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Green Synthesis, Spectroscopic Analysis, and Stabilisation Energies of Copper and Manganese Oxide Nanoparticles from Aqueous *Mentha piperita* leaf Extract

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Abstract

Manganese and copper oxide nanoparticles synthesized from the leaf extract of M. piperitha leaf extract were characterized using UV-visible spectrophotometry, FTIR, and SEM. In the UV- visible spectra strong absorption bands were observed at 600 and 403 nm for the manganese oxide and copper oxide nano particles respectively and these were ascribed to the plasmon resonance phenomenon, Significant but weak peaks observed at 617 cm^{-1} in the FTIR spectra of CuO NPs and 538 cm^{-1} in MnO NPs but totally absent from that of the plant extract were assigned to the metal – oxygen (M – O) stretching vibration. The detection of the M – O bond at low frequencies strongly confirms the formation of the NPs. The stabilization energies of the synthesized nano particles were calculated using Planck's Quantization energy at their wavelengths of maximum excitation were found to be 299.3 and 200 kJ/mol at 400 nm and 600 nm for CuO and MnO NPS respectively

Keywords: Green synthesis, CuO, MnO Nanoparticles, *Mentha piperita*, and Stabilisation Energies

INTRODUCTION

Green synthesis of nanomaterial from organic sources has attracted a lot of interest in the last decade whereby Nanoparticles (NPs) are synthesized through oxidation/reduction of metallic ions. The literature is well stocked with green synthesis of metallic NPs from plant extracts. Murthy *et al*. (2020) synthesized Cu NPs from *Hagenia abyssinica (Brace). JF. Gme*. leaf extract and evaluated its antimicrobial properties while Amaliyah *et a*l, (2020) synthesized NPs and explored its use as a biodiesel and capping agent. Ghosh *et al*. (2020) obtained Cu NPs from *Jatropha curcas* leaves aqueous extract for CT-DNA binding and photocatalytic activity. Jayandran *et al* (2015) reported the green synthesis of Mn NPs from turmeric extract.

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On the other hand the biosynthesis of NPs using *Mentha piperita* (MP) has been reported (Abhirami *et al*., 2019). Jadoun *et al* (2021) presented principles of green chemistry and reviewed plant-mediated synthesis of NPs and their recent applications with regards to Au, Cu, Pd, Pt, ZnO and TiO_2 NPs. Alshehri *et al* (2017) used *Hibiscus sabdariffa* flower extracts to synthesise Fe NPs and proposed a mechanism for the enhanced catalytic activity of the Fe NPs but Gebre (2023) reviewed comprehensively the green synthesis of metal and metal oxide NPs highlighting reaction mechanisms and the role of biomolecules in the synthesis and It has been established that phytochemicals act as a reducing, capping and stabilisation agent in the synthesis of NPs (Ezealisiji, *et al*., 2019, Ghosh, *et al*., 2020 and Karu, *et al*. 2020). Though Ezealisiji *et al*. (2019) provided a mechanism of the role of the phytochemical acting both as a reducing and capping agent no report has appeared on the actual estimate of the stabilisation energies provided by the phytochemicals acting as a stabilization agent. The present work aims at synthesizing some metallic NPs (MnO and CuO) and providing the stabilizing energy using the crystal field approach and following a calculation as shown by Murray and Fay (2008).

MATERIALS AND METHODS

All chemicals and reagents used in this study were of analytical grade as supplied.

10% NaOH solution

NaOH pellets (10g, 0.35 mol) pellets were placed in a 250 cm^3 beaker to which 90 cm^3 of distilled water was added with stirring to dissolve it.

0.1M and 0.01 M NaOH solutions

Approximately 0.1M NaOH was prepared by dissolving NaOH pellets (1g , 0.25 mol) in 100 cm^3 beaker to which 100 cm^3 of distilled water was added to dissolve it. The solution was then quantitatively transferred into a 250 cm^3 volumetric flask and diluted to the mark with distilled water. 10 cm^3 of the prepared 0.1M NaOH solution was pipetted into a 100 cm^3 volumetric flask and then diluted to the mark with distilled water.

1% Lead acetate solution

Hydrated lead (II) acetate, $Pb(CH_3COO)_2.3H_2O$, (1g, 0.003 mol), was placed in a 250 cm^3 beaker to which 100 cm^3 of distilled water was added with stirring to dissolve it.

2M H_2SO_4

Distilled water (150 cm^3) was initially was measured into 500 cm^3 volumetric flask and 54.5 $cm^3$of conc. H_2SO_4 was added and finally diluted to the mark with distilled water.

2M HCl

Distilled water (150 cm^3) was taken in 500 cm^3 volumetric flask and 83.8 cm^3 of conc.HCl was added and diluted to the mark with distilled water

0.0147 M $CuCl_2$. $2H_20$ Solution

$CuCl_2.2H_20$ (2.49 g, 0.0147 mol) was placed in 1000 cm^3 volumetric flask to which about 100 cm^3 of distilled water was added to dissolve it. It was then made up to the mark with distilled water.

MnO_2 solution

Approximately 0.1 M was prepared by dissolving 8.6g (0.09 mol) of MnO_2 salt into 1000 cm^3 volumetric flask, to which about 100 cm^3 of distilled water was added to dissolve it. The solution was then diluted to the mark with distilled water.

Preparation of Aqueous *Mentha piperita* Leaf Extract

A bunch of matured leaves of *Mentha piperita* were collected from Tumfure, a suburb of Gombe Metropolis, Nigeria and was identified and authenticated at the University Herbarium of the Department of Botany Gombe State University. The leaves were washed four times with tap water and then rinsed with distilled water to remove any dirt adhered to it. They were then air-dried, ground using a wooden mortar and pestle and then sieved into powder. Using a literature method (Igwe and Ikebo, 2018), 20 g of the powdered leaf sample was weighed and dispersed into 400 cm^3 of distilled water in 500 cm^3 beaker and boiled at 80℃ for 60 minutes and then allowed to cool to room temperature. The mixture was filtered using Whatman filter paper. The filtrate was used immediately for the synthesis of nanoparticles.

Preparation of the Copper Nanoparticles (CuO NPS)

Following a literature method reported by DinkerPawar *et al*., (2017), $CuCl_2$ was used instead of $CuSO_4$. 0.0147 M $CuCl_2$ solution (80 cm^3) was added drop-wise into 20 cm^3 solution of the plant extract that is in a ratio of 2:8 with constant stirring at 80℃ for 60 minutes using magnetic stirrer. Within the first 30 minutes the colour changed from blue to dark brown indicating the reduction of Cu(II) and formation of the nanoparticles.. The NPs were allowed to aggregate for 24 hours after which the solution was then decanted leaving the nanoparticles in the beaker. It was air–dried, ground into powdered form and then transferred into a sample bottle and kept for further analysis.

Preparation of the Manganese nanoparticles (MnO NPs).

By using slightly modified method as reported by Igwe and Ekebo (2018), the prepared MnO_2 solution was added drop - wise into the plant extract in a ratio of 1:40 for easy dissolution (that is 10 cm^3 extract and 400 cm^3 metal precursor) in a 500 cm^3 beaker with constant stirring at 60^0C for 60 minutes using magnetic stirrer. Within the first 15 minutes the colour changed from dark brown to black which indicated the reduction of Mn(IV) to Mn(II) by the plant phytochemical and the formation of NPs. The NPs were then allowed to aggregate for 24 hrs after which the solution was then decanted leaving the NPs in the beaker. The NPs were then transferred into a 100 cm^3 beaker and dried at 100^oC for 2 hrs. The NPs were then ground into a powder and transferred to a sample bottle and kept for further analysis.

Phytochemical analysis

Mentha piperita (MP) leaf extract was subjected to preliminary phytochemical screening for detection of the following constituents as reported by Madike *et al*., (2017), Jaradat *et al*., (2015) and Deshmukh *et al*. (2018).

Saponins

About 1cm^3 of the extract was added to 2 cm^3 distilled water in a 100 cm^3 beaker and shaken vigorously and bubbles of gas were given off. The formation of bubbles was taken as a positive test for saponins constituents.

Flavonoids Alkaline Reagent Test:

The MP extract (3 cm^3) was measured into a test tube and treated with 1 cm^3 of 10% NaOH solution. The formation of an intense yellow colour observed that disappeared after the addition of few drops of dilute acid (H_2SO_4) was taken as an indication of the presence of flavonoids

Phenols and Tannins:
Lead acetate Test: The extract was taken (10 cm^3) in a test tube to which 0.5 cm^3 of 1% lead acetate solution was added from a 1 cm^3 graduated pipette. A dark brown precipitate was formed indicating the presence of tannins and phenolic compounds.

Characterisation.
The synthesized CuO and MnO NPs were characterised by UV-visible spectroscopy, FTIR, and X-Ray diffraction (XRD) and scanned electron microscopy (SEM). UV-visible spectrum was recorded on a PerkinElmer UV-visible spectrophotometer model 725 and scanned between 200–800 nm wavelength region in order to confirm the formation of nanoparticles at the wavelength of maximum absorbance due to surface plasmon resonance vibration and excitation. In order to ascertain the phytochemical agent responsible for the reduction, capping and stabilisation of the NPs, Fourier Transform Infrared (FTIR) was undertaken. FTIR analysis was done on both the plant extract and also on the NPs (CuO and MnO) with Perkin Elmer spectrophotometer model 10.03.09 using the KBr pellet technique. In order to determine the morphology and the size of the synthesized nanoparticles, SEM analysis was done at the Centre for Energy Research and Training (CERT), Zaria Nigeria.

RESULTS AND DISCUSSION

Phytochemical Analysis,
The findings of the phytochemical analysis are presented in Table 1. The results indicate the presence of flavonoids, tannins, saponins and phenolic compounds.

Table 1 Phytochemical analysis of NP

S/N	Phytochemical Test		Remark
1	Flavonoids		+
2	Tannins	+	
3	Saponins		+
4	Phenol		+

UV – Visible Spectra Analysis

MnO NPs
The UV – Visible spectra of the MnO NPs is presented in Fig. 1. Two absorbance maxima are observed at 400 and 600 nm. From the work by Jayandran and co-workers (2015) on the green synthesis and characterization of manganese nanoparticles, a strong broad peak was observed at 425 nm and this was ascribed to transition from non-bonding orbitals to anti-bonding pi orbitals (n→ π *) or a combination of transition from pi bond to ant-pi pi (π → π* and n→ π*) or both. Gabriela *et al.,* (2017) reported a similar absorption between 438 – 470 nm and these peaks in both studies were attributed to surface plasmon phenomenon. Ahmad *et al*.(2020) reported that surface plasmon resonance depends on several factors such as particle size, shape, and type of solvents. The strong absorption band at 600 nm obtained in the present research could be ascribed to the surface plasmon resonance.

CuO NPs
The UV-Visible spectrum for the CuO NPs is presented in Fig 2. A strong absorption peak is observed at around 400 nm. This is in good agreement with a study by Kiranmai *et al.* (2017) and also Murthy et al (2020) on the synthesis of green copper nanoparticles reported a λ_{max} at 403 nm as due to the surface plasmon resonance. They also argued that this depended on the particle size and the plant extract. However, Amaliyah *et al* (2020) in their work on the green

π π

synthesis and characterization of copper nanoparticles found the absorption maxima at 207 nm to be due to pi to pi star anti-bonding (→ *) transitions of polyphenolic compounds and another peak at around 234–255 nm as the surface plasmon resonance.

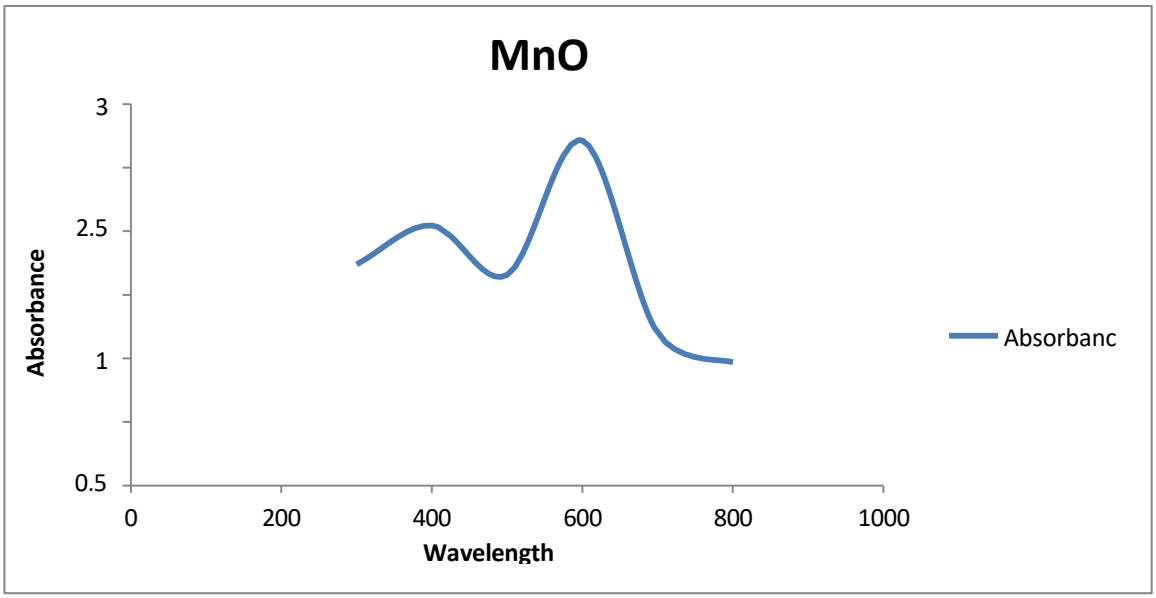

Fig 1: U.V. Absorbance spectrum of MnO NPs in ethanol. The spectrum was acquired on a Jenway 6705 UV-vis spectrophotometer in a 10 mm path-length quartz cuvette with ethanol as reference.

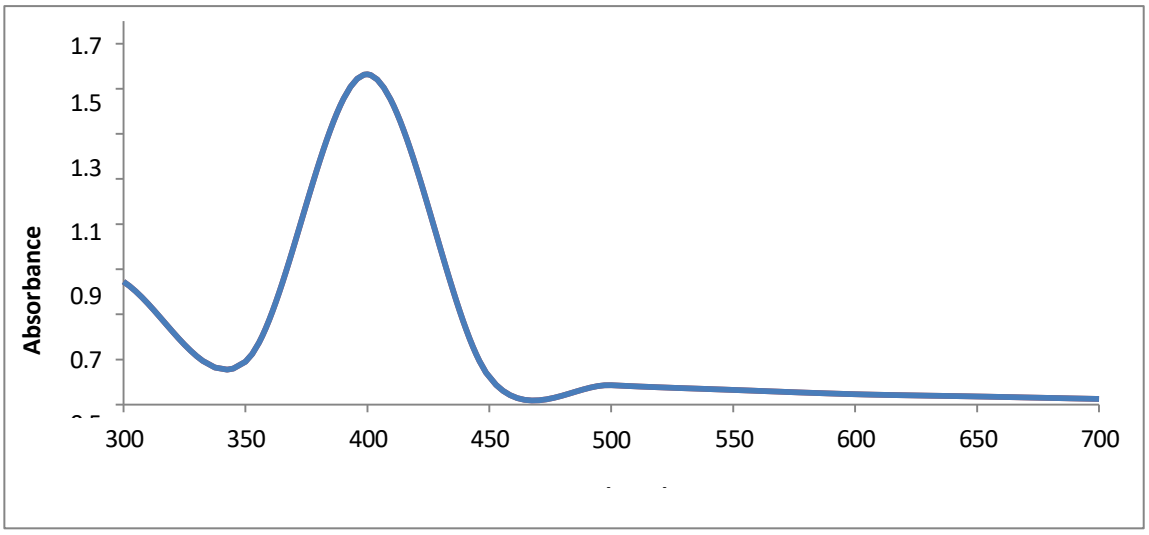

Fig 2. Absorbance spectrum of CuO NPs in ethanol. The spectrum was acquired on a Jenway 6705 UV-vis spectrophotometer in a 10 mm path-length quartz cuvette with ethanol as reference.

Calculation of the stabilisation energies of the synthesised nanoparticles

Most literature has been silent on the quantum value of stabilization energies but only state the role of phytochemicals as stabilizing the nanoparticles. Here we present an attempt to calculate the stabilizing energy using the surface plasmon resonance wavelength and relating it to Plank's Quantization Energy

$E = hv$

$= hc/\lambda$ (1)

Where

h is Plank constant,

c = velocity of light and

λ = wavelength of maximum absorbance in the UV-Vis spectra.

The value for excitation of 1 NP is given by equation 2 and for one mole of NPs, it is multiplied by Avogadro's number (Murray and Fay, 2008). The stabilization energies at their wavelengths of maximum excitation were found to be 299,3 and 200 kJ/mol at 400 nm and 600 nm for CuO and MnO NPS respectively

Infrared Analysis

The IR analysis of the synthesized of CuO and MnO nanoparticles was undertaken in order to know the functional groups involved in the reduction, stabilization and capping and the formation of the nanoparticles.

The IR spectra of the Copper nanoparticles (CuO and MnO NPs) are presented in Fig. 3 and 4, and the absorption frequencies in Table 2.

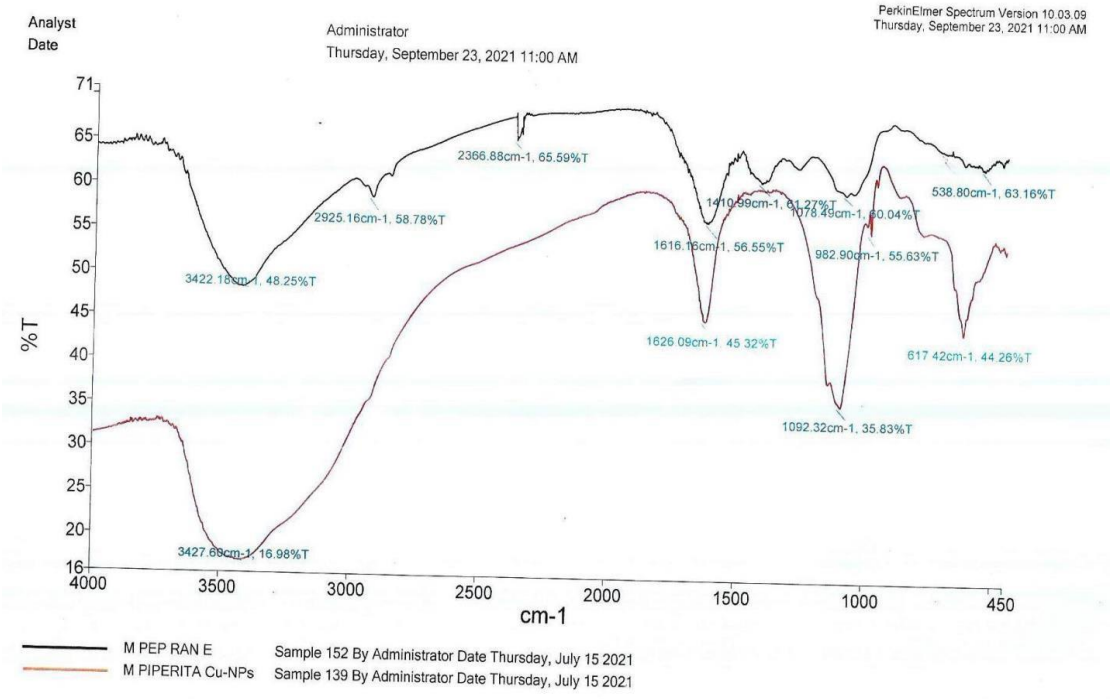

Fig. 3. FTIR spectra of CuO NPs and *M. piperita* leaf extract.

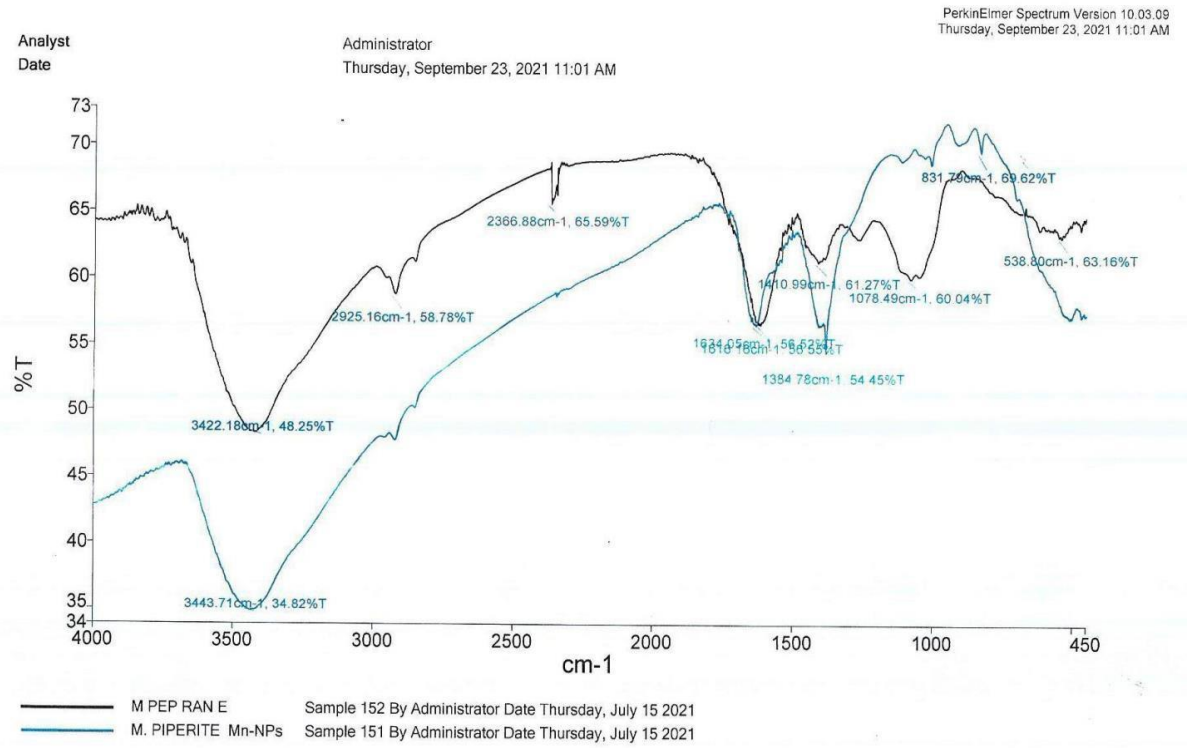

Fig. 4 Showing the FTIR spectra for Mn0 NPs and Plant Extract

Table 2. IR absorption frequencies (cm^{-1})

Mentha Piperita Extract	CuO NPs	MnO NPs	Assignment	Probable source
3422br	3427br	3443br	v(OH)	OH from water, alcohol, carboxylic acid, flavonoids, phenols, tannins
2925m	n.o	n.o	v(C-H)	Alkanes
1616 & 1634m	1626m	1634	v(C=O)	Carbonyl functional group, from flavonoid
1410w	n.o	1410	δOH (deformation mode)	OH from water, Alcohol
1078m	1092s	1078s	v(C-O)	Phenolic group, tannins,
1002w	1007s	n.o	v(C-N)	flavonoid Aliphatic amines
	617m	538m	v(CuO)	CuO nanoparticles

Note: br = broad, s = strong, m = medium, w = weak and n.o = not observed, v = stretching vibration, δ= bending or deformation mode.

The IR spectra for the NPs and the Plant extract are shown under Figures 3 & 4 while the absorption frequencies are presented in Table 2

The broad peaks that appear around 3400-3500 cm^{-1} that occurs in both the plant extract and the NPs is undoubtedly the OH stretching v(OH) vibration probably arising from water,

phenol, alcohol, carboxylic acid, or tannins. Also the weak bands observed at 2925 cm^{-1} in the plant extract but not in both the CuO and MnO NPs is due to C – H stretching vibration v(C - H) of alkanes. Bands observed between 1616 1634 cm^{-1} and 1070 – 1098 cm^{-1} respectively are assigned to the carbon – oxygen double bond, v(C = O), and carbon – oxygen single bond v(C - O) stretching vibrations arising from the carbonyl functional group of the carboxylic group, flavonoids or tannins. This assignment follows the pattern by Amaliyah, *et al*. (2020). A significant but weak peak observed at 617 cm^{-1} in the CuO NPs and 538 cm^{-1} in MnO NPs but totally absent from that of the plant extract is assigned to metal – oxygen (M – O) stretching vibration and this strongly confirms the formation of the NPs. The detection of the M – O bond at low frequencies is in line with that by Bhuiyan, *et al*., (2020), Rufus, *et al*. (2016) and Amaliyah, *et al*. (2020). Also the bands observed at 1410 cm^{-1} in both the plant extract and the MnO but not in CuO NPs are assigned to the deformation mode (δOH) of OH group probably from water, carboxylic or phenolic groups. The assignments are in good agreement with literature (Jayandran, *et al*. 2015, and Ghosh, *et al*. 2020) and all these provide strong evidence of the phenolic group, flavonoids or tannins acting as the reducing, stabilizing and capping agent for the synthesized NPs.

SEM Analysis

The SEM images for the NPs are presented under Figures 5 & 6.

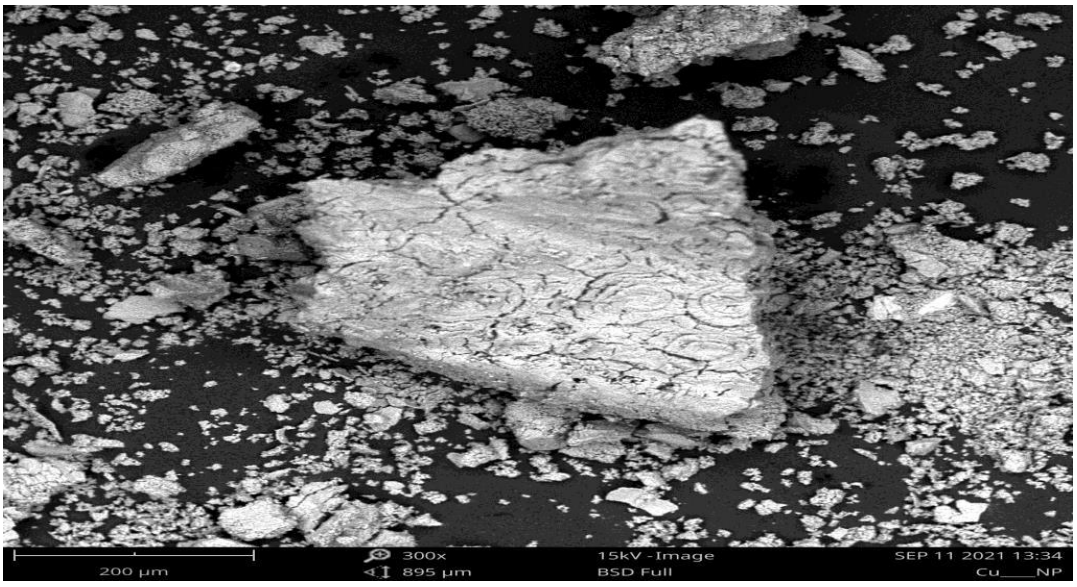

Fig: 5 showing SEM result for CuO NPs

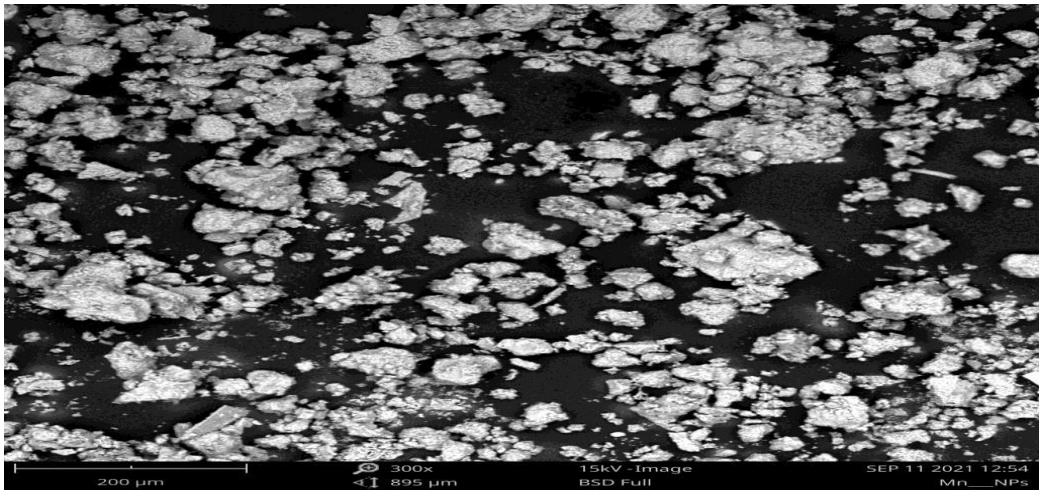

Fig 6 showing SEM result for MnO NP

CuO NPs

The SEM results, presented in Fig. 5 showed that the copper nanoparticles (CuO NPS) have mono dispersed morphology which range between 23-31 nm in diameter together with some percentage of copper and sulphate ions present. The result obtained is in agreement with the literature (Kiranmai & co-worker 2017) which showed mono dispersed morphology for the green synthesized copper nanoparticles.

MnO

The SEM images obtained for (MnO NPs) nanoparticles are shown in Fig. 6. The particles are found to be crystalline and partially spherical in nature. Similar result was reported by Jayadran *et al.,* (2015).

CONCLUSION

MnO and CuO nano particles were successfully synthesized from *M. piperitha* leaf extract and characterized by spectroscopic techniques. The stabilization energies at their wavelengths of maximum excitation were found to be 299,3 and 200 kJ/mol at 400 nm and 600 nm for CuO and MnO NPS respectively

X-ray Diffraction (XRD) analysis

The X-Ray Diffraction pattern of the synthesized Cu O and MnO NPs are shown in Figures 7 & 8.

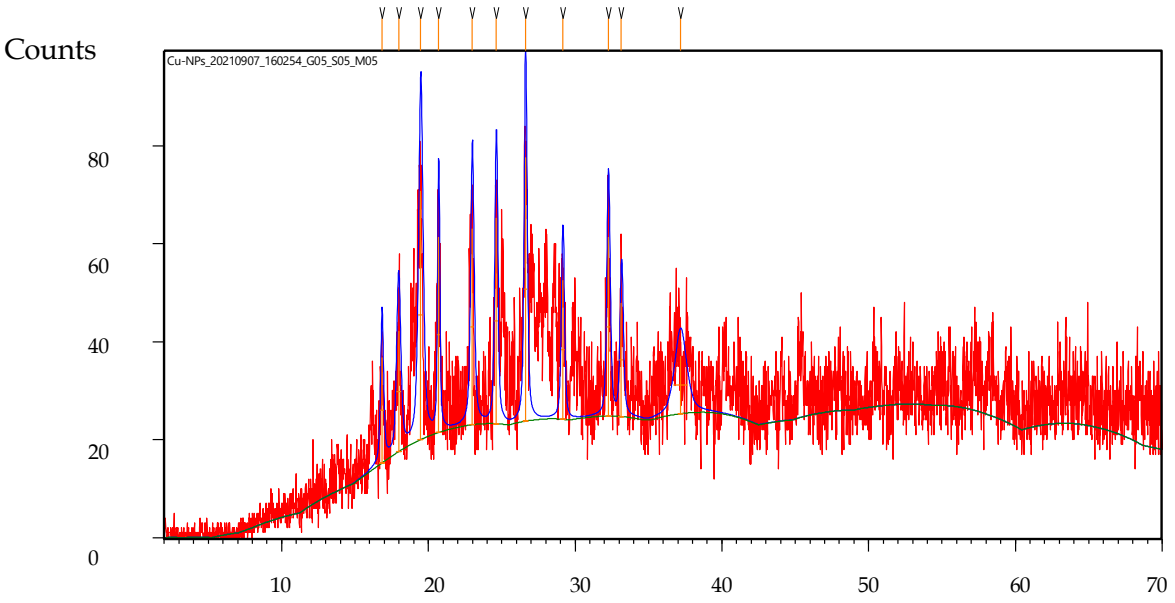

Fig: 7 showing XRD result for CuO NPS

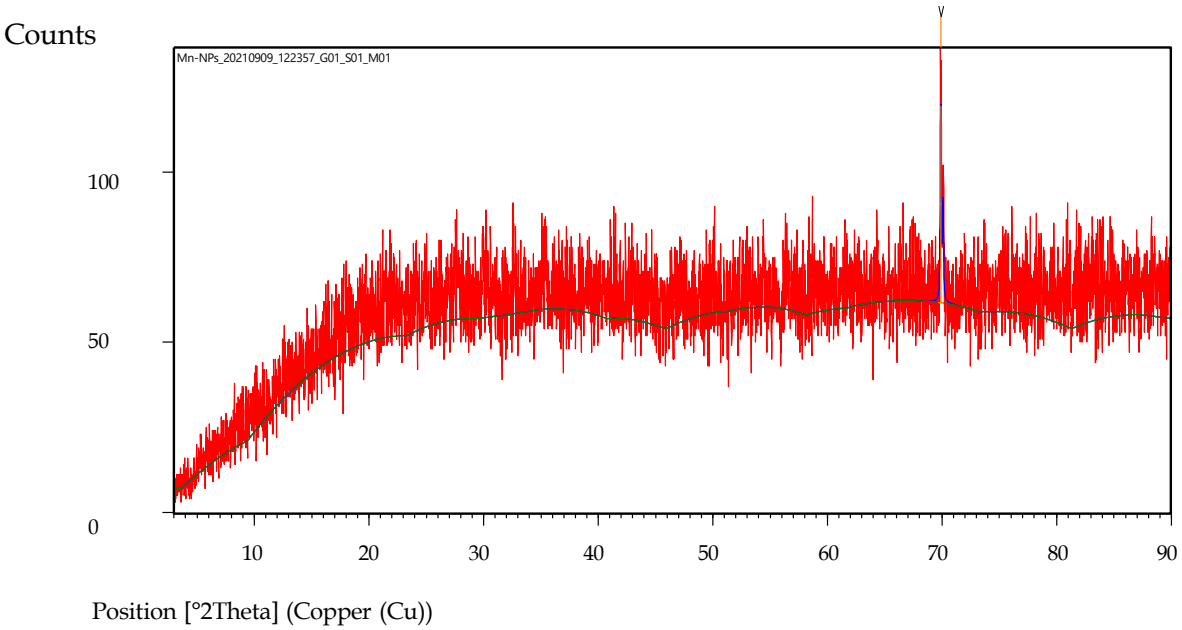

Fig: 8 showing XRD result of MnO NPs

CuO NPs

From the XRD analysis of the copper nanoparticles with the Braggs angle of 5.28-100 observed along with the weak peaks, three prominent peaks were observed at 2θ =19.47,24.60, and 26.61 with respect to the plane of (110), (111), and (220). This shows Face Centered Cubic [FCC] structure and with an average crystalline size of 23.76, 35.95 and 31.93 nm as obtained from Scherer equation.

$$D = K\lambda/\beta\cos\theta \quad (2)$$

Where D = the crystallite size of NPs

MnO NPs

The X-Ray Diffraction pattern of the synthesized Mn ONPs is shown in Fig. 8.

The synthesized manganese nanoparticles showed a single prominent peak at 2θ = 69.88˚with respect to the plane of (101), It shows Face Centered Cubic [FCC] structure and an average crystalline size of 84.34 nm.as calculated from Scherer equation. This analysis corresponds to that from literature (Benakashani *et al.,* 2017) that showed face centered cubic (FCC) structure as found for the green silver nanoparticles using *tapidium draba*weed extract.

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