SYNTHESIS OF ZINC OXIDE NANOPARTICLE FROM FRUIT OF CITRUS AURANTIFOLIA BY CHEMICAL AND GREEN METHOD

P. Ramesh*1, A. Rajendran1, Arumugam Subramanian2

1PG and Research Department of Physics, Nehru Memorial College (Autonomous), Puthanampatti, Tiruchirappalli, Tamil Nadu, India.
2PG and Research Department of Chemistry, Nehru Memorial College (Autonomous), Puthanampatti, Tiruchirappalli, Tamil Nadu, India.

ABSTRACT
Presently the progress of green chemistry in the synthesis of nanoparticles with the use of plants has engrossed a great attention. Zinc oxide nanoparticles have received potential interest due to their vast applications in the food industry. For such purpose, the development of novel and biological techniques is in considerable demand for raising these materials to an industrial level. This letter portrays a novel method for the biosynthesis of ZnO nanoparticles using a Citrus aurantifolia for the first time. The morphology structure and stability of the synthesized ZnO nanoparticles were studied using scanning electron microscope (SEM), UV-spectro photometer and Fourier Transform Infrared (FTIR) spectroscopy. The results depicted that the synthesized nanoparticles are moderately stable, roughly spherical with maximum particles in size range within 9-10 nm in diameter.

KEY WORDS
Citrus aurantifolia, Bio synthesis, ZnO nanoparticles and Scanning electron microscope.

INTRODUCTION
Nanotechnology is the production and use of materials at the smallest possible scale. Nanotechnology has considerably improved and revolutionized several technology and industrial sectors including medicine, food safety, and many others. More recently, ZnO nanoparticles has entered the scientific spotlight, for its semi conducting properties, unique antibacterial, antifungal, wound healing and UV filtering properties,
high catalytic and photochemical activity. Zinc oxide nanoparticles have gained immense popularity in the scientific world due to their distinctive and fascinating properties. The synthesis and assembly of nanoparticle would benefit from the development of clean, nontoxic and environmentally acceptable "green chemistry" approaches for nanoparticles. *Citrus aurantifolia* (Family: *caesalpiniaceae*) commonly known as lime, is distributed through hot deciduous forests of India and holds a very prestigious position in Ayurveda and siddha systems of medicine. The plant used in the traditional systems of medicine for urinary disorders, female anti fertility, leprosy, worm infestation, disease of pittam; bark used in skin conditions; bark as astringent; leaves, *Citrus aurantifolia* liquids, and fruits as anthelmintic; seeds for eye troubles, diabetes. During the last two decades, the bio synthesis of noble metal nano particles has received considerable attention due to the growing need to develop environmentally sociable technogies in material synthesis. *Citrus aurantifolia* it is a tall, much branched in syrup with large bright yellow *Citrus aurantifolia* liquids, bark smooth, reddish brown; branch lets finely pubescent leaves. It is widely distributed in dry regions of the central provinces and the western peninsula. It is grown in Rasputin desert. It is obtained from both wild and cultivated plants produced in many parts of palladium India and Srilanka.

ZnO nanoparticles were synthesized by several different methods, such as thesol-geltechniques\(^1\), wet chemical method\(^2\), green chemistry\(^3\) and microwave method\(^4\). The biosynthesis of ZnO nanoparticles of different sizes, ranging from 1-70nm, and shapes, including spherical, triangular and hexagonal has been conducted using bacteria, fungi, plant extracts\(^5\)\(^-\)\(^8\). Biological synthesis of nanoparticles has gained more attention by the researchers for its potential applications\(^9\)\(^-\)\(^10\). While interaction of nanomaterials with cells and its macromolecular components is critical in many applications such as imaging and drug/gene delivery, the same features are a concern with respect to their safety. The potential of nanoparticles to interact with biological systems has been acknowledged in recent years by the scientific community. Almost all type of biological entity has been used for the synthesis of nanoparticles with different size and shape\(^11\)\(^-\)\(^15\).

In the present report, we report the synthesis and Characterization of ZnO nanoparticles using a fruit of *Citrus aurantifolia* for the first time. The morphology structure and stability of the synthesized ZnO nanoparticles were studied using scanning electron microscope (SEM), UV-spectro photometer and Fourier Transform Infrared (FTIR) spectroscopy.

**MATERIALS AND METHOD**\(^16\),\(^17\)

**Preparation of extract**

*Citrus aurantifolia* were collected and it is washed several times with water to remove the dust particles and then to remove the residual moisture. The extract used for the reduction of zinc ions (Zn\(^{2+}\)) to zinc nanoparticles (ZnO) was prepared by placing 50g of washed dried fine cut *Citrus aurantifolia* leaves extract was taken and boiled to 60-80 degree Celsius using a stirrer heater. 5 grams of Zinc Nitrate was added to the solution as the temperatures reached 60 degree Celsius. This mixture is then boiled until it reduced to a deep yellow colored paste. This paste was then collected in a ceramic crucible and heated in an air heated furnace at 400 degree Celsius for 2 hours. A light white colored powder was obtained and this was carefully collected and packed for characterization.
purposes. The material was mashed in a mortar-pestle so as to get a finer nature for characterization.

RESULTS AND DISCUSSION

Phytochemical Analysis
The Citrus \textit{aurantifolia} fruit extract were subjected to chemical test for different phyto constituents viz. alkaloids, phenols, flavonoids, amino acids, saponins and tannins. Chemical tests were carried out on the aqueous extracts using procedures to identify the phytochemicals as described by phytochemical methods. Alkaloids, phenols, flavonoids, amino acids, saponins and tannins were qualitatively analyzed.

Characterization of Zinc oxide Nanoparticles

UV-Vis Spectra analysis
Electromagnetic radiation such as visible light is commonly treated as a wave phenomenon, characterized by a wavelength or frequency. Wavelength is defined on the left below, as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers (10^{-9} meters). Visible wavelengths cover a range from approximately 400 to 800 nm. Optical properties of the as-prepared ZnO nanostructure sample was revealed by UV–Vis spectrum and photoluminescence spectroscopy at room temperature, as shown in Figure No.1. It can be seen from the Figure No.1 that there was intensive absorption in the ultraviolet band of about 300-1100 nm. The absorption wavelength at about 208 and 215 nm of ZnO suggested the excitonic character at room temperature. Photoluminescence (PL) studies were performed to emphasize its emission properties as shown in Figure No.1. The photoluminescence of ZnO sample suggested emitting bands, 208 and 215 been observed in as-prepared ZnO sample. The PL of the ZnO sample in our case is considerably different from the typical observation in ZnO crystals.

FTIR Spectra analysis
Two milligram of Zno nanoparticles were prepared by mixing with 200 mg of spectroscopic grade KBr. FTIR spectra were recorded using a Nicolet 520P spectrometer with detector at 4000-400 cm^{-1} resolution and 20 scans per sample. FTIR Spectra of aqueous Zinc oxide nanoparticles prepared from the \textit{Citrus aurantifolia} fruit extract was carried out to identify the possible biomolecules responsible for capping and efficient stabilization of the metal nanoparticles synthesized by leaf broth (Figure No.3).

SEM analysis of Zinc oxide Nanoparticles
Size and structure of the nanoparticles analysis was done by using Vega3 Tuscan Scanning Electron Microscope machine. Thin films of the sample were prepared on a carbon coated copper grid by just dropping a very small amount of the sample on the grid, extra solution was removed using a blotting paper and then the film on the SEM grid were allowed to dry by putting it under a mercury lamp for 5 min. SEM studies were revealed to visualize the size and shape of Zinc oxide nanoparticles and (Figure No.4) and show the typical bright - field SEM micrograph of the synthesized Zinc oxide nanoparticles. In this study, it was appeared with that most of spherical in shape.
Table No.1: Results of Phytochemical Analysis of Aqueous Extract of *Citrus aurantifolia* fruit

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of the Phytochemical Constituents</th>
<th>Aqueous extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alkaloid</td>
<td>+</td>
</tr>
<tr>
<td>2</td>
<td>Glycoside</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Reducing sugar</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Tannins</td>
<td>+</td>
</tr>
<tr>
<td>5</td>
<td>Flavonoid</td>
<td>+</td>
</tr>
<tr>
<td>6</td>
<td>Steroid</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Sponins</td>
<td>+</td>
</tr>
<tr>
<td>8</td>
<td>Phenol</td>
<td>+</td>
</tr>
<tr>
<td>9</td>
<td>Amino acid</td>
<td>+</td>
</tr>
<tr>
<td>10</td>
<td>Protein</td>
<td>+</td>
</tr>
</tbody>
</table>

+: Indicates the presence and -: Indicates the absence of phytoconstituents.

Table No.2: FT-IR Analysis of Wave Number of Peak Assignments

<table>
<thead>
<tr>
<th>S.No</th>
<th>Wave number (cm(^{-1}))</th>
<th>Peak assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3411.30</td>
<td>O-H Stretching</td>
</tr>
<tr>
<td>2</td>
<td>2469.38</td>
<td>P-H Phosphine</td>
</tr>
<tr>
<td>3</td>
<td>2174.39</td>
<td>C=O=O Stretching</td>
</tr>
<tr>
<td>4</td>
<td>1557.44</td>
<td>C=O Vibration</td>
</tr>
<tr>
<td>5</td>
<td>1409.53</td>
<td>CH(_2) Bending</td>
</tr>
<tr>
<td>6</td>
<td>1117.32</td>
<td>O-C Stretching</td>
</tr>
<tr>
<td>7</td>
<td>1085.04</td>
<td>O-C Stretching</td>
</tr>
<tr>
<td>8</td>
<td>1020.47</td>
<td>P-OR Esters</td>
</tr>
<tr>
<td>9</td>
<td>865.44</td>
<td>= CH(_2) Stretching</td>
</tr>
<tr>
<td>10</td>
<td>842.14</td>
<td>P-O Stretching</td>
</tr>
<tr>
<td>11</td>
<td>654.00</td>
<td>C-H Bending</td>
</tr>
<tr>
<td>12</td>
<td>548.98</td>
<td>Zn-OH Rocking</td>
</tr>
</tbody>
</table>

Figure No.1: UV-Visible spectral analysis
Figure No.2: UV-Visible spectral analysis of water extract of *Citrus aurantifolia*

Figure No.3: FT-IR Spectrum of water extract of *Citrus aurantifolia*
CONCLUSION
To conclude we have used unreported, inexpensive, nontoxic, ecofriendly and abundantly available Citrus aurantifolia for the rapid synthesis of ZnO NPs in the range of 9-10nm. FT-IR studies of aqueous Citrus aurantifolia extract reveals the presence of phyto constituents like alcohol, aldehyde and amine which were the surface active molecules stabilized the nanoparticles and this phytochemicals have interacted with the zinc surface and aids in the stabilization of zinc oxide nanoparticles. This green synthesis approach shows that the environmentally benign and renewable Citrus aurantifolia extract can be used as an effective stabilizing as well as reducing agent for the synthesis of zinc oxide nanoparticles.

ACKNOWLEDGEMENT
The authors would wish to acknowledge the management and Principal of Nehru Memorial College for providing research facilities and encouragements.

CONFLICT OF INTEREST
We declare that we have no conflict of interest.

BIBLIOGRAPHY


