JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

NATURAL PRODUCTS ASSISTED SYNTHESIS OF CuO AND ZnO NANOPARTICLES FOR THE CATALYTIC DEGRADATION OF METHYLENE BLUE DYE FOR LONGER PERIOD

[1]Shubhangi P. Patil1 *, [2]Arslan M. Shaikh, [3]Rahul R. Baviskar, [4]Guruprasad R. Mavlankar, [5]Minakshi N. Bhatu

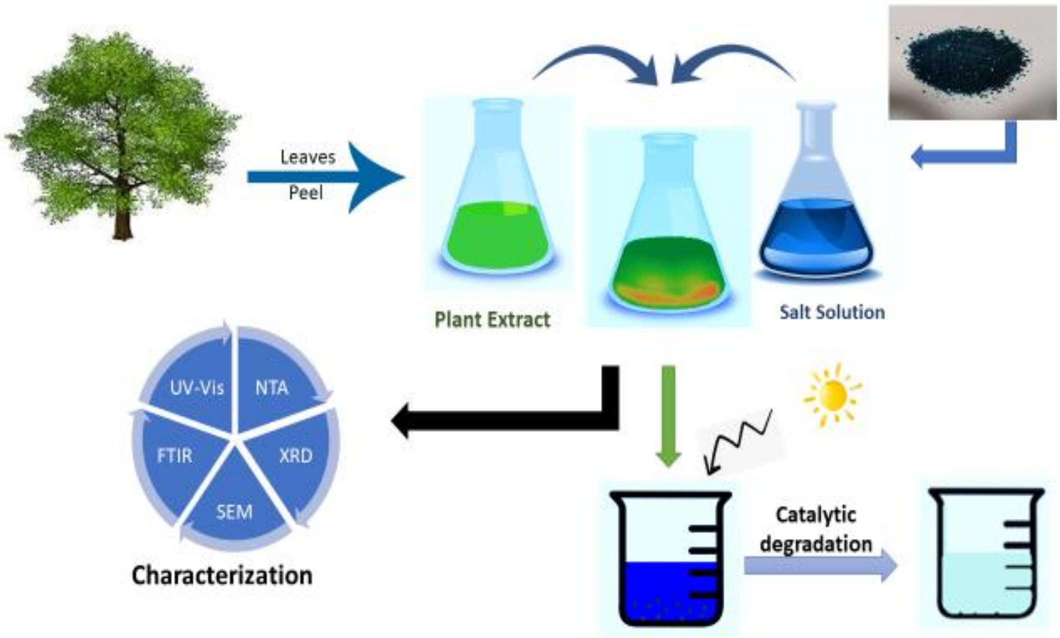
[1]Assistant Professor, [2]M.SC.Chemistry student, [3]M.SC.Chemistry student, [4]Ph.D. Student, [5]Ph.D. Student

[1] Department of Chemistry, Institute of Science,
15, Madam Cama Road, Mantralaya, Fort, Mumbai,
Maharashtra 400032, India

ABSTRACT

With the world gravitating towards a greener and sustainable method in various sectors, the synthesis of metal oxide nanoparticles is also seen to be shifting from convectional to economically sound methods. In this context, herein, an eco-friendly phytochemical method has been used to synthesize and evaluate photocatalytic activity of CuO and ZnO nanoparticles. The phytochemical extract was prepared by using *Azadirachta indica* (neem) leaf, *Hylocerus undatus* (dragon fruit) fruit peel and *Vigna unguiculate* (Black-eyed beans) sprouting water. Further, the samples which showed good photocatalytic reduction were characterized by using nanoparticle tracking analysis (NTA) which revealed the mean sizes of the particle to be 61 nm, 45 nm & 37 nm for ZnO (neem), ZnO (dragon fruit) & CuO (neem) respectively. The X-ray diffraction (XRD) study disclosed that the samples were more amorphous in nature. Surface analysis of samples using scanning electron microscopy (SEM) revealed the agglomeration of spherical and irregular - shaped particles. The presence of reducing agents i.e., various functional molecules & metal-oxide nanoparticles were further confirmed by FTIR analysis. The photocatalytic study of the CuO (neem) nanoparticles with methylene blue revealed 90.43% degradation of the dye in the period of 15 minutes while the reaction was studied for 120 minutes.

GRAPHICAL ABSTRACT



KEYWORDS

Metal Oxide Nanoparticles, Phytochemical Synthesis, Catalytic degradation, Long time Reaction.

1. INTRODUCTION

With the expansion of work in science and technology, various areas are blooming at their best. One of those is Nanotechnology, which covers a large area of food security, electronics, automotive, environment, textiles, cosmetics, and many more [1,2]. The core of nanotechnology is nanoparticles or ultrafine particles and currently, they are synthesized using various conventional methods such as hydrothermal, flame spray pyrolysis, sonochemical, sol-gel, vapor phase, co-precipitation method, etc. However, the conventional methods require a long processing time and high energy, the use of toxic organic reagents. Eventually, the green synthesis of nanomaterials has gained vast dimensions compared to traditional methods. Green methods mainly focus on low cost and low energy requisite, high yield rate and environment friendly techniques [2,3]. They lessen the usage of chemicals as the reduction part is carried by phytochemicals present in the plant extract as well as by the microorganisms like bacteria, algae, and fungi [4,5]. Plenty of bioactive compounds such as proteins, flavonoids, sugar, phenolic compounds and alkaloids can be directly extracted through plant extract without following any hazardous procedure which in turn can reduce specific metal ions into nanoparticles [6].

Noble metals like gold, silver and platinum are mainly used for the synthesis of nanoparticles [7-9], but due to their high economic value, they are replaced by new studies emerging in nanoparticle synthesis using transition metals like zinc, copper, iron, magnesium, etc. Due to their low toxic nature and easy availability, zinc and copper is used widely all over the world [10-13]. Nanoparticles of ZnO and CuO have various applications in energy, electronics and some are related to future applications for curing fatal diseases like cancer [14-17]. Nanoparticle has reduced particle size that imparts increased surface area due to which nanoparticles show good anti-microbial activity [18]. ZnO and CuO are bio-safe materials that possess photo-oxidizing and photocatalytic properties that impact biological and chemical species [19,20]. Variety of plants and fruits have antioxidant compounds present which are used for curing life-threatening diseases such as diabetics, cancer, and multiple heart problems. Also harmful dye released from various industries can be broken down into simpler compounds using nanoparticles. Nanoparticles have not only deepened in the biological world but also into the physical world by reducing harmful organic pollutant like dyes, nitro aromatic compounds, phenols, etc. [7-10]

Currently, the researchers are focusing on the green synthesis of metal oxide nanoparticles using phytochemicals extracted by different parts of the plant such as root hair [21], leaves [22,23] and fruit peel [24,25]. In this frame of reference, various plants such as *Azadirachta indica* [26,27], *Psidium guajava* [28], *Ocimum tenuiflorum [29,30]*, *Carica papaya [31]*, *aloe-vera [32]*, *etc.* have been studied for the biosynthesis of metal oxides nanoparticles. **Table.1** shows different synthesized nanoparticles using various plant extracts.

Hence, in the current study, we have discussed an energy – efficient synthesis of CuO and ZnO nanoparticles by using the following phytochemicals sources like *Azadirachta indica*, *Hylocerus undatus*, *Vigna unguiculata*. Further, the reach of this research article is focused on the green synthesis of ZnO and CuO nanoparticles for their application in the photocatalytic study for the degradation of water polluting dye, Methylene Blue (MB). According to the literature review, the catalytic reduction reactions were studied for short times such as 2 to 5 minutes intervals for 24 to 30 minutes. Here, in the present study, we have planned to observe the reaction for a longer period with 15 minutes time intervals for 120 minutes and to study the time dependency of catalytic reaction.

Table.1 Synthesized nanoparticles using various plant extracts

Year	Nanoparticle	Plant Name	Size(nm)	Morphology	Application	Ref
2020	ZnO	Melia azedarach	33-96	Spherical	Antioxidant	[33]
2020	ZnO	Euphorbia hirta	20-25	Spherical	Antimicrobial	[34]
2020	ZnO	Calotropis gigantea	31	Hexagonal and pyramidal	Photocatalytic	[35]
2014	CuO	Tea leaf and coffe powder	50	Spherical	Antimicrobial	[36]
2017	CuO	Banana peel	60	Spherical	Photocatalytic	[37]
2020	CuO	Walnut shell	15-22	-	Anticancer	[38]
2020	Au	Hibiscus sabdariffa	15-45	Spherical	Antiacute myeloid leukemia	[39]
2020	Au	Pimenta dioica	9-17	Spherical	Anticancer	[40]
2020	Au	Litsea cubeba	8-18	Spherical	Catalytic reduction of 4-Nitrophenol	[41]
2020	TiO_2	Lemon peel Extract	80-140	Spherical	Antimicrobial	[42]
2020	TiO_2	Mentha arvensis	20-70	Spherical	Antimicrobial	[43]
2020	TiO_2	Syzygium cumini	11	Spherical	Photocatalytic removal of lead	[44]
2020	Ag	Dionaea muscipula	5-10	Quasi-Spherical	Antioxidant	[45]

2020	Ag	Cestrum nocturnum	20	Spherical	Antibacterial	[46]
2020	Ag	Nauclea latifolia	12	Irregular	Antimicrobial	[47]

2. MATERIAL AND METHOD

2.1 Materials

Copper acetate [$Cu(CH_3COO)_2$], Zinc chloride ($ZnCl_2$) were obtained from Merck Pvt. Ltd. and were used without any further purification. Distilled water was used as a solvent and Methylene blue was obtained from Sigma-Aldrich Pvt. Ltd. *Azadirachta indica (*Neem) leaves from Vishnu baug (plant nursery), *Hylocerus undatus* (dragon fruit) fruit peel and *Vigna unguiculate* (sprouting water of Black-eyed beans) were taken from a nearby market.

2.2 Methods

2.2.1 Preparation of the extract

***Hylocerus undatus* (Dragon Fruit) peel extract**: The peels of *Hylocerus undatus* (Dragon Fruit) were collected and washed entirely first with tap water and then with distilled water. The washed peels were shade dried for 4-5 days to eliminate the moisture from the surface. 20 g of peels were accurately weighed and extracted in 100 ml distilled water at 60 ℃ for about 30 minutes. The extract was cooled at room temperature and filtered using Whatman filter paper No.1. This extract solution was then labeled and stored in a refrigerator for the further procedure in synthesis [48].

***Azadirachta indica* (Neem) leaves extract:** *Azadirachta indica* (neem) leaves were collected, washed, and dried at room temperature. 20 g of leaves were boiled in 100 ml distilled water for 20 min at 60 ℃ till the color of the solution turns light yellow. This light yellow colored extract solution was filtered using Whatman filter paper No.1 and stored for the further procedure in synthesis [23].

***Vigna unguiculate* (Black-eyed beans) sprouting water**: Black-eyed beans were collected and soaked in water overnight. Further, the peas were removed and water was collected which was filtered using Whatman filter paper No.1 and stored for the further procedure in synthesis.

2.2.2 Synthesis of CuO Nanoparticles

The CuO nanoparticles were synthesized by weighing 2.0 g of copper acetate and by dissolving it in 100 ml of distilled water under the constant stirring conditions on a magnetic stirrer at room temperature until the dissolution of salt. Subsequently, Dragon Fruit peel extract was added dropwise under constant stirring, after sometime solution changes color from blue to green. The obtained mixture was left under constant stirring at room temperature. After about 60 minutes, green colored solution changed to a dark green colored solution. The mixture is then centrifuged and washed first with distilled water and then with ethanol. CuO nanoparticles were then collected, weighed, and stored for further studies.

10 ml copper acetate salt solution was added to 20 ml neem leaves extract dropwise under constant stirring at 60 °C. The mixture was kept at room temperature then after 10 to 15 minutes, brownish black precipitate was observed. This precipitate was centrifuged and washed with distilled water first and then with ethanol. The obtained CuO nanoparticles were then collected, weighed and stored for further studies.

1.0 g of copper acetate was dissolved in 100 ml distilled water under constant stirring. Black-eyed beans sprouting water extract was added to the copper acetate solution under constant stirring in the presence of sunlight until the solution changed from blue to green indicating the formation of nanoparticles. The nanoparticles were then obtained using centrifugation followed by washing, first with distilled water and further with ethanol. The nanoparticles were collected, weighed and stored for further studies.

2.2.3 Synthesis of ZnO Nanoparticles

The ZnO nanoparticles were synthesized by weighing 1.0 g of zinc chloride in 10 ml of distilled water. This solution is then heated to 70–80 °C and 7-10 ml of dragon fruit peel extract was added dropwise in the constant stirring conditions on a magnetic stirrer. The solution was then heated to form a gel like product~~,~~ which was transferred to a crucible. This product was heated in a muffle furnace at 400 °C for 2 hours to obtain the nanoparticles. The particles were separated by using the centrifugation method followed by washing, first with distilled water and further with ethanol. The obtained ZnO nanoparticles were collected, weighed and stored for further studies.

2.0 g of zinc chloride crystals were dissolved in 20 ml of neem leaves extract with constant stirring. Then the mixture was boiled at 60–80 °C under constant stirring until a deep yellow paste was formed. The paste was heated in a muffle furnace at 400 °C for 2 hours. Then the nanoparticles were obtained using centrifugation followed by washing, first with distilled water and further with ethanol. The obtained ZnO nanoparticles were collected, weighed and stored for further studies.

1.0 g of Zinc Chloride was dissolved in 100 ml distilled water. Then the black-eyed beans, sprouting water extract was added under constant stirring in the presence of sunlight until the formation of a turbid solution, which was centrifuged and washed first with distilled water and further with ethanol to obtain the nanoparticles. The ZnO nanoparticles were collected, weighed and stored for further studies.

Table.2 shows all synthesized nanoparticles via the green method using the extract from different plant materials in this study.

Table: 2 Synthesized nanoparticles via the green method using the extract from different plant materials in this study.

Metal salt used	Name of the plant	Part of the plant	Synthesized nanoparticle
Copper acetate	Hylocerus undatus	Fruit peel	CuO
Zinc chloride	Hylocerus undatus	Fruit peel	ZnO
Copper acetate	Azadirachta indica	Leaves	CuO
Zinc chloride	Azadirachta indica	Leaves	ZnO
Copper acetate	Vigna unguiculuta	Sprouting water of Beans	CuO
Zinc chloride	Vigna unguiculuta	Sprouting water of Beans	ZnO

2.3 Photocatalytic property of Nanoparticles

The photocatalytic study of synthesized nanoparticles was performed in the presence of the natural source of UV light i.e. Sunlight. Investigation of photocatalytic activity of synthesized ZnO and CuO nanoparticles as per **Table no.2** were studied against 50 ml aqueous solution of 5 ppm MB dye solution. The weight of the nanoparticle taken to study the photocatalytic activity was 10 mg. The degradation of methylene blue dye was analyzed by using a UV- visible spectrophotometer at λ=664.84 nm at a time interval of 15 minutes. The percentage degradation of MB dye as per **Figure.1** and **Figure.2** reveals that CuO (neem), ZnO (dragon fruit) and ZnO (neem) nanoparticles showed better results hence were characterized for further studies.

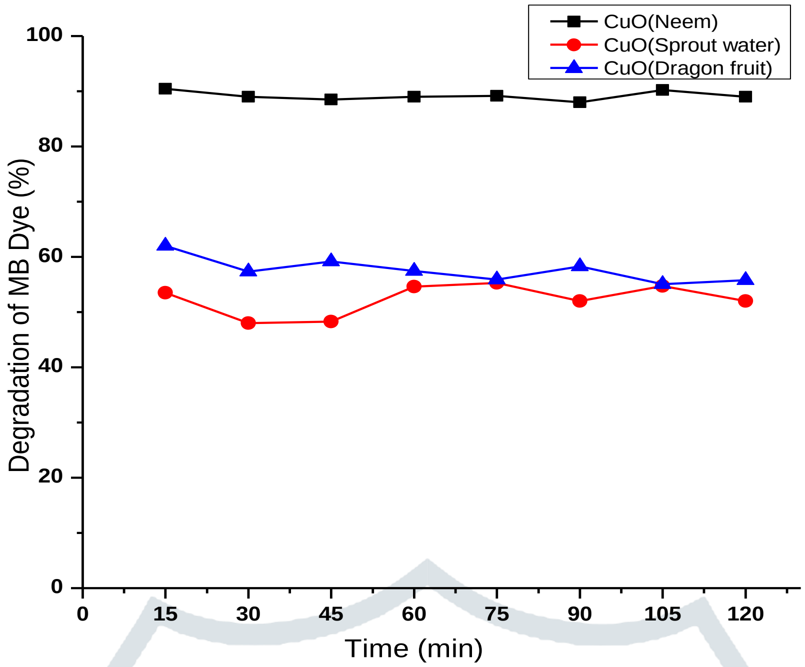


Figure 1: Percentage degradation of MB dye in the presence of CuO nanoparticles.

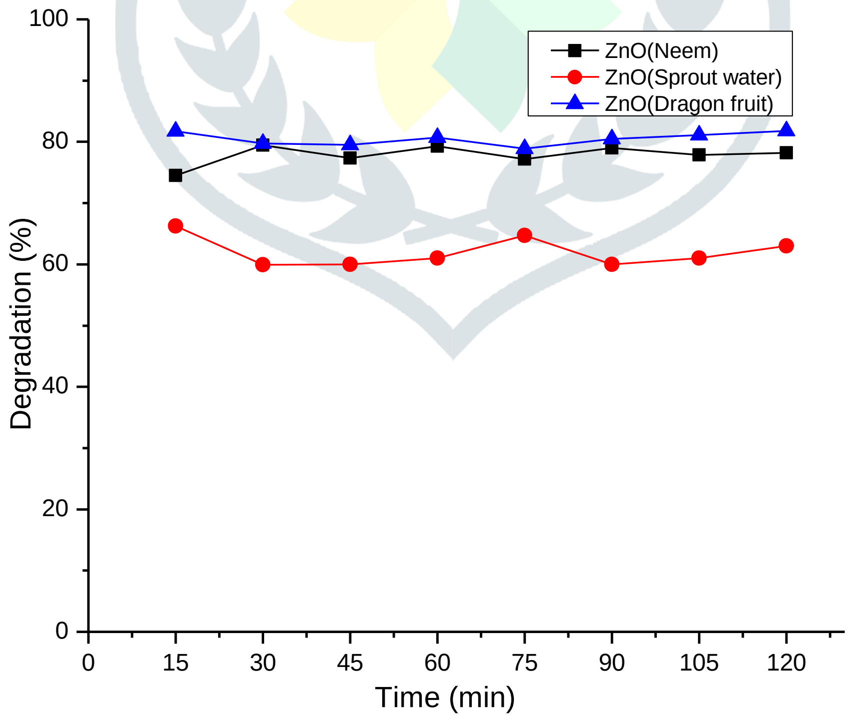


Figure 2: Percentage degradation of MB dye in the presence of ZnO nanoparticles.

2.4 Characterization

The authenticity of the so-synthesized nanoparticles was confirmed by using the following standard characterization techniques: UV-Visible, NTA, XRD, SEM and FTIR. The absorbance of the Methylene Blue (MB) dye solutions was measured using a UV-Visible spectrophotometer of Thermo Scientific (Model Evolution 260 bio). The mean size of synthesized particles was obtained by performing Nanoparticle tracking analysis using the Nanosight LM20 nanoparticle tracking analysis instrument. The crystallinity of the synthesized nanoparticles was studied using MiniFlex II X-Ray Diffractometer. The morphology of synthesized nanoparticles was studied by using the Scanning Electron Microscope of Tescan, (Model Vega3) with an accelerating voltage of 20 kV. The Fourier Transfer Infrared (FTIR) spectroscopy was used for the identification of functional groups present in the nanoparticles. Spectra were obtained using the Perkin Elmer spectrometer within the range of 400 - 4000 cm^{-1} by using the KBr palette method.

3. RESULTS AND DISCUSSION

3.1 Nanoparticle Tracking Analysis (NTA):

NTA analysis of so-synthesized nanoparticles discloses that the mean size of the nanoparticles was 37nm, 45nm & 61nm for CuO (neem), ZnO (dragon fruit) & ZnO (neem) respectively as shown in **Figure.3(A), Figure.3(B)** and **Figure.3(C).** The standard deviation of the so-synthesized nanoparticles was 56 nm, 36 nm & 50 nm for CuO (neem), ZnO (dragon fruit) & ZnO (neem) respectively. Researchers have reported certain important applications of NTA for the establishment of size; size distribution and concentration of particles in ecotoxicology, environmental and nanotoxicology studies [49,50].

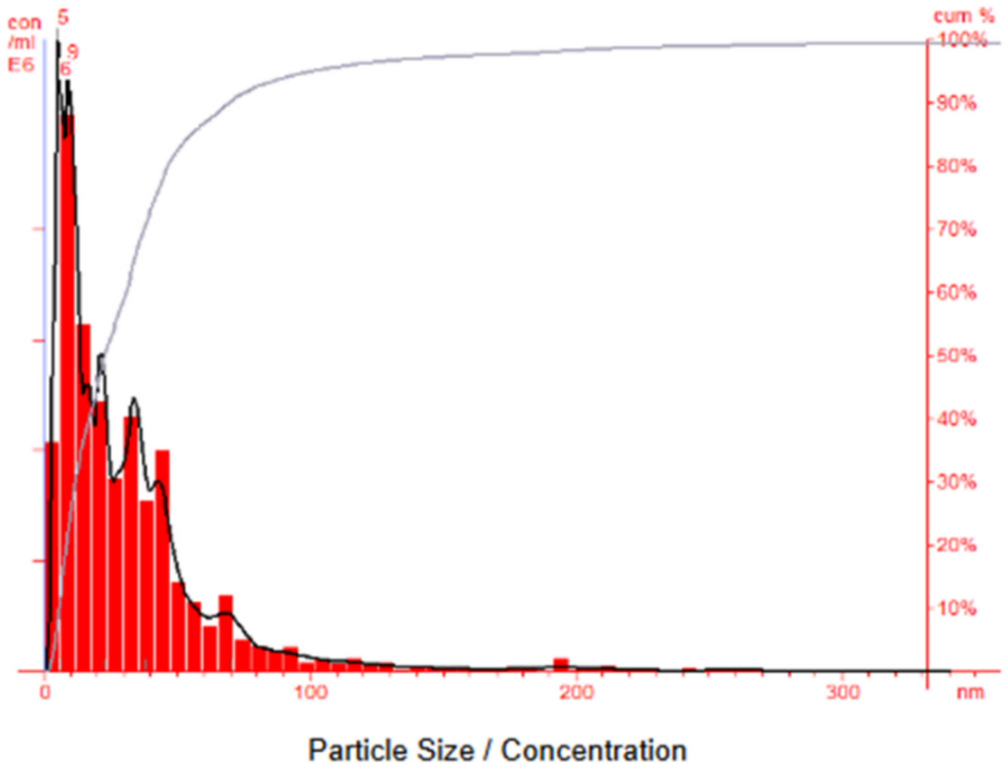


Figure.3 (A) NTA graph showing mean size of CuO nanoparticles (neem)

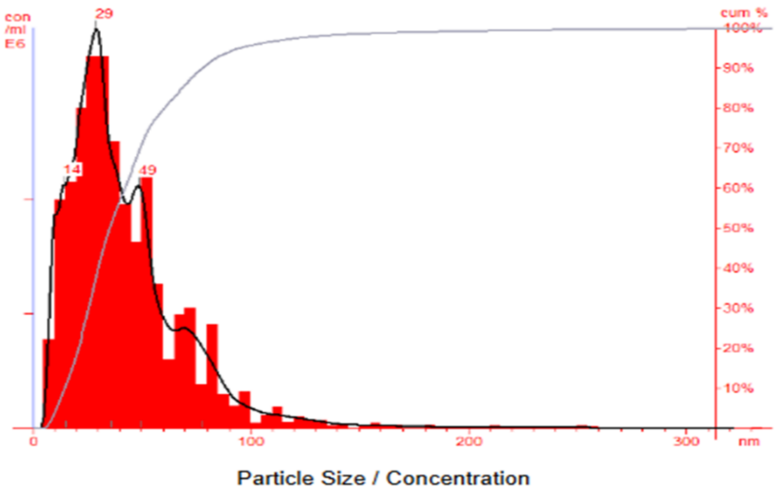


Figure.3 (B) NTA graph showing mean size of ZnO nanoparticles (dragon fruit)

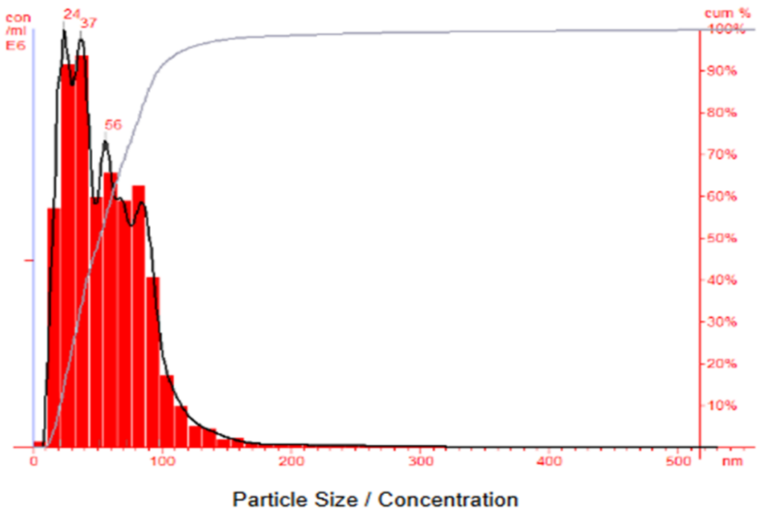


Figure.3 (C) NTA graph showing mean size of ZnO nanoparticles (neem)

3.2 X-Ray Diffraction (XRD)

XRD analysis of so-synthesized nanoparticles reveals the crystalline or amorphous nature of the particles under study. **Figure.4** shows the XRD pattern of CuO (neem), ZnO (dragon fruit) and ZnO (neem) nanoparticles. The 2θ value of CuO (Neem) were correlated with the 2θ values of 23.7, 29.6, 32.4, 35.5, 38.9 & 44.1 [2]. This indicates the presence of the CuO phase as per the 2θ values. Similarly, the 2θ values of ZnO (Dragon fruit) were correlated with, the 2θ value of 22.4, 24.9, 31.4, 32.5, 34.7, 36.6, 38.2, 45.1, 54.3, 58.6 & 63.1 [1] which revealed the presence of ZnO phase. Lastly, the 2θ value of ZnO (Neem) were again correlated with, the values of 31.4, 34.4, 36.6, 47.06, 63.28 & 68.8 indicating the presence of CuO phase [1]. It can be seen in **Figure.4** that the peaks corresponding to 2θ values are comparatively less intense. This indicates that the so-synthesized nanoparticles are comparatively more amorphous in nature than crystalline.

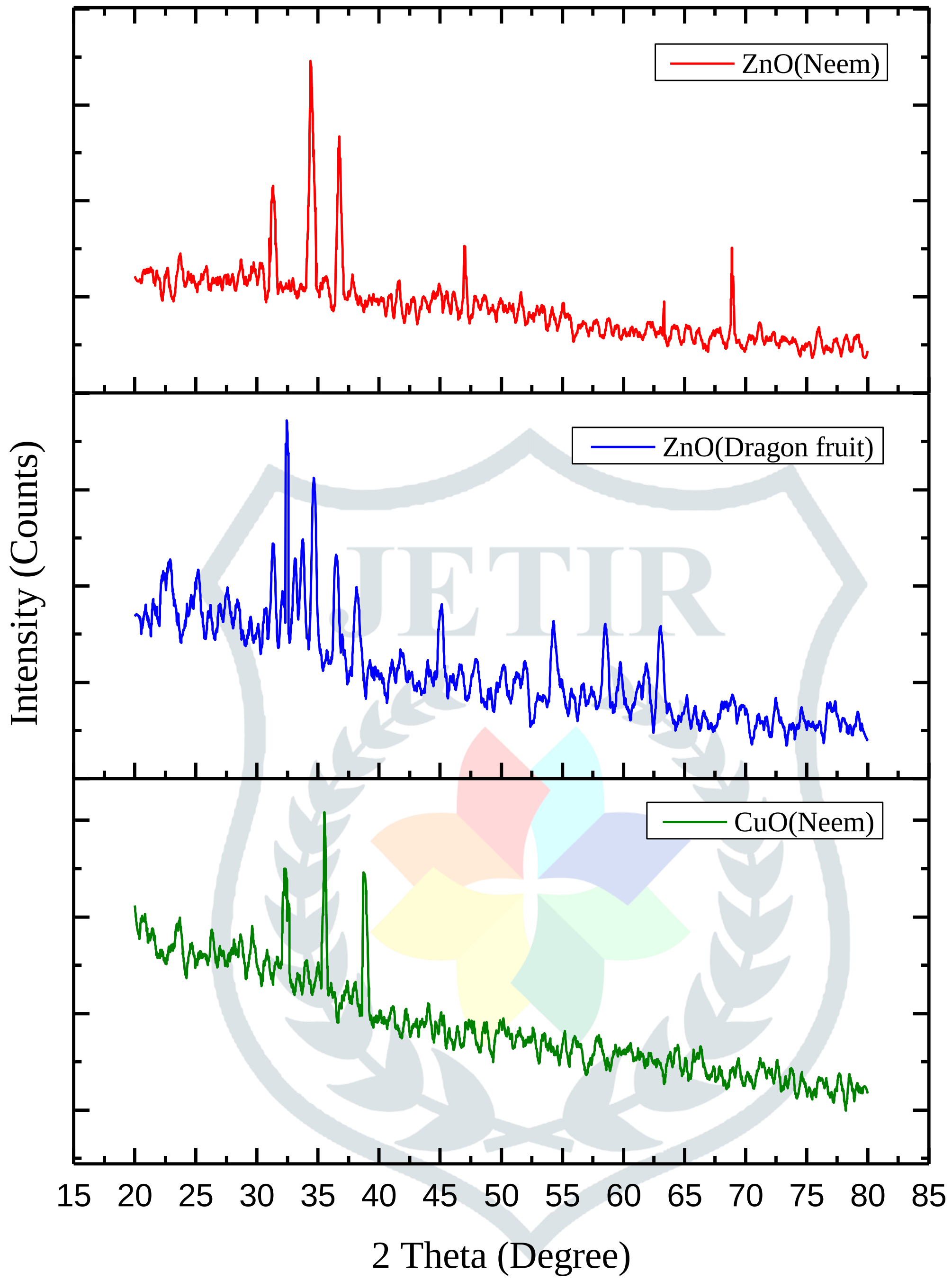
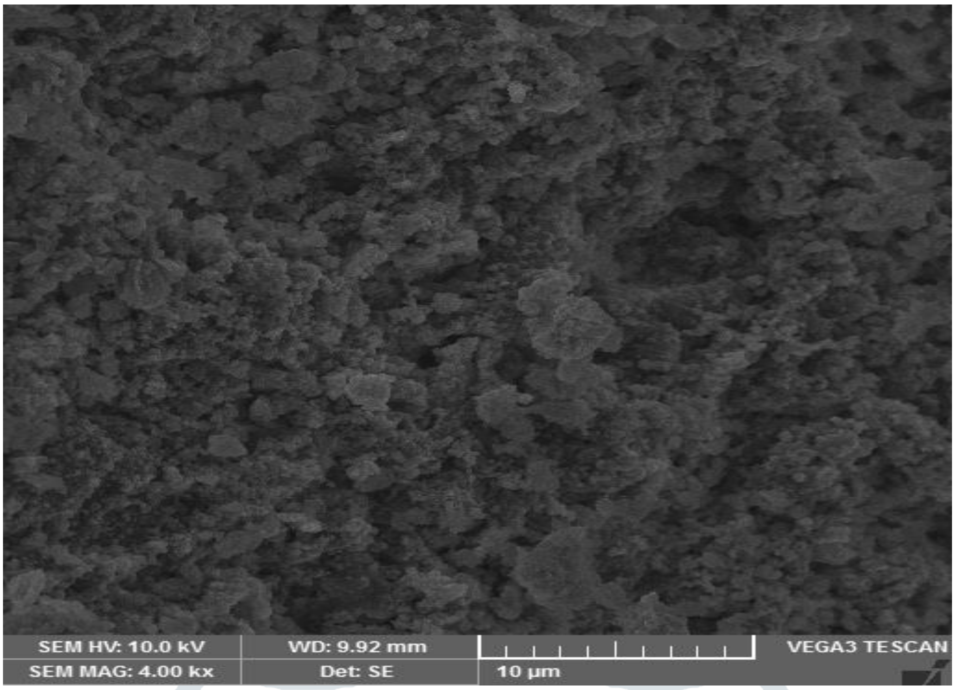


Figure 4: XRD pattern of CuO (neem), ZnO (dragon fruit) and ZnO (neem) nanoparticles

3.3 Scanning Electron Microscopy (SEM)

The scanning electron microscopy technique was used to analyze the morphologies of so-synthesized nanoparticles. The SEM images of CuO nanoparticles synthesized using *Azadirachta inidica* leaf extract; **Figure.5** reveals that the particles are agglomerated in nature and have irregular morphology. The SEM images of ZnO nanoparticles synthesized using *Hylocerusundatus* peel extract; **Figure.6** reveals that the particles are agglomerated in nature and possess spherical morphology. Whereas, the SEM images of ZnO nanoparticles synthesized using *Azadirachta indica* leaf extract; **Figure.7** reveals that they possess irregular morphology.



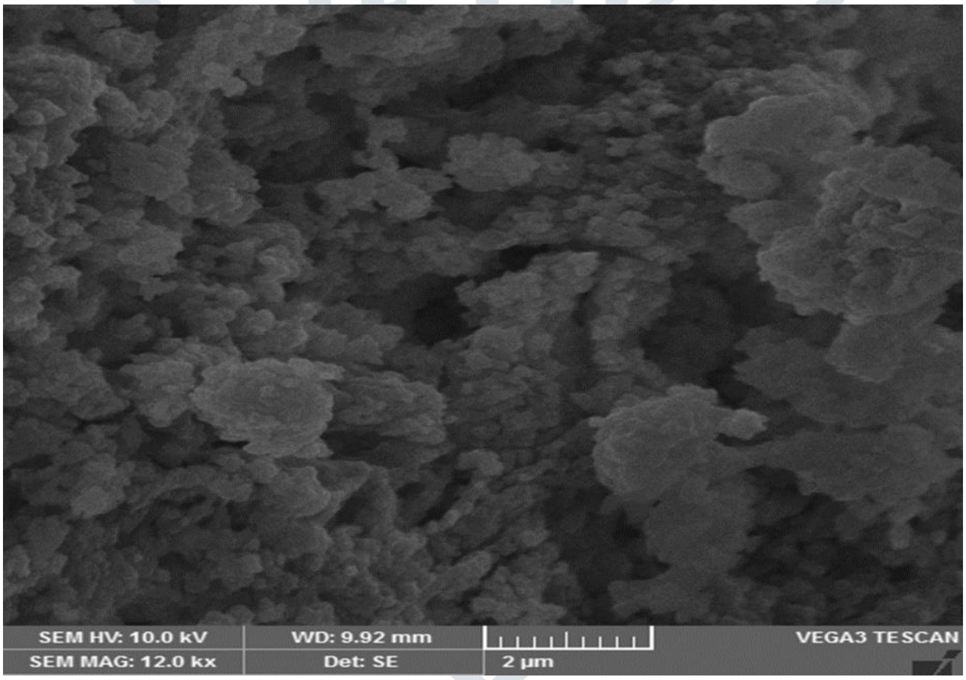
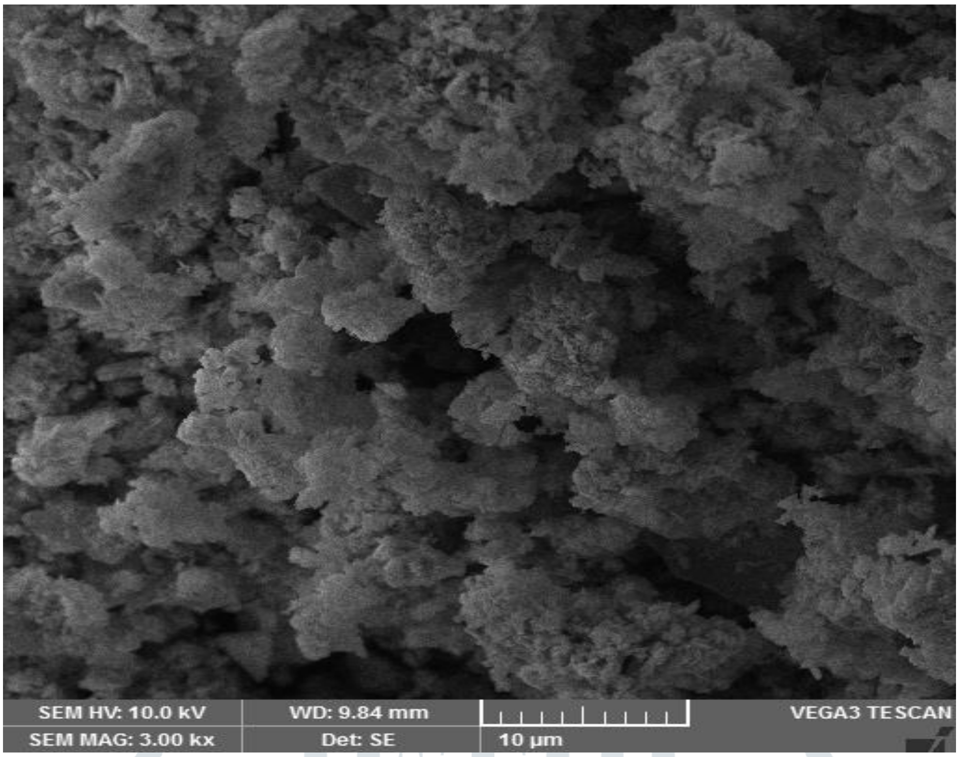


Figure 5: SEM images of CuO nanoparticles synthesized using Azadirachta indica (neem) leaf extract.



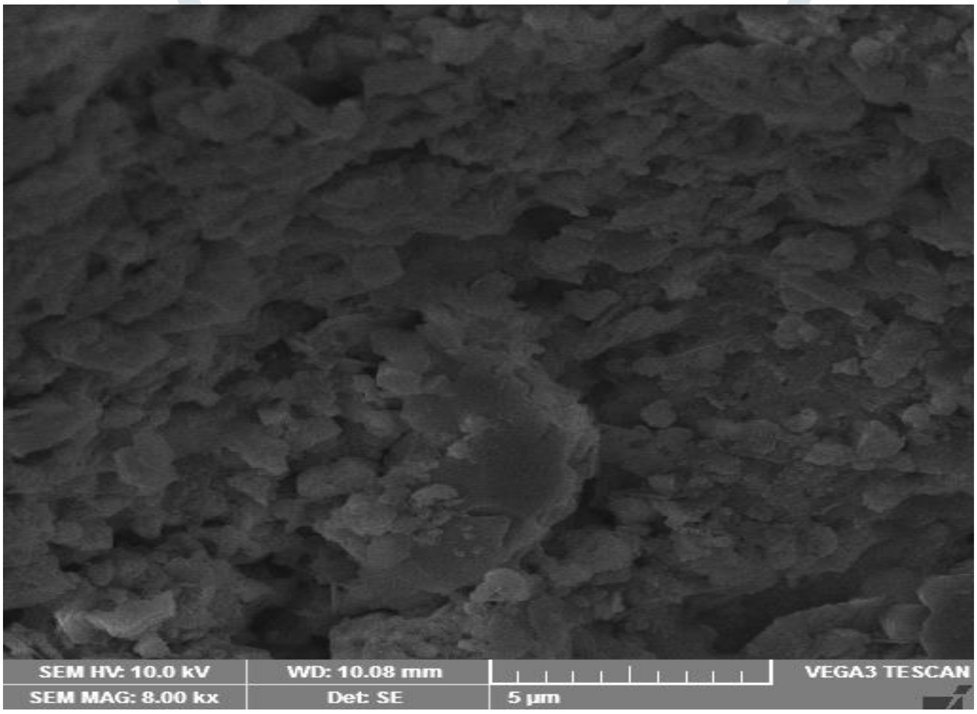
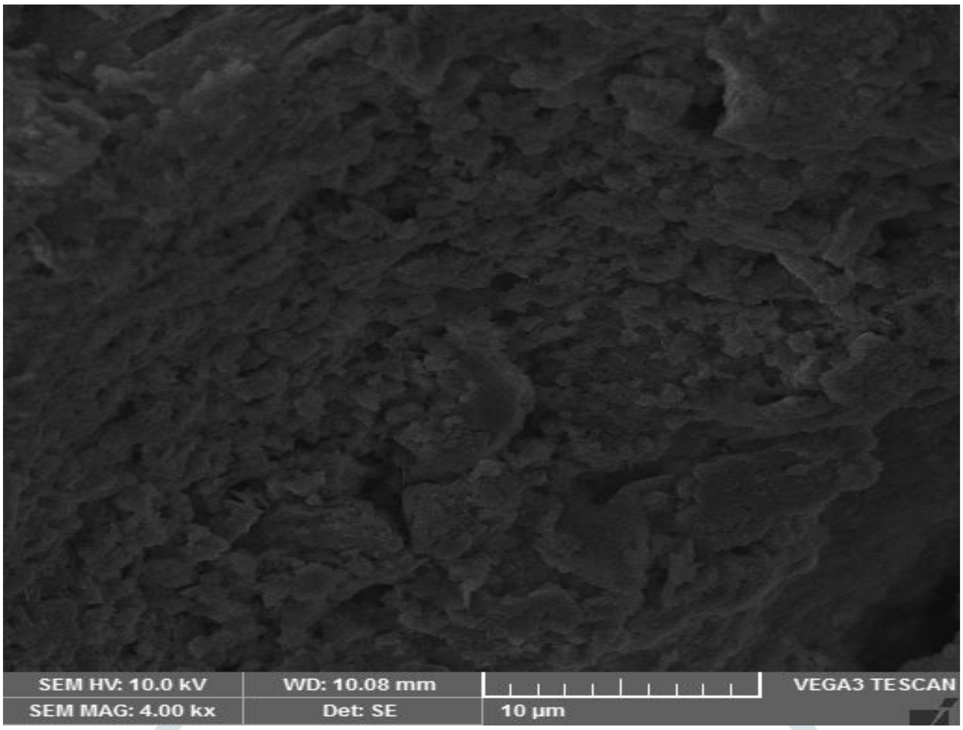


Figure 6: SEM images of ZnO nanoparticles synthesized using Hylocerus undatus (Dragon fruit) peel extract.



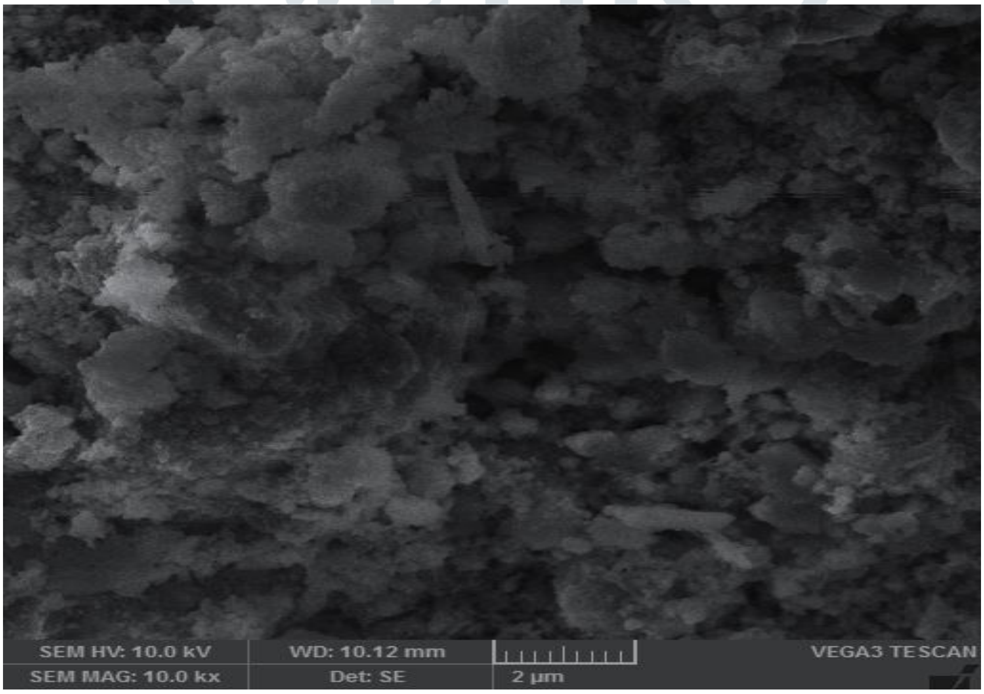


Figure 7: SEM images of ZnO nanoparticles synthesized using Azadirachta indica (neem) Leaf extract.

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of CuO nanoparticle synthesized using *Azadirachta indica* (Neem) leaf extract is shown in **Figure.8**. The peak at 3446 cm^{-1} shows aliphatic and aromatic O-H stretching vibration [11]. The peak at 1617 cm^{-1} corresponds to the stretching vibration of the primary amine and the band at 1040 cm^{-1} is assigned to C-O stretching vibration [26]. The band at 900 and 709 cm^{-1} is due to aromatic C-H bending. The peak at 458 cm^{-1} corresponds to Cu-O (metal-oxygen) vibration [26].

The FTIR spectra of ZnO nanoparticle synthesized using *Hylocerus undatus* (Dragon fruit) peel extract is shown in **Figure 8**. The peak at 1051 cm^{-1} refers to C-N stretching vibration [33]. The band at 1413 cm^{-1} corresponds to C-C stretching vibration. FTIR spectra band at 1584 cm^{-1} & 2351 cm^{-1} is due to N-H bending vibration and O-H bending vibration respectively and the broad peak at 3338 cm^{-1} corresponds to aromatic O-H stretching vibration. The bands at 610 cm^{-1} & 560 cm^{-1} are assigned to Zn-O (metal-oxygen) vibration [26].

The FTIR spectra of ZnO nanoparticle synthesized using *Azadirachta indica* (Neem) leaf extract is shown in **Figure.8**. The bands at 3344 cm^{-1} and 2908 cm^{-1} indicate the presence of O-H and C-H stretching of polyols [17]. The peak at 1600 cm^{-1} indicates the presence of C=C stretching vibration of the aromatic ring. The bands at 1041 cm^{-1} and 716 cm^{-1} represented C-N & N-H stretching vibration of amines respectively [17]. The peak at 3448 cm^{-1} is assigned to O-H stretching of the aromatic ring. The band at 902 cm^{-1} corresponds to C-H aromatic stretching vibration. FTIR bands in the range 600-450 cm^{-1} are assigned to Zn-O (metal-oxygen) vibration [34].

The FTIR spectral study showed various bands corresponding to different functional groups which indicate the presence of a plethora of phytochemicals such as alkaloids, flavonoids, polyphenols & terpenoids etc. These phytochemicals were responsible for the reduction and synthesis of metal oxide nanoparticles [26,33].

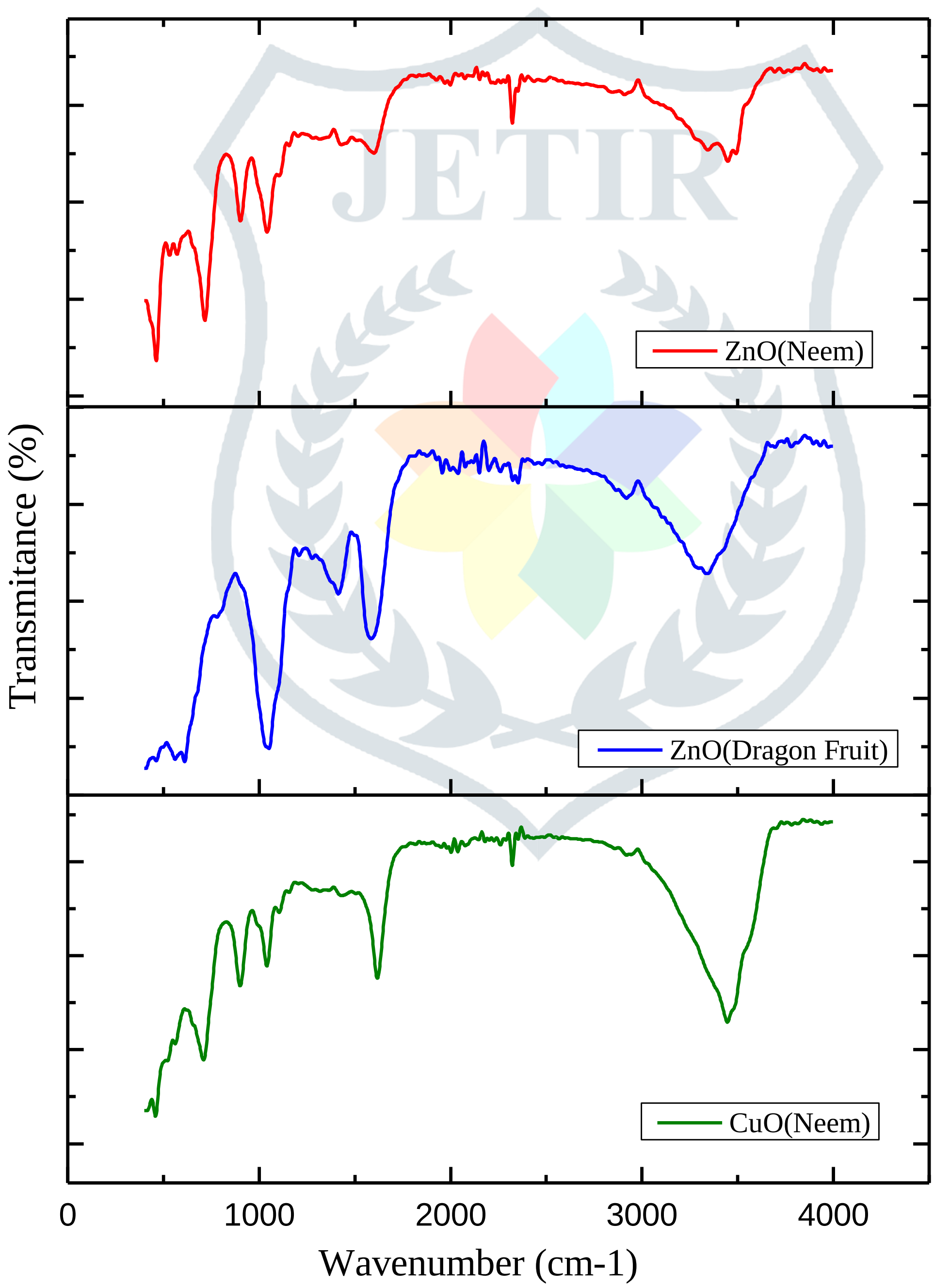


Figure 8 : FTIR spectrum of CuO (neem), ZnO (dragon fruit) and ZnO (neem) nanoparticles

3.5 Photocatalytic Activity

The photocatalytic activity of so-synthesized nanoparticles was studied by investigating the degradation of methylene blue (MB) dye by recording UV-visible absorbance spectra of the dye (λ= 664.84 nm) at a time interval of 15 minutes. The absorbance spectra of the dye degradation of different nanoparticles with ZnO (neem), ZnO (dragon fruit) & CuO (neem) was recorded in the presence of sunlight. Later, by using equation (1) the percentage degradation of dye was calculated, by measuring the change in absorbance at an expense of time.

$$\% \, Degradation = \frac{A_o - A_t}{A_o} \times 100 \qquad (1)$$

Where, A_o is the absorbance of pure dye solution and A_t is the absorbance of the solution containing dye and nanoparticle (i.e., reaction mixture) at time t.

All the synthesized nanoparticles as shown in **Table.2** were investigated for photocatalytic activity. Every nanoparticle which was synthesized behaved as a catalyst for the degradation of methylene blue in presence of sunlight. The extent of degradation of MB dye shown by each nanoparticle was different. The graph of percentage degradation vs time for ZnO nanoparticles & CuO nanoparticles is shown separately in **Figure.1** and **Figure.2** which revealed that CuO (neem), ZnO (dragon fruit) & ZnO (neem) showed better results as compared to others. So, they are selected for further studies.

3.5.1 Photocatalytic activity of CuO (neem)

CuO nanoparticle synthesized using *Azadirachta indica* leaf extract behaved as a catalyst by showing degradation of methylene blue (MB) dye in the presence of sunlight. The highest degradation shown by CuO (neem) nanoparticle was in the first 15 minutes of the time interval where the dye degraded to 90.43% as shown in **Figure.1**. Further the reaction was studied for upto 120 minutes but no specific changes were observed in percentage degradation. Thus it was observed that after a particular period the degradation of MB dye stopped in presence of CuO (Neem) nanoparticles.

3.5.2 Photocatalytic activity of ZnO (dragon fruit)

ZnO nanoparticle synthesized using *Hylocerus undatus peel* extract behaved as a catalyst by showing degradation of methylene blue (MB) dye in presence of sunlight. The dye was degraded to 81.71% in the first 15 minutes of the time interval by ZnO (dragon fruit) nanoparticles. The graph of percentage degradation vs time shown in **Figure 2.** indicates that elongation of period for reaction did not show any increase in percentage degradation. Thus no further degradation of the MB dye takes place after 15 minutes.

3.5.3 Photocatalytic activity of ZnO (neem)

ZnO nanoparticle synthesized using *Azadirachta indica* leaf extract behaved as a catalyst by showing degradation of methylene blue (MB) dye in presence of sunlight. The degradation shown by ZnO (neem) nanoparticle in the first 15 minutes of time interval is 74.5% and the highest degradation of the dye shown by ZnO (neem) nanoparticle was 79.43% after 30 minutes of time interval. The graph of percentage degradation vs time shown in **Figure.2** after first 30 minutes of the reaction no further degradation was observed when the reaction was carried for 120 minutes.

The nanocatalysts were recovered from the solution (i.e., reaction mixture) by centrifugation at 6000 rpm for 20 minutes. The recovered nanoparticle can be reused for another photocatalytic cycle.

3.5.4 Comparative Study of Photocatalytic Activity

CuO (neem), ZnO (dragon fruit) and ZnO (neem) nanocatalysts showed catalytic activity for the degradation of Methylene Blue dye in the presence of sunlight. Among the three nanoparticles, CuO (neem) showed the highest percentage degradation which was 90.43% in the initial 15 minutes, followed by ZnO (dragon fruit) which was 81.71% in the initial 15 minutes and lastly by ZnO (neem) which was 79.43 % in the initial 30 minutes of the time interval. **Figure. 9** shows the comparative study of these three catalysts.

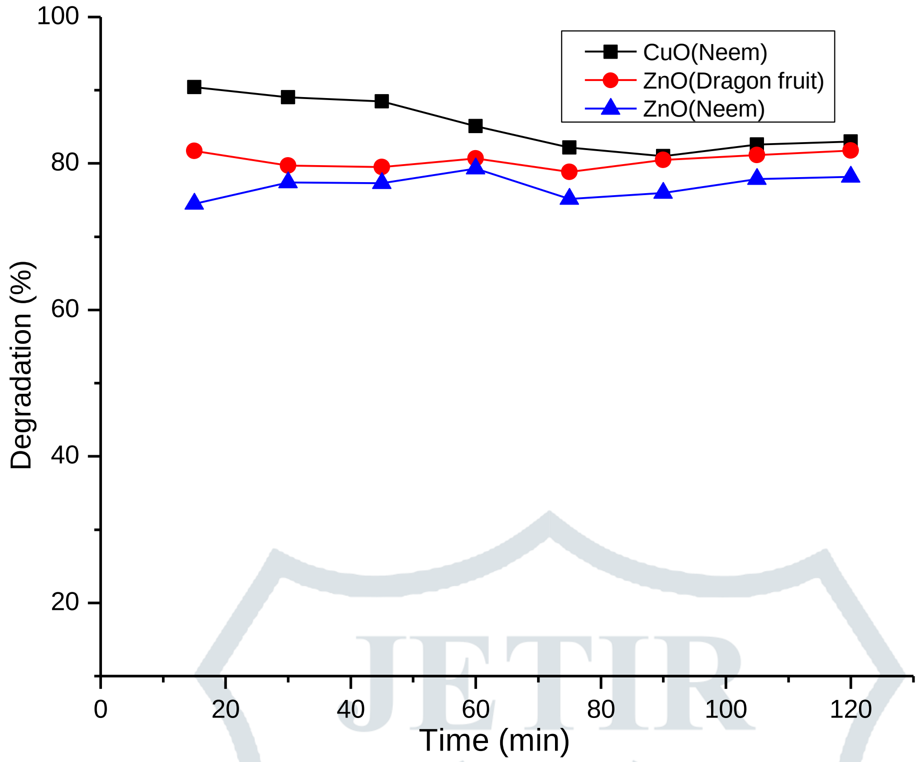


Figure 9: Comparative study of Percentage degradation of MB dye with nanoparticles showing highest activity

The study of the photocatalytic degradation of so-synthesized nanoparticles indicates that after a certain period the reaction does not proceed further which means maximum degradation of MB dye was achieved. This reveals that the catalysts possess specific activity for degradation of MB dye at a specific time. After that time the further reaction is not carried out in presence of a catalyst or elongation of the reaction time. Reusability is the wonderful phenomenon of the catalyst. CuO (Neem) nanoparticles were selected as it showed the highest activity to check the reusability of the catalyst, by running five repeated cycles for the degradation of MB. For the first cycle the percentage degradation of MB was 90.43 % after period of 15 minutes. The used catalyst was recovered by simple centrifuge method and then washed with ethanol and dried at 60 °C. The same catalyst was used for the second cycle and we found 84.34 % degradation of MB. As the same procedure was repeated for the next three cycles we found a steadily decreasing order of percentage degradation 81.45 %, 73.73 % and then 65.54 % as shown in

Figure.10. The catalysts showed good activity in each cycle, however decreasing results in percentage degradation may be due to the loss of the catalyst while recollecting it after every cycle.

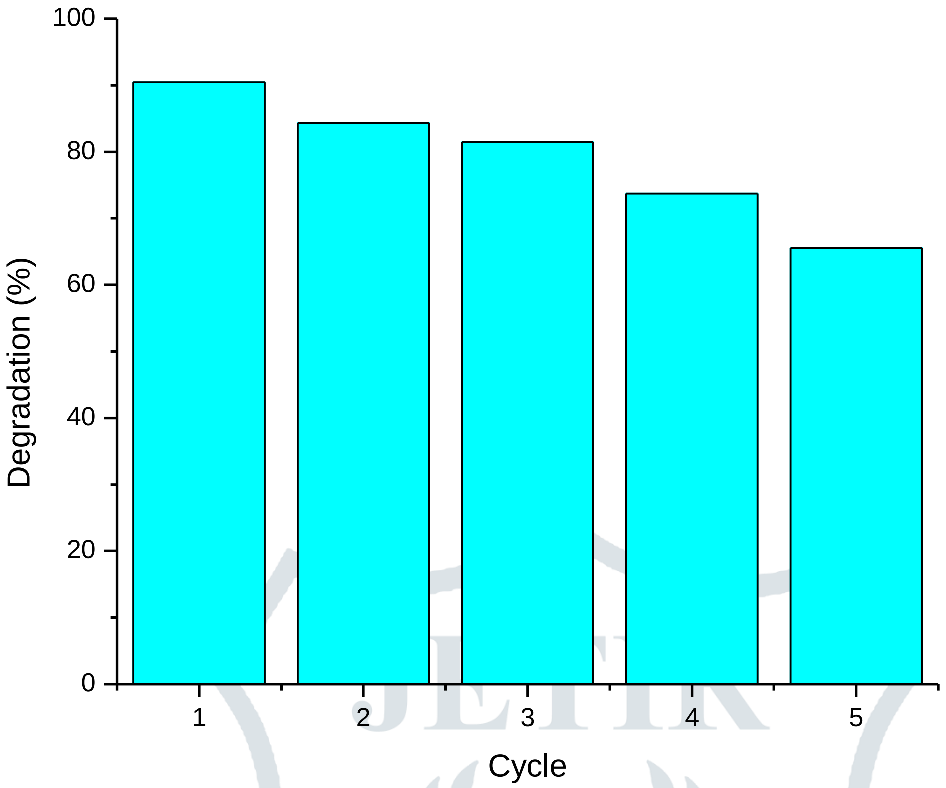


Figure 10: Percentage degradation of MB dye by using CuO (neem) nanoparticles upto five cycles

4. CONCLUSIONS

The metal oxide nanoparticles have been synthesized through economical & sustainable methods using various plant extracts. The NTA analysis of so-synthesized nanoparticles revealed the mean sizes which were 37 nm, 45 nm & 61 nm for CuO (neem), ZnO (dragon fruit) & ZnO (neem) respectively. The XRD analysis showed that the so-synthesized nanoparticles were more amorphous in nature. The SEM images disclosed that the nanoparticles were irregular & spherical in shape with agglomeration. The presence of reducing agents i.e., various functional molecules & metal-oxide nanoparticles were further confirmed by FTIR analysis. The applicability of so synthesized nanoparticles was evaluated by the photocatalytic study. Excellent photocatalytic efficiency was exhibited by the so-synthesized nanoparticles by degrading 50 ml of 5 ppm solution of MB dye in the time duration of 120 minutes in the photocatalytic experiment. The highest degradation of MB dye was shown by CuO (neem) nanoparticle which was about 90.43 % in the initial 15 minutes of time duration, followed by ZnO (dragon fruit) nanoparticle which was about 81.71 % and lastly by ZnO (neem) nanoparticle which was about 79.43 %. The highest percentage degradation was observed in the initial 15 to 30 minutes of time duration.

References

[1] Siti Nur Amalina Mohamad Sukri, Kamyar Shameli, Magdelyn Mei-Theng Wong, Sin-Yeang Teow, Jactty Chew, Nur Afini Ismail,Cytotoxicity and antibacterial activities of plant-mediated synthesized zinc oxide (ZnO) nanoparticles using Punica granatum (pomegranate) fruit peels extract,Journal of Molecular Structure,Volume 1189, 2019, https://doi.org/10.1016/j.molstruc.2019.04.026.

[2] Saurabh Sharma, Kuldeep Kumar, Naveen Thakur, Suvarcha Chauhan, Mohinder Singh Chauhan,Eco-friendly Ocimum tenuiflorum green route synthesis of CuO nanoparticles: Characterizations on photocatalytic and antibacterial activities,Journal of Environmental Chemical Engineering,Volume 9, Issue 4, 2021, https://doi.org/10.1016/j.jece.2021.105395.

[3] G. Maheshwaran, A. Nivedhitha Bharathi, M. Malai Selvi, M. Krishna Kumar, R. Mohan Kumar, S. Sudhahar,Green synthesis of Silver oxide nanoparticles using Zephyranthes Rosea flower extract and

evaluation of biological activities,Journal of Environmental Chemical Engineering,Volume 8, Issue 5,2020, https://doi.org/10.1016/j.jece.2020.104137.

[4] Chetan Pandit, Arpita Roy, Suresh Ghotekar, Ameer Khusro, Mohammad Nazmul Islam, Talha Bin Emran, Siok Ee Lam, Mayeen Uddin Khandaker, David Andrew Bradley,Biological agents for synthesis of nanoparticles and their applications,Journal of King Saud University - Science,Volume 34, Issue 3,2022, https://doi.org/10.1016/j.jksus.2022.101869.

[5] R.Vasanth Kumar, S. Vinoth, V. Baskar, M. Arun, P. Gurusaravanan,Synthesis of zinc oxide nanoparticles mediated by Dictyota dichotoma endophytic fungi and its photocatalytic degradation of fast green dye and antibacterial applications,South African Journal of Botany,2022, https://doi.org/10.1016/j.sajb.2022.03.016.

[6] Sivakami M., Renuka Devi K., Renuka R., Thilagavathi T.,Green synthesis of magnetic nanoparticles via Cinnamomum verum bark extract for biological application,Journal of Environmental Chemical Engineering,Volume 8, Issue 5,2020, https://doi.org/10.1016/j.jece.2020.104420.

[7] Mamatha Susan Punnoose, D. Bijimol, Beena Mathew,Microwave assisted green synthesis of gold nanoparticles for catalytic degradation of environmental pollutants,Environmental Nanotechnology, Monitoring & Management,Volume 16,2021, https://doi.org/10.1016/j.enmm.2021.100525.

[8] Shivali Singla, Abhishek Jana, Reena Thakur, Chinu Kumari, Sachin Goyal, Joohee Pradhan,Green synthesis of silver nanoparticles using Oxalis griffithii extract and assessing their antimicrobial activity,OpenNano,Volume 7,2022, https://doi.org/10.1016/j.onano.2022.100047.

[9] Abdelazeem S. Eltaweil, Manal Fawzy, Mohamed Hosny, Eman M. Abd El-Monaem, Tamer M. Tamer, Ahmed M. Omer,Green synthesis of platinum nanoparticles using Atriplex halimus leaves for potential antimicrobial, antioxidant, and catalytic applications,Arabian Journal of Chemistry,Volume 15, Issue 1,2022, https://doi.org/10.1016/j.arabjc.2021.103517.

[10] Rafique, M., Shaikh, A.J., Rasheed, R. *et al.* Aquatic Biodegradation of Methylene Blue by Copper Oxide Nanoparticles Synthesized from *Azadirachta indica* Leaves Extract. *J Inorg Organomet Polym* **28,** 2455–2462 (2018). https://doi.org/10.1007/s10904-018-0921-9

[11] Vasi Uddin Siddiqui, Afzal Ansari, Ruchi Chauhan, Weqar Ahmad Siddiqi,Green synthesis of copper oxide (CuO) nanoparticles by Punica granatum peel extract,Materials Today: Proceedings,Volume 36, Part 3,2021, https://doi.org/10.1016/j.matpr.2020.05.504

[12] J. Amin Ahmed Abdullah, Laouini Salah Eddine, Bouafia Abderrhmane, M. Alonso-González, A. Guerrero, A. Romero,Green synthesis and characterization of iron oxide nanoparticles by pheonix dactylifera leaf extract and evaluation of their antioxidant activity,Sustainable Chemistry and Pharmacy,Volume 17,2020, https://doi.org/10.1016/j.scp.2020.100280

[13] Asifa Nadeem, Sumbal, Joham Sarfraz Ali, Muhammad Latif, Zarrin Fatima Rizvi, Sania Naz, Abdul Mannan, Muhammad Zia,Green synthesis and characterization of Fe, Cu and Mg oxide nanoparticles using Clematis orientalis leaf extract: Salt concentration modulates physiological and biological properties,Materials Chemistry and Physics,Volume 271,2021, https://doi.org/10.1016/j.matchemphys.2021.124900

[14] Neeraj Gupta, Amit Kumar, Hrishikesh Dhasmana, Vivek Kumar, Avshish Kumar, Prashant Shukla, Abhishek Verma, Gautam V. Nutan, S.K. Dhawan, V.K. Jain,Enhanced thermophysical properties of Metal oxide nanoparticles embedded magnesium nitrate hexahydrate based nanocomposite for thermal energy storage applications,Journal of Energy Storage,Volume 32,2020, https://doi.org/10.1016/j.est.2020.101773

[15] Shahroz Saleem, Muhammad Hasnain Jameel, Naheed Akhtar, Nousheen Nazir, Asad Ali, Abid Zaman, Ateequr Rehman, Shoaib Butt, Fozia Sultana, Muhammad Mushtaq, Jing Hui Zeng, Mongi Amami, Khaled Althubeiti,Modification in structural, optical, morphological, and electrical properties of zinc oxide (ZnO) nanoparticles (NPs) by metal (Ni, Co) dopants for electronic device

applications,Arabian Journal of Chemistry,Volume 15, Issue 1,2022, https://doi.org/10.1016/j.arabjc.2021.103518

[16] Govindasamy Sharmila, Marimuthu Thirumarimurugan, Chandrasekaran Muthukumaran,Green synthesis of ZnO nanoparticles using Tecoma castanifolia leaf extract: Characterization and evaluation of its antioxidant, bactericidal and anticancer activities,Microchemical Journal,Volume 145,2019, https://doi.org/10.1016/j.microc.2018.11.022.

[17] Lakshmi Kalyani Ruddaraju, S.V.N. Pammi, P.N. Vijay Kumar Pallela, Veerabhadra Swamy Padavala, Venkata Ramana Murthy Kolapalli,Antibiotic potentiation and anti-cancer competence through bio-mediated ZnO nanoparticles,Materials Science and Engineering: C,Volume 103,2019, https://doi.org/10.1016/j.msec.2019.109756

[18] Gusliani Eka Putri, Yetria Rilda, Syukri Syukri, Arniati Labanni, Syukri Arief,Highly antimicrobial activity of cerium oxide nanoparticles synthesized using Moringa oleifera leaf extract by a rapid green precipitation method,Journal of Materials Research and Technology,Volume 15,2021, https://doi.org/10.1016/j.jmrt.2021.09.075

[19] M. Hussain, R. Ceccarelli, D.L. Marchisio, D. Fino, N. Russo, F. Geobaldo,Synthesis, characterization, and photocatalytic application of novel TiO2 nanoparticles,Chemical Engineering Journal,Volume 157, Issue 1,2010, https://doi.org/10.1016/j.cej.2009.10.043

[20] Lequan Liu, Xinnan Zhang, Lufeng Yang, Liteng Ren, Defa Wang, Jinhua Ye, Metal nanoparticles induced photocatalysis, *National Science Review*, Volume 4, Issue 5, September 2017, Pages 761–780, https://doi.org/10.1093/nsr/nwx019

[21] Vinayak H. Lokhande, Subhash Kudale, Ganesh Nikalje, Neetin Desai, Penna Suprasanna,Hairy root induction and phytoremediation of textile dye, Reactive green 19A-HE4BD, in a halophyte, Sesuvium portulacastrum (L.) L.,Biotechnology Reports,Volume 8,2015, https://doi.org/10.1016/j.btre.2015.08.002.

[22] Sagar Raut, D. P., and R. Thorat. "Green synthesis of zinc oxide (ZnO) nanoparticles using OcimumTenuiflorum leaves." *International journal of science and research* 4.5 (2015): 1225-1228.

[23] K. Elumalai, S. Velmurugan,Green synthesis, characterization and antimicrobial activities of zinc oxide nanoparticles from the leaf extract of Azadirachta indica (L.),Applied Surface Science,Volume 345,2015, https://doi.org/10.1016/j.apsusc.2015.03.176

[24] Mohammod Aminuzzaman, Pei Sian Ng, Wee-Sheng Goh, Sayaka Ogawa & Akira Watanabe (2019): Value-adding to dragon fruit (Hylocereuspolyrhizus) peel biowaste: green synthesis of ZnO nanoparticles and their characterization, Inorganic and Nano-Metal Chemistry, DOI: 10.1080/24701556.2019.1661464

[25] Alaa Y. Ghidan, Tawfiq M. Al-Antary, Akl M. Awwad,Green synthesis of copper oxide nanoparticles using Punica granatum peels extract: Effect on green peach Aphid,Environmental Nanotechnology, Monitoring & Management,Volume 6,2016, https://doi.org/10.1016/j.enmm.2016.08.002

[26] Aditi Dey, Subhankar Manna, Sourav Chattopadhyay, Dipankar Mondal, Dipankar Chattopadhyay, Anupam Raj, Subhajit Das, Braja Gopal Bag, Somenath Roy,Azadirachta indica leaves mediated green synthesized copper oxide nanoparticles induce apoptosis through activation of TNF-α and caspases signaling pathway against cancer cells,Journal of Saudi Chemical Society,Volume 23, Issue 2,2019, https://doi.org/10.1016/j.jscs.2018.06.011

[27] B.K. Thakur, A. Kumar, D. Kumar,Green synthesis of titanium dioxide nanoparticles using Azadirachta indica leaf extract and evaluation of their antibacterial activity,South African Journal of Botany,Volume 124,2019, https://doi.org/10.1016/j.sajb.2019.05.024

[28] Raunak Saha, Karthik Subramani, Subbiah Arunachala Kumar Petchi Muthu Raju, Suriyaprabha Rangaraj, Rajendran Venkatachalam,Psidium guajava leaf extract-mediated synthesis of ZnO

nanoparticles under different processing parameters for hydrophobic and antibacterial finishing over cotton fabrics,Progress in Organic Coatings,Volume 124,2018, https://doi.org/10.1016/j.porgcoat.2018.08.004

[29] Rupali S. Patil, Mangesh R. Kokate, Sanjay S. Kolekar,Bioinspired synthesis of highly stabilized silver nanoparticles using Ocimum tenuiflorum leaf extract and their antibacterial activity,Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,Volume 91,2012, https://doi.org/10.1016/j.saa.2012.02.009

[30] R. Subbiah, S. Muthukumaran, V. Raja,Biosynthesis, structural, photoluminescence and photocatalytic performance of Mn/Mg dual doped ZnO nanostructures using Ocimum tenuiflorum leaf extract,Optik,Volume 208,2020, https://doi.org/10.1016/j.ijleo.2020.164556

[31] Renu Sankar, Perumal Manikandan, Viswanathan Malarvizhi, Tajudeennasrin Fathima, Kanchi Subramanian Shivashangari, Vilwanathan Ravikumar,Green synthesis of colloidal copper oxide nanoparticles using Carica papaya and its application in photocatalytic dye degradation,Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,Volume 121,2014, https://doi.org/10.1016/j.saa.2013.12.020

[32] Kumar, P.P.N.V., Shameem, U., Kollu, P. *et al.* Green Synthesis of Copper Oxide Nanoparticles Using *Aloe vera* Leaf Extract and Its Antibacterial Activity Against Fish Bacterial Pathogens. *BioNanoSci.* **5,** 135–139 (2015). https://doi.org/10.1007/s12668-015-0171-z

[33] Kayal Vizhi Dhandapani, Devipriya Anbumani, Arumugam Dhanesh Gandhi, Purandaradas Annamalai, Bala Sundaram Muthuvenkatachalam, Purushothaman Kavitha, Babujanarthanam Ranganathan,Green route for the synthesis of zinc oxide nanoparticles from Melia azedarach leaf extract and evaluation of their antioxidant and antibacterial activities, Biocatalysis and Agricultural Biotechnology,Volume 24,2020,https://doi.org/10.1016/j.bcab.2020.101517

[34] Waseem Ahmad, Divya Kalra,Green synthesis, characterization and anti microbial activities of ZnO nanoparticles using Euphorbia hirta leaf extract,Journal of King Saud University - Science,Volume 32, Issue 4,2020, https://doi.org/10.1016/j.jksus.2020.03.014

[35] Kumar, C.R.R., Betageri, V.S., Nagaraju, G. *et al.* One-Pot Synthesis of ZnO Nanoparticles for Nitrite Sensing, Photocatalytic and Antibacterial Studies. *J Inorg Organomet Polym* **30,** 3476–3486 (2020), https://doi.org/10.1007/s10904-020-01544-3

[36] Sutradhar, P., Saha, M. & Maiti, D. Microwave synthesis of copper oxide nanoparticles using tea leaf and coffee powder extracts and its antibacterial activity. *J Nanostruct Chem* **4,** 86 (2014). https://doi.org/10.1007/s40097-014-0086-1

[37] M. Aminuzzaman, L.M. Kei, W.H. Liang, Green synthesis of copper oxide (CuO) nanoparticles using banana peel extract and their photocatalytic activities, in: AIP Conference Proceedings, AIP Publishing LLC, 2017, 020016. https://doi.org/10.1063/1.4979387

[38] Tooraj Mehdizadeh, Asghar Zamani, Seyyed Meysam Abtahi Froushani,Preparation of Cu nanoparticles fixed on cellulosic walnut shell material and investigation of its antibacterial, antioxidant and anticancer effects,Heliyon,Volume 6, Issue 3,2020, https://doi.org/10.1016/j.heliyon.2020.e03528

[39] Zangeneh MM, Zangeneh A (2020) Novel green synthesis of Hibiscus sabdarifa fower extract conjugated gold nanoparticles with excellent anti-acute myeloid leukemia efect in comparison to daunorubicin in a leukemic rodent model. Appl Organomet Chem. https://doi.org/10.1002/aoc.5271

[40] Kharey P, Dutta SB, Gorey A et al (2020) Pimenta dioica mediated biosynthesis of gold nanoparticles and evaluation of its potential for theranostic applications. ChemistrySelect 5:7901–7908. https://doi.org/10.1002/slct.202001230

[41] Doan V-D, Thieu AT, Nguyen T-D et al (2020) Biosynthesis of gold nanoparticles using Litsea cubeba fruit extract for catalytic reduction of 4-Nitrophenol. J Nanomater 2020:4548790. https://doi.org/10.1155/2020/4548790

[42] Nabi G, Ain Q-U, Tahir MB et al (2020) Green synthesis of TiO2nanoparticles using lemon peel extract: their optical and photocatalytic properties. Int J Environ Anal Chem. https://doi.org/10.1080/03067319.2020.1722816

[43] Ahmad W, Jaiswal KK, Soni S (2020) Green synthesis of titanium dioxide (TiO2) nanoparticles by using Mentha arvensis leaves extract and its antimicrobial properties. Inorg Nano-Met Chem. https://doi.org/10.1080/24701556.2020.1732419

[44] Sethy, Naresh Kumar, Arif, Zeenat, Mishra, Pradeep Kumar and Kumar, Pradeep. "Green synthesis of TiO2 nanoparticles from Syzygium cumini extract for photo-catalytic removal of lead (Pb) in explosive industrial wastewater" Green Processing and Synthesis, vol. 9, no. 1, 2020, pp. 171-181. https://doi.org/10.1515/gps-2020-0018

[45] Rafal Banasiuk, Marta Krychowiak, Daria Swigon, Wojciech Tomaszewicz, Angelika Michalak, Agnieszka Chylewska, Magdalena Ziabka, Marcin Lapinski, Barbara Koscielska, Magdalena Narajczyk, Aleksandra Krolicka,Carnivorous plants used for green synthesis of silver nanoparticles with broad-spectrum antimicrobial activity,Arabian Journal of Chemistry,Volume 13, Issue 1,2020, https://doi.org/10.1016/j.arabjc.2017.11.013

[46] Anand Kumar Keshari, Ragini Srivastava, Payal Singh, Virendra Bahadur Yadav, Gopal Nath,Antioxidant and antibacterial activity of silver nanoparticles synthesized by Cestrum nocturnum,Journal of Ayurveda and Integrative Medicine,Volume 11, Issue 1,2020, https://doi.org/10.1016/j.jaim.2017.11.003

[47] Michael Ayodele Odeniyi, Vivian Chikodiri Okumah, Bukola Christianah Adebayo-Tayo, Olubusola Ayoola Odeniyi,Green synthesis and cream formulations of silver nanoparticles of Nauclea latifolia (African peach) fruit extracts and evaluation of antimicrobial and antioxidant activities,Sustainable Chemistry and Pharmacy,Volume 15,2020, https://doi.org/10.1016/j.scp.2019.100197

[48] B. Vishnupriya, G.R. Elakkiya Nandhini, G. Anbarasi,Biosynthesis of zinc oxide nanoparticles using Hylocereus undatus fruit peel extract against clinical pathogens,Materials Today: Proceedings,Volume 48, Part 2,2022, https://doi.org/10.1016/j.matpr.2020.05.474

[49] Julian A. Gallego-Urrea, Jani Tuoriniemi, Martin Hassellöv,Applications of particle-tracking analysis to the determination of size distributions and concentrations of nanoparticles in environmental, biological and food samples,TrAC Trends in Analytical Chemistry,Volume 30, Issue 3,2011, https://doi.org/10.1016/j.trac.2011.01.005

[50] Rajesh Warluji Raut, Vijay Damodhar Mendhulkar, Sahebrao Balaso Kashid,Photosensitized synthesis of silver nanoparticles using Withania somnifera leaf powder and silver nitrate,Journal of Photochemistry and Photobiology B: Biology,Volume 132,2014, https://doi.org/10.1016/j.jphotobiol.2014.02.001