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Green Synthesis and Characterization of Zinc Oxide Nanoparticles Using Black Currant Extracts

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Abstract. The goal of the current research was to synthesis zinc oxide nano-particles (ZnONPs) via simple, cheap and eco-friendly method which include reduction of zinc acetate dehydrate to ZnONPs by using of black currant aqueous extract (BC) as a reducing-agent. The characterization of stability, size, morphology, and present the functional groups on the surface of synthesized ZnOBCNPs were achieved by SEM, X–ray diffraction, and FTIR spectroscopy.

Keywords. eco-friendly, Zinc oxide, black currant

INTRODUCTION

Nanotechnology has grown dramatically in the last decade as a function of its applications in health, biotechnology, and chemistry. (1-3). The evolution of this discipline has opened up new frontiers in nano-science, particularly in nanomedicine, biosensing, drug delivery, and gene delivery. (4, 5). Nanoparticles have a high surface-to-volume ratio, which is one of their most attractive properties makes them so intriguing. (6) Thus, nanoparticles atoms on the surface are more active than those in the middle, making the surface more reacting than the bulk material. (7, 8). Chemical, physical, and biological approaches are widely used to produce nanoparticles like laser ablation, lithography, hydrothermal, sol-gel synthesis, etc. All these methods need to use of costly equipment, large space area for setting up of machines, high temperature and pressure (9). The nanoparticles produced by the green synthesis approach have been proven to be Biodegradable, cost-effective, and non-toxic. (10, 11). The development of eco-friendly technologies for synthesizing nanostructured materials has been a key focus of material scientists in recent years. In this regard, green synthesis method, particularly employing extracts from various plants, is an emerging trend in green chemistry because it is simple, inexpensive, and safe. (12). Nano-technology has also raised the standard of living for humans by tackling various common challenges, such as: climate change, the beauty, energy sufficiency, textile, and health industries, including the healing of severe diseases like cancer and Al-zheimer's. (13)

ZnONPs in particularly, show ease of synthesis, bio-safe, environment friendly, non-toxic, biocompatible and display excellent bio-medical applications such as anti-inflammatory (14), anti-cancer (15), antimicrobial, drug delivery (16), wound healing (17), and bioimaging (18). Furthermore, Zinc Oxide (ZnO) and the other four zinc

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compounds have been designated as GRAS (generally recognized as safe) materials by the US Food and Drug Administration. (19).

The development of green approaches for the synthesis of ZnONPs is a critical method that remains a problem for materials scientists. Plant extracts have recently been proposed as an environmentally acceptable alternative to chemicals in the manufacture of ZnONPs (20). Using plants to synthesis NPs could potentially alleviate the toxicity issues associated with chemical procedures, making these NPs more biocompatible than those created using chemical means.(21).

This study aims to synthesis and characterize zinc oxide nanoparticles (ZnONPs) using a biogenic technique utilizing aqueous black currant extract, based on the large quantity of active substances that act as inducing agents in the black currant, such as flavonoids, polyphenol, lignins, and sugar.

MATERIALS AND METHODS

Materials and Instruments

Black currant without seed (*Vitis vinifera*) was purchased from the local market of AL- Diwaniya, Iraq. The rating of black currant was done by the Ministry of Agriculture/ Stat Board for seed testimony in Abu Graib/ Baghdad, Iraq. All other chemicals are provided by Fluka, BDH and Sigma-Aldrich. the crystalline amorphous zinc oxide nano-particles were determined by X-ray diffraction (Shemadzu-6000 Japan). Furthermore, functional groups of Black currants without seed (*Vitis vinifera*) and prepared nano-particles were identified by Fourier-transform infrared spectroscopy (Shemadzu-8400s, Japan 4000 - 400 cm^{-1}). surface topography, partials size and important composition of the ZnONPs was identified by scanning electron microscopy (SEM), Tescan VegaII, Czech.

Extraction of Black currant

About 100 gm of black currant without seed was washed by distilled water for several times and dried at 40°C (incubator) and grinded by blender. A solution of 10 gm of black currant in distilled water (100 mL) was stirred at 45-50°C for 10-20 min by magnetic stirrer with hotplate, and then left at room temperature overnight. The solution was centrifuged at 1000 rpm /15 min. The supernatant was separated and filtered using Whatman® filter paper No.4. Centrifugation and filtration were repeated twice (22).

Green Synthesis of Zinc Oxide Nanoparticles

0.25g zinc acetate dihydrate [Zn $(CH_3CO_2)_2.2H_2O$] (0.2 M) was dissolved in deionized water(50 mL). Then, slowly add (4 ml) of the aqueous BC, drop by drop, with stirring for 10 minutes. By adding two moles of NaOH drop by drop while stirring, the pH of the solution was raised to 12. The pellets (0.1g) were collected and rinsed twice with ethyl alcohol (70 percent) followed by deionized distilled water after the precipitate was separated in a centrifuge at 4000 rpm for 15 minutes. To obtain the ZnONPs, the pellets were dried at 60°C. (23).

RESULTS AND DISCUSSION

The present work includes the preparation of zinc oxide nano-particles (ZnONPs) by a new green method. This method involves the reduction of zinc acetate dihydrate by an aqueous extract of black currant (BC). The presence of different phytochemical compounds in black currant (BC) aqueous extract such as phenols, ketones, terpenoids, aldehydes, polyphenolic, polysaccharides, alkaloids, vitamins(C, A and B3), amides, and amino acids are capable of the nanoparticle's production by phytochemical reduction reaction (24, 25). In particular, flavonoids can act as powerful reducing agents, which are respons-ible for metal reduction and the formation of nanoparticles because of their transition from keto to enol form. Flavonoids have been shown in several studies to behave as chelating agents. For example, quercetin can chelate in three situations, including carbonyl, hydroxyl, and catechol groups, which play an important role in the bio-reduction step and the start of nanoparticle formation and aggregation (26, 27). After adding BC extract, the reduction reaction of zinc acetate dihydrate started, and the color of the precipitate changed to pale yellow from white after a few minutes. The pale-yellow precipitate formation continues spontaneously for 8 hours at room temperature. The reduction rate and ZnONPs formation could be increased by increasing the incubation time. The pH and temperature of the reaction mixture are also important regulating

parameters in the biosynthesis of nanoparticles. As a result, raising the pH to 12 increases the ZnONPs weight during the synthesis process produced as the final product, whilst lowering the pH produces purer ZnONPs. Temperature is also acknowledged as one of the primary effectors in the creation of nanoparticles. It may also affect the weight and color of nanoparticles that have been created. (28). Figure 1. shows the ZnONPs during the synthesis process.

FIGURE 1. (A) pale yellow ZnONPs after mixing with BC. (B) ZnO nano powder dried in oven at 60 ^{0}C.

Figure 2. illustrates SEM images that were seen in magnification (500 nm), which demonstrated the presence of crystal shapes with a mean aver-age diameter of 50.13 nm for ZnONPs formed from BC. The green synthesis of ZnONPs from BC manifested as a close packed periodic array of crystal structure, with particle sizes predicted using the Debye Scherrer equation. These differences in nanoparticle shape could be attributed to the fact that the many samples were not homogeneous in size, allowing only the particles on the sample's surface to be examined by SEM. The existence of negative charges on the surface of nanoparticles, on the other hand, contributed to their stability, while the soluble state acts to prevent their accumulation by enhancing electrostatic repulsion between particles. (29). Many earlier research demonstrated that this amount of negative charges was insufficient to stabilize nanoparticle sustainability, thus the remaining nano-particles in soluble condition can lead to additional accumulation and increase particle size. (30).

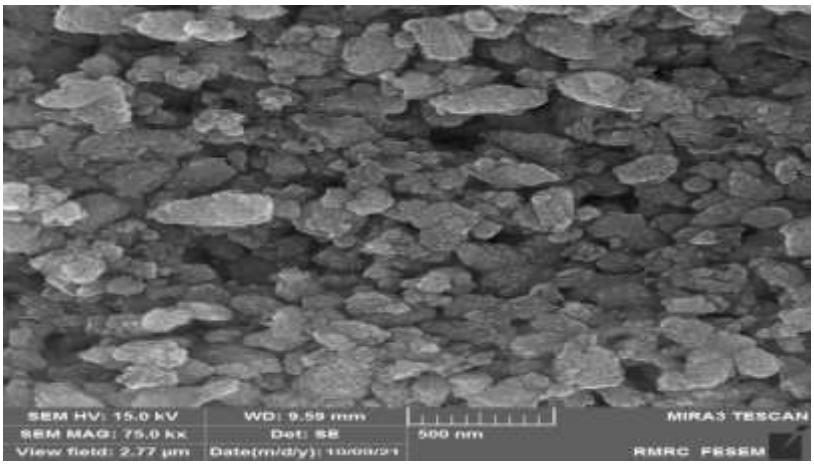

FIGURE 2. SEM image (500nm) of the Zinc oxide nano-particles

The diffractogram of XRD ZnO of nanoparticles shows the intensity of the diffracted rays as a function of diffract-tion angles. In the current study, a pattern of X-ray diffraction peaks at theta angle-2 value of 30.98 , 35.87, 47.26, 55.85, 61.93, 66.78 and 69.02, respectively, correspondent to hkl values of (100), (002), (101), (102), (110), (103), (112), and (201), as shown in Figure 3. The Debye Scherrer equation was used to calculate the size of the nanoparticles.

$$D = \frac{k\lambda}{\beta \cos\theta} \text{ Å}$$

Where D denotes the average crystalline particle size, is the Xray wavelength (1.5406), k denotes the form factor or Scherer's constant (0.9), θ is the Bragg's diffraction angle, and is the XRD peak full width at half maximum.

The average crystalline size of the nano-particles generated was determined using Scherrer's-formula and found to be 50.13 nm. The peaks were found to correspond with the ICDD card number 01-079-0207. The nanoparticles were discovered to be hexa-gonal in nature, with lattice para-meters a (=b) equal to: 3.2568 A^0 and c equal to: 5.2125 A^0, which correspond to previously published values.(31)

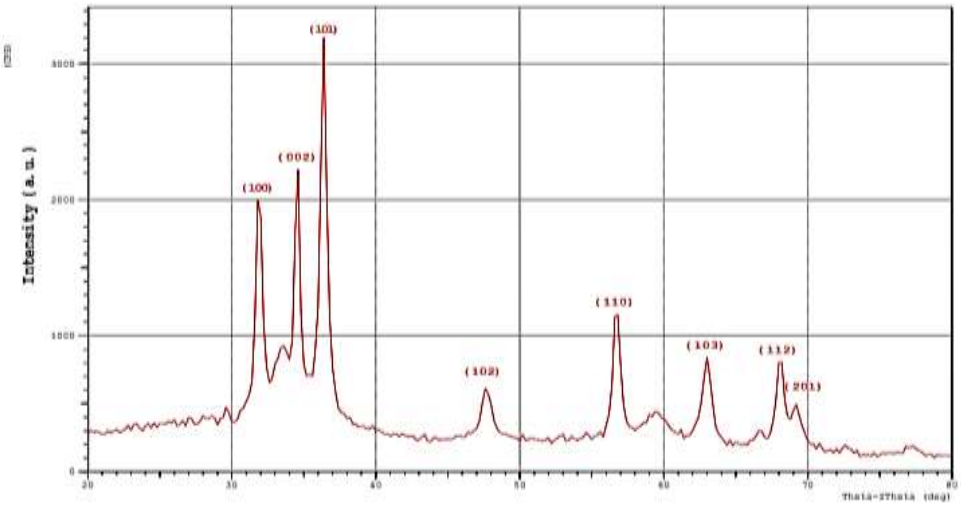

FIGURE 3. X-ray diffraction pattern for of the Zinc oxide nanoparticles

Figure 4 represents the infrared spectrum of the prepared nanoparticles. It shows the types of bonds and functional groups formed in the resulting compound. The bands observed at (3246, 2920, 1563 and 1324 cm^{-1}) represent the stretched frequency of the (OH, C-$H_{alph.}$, C=C , and C-O) bonds respectively. While the band appeared at (480 cm^{-1}) represent Zn-O bond and confirm the formation of nanoparticles. (32)

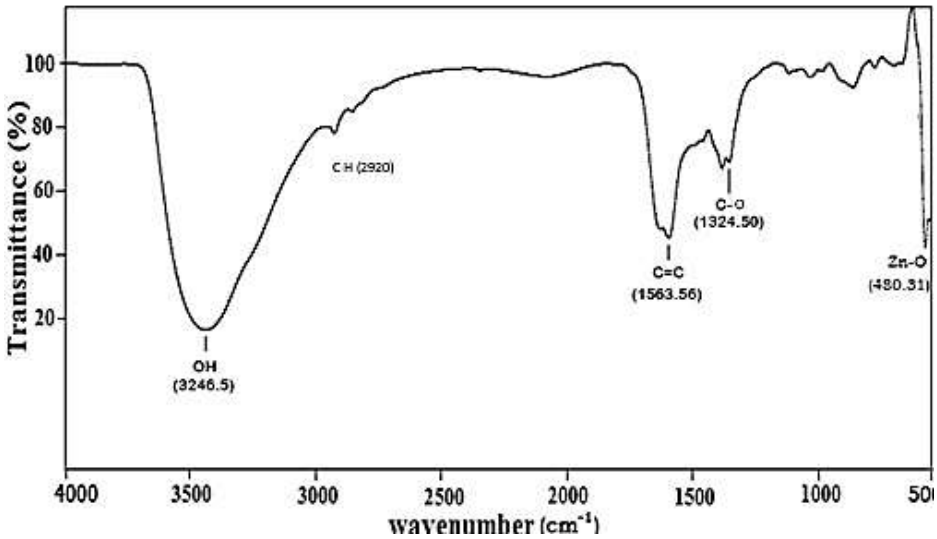

FIGURE 4. FT-IR spectroscopy for the Zinc oxide nanoparticles

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