The zone of inhibition, expressed as millimeter in diameter, was measured after 24 hours of incubation. The MIC was investigated using different concentrations of Ag_2SNPs. The experiments were performed in triplicates.

RESULTS AND DISCUSSION

Ultraviolet-visible spectroscopy (UV-Vis) analysis

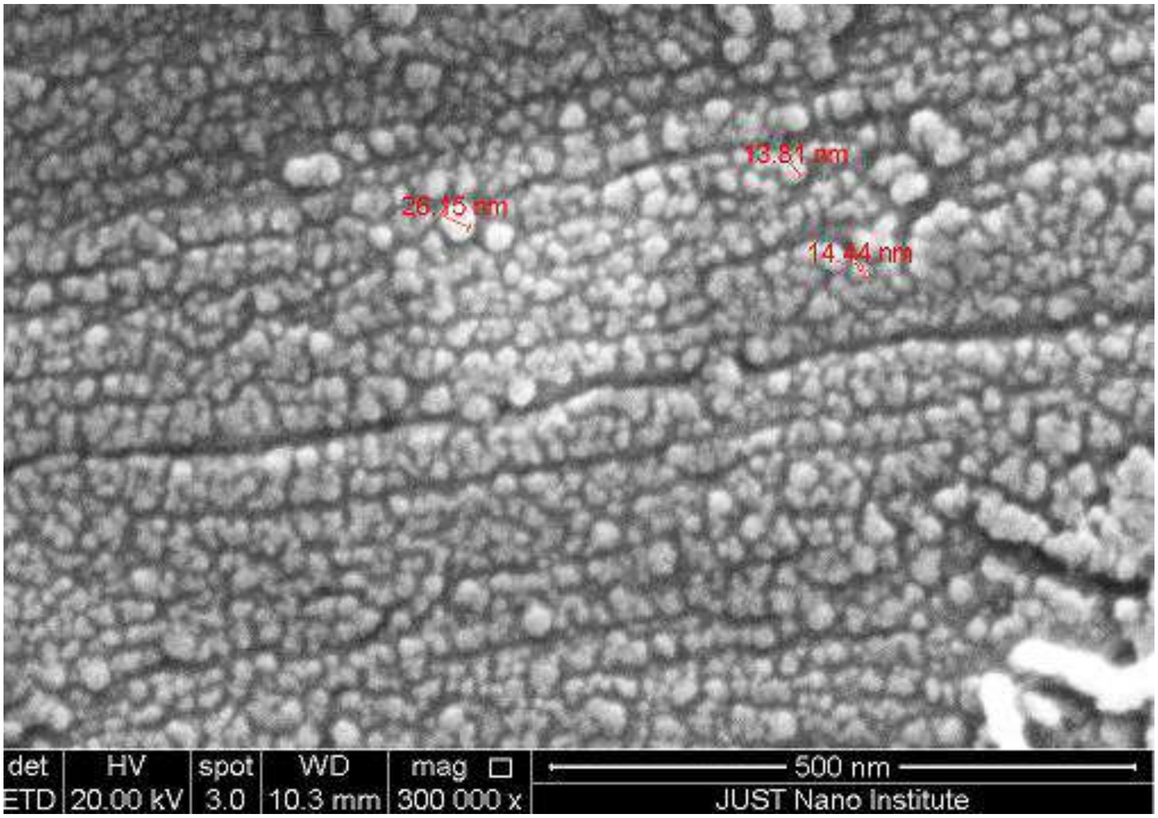

Fig. 5: SEM pattern of synthesized Ag_2SNPs

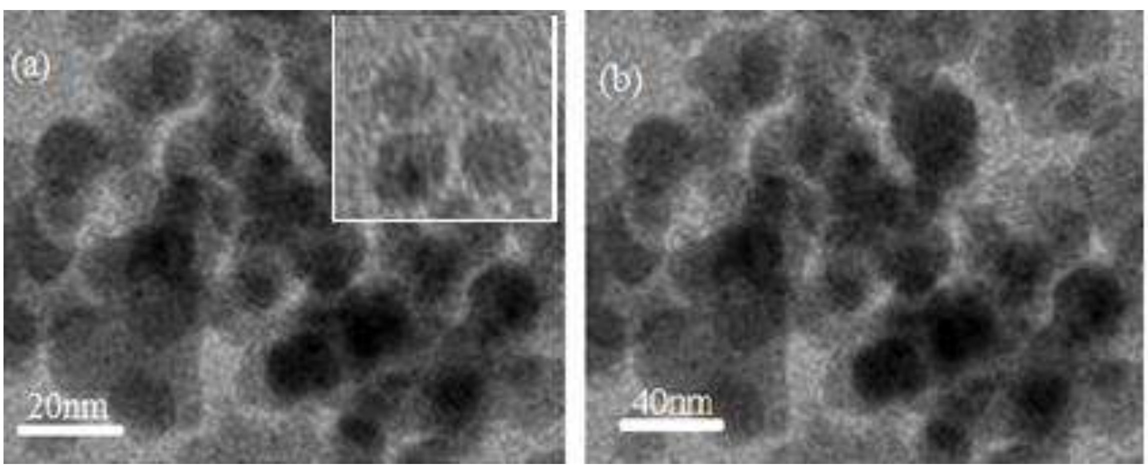

Fig. 6: TEM images of synthesized Ag_2SNPs

In the present study, the absorption spectrum of silver sulfide (Ag_2S) nanoparticles synthesized by green route using rosemary leaves aqueous extract revealed the conversion of silver and sulfur ions to silver sulfide nanoparticles with almost 100% as evidenced by qualitative testing of supernatant after the purification of silver sulfide nanoparticles. The difference in the rate of Ag_2S formation observed may be assign to the differences in the activities of the amino acids, poly phenols and flavonoids present in rosemary leaves extract. The entire reaction mixture is turned to black color, and exhibit an absorbance peak around 355 nm characteristic of Ag_2SNPs nanoparticle, due to its surface Plasmon resonance absorption band. In present investigation, the reaction mixtures showed a single SPR band revealing spherical shape of silver sulfide nanoparticles, which was further confirmed by SEM and TEM images. Fig. 2 showed SPR bands of the colloidal silver sulfide nanoparticles were centered at around 355 nm and rosemary aqueous extract at 300 nm.

Fourier transforms infrared analysis

FT-IR spectrum of rosemary leaves aqueous extract, Fig. 3 showed a number of peaks thus reflecting its complex nature. Strong broad absorption band at 3437 cm^{-1} is characteristic of the alcohol/phenol –OH stretching vibration, carboxylic acid –OH stretch and N-H stretching of amides. The strong peak at 1640 cm^{-1} is characterized to –NH stretch of primary amines. Peak at ~ 752 cm^{-1} refers to O-C=O bending in carboxylic acids, N-C=O, and C-N-C bending mines.

X-ray diffraction (XRD) analysis

A comparison of XRD spectrum, Fig. 4 with the standard confirmed that the silver sulfide particles formed in our experiments were in the form of nanocrystals, as evidenced by the peaks at 2θ values of 22.8°, 25.7°, 28.9°, 31.4°, 34.6°, 36.7°, 37.8°, 40.7°, 43.3°, 45.4°, 48.6°, 53.2°, 57.9° and 63.9° corresponding to (-101),(101), (111), (112), (-121), (121), (031), (200), (210), (-212), (-213), (-223), and (-134) Bragg reflections, respectively, which may be indexed based on the structure of silver sulfide. X-ray diffraction results clearly show that the silver sulfide nanoparticles formed by using rosemary leaves extract are crystalline in nature. It was found that the average size from XRD data and using the Debye-Scherrer equation (Eq. 1) (Klug and Alexander, 1959) is 20 nm.

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

Where, D is the crystallite size of silver sulfide nanoparticles, λ represents wavelength of x-ray source 0.1541 nm) used in XRD, β is the full width at half maximum of the diffraction peak, K is the Scherrer constant with value from 0.9 to 1 and θ is the Bragg angle.

Scanning electron microscopy (SEM) analysis

The suspended silver sulfide nanoparticles in sterile distilled water were used for scanning electron microscope analysis by fabricating a drop of suspension onto a clean electric stubs and allowing water to completely evaporate. Fig. 5 shows the SEM images of the silver sulfide nanoparticles synthesized by different concentrations are homogenously dispersed and ranges approximately from 5-40 nm. The shape of the silver sulfide nanoparticles is spherical with few exceptional as ellipsoidal. The larger silver sulfide particles may be due to the aggregation of the smaller ones, due to the SEM measurements.

Transmission electron microscopy (TEM) analysis

Typical TEM micrograph for as prepared Ag_2SNPs is shown in Fig. 6. The TEM micrograph clearly showed nanostructure homogeneities with spherical morphologies of Ag_2SNPs. The TEM observation showed the nanospheres with an average diameter of 14 nm. This slight deviation of the particle size estimation compared to that calculated from XRD analysis can be attributed to the deviation of the spherical shape of the particles that is required for the Debye–Scherrer formula and the detection limit of the XRD diffractometer. From the Fig. 6, spherical particles with 5-40 nm have been observed. The magnified TEM image as shown confirms the uniform and regular spherical morphology.

Antibacterial activity

Biosynthesized silver sulfide nanoparticles by this method were studied for antimicrobial activity against pathogenic bacteria by disc diffusion method; it was observed that silver sulfide nanoparticles have antibacterial activities at different concentration. Chloromphenical was used as a control antimicrobial agent. The silver sulfide nanoparticles biosynthesized by rosemary leaves aqueous extract showed inhibition zone against Gram negative *Escerichia coli*, and Gram positive *Staphyococcus aureus, Shigella , Listeria bacteria*. Maximum zone of inhibition (MZI) are listed in Table 1. It was observed that an increase in Ag_2SNPS concentration increases the MZI of *Escherichia coli*, *S. aureus*, *Shigella* and *Listeria* bacteria. Our results showed that the MZI for bacteria are higher than those reported in the literature (Jafari et al., 2017 and Sibiya and Moloto, 2018). This difference is due to the particles size of NPs prepared and capping agents used in the preparation process (Andra et al., 2019; Baygar et al., 2019; Manjunath Hulikere and Joshi, 2019; Soliman et al., 2018; Soto et al., 2019).

Table 1: Antibacterial activity of silver sulfide nanoparticles

Ag_2S NPs	Zone of inhibition (mm)			
Conc.	*E. coli*	*S. aureus*	*Shigella*	*Listeria*
80 mg/ml	14	16	12	17
40 mg/ml	14	16	11	16
20 mg/ml	13	14	10	14
10 mg/ml	12	13	9	13
Ref. Drug	18	20	16	20

CONCLUSIONS

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 sulfide nanoparticles using rosemary leaves aqueous extract with a diameter range of 5-40 nm. These particles are monodispersed and spherical. No chemical reagent or surfactant template was required in this method, which consequently enables the bioprocess with the advantage of being environmental friendly. Color change occurs due to the reaction with the plant components present in the plant leaves extract results in the formation of silver sulfide nanoparticles which is confirmed by UV–vis, XRD, FT-IR and TEM, having average mean size of 14 nm had fcc structure. The antibacterial activity of synthesized silver sulfide nanoparticles was evaluated against *E. coli and S. aureus, shigella and listeria* showing an effective bactericidal activity.

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