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ORIGINAL RESEARCH PAPER

Green Route Synthesis of Manganese Oxide Nanoparticles by Using Methanolic Extract of Sapindus mukorossi (reetha)

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ABSTRACT

Nanoparticles of manganese oxide have been synthesized by a green chemistry approach using manganese chloride ($MnCl_2.2H_2O$), potassium permanganate ($KMnO_4$), and methanolic extract of *Sapindus mukorossi* (reetha). In this study, we report here a simple ecofriendly green route to synthesize MnO_2 nanoparticles. Manganese oxide nanoparticles were characterized by Fourier Transform Infra-Red (FTIR), UV-Vis spectral analysis, High-Resolution Transmission Electron Microscope (HRTEM), and Scanning Electron Microscope (SEM). The surface morphology showed that the MnO_2 nanoparticles were uniformly dispersed. The average particle size was found 16 nm obtained by X-ray Diffraction (XRD), analysis. To find particle size DLS analysis has been done. The thermal stability of the nanoparticles with the temperature increase has been determined by Thermo-gravimetric Analysis (TGA) measurement. The synthesized manganese oxide nanoparticles were screened for antibacterial activities on gram-positive bacteria *Staphylococcus aureus, Bacillus subtilis,* and gram-negative bacteria *Pseudomonas aeruginosa, Escherichia coli*. The results of the antibacterial study suggest that the manganese oxide nanoparticles can be useful for effective growth inhibitors in microorganisms with applications to medical devices and antimicrobial-controlled systems. The order of the reactivity towards the zone of inhibition of microorganisms observed in the order of *Escherichia coli (9mm) > Pseudomonas aeruginosa (8.3mm) > Bacillus subtilis (7.3mm) > Staphylococcus aureus (5.3mm).*

Keywords: *Green chemistry approach, MnO_2 nanoparticles, Sapindus mukorossi, Antibacterial activity*

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INTRODUCTION

Transition metal oxides have scientific and technological importance for the last decades due to their specific properties related to optical, catalytic, electric, and magnetic fields [1]. Metallic nanoparticles of various sizes and shapes find specific areas of application [2]. Manganese oxides are largely studied because of their abundant nature and are used as green catalysts in the field of catalysis. Recently various methods have been used for the synthesis of metal nanoparticles such as chemical reduction [3], sonochemical method [4], one-step solution method at room temperature [5], electrochemical techniques [6], hydrothermal method [7], polyol method [8], microemulsion method [9] and nowadays green chemistry route [10]. The use of benign material like plant leaf extract [11], bacteria [12], fungi [13], and enzymes [14], in the synthesis of nanoparticles is more cost-effective, environmentally friendly, having biomedical application due to the use of non-toxic material [15].

Secondary metabolites called Sapindus are produced by a wide variety of plant species. *Sapindus mukorossi*, a member of the family Sapindaceae, is commonly known by several names such as soapnut, soapberry, washnut,

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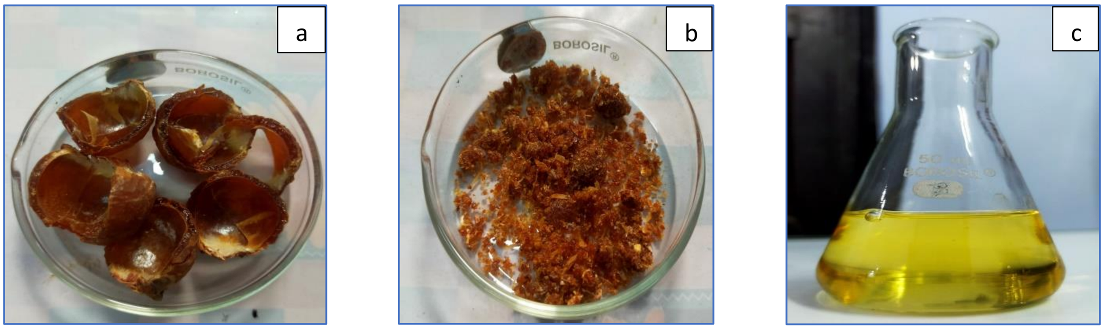

Fig. 1. Schematic representation of soapberry (a) soapberry fruits, (b) powdered extract of fruit pericarp, (c) methanolic extract of fruit pericarp of soapberry.

reetha, aritha, and dodan [16]. *Sapindus mukorossi* possesses antibacterial activity, insecticidal activity, spermicidal activity, anti-cancer activity, anti-inflammatory activity, antiplatelet aggregation activity, molluscicidal activity, and fungicidal activity [17]. In recent years manganese dioxide nanoparticles achieved a high rate of interest in the research field of material science due to their extensive applications in various fields like catalysts, lithium-ion batteries, biological fields, medicinal drug delivery, sensor and imaging techniques, etc. [18]. Due to its non-toxic behavior, it is safe to use in laboratory reactions, products made from manganese are biocompatible and non-hazardous. Manganese oxide nanoparticles have attracted extensive attention in fundamental and potential technological applications in various fields. From various studies, it is well known that MnO_2 has different crystal structures. As we concluded based on previous studies MnO_2 nanoparticles are easy to prepare by using a wet chemical method for its synthesis and have great stability and durability [19].

As for the environmental approach, plant extracts using reduction methods can be considered as more effective green approaches for synthesizing metal oxide nanoparticles. Green synthesis of metal oxides can be performed under mild conditions such as low temperature or at room temperature [20]. Recent reports on the use of *Sapindus mukorossi* extracts in the synthesis of other metal nanoparticles have motivated us to synthesize manganese dioxide nanoparticles using *Sapindus mukorossi*. MnO_2, due to its significant electrochemical performance, limited environmental toxicity, and lower production cost, has extensive applications in energy storage devices [21]. It is known that the phases, sizes, and morphologies of nanomaterials have a great influence on their properties and applications; therefore, many research efforts have focused on rational control of the phase, shape, size, and dimensionality of nanomaterials [22]. In the present study, we have focused on the synthesis of manganese oxide nanoparticles and its characterization has been done by analytical instrumentation, along with SEM, TEM, XRD, FT-IR, TGA, and UV-Vis, DLS. The biologically synthesized nanoparticles were achieved by antibacterial activity against selected organisms using *S. aureus (+ve), B. subtilis(+ve), P. aeruginosa(-ve), and E. coli(-ve)*. The metal oxide nanoparticles of manganese oxide (IV) have been tested against gram-positive and two gram-negative bacteria.

MATERIALS AND METHODS

Every chemical and solvent that was used came from the analytical reagent grade Merck (India) Ltd and all the samples were prepared by using fresh double-distilled water. In a typical synthesis, Potassium permanganate ($KMnO_4$), double distilled water, manganese (II) chloride, and methanolic extract of *Sapindus mukorossi* have been utilized to synthesize MnO_2 nanoparticles in a round bottom flask, under constant magnetic stirring. After that, the product was filtered, washed, and dried for further characterization.

Plant material collection and extraction:

The fruits of *Sapindus mukorossi* were collected from Bhatronjkhan Ranikhet district Almora Uttarakhand, directly from the natural trees. The collected fruits were washed thrice with distilled water and dried in sunlight. The peel of the fruits was separated from the seeds by cutting the whole fruit. The peel portion was used for the extraction of plant surfactant. The peel material was crushed

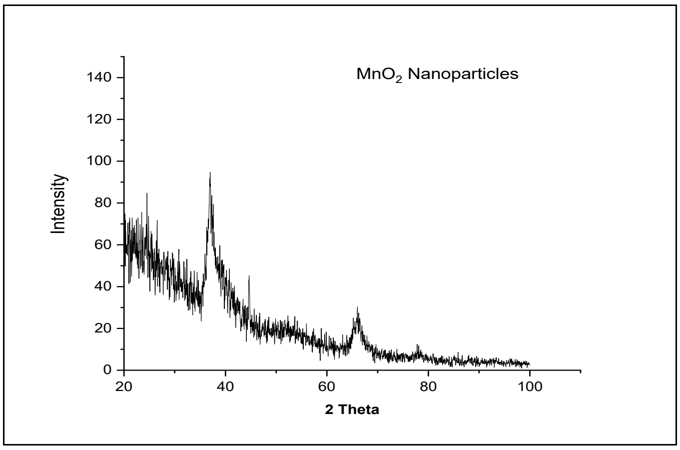

Fig. 2. XRD pattern of MnO_2 nanoparticles synthesized with Sapindus mukorossi.

in a grinder and then in a mortar to prepare the small particle size. The crushed material of peels was 12.5 gr in 250 mL of methanol and was kept for seven days at room temperature. Finally, the content was heated up to 35 ^{0}C and an extract of the surfactant was collected by centrifuge with the speed of 3700 rpm (medico centrifuge). The extract obtained has a light yellow color which was used in the present study and mentioned in Fig. 1. The extract was collected in a clean and dried container and it was stored for further uses.

Synthesis of manganese dioxide nanoparticles

Synthesis of manganese dioxide nanoparticles was performed by using the sol-gel method. The method was performed by using manganese (II) chloride of (3.76 gr), in 100 mL of double distilled water containing methanolic extract of *Sapindus mukorossi* which was dissolved in 100 mL aqueous solution of potassium permanganate (4.76 gr), under continuous magnetic stirring at room temperature for 1 hour. The resulting black precipitate was filtered and washed with ethanol and double distilled water and kept in the air for 24 hours. The powdered black precipitate of MnO_2 nanoparticle was dried at 80 ^{0}C for 15 hours.

Characterization of MnO_2 nanoparticle

In our studies, the MnO_2 nanoparticles were synthesized and characterized by XRD (PW3050/60 X-ray diffractometer), UV-Vis spectroscopy (λ= 750 (Perkin Elmer) UV-Vis NIR Spectrophotometer), FTIR (FT-IR Spectrum 2 Perkin Elmer), TGA (STA 6000 (Perkin Elmer), SEM (Carl Zeiss EVO 40 used at 20 KV (Cambridge UK), HRTEM (HRTEM, Tecnai G2 20 S-TWIN [FEI], 200 kV) have been obtained to confirm the nano size of the materials. Powder XRD analysis has been carried out to examine the crystallinity and to check the purity. The optical properties of the nanoparticle were analyzed using UV-Vis spectroscopy. The presence of chemical bonds was analyzed by FTIR spectroscopy. The thermal stability of the synthesized nanoparticle was analyzed by TGA. Particle size and Morphology of the synthesized manganese dioxide nanoparticles were analyzed using HRTEM, antibacterial activity test against *S. aureus B. subtilis, P. aeruginosa, and E. coli* by zone inhibition method. For antibacterial activity, Bacterial Culture (*S. aureus*, MTCC96 *B. subtilis* MTCC 1133, *P. aeruginosa* MTCC3541, *E. coli* MTCC- 452), Mueller-Hilton Agar (MHA-SRL Chem-24756) Plates have been utilized. To detect particle size DLS analysis has been done in (LENOVO Litesizer 500 in an advanced cumulent model).

RESULTS AND DISCUSSION

The chemical synthesis of manganese dioxide nanoparticles shows different characterization patterns like XRD, UV-Vis spectrum, TGA, FTIR, HRTEM, SEM, DLS, and antibacterial activity. All the characterized data is discussed below.

X-Ray Diffraction Analysis

The phase and purity of the products are examined by X-ray diffraction (XRD), from the XRD pattern it is clear that manganese dioxide metal nanoparticles synthesized were purely crystalline. X-ray diffraction (XRD) analysis was

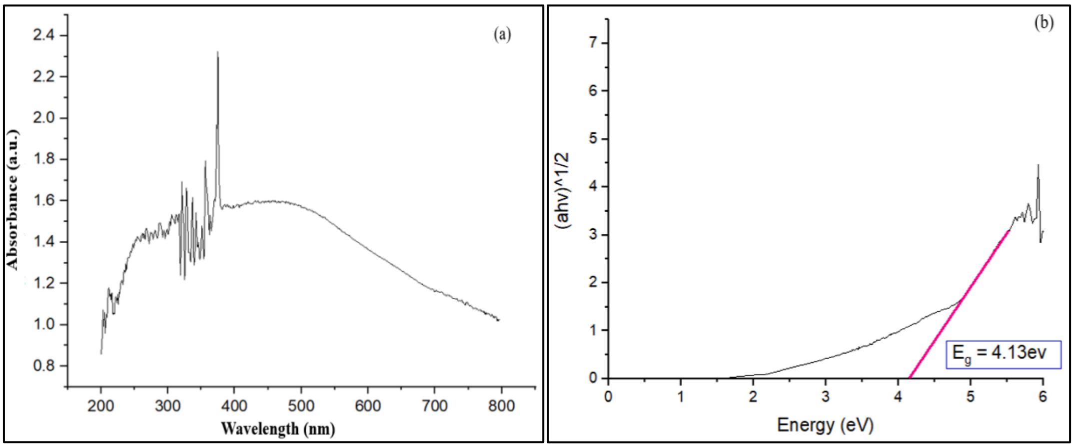

Fig. 3. (a) UV-Vis spectrum of MnO_2 nanoparticle (b) Energy band gap of MnO_2 nanoparticle synthesized with Sapindus mukorossi.

carried out in powder form and typical diffraction patterns are shown in Fig. 2. The intensity of the peaks indicates the crystallinity of the biologically synthesized nanoparticle [23]. The size of crystalline nanoparticles was calculated by using Debye-Scherrer equation, Where D is the mean size of the crystal, λ denotes the wavelength of the incident x-ray, β is full-width half maxima, and θ is Bragg's angle. The particle size of the nanoparticle was estimated to be 8 nm and 24 nm and the average particle size was approximately 16 nm [24].

UV-Vis Spectroscopy

UV-visible absorption study is one of the most convenient techniques for characterizing nanoparticles and thus provides information about the optical properties of nanoparticles [25]. The electronic absorption spectrum of synthesized MnO_2 nanoparticles showed absorption maxima (λ_{max}) at 380 nm which indicated the formation of MnO_2 nanoparticles [26]. UV-Vis provides high stability and accuracy performance. The UV-Vis absorption spectra were used to estimate optical band gaps [27], the optical band gap (Eg) value is 4.13 eV with increasing the MnO_2 percentage as can be seen in Fig. 3, (b). This can be attributed to the photoexcitation of electrons from the valence band to the conduction band [28].

FT-IR Analysis

FTIR spectroscopy is used to determine the presence of functional groups on the synthesized nanoparticles. In the FTIR spectra of manganese dioxide nanoparticles assisted with methanolic extract of *Sapindus mukorossi* sample. The wave numbers of the maximum intensity in the spectra of manganese dioxide are measured from 400-4000cm^{-1}. The first peak at 530.99cm^{-1} reveals the presence of a metal-oxygen stretching vibration band of manganese in the oxide state and confirms the formation of manganese dioxide. The presence of a broad peak at 3430cm^{-1} corresponds to the vibrations of the alcoholic O-H group, another peak is obtained at 1059cm^{-1} due to the C=O stretching of carbinol. The absorption band near 1631cm^{-1} confirms the presence of carboxylic groups. The bands at 1222 and 1383cm^{-1} may be due to the hydrocarbon chain of soapnut assigned to C-O and C=C stretching [29]. The FTIR spectra observed in this study are consistent with reported literature [30]. It is important to mention here that during the synthesis of manganese oxide, we have synthesized the nanoparticles at low temperatures due to which the absorption of precursors at the surface of the particles has a significant influence in the spectra. The changes in the intensity or small shifts of the various spectral bands may be due to the interactions between the nanoparticles and their precursors. The bands at 2919 cm^{-1} and 2850 cm^{-1} can represent the absorption of a phenolic ring of saponin present in soapnut extract or C-H stretch of alkenes as reported in the literature [31]. The FTIR spectrum of the methanolic extract of *Sapindus mukorossi* was recorded to compare the FTIR spectrum of the MnO_2 nanoparticle. The spectrum is shown in Figs. 4 (b) and (a). It is clear from Fig. 4 (a and b) that the presence of peaks in both the spectra at 3324 cm^{-1} and 3430 cm^{-1} are

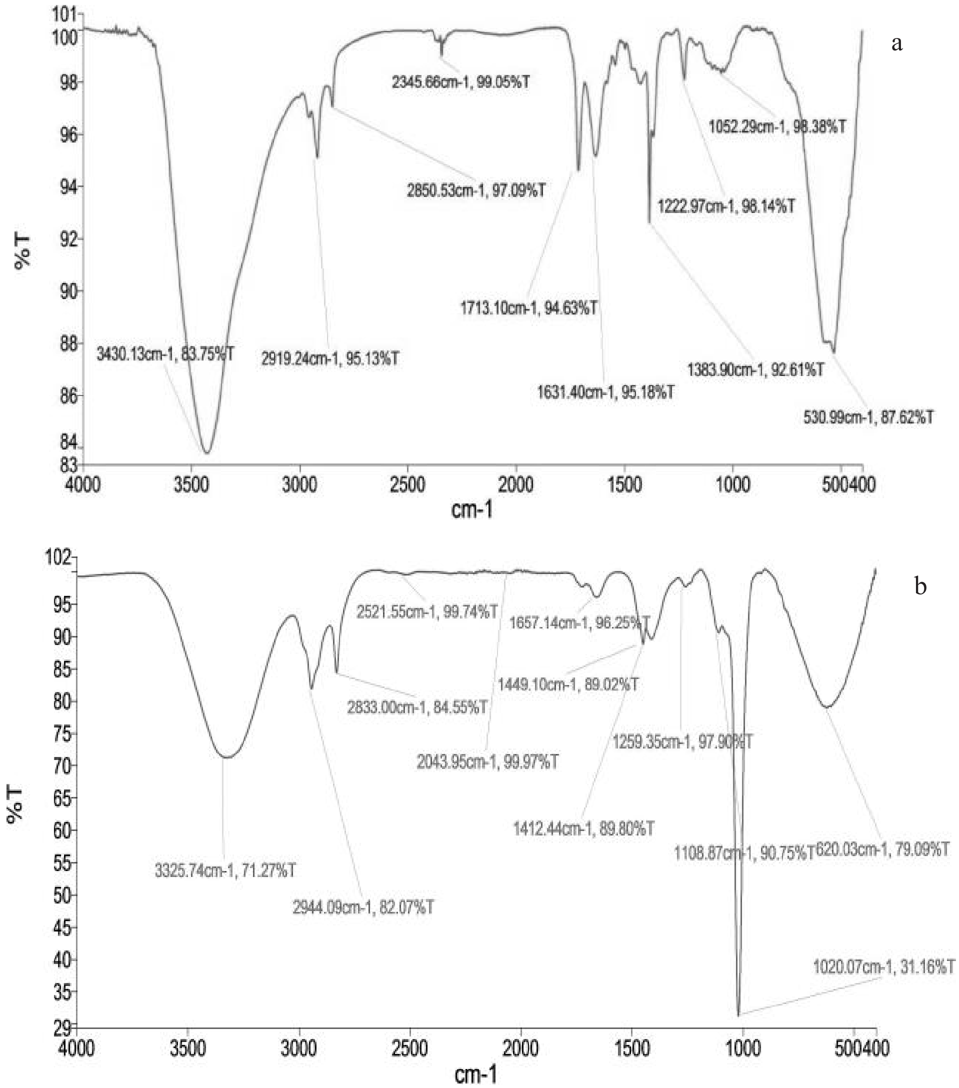

Fig. 4. (a) FT-IR spectrum Plot between wave number (cm^{-1}) and transmittance (%) of MnO_2 nanoparticle synthesized with Sapindus mukorossi (b) FT-IR spectrum of methanolic extract of soapnut.

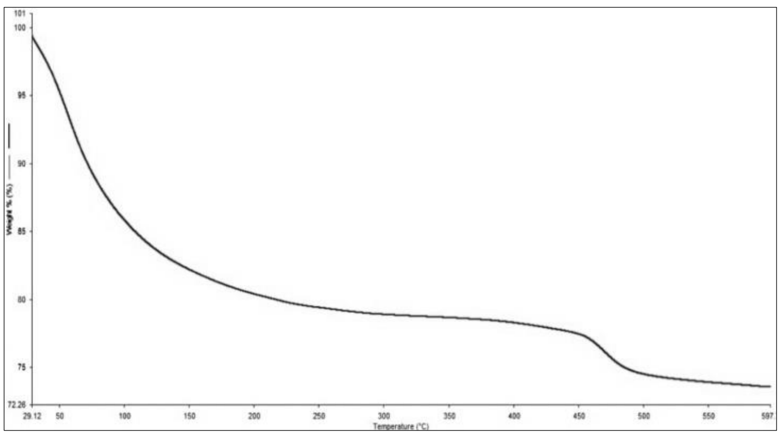

Fig. 5. TGA analysis of MnO_2 nanoparticle plot between temperature and weight % synthesized with Sapindus mukorossi.

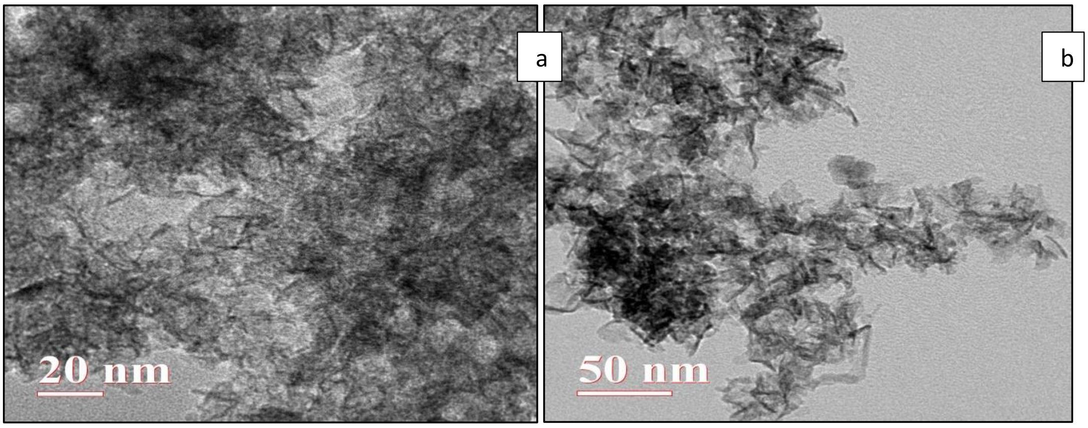

Fig. 6. TEM images of MnO_2 nanoparticle synthesized with Sapindus mukorossi (a) 20nm scale (b) 50nm scale.

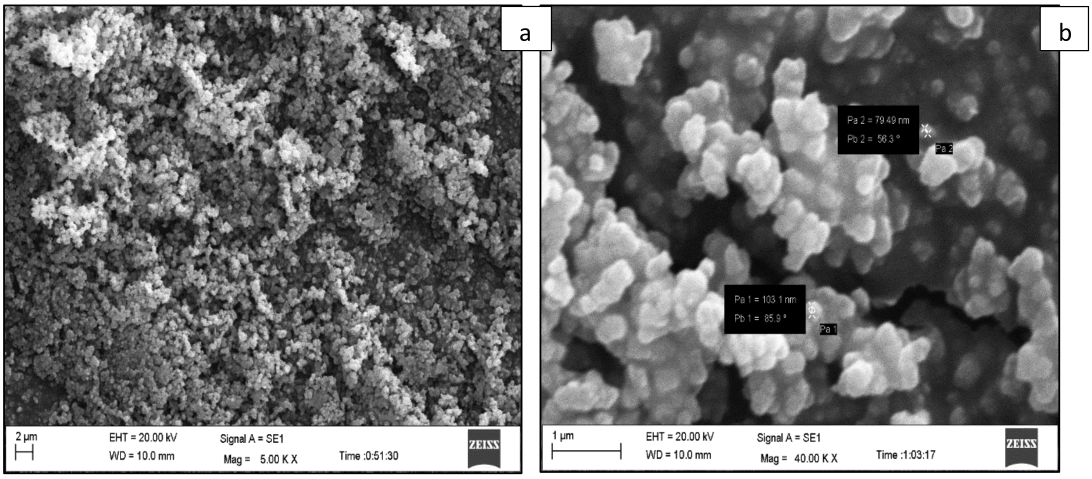

Fig. 7. SEM images of MnO_2 nanoparticle synthesized with Sapindus mukorossi (a) 2μm (b) 1μm.

in the same region which is the characteristic of O-H alcoholic stretch and H-bonding of water molecules. The peaks at 1119 cm^{-1}, 1417 $cm^{-1,}$ and 1222 cm^{-1} are the C-C stretch in aromatic rings whereas 620 cm^{-1} represents the presence of N-H amine group which confirms the metal oxide characteristics bond at 530 cm^{-1} in the case of nanoparticle spectra.

TGA Analysis

TGA analysis was used to demonstrate the thermal stability of the synthesized nanoparticles. The analysis was carried out in the range of 30-600 ^{0}C [32]. The data shows the reduction in the weight percentage of the nanoparticle with an increase in the temperature, which is attributed to the decomposition of water molecules present on the surface of the nanoparticles [33]. It is visible from Fig. 5 that the nanoparticle favors the thermal gravimetric analysis by its decreasing weight percent. In this study, stable nanoparticles of MnO_2 were produced by using the *Sapindus mukorossi* at room temperature. The thermal stability of MnO_2 nanoparticles was accomplished by thermal gravimetric and differential thermal analysis from 30 to 600 ^{0}C temperature and weight percentage from 72.16 to 100% which shows the TGA behavior of MnO_2 nanoparticles.

HRTEM Analysis

HRTEM image gives detailed information about the interior structural characteristics of as-prepared MnO_2 nanoparticles. HRTEM images give a clear shape and size of the nanoparticle. It is clear from HRTEM images that the nanoparticles are grown in needle shape. In the TEM image

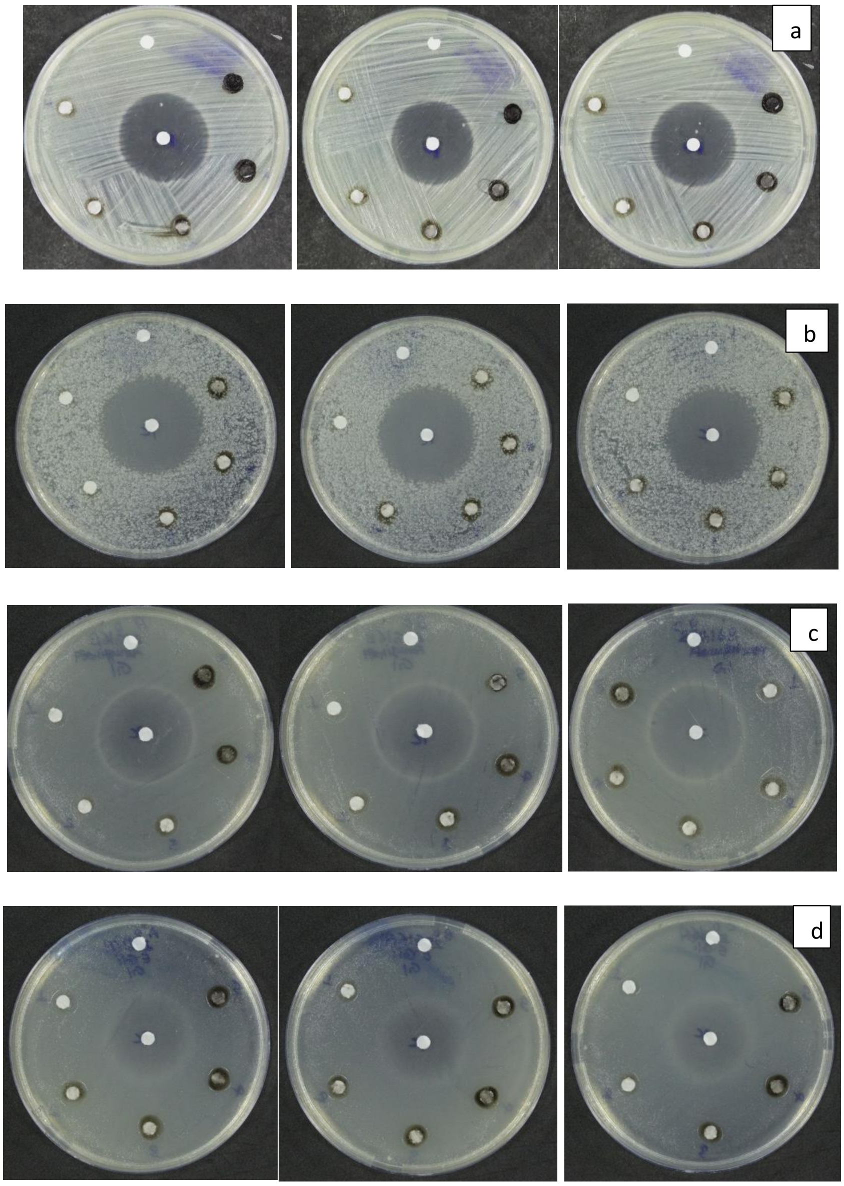

Fig. 8. The plates of (a) S. aureus, (b) B. subtilis, (c) P. aeruginosa, (d) E. coli showing bacterial culture of MnO_2 nanoparticle synthesized with Sapindus mukorossi by following Zone Inhibition Method through disc diffusion method.

shown in Fig. 6, the crystalline shape of the particle/crystals is more distinguished the scale used is also large 50nm. From this figure, the needle-to-needle distance was calculated for eight samples. The average of the eight data is 14.953, 11.983, 15.285, 10.986, 16.213, 3.963, and 5.151 the average size of the particle obtained from the data was 10.7 nm which is justified with the size calculated from the XRD spectra 8.0 nm in the experimental limit.TEM images have been observed extremely small in size [34].

SEM *Analysis*

SEM technique was used to examine the surface morphology of the manganese oxide nanoparticles. The image represented in Fig. 7, shows the irregular spherical shape due to their external small dimension and high surface energy [35]. It is well acknowledged that surface morphology has an important impact on the performance of nanostructure materials. SEM micrograph reveals the overall appearance of the combustion-derived product [36]. SEM morphology of MnO_2 nano-crystalline particles

Table 1. Antibacterial activity of MnO2 nanoparticles against S. aureus, B. subtilis, P. aeruginosa, and E. coli showing maximum zone inhibition under different concentrations.

S. No.	Microorganism	Max. ZI (mm)	conc. (µg)	PC (conc. in µg)
1.	*S. aureus*	5.3mm	50 µg	50 µg
2.	*B. subtilis*	7.3mm	50 µg	10 µg
3.	*P. aeruginosa*	8.3mm	50 µg	50 µg
4.	*E. coli*	9mm	250 µg	10 µg

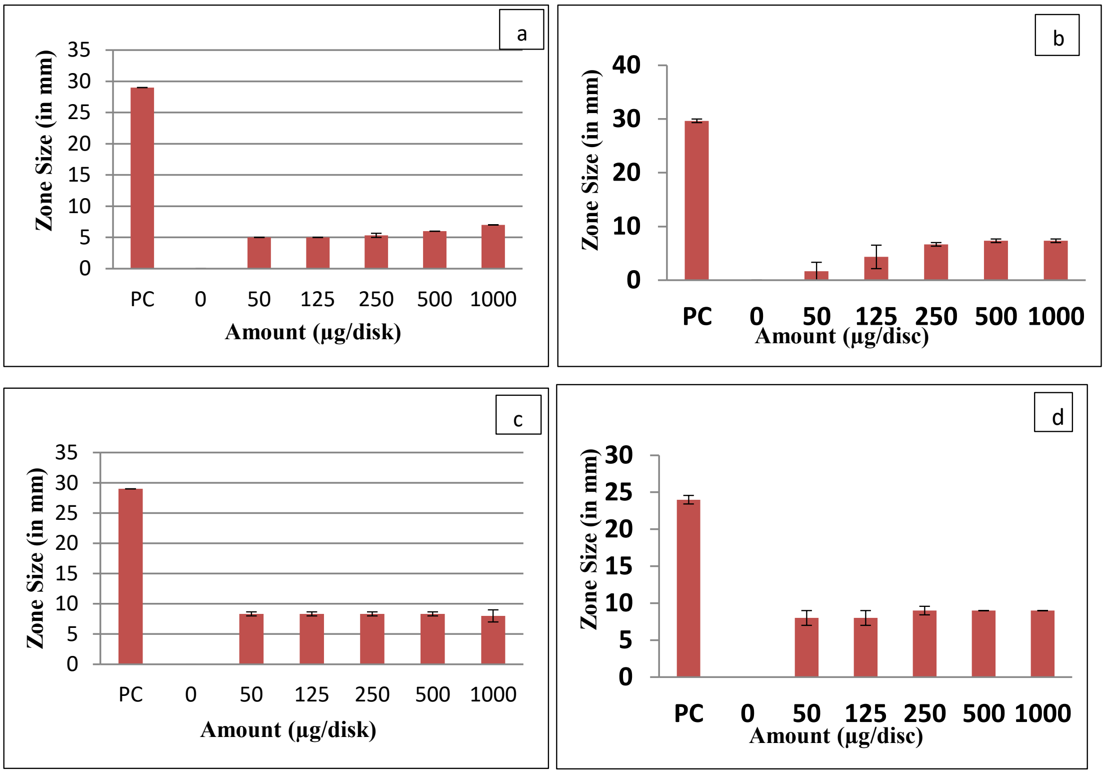

Fig. 9. Graphical representation of antibacterial activity for MnO_2 nanoparticle synthesized with Sapindus mukorossi against (a) S. aureus, (b) B. subtilis, (c) P. aeruginosa, (d)E. coli, between zone size (in mm) and amount (µg/disc).

found to have an irregular spherical shape, harshly agglomerated, and aggregated between the observed particles. The SEM pictures of prepared MnO_2 nanoparticles at different diameters, at 2 µm and 1 µm were supported with the previously published data [37]. The MnO_2 nanoparticles consist of separated nanostructures, due to the activation of the surface of nanoparticles, some areas have been ruptured and also show small cubic-shaped nanoparticles [38]

Antibacterial activity

The Antibacterial activity was checked by following the Zone Inhibition Method (Kirby-Bauer method). The MHA plates were inoculated by spreading with 100 µl of Bacterial culture, *S. aureus, B. subtilis, P. aeruginosa, and E. coli* (adjusted to 0.5 McFarland Unit - approx cell density (1.5 X 10^8 CFU/mL) and followed by placing the discs containing 10 µl of different

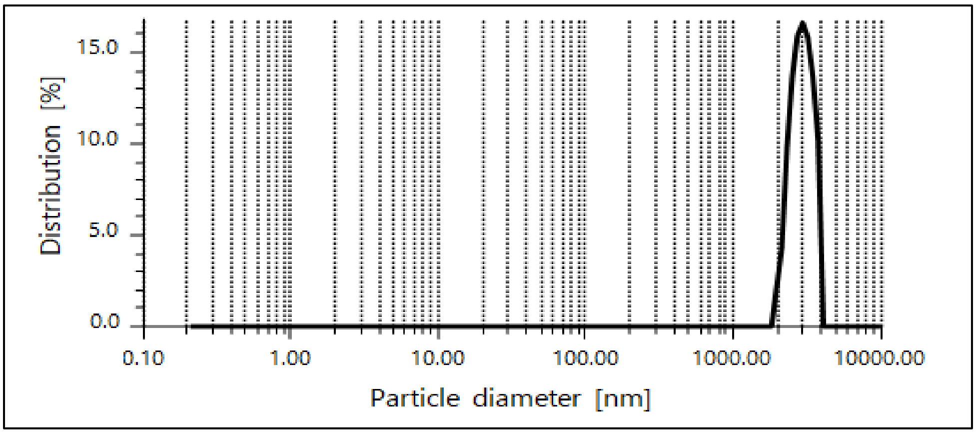

Fig. 10. DLS of MnO_2 nanoparticle synthesized with Sapindus mukorossi showing particle size distribution intensity.

Table. 2. Representation of DLS measured hydrodynamic diameter of MnO2 nanoparticles synthesized with Sapindus mukorossi.

Hydrodynamic diameter	4762 nm	Mean intensity	264.0 kcounts/s
Polydispersity index	54.9 %	Absolute intensity	337996.9 kcounts/s
Diffusion coefficient	0.1 $\mu m^2/s$	Intercept $g1^2$	0.6097
Transmittance	2.1%	baseline	1.062

concentration (0 to 100 mg/ml). 10 % of the sample was taken and serially diluted to achieve the required amount to be loaded on the disc. One disc in each plate was loaded with solvent alone which served as vehicle control (Dimethyl Sulfoxide, SRL Chem- 28580) and Ciprofloxacin disc (10μg) (SRL Chem-78079), 2mg/ml was taken as a positive control. The plates of *S. aureus, B. subtilis, P. aeruginosa, and E. coli* were incubated (Basil Scientific Corp. India) at 37 °C for 24 hours. Clear zones created around the disc were measured and recorded.

Based on the results obtained from the study, when the test organism was treated with different amounts of sample on an agar plate, it was found that MnO_2 nanoparticles achieved the maximum zone of inhibition (ZI) estimated as mentioned in Table 1. having antibacterial activity against the test organisms *S. aureus*, *B. subtilis*, *P. aeruginosa*, and *E. coli* as compared to positive control. The zone of inhibition is an area around a disc on an agar plate where no bacterial growth is observed due to the presence of an antimicrobial agent. It is used to determine whether a particular test organism is susceptible to the action of a particular antimicrobial agent or not.

We also looked at the broad-spectrum antibacterial activity of MnO_2 nanosheets and their ability to inhibit *S. aureus* , *B. subtilis, P. aeruginosa, and E. coli* by the surface plate assay a significant dose-dependent inhibitory effect was observed after exposure of different concentrations of MnO_2 nanoparticles. Different concentration of MnO_2 nano-sheet shows higher inhibitory effects on *S. aureus, B. subtilis, P. aeruginosa, and E. coli,* and the inhibition rate was higher to control the antimicrobial growth. These results indicated that MnO_2 nano-sheets have antibacterial activity against Gram-positive bacteria and Gram-negative bacteria [39].

DLS Analysis

To confirm the size of the MnO_2 nanoparticle synthesized using methanolic extract of the soapnut dynamic light scattering (DLS) analysis was conducted to calculate the particle size. Table 2 shows the the hydrodynamic particle sizes of MnO_2 nanoparticles that were analyzed to detect the Brownian motion of particles, which is correlated to the particle size [40]. Based on the DLS analysis the results revealed that the size of the Mno_2 nanoparticle which is in agreement with the size obtained from XRD 8.0 nm there is only a variation of percent in results obtained from DLS and XRD (Fig. 10). The size of the nanoparticle obtained in our study is seven times smaller than the size obtained in using Tridax procumbers [41].

CONCLUSION

Green synthesis of nanoparticles has a significant role in the field of nanotechnologies due to its non-toxic and environmentally friendly nature, the green route synthesis of nanoparticles is a significant step in the field of nano-chemistry. There is a massive difference between classical synthesis and green synthesis due to its cost-effectiveness and feasibility. MnO_2 nanoparticles have been successfully synthesized by using an eco-friendly method followed by a green synthesis route at room temperature in the aqueous medium of methanolic extract obtained from *Sapindus mukorossi* (soapnut). The synthesized manganese oxide nanoparticles have an extremely small size 8 nm which has potent antibacterial activity against *S. aureus, B. subtilis, P. aeruginosa, and E. coli*. The study is a primary step towards the application of antibacterial agents against other microorganisms.

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CONFLICT OF INTEREST

The authors hereby declare that there is no conflict of interest.

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