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Comparative Green synthesis of Al-doped ZnO nanoparticles from Bitter leaf and Neem leaf Extracts

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Abstract: *Aluminum doped Zinc Oxide nanoparticles (Al-doped ZnO Nps) is known for its wide applications in biosensors, blue-UV light emitting diodes, transparent conducting oxide, semi-conductors, selective gas sensor and as efficient catalyst support. It is often synthesized through physical and chemical techniques which require toxic reagents, high vacuum structures and elevated temperatures which are expensive and hazardous. The need for healthier, eco-friendly and cost effective way of synthesizing this nanoparticle for use has made researchers to look into green synthesis. Green synthesis allows the metal oxide nanoparticles to be synthesized using natural plant extract as reducing agent on metal salt. This research work looks at the comparative green synthesis of Al-doped ZnO Nps using extracts of Neem leaf (Azadirachta Indica) and Bitter leaf (Vernonia Amygdalina) and their mixture to bio-reduce zinc acetate precursor. The synthesized Al-doped ZnO Nps were characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD result show that Al-doped ZnO Nps formed using bitter leaf extracts had better peaks and highest amount of the nanoparticles formed (3.72 grams) using the same precursors compared to neem leaf extract and 50:50 neem/bitter leaf extracts mixture. Bitter leaf extract had thirteen diffraction peaks at 2θ values of 20^0, 25.16^0, 27.1^0, 30^0, 32.46^0, 34.69^0, 37.12^0, 44.60^0,56.6^0, 57.62^0, 63^0, 68.8^0 and 76.76^0 indexed to (111), (004), (013), (020), (100), (014), (101), (320), (110), (107), (103), (112) and (202) planes of Al-doped ZnO Nps with an average crystallite size of 8nm. Neen leaf extracts had five diffraction peaks at lower 2θ values of 20.59^0, 25.11^0, 27.20^0, 37.29^0 and 44.01^0 indexed to (111), (004), (013), (101) and (320) planes of Al-doped ZnO Nps with average nanoparticles size of 7nm. The 50:50 mixtures of both extracts had five peaks at 25.04^0, 37.86^0, 43.44^0, 48.58^0 and 74.93^0 indexed to (004), (101), (320) (102) and (202) planes of Al-doped ZnO Nps. The nanoparticles had hexagonal structures of Al-doped ZnO Nps. The slight deviation observed in some peaks compared to Joint Committee on Powder Diffraction Standards might be attributed to the presence of metallo proteins or bio-organics present in the extracts. The SEM image showed rough morphologies for all the Al-doped ZnO Nps synthesized using the different leaf extracts and their 50:50 mixture.*

Keywords— Zinc oxide nanoparticles; Aluminum doped; Green synthesis; Bitter leaf; Neem leaf; SEM, XRD

1. INTRODUCTION

Metal oxide nanoparticles such as Magnesium Oxide (MgO), Zirconium Oxide (ZrO), Cerium dioxide (CeO_2), Titanium dioxide (TiO_2), Zinc Oxide (ZnO), Iron Oxide (Fe_2O_3), Tin Oxide (SnO), have unique properties such as catalytic activities, electronic properties, antibacterial properties and magnetic properties that has made them widely acceptable in engineering, science and medical fields. Among these nanoparticles, zinc oxide (ZnO), also known as Zincite has been investigated by many researchers because of its wide applications. Zinc oxide nanoparticle have a tremendous potential application in electronics, sensor, cosmetics, environmental protection, biological sensing, biological labelling, gene delivering, drug delivery and antibacterial agents [1-2]

Modification of Zinc oxide nanoparticle by doping molecules influences its size confinement, physical properties and enhances its electrical, optical and biological performance. Elements such as aluminum, copper, manganese, calcium, cobalt etc. can be used as dopants for Zinc oxide nanoparticle. Aluminum is the most commonly used dopant due to its small ionic radius, low material cost and conductivity. Aluminum doped Zinc Oxide nanoparticles (Al-doped ZnO Nps) are used as transparent and conducting coating in solar cells, production of polymers display, antibacterial agents and enhancing biosensor sensitivity [2-3].

Al-doped ZnO Nps can be synthesized through different method such as physical, biological (green synthesis) and chemical methods. The physical and chemical methods require high energy demand, involves toxic and hazardous chemicals which are dangerous to the human health. In contrast, the biological method is eco-friendly, less expensive, less toxic and biocompatibility for pharmaceutical and biomedical applications.

Green synthesis technique uses micro-organisms, enzymes, part of plant and plant extracts as reducing agent on the metal salt to synthesize nanoparticles. Researchers have focused attention on this technique because of its advantages and gained wide acceptance.

Al-doped ZnO nanoparticles have been synthesized through this method using extracts from different plants such as brown marine Sorgassum Myriocystum, sea weeds, Calotropis Gigantea leaves, Camellia Sinensis leaves,

Ocinum Tenuiflorum leaves, Calatropis Procera milky latex, Arathosoma Betulina [4-10]. Plant phytochemicals such as phenols, terpenoids, aldehydes and amides have been reported as the reducing agent found in plant extracts responsible for the green synthesis of metal oxide nanoparticles from their salts [11-13].

However, in this work, we report the comparative green synthesis of Al-doped ZnO nanoparticles using bitter leaf and neem leaf extracts as reducing agents on aqueous solution of zinc salt (acetate) as precursor. The characterization of the nanoparticles was done using XRD and SEM.

Bitter leaf botanically known as Vernonia amygdalina is a shrub that grows up 3-meter-high in African tropics and other parts of Africa, particularly, Nigeria, Cameroon and Zimbabwe. It is known for its health benefits such as its resistance to bacteria, malaria parasites, and ability to reduce diabetes, inflammation, helminths, oxidation, etc. [14-16]. They contain phytochemicals which are responsible for their biological active properties. Research have shown that they contain the following phytochemicals, 2.15 % saponins, 14.91% alkaloids, 1.30 % terpenoids, 0.34 % flavonoids, 0.19 %phenolic acids at room temperature with other components such as steroids, lignans, xanthones and anthraquinone edotides [17].

Neem (Azadirachta indica) is a fast growing tree of the mahogany family (Meliaceae). It was originally found in Indian sub-continent and dry areas of South Asia before been introduced to Africa, the Caribbean, and numerous countries in south and Central America. Neem tree grow up to 15-30 meter in height and have attractive rounded crowns and thick furrowed bark. The compound leaves have toothed leaflets and are typically evergreen but do chop during periods of extreme drought. The fruit of neem tree is a smooth yellow green drupe with a sweet flavoured pulp. Research have shown that neem leaf contains the following biologically active compounds such as saponins, alkaloids terpenes, glycosides, reducing sugar, steroids coumarins, flavonoids, phenolic acids lignans etc. [18-20].

2. MATERIALS AND METHOD

2.1 Materials and Equipment

Zinc acetate dihydrate, aluminum chloride, sodium hydroxide, ethanol, Fresh Vernonia amygdalina and Azadirachta indica leaf were bought from Amassoma market in southern Ijaw Local Government Area of Bayelsa State in Nigeria, Magnetic stirrer and hot plate, Whatman filter paper No. 42, Beakers (500 ml), volumetric flasks (100 ml). Scanning Electron Microscope (JSM-6480 LV), X-ray diffractometer (PANalytical X'pert Pro MPD).

2.2 Method

2.2.1 Preparation of Plant Extract

Fresh neem leaves were collected and washed several times with distilled water. The aqueous extract of the sample was prepared by chopping and heating 100 g of the fresh leaves in 500 ml glass beaker with 400 ml of double distilled water at 60˚C for 20 minutes. The mixture was continuously stirred until the colour of the aqueous solution turns light brown. The extract was cooled to room temperature and filtered using Whatman filter paper. The extract was stored in a refrigerator for use in subsequent experiments. Fig. 1 shows the fresh neem leaves in (a) and the neem leaves extracts in (b).

Fig. 1 (a) fresh neem leaves and (b) neem leaf extract.

The same procedure was followed for the extraction of bitter leaves extracts from fresh bitter leaves. The extracts also have a light brown colour as shown in Fig. 2. The extract was stored in a refrigerator for us in subsequent experiments. Fig. 2 (a) shows the fresh bitter leaves and (b) the extracts from the fresh bitter leaves.

Fig. 2 (a) fresh bitter leaves and (b) bitter leaf extract

2.2.2 Synthesis of Aluminum doped zinc oxide Nanoparticles

Al-doped ZnO Nps was synthesized by mixing 75 ml Zinc Acetate dihydrate (0.5033M) solution and 20 ml aluminum chloride solution (0.02077M) in 75 ml of neem leaf extract in a 500 ml beaker. The mixture was stirred continuously for 2 hours using magnetic stirrer and the solution pH

maintained at pH 7.0 by drop wise addition of 0.5 M sodium hydroxide solution at room temperature. The precipitates formed was filtered and washed repeatedly with distilled water followed by ethanol in order to remove impurities. It was then dried in an oven at 60°C overnight and ground to fine powder. The fine powder was calcined at 400°C for 1 hour in Muffle furnace under air atmosphere. This same procedure was repeated for bitter leaf extract and the 50:50 mixture of neem and bitter leaf extracts.

3. RESULT AND DISCUSSION

Fig. 3 shows the colour change and precipitates formed in the synthesized Al-doped ZnO Nps. In the figure, (a) mixture of zinc acetate dihydrate solution, aluminum chloride solution and neem leaf extract, (b) mixture of zinc acetate dihydrate solution, aluminum chloride solution and bitter leaf extract and (c) mixture of zinc acetate dihydrate solution, aluminum chloride solution, neem leaf extract and bitter leaf extract (50:50).

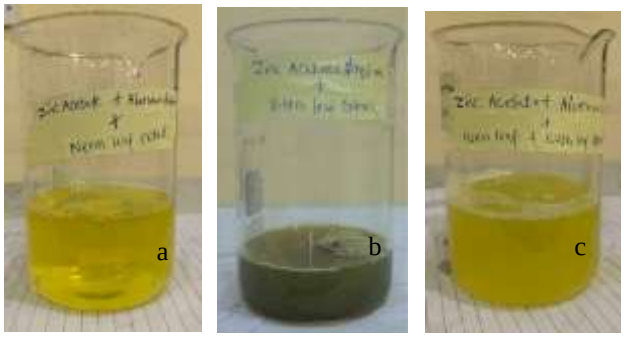

Fig. 3 (a) mixture of neem leaf extract and precursor, (b) mixture of bitter leaf extract and precursor and (c) mixture of neem and bitter leaf extract and precursor

Fig. 4 shows the centrifuged precipitates of synthesized Al-doped ZnO Nps from neem leaf extract, mixture of both leaf' extracts and bitter leaf extracts.

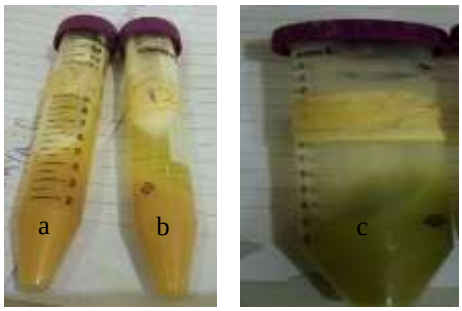

Fig. 4 Precipitates of Al-doped ZnO nanoparticles (a) 50:50 neem/bitter leaf mixture (b) neem leaf (c) bitter leaf

Fig. 5 shows the synthesized, calcined and dried samples of the Al-doped ZnO Nps

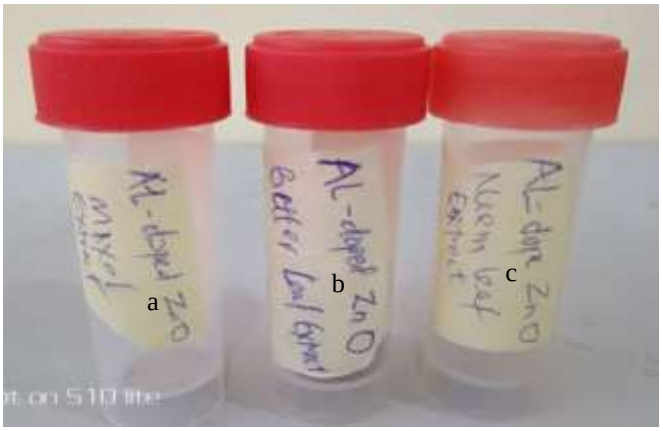

Fig. 5 Synthesized, dried and calcined nanoparticles from (a) 50:50 mixture of both leaf extracts (b) bitter leaf extract and (c) neem leaf extract,

Fig. 6, 7 and 8 shows the morphology of neem leaf extract synthesized Al-doped ZnO Nps, bitter leaf extract and 50:50 mixture of neem and bitter leaf extract Al-doped ZnO Nps respectively. The scan shows that the Al-doped ZnO Nps synthesized are solid and aggregated with rough surfaces. The crystallite nature and size of the Al-doped ZnO Nps were studied using XRD at 2θ range 5-80 degrees as shown in Fig. 9, 10 and 11 for neem leaf extract synthesized, bitter leaf extract synthesized and 50:50 mixture of neem/bitter leaf extract respectively.

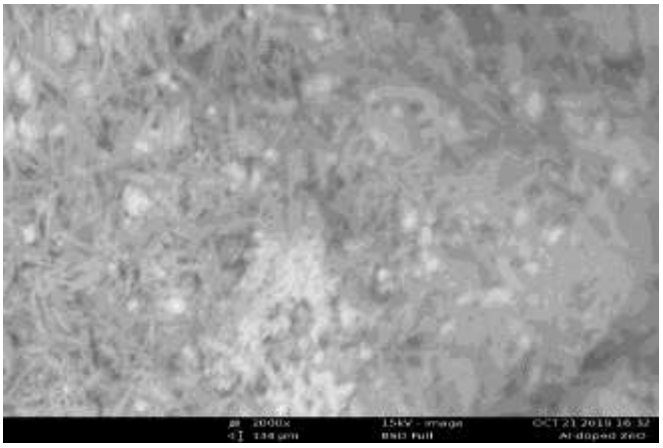

Fig.6. SEM image of Al-doped ZnO nanoparticles synthesized with bitter leaf extract.

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Fig. 7 SEM image of Al-doped ZnO Nps synthesized with neem leaf extract.

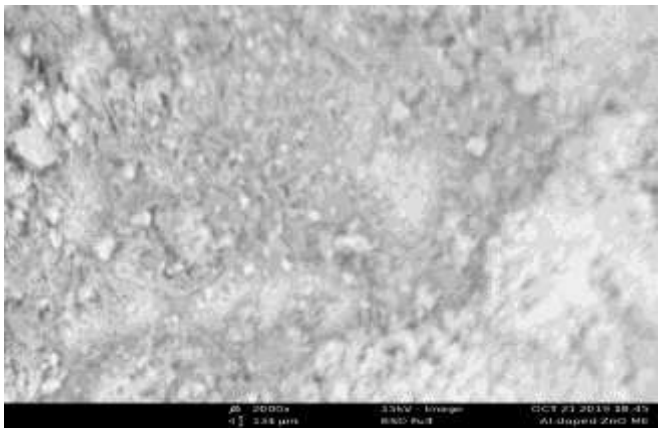

Fig. 8 SEM image of Al-doped ZnO nanoparticles synthesized with 50:50 mixture bitter-neem leaves extracts.

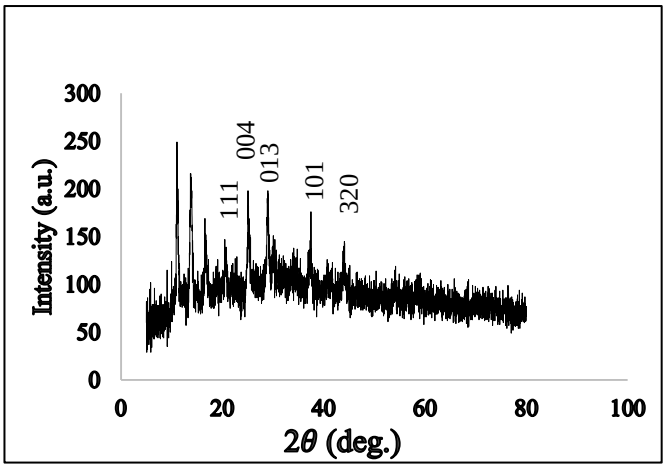

Fig. 9 XRD spectrum of Al-doped ZnO nanoparticle synthesized with neem leaf extract.

The XRD pattern in Fig. 9 shows five distinct diffraction peaks at lower 2θ values of 20.59^0, 25.11^0, 27.20^0, 37.29^0 and 44.01^0 which have been identified to be due to the presences of Al-doped ZnO particles corresponding to the Miller indices (hkl) values of (111), (004), (013), (101) and (320) planes of Al-doped ZnO Nps. The peaks compared with standard data from Joint Committee on Powder Diffraction Standards (JCPDS) File (No.36-1451), (No.80-0075) and (No.023-1491) confirms the formation of Al-doped ZnO Nps with neem leaf extract. The nanoparticles have hexagonal structure with face centered cubic nature of ZnO. Although slight shift from the standard peaks was observed, it might be due to the composition of the leaf extracts and the presence of bioorganic or metallo-proteins in the supernatant that aids stabilization of the nanoparticles. The shift in diffraction peaks is also affected by the synthesis technique and the concentration of doped aluminum on the ZnO Nps. The extra three peaks observed in XRD patterns at 11.08^0, 13.82^0 and 16.68^0 might be as a result of impurity or unreacted zinc acetate dehydrate. The average crystallite size of Al-doped ZnO nanoparticles was estimated by applying the Scherer's equation's shown in equation 1

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad 1$$

Where λ is the wavelength of Cu Kα radiation (0.154nm), θ is the Braggs angle in radians and β is the full width at half maximum of the peak in radians. From this equation, the average size of the Al-doped ZnO nanoparticles synthesized with neem leaf extract was estimated to be approximately 8nm. The small nanoparticles size indicates that thin film of aluminum was doped on the ZnO nanoparticles.

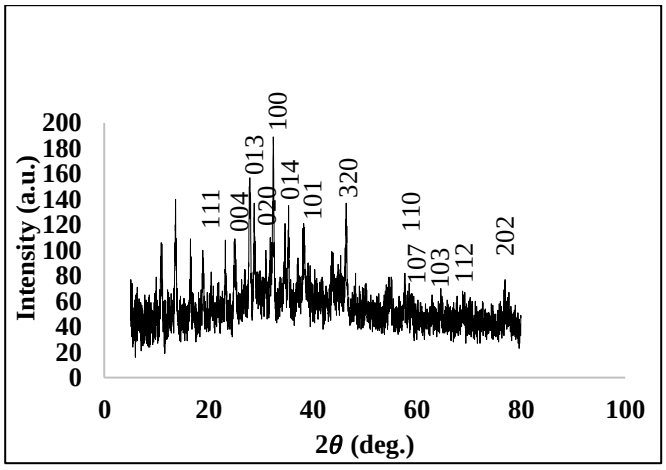

Fig. 10 XRD spectrum of Al-doped ZnO nanoparticle synthesized with bitter leaf extract.

Fig. 10 shows the XRD spectrum of Al-doped ZnO Nps synthesized using bitter leaves extracts. The XRD pattern shows thirteen distinct diffraction peaks at 2θ values of 20^0, 25.16^0, 27.1^0, 30^0, 32.46^0, 34.69^0, 37.12^0, 44.60^0,56.6^0, 57.62^0, 63^0, 68.8^0 and 76.76^0 which can be indexed (111), (004), (013), (020), (100), (014), (101), (320), (110), (107), (103), (112) and (202) planes of Al-doped ZnO Nps. The observed peaks were compared with the standard data powder diffraction card of JCPDS (No.36-1451), (No.80-0075) and No. 023-1491). The XRD analysis result confirms that the resultant particles is Al-doped ZnO Nps with face centered cubic nature. The peaks in this case were more standardized compared to Al-doped ZnO Nps peaks from neem extracts. Although slight shift in Al-doped ZnO Nps peaks was recorded. The average crystalline size of the Al-doped ZnO nanoparticles synthesized with bitter leaf extract was calculated to be approximately 7 nm.

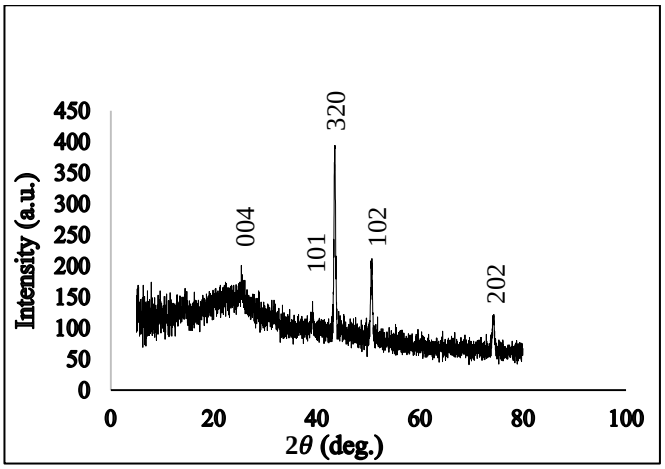

Fig. 11 XRD spectrum of Al-doped ZnO Nps synthesized with 50:50 mixture of neem/bitter leaf extracts

Fig. 11 shows XRD pattern of the synthesized Al-doped ZnO Nps with 50:50 ratio mixture of bitter leaf and neem leaf extract. The XRD pattern reflected peaks at 2θ of 25.04^0, 37.86^0, 43.44^0, 48.58^0 and 74.93^0 which can be indexed (004), (101), (320) (102) and (202) planes of Al-doped ZnO Nps. This shows that Al-doped ZnO Nps was formed using mixture of both leaf extracts as indicated by the XRD peaks compared with JCPDS standard data. Although slight shift in peaks occurred, no extra peaks was observed at lower 2θ angle as was seen in the case of neem leaf or bitter leaf extract respectively. This might be due to chemical reaction of constituent in the mixture which suppresses the formation of those peaks. The average size of the Al-doped ZnO nanoparticles synthesized was estimated to be approximately 7nm.

The quantity of nanoparticles synthesized using equal volume of precursors is shown in table 1. From the table Al-doped ZnO Nps synthesized with bitter leaf extract had the highest amount of nanoparticles (3.72grams) compared to neem and the 50:50 mixture of neem and bitter leaf.

Table 1 Volumes of leaf extract, Precursors and amount of Al-doped ZnO Nps synthesized

Extract	Volume (ml)			
	Extract	Zinc acetate dihydrate	Aluminum chloride solution	Al-doped ZnO Nps (grams)
Neem	75	75	20	3.31
Bitter	75	75	20	3.72
Neem+ bitter	75	75	20	3.42

4. CONCLUSION

The experimental results confirmed that aluminum doped zinc oxide nanoparticles were prepared through green synthesis method using neem leaves, bitter leaves and neem/bitter leaves extract mixtures. The SEM results showed that the nanoparticles synthesized had rough morphologies and the XRD result shows that the nanoparticles have the hexagonal wurtzite structure of Zinc oxide. The Al-doped ZnO Nps synthesized using bitter leaf extracts had thirteen peaks to relative to standard data with average nanoparticles size of 8nm. This indicates that bitter leaf extract phytochemicals performed better as reducing agents on the Zinc salt compared to neem leaf extract and neem/bitter leaf extracts. The average crystallite size for Al-doped ZnO Nps formed using neem leaf extract is 7nm and same for 50:50 mixture of both extracts with hexagonal structure respectively. Bitter leaf extract also gave the highest quantity of Al-doped ZnO Nps compared to neem leaf and 50:50 ratio of both mixtures using the same quantity of salt and precursors.

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