

Plant-Mediated Green Synthesis of MnO₂ Nanoparticles Using *Annona muricata* Flower Extract for Antibacterial and Antifungal Applications

M. Baskaran¹, P. Rajesh², S. Syed Illyas³, J. Kalimuthuraj⁴

^{1,2,3,4}PG & Research Department of Chemistry, Government Arts College (Autonomous), Coimbatore, India.

Abstract:

The current work deals with a green and sustainable approach for the biosynthesis of manganese dioxide (MnO₂) nanoparticles by using *Annona muricata* flower extract as a reducing, capping and stabilizing agent. The phytoconstituents present in the flower extract reduce the Mn precursor solution to form MnO₂ nanoparticles. MnO₂ nanoparticles were synthesized by treating an aqueous solution of manganese precursor with various concentrations of *A. muricata* flower extract under optimized conditions, which resulted in a prominent colour change. The formed MnO₂ nanoparticles were isolated and characterized by XRD, FT-IR, UV-Visible, FE-SEM and EDX analysis. UV-visible spectrophotometry confirmed the formation of MnO₂ nanoparticles based on their characteristic absorption bands. The crystal structure and phase purity were analysed by X-ray diffraction. The surface morphology and nano structural features were examined by field emission-scanning electron microscopy. The characteristic elemental composition was analysed by energy-dispersive X-ray spectroscopy. Fourier-transform infrared (FT-IR) spectroscopy established the participation of phytochemical functional groups in reducing, stabilizing, and forming Mn-O bonds. The green-synthesized MnO₂ nanoparticles demonstrated considerable antibacterial activity against the tested pathogenic bacteria and good antifungal activity against the tested pathogenic fungi. The comparison between the biologically synthesized and chemically synthesized MnO₂ nanoparticles revealed the benefits of the green approach. In general, the present study offers a new protocol for MnO₂ nanoparticle synthesis using *Annona muricata* flower extract that is easy to perform, economical, environmentally friendly, and promising in biomedical and antimicrobial applications.

Keyword: *Annona muricata* flower extract, MnO₂ nanoparticles, Antibacterial activity, X-ray diffraction, FE-SEM, EDX.

1. Introduction

The properties of nanomaterials and their unique characteristics triggered a disruptive innovation in science and technology. Nanotechnology has led to the development of many promising routes, including biomedical and pharmaceutical products, new approaches in food packaging and engineering, renewable energy, water treatment and recycling technologies in various industries [1-3]. The food production sector has likewise experienced impacts, as nanoparticles substantially affect seed germination, plant growth and

overall crop yield [4]. In medicine, the integration of nanotechnology has revolutionized the diagnosis and treatment of numerous diseases, particularly cancers and tumours. Thanks to their distinctive properties, nanoparticles have transformed the development and performance of therapeutic agents, enhanced the precision and effectiveness of drug delivery systems, and reduced the adverse side effects commonly associated with anticancer treatments [5-7]. Moreover, nano-medicine enables the combined delivery of multiple drugs at once, allows ongoing tracking of targeted drug pathways using advanced multidimensional imaging techniques, and improves the transport of drugs that are poorly soluble in water. Numerous biological resources have been explored for the green synthesis of ZnO nanoparticles, including *Mangifera indica* leaves,[8] *Capsicum annuum* fruits [15], *Tabernaemontana divaricata* leaves [9], *Nyctanthes arbor-tristis* flowers [10], as well as marine-derived seaweeds and microorganisms [11,12]. Among these biological resources, seaweeds represent a rich reservoir of structurally diverse bioactive compounds that exhibit a wide range of biological activities [13] making them promising candidates for the efficient synthesis of nanoparticles for biomedical applications [14,15]. Notably, the bioactive constituents present in the brown seaweed *Sargassum myriocystum* have been reported to facilitate the successful formation of ZnO NPs, whereas extracts derived from the green and red seaweeds *Caulerpa peltata* and *Hypnea valencia*, respectively, were unsuccessful in producing ZnO NPs under the reported conditions [16].

Nanomaterials known to display some degree of antibacterial activity can currently be divided into two main categories. The first includes two-dimensional (2D) materials such as graphene oxide (GO), reduced graphene oxide (rGO), molybdenum disulfide (MoS_2), and tungsten disulfide (WS_2) [17,18]. The second consists of metal and metal oxide nanoparticles, including silver nanoparticles (Ag NPs), zinc oxide (ZnO), gold nanorods (Au NPs), and titanium dioxide (TiO_2) [19,20]. Among these, 2D materials with nanoscale thickness show particularly strong potential as antibacterial agents. Manganese dioxides are quite popular because of their excellent physicochemical properties, wide structural variety, low cost, and environmental friendliness [21]. They find numerous potential applications in ion exchange, molecular adsorption, catalysis, and electrochemical energy storage and conversion [22,23]. Manganese dioxide (MnO_2) is a widely studied transition-metal oxide, valued for its unique physicochemical characteristics and diverse potential uses. Nanoparticles of MnO_2 display a range of beneficial properties, such as antimicrobial, antifouling, antioxidant, photocatalytic, catalytic, electrochemical, and biosensing capabilities [24-26]. Their strong redox activity, large surface area, adjustable shape, and high chemical stability make them suitable for applications in environmental remediation, energy storage, and biomedicine. Among the various methods to produce MnO_2 nanoparticles, biological or green synthesis has become increasingly prominent due to its simplicity, low cost, minimal toxicity, eco-friendliness, and sustainable nature [27,28]. This method utilizes natural biomolecules such as polyphenols, flavonoids, proteins, amino acids, alkaloids, terpenoids, and carbohydrates found in biological extracts to facilitate the reduction, nucleation, growth, and stabilization of the nanoparticles. These bioactive compounds also act as capping and stabilizing agents, helping to regulate particle size and structure while improving colloidal stability and overall performance. As a result, biologically derived MnO_2 nanoparticles offer a sustainable alternative to traditionally produced nanomaterials and show significant promise for antimicrobial and other advanced technological applications [29,30]. A variety of biological materials have been employed in the synthesis of zinc oxide nanoparticles (ZnO NPs), including leaves of *Mangifera indica* [31], fruit of *Capsicum annuum* [32], leaves of *Tabernaemontana divaricata* [33], flowers of *Nyctanthes arbor-tristis* [34], as well as marine-based seaweeds and microorganisms [35,36].

The present study aimed to investigate the antibacterial and antifungal potential of biosynthesized (MnO_2) nanoparticles by using *Annona muricata* flower extract. The synthesized MnO_2 nanoparticles were comprehensively characterized to elucidate their morphological, crystalline, elemental, and surface functional-group characteristics. Their antibacterial activity was evaluated against four bacterial strains, including the Gram-positive bacteria *Staphylococcus aureus* (MTCC 87) and *Staphylococcus epidermidis* (MTCC 435), and the Gram-negative bacteria *Pseudomonas aeruginosa* (MTCC 1688) and *Klebsiella pneumoniae* (MTCC 530). Furthermore, their antifungal activity was assessed against four fungal strains, namely *Candida albicans* (MTCC 183), *Candida vulgaris* (MTCC 429), *Aspergillus niger* (MTCC 282), and *Aspergillus flavus* (MTCC 277). All microbial strains were obtained from the Microbial Type Culture and Collection (MTCC). The obtained results demonstrate the promising antibacterial and antifungal properties of the seaweed-mediated ZnO nanoparticles, highlighting their potential for applications in antimicrobial materials and biomedical fields. To the best of our knowledge, the present study provides a systematic investigation of MnO_2 nanoparticles synthesized using *Annona muricata* flower extract with particular emphasis on their antibacterial and antifungal activities.

2. Experimental section

2.1. Materials

Fresh *Annona muricata* flowers were collected from the campus of Arts College, Coimbatore, Tamil Nadu, India. The plant material was authenticated by a qualified taxonomist in the Department of Botany, Arts College, Coimbatore. The collected flowers were thoroughly washed with distilled water to eliminate adhering dust and other surface contaminants and were subsequently used for the synthesis of MnO_2 nanoparticles. Manganese (II) sulphate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 98% purity) was procured from Merck and used as the manganese precursor without further purification.

2.2. Preparation of *Annona muricata* Flower Extract

Fresh flowers of *Annona muricata* were collected from a local source and authenticated by a qualified botanist. The collected flowers were thoroughly washed with tap water followed by distilled water to remove adhering dust and other surface impurities. The flowers were then shade-dried at room temperature for 7-10 days until a constant weight was achieved. The dried flowers were subsequently pulverized into a fine powder using a mechanical grinder. For the preparation of the flower extract, 10 g of the powdered flower material was transferred into a conical flask containing 100 mL of distilled water. The mixture was maintained at 60-70°C for 30-60 min under continuous stirring to facilitate the extraction of bioactive phytochemicals. After extraction, the mixture was allowed to cool to room temperature and filtered through Whatman No.1 filter paper to remove the residual plant material. The resulting filtrate was concentrated by solvent evaporation using a rotary evaporator to obtain a crude *A. muricata* flower extract. The concentrated extract was stored at 4°C until further use for the green synthesis of MnO_2 nanoparticles.

2.3. Synthesis of MnO_2 Nanoparticles

The MnO_2 nanoparticles were synthesized by adopting green co-precipitation techniques, with aqueous *Annona muricata* flower extract as a reducing agent, capping agent, and stabilizing agent in this process. The phytochemicals that were present in the flower extract had active functional groups that helped to reduce Mn species and stabilize the growth of MnO_2 nanoparticles. For the production of MnO_2 nanoparticles by a green approach, 30, 60, 90, and 120 mL of aqueous *A. muricata* flower extract were separately introduced into beakers. To each beaker containing the plant extract, 100 mL of an aqueous solution of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.1 M) was added under magnetic stirring. The obtained solution was stirred for

1 h at room temperature to allow for effective interaction of the manganese precursor with phytochemicals in the plant extract. The pH of the mixture was adjusted by dropwise addition of an aqueous solution of alkali, with continuous stirring, to obtain the precipitate. The obtained precipitate was separated from the top layer of the solution by centrifugation at 10,000 rpm for 15 min. The precipitate was washed several times with ethanol to remove excess reagents and organic impurities. The obtained powder was dried at 80 °C in a hot-air oven to yield green MnO_2 nanoparticles. The MnO_2 powder was used for further analysis.

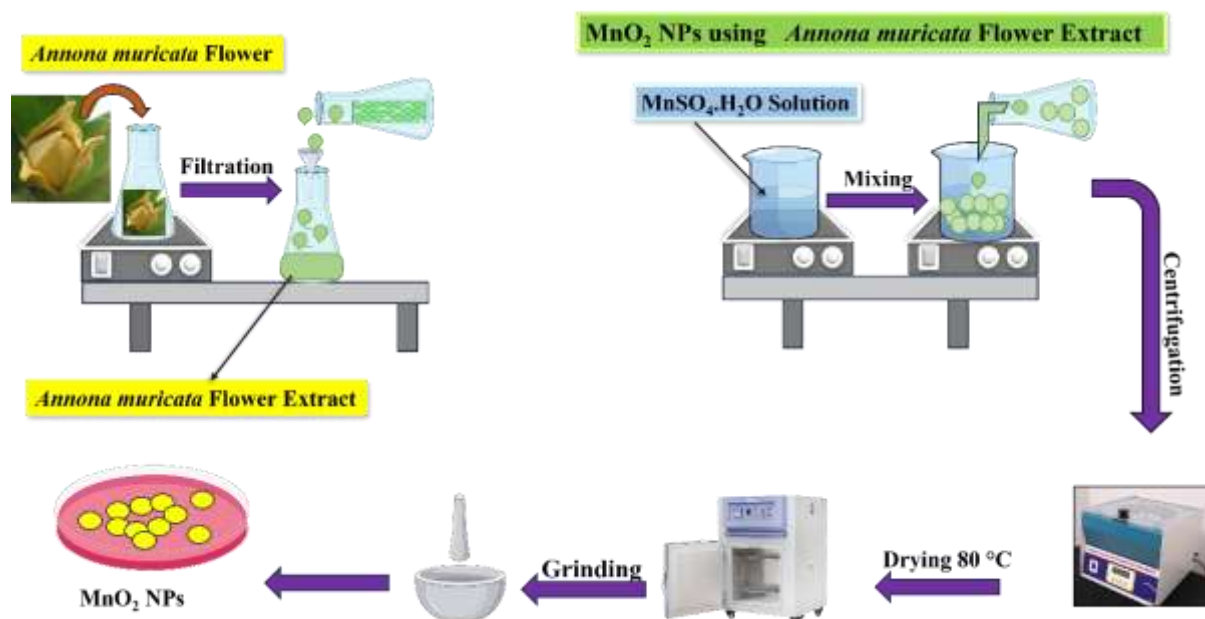


Figure.1 Schematic illustration of the green synthesis of MnO_2 NPs using *Annona muricata* flower extract.

2.4. Characterization of Manganese oxide nanoparticles

The green-synthesized MnO_2 nanoparticles were systematically characterized using a range of analytical techniques to elucidate their optical, structural, morphological, functional, and elemental properties. The optical absorption characteristics of the synthesized MnO_2 nanoparticles were investigated using UV-visible spectroscopy. The functional groups associated with the *Annona muricata* flower extract and their possible interactions with the MnO_2 nanoparticle surface were analysed by Fourier-transform infrared (FT-IR) spectroscopy using a Shimadzu IR Affinity-1 double-beam spectrometer over the wavenumber range of 4000-400 cm^{-1} . The crystalline structure, phase composition, and degree of crystallinity of the synthesized MnO_2 nanoparticles were determined by X-ray diffraction (XRD) using an Empyrean Malvern Panalytical diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.540 \text{ \AA}$). The surface morphology and microstructural characteristics were examined by field-emission scanning electron microscopy (FE-SEM; Carl Zeiss, USA, Sigma model with Gemini column). Energy-dispersive X-ray spectroscopy (EDS/EDX) was employed to determine the elemental composition and confirm the presence of manganese and oxygen in the synthesized nanoparticles. Collectively, these characterization techniques provided comprehensive insights into the physicochemical properties of the green-synthesized MnO_2 nanoparticles.

2.5 Anti-bacterial Activity

The disk diffusion technique is used to evaluate the antibacterial activity of the material. Sterile petri dishes with a diameter of 60 mm were filled with 10 milliliters of Mueller-Hilton agar medium and infected with the test organism. Sterile filter paper disks with varying sample concentrations of 60, 80, and 100 $\mu\text{g/ml}$ were placed over Mueller-Hilton agar plates. A filter paper disk with five micrograms of amoxicillin was used as a positive control. After the plates were incubated at 37°C for a whole day, the experiment was performed twice, and the zone of inhibition was measured in millimeters.

2.6 Anti-fungal Activity

The disk diffusion technique was used to evaluate the sample's antifungal activity against test microbes. In 60 mm petri plates filled with Sabouraud's dextrose agar (SDA), a sterile filter paper disk (diameter 6 mm, Whatmann paper no. 3) was seeded with 0.3 ml of the test organism. The sterile disk was saturated with ten microliters of samples at various concentrations of 60, 80, and 100 $\mu\text{g/ml}$. The zones of growth inhibition surrounding the disk were measured after a 24-hour incubation period at 37°C . The positive control used was fluconazole.

3. Results and discussions

3.1. XRD analysis

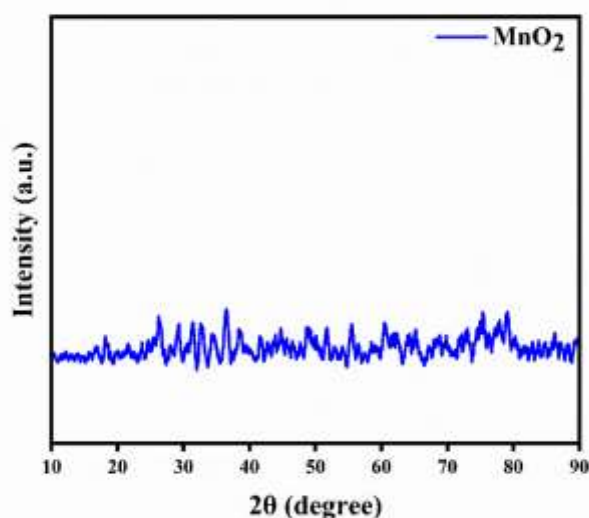


Figure.2. XRD pattern of MnO_2 NPs using *Annona muricata* flower extract.

Figure 2. confirms the successful formation of manganese dioxide (MnO_2), as evidenced by the good agreement between the observed diffraction pattern and the standard JCPDS card No. 00-044-0141. The diffraction peaks observed at $2\theta = 12.7^\circ, 25.7^\circ, 28.8^\circ, 36.6^\circ, 39.01^\circ, 41.2^\circ,$ and 47.3° are indexed to the (110), (220), (310), (400), (330), (420), and (510) crystallographic planes, respectively. These diffraction peaks are characteristic of the crystalline MnO_2 phase and confirm the successful formation of the desired manganese oxide structure. The crystal structure is assigned to a tetragonal crystal system.

3.2. FT-IR analysis

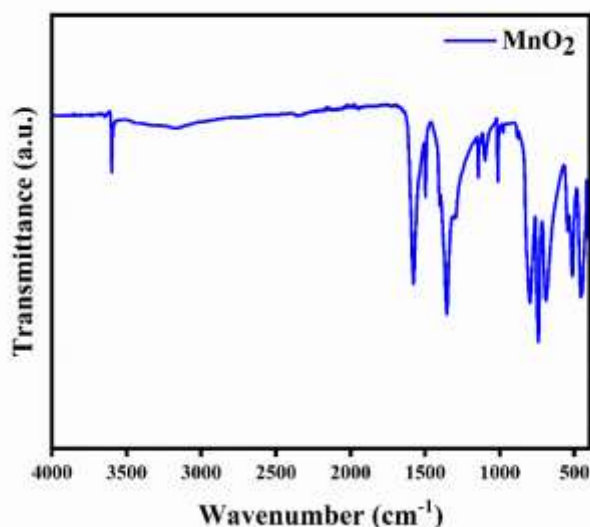


Fig.3. FT-IR spectra of MnO₂ NPs using *Annona muricata* flower extract.

The FTIR spectrum of the synthesized MnO₂ nanoparticles is presented in Fig. 3. The broad absorption band observed around 3400–3500 cm⁻¹ can be attributed to the O-H stretching vibration of surface hydroxyl groups and adsorbed moisture. The band near 1600 cm⁻¹ is associated with the bending vibration of absorbed H₂O molecules, while the bands in the 1400-1000 cm⁻¹ region may be related to residual organic functional groups originating from the *Annona muricata* flower extract. The characteristic absorption bands in the lower-wavenumber region, particularly below 700 cm⁻¹, are assigned to Mn-O stretching vibrations, confirming the formation of MnO₂. The presence of these characteristic Mn-O vibrational bands support the successful synthesis of MnO₂ nanoparticles through the green synthesis route.

3.3. UV-Visible Spectra Analysis

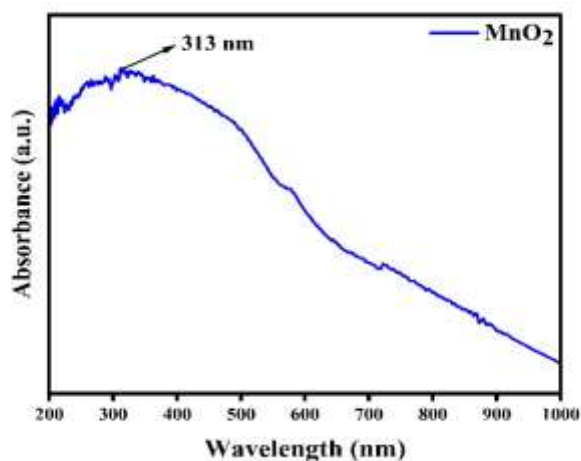


Figure 4. UV-visible diffuse reflectance spectrum of MnO₂ nanoparticles synthesized using *Annona muricata* flower extract.

The UV-visible diffuse reflectance spectrum (UV–DRS) of the synthesized MnO_2 nanoparticles is shown in Fig. 4. The MnO_2 nanoparticles exhibit strong absorption in the UV region, with a broad absorption band extending from approximately 200 to 450 nm and a maximum absorption around 380–390 nm. The absorption intensity decreases markedly beyond 400 nm and approaches the baseline in the visible region, indicating the predominant UV-light absorption characteristics of the synthesized MnO_2 nanoparticles. The observed absorption behaviour can be attributed to the electronic transitions associated with the Mn–O framework and confirms the optical response of the prepared MnO_2 nanoparticles.

3.4. SEM and EDX analysis

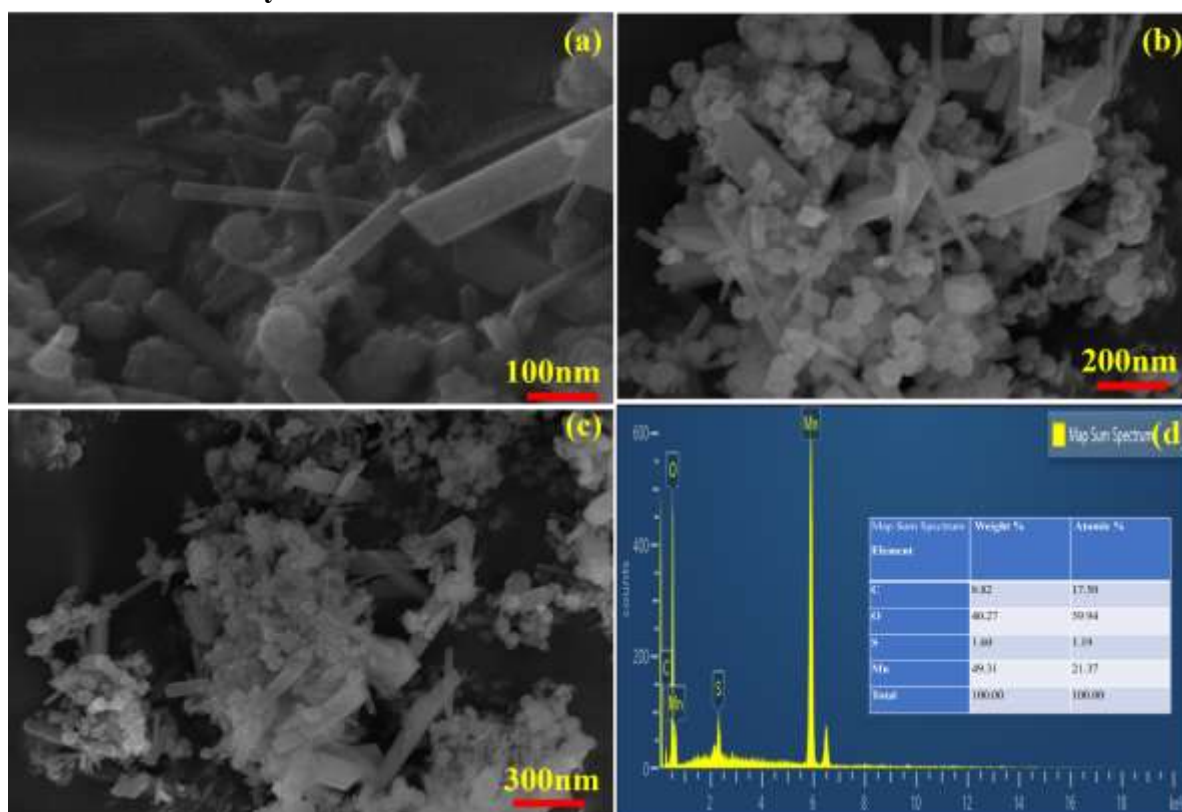


Figure 5. SEM images and EDX analysis of green-synthesized MnO_2 nanoparticles using *Annona muricata* flower extract: (a-c) SEM images at different magnifications and (d) corresponding EDX spectrum.

The SEM images in Fig. 5(a-c) reveal that the synthesized MnO_2 nanoparticles exhibit a heterogeneous morphology consisting predominantly of rod/plate-like structures accompanied by numerous irregular granular nanoparticles. The particles are strongly agglomerated and form interconnected clusters, which can be attributed to the high surface energy and interparticle interactions of the nanosized MnO_2 particles. The images recorded at different magnifications (100, 200, and 300 nm scale bars) confirm the formation of nanoscale MnO_2 structures with non-uniform morphology and considerable particle aggregation.

3.5 Applications

3.5.1 Antibacterial Activity



Staphylococcus aureus

Pseudomonas aeruginosa



Staphylococcus epidermidis

Klebsiella pneumonia

Fig 6. Antibacterial activities of Manganese oxide nanoparticles

The antibacterial activity of Manganese oxide nanoparticles prepared by the proposed method using the extract of the flower of *Annona muricata* was checked for a particular bacterium by the disc diffusion method. The antibacterial activity of Manganese oxide nanoparticles synthesized by the proposed method was checked for two Gram-positive bacteria, namely, *Staphylococcus aureus* (MTCC 87) and *Staphylococcus epidermidis* (MTCC 435), and two Gram-negative bacteria, namely, *P. aeruginosa* (MTCC 1688) and *K. pneumoniae* (MTCC 530). Manganese oxide nanoparticles react with the antibacterial of the synthesized material by the proposed method, which was tested by determining the zone of inhibition (mm) for various concentrations of the sample (60, 80, and 100 $\mu\text{g/mL}$) and compared with a standard antibiotic, amoxicillin (10 $\mu\text{L/disc}$). The results showed the concentration-dependent antibacterial activity of the sample against all the test microorganisms. In the case of *Staphylococcus aureus*, the sample showed zones of inhibition of 6 mm, 8 mm, and 9 mm at concentrations of 60, 80, and 100 $\mu\text{g/mL}$, respectively. On the other hand, the standard drug showed a zone of inhibition of 11 mm. Similarly, for *Staphylococcus epidermidis*, the sample showed zones of inhibition of 3 mm, 4 mm, and 6 mm at concentrations of 60, 80, and 100 $\mu\text{g/mL}$, respectively. However, the standard drug showed a zone of 8 mm. For *Pseudomonas aeruginosa*, the sample showed inhibition zones of 8 mm, 9 mm, and 10 mm as the concentration increased from 60 $\mu\text{g/mL}$ to 100 $\mu\text{g/mL}$, while the standard antibiotic showed an inhibition zone of 11 mm. On the other hand, the antibacterial activity of the sample increased from 4 mm to 7 mm as the concentration increased from 60 $\mu\text{g/mL}$ to 100 $\mu\text{g/mL}$, while the standard antibiotic showed an inhibition zone of 9 mm.

The aqueous control did not show any activity against the microorganisms. Overall, the results show that the sample prepared by the method has moderate antibacterial properties against Gram-positive as well as Gram-negative bacteria. The antibacterial properties of the sample were found to increase with an increase in the concentration of the sample. This shows that the sample has the potential for antibacterial properties, though the properties are less compared to that of the standard drug amoxicillin. From the results, it is clear that the sample prepared by the method can be used as an antibacterial agent. The antibacterial activity of the sample was seen to increase with increasing concentrations of the sample. It is, therefore, clear that there are possibilities of antibacterial activities in the sample but the antibacterial activity is lower than that of amoxicillin, which is considered to be the standard antibiotic. From the results obtained, it is evident that the sample can be used as an antibacterial agent.

Table-1: In Vitro Antibacterial activity of samples

Samples	Concentrations (µg/ml)	Organisms/Zone of inhibition (mm)			
		Staphylococcus aureus	Staphylococcus epidermis	Pseudomonas aeruginosa	Klebsiella pneumonia
Samples	60	6	3	8	4
	80	8	4	9	5
	100	9	6	10	7
Standard Amoxicillin	10 µl/disc	11	8	11	9
AQUEOUS	10 µl/disc	0	0	0	0

3.5.2. Anti-Fungal Activity



Candida albicans



Candida vulgaris



Aspergillus niger

Aspergillus flavus

Fig 7. Antifungal activities of Manganese oxide nanoparticles

The antifungal potential of nanoparticles synthesized using *Annona muricata* flower extract was investigated by the disc diffusion method using fungal pathogens, such as *Candida albicans*, *Candida vulgaris*, *Aspergillus niger*, and *Asp. flavus*. Antifungal properties were also investigated against *Candida albicans* (MTCC 183), *Candida vulgaris* (MTCC 429), *Asp. Niger* (MTCC 282), and *Asp. flavus* (MTCC 277). The antifungal activity of the nanoparticles was assessed based on the zone of inhibition (mm) at different concentrations of the synthesized sample, which was analysed (60, 80, and 100 $\mu\text{g/mL}$) and compared with the standard antifungal drug fluconazole (10 $\mu\text{L/disc}$). The results revealed that the synthesized nanoparticles had concentration-dependent antifungal activity for all tested fungal strains. In the case of *Candida albicans*, the inhibition zones were recorded as 4 mm, 5 mm, and 6 mm for 60, 80 and 100 $\mu\text{g/mL}$, respectively. However, the standard drug recorded an inhibition zone of 7 mm. In the case of *Candida vulgaris*, the inhibition zones recorded for the synthesized nanoparticles were 3mm, 4mm, and 5mm for the same concentrations. On the other hand, for the standard recorded inhibition zone was 8mm. For instance, the same was the case for *Aspergillus niger* where the synthesized sample exhibited inhibitions of 2 mm, 5 mm, and 7 mm at different concentrations ranging from 60 $\mu\text{g/mL}$ to 100 $\mu\text{g/mL}$; the inhibition for the drug fluconazole was 8 mm. For *Aspergillus flavus*, inhibition zones of 6 mm, 7 mm, and 8 mm were observed at concentrations of 60 $\mu\text{g/mL}$, 80 $\mu\text{g/mL}$, and 100 $\mu\text{g/mL}$, respectively while the standard exhibited inhibition of 9 mm. On the other hand, water control did not exhibit any fungal activity. To sum up, it can be concluded that from the results obtained in the study, it can be concluded that the nanoparticle synthesized using *Annona muricata* flower extract is highly effective against fungi like *Candida* and *Aspergillus*

Table-2: In Vitro Antifungal activity of sample

Samples	Concentrations ($\mu\text{g/ml}$)	Organisms/Zone of inhibition (mm)			
		<i>Candida albicans</i>	<i>Candida vulgaris</i>	<i>Aspergillus niger</i>	<i>Aspergillus flavus</i>
Samples	60	4	3	2	6
	80	5	4	5	7
	100	6	5	7	8

Standard (Fluconazole)	10 µl/disc	7	8	8	9
AQUEOUS	10 µl/disc	0	0	0	0

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