

Green Synthesis of ZnO Nanoparticles Using *Prosopis fracta* Extract with Two Solvents and Study of Their Biological Activities

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ABSTRACT- *The main goal of this paper is a green synthesis of zinc oxide nanoparticles with extracts of Prosopis fracta (growing in the Iraqi Kurdistan region) using two solvents, first with water (Zn-NPs-W) and second with methanol (Zn-NPs-M). The prepared nanoparticles characterizations were confirmed by UV-Vis absorption spectrophotometry; Fourier transforms infrared spectroscopy (FT-IR); scanning electron microscopy (SEM); X-ray Diffraction (XRD); and Transmission Electron Microscopy (TEM), in order to determine which solvent is more favorable in terms of particle size, particle agglomeration, and particle separation. The particle size of Zn-NPs-W was found to be 25 nm with a rod shape, while Zn-NPs-M had a particle size of 35 nm which is a wide range and gives a deformed rod shape. Further, it has been shown after testing the antibacterial activity of the two different sizes of the Zn-NPs (25, 35) nm against both gram-positive bacteria such as micrococcus species (M. species) Staphylo epidermidis (S.epidermidis); gram-negative such as Acinetobacter baumannii (A. baumannii), Pseudomonas aeruinososa (P. aeruinososa), and yeast Candida Albicans (C.albicans), with a different effect on bacteria. The most critical advantages of this process are the environmentally friendly and fast synthesis for both Zn-NPs-W and Zn-NPs-M.*

Keywords- ZnO- nanoparticles, *Prosopis fracta*, Green Synthesis, Biological Activity.

I INTRODUCTION

In the last decade, nanoparticles are being employed in a wide range of applications due to its varying properties on scaling down from bulk to nanometer size [1]. Most usually, zinc nanoparticles are generated through chemical methods [2], like precipitation and electro-deposition method [3]. Zinc oxide nanoparticles have been used in multiple fields of our lives, like solar cells [4], gas followed [5], ceramics [6], catalysts [7].

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The growing need for environmental-friendly nanoparticles and Zn-NPs carried out using different plant extracts and green method for the synthesis [8, 9].

The aim of this work was to synthesize, the zinc nanoparticles using *Prosopis fracta* extracts with different solvents (methanol and water). Further zinc nanoparticles were optical charcoal characterization using UV-Vis, FT-IR spectrometer, structural characterization using scanning electron microscopy (SEM, EDAX, TEM, and XRD); finally the antimicrobial activity studies were also investigated towards some gram-positive, gram negative and yeast.

II EXPERIMENTAL

A. Materials

The following analytical grade materials were used without any further purification: zinc sulfate heptahydrate ($M = 287.49 \text{ g/mol}$), and absolute methanol. All glasses were washed with distilled deionized water and dried in a hot oven before use.

B. Instruments

The morphology and size of nanoparticles were investigated using Transmission Electron Microscopy (TEM) (CM120 Philip), and Scanning Electron Microscopy (SEM) (Czech Republic), Fourier transform infrared spectroscopy (FTIR) [CE 3021(3000 SERIES)], X-Ray Diffraction (XRD) (P-Analytical) analysis were also obtained. Some drops of NPs were port on 1.0 cm^2 glass slide coated with gold, left under argon gas (for 24 h) then transferring to XRD chamber. UV-Vis absorption spectra were obtained on a double-beam Cary 50 spectrophotometer to ensure the formation of NPs.

C. Plant Collection

The *Prosopis fracta* fruits collected from Iraq – Erbil City and dried at room temperature. Samples were crushed and transferred into glass containers and preserved until the extraction procedure was performed in the laboratory.

D. Preparation of Prosopis Fracta (P.F) extract

In this extraction process two different solvents were utilized:

- i) First water as a solvent extract (P.F-W): fruit powder weighing 5.0 mg were put it into 100 mL distilled deionized water and boiled to $60\text{-}70^\circ\text{C}$ for about 15 min , left it at room temperature overnight, then the crude extract filtered using Buchner funnel through Whatman filter paper (No. 1).
- ii) Second absolute methanol as a solvent extract (P.F-M): using the same method (i) and the same quantities, but instead of water using absolute methanol solvent.

E. Synthesis of Zn oxide nanoparticles

- Synthesis of (Zn-NPs-W) and (Zn-NPs-M) using zinc sulfate:

For the synthesis of (Zn-NPs-W) take 100 mL (0.1 M) of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) solution (which was prepared by water in a 100 mL volumetric flask) and added slowly 30 mL of *Prosopis frakta* extract (P.F-W) then add (0.1 M) NaOH drop by drop until the pH arrive to 12 with heating at 70 oC with continuous steering for about 2 h, then cooled and the product was subjected to filtrate using Whatman filter paper (No.1) to remove the fruit debris and drying in the oven then use it for diagnosis [10].

For the synthesis of (Zn-NPs-M) prepare 0.1M of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) solution with methanol and completed in to 100 mL volumetric flask then added slowly 30 mL of (P.F-M), finally added drop by drop (0.1 M) NaOH until pH =12 and then continue as in the same method of (Zn-NPs-W) to obtain the (Zn-NPs-M). Figure (1) showed the steps for preparation of both (Zn-NPs-W) & (Zn-NPs-M).

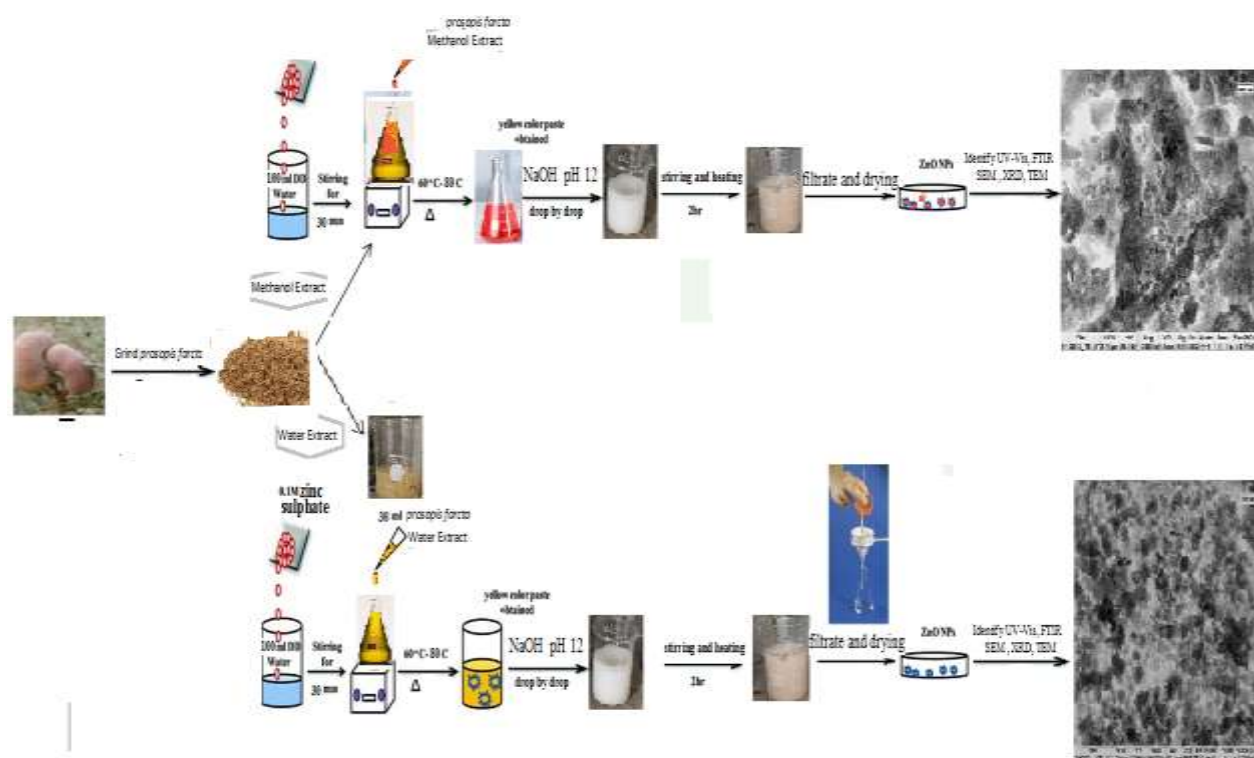


Figure (1): Preparation of both (Zn-NPs-W) & (Zn-NPs-M)

III RESULTS AND DISCUSSION

UV-Vis Spectra Analysis

UV-Vis spectrum of ZnO nanoparticles was recorded using UV-Vis spectrophotometer in the wavelength region 200 - 800 nm, by taking 0.1 mL of the sample and diluting it with 2.0 mL distilled deionized water. Figure (2) had showed the UV-Vis spectra of ZnO nanoparticles prepared from the extracts of *Prosopis frakta*. (A) For the water extracted and (B) for the methanol extracted. The absorption peak observed at 310 nm confirms the formation of Zn-NPs-W, while the peak at 290 nm corresponded to the Zn-NPs-M [11]. The UV-

Vis absorption bands are broad because each electronic energy level has multiple vibrational and rotational energy levels associated with it.

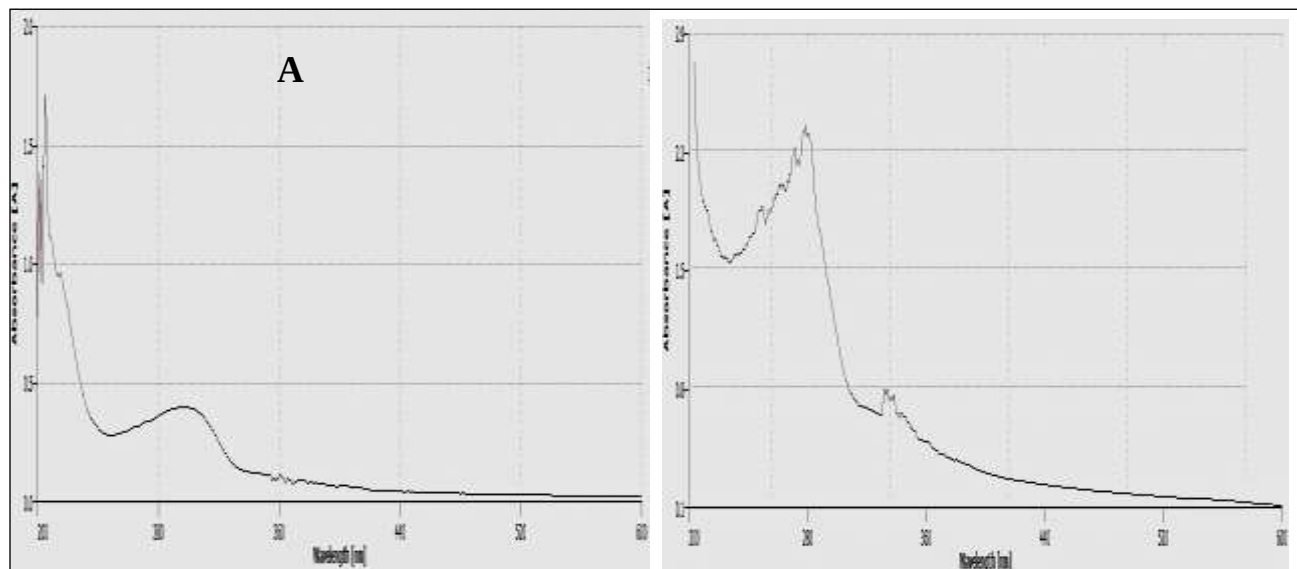


Figure (2): UV-Vis spectra showing absorption of (a) Zinc nanoparticles (Zn-NPs-W) synthesized using prosopis fracta aqueous

FT-IR Spectra Analysis

FTIR- spectra were recorded in order to characterize the surface structure and functional groups involved in the ZnO particles prepared from the fruit extract of Prosopis fracta. Figure (3) shows FTIR analysis for ZnO nanoparticles, a strong and broad absorption band at 3340 cm^{-1} (O-H stretching), the shoulder peak at 1708 cm^{-1} assigned for C=O group of carboxylic acids, the weak band at 1026 cm^{-1} can be assigned to the C-O-H stretching vibrations of Prosopis fracta and 1303 cm^{-1} correspond to C-H bond in alkenes [12].

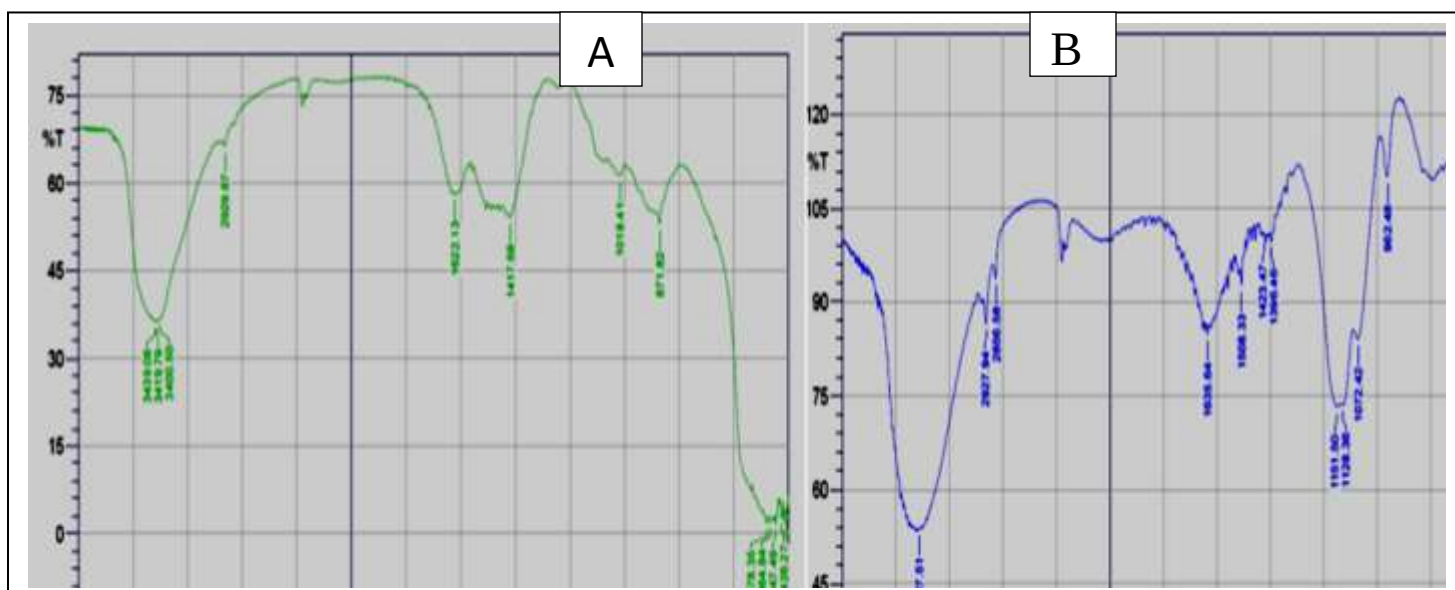


Figure (3): FT-IR spectra showing absorption of (a) Zinc nanoparticles (Zn-NPs-W) synthesized using prosopis fracta aqueous extract (b) Zinc nanoparticles (Zn-NPs-M) synthesized using prosopis fracta Methanol extract.

Scanning Electron Microscopy (SEM)

SEM analysis images of ZnO-NPs were obtained to determine the shape and size of prosopis fracta extract with water (Zn-NPs-W), as shown in Figure (4-A) the particle size was found to be 25 nm, with the shape clearly spherical, it showed more black holes and a less white area which increases surface area, and [Figure (4-B) showed EDAX spectra revealed that the required phase of Zn and O is present in the samples and confirmed high –purity for synthesized (Zn-NPs-W)], the expected stoichiometric mass percent of Zn and O are 84.7% and 15.3%, but when uses menthol solvent of (Zn-NPs-M) as shown in Figure (5-A) synthesized (Zn-NPs-M). Theoretically with 35 nm particle size and the shape aggregation of capped and fewer holes that little surface like , while Figure (5-B) showed [synthesized (Zn-NPs-M)], the EDAX analyses also approximately similar results for both synthesized composition of zinc and oxygen which was reported 83.4 % and 16.6% [13].

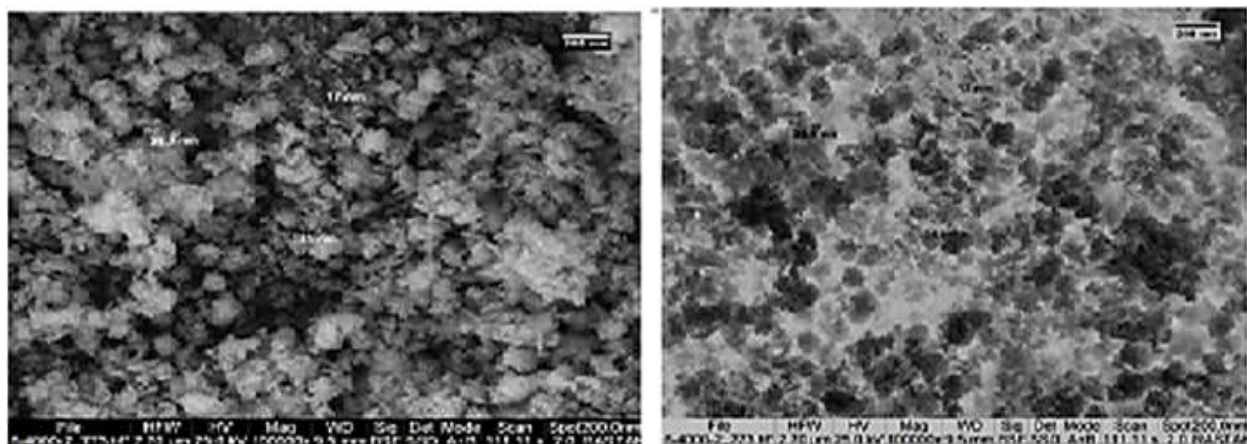


Figure (4):A- shows the Scanning Electron Mikroskop (SEM) image of zinc oxide nanoparticle's(ZNPsw)

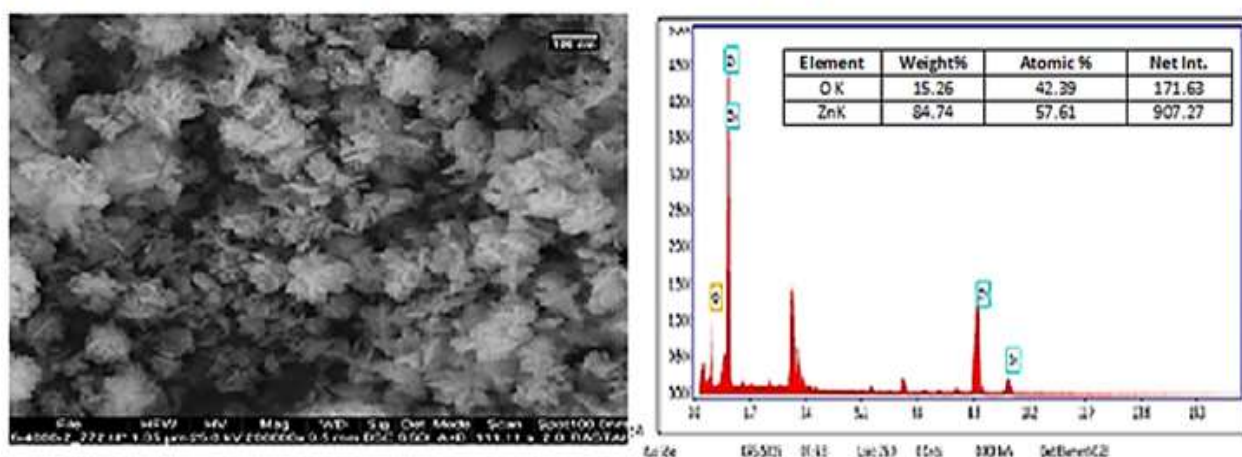
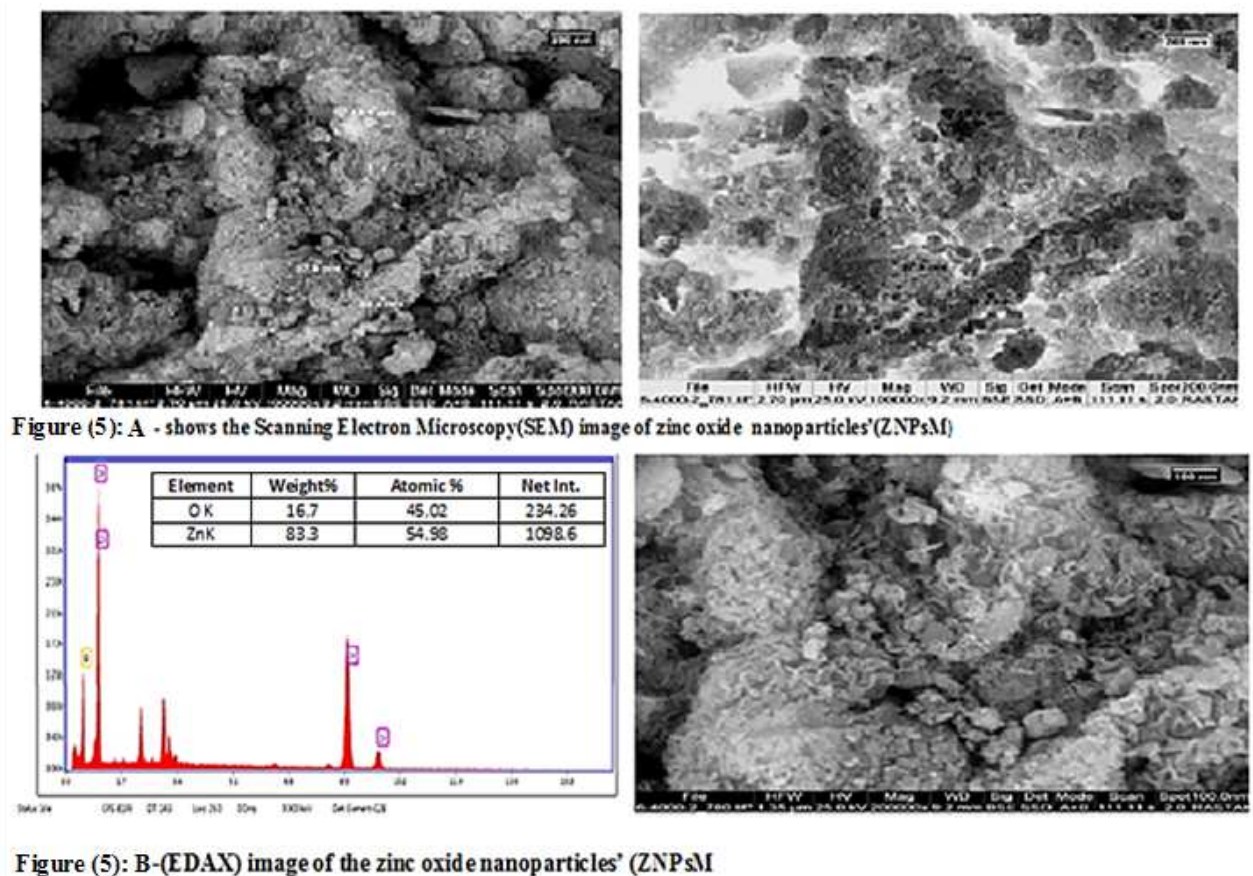


Figure (4):B- (EDAX) image of the zinc oxide nanoparticles' (ZNPsw)



X-Ray Diffraction (XRD)

The XRD of synthesized (Zn-NPs-W) as shown in Figure (6) show peaks with values $\Theta = 31.4, 34.0, 35.9, 47.2, 56.3, 62.5$ and 68.0° which are specific types for ZnO structure, this is an indication of synthesized in the nanometer range. The average particle size from the full width at half maximum (FWHM) of the diffraction peaks using Scherer's equation, which is given as $y = 0.9 \lambda (\beta \cos \Theta)$; where λ is the wavelength of X-ray (1.54 nm) and β is the FWHM with the average size of (Zn-NPs-W) has been found 25 nm. But XRD of synthesized (Zn-NPs-M) show peaks with values $\Theta = 32.2, 34.7, 36.6, 47.9, 56.8$ and 68.1° , with the average size of 35 nm.

Suggest the face-centered cubic (fcc) crystal structure of nanoparticles – Joint committee on powder diffraction standards (JCPDS) was used as a reference to assign the lattice planes according to the peaks obtained [14].

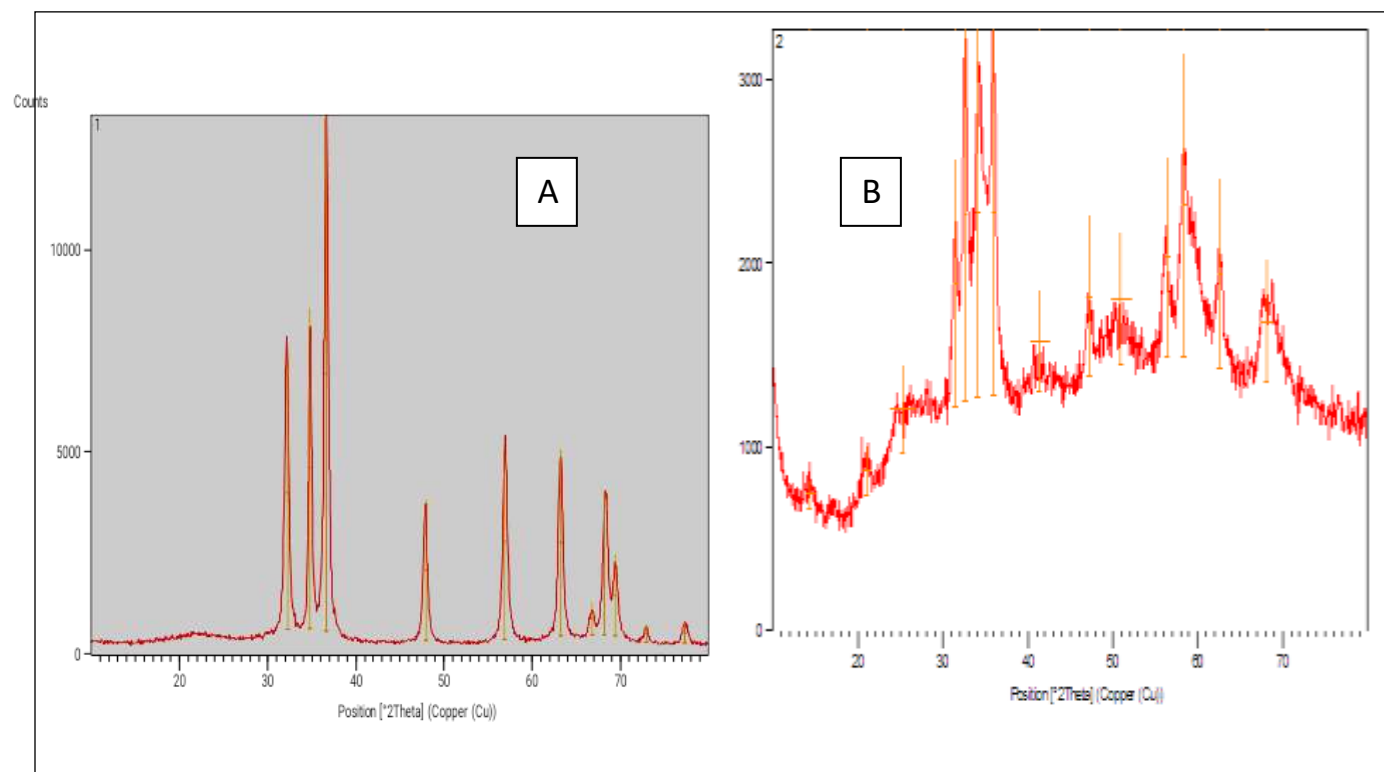


Figure (6): XRD spectra - (A) zinc oxide of (Zn-NPs-W) and (B) zinc oxide of (Zn-NPs-M) prepared using *prosopis fracta*

Transmission Electron Microscopy (TEM)

The size and morphology of the ZnO-NPs synthesized using *prosopis fracta* were studied by TEM. As can be seen from Figure (7-A) the images for (Zn-NPs-W) were well dispersed with their dimensions ranging from 25 nm most of the particles are observed spherical with some rod and shoulder shape. While, Figure (7-B) the image for (Zn-NPs-M) was well dispersed with their dimensions ranging about 35 nm most of the particles are observed spherical shape [15, 16].

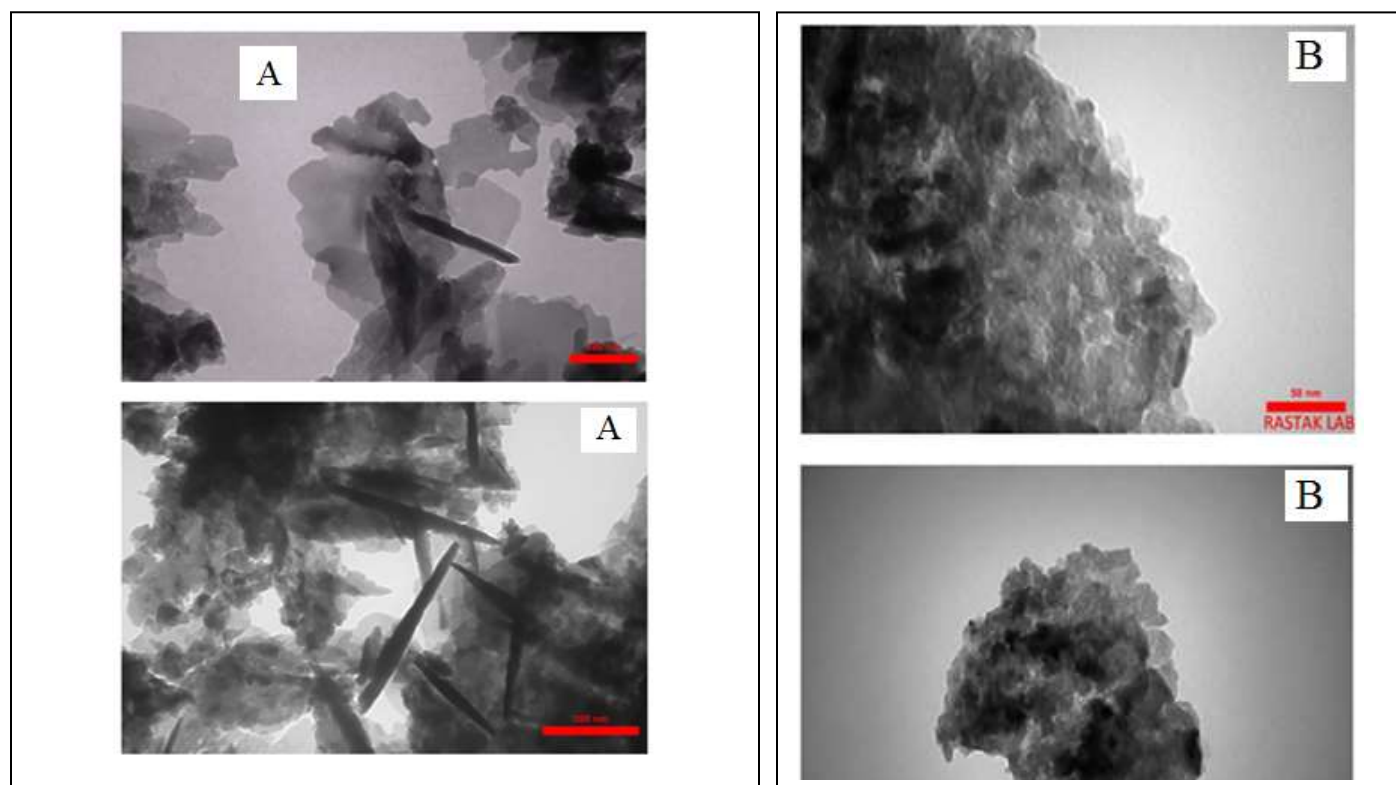


Figure (7): (A) TEM Analysis image of (Zn-NPs-W); (B) TEM image of (Zn-NPs-M)

Antimicrobial activity

The ZnO nanoparticles synthesized showed inhibition for an antibacterial, in a dose-dependent behavior zone against the studied bacterial species shown in the Table (1). The results depict that the nanoparticles are efficient in giving a zone of inhibition and inhibit the pathogens. It has been shown that Zn-NPs-W effect on the ability to inhibit the growth of various pathogenic microorganisms species (M. species) like *S. epidermidis*, *A. baumannii*, is very effective, as well as on yeast *C. albicans* and Zn-NPs-M, has an effect only on bacteria *P. aeruginosa* which is very effective as shown in Figure (8) [17, 18].

Table (1): Zone of inhibition of Zn-NPs (mm)

Bacterial Strains	Zone of inhibition (mm)		
	Antibiotics	Zn-NPs-W	Zn-NPs-M
<i>M. species</i> (Gram-positive)	1.5± 0.02	1.5± 0.07	0.3± 0.02
<i>S. epidermidis</i> (Gram-positive)	10± 0.14	1.8± 0.05	-ev
<i>A. baumannii</i> (Gram -negative)	10 ± 0.01	1.2± 0.06	0.2± 0.05
<i>P. aeruginosa</i> (Gram -negative)	10 ± 0.16	-ev	1.8± 0.12
<i>C.albicans</i> (yeast)	10 ± 0.11	1.2± 0.08	0.7± 0.08

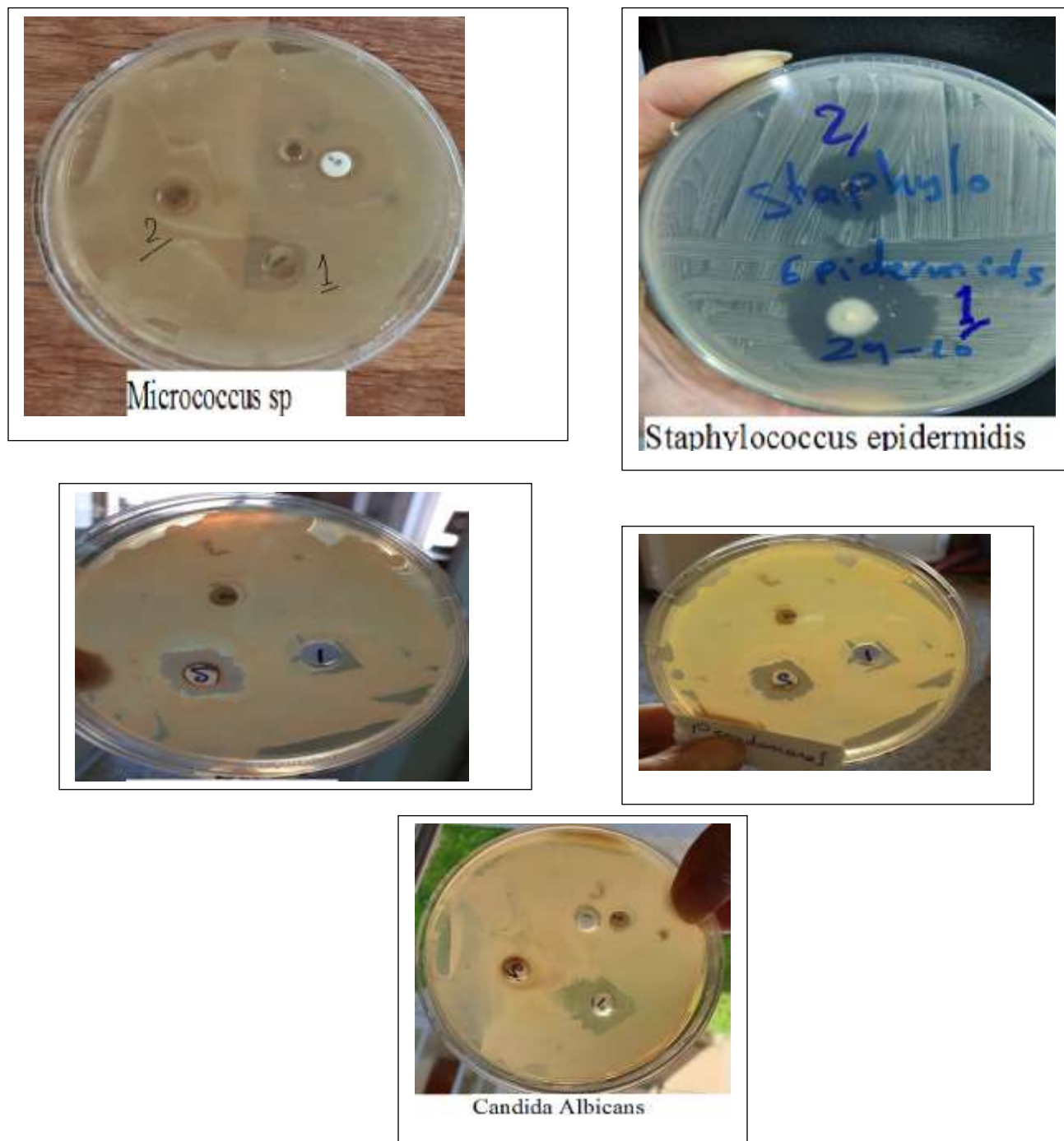


Figure (8): Antimicrobial activity of Zn-NPs-W, Zn-NPs-M nanoparticles With Microorganism species.

IV Conclusions

A facile synthetic method was proposed for the preparation of ZnO-NPs using *Prosopis fratta* extracts with two different solvents (water and methanol). The nanoparticles were successfully characterized by UV-Vis absorption spectroscopy, SEM, TEM, XRD, and FTIR. The size of the particles were found from SEM and TEM images, (25 nm) for *Prosopis fratta* extract with water, while 35 nm for the same plant but with methanol extract, and comparable with Scherer's results. The essential advantages of this procedure are short reaction time, fast, discrete stage, green synthesis of the ZnO nanoparticles, removal of a hurtful component, and reproducibility of the process, comparing with the conventional methods. Although this method is very cheap and simple, therefore it can be a predictable candidate for various medicinal and water purification applications. For the clear to know that the Zn-NPs-W also have the ability to inhibit the growth of several pathogenic microorganisms like *S. epidermidis*, *A. baumannii*, has proved that these can be used as a potent antibacterial agent against- immunosuppressed patients, (biofilms to grow on plastic devices placed within the body), (bacteria to resist antibiotics) but the Zn-NPs-M ability to inhibit the growth of pathogenic microorganisms like *P. aeruginosa* has proved that these can be used against superficial infection on mucous membranes in the mouth or vagina.

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REFERENCES

1. U. Abhulimen, Mater. Rassoc, "Transparent ZnO/polycarbonate nanocomposite for food packaging application" J. Nanocomposites, 1 (2015) 106-112 , doi.org/10.1179/2055033215Y.0000000004
2. A. M. Saad, M. A. Ghareeb, M. S. Abdel- Aziz, H. M. Fawzy Madkour ; "Chemical constituents and biological activities of different solvent extracts of *prosopis farcta* growing in Egypt"; J. Pharm.Phyto.Sci. Rev. Res., 9 (2017) 67- 76. DOI: 10.5897/JPP2017.0452
3. F.Sultana, J. Barman, M. C. Kalita; "Biogenic synthesis of ZnO Nanoparticles using *Polygonum chinense* leaf extract and their Antibacterial activity"; Int. J. Nanotechnology and Application . 2, (2017) 155-165.
4. A. C. Mohon, B. Renjanadevi; "Preparation of Zinc Oxide Nanoparticles and its Characterization Using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD)"; J. Procedia Tech ,24, (2017), 761-766. DOI: 10.1016/ j. protcy.2016.05.078
5. S. Devasenan, N. H. Beevi, S. S. Jayanthi; "Green synthesis and characterization of zinc Nanoparticle using *Andrographis paniculata* Leaf Extract"; Int. J. pharm. Sci. Rev. Res,1(2016), 243-247.

6. S. Saeidi, E. Javadian, M. Birjandi, F. Javadi; "Antimicrobial Activity of synthesized Nanoparticles using prosopis farcta Extract Against Pseudomonas aeruginosa Isolated From patients"; J . Nano Drug Science, 1 (2018), 1-4.
7. S. Fakhari, M. Jamza, H. K. Fard; "Green synthesis of zinc oxide nanoparticles: a comparison"; J. Green chemistry letters and Reviews. 12 (1), (2019),19-24 , DOI: 10.1080/17518253.2018.1547925
8. A. Husen, S. K. Siddiqi; "Plants and microbes assisted selenium nanoparticles: characterization and application"; J. Nanobiotechnol. 1 (2014) 12, 28. <http://dx.doi.org/10.1186/s12951-014-0028-6>.
9. J. Jeevanandam, S. Y. Chan, K. M. Danquah, "Biosynthesis of metal and metal oxide nanoparticles". Chem. Bio. Eng. Rev.; 3 (2016), 55–67. <http://dx.doi.org/10.1002/cben.201500018>.
10. P. Jamdagui, P. Khatri, J. S. Rana; "Green synthesis of Zinc oxide nanoparticles using flower extract of Nyctanthes arbor-tristis and their antifungal activity", J . King Saud Univ –Sci, (2016), DOI: 10 . 1016 / J. / Jksus.2016.10.002.
11. P .J. Bora, P. J. Barman, C. K. Sarma; "Effect of pH on ZnS nanocrystalline thin film embedded in a polyvinyl alcohol matrix", J. Inte. phys. 29 (2010), 5663–5673.
12. V. Mishra, R. Sharma; "Green synthesis of zinc oxide nanoparticles using fresh peels extract of Punica granatum and its antimicrobial activities", Spectrochim- ica Acta–Part A 143 (2015), 158–164, DOI: 10.1016/j.saa.2015.02.011.
13. N. Bala, S. Saha, M. Chakraborty, M. Maiti, S. Das, R. Basu, P. Nandy, "Green syn- thesis of zinc oxide nanoparticles using Hibiscus subdariffa leaf extract: effect of temperature on synthesis, anti-bacterial activity and anti-diabetic activity", RSC Adv. 5 (2015), 4993–5003, DOI: 10.1039/C4RA12784F .
14. S. Fakhari, M. Jamzad , H.K. Fard, "Green synthesis of zinc oxide nanoparticles: a comparison";J.Green.Chem.Lett& Revi. 41(7), (2019), 19-24. doi.org/10.1080/17518253.2018.1547925
15. J. J. Cheng, S. M. Nicaise, K. K. Berggren, S. Gradecak; "Dimensional tailoring of hydrothermally grown zinc oxide nanowire arrays", J. Nano Lett. 16 (2015), 753–759.
16. J. Zhou, F. Zhao, Y. Wang, Y. Zhang, Y. Yang; "Size controlled synthesis of ZnO nanoparticles and their Photoluminesnce properties", J. Lumin. 1(2), (2015), 195-197.
17. V. Mishra, R. Sharma; "Green synthesis of zinc oxide nanoparticles using fresh peels extract of Punica granatum and its antimicrobial activities"; Spectrochim- ica Acta–Part A 143 (2015), 158–164, DOI: 10.1016/j.saa.2015.02.011.
18. Y. Xie, Y. He, P. L. Irwin, T. Jin, X. Shi; "Antibacterial activity and mechanism of action of zinc oxide nanoparticles against Campylobacter jejuni"; Appl. Environ. Microbiol. 77 (2011), 2325–2331, DOI: 10.1128/AEM.02149-10.