THE EFFECT OF CALCINATION TEMPERATURES ON THE PROPERTIES OF ZNO NANOPARTICLES SYNTHESIZED BY USING LEAVES EXTRACTS OF PINUS BRUTIA TREE

Sherwan M. Mahdi Ismail 1,2*, Sabah M. Ahmed 1

1 Department of Physics, College of Science, University of Duhok, Kurdistan Region, Iraq

Received: 15 Dec., 2022 / Accepted: 8 Jan., 2023 / Published: 7 June, 2023
https://doi.org/10.25271/sjuoz.2023.11.2.1087

ABSTRACT:

Pinus Brutia (PB) tree leaf extracts were used to produce zinc oxide (ZnO) nanoparticles. The study of the PB tree extracts at several calcination temperatures from (200 to 500) °C on the formation of ZnO NPs’ characteristics has been investigated using various characterization techniques. The chosen plant PB had its findings at both examinations of FTIR and UV-Visible spectroscopies shown and offered to be a superior option for the GS ZnO NPs at various pH levels. PB tree leaf extracts’ UV-visible spectra revealed one distinguishable absorption peak at 275.3 nm. The study of the FESEM results showed that the Green Synthesized (GS) ZnO NPs’ orientation, shape, and dimensions are significantly impacted by the calcination temperatures. The ZnO NPs are also shown by the XRD data to have hexagonal wurtzite crystal structures that have particle sizes at (002) peak falling within the range between (10 to 24) nm. The UV-Visible study of the ZnO NPs showed a strong peak absorbance for ZnO NPs that were calcined at various temperatures, with high UV absorption below 400 nm. The obtained energy band gap (Eg) is located in the region between (2.65 and 2.747) eV, narrowing as the calcination temperature rises. The ZnO NPs that were calcined at a temperature of 500 °C also had superior quality and outperformed those produced at other calcination temperatures, according to all of the analyzed results and properties of the ZnO NPs.

Keywords: Calcination Temperature, ZnO NPs, Pinus Brutia, Green Method, Tree Extract

1. INTRODUCTION

One of the most rapidly developing and ever-evolving fields is nanotechnology, regarded as the industrial revolution of this time. With the potential to form and underpin an advancement in a wide range of biotechnology and technology (Azeez et. al., 2020). Many research and commercial fields, including electronics, information technology, biology, agriculture, chemistry, and physics, have used nanotechnology (Abdelbaky et. al., 2022). Due to the advanced chemical and biological properties of nanoparticles, they have many applications in science. These advanced properties of nanoparticles can’t be found in the bulk material of the same chemicals (Khan et. al., 2019).

The unique property of nanoparticles (NPs) is that they have a high surface-to-volume ratio. This makes them good candidates for performance-oriented applications like cosmetics, creating gas sensors, energy storage, electronics devices, food packaging, and environmental remediation, which promotes their incorporation into a wide range of technology (Nilavukkarasi et. al., 2020; Zheng, et. al., 2020). It is believed that metal oxide nanoparticles are more advantageous than other nanoparticles due to their unique physical, chemical, and biological properties (Waseem et. al., 2020). ZnO nanoparticles, known for their remarkable piezoelectric, optoelectronics, pyroelectric, semiconducting, catalysis, and antimicrobial properties, are among them. They have been recognized as a material with great potential in all fields, such as physics, biology, engineering, chemistry, and so on (Bettini et. al., 2015; Hong et. al., 2011).

Numerous negative side effects and toxicities are brought on by the reduction and capping of nanoparticles with toxic chemicals. Consequently, the use of plant extracts in the synthesis of metal oxide nanoparticles has grown in significance (Meron et. al., 2020). Compared to conventional chemicals, this method is more environmentally friendly and has a quicker reaction time. Plant extracts have a variety of bioactive molecules that help stabilize and reduce nanoparticles (Seyyed et. al., 2020).

According to past research, researchers managed to form Zinc Oxide NPs through plant extracts; a large number of plants that are used to synthesize ZnO NPs can be found in literature, for example, Trifolium pratense, Alse vera, Vitex trifolia, Matricaria chamomilla, Camellia sinensis, Azadirachta indica, Artocarpus gomezianus, Olea europaea, and Duranta erecta (Meron et. al., 2020).

A green chemical and environmentally benign approach for the synthesis of zinc oxide (ZnO) nanostructure has been explored using aqueous solution of Gum Arabic (GA) (Taha et. al., 2019). Agarwal et. al. (2019) focus on the fabrication of nano-sized ZnO particles by using zinc oxide as a precursor molecule and leaf extract of Cinnamomum Tamala as a reducing and capping agent. The structural analysis confirmed that copper ions substitute Zn ions without altering their wurtzite structure and a crystallite size of 10–16 nm with high degree of crystallization (Vanaja et. al., 2019). Kanmorhi et. al. (2019) have prepared zinc oxide by high pressure homogenization process and the resultant zinc oxide was evaluated as fibers in CS/PVA/MC3 films. Ghalawat et. al. (2019) reviewed the progress made in recent years on nanoparticle biosynthesis by microbes. Zhou et. al. (2020) present a highly selective transformation of methane to methanol using gold modified zinc oxide as a photocatalyst under full light spectrum irradiation at atmospheric temperature. Chauhan et. al. (2020) explore removal of carcinogenic cationic and anionic dyes from aqueous medium using green fabricated zinc oxide nanoparticles (ZnO-NPs). Plants contain biomolecules that can act as capping, oxidizing and reducing agents that increase the rate of reaction and stabilizes the NPs. Rahman et. al. (2021) emphasize and compiles different types of plants and parts of plant used for the synthesis of ZnO and its potential applications at one place. Other influential work includes (Patil et. al., 2020 and Sekar et. al., 2021).

The subject of (Faye et. al., 2021) was to synthesise ZnO and nickel doped ZnO nanoparticles using Euphorbia abyssinica bark extract for antimicrobial activity studies via agar disk diffusion method against some selected microbes. Diab et. al. (2022)
evaluate the effects of green-synthesized zinc oxide nanoparticles (ZnO-NPs) using Ulva fasciata extract as an anti-fungal agent against Candida albicans (C. albicans) in vitro and in vivo in O. niloticus. Irfan et. al. (2022) develop zinc oxide nanoparticles (ZnO-NPs) based surgical sutures for the accelerated wound healing process. The NPs synthesized by the method are also free from toxicity properties. Chandrasekaran et. al. (2022) describe one such green synthesis method for zinc oxide nanoparticles (ZnO NPs) using the aqueous flower extract of Senna auriculata. Biogenic ZnO NPs were synthesized using seed extract by a simple, cost-effective, and green chemistry approach (Sakthivel et. al., 2022).

This study was aimed at the environmentally friendly fabrication of ZnO-NPs from plant extract (Awan et. al., 2022). Other influential work includes (Ari et. al., 2021; Hasan et. al., 2022; Nitnavare et. al., 2022 and Mutukwa et. al., 2022).

This research focuses on the production of ZnO nanoparticles through the green method from Pinus Brutia (PB) tree leaf extracts. The effect of different calcination temperatures in the range of (200 to 500) °C on the quality characteristics of GS ZnO NPs has been studied. The importance of this research is highlighted by a thorough examination of the various factors that influence the shape, size, particle size distribution, optical properties, crystal structure, and energy band gap of ZnO NPs. The role of green plant biomolecules in the bioreduction of metal salts during nanoparticle extraction has been demonstrated.

2. EXPERIMENTAL METHOD

The zinc salt (Zinc nitrate hexahydrate) [Zn (NO\(_3\))\(_2\) \(\cdot\) 6H\(_2\)O] with molecular weight (297.48 g/mol) and purity greater than (99%) as well as sodium hydroxide powder ([NaOH] molecular weight (40 g/mol)) were purchased from Sigma-Aldrich and used for this study with no further treatment.

The 60 grams of fresh green PB tree leaves were collected, washed thoroughly with distilled water to remove any dust or pollution, cut into small pieces, and then placed in 600 ml of distilled water. The mixture was heated at 75 °C for 50 minutes, after which the PB leaf extracts were filtered many times using filter paper with pore sizes of 8 μm and centrifuged extensively (Karam et al., 2022). The characterization using a UV-V spectrometer and FTIR were checked, and the extracts were stored in a cold place for future use.

To prepare the GS ZnO NPs at different calcination temperatures, 60 ml of PB tree extracts from the leaf were added dropwise to (0.1 M) in 60 ml of zinc nitrate hexahydrate [Zn (NO\(_3\))\(_2\) \(\cdot\) 6H\(_2\)O] dropwise under magnetic stirring at 75 °C degrees for 30 minutes. Later, the pH of the prepared GS mixture was adjusted to 8 by adding drops of (NaOH) sodium hydroxide while the magnetic stirrer was turned on. A pH meter was used to monitor the pH of the solution continuously. The color and transparency of the mixture began to change as the pH was adjusted, indicating that a reaction between the metal salt and the plant extracts occurred, and ZnO NPs were formed. For 8 hours, the setup was kept on magnetic stirring at 75 °C until all of the water evaporated (Amad et. al. 2022). After 8 hours on the heater stirrer, the leftovers from the mixture were calcined and purified in the annealing furnace for 2 hours at several calcination temperatures. The final product of GS ZnO NPs was then stored in a tube for characterization, as shown in Figure 1. For different calcination temperatures of the GS mixture, such as (200, 300, 400, and 500) °C and the fabricated samples were labeled (a), (b), (c), and (d), respectively.

![Figure 1. Schematic Diagram representation of the ZnO NPs using Green Synthesized at different Calcinations Temperatures using Leaf extracts of the PB tree.](image-url)
shape, chemical composition, size, and orientation of ZnO NPs, studying the size and crystal formation, stress and strain, and quality of the produced Zinc Oxide nanoparticles at different calcination temperatures were all carried out using PB leaf extracts and the various functional groups that appeared in them (Nicolet IS10, Thermo Scientific, Waltham, MA, USA).

The testing range for Fourier Transform Infrared Spectroscopy (FTIR) was set to begin at 400 to 4000 cm\(^{-1}\), followed by using the Supra 55VP from Carl Zeiss AG. We performed (EDX) energy-dispersive X-ray spectroscopy and (FE-SEM) field emission scanning electron microscopy with CuK radiation at 1.54050 angstroms and scanning angles between 20 and 80 degrees.

3. RESULTS AND DISCUSSION

The Fourier Transform functional groups (FTIR) associated with reductive biomolecules have been investigated using infrared of the tree extract spectra and the functional groups that support the reduction of ZnO (Aswathy et. al., 2021; Barzinjy et. al., 2020). Figure 2 depicts the FTIR spectrum of the PB tree leaf extracts. As can be seen, this spectrum exhibits many peaks between (400-4000) cm\(^{-1}\). In essence, the FTIR spectrum may be separated into two regions: first, from (0-1500) cm\(^{-1}\) is the region that can be called the fingerprint; in this region, it is possible to see that plant extract that is utilized to create ZnO nanoparticles. Second, the functional group region spans the range of (1800-4000) cm\(^{-1}\). FTIR spectra typically provide information about the composition of internal components that connect all stages of matter (Norouzi et. al., 2019; Srivastava, et. al. 2013 and Zandi et. al., 2011). Peak absorption at 815 cm\(^{-1}\) is mostly caused by C-H bond 1,4-disubstitution (para). The phosphate ion of common inorganic ions is the peak that was observed at 1072 cm\(^{-1}\). The measured absorption peak for the aryl-O stretch of ether and oxy molecule, which includes aromatic ethers, is at 1253 cm\(^{-1}\). At 1340 cm\(^{-1}\), CN stretch, the aromatic primary amine is at its highest absorption. Additionally, the peak of primary amine, or 1608 cm\(^{-1}\) NH bend, is seen. The 2931 cm\(^{-1}\) peak under investigation is a Methylene C-H asym./sym. stretch (>CH2). The aliphatic secondary amine and >N-H stretch of secondary amino, respectively, peak at 3334 cm\(^{-1}\) and 3363 cm\(^{-1}\). Additionally, aliphatic primary amine and NH stretch peaks at 3385 cm\(^{-1}\). Meanwhile, the obtained peak at 3421 cm\(^{-1}\) is an NH stretch and an aromatic primary amine (Kim et. al., 2001).

![Figure 2. FTIR Spectrum Analysis of the PB Tree Leaf Extracts](image-url)

The leaf extracts' UV-visible spectrum of the PB tree is shown in Figure 3. One maximum peak was visible at a wavelength of (275.3) nm. This peak can be explained by the phytochemicals found in the leaf extracts of the PB tree, which is plausible given that OH groups serve as numerous stabilizing agents. NPs can be created by bio-reducing (Singh et. al., 2016). Since these phytochemicals are antioxidants and free of hazardous substances, they continue to be very effective at reducing metal ions and their stability at the nanoscale. Phytochemicals can produce nanoparticles of varied shapes and sizes simultaneously (Hocine et. al., 2016). Electromagnetic waves carry out the creation of NPs, and the spectra of the (UV-Vis.) indicated the absorption peak (SPR) surface plasmon resonance and retains electron (e) oscillations in the conduction-band reactive metal ion reduction (Pai 2019).
The size, density, distribution, shape, formation, and orientation at different calcination temperatures for ZnO nanoparticles have been studied by using the FESEM analysis, as shown in Figure 4. It can be observed that the ZnO nanoparticles were formed by using Pinus Brutia tree leaf extraction and modified by increasing several calcination temperatures from 200 °C to 500 °C. Also, it is noticeable from Figures 4 (a) to 4 (c) that the ZnO NPs were successfully produced with high density and had a high rate of agglomeration due to the electrostatic charge. Due to a high agglomeration rate, the average size distribution was not estimated for the ZnO NPS samples synthesized with calcination temperatures 200, 300, an. The agglomeration makes the NPs stick together, making it challenging to observe the NPs. Whereas, the shape and size of Zinc oxide nanoparticles increase with increasing the calcination temperature. The novelty of this study is giving a good idea about understanding the calcination temperature of the final product of ZnO NPs.

In Figure 4, as the calcination temperature increases, one can clearly understand that the calcination temperature plays an essential role in the deagglomeration of the ZnO NPs.

Figure 3. UV-Vis. Spectrum Analysis of the Pinus Brutia Tree Leaf Extracts

Figure 4. The effect of Various Calcination Temperatures on the Morphological Properties of Zinc Oxide Nanoparticles Produced by utilizing the leaf Extracts of the Tree of Pinus Brutia: (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.
The green synthesis nanoparticles, distinguished by significant aggregation formation, are where ZnO NPs are typically found. This is a result of the larger surface area and lasting affinities of biosynthetic NPs that cause them to clump or aggregate together (Vidy et al., 2013). One might assert that ecological factors significantly affect stability and NP agglomeration. As a result, as the nanoparticles grew, they came together, and a symmetrical cluster appeared on its own (Shim et al., 2019). While the calcination temperature the size, shape, and other characteristics have been studied. When the temperature is increased to 500 °C, the ZnO NPs have been in spherical shapes, and the majority of these NPs were gathered together to form clusters with high distribution densities as shown in figure 4, which shows that the ZnO NPs have narrow size distribution, shape, and low rate of agglomerations. They have an average size of about 65.70 nm.

The elemental chemical composition of the biosynthesized ZnO NPs is investigated and evaluated using EDX spectroscopic analysis in different calcination temperatures in the range of (200-500) °C. One can notice that the EDX analysis. It is apparent that both the Oxygen (O) and Zinc (Zn) elements are present, eliminating the possibility of any impurity’s indicators with respect to the orientation of the features structures of the green synthesis ZnO NPs. The Au energy was observed because the ZnO NPs were coated with gold NPs before taking the EDX and FESEM analysis. ZnO nanoparticles exhibit unique features, as evidenced by the two highly directed Zn peaks in the EDX spectrums that were about 1.1 and 8.7 keV and an oxygen signal at 0.5 keV (Amad et al., 2022). All green synthesis ZnO NPs made at different pH levels have approximately the same zinc (Zn) to oxygen (O) atomic ratio. Quantitative characterizations from (EDX) show that the studied nanoparticles are pure GS ZnO because the computed (MR) molecular ratio of Zinc. Oxygen in the generated nanoparticles is 1:1. The weight percentage of GS ZnO nanoparticles composition has been obtained using EDX analysis at numerous calcination temperatures which are Zn (70.2%, 70.8%, 82.6%, and 82.4%) and O (29.8%, 29.2%, 17.4%, and 17.6%) for calcination temperatures 200 °C, 300 °C, 400 °C, and 500 °C, respectively.

![Figure 5](image_url)

Figure 5. The effect of the Various Calcination Temperatures on the Elemental Chemical Compositions (EDS) of Zinc Oxide Nanoparticles Produced by utilizing the leaf Extracts of the of Pinus Brutia Tree: (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

The structural properties of the fabricated ZnO NPs from Pinus Brutia plant leaf extracts with various calcination temperatures were investigated using the non-destructive XRD technique, as shown in Figure 6. The investigated diffractions for all XRD patterns of ZnO NPs were biosynthesized with hexagonal (wurtzite) polycrystalline crystal structures and indexed with the standard XRD database (JCPDS card number 98-009-4004). Further evidence that the ZnO NPs made from Pinus Brutia tree leaf extracts at various calcination temperatures were formed with extremely high purity of ZnO nanocrystal phases came from the lack of peak diffraction from other defects (impurities). Figure 6 shows that (100), (002), and (101), which are the three main and firm diffraction peaks with changing intensities that are present in the X-ray diffraction peaks for all calcination temperatures, changed in intensity as the ZnO NPs were calcinated at various temperatures. The diffraction peaks along the (101) plane are also more apparent and robust; also, the XRD results and behaviors displayed are completely consistent with other studies (Barzinjy et al., 2020, Dey et al., 2022, Abdo et al. 2021, Abel et al. 2021).
The average particle size of ZnO NPs produced at various calcination temperatures of the three dominant planes, (100), (002), and (101), is determined using the Debye-Scherrer equation (Abdulrahman et. al., 2020): Table 1 displays the results of (D).

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]  

(1)

where \( K \), \( D \), the angle of diffraction, the wavelength of the X-ray beam, and the shape factor of the crystallite are, in turn, the (FWHM) Full Width at Half Maximum of the peak, respectively. When ZnO NPs are calcinated from 200 °C to 500 °C, the average particle size has been changed. The annealing process causes the particles to reorient due to heat energy, which also helps to reduce crystal structural flaws. At the same time, it results in variations in the average size of the particles of ZnO NPs (Korake et. al., 2014).

The dislocation density (\( \delta \)) of ZnO NPs produced with various calcination temperatures in the range between (200 to 500) °C, which is computed using the equation below, coupled with the dislocation density of synthesized ZnO NPs (Abdulrahman et. al., 2020), represents the number of defects present in the Zinc Oxide NPs (Abdulrahman et. al., 2020), which is caused by internal strain. The obtained results of (\( \delta \)) have been listed in Table 1:

\[
\delta = \frac{1}{D^2}
\]  

(2)

Where D is the crystallite size

From Table 1, one can conclude that the calcination temperature significantly affects the number of defects present in the Zinc Oxide NPs. The following equations (Abdulrahman et. al., 2020) have been implemented to evaluate the effect of various calcination temperatures on the length of the bond as well for hexagonal-cell volume of produced ZnO nanoparticles along the planes of (100), (002), and (101). The results are reported in Table 1.

\[
L = \frac{a^2}{c} + \left( \frac{1}{2} - u \right)^2 c^2
\]  

(3)

The length of the "c" axis is a parameter related to the ratio of "c/a," and "u" represents the distance that the atoms traveled in the direction of the subsequent atoms, according to the formula below (Abdulrahman et. al., 2020):

\[
u = \frac{a^2}{3c} + 0.25
\]  

(4)

To investigate (V) the hexagonal cell's volume, the below formula has been employed (Abdulrahman et. al., 2020):

\[
V = \frac{\sqrt{3} a^2 c}{2}
\]  

(5)

Table 1: The effects of the calcination temperatures on the ZnO nanoparticle's volume, bond length, dislocation density, crystal size, and (100), (002), and (003) peak diffraction planes (101)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Plane</th>
<th>D (nm)</th>
<th>( \delta \times10^5 ) (Å(^2))</th>
<th>V(Å(^3))</th>
<th>L (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>100</td>
<td>23.989</td>
<td>1.737</td>
<td>50.946</td>
<td>2.025</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>41.951</td>
<td>0.568</td>
<td>52.318</td>
<td>2.044</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
<td>20.989</td>
<td>2.269</td>
<td>51.033</td>
<td>2.027</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>23.991</td>
<td>1.737</td>
<td>50.814</td>
<td>2.024</td>
</tr>
<tr>
<td>200</td>
<td>002</td>
<td>21.131</td>
<td>2.239</td>
<td>40.674</td>
<td>1.879</td>
</tr>
<tr>
<td>300</td>
<td>002</td>
<td>10.563</td>
<td>8.961</td>
<td>40.903</td>
<td>1.883</td>
</tr>
<tr>
<td>400</td>
<td>002</td>
<td>16.914</td>
<td>3.495</td>
<td>40.003</td>
<td>1.869</td>
</tr>
<tr>
<td>500</td>
<td>002</td>
<td>24.154</td>
<td>1.714</td>
<td>40.468</td>
<td>1.875</td>
</tr>
<tr>
<td>200</td>
<td>101</td>
<td>42.488</td>
<td>0.554</td>
<td>34.759</td>
<td>1.783</td>
</tr>
<tr>
<td>300</td>
<td>101</td>
<td>33.974</td>
<td>0.866</td>
<td>35.218</td>
<td>1.791</td>
</tr>
<tr>
<td>400</td>
<td>101</td>
<td>21.248</td>
<td>2.215</td>
<td>34.546</td>
<td>1.779</td>
</tr>
<tr>
<td>500</td>
<td>101</td>
<td>24.286</td>
<td>1.700</td>
<td>34.489</td>
<td>1.778</td>
</tr>
</tbody>
</table>

By applying Bragg's law (Ahmed et. al., 2020), (a & c) the lattice constants, with the three main planes (100), (002), and (101) of hexagonal Zinc Oxide NPs structure with various...
calcination temperatures have been calculated. The results of (a & c) are shown in Table 2.

$$a = \frac{\lambda}{2 \sin \theta}$$
$$c = \frac{\lambda}{\sin \theta}$$

(6)

(7)

The diffraction peak's angle is denoted by the symbol "θ" and "λ" also denotes the X-ray source's wavelength.

Because of the following equations (Ahmed et. al., 2020), the strains (ξc) and (ξa), the main planes of the a-axis and c-axis, respectively, of the Zinc Oxide Nanoparticles produced at different calcination temperatures, are considered. The results of (ξc) and (ξa) are listed in Table 2.

$$ξ_a = \frac{a - a_0}{a_0} \times 100\%$$

(8)

$$ξ_c = \frac{c - c_0}{c_0} \times 100\%$$

(9)

Because of the following equations (Ahmed et. al., 2020; Ahmed et. al., 2021), the optical characteristics of GS ZnO NPs with the Sharper Peaks Diffraction planes of (100), (002), and (101) have been used:

$$\frac{1}{\sin \theta} = \frac{4}{3} \left( \frac{h^2 + h^2 + k^2}{a^2} \right) + \frac{1}{c^2}$$

(10)

Anywhere h, k, and l are situated Miller indices as per X-Ray diffraction peaks.

Table 2: Impact of Several Calcination Temperatures on the Lattice Parameters and Zinc Oxide (wurtzite-hexagonal) Structure properties of the produced Zinc Oxide Nanoparticles with the Sharper Peaks Diffraction planes of (100), (002), and (101)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Plane</th>
<th>FWHM</th>
<th>2θ</th>
<th>c (Å)</th>
<th>ξc%</th>
<th>a (Å)</th>
<th>ξa%</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>100</td>
<td>0.3444</td>
<td>31.883</td>
<td>5.609</td>
<td>7.807</td>
<td>3.238</td>
<td>-0.262</td>
<td>2.805</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>0.1968</td>
<td>31.5944</td>
<td>5.659</td>
<td>8.766</td>
<td>3.267</td>
<td>0.625</td>
<td>2.829</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
<td>0.3936</td>
<td>31.8645</td>
<td>5.612</td>
<td>7.868</td>
<td>3.240</td>
<td>-0.206</td>
<td>2.806</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>0.3444</td>
<td>31.9114</td>
<td>5.604</td>
<td>7.714</td>
<td>3.236</td>
<td>-0.349</td>
<td>2.802</td>
</tr>
<tr>
<td>200</td>
<td>002</td>
<td>0.3936</td>
<td>34.4427</td>
<td>5.203</td>
<td>0.011</td>
<td>3.004</td>
<td>-7.474</td>
<td>2.602</td>
</tr>
<tr>
<td>300</td>
<td>002</td>
<td>0.7872</td>
<td>34.3765</td>
<td>5.213</td>
<td>0.198</td>
<td>3.009</td>
<td>-7.302</td>
<td>2.606</td>
</tr>
<tr>
<td>400</td>
<td>002</td>
<td>0.3444</td>
<td>34.5031</td>
<td>5.195</td>
<td>-0.158</td>
<td>2.999</td>
<td>-7.631</td>
<td>2.597</td>
</tr>
<tr>
<td>200</td>
<td>101</td>
<td>0.1968</td>
<td>36.3581</td>
<td>4.938</td>
<td>-5.092</td>
<td>2.851</td>
<td>-12.197</td>
<td>2.469</td>
</tr>
<tr>
<td>300</td>
<td>101</td>
<td>0.246</td>
<td>36.194</td>
<td>4.959</td>
<td>-4.677</td>
<td>2.863</td>
<td>-11.812</td>
<td>2.479</td>
</tr>
<tr>
<td>400</td>
<td>101</td>
<td>0.3936</td>
<td>36.4351</td>
<td>4.928</td>
<td>-5.286</td>
<td>2.845</td>
<td>-12.376</td>
<td>2.463</td>
</tr>
<tr>
<td>500</td>
<td>101</td>
<td>0.3444</td>
<td>36.4558</td>
<td>4.925</td>
<td>-5.339</td>
<td>2.844</td>
<td>-12.424</td>
<td>2.463</td>
</tr>
</tbody>
</table>

The optical characteristics of GS ZnO NPs which were calcinated with different temperatures from 200 °C to 500 °C were studied using the double beam UV-Visible spectrophotometer by observing the absorption spectrum. The absorption spectrums of GS ZnO NPs produced using extracts of the leaf of PB tree at different calcination temperatures in the wavelength range between (300 to 800) nm is shown in Figure 7. The GS ZnO NPs powder exhibits strong (UV) absorption, a high rate of absorbance less than 400 nm, remarkable clarity, and a narrow visible absorption range when the calcination temperature is varied (Roza et. al., 2015).
Figure 7. The effect of the Various Calcination Temperatures on the Optical Absorption Properties of Zinc Oxide Nanoparticles Produced by utilizing the leaf Extracts of the Tree of Pinus Brutia

Low absorption values at long wavelengths are caused by defects in GS ZnO NP that rely on the crystal's quality, lattice parameters, crystal size, and oxygen vacancies that exist as donor impurities (Shabannia et. al., 2014). In the wavelength range of (381-388.5) nm, exciton absorption and a strong UV absorption edge have been observed. These phenomena are connected to the (Eg) optical Energy Band-gap of the GS ZnO nanoparticles at varied calcination temperatures. When the peak is sharpened, monodispersed ZnO NPs are produced as a result of the (SPR). Rather than following the rule of thumb, the maximum peak absorption of Zinc Oxid Naneoparticles was discovered to be in the range between 350 and 400 nm. The value obtained is smaller than the one that bulk Zinc Oxide anticipated using 381 nm to 388.5 nm wavelengths, and it also exhibited a blue shift in excitonic absorption, suggesting a slight quantum confinement effect (Barzinjy et. al., 2020).

Figure 8. The projection of the linear component of (αhv)^2 versus (h) using transmittance spectra. The Tauc formula is then used to determine the optical band-gap energy of GS ZnO NPs using PB tree leaf extracts at various calcination temperatures (Abdulrahman et. al., 2022):

\[
(\alpha \cdot h \cdot v)^2 = A(h \cdot v - E_g)^n \tag{11}
\]

Where \( \alpha \), \( h \), \( A \) and \( E_g \) are the absorption coefficient, photon’s energy, constant, and optical band gap energy. Also, \( n \) depends on the transmission, and it is equal to 1/2 for allowed direct transmission.

The \( (\alpha) \) coefficient container’s major focus is the transmittance spectrum, which is used in conjunction with (Abdulrahman et. al., 2022).

\[
\alpha = \frac{\ln(T)}{d} \tag{12}
\]

\( T \) “and “d” are the transmittances and thickness aimed at ZnO samples.

Figure 8. The Influence of the Different Calcination Temperatures on the Optical Energy Band Gap of Zinc Oxide Nanoparticles Produced by utilizing the leaf Extracts of the Tree of Pinus Brutia. Tauc-plot Versus Eg.
From Figure 8, one can see that the transition region of the produced GS ZnO NPs with various calcination temperatures is roughly in the range of (2.65-2.7) eV, which is represented by the Eg corresponding to the transition band between both valance and conduction bands, that denotes the Eg of the semiconductor ZnO NPs (Roza et. al., 2015). Also, from the plots in Figure 8, the obtained Eg of synthesized GS ZnO NPs with different calcination temperatures are (2.747, 2.711, 2.675, and 2.625) eV, and (200, 300, 400, and 500) °C, respectively. The Eg is decreased with increasing the calcination temperature from 200 °C to 500 °C. This decrease in the Eg of the nanoparticles is due to the change in the lattice constant of the tree’s leaf extracts, because of the use of plant extracts, a lowering in the band gap is expected (Khan et. al., 2019). This discovery, which was made primarily in GS NPs, is not contradictory with quantum (effect) confinement occurrences. GS NPs are typically more active than NPs produced by other fabrication methods.

FTIR spectrum analysis has been employed to examine and study the functional group, purity, and composition of the obtained ZnO nanoparticles produced via the GS technique, and by displaying in Figure 9. Figure 9 demonstrates that no peaks were apparent in the observation range and showed the purity of the GS ZnO nanoparticles which were calcinated with different temperatures. The FTIR spectrum of ZnO NPs calcinated with the temperature of 200 °C shows different absorption peaks. The peaks 538 cm⁻¹ and 817 cm⁻¹ are related to the Aliphatic Iodo compounds, C-I stretch, peroxides, and C-O-O- stretch, respectively. Also, the obtained peaks (1049, 1310, 1387,1541, 1643, 1804, and 1935) cm⁻¹ are related to compounds of Primary amine, CN stretch, Aromatic tertiary amine, CN stretch, Common inorganic ions, Nitrate ion, Carboxylate (carboxylic acid salt), Quinone or conjugated ketone of Carbonyl compound, cm⁻¹ Carbonyl compound of Acid (acyl) halide, and Aromatic ring (aryl) of Aromatic combination bands, respectively. The investigated peak (2220, 2850, 2921, 3409, 3605, 3695, and 3872) cm⁻¹ are related to the compound of C≡C Medial alkyne (disubstituted), Methoxy, C-H stretch (CH3-O-), Methylene C-H asym./sym, Stretch, Normal “polymeric” OH stretch, Nonbonded hydroxy group, OH stretch, Primary alcohol, OH stretch, and O-H stretching of alcohol, respectively.

The FTIR spectrum of ZnO NPs shows several absorption peaks, which include (632, 781, 1049, 1425, 1541, 1643, and1864) cm⁻¹ that are related to Acetylenic(alkyne) of Alkylene C-H bend, Aromatic ring (aryl) of C-H 1,3-Disubstitution (meta), Primary amine, CN stretch, Methylene (>CH2) of Methylene C-H bend, Carboxylate (carboxylic acid salt), Quinone or conjugated ketone of Carbonyl compound, and Carbonyl compound of Acid (acyl) halide, respectively. While the obtained peaks (2196, 2481, 3415, 3687, 3742, and 3871) cm⁻¹ were related to the compounds C≡C Medial alkyne (disubstituted), strong O= C=O stretching carbon dioxide, Normal “polymeric” OH stretch, Nonbonded hydroxy group, OH stretch, Primary alcohol, OH stretch, and O-H stretching of alcohol, respectively.

Different absorption peaks were seen in the ZnO Nanoparticles’ FTIR spectrum that was calcinated with the temperature of 400 °C as shown in Figure 9. The observed peaks were (669, 716, 1102, 1425, 1541, and 1643) cm⁻¹ that were related to the compounds of Acetylenic(alkyne) of Alkylene C-H bend, Aromatic ring (aryl) of C-H 1,3-Disubstitution (meta), Secondary alcohol, C-O stretch, Common inorganic ions of Carbonate ion, Nitrogen-oxy compounds of Aliphatic nitro compounds, and Quinone or conjugated ketone of Carbonyl compound, respectively. While peaks (2273, 2356, 2494, 2886, 3469, 3611, 3736, 3801, and 3872) cm⁻¹ are concerned with C≡C Medial alkyne (disubstituted), stretching O=C=O carbon dioxide, strong O=C=O stretching carbon dioxide, Methoxy, C-H stretch (CH3-O-), Normal “polymeric” OH stretch, Nonbonded hydroxy group, OH stretch, Primary alcohol, OH stretch, and O-H stretching of alcohol, respectively.

In addition, when ZnO NPs are calcinated at 500 oC, several absorption peaks are investigated, as shown in Figure 9. The absorption peaks observed at (574, 627, 835, 878, and 991) cm⁻¹ are related to the Disulfides (C-S stretch), and Alkylene C-H bend, Peroxides, C-O-O- stretch band, and Aromatic C-H in-plane bend, respectively. Additionally, the seven peaks absorption were seen in the (1000-2000) cm⁻¹, which are (1134, 1343, 1425, 1521, 1652, 1747, and 1813) cm⁻¹ that are owing to the bands of
the Aliphatic fluoro compounds, C-F stretch primary or secondary, OH in-plane band, Carbonate ion of Common inorganic ions, Carbonate (carboxylic acid salt), Amide of Carbonyl compound, Ester of Carbonyl compound, and Acid (acyl) halide, respectively. Additionally, the examined absorption peak lies in the region between 2000 cm-1 to 4000 cm-1, including (2189, 2870, 2976, 3566, 3739, and 3876) cm-1, which are related to the bands of Cyanide ion, thiocyanate ion, related ions, Methyl C-H asym/sym, Stretch, internally bonded OH stretch, and O-H stretching of alcohol, respectively.

4. CONCLUSION

The ZnO NPs have been successfully produced at a low cost using the extracts from the leaf of the Pinus Brutia tree. The influence of the tree extracts from PB and ZnO NPs’ properties, including their crystal structure, size, orientation, average size, shape, density distribution, functional group, elemental composition, and optical characteristics, have been studied at various calcination temperatures. According to the PB tree leaf extracts analysis, the PB tree is a better option for the biosynthesis of GS Zinc Oxide Nanoparticles at different calcination temperatures. Also, the results displayed that the change in the calcination (annealing) temperature significantly affects all of the obtained properties of the ZnO NPs. The calcination temperature change greatly impacts the quality and average crystal size of the generated hexagonal-wurtzite Zinc Oxide Nanoparticles. The FESEM analysis showed that the Zinc Oxide Nanoparticles are significantly affected in their orientation, shape, and size by the calcination temperatures. The GS ZnO nanoparticles’ UV-Visible analysis revealed a significant peak for all Zinc Oxide NPs made at various temperatures of calcination, a considerable absorbance in the UV region and below 400 nm, and a poor absorption rate in the visible region. The (Eg), which denotes the Energy Band Gap, lays between the (2.65-2.747) eV region, and it decreases as the calcination temperature increases.

Additionally, the FTIR spectra of formed ZnO NPs with various calcination temperatures showed no apparent peak in the visible range, demonstrating pure Zinc Oxide Nanoparticles produced by employing PB tree leaf extracts. In addition, according to all of the investigated results and properties of the Zinc Oxide Nanoparticles, the Zinc Oxide Nanoparticles that are calcinated at 500°C had higher quality. They performed better than those made at other calcination temperatures.

REFERENCES


[37] Geeta Gahlawat; Anirban Roy Choudhury; “A Review on The Biosynthesis of Metal and Metal Salt Nanoparticles By Microbes”, RSC ADVANCES, 2019. (IF: 5)

[38] Wencui M. Zhou; Xueying Qiu; Yuheng Jiang; Yingying Fan; Shilei Wei; Dongxue Han; Li Ni; Zhiyang Tang; “Highly Selective Aerobic Oxidation of Methanol to Methanol Over Gold Decorated Zinc Oxide Via Photocatalysis”, JOURNAL OF MATERIALS CHEMISTRY, 2020. (IF: 3)


[40] Amit Kumar Chauhan; Navish Kataria; V. K Garg; “Green Fabrication Of ZnO Nanoparticles Using Eucalyptus Spp. Leaves Extract And Their Application In Wastewater Remediation”, CHEMOSPHERE, 2020. (IF: 3)

[41] Anithadevi Sekar; Rakhi Yadav; “Green Fabrication of Zinc Oxide Supported Carbon Dots for Visible Light-Responsive Photocatalytic


[46] Hadiza Abdullahi Ari; Alani Olushola Adewole; Adamu Yunusa Ugya; Otaru Habiba Asipita; Makiyyu Abdullahi Musa; Wei Feng; “Biogenic Fabrication and Enhanced Photocatalytic Degradation of Tetracycline By Bio Structured ZnO Nanoparticles”, ENVIRONMENTAL TECHNOLOGY, 2021.

[47] Amany M Diab; Basma T Shokr; Mustafa Shukry; Foad A Farrag; Radi A Mohamed; “Effects of Dietary Supplementation with Green-Synthesized Zinc Oxide Nanoparticles for Candidiasis Control in Oreochromis Niloticus”, BIOLOGICAL TRACE ELEMENT RESEARCH, 2022.


[52] Selvakumar Sakhthivel; Anand Raj Dhanapal; Lilly Pushpa Pauraj; Annadurai Gurusamy; Baskar Venkidasamy; Muthu Thiruvengadam; Rajakumar Govindasamy; Mohammad Ali Shariati; Abdelhakim Bouyahya; Gokhan Zengin; Mohammad Mehedi Hasan; Pavel Burkov; “Antibacterial Activity of Seed Aqueous Extract of Citrus Limon (L.) Mediated Synthesis ZnO NPs: An Impact on Zebrafish (Danio Rerio) Caudal Fin Development”, HELIYON, 2022.


[54] Shahid Shabbir Awan; Rizwan Taj Khan; Ansar Mehmood; Muhammad Hafeez; Syed Rizwan Abass; Munazza Nazir; Muhammad Raffi; “Ailanthus Altissima Leaf Extract Mediated Green Production of Zinc Oxide (ZnO) Nanoparticles for Antibacterial and Antioxidant Activity”, Saudi Journal Of Biological Sciences, 2022.