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Facile and Green Synthesis of Zirconium Dioxide Nanoparticles Using Mountain Ebony Leaf Extract

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ABSTRACT

Nanoparticle are gaining importance in research for the treatment of various diseases. The production of nanoparticles is eco-friendly, biocompatible, and cost-effective. In this study, Zirconium dioxide (ZrO_2) nanoparticles were synthesized from the leaf extract of Mountain ebony (*Bauhinia variegata)*. The leaf acts as a capping, stabilizing, and reducing agent. The particles were characterized for their size and shape using transmission electron microscopy (TEM). Fourier transform infrared spectroscopy (FTIR) was conducted to identify the functional groups on the surface of the nanoparticles. The optimal synthesis conditions were obtained by considering the following parameters: pH, concentration, temperature, reaction time, and ratio of substrate. The analysis showed sizes ranges of 0.22 nm to 5.80 nm, with spherical shaped nanoparticles. The FTIR showed the presence of polyphenol compounds at 3778 cm^{-1} and symmetric stretching vibration of Zr-O-Zr at 367 cm^{-1}. The optimal values are pH 9, concentration 0.5 M, temperature 60 °C, reaction time 60 min, and ratio of substrate 1:3. The synthesized ZrO_2 nanoparticles from mountain ebony leaf showed acceptable size and shape of nanoparticles.

Keywords: Fourier transform infrared spectroscopy, leaf extract of Mountain ebony, Transmission electron microscopy, UV spectroscopy, ZrO_2 nanoparticles

INTRODUCTION

In a world where size matters, nanotechnology emerges as a groundbreaking project that transforms the very essence of matter itself. At its core, nanotechnology revolves around manipulating materials, structures, and devices at the nanoscale and is utilized in fields like medicine, biotechnology, pharmaceuticals, and environmental remediation [1].

Nanoparticles (NPs) are nanometer-sized (<100 nm) atomic or molecular scale solid particles having excellent physical properties compared to bulk molecules, depending on their size and morphology [2].

Applications of nanotechnology are remarkable due to the size-dependent physiochemical properties of nanomaterials. These have led to the development of protocols for synthesizing nanomaterials over a range of sizes, shapes, and chemical compositions [3]. In the medical field, it facilitates precise drug delivery, accurate imaging, and advancements in regenerative medicine, leading to improved patient outcomes and reduced side effects. Nanoparticles can be synthesized using different methods like physical, chemical, and biological synthesis [4]. Traditional physical and chemical approaches often release highly toxic chemicals, are time-consuming, expensive, and require high energy. To control these issues, green approaches are now applicable. Plants contain biomolecules like tannins, sugars, steroids, enzymes, phenol, amino acids, flavonoid, and others that help stabilize ZrO_2 nanoparticles and are beneficial in medicine [5]

Mountain ebony, commonly known as the Pink Orchid tree, belongs to the Fabaceae family [6]. It is native to Madagascar and is characterized by deeply bilobed leaves and nitrogen-fixing properties. Traditionally, its leaves are used for their anti-inflammatory, anti-diabetic, and antibacterial properties [7]. They are rich in vitamin C, iron, and calcium and are also used in culinary practices. Several leaves, roots, flowers and fruits have been used to synthesis ZrO_2 nanoparticles expect the leaf of Mountain ebony. The synthesis was done under different conditions

This study was aimed at green synthesizing zirconium dioxide nanoparticles using the leaf of mountain ebony. Laboratory optimization was used to optimize the synthesis of the nanoparticles. The optimized values were used to synthesize ZrO_2. The biosynthesis of nanoparticles using microbial strains, enzymes, plant extracts, and biodegradable products has been explored in previous studies [8-10]. In this study, ZrO_2 nanoparticles were biosynthesized by mixing Zirconium(IV) oxychloride octahydrate ($ZrOCl_2.8H_2O$) with mountain ebony leaf extract. The reduction of zirconium ions by the aqueous extract results in nanoparticle formation. Characterization was done using UV–visible spectrophotometry, TEM, and FTIR.

MATERIALS AND METHODS

Mountain ebony leaves were collected from Federal University of Technology, Akure. It was identified and authenticated by a Forestry and Wood Technologist at the Federal University of Technology, Akure, Nigeria. Zirconium(IV) oxychloride octahydrate ($ZrOCl_2.8H_2O$), Sodium hydroxide, (NaOH), and Hydrochloric acid, (HCl) were purchased from BDH and Sigma-Aldrich, India.

Preparation of the aqueous leaf extract of Mountain ebony and 0.1M of $ZrOCl_2.8H_20$

Fresh leaves of Mountain ebony (25 g) were diced into fine pieces and transferred to sterile 250 mL conical flask. Approximately 200 mL distilled water was added to the flask and heated at 60 °C for 5–10 min and incubated on sand bath for 30 min. to facilitate the formation of aqueous extract. The extract was filtered using Whatman No. 1 filter paper and the filtrate was stored at 4 °C in refrigerator for further use. In preparation of 0.1 M of $ZrOCl_2.8H_20$ into distilled water, 23.3 g of the salt was measured using weighing balance and dissolved into 1000 ml of distilled water in a standard flask, shaken vigorously and allowed to dissolved evenly [11]. This method was also used to prepared different concentration of salt with different quantity.

Synthesis of ZrO_2 Nanoparticles

pH Studies

The optimization of pH in nanoparticle synthesis is crucial as it profoundly influences the formation and characteristics of nanoparticles. The pH level not only affects the stability of the colloidal system but also plays a pivotal role in controlling the size, shape, and surface charge of the nanoparticles. Maintaining an optimal pH ensures favorable conditions for the nucleation and growth of nanoparticles. In this study, a 20 ml portion of a 0.1 M zirconium (IV) oxychloride octahydrate salt solution was measured and combined with 20 ml of leaf extract. Then, the samples were tested at various pH levels (1, 3, 5, 7, 9, 11) with a temperature of 50 °C. Stirring was carried out using a magnetic stirrer for 60 minutes. Notably, extract exhibited a color change from dark brown to yellowish brown signifying nanoparticles formation. The pH of both were adjusted using solution of NaOH and HCl acid. The resulting solutions were then subjected to a 24-hour period in the oven, followed by calcining inside a furnace at 500 °C for three hours, resulting in a powdery form. This was done with the aim of eliminating any organic compounds present, in order to obtain nanoparticles that were as pure as possible. After being calcined, the

nanoparticles were cooled in a desiccator, then weighed, and finally kept for analysis in sterile containers. The sample was taken for UV analysis in order to determine the optimal pH value.

Reaction time studies

The reaction time in nanoparticle synthesis is crucial for controlling particle size, morphology, and overall product characteristics. In this study, a 20 ml portion of a 0.1 M zirconium(IV) oxychloride octahydrate salt solution salt was combined with 20 ml of leaf extract. The samples were tested at various time intervals (20, 30, 40, 50, 60, 70 minutes). Maintaining a constant temperature of 60 °C, pH levels were adjusted to 11, based on UV analysis results. Stirring at different time points using a magnetic stirrer ensured effective mixing. Subsequently, the resulting solutions were subjected to a 24-hour period in the oven to promote synthesis. Post-oven treatment involved calcining inside a furnace at 500 ^{o}C for three hours, yielding a powdery form. The sample was taken for UV analysis in order to determine the optimal time value.

Concentration optimization studies

Optimizing concentration in nanoparticle synthesis is essential for tailoring the properties of the resulting nanoparticles. In this study, the concentration of the samples was systematically varied by measuring 20 ml of Zirconium(IV) oxychloride octahydrate salt solution at different concentrations (0.1M, 0.2M, 0.3M, 0.4M, 0.5M) into 20 ml of leaf extract. The temperature, a critical parameter in nanoparticle synthesis, was set to 60 °C. pH levels were adjusted to 11. Stirring using a magnetic stirrer was performed at 70 min. based on UV analysis results. The resulting solutions were then placed into the oven for a 24-hour period, followed by calcining inside a muffle furnace at 500 ^{o}C for three hours to yield a powdery form. Subsequent UV analysis of the samples provided valuable insight into the influence of concentration on nanoparticle synthesis efficiency and characteristics

Ratio of substrate studies

Optimizing the ratio of substrate in nanoparticle synthesis is also a crucial step to achieving a desired characteristics and properties. In this study, the samples were varied systematically at different ratios to the substrate (1:1, 1:2, 1:3, 1:4, 1:5). The temperature was set at 60 °C to ensure controlled reaction kinetics. The pH, time and concentration values were done at obtained values and stirring was carried out using a magnetic stirrer Subsequently, the resulting solution was placed into the oven for a 24-hour period to facilitate further synthesis and stabilization.

Following this, the samples underwent calcining inside a furnace at 500 ^{o}C for three hours. After being calcined, the nanoparticles were cooled in a desiccator, then weighed, and kept for analysis in sterile containers. Finally, samples were collected for UV analysis**.**

Temperature studies

In this study, the substrate ratio was set at a constant 1:5 of salt solution and leaf extract respectively and the samples underwent meticulous optimization at different temperature levels (20, 30, 40, 50, 60 ^{o}C). The pH**,** time and concentration values were done at optimal values and **s**tirring was carried out using a magnetic stirrer. Subsequently, the resulting solution was subjected to a 24-hour period in the oven to enhance synthesis. Post-oven treatment involved calcining inside a furnace at 500 ^{o}C for three hours, transforming the samples into a powdery form. After being calcined, the nanoparticles were cooled in a desiccator, then weighed, and finally kept for analysis in sterile containers. Samples were then collected for UV analysis, providing the optimal temperature.

Characterization of Mountain Ebony Leaf ZrO_2 Nanoparticles

UV–visible spectrometric analysis of ZrO_2 nanoparticles

An ELICO SL-159 UV–visible spectrophotometer was employed for the spectrometric analysis of biosynthesized ZrO_2 nanoparticles. The reduction of Zirconium salt was measured periodically at 200–800 nm. A spectrum of ZrO_2 nanoparticles was plotted with wavelength on x-axis and absorbance on y-axis.

Fourier transform infrared analysis of ZrO_2 nanoparticles

Fourier-transform infrared spectroscopy was employed to characterize the chemical composition and bonding of the biosynthesized ZrO_2 nanoparticles and compare them to the aqueous leaf extract used in their synthesis. Figure 7 presents the FTIR spectra of both the ZrO_2 nanoparticles and the aqueous leaf extract in the range of 4500-500 cm^{-1}.

Transmission electron microscopy

Transmission electron microscopy was used to obtain the morphology of the ZrO_2 nanoparticles. Transmission electron microscope (TEM; Philips model CM 200) was used for the study. The instrument was operated at an accelerating voltage of 200 kV with ultra-high-resolution of 0.2 nm and magnification of 10000 to 100000X. TEM's grid size is 3 mm diameter which was

prepared placing a 5 µL of the ZrO_2 nanoparticles solutions on carbon-coated copper grids and drying under mercury lamp and then analyzed. The size of the ZrO_2 nanoparticles was determined by using the image magnifying software and this software magnified the particles with size less than 10 nm and gave clear morphological data. Figure 8 presents the TEM spectra of both the ZrO_2 nanoparticles.

RESULTS AND DISCUSSION

The absorbance peaks are shown in Figures 1 – 5

pH studies

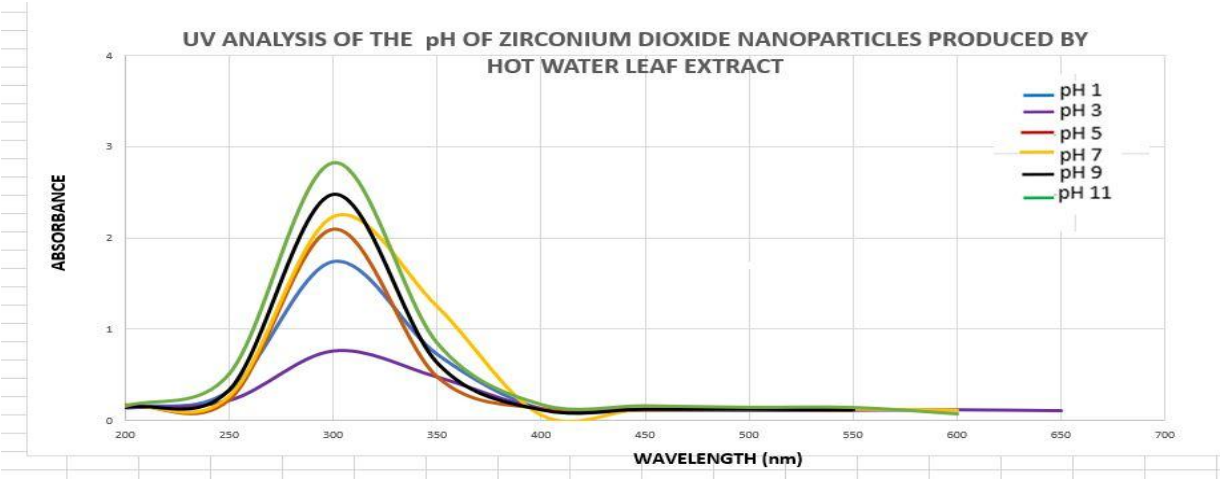


Figure 1: Absorption spectra of Zirconium dioxide (ZrO_2) nanoparticles at different pH values (pH 1, 3, 5, 7, 9, 11) of the reaction mixture of the aqueous extract

Concentration studies

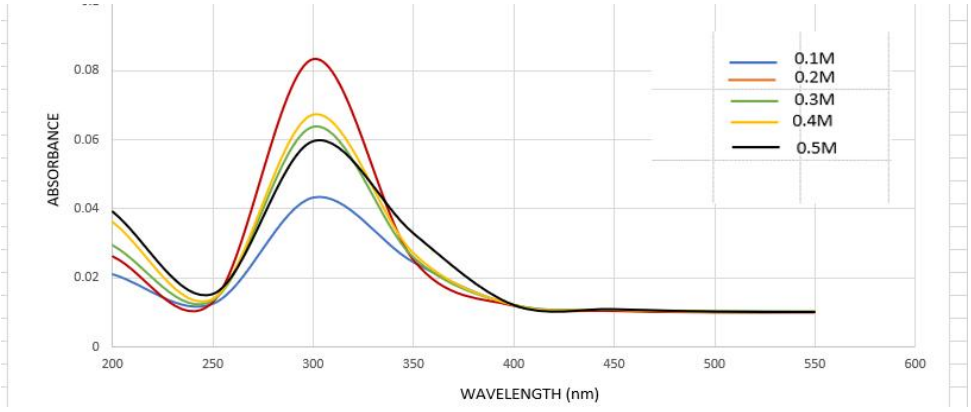


Figure 2: Absorption spectra of Zirconium dioxide (ZrO_2) nanoparticles at concentration (0.1 M, 0.2 M, 0.3 M, 0.4 M, 0.5 M) of the reaction mixture

Temperature studies

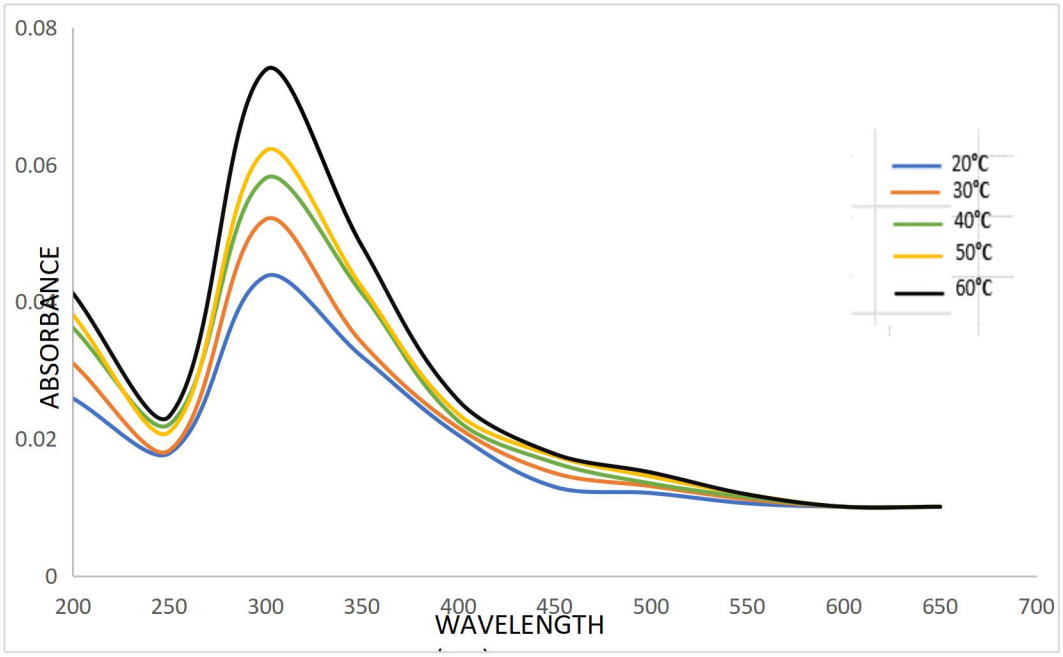


Figure 3: UV-Vis spectra of the temperature Optimization for ZrO_2 nanoparticles by aqueous leaf extract

Reaction time studies

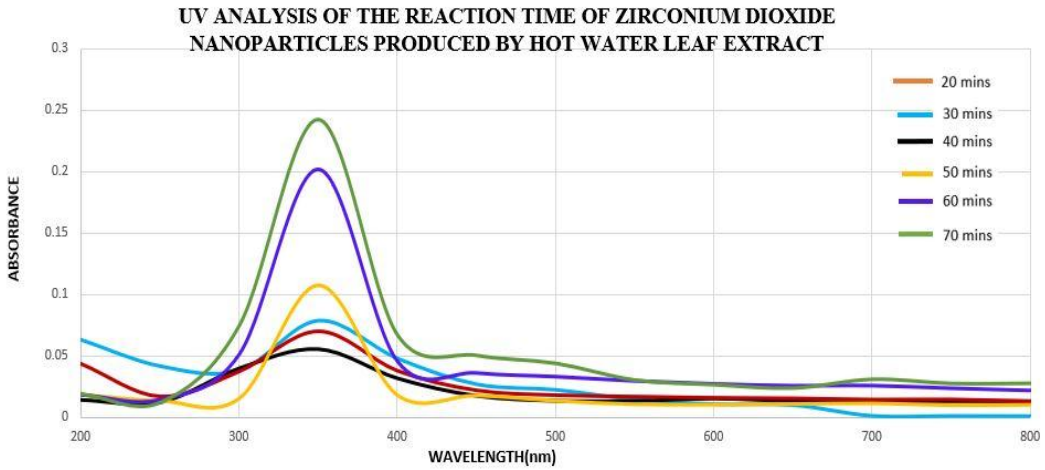


Figure 4: Absorption spectra of Zirconium dioxide (ZrO_2) nanoparticles at different reaction time (20,30,40,50,60,70 mins) of the reaction mixture of the aqueous extract.

Ratio of substrate studies

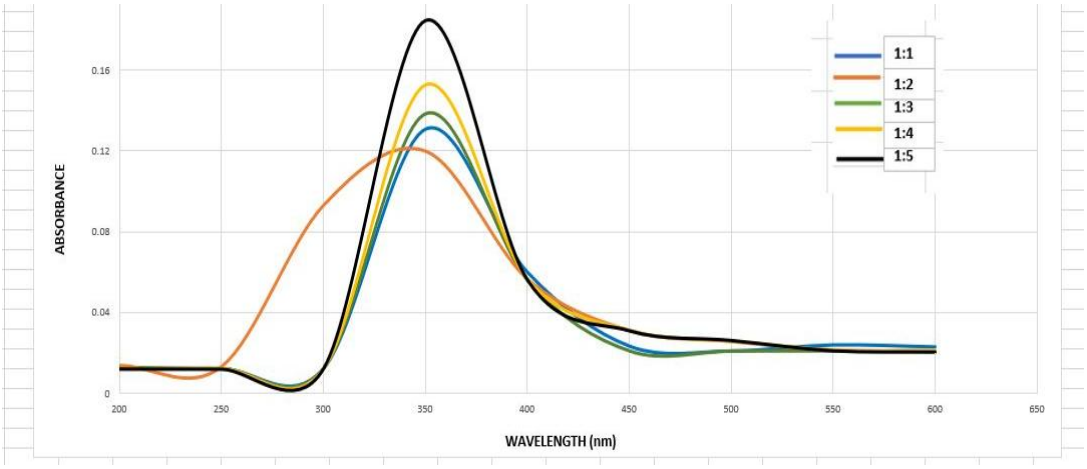


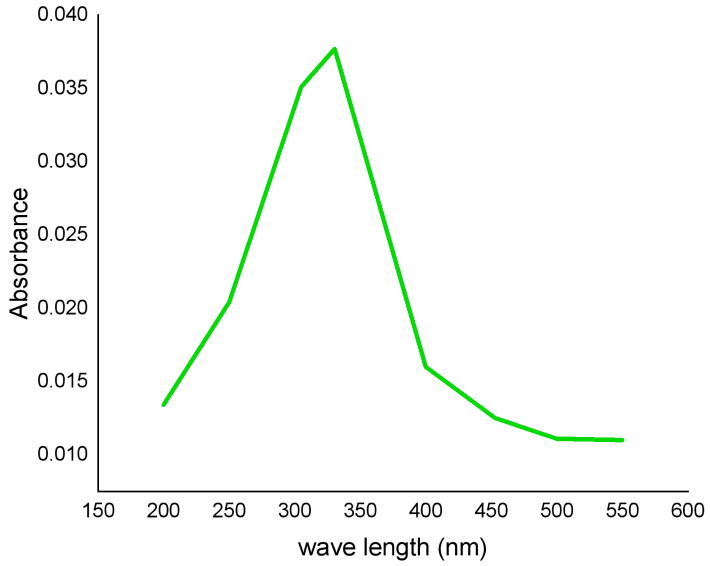
Figure 5: UV-Vis spectra of the ratio of substrate for ZrO2nanoparticles by aqueous leaf extract.

Table 1 shows the best values at which ZrO_2 can be synthesized and the wavelength of the maximum absorbance.

Table I: Best values of ZrO_2 nanoparticles obtained from aqueous leaf extract

Parameters	Value	Wavelength
pH	11	300
Concentration	0.2 M	320
Temperature	60^{o}C	350
Reaction time	70 minutes	350
Ratio of substrate	1:5	350

When the ZrO_2 was synthesized under the above condition or values the spectra of the UV is shown in Figure 6.



Figures 6: UV–visible spectra of Mountain ebony leaf-ZrO_2 nanoparticles done at optimal value and wavelength maximum absorbance noted at 330.5 nm

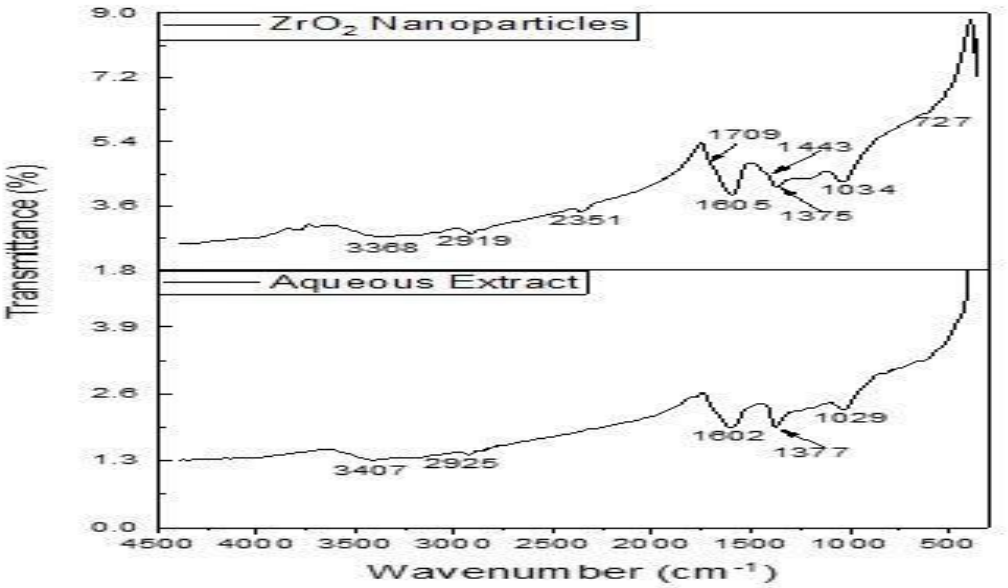


Figure 7: FTIR spectra of both the ZrO_2 nanoparticles and the aqueous leaf extract

The UV absorption spectrometric analysis of ZrO_2 nanoparticle showed absorbance spectra at 330 nm when synthesized at the optimal values. From Table 1, different parameters have different optimal wavelength. The optimal pH, concentration, temperature, reaction time and

ratio of substrate are 11, 0.2 M, 60 ºC, 70 minutes and 1:5 respectively. suggesting bio reduction of into zirconium (IV) oxychloride octahydrate ($ZrOCl_2.8H_2O$) (Figure 6). The FTIR analysis spectrum showed sharp absorbance between 500 and 4000 cms−1. There are other peaks in the spectrum of leaf extract at 1029,1377,1602,2925 and 3407 cms^{-1} which could be carbonyl, phenol and alkyl. There are other peaks in the spectrum of synthesized ZrO_2 at 727, 1034, 1375, 1443, 1605, 1709, 2351, 2919 and 3368 cms^{-1} which could be the symmetric stretching vibration of Zr-O-Zr, carboxylic, phenol, esters or aromatic compounds.

The TEM analyses showed the particle size between 0.22 to 5.80 nm and with a spherical morphology (Figure 8).

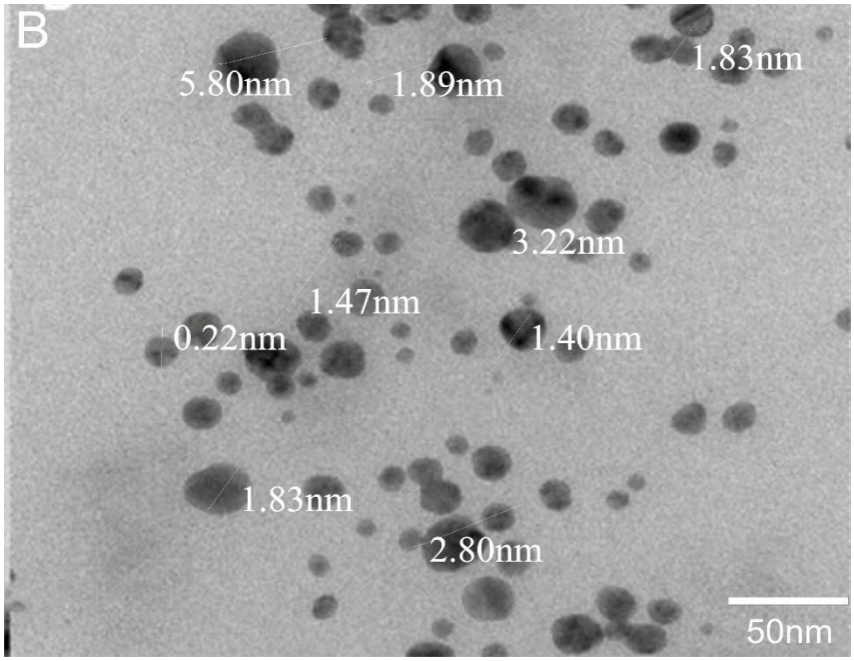


Figure 8: Transmission electron microscopy micrographs of green synthesized ZrO_2

Nanomaterials have proven to be efficient modes of drug delivery in modern science [9]. The use of medicinal plant materials and microbes for nanoparticle synthesis has revolutionized the field and could serve as an alternative to antibiotics [12] In the present study, ZrO_2 nanoparticles showed particle sizes ranging between 0.22 and 5.80 nm.

The characterization of nanoparticles was done using UV–visible spectroscopy, TEM, and FTIR. The results aligned with literature in the field [8, 10]. Bio-compounds in leaf extract with carbonyl groups are believed to reduce zirconium salt to unsaturated carbonyl groups through auto-oxidation [12]. Surface plasmon resonance of metal UV–visible spectra showed a sharp

peak at 330 nm, with a band gap of 3.75 eV, indicating ZrO_2 nanoparticle formation [5] FTIR spectra showed peaks indicating interactions between proteins and ZrO_2 nanoparticles, with OH groups indicating alcohol and phenolic presence [13, 15]

CONCLUSION

The green synthesis and characterization of ZrO_2 nanoparticles was confirmed by UV–visible spectrophotometery, FTIR, and TEM techniques. The nanoparticles appeared spherical with smooth surfaces and sizes varying from 0.22 to 5.80 nm. The band gap was 3.75 eV. Optimization showed that at pH 11, concentration 0.2 M, temperature 60 °C, reaction time 70 min. and substrate ratio 1:5, ZrO_2 nanoparticles can be synthesized with good results.

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