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Green Synthesis of Zinc Oxide Nanoparticles Using Tropical Plants and Their Characterizations

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Abstract – Green synthesis is one of the most popular methods in nanotechnologies. Different tropical plants have a characteristic feature of medicinal effects that are associated with metallic nanoparticles present in the plants. Nanoparticles are used immensely due to its small size, orientation, physical properties, which are reportedly shown to change the performance of any other material which is in contact with these tiny particles. These particles can be prepared easily by different chemical, physical, and biological approaches. The green synthesis was done by using the aqueous solution of Neem*(Azadirachta indica*) leaf extracts and zinc nitrate solution as well as aqueous solution of Golden shower (*Cassia fistula*) leaf extracts and zinc acetate solution. Moreover, the synthesized zinc oxide nanoparticles were characterized by using ultraviolet-visible (UV-Visible) spectroscopy, Fourier Transform Infrared spectroscopy (FT IR), Energy Dispersive X-ray fluorescence (EDXRF), X ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) analyses.

Keywords : EDXRF, Golden shower, Green synthesis, Neem, XRD, SEM, Zinc oxide nanoparticles

1 INTRODUCTION

Nowadays, the production of new materials synthesized by researchers increases with an increased population rate of global world. Researchers carry out extensive innovations for the synthesis of nanoparticles using the extract obtained from different plants and succeeded in the synthesis of Zinc oxide nanoparticles (ZnO Nps), Silver nanoparticles (Ag Nps) and Titanium oxide nanoparticles (TiO_2 Nps) etc., in the field of biotechnology and pharmaceutical science. Various chemical methods have been proposed for the synthesis of zinc oxide nanoparticles, such as reaction of zinc with alcohol, vapor transport, hydrothermal synthesis, precipitation method etc [1], [2], [3], [4]. Nanoparticles are particles having nanoscale dimension, and nanoparticles are very small sized particles with enhanced catalytic activity , thermal conductivity, non- linear optical performance and chemical steadiness owing to its large surface area to volume ratio.

Nanoparticles are particles having nanoscale dimension, and nanoparticles are very small sized particles with enhanced catalytic activity, thermal conductivity, non- linear optical performance and chemical steadiness owing to its large surface area to volume ratio. NPs have started being considered as nano antibiotics because of their antimicrobial activities. Nanoparticles have been integrated into various industrial, health, food, feed, space, chemical, and cosmetics industry of consumers which call for a green and environment-friendly approach to their synthesis (Venkat Kumar, *et al*., 2017).

Zinc Oxide nanoparticles are presently under intensive study for applications in the field of optical devices, sensors, catalysis, biotechnology as a catalyst, DNA labeling, drug delivery, medical, chemical and biological sensors as catalysts. Nanomaterials can be used in multidisciplinary field due to their unique properties. The selected application fields are as follows (Sajad Bashir, *et al*., 2015).

Aim

The present study concerns with the comparison between the preparation of ZnO Nps using neem and Golden shower in the middle of Myanmar as a green synthesis and to characterize them by some spectroscopic methods.

2 MATERIAL AND METHODS

2.1 Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 . 6H_2O$), Zinc acetate dehydrates ($(CH_3COO)_2Zn.2H_2O$), distilled water and leaf extracts of Neem (Tamar in Myanmar) and Golden shower (Ngu Wha in Myanmar), deionized water, ethanol and acetone solvents are used for the preparation of ZnO Nps .

2.2 Methods

- UV Visible Spectroscopy UV-Vis)

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- X-ray diffraction method
- Energy Dispersive X-ray fluorescence (EDXRF)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Scanning Electron Microscopy (SEM)

2.3 Sample Collection

Neem (*Azadirachta indica* L.) and Golden Shower (*Cassia fistula*) leave were collected from University of Mandalay, Mandalay Region, Myanmar.

Fig. 1. Neem (*Azadirachta indica* L.) Leaves

Fig. 2. Golden Shower(*Cassia fistula*)

2.4 Botanical Description *Azadirachta indica* L.

Botanical name	- *Azadirachta indica* L.
English name	- Margosa tree (or) Neem tree
Myanmar name	- Tama
Family	- Meliaceae
Genus	- *Azadirachta*
Part use	- Leaves

2.5 Botanical Description *Cassia fistula* Linn

Family name	- Fabaceae
Botanical name	- *Cassia fistula* Linn
Myanmar name	- Ngu Wah
English name	- Golden Shower
Part used	- Leaves

2.6 Preparation of Aqueous Extract from *Azadirachta indica* Leaves

Green leaves of *Azadirachta indica* were collected from Mandalay region, Myanmar and washed with distilled water many times for the removal of dust particles. The leaves are dried in the shade and then grinded with the help of motor and pestle until the leaves turned into fine powder. 5g of dried powder is sterilized as well as boiled with deionized water at different temperature ranges (30^0C to 120^0C). Whatman filter paper is used to filter the leaf solution and collected the leaf extract. The collected sample is cooled in a refrigerator and stored at 16^oC.

2.7 Preparation of Aqueous Extract from *Cassia fistula* Leaves

Green leaves of *Azadirachta indica* are collected from Mandalay region, Myanmar and washed with distilled water many times for the removal of dust particles. The leaves are dried in the shade and then grinded with the help of motor and pestle until the leaves turned into fine powder. 5g of dried powder is sterilized as well as boiled with deionized water at different temperature ranges (30^0C to 120^0C) and the remaining procedure are mentioned as the above.

2.8 Green Synthesis of ZnO Nanoparticles Using *Azadirachta indica* Leaf Extract

10 M of zinc nitrate solution is firstly prepared and stored in a 100ml of volumetric flask. The fresh prepared zinc nitrate solution is mixed with 20 mLl of leaf extract solution prepared at 30^oC after that mixed solution is placed in a beaker as well as stirred by the use of magnetic stirrer at room temperature. The solution is then centrifuged about 14000 rpm for 30 minute. The solution is decanted and the precipitateis rewashed with distilled water.

The process of centrifuging, decantation, re-washing and re centrifuging are repeated at least three times. Finally, the precipitate is dried in an oven in the temperature range of 120-130 ^{o}C for a day and again purified with the help of ethanol and acetone solvents that purified nanoparticles are annealed about 600°C for 2 h in Muffle furnace. Similarly, the same process is carried on for the synthesis of zinc oxide nanoparticles from the leaves extract solutions boiled at 50^oC, 75^oC, 100^oC and 120^oC.

2.9 Green Synthesis of ZnO Nanoparticles Using *Cassia fistula* Leaf Extract

10 M of zinc acetate solution is firstly prepared and stored in a 100 mL of volumetric flask. The fresh prepared zinc nitrate solution is mixed with 20 mL of leaf extract solution prepared at 30^oC after that mixed solution is placed in a beaker as well as stirred by the use of magnetic stirrer at room temperature. The solution is then centrifuged about 14000 rpm for 30 minute. The solution is decanted and the precipitate is rewashed with distilled water.

The process of centrifuging, decantation, rewashing and recentrifuging are repeated at least three times. Finally, the precipitate is dried in an oven in the temperature range of 120-130 ^{o}C for a day and again purified with the help of ethanol and acetone solvents that purified nanoparticles are annealed about 600°C for 2 h in Muffle furnace.

Similarly, the same process is carried as the mentioned above at 50^{o}C, 75^{o}C, 100^{o}C and 120^{o}C.

3 RESULT AND DISCUSSION

Fig. 3 Synthesized Zinc Oxide Nanoparticles

3.1 Yield Percent of Prepared ZnO Nanoparticles from Neem at Different Temperature

Table 1 Yield Percent of Prepared ZnO Nanoparticles from Neem at Different Temperatures

Leaf sample (g)	Yield percent of ZnO NPs at different temperatures (%)			
	50°C	75°C	100°C	120°C
5	0.01	0.02	0.04	0.03
10	0.02	0.03	0.05	0.04
15	0.025	0.035	0.055	0.045

Table 2 Yield Percent of Prepared ZnO Nanoparticles from Golden Shower at Different Temperatures

Leaf sample (g)	Yield percent of ZnO NPs at different temperatures (%)			
	50°C	75°C	100°C	120°C
5	0.01	0.02	0.04	0.03
10	0.02	0.04	0.08	0.06
15	0.025	0.050	0.010	0.075

Table (1) and (2), According to above table, the yield percent of ZnO NPs extracted from the leaves of *Azadirachta Indica L.* and *Cassia fistula* depends on the temperature ranges. The higher the temperature, the greater the amount of ZnO NPs extracted. But, at the temperature of 120˚C, it yield percent decreases again. So, the optimum temperature is found to be 100˚C.

3.2 UV Visible Spectra Analysis

ZnO nanoparticles prepared using the extract obtained from the leaves of Neem and Golden shower are subjected to record UV-Vis spectroscopy. Figures shows the photograph of the UV-Vis spectra of ZnO nanoparticles prepared from the extracts of Neem and Golden shower. The absorption peaks is obtained at the wavelength 375 nm and 376 nm for ZnO particles prepared from leaves of Neem and Golden shower. From the UV-Vis graphs, energy band gap is obtained as 3.3 and 3.29eV using the formula

$$Eg = 1240/\lambda_{max} eV$$

3.3 Fourier Transformer Infrared Spectroscopic Analysis (FT-IR)

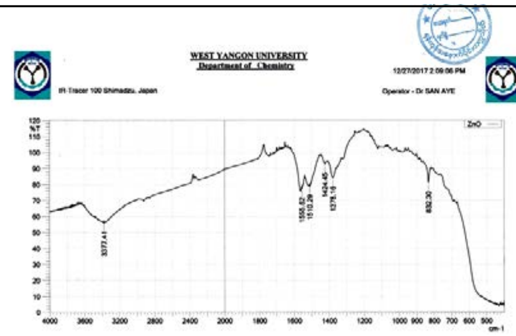

Fig. 5 FT-IR Spectra of Leaves Extract of Green Synthesized ZnO NPs

Table 3 FT-IR Assignment of ZnO NPs

No	Wave Number (cm^{-1})	Functional group
1	3377.41	O-H and N-H stretching frequencies
2	1555.62, 1510.29	N-H bending
3	832.30	Zn-O stretching

FT-IR Assignments of Pure Compound

In the region of longer wavelength or low frequency the identification of different instrument requires for its execution is Fourier transform infrared (FTIR) spectrometer.

The FT-IR spectrum of ZnO NPs is shown in Figure (6). In the spectrum, the broad bands which appear at 3377.41 cm^{-1} represents the O-H and N-H stretching frequencies of alcohol and amine groups. The bands at 1555.62 cm^{-1} and 1510.29 cm^{-1} indicates the N-H banding vibration of amine group. The band at 832.30cm^{-1} displays the Zn-O stretching frequency of metal oxygen band.

3.4 SEM Report for ZnO NPs

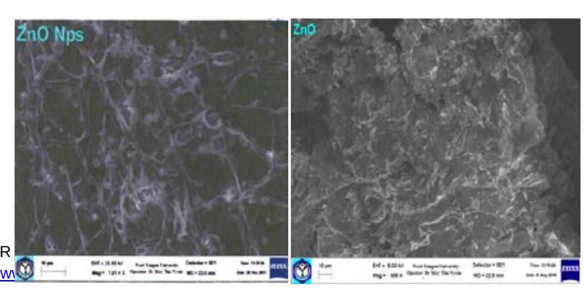

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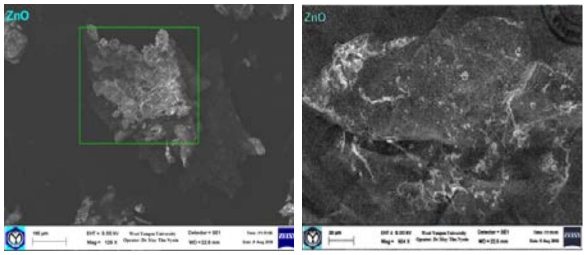
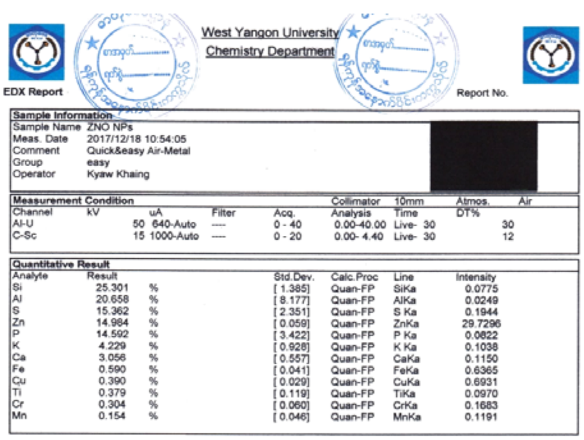
Fig. 6 SEM Micrograph of Zinc Oxide Nanoparticles



According to SEM micrograph, ZnO NPs was spindle shape and image sometime nanoflake. It is inconsistent with the shape of ZnO nanoparticles. SEM studies provided further insight into the morphology and size details of the ZnO nanoparticle. The results of the SEM studies on Zinc Oxide Nanoparticles synthesized using Neem leaves extract revealed the formation of stable Zinc Oxide Nanoflakes and spindle shaped nanoparticles. The size of the ZnO Nanoparticles synthesized using Neem leaf extracts were recorded to be 10 µm.

3.5 The EDX Report for ZnO NPs

Table 4 Elemental Analysis of ZnO NPs



West Yangon University
Chemistry Department

EDX Report

Report No.

Sample Information

Sample Name	ZNO NPs
Meas. Date	2017/12/18 10:54:05
Comment	Quick&easy Air-Metal
Group	easy
Operator	Kyaw Khaing

[redacted]

Measurement Condition Collimator 10mm Atmos. Air

Channel	kV	uA	Filter	Acq.	Analysis	Time	DT%
Al-U	50	640-Auto	----	0 - 40	0.00-40.00	Live- 30	30
C-Sc	15	1000-Auto	----	0 - 20	0.00- 4.40	Live- 30	12

Quantitative Result

Analyte	Result		Std.Dev.	Calc.Proc	Line	Intensity
Si	25.301	%	[1.385]	Quan-FP	SiKa	0.0775
Al	20.658	%	[8.177]	Quan-FP	AlKa	0.0249
S	15.362	%	[2.351]	Quan-FP	S Ka	0.1944
Zn	14.984	%	[0.059]	Quan-FP	ZnKa	29.7296
P	14.592	%	[3.422]	Quan-FP	P Ka	0.0822
K	4.229	%	[0.928]	Quan-FP	K Ka	0.1038
Ca	3.056	%	[0.557]	Quan-FP	CaKa	0.1150
Fe	0.590	%	[0.041]	Quan-FP	FeKa	0.6365
Cu	0.390	%	[0.029]	Quan-FP	CuKa	0.6931
Ti	0.379	%	[0.119]	Quan-FP	TiKa	0.0970
Cr	0.304	%	[0.060]	Quan-FP	CrKa	0.1683
Mn	0.154	%	[0.046]	Quan-FP	MnKa	0.1191

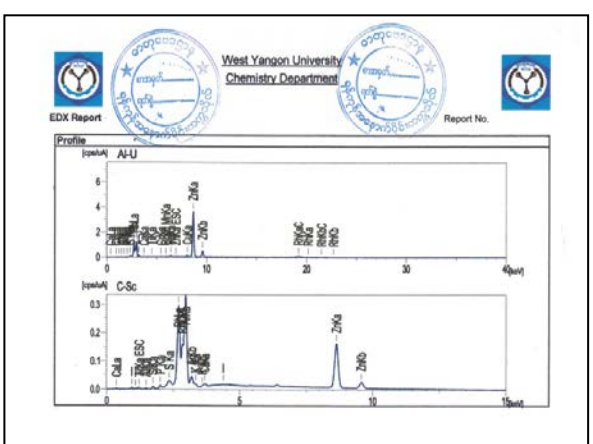


Fig. 7 EDX Pattern of ZnO NPs

The EDX Report for ZnO NPs

The EDX Spectrometry can analyse the element from Si to U under non vacuum condition. It can be utilized for qualitative identification and quantitative estimation of elements is solids, powders and liquids with appropriate sample preparation techniques. EDX-700 spectrometer can perform two different types of quantitative analysis, namely Fundamental Parameter (FP) method and Calibration Curve method. In the FP method, theoretical results are calculated when standard samples are not available. This method can be applied to most samples, but the accuracy must be checked in advance. In calibration curve method, experimental results can be obtained by using standard samples. Only limited samples can be applied, but accuracy is high (Becheri, 2008).

The EDX Report of the leaf extract of ZnO Nps was determined at the department of Chemistry, West Yangon University. The percent contents of elements Si, Al, S, Zn, P, K, Ca, Fe, Cu, Ti, Cr were found to be as shown in the Figure (4.3). According to this EDX spectrum, the percent composition of Si was 25.301 % that was the highest amount from the leaf extract. The percent composition of Zn was 14.984 % which is a medium content of leaf extract.

3.10 XRD Assignment for ZnO NPs

Unique characteristic X-ray diffraction pattern of each crystalline solid gives the designation of “fingerprint technique” to XRD for its identification. XRD may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. From these points it can be concluded that X-ray diffraction has become a very important and powerful tool for the structural characterization in solid state physics and materials science (Rajendran, 2010). In this study, the powder of ore sample was measured by XRD diffractogram. The peaks related to impurities were found in the XRD diffractogram.

Scherer’s Equation for estimation of crystalline size

$$D = \frac{K\lambda}{\beta \cos\Theta} \quad A^{\circ}$$

Where, D = the average crystalline size in A°

K = the shape factor

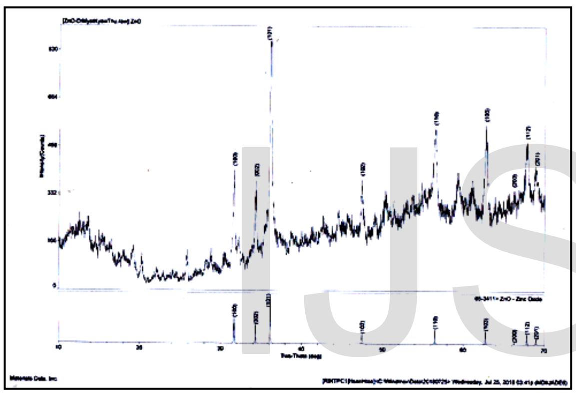
λ = the wavelength of X-ray (1.5406 A°)

ß = the corrected line broadening of the NPs

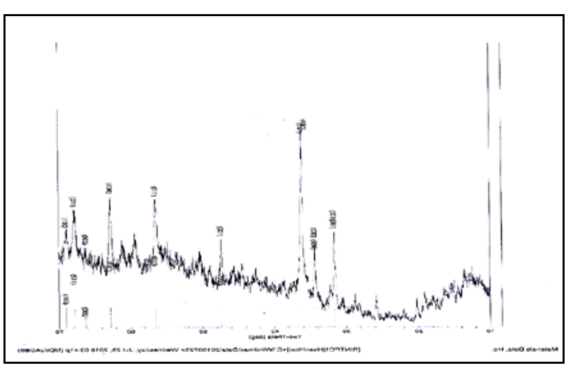
ϴ = the Bragg angle

Table 5 The Structure and Geometric Parameters of ZnO NPs

2Θ (°)	FWHM (ß in radians)	d-spacing (A°)	Cos Θ	Crystalline size(nm)
31.643	0.0055	2.8252	0.9621	25.91
34.354	0.0049	2.6082	0.9554	29.29
36.158	0.0068	2.4822	0.9506	21.21
47.423	0.0045	1.9155	0.9156	33.28
56.477	0.0077	1.6280	0.8809	20.21
62.744	0.0062	1.4796	0.8538	25.90
66.186	0.0100	1.4108	0.8377	15.74
67.823	0.0065	1.3807	0.8299	25.42
69.007	0.0068	**1.3598**	**0.8241**	**24.47**
			Average	24.60



[ZnO-T100C-EiNgeSaw.raw] ZnO											Peak Search Report
SCAN: 10.0/70.0/0.02/0.12(sec), Cu(40kV,40mA), I(max)=46, 01/17/18 14:19											
PEAK: 9-pts/Parabolic Filter, Threshold=1.0, Cutoff=0.1%, BG=1/1.0, Peak-Top=Parabolic Fit											
NOTE: Intensity = Counts, 2T(0)=0.0(deg), Wavelength to Compute d-Spacing = 1.54056Å (Cu/K-alpha1)											
#	2-Theta	d(Å)	(h k l)	BG	Height	Height%	Area	Area%	FWHM	XS(Å)	P/N
1	31.204	2.8639	(1 0 0)	19	6	35.3	65	16.5	0.184	533	0.6
2	33.634	2.6624	(1 1 1)	18	6	35.3	94	23.8	0.266	336	0.6
3	34.768	2.5781	(0 0 2)	18	6	35.3	84	21.3	0.238	385	0.6
4	35.880	2.5008	(1 0 1)	15	11	64.7	106	26.8	0.164	644	1.1
5	38.772	2.3206	(2 0 0)	14	17	100.0	395	100.0	0.395	220	1.5
6	47.122	1.9270	(1 0 2)	17	12	70.6	242	61.3	0.343	264	1.1
7	56.230	1.6346	(2 2 0)	14	10	58.8	72	18.2	0.122	>1000	1.0
8	64.695	1.4396	(2 0 0)	12	10	58.8	299	75.7	0.508	189	1.1



X-ray powder diffraction (XRD) is a rapid methodical technique primarily used for phase identification of a crystalline material and provides information on unit cell dimensions. Structure and peak purity of the samples were acknowledged from XRD prototype of the synthesized ZnO nanoflowers and flakes from aqueous leaf extract of neem Figure (4.4). The peaks obtained for are ZnO Nps analogous to (100), (111), (002), (101), (200), (102), (220) and (200) planes in the hexagonal phase of ZnO. The XRD patterns of the ZnO nanoparticle are in high quality accord with the values of stand card (JCPDS NO: 36-1451). More over predominantly broad peaks at about 31° and 36° are indicative of nano-crystalline nature of the ZnO phase. No other contamination peaks are observed. From the XRD measurements the estimation of the average crystallite size of ZnO Nps was found to be 37.79 nm and 24.60 nm by using leaf extracts of neem and golden shower, respectively.

4 CONCLUSION

In the present study, zinc oxide nanoparticles (ZnO NPs) were successfully synthesized by using zinc nitrate and aqueous leaves extracts of (neem and golden shower) as the reducing agent as well as stabilizing agent.

The synthesized ZnO nanoparticle solution exhibited absorbance bands at 328 nm attributed to the excitation of valence electrons of ZnO arranged in the nanoparticles.

The FT-IR spectrum of the aqueous neem extract showed the presence of O-H stretching frequency at 3377.41cm^{-1} from the leaves extract of Neem and the characteristic absorption peak of Zn-O bond was observed at 832.30 cm^{-1}.

The EDXRF gave strong signal for zinc at energies 29.7296 units and its amount was found to be 14.984% .

The sharp peaks in the XRD pattern clearly illustrated the high crystallinity of the nanoparticles and were all indexed to standard JCPDS card no.36 -1451. According to XRD peak search report of ZnO NPs at 100°C, the crystallite size of the ZnO nanoparticles at 100°C was found to be 37.79 nm and 24.60 nm.

SEM studies revealed the formation of nanoflakes and spindle shaped nanoparticles for the green synthesized ZnO. Thus the progress of green chemistry with the use of plants in the synthesis of nanoparticles has engrossed a great attention.

From my research, the synthesized zinc oxide nanoparticles using Neem and golden shower leaves so as to confirm the extract chemicals that lead to bio-functionalization of Zn ions to ZnO NPs can be furthered used for the nano drug productions and other applications such as vitamin, anti-oxidants, suncreams.

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