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RESEARCH PAPER

Cinnamon Zeylanicum Extracts-Mediated Biosynthesis of Zinc Oxide Nanoparticles by using Two Zinc Precursors (Zinc Acetate and Zinc Sulfate)

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ABSTRACT

Two different Zinc precursors Zinc acetate A (C_4 H_6O_4 Zn.$_2$.$2H_2O$) (ZnOA) and Zinc sulfate heptahydrateS ($ZnSO_4.7H_2O$) (ZnOS) were used for synthesis ZnO nanoparticles (Nps) by green synthesis method using cinnamon zeylanicum. The green synthesis of zinc Nps is eco-friendlier, simple, cost effective and less toxic than other chemical methods and physical method. Cinnamon zeylanicum extract in present study was used as reducing and cupping agent for green synthesis of zinc oxide NPs which have different medical and biological uses because by its natural photochemical elements which enhance stabilizing of zinc oxide nanoparticle by reducing Zinc ion to ZnO NPs and discarding noxious substance. Zinc acetate and zinc sulfate were used as precursor for utilizing zinc oxide nanoparticle to detect their effective ness for synthesizing zinc oxide NPs. UV-vis visible spectroscopy, XRD X-ray diffraction, FT-IR Fourier Transform Infrared Spectroscopy , FE-SEM Field emission scanning electronic microscope, EDS energy dispersive spectroscopy, and MAPS were used for characterization superlatively for each precursors of zinc oxide nanoparticle by mean of cinnamon zeylanicum this characterizations were confirmed the green synthesis of ZnO Nps by cinnamon zeylanicum .Also ZnO Np that performed by zinc acetate precursor recorded smaller particle size less agglomerations and more purified ZnO NPs than ZnO NPs that performed by zinc sulfate precursor.

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INTRODUCTION

Nanoparticles size is range from 1–100 nm. The small sizes and variety of nanomaterial shapes will affect different properties of nanomaterial including physical, chemical and optical character. For example, decreasing the size of particle the band gab of nanoparticle will increase [1]. Green synthesis is an effective, quick, simple, feasible, less cost, ecofriendly, and non-toxic process for synthesizing of nanoparticle, green synthesis is more beneficial processes than other chemical and physical process. Different parts of plants have

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wide range of medical uses due to presence of chief compound, biocompatibility, and cheap [2]. Therefore, cinnamon conceders as one of natural plants which have wide ranges of medical uses by its chief compound like flavonoid, alkaloid, phenol and cinnamon aldehyde and in which attract the researcher's attention [3,4].

Cinnamon zeylanicum bark use as multi factors such as medicine, nutrition and edible plant also use as antioxidant, antifungal anti-cancer and antibacterial for food protection [5]. The cinnamic acid found in the cinnamon acts as the capping agent [1]. The type of metal affects the green synthesis of metal and metal oxide nanoparticle and potential use of metal and metal oxide Nps depends upon the metal used for the biogenic synthesis of Nps. Through using green synthesis process different type of metal and metallic oxide nanoparticle were manufactured, such as Ag, Cu, CuO, Fe_3O_4, ZnO, and many others, for different biological and medical uses [6, 7].

Zinc Oxide (ZnO) is an inorganic metal oxide that consists of nanomaterials in a vast range, ZnO has specific properties that make it different from another substance such as strong optical stability, strong chemical stability, strong electrochemical connection factor, minimal toxicity, and wide range radiation absorption [8]. ZnO is an intriguing material in the scientific field of medical because of its durability, biocompatibility, and biodegradability [8]. ZnO can adsorb UV-A and UV-B. Nowadays ZnO is used in many sunscreen lotions, ointments, sun creams, dental pastes, and medicines and it found that ZnO has wound-healing properties which are used in inflammation and allergy. Green synthesis Zinc oxide nanoparticles have several biological and biomedical usage including anticancer, antimicrobial, antibacterial, and antifungal activities [8].

Green synthesis of zinc oxide nanoparticle using plant extract have several advantages over other biological processes because of the its bioactive component which has several anti-oxidant and antimicrobial effect [8]. Studies indicated that type of zinc salt precursor affect Synthesis of ZnO NPs because zinc salts have different counter ions (chlorides, sulfates, acetates and nitrates) lead to different nucleation and growth kinetics [9]. Also studies reported that different precursors in different state will affect size, morphology, crystallographic and photoluminescence character of Their influence on the of ZnO NP [9].

The aim of the present study was green synthesis and characterization of ZnO NPs from two different zinc salt precursors zinc (acetate and zinc sulfate) by cinnamon zeylanicum powder.

MATERIAL AND METHOD

Preparation of plant extract

10 g of cinnamon zeylanicum powder were mixed to 100ml of distal water,the mixture were boiled for 15min on magnetic stirring device in 70◦c 1500 rpm,when the solution cooled it filtered by four layers of sterilized gauze, then the mixture were filtered again by Whatman filter paper 0.01then stored in cool place 40 ℃ [10].

Green synthesis of ZnO NPs

In the present study for synthesizing ZnO Nps two different precursors were used 2.5 g of zinc acetate $Zn(C_4H_6O_4)_2.2H_2O$) (M.W 219.4) and 3.2 g of zinc sulfate heptahydrateS ($ZnSO_4.7H_2O$)(M.W 287.54) each one were dissolved separately in 250 ml of di ionized water then stirred continuously for 15min in 37◦c 1500 rpm until no zinc precursor particle remain .For mixing the solution 45 ml of cinnamon zeylanicum extract were added drop by drop to the zinc per courser solution by continuous stirring the solution and heating in 70◦c in 1500rpm for 3 hrs until the color changed to yellowish suspension. The mixing conical tube were covered by aluminum foil to prepare the nano particle in a dark area. Before cooling the mixtures, the PHs of both mixtures adjusted by using drop by drop of diluted solution of NaOH in which (2g of NaOH dissolved in 50ml of distal water) to value of 9.

Then the mixtures separately were in cubed for 72 hrs. The mixtures were centrifuged then spread on Petri dish placed and dried in oven for 3hr at 80◦c until dry brown material obtained after that the material farther dried and purified by calcination in 500 ◦c for zinc acetate and 600◦c because zinc sulfate has larger particle size, to confirm the synthesis of ZnO nanoparticle the sample were characterized by UV-vis spectra, XRD, FT-IR, FE-SEM, EDS, and MAPS. The sequences of ZnO Nps synthesis shown in Fig. 1.

Characterization of ZnO NPs

Different Characterization of ZnO NP were performed by different sample tests such as UV-vis visible spectroscopy were used in wave length(200-600nm) through Uv- vis spectrometer

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1900i (SHIMADZU Japan), XRD X-ray diffraction were used to record crystalline structure of ZnO NPs by (PHILIPS, PW1730, the Netherland) with Position. (°2Theta Cu Ka) radiation, FT-IR Fourier Transform Infrared Spectroscopy were used for characterization of ZnO NPs surface structure (SHIMADZU Japan), FE-SEM Field emission scanning electronic microscope were used for detection of surface morphology and shape of ZnO NPs, (FESEM device, TESCAN, MIRA3:Japan), EDS energy dispersive spectroscopy and MAPS were used to detect element amount of Zinc,Oxygen and other trace elements FESEM device, (TESCAN, MIRA3: Japan).

RESULT AND DISCUSSION

UV-Vis spectroscopy

UV-Vis spectroscopy was used to certify the optical properties and characteristics of cinnamon derived zinc oxide nanoparticle and to determine the synthesis of zinc oxide nanoparticle as shown in Fig. 2 UV-Vis spectroscopy reported the highest

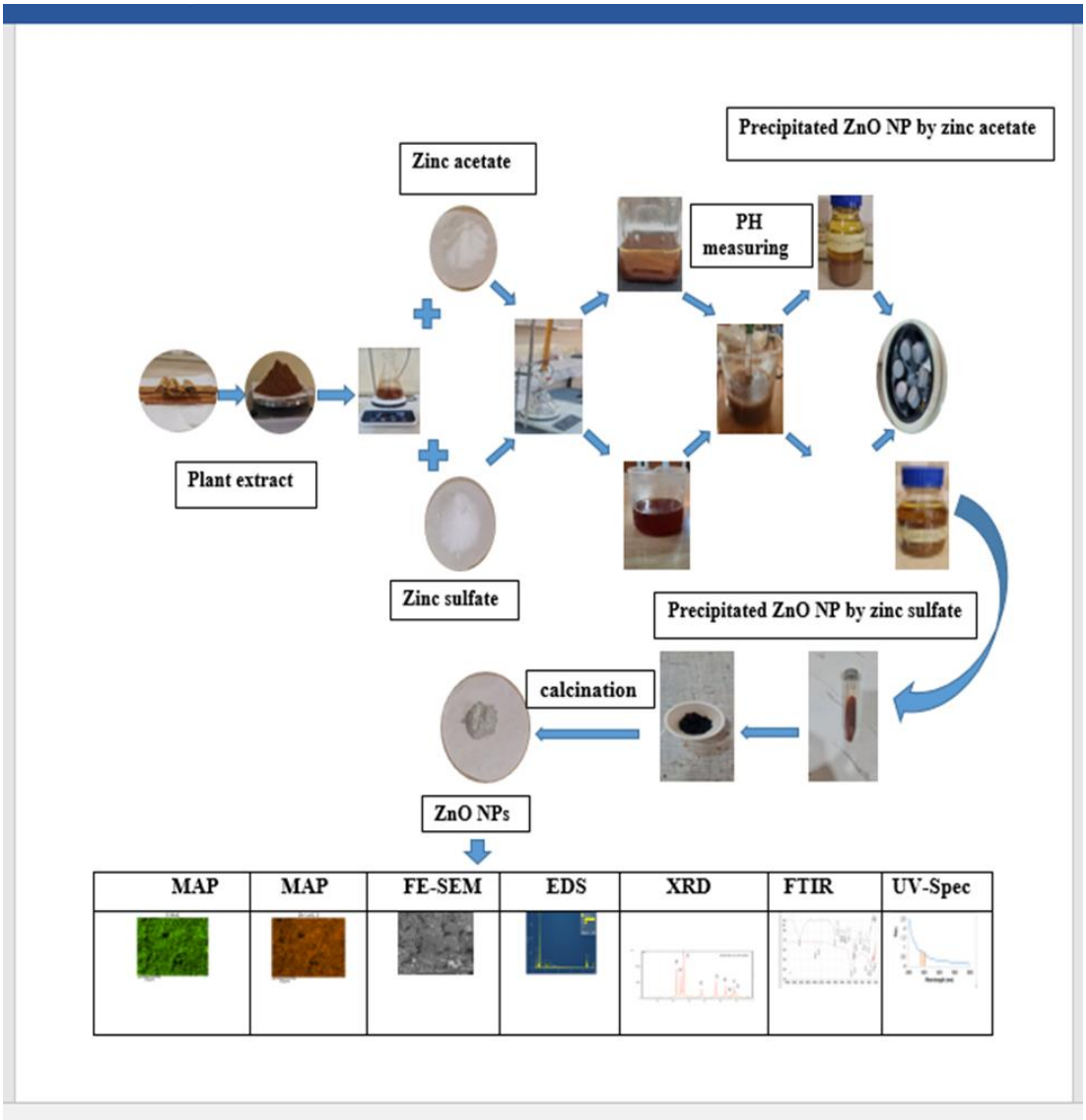

Fig. 1. A diagram representation of Zinc oxide nanoparticles (ZnO Nps) synthesized from cinnamon zeylanicum plants extract utilizing zinc acetate and zinc sulfate precursors

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absorbance peak at 280-320nm for both precursors which indicated the synthesis of ZnO nanoparticle by means of cinnamon zeylanicum. As revealed in the Fig. 2 the biosynthesis of ZnO nanoparticle is pure because there are no other peaks recorded. However; the maximum absorbance band were absorbed at for both precursors 320nm this may be related to ZnO existing absorbent band gab produced by transition of electron from valence (EV) band to conduction band (EC)(O2p-Zn3d). [4, 11] The energy band gab (EG) of ZnO nanoparticle was calculated by means of this formula :EG=hc/λ in which (h) is Planck's constant (6.626 × 10−34 Js), (c) is the velocity of light (3 × 108 m/s) and (λ) is the wavelength 320nm in which in good agreement with .[4, 11] The energy band gab for present study for both precursors were 3.87 eV in which indicated that ZnO NP can utilize metal oxide semiconductor-based systems this in agreement with [12, 13].

Because of wide energy band gab of ZnO nanoparticle and ability for protection against UV

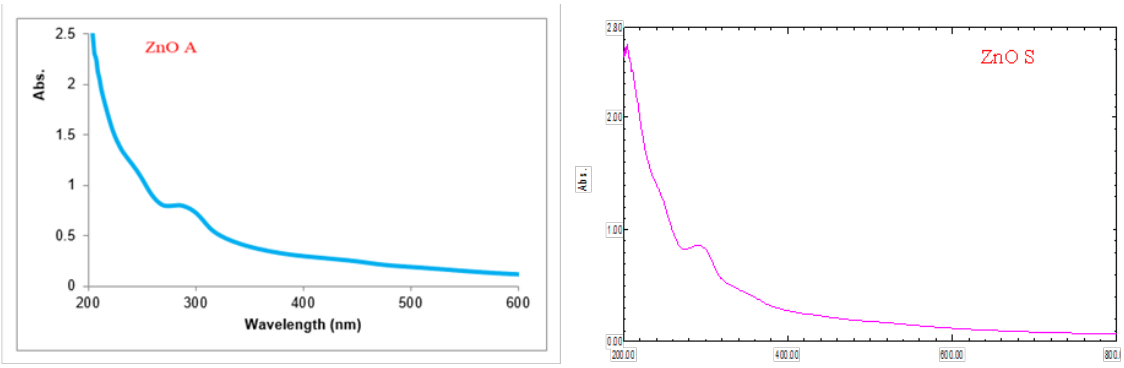

Fig. 2. UV-vis spectrum of ZnO NPs synthesized by cinnamon zeylanicum using zinc acetate (ZnO A) and zinc sulfate (ZnO S) precursors.

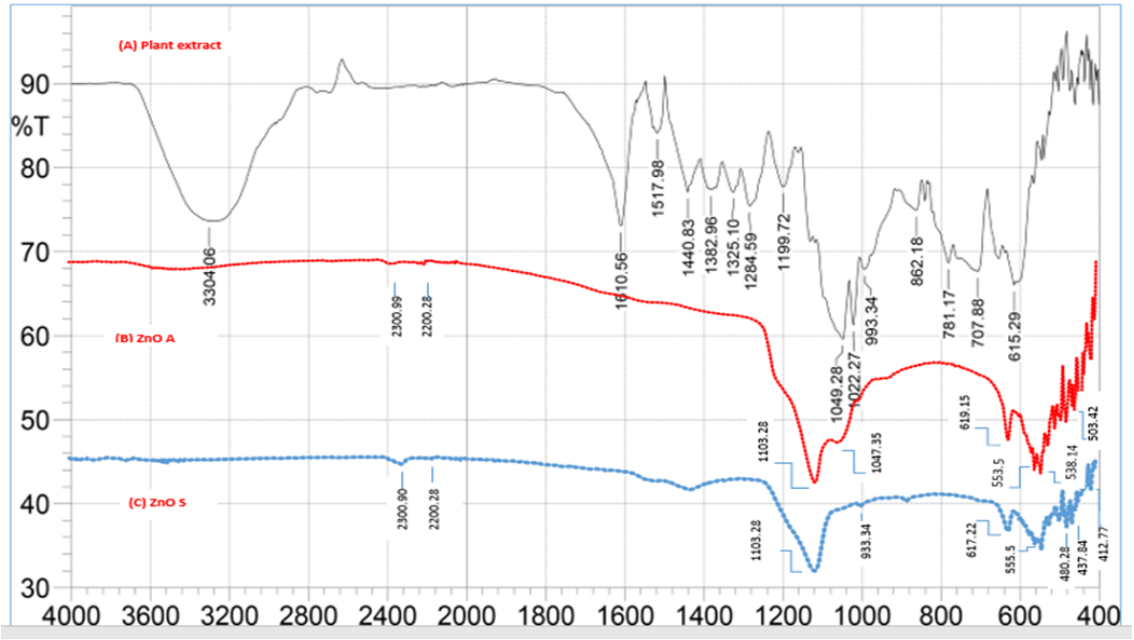

Fig. 3. FTIR spectra of (A) cinnamon zeylanicum extract, (B) ZnO NPs and organic compound related to cinnamon zeylanicum when zinc acetate(ZnO A) used as precursor and, C (ZnO S) is zinc sulfate precursor.

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absorption has several medical applications like sunscreen and antimicrobial and wound healing activity [11,13].

FTIR spectrum for ZnO nanoparticle

FTIR spectrum for ZnO nanoparticle synthesis using cinnamon zeylanicum shows distinct peaks that align with typical functional groups associated with both ZnO nanoparticle and organic compound from cinnamon zeylanicum were showed in Fig. 3B. FT-IR spectra and functional group related to ZnO nanoparticle formation demonstrated peaks

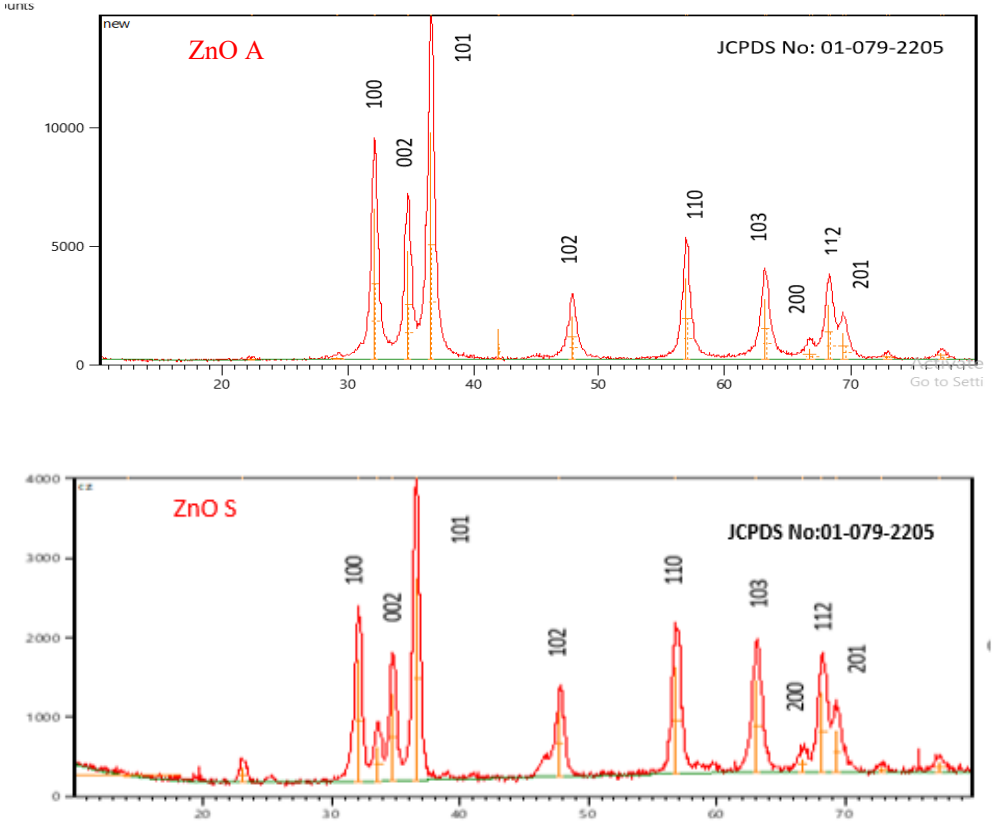

Fig. 4. XRD image of ZnO NPs using zinc acetate (ZnO A) and zinc sulfate (ZnO S) precursors.

Table 1. 2Th values, FWHM, Diameter (nm) and average diameter of XRD pattern form of synthesized ZnO nanoparticle by zinc acetate and zinc sulfate precursors.

Zinc sulfate XRD pattern				Zinc acetate XRD pattern				
°2Th	FWHM	Diameter (nm)	Average diameter(nm)	°2Th	FWHM	Diameter(nm)	Average diameter(nm)	hkl
32.039	0.600	13.77		32.103	0.544	15.19		(100)
34.727	0.558	14.91		34.830	0.569	14.63		(002)
36.532	0.597	14		36.5680	0.598	13.93		(101)
47.754	0.64	13.56		47.982	0.761	11.42		(102)
56.816	0.677	13.33	13.42	57.071	0.683	13.24	12.74	(110)
63.072	0.761	12.24		63.169	0.741	12.58		(103)
66.61	0.72	13.19		66.93	1.05	9.07		(200)
68.167	0.73	13.13		68.258	0.748	12.83		(112)
69.28	0.76	12.70		69.598	0.82	11.79		(201)

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is between 500–4000 cm−1, the present study includes absorptions peak of zinc acetate (ZnO A) precursor was at 503.42, 520.78, 538.14, 553.57, 619.15. 1047.35, 1103.28,2200.28 and 2300.99 cm-1 and zinc for sulfate (ZnO S) precursors was at 412.77,437.84,480.28,555.50,617.22,993.34 ,1103.28, 2200.28, and 2300.9 The broad area adjacent to 2300.99 may related to C-O stretching vibration, and the prominent peaks between 1103.28 and 2200.28 cm^{-1} may arise from 0-H, N-H, C-C and C-H, stretching vibration in which H-bonds alcohol, phenol and the amide group. The prominent peaks between 503.42 and 619.15 cm^{-1} is representing the formation synthesis ZnO NPs. This is in agreement with [14]. The FTIR spectra of plant extract were shown in Fig. 3A: which clarified that a wide peak achieved at 3304.06 is related to O-H stretching this result is same as the result that obtained by [15].

XRD characterization of zinc oxide nanoparticles

Fig. 4: Position (2ThCopper (Cu) shows the XRD Spectra illustrate the synthesis of ZnO NPs using cinnamon zylanicum extract, (ZnO A) and (ZnO S) as precursor. The X-ray peaks diffraction of (ZnOA) was attained at 32.103°, 34.830°, 36.5680°, 47.982°, 57.071°,63.169°, 66.93°, 68.258°and 69.598°, correlate with the lattice plane of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (103), (200) (1 1 2), (2 0 1) and (ZnO S) at 32.039°, 34.727°, 36.532°, 47.754°, 56.818°,63.072°, 66.61°, 68.167°and 69.28°, correlate with the lattice plane of (1 0 0),(0 0 2), (1 0 1), (1 0 2), (1 1 0), (103), (200) (1 1 2), (2 0 1) indicated the crystallization of ZnO NPs structure. The nano particle dimeter size was determined by using Debye–Scherer equation = in which D = Kλ/ βcosθ where, D- is particle size in nm, λ- X-ray wavelength, β- FWHM, θBragg's angle of reflection. The average size of ZnO nanoparticle crystallite dimeter of present study of (ZnO A) was (12.74 nm) and (ZnO S) was (13.42) which indicates the good crystallization of ZnO nanoparticle as shown in the Table 1 and the Joint Committee on Powder Diffraction Standards JCPDS of (ZnO A) No. in present study was:(01-079-2205) and (ZnO S) was also :(01-079-2205) in which applied as reference to determine lattice planes in relation to induced plain. The strongest peak of (ZnO A) and (ZnO S) in the present study was seen at (101). XRD patterns of both ZnO NPs in present study showed hexagonal wurtzite structure, the obtained patterns identified our prepared material

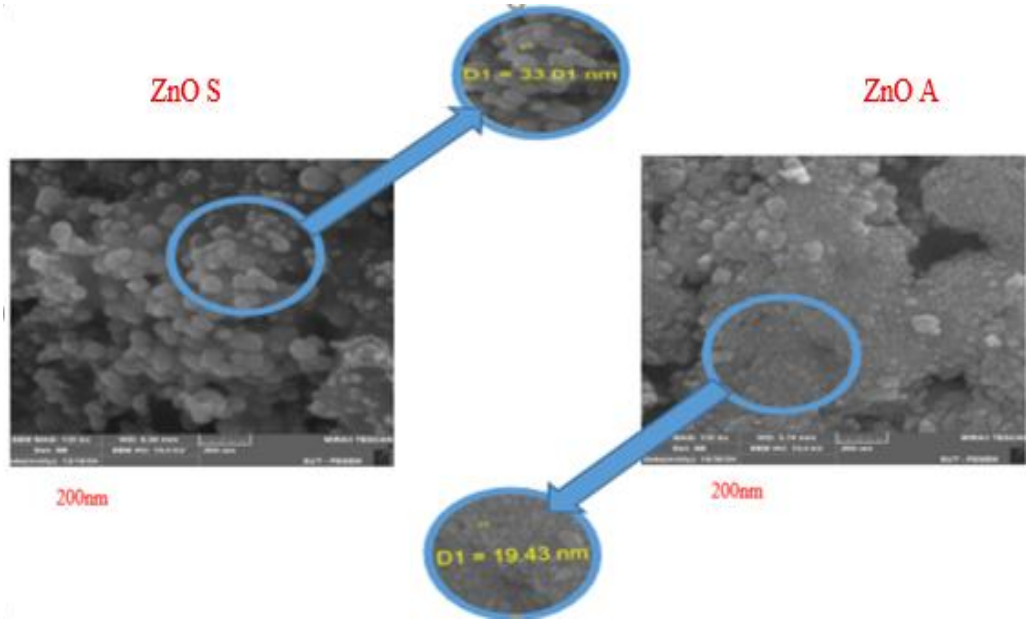

Fig. 5. FeSem images of ZnO of ZnO nanoparticle using zinc acetate (ZnOS), zinc sulfate(ZnOA) precursors and cinnamon zeylanicum as plant extract.

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as ZnO structure with lattice parameters of a = b = 249 and c = 206, as mentioned in [14, 16, 17].

FE-SEM Characterization of ZnO nanoparticle

The surface morphology of cinnamon ZnO Acetate NPs were confirmed by Sem images in Fig. 5,where indicated that all shapes of ZnO NP were nearly same they were appeared as spherical, hexagonal,clearly defined borders, this due to basic media and well distribution of hydroxyl group also less aggregated than zinc sulfate precursors due to acetate stabilize the particle during its synthesis, the present study in accordance with [11] were using other plant extract Salvadora Persia leaf extract with zine acetate as precursor [18] .FeSEM image in Fig. 5 also indicated that the size of nanoparticle was (19.43nm)for (ZnO A) and (33.01nm) for (ZnO S) while other study reported 70nm when zinc sulfate were used as precursor[19] . This result is in agreement with the result of XRD of our present study in which indicates that the particle size is less than 100nm [20].

EDS and MAPS Characterizations of ZnO nanoparticle

Figs. 6, 7A, and 7B: both EDS and MAPs were explaining and confirm the formation of ZnO Nps and EDS showed the component of ZnO NPs in which the presence of maximum peaks of Zinc and Oxygen and the highest peaks of Zinc were observed at 1 eV and 8.6 eV, while the Oxygen signal appeared at 0.5 eV.as showed in Fig. 6 identified the green synthesis of pure ZnO NPs. It was about %80 for (ZnO A) and about %60 and for (ZnO S) in which in agreement [19], [21] while other studies reported %17.81 of ZnO NP by zinc acetate precursor from Wodyetia bifurcata fruit peel extract [8]. The biomolecules in cinnamon zeylanicum are the source of trace

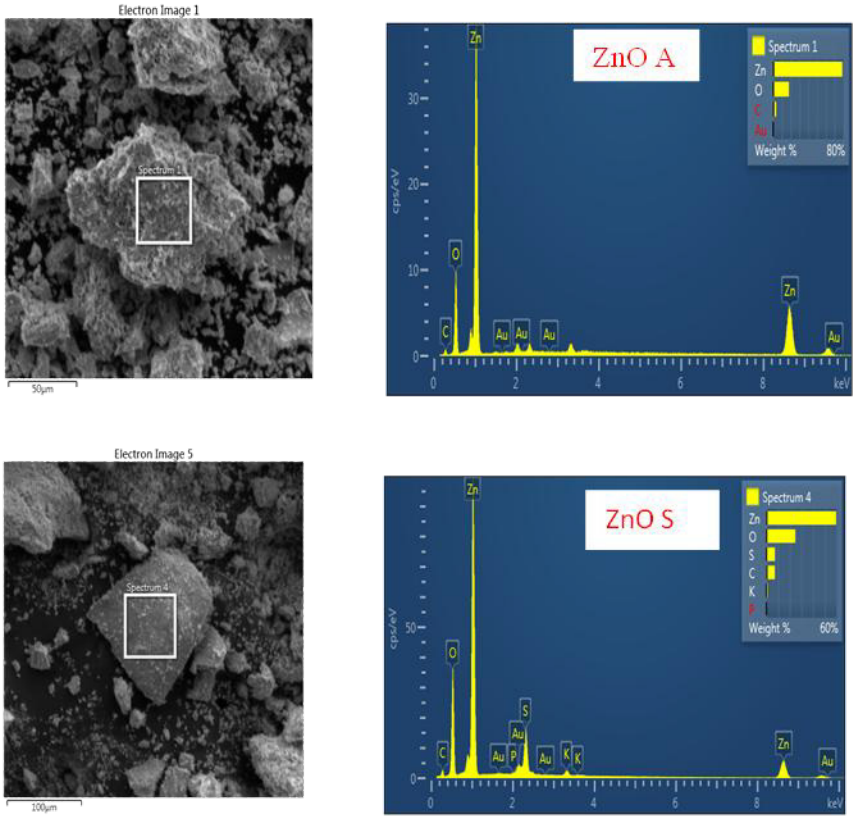

Fig. 6. Image of EDX of ZnO nanoparticle using zinc acetate (ZnO A), zinc sulfate (ZnO S) precursors and cinnamon zeylanicum as plant extracts.

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amounts of (C) as well as Au, P, S, and K of both precursors indicates the capping agents of plant photochemical elements [22].

CONCLUSION

Green synthesis of ZnO NP by cinnamon zeylanicum is easy,ecofriendly less toxic, less

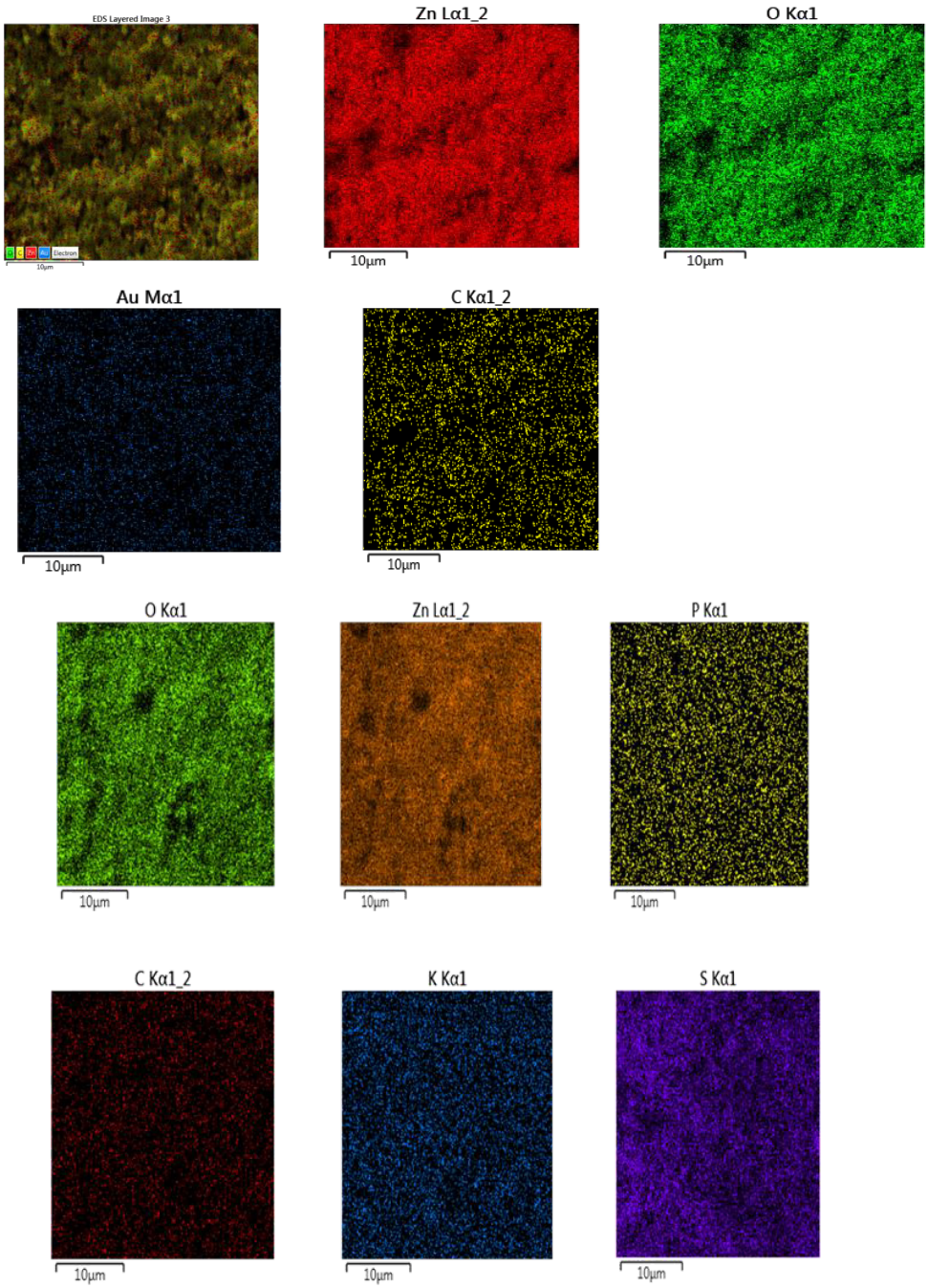

Fig. 7. A) image of MAP of ZnO nanoparticle using zinc acetate (ZnO A), precursors and cinnamon zeylanicum as plant extract confirms the formation of pure ZnO NP, B): image of MAP of ZnO nanoparticle and trace elements using zinc sulfate (ZnO S) precursors and cinnamon zeylanicum as plant extract confirms the formation of pure ZnO NP.

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time consuming and act as good reducing and capping agent for synthesis ZnO NPs by both precursors (ZnO A) and (ZnO S)all of each following characterizations including UV vis spectrometer,FTIR,XRD,FESEM,EDS and MAPS confirm the green synthesis of ZnO NP by cinnamon zeylanicum, however the present study zinc acetate recorded smaller particle size less agglomerations and more purified ZnO NP than zinc sulfate, that's why zinc acetate is faster and better absorption in water.

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