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Green synthesis, characterization and applications of manganese oxide nanoparticles

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ABSTRACT

Nanotechnology is a promising and rapidly evolving field. Nanotechnology has received increased attention in recent years due to the need to create biocompatible materials for a variety of applications in fields such as health, medicine, water treatment and purification, and so on. Metal and Metal Oxide is one element of nanoscience and nanotechnology that has various applications in a variety of fields and has piqued the curiosity of academics. However, manganese and manganese oxide have received less attention as a high-performance metal in a variety of applications, including medicine, biomedicine, biosensors, water treatment and purification, electronics, electrochemistry, photo-electronics, catalysis, and so on. The standard methods of synthesizing nanoparticles can be harmful to the environment and living things. Thus, the greener way to nanoparticles (NPs) synthesis is recommended. It has various advantages, including being non-toxic, environmentally friendly, clean, less expensive, and almost new, as well as the ability to be done at room pressure and temperature. This review focuses on collection of comprehensive information from recent developments in the synthesis, characterization and applications from previous scientific findings on the biological method of synthesizing manganese oxide nanoparticles (MnO NPs) due to the aforementioned advantages. Green synthesis of MnO NPs leverages the benefits of bioactive compounds from plant extracts, which help in controlling the size, shape, and surface characteristics of the nanoparticles. This results in enhanced antibacterial activity, catalytic activity, electrochemical performance, magnetic behavior, and fluorescent properties while ensuring biocompatibility and environmental safety. Consequently, MnO NPs synthesized via green methods are highly suitable for a wide range of applications, including environmental remediation, electronics, biomedical imaging, and nutritional supplements.

Keywords: Nanoparticles, Manganese oxide, Green synthesis, Biomedicine, Characterization.

INTRODUCTION

Nanomaterials, with a length scale of less than 100 nm, have garnered significant attention not only for their fundamental scientific value but also for their remarkable applications stemming from unique electrical, magnetic, and catalytic capabilities.[1] These nanoparticles are of interest due to their potential applications across diverse fields, including medicine, wastewater treatment, agriculture, energy production, and environmental remediation.[2,3] Metal nanoparticles (NPs), in particular, exhibit exceptional surface area-to-volume ratios, high surface energy, spatial confinement, and minimal defects, alongside superior physicochemical, electrical, mechanical, magnetic, thermal, dielectric, optical, and biological properties compared to as compared with other materials.[4–7]

Among the 3D transition metal oxides, manganese oxides, including MnO, Mn_5O_8, Mn_2O_3, MnO_2, and Mn_3O_4, have piqued researchers' interest due to their numerous structural and compositional variations.[8] Manganese oxide nanoparticles show significant promise for sustainable nanotechnology.[9] They find extensive applications in imaging contrast agents, magnetic storage devices, water treatment, and purification, owing to their advantageous physical and chemical properties.[10–16]

Various methods, such as chemical precipitation, sol-gel, solvothermal/hydrothermal, solid-state synthesis, electrochemical, and photochemical reduction techniques, are widely employed for the synthesis of nanoparticles.[17–19] However, physical and chemical methods often involve energy-intensive, costly processes and the use of toxic substances.[20] In contrast, green synthesis offers an alternative route to producing biocompatible nanoparticles. This eco-friendly, cost-effective, and less energy-demanding approach utilizes biological materials such as bacteria, fungi, algae, yeast, and plant extracts as reducing agents.[21–23] Among these, plant-based synthesis has garnered particular interest due to its simplicity and efficiency.[24–26] Plant phytochemicals, such as alkaloids, polyphenols, flavonoids, and terpenoids, have demonstrated their ability to reduce metal ions and synthesize stable nanoparticles.[27,28] Moreover, biogenic plant phytomolecules can enhance the nanoparticles' intrinsic properties, such as antioxidant, antibacterial, and anticancer activities, compared to their extracts.[29–31]

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This article provides a comprehensive review of green synthesis approaches for MnO NPs to address the limitations of traditional physical and chemical synthesis methods. It begins by exploring various synthesis methods, with a focus on green synthesis and the effects of experimental parameters on MnO NPs production. Next, characterization techniques are reviewed, highlighting their role in understanding the morphology, optical properties, crystallinity, and surface chemistry of MnO NPs. Finally, the article highlights the diverse applications of MnO NPs, including antibacterial activity, dye degradation, electrochemical properties, magnetic behavior, fluorescence, and their potential as nutritional supplements. Through this structured analysis, the review aims to provide a detailed understanding of the green synthesis of MnO NPs using plant extracts as reducing and stabilizing agents, along with their emerging applications.

SYNTHESIS OF MnO NPs

Manganese oxide nanoparticles with various shapes and exceptional qualities have been synthesized via several innovative and novel methods, including the hydrothermal method, chemical method[32], sol-gel synthesis method[33], ultrasonic bath method[34], thermal decomposition method[35,36], laser ablation method[35], and green synthesis method.[16] The chart showing the various methods of MnO NPs synthesis are showed in Figure 1.

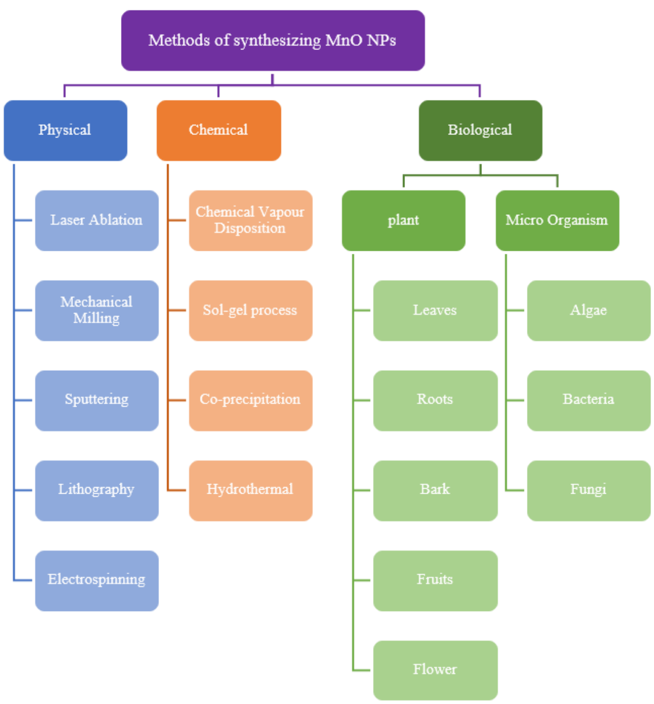

Figure 1. Flow chart representing the various methods of synthesis of MnO NPs.

Chemical Method

Atoms, molecules, and clusters are used in chemical processes to construct Manganese oxide NPs structures. As a result, the majority of these approaches rely on a bottom-up approach that employs appropriate precursors and additives.[37]. Wet chemical, chemical vapor disposition, direct precipitation, solvothermal, hydrothermal, sonochemical, microwave-assisted combustion, electrode-position, homogeneous precipitation, sol-gel, spray drying, microwave irradiation, reverse micelles, and spray pyrolysis methods, as well as the manganese-alcohol reaction, are examples of chemical processes.[38–40] Although chemical procedures are simple, economical, and continuous processes with high efficiency[41,42], they can be harmful to persons and the environment due to the presence of dangerous substances. Some of the substances utilized in chemical and physical techniques may remain on the NPs, providing major dangers to medical applications.[43] Advantages and disadvantages of this methods are shown in Table 1. In Sol-Gel Method, this technique involves the hydrolysis and condensation of metal alkoxides to form a gel, which is then calcined to produce MnO NPs. Sol-gel synthesis enabled precise control over particle morphology and crystallinity.[44] MnO_2 was successfully fabricated using a gel formation process followed by calcination at 400°C (MnO_4) and 700°C (MnO_7) in the presence of air.[44] The structural and morphological analyses revealed to be a body-centered tetragonal crystal lattice with a nano-tablet-like porous surface with size of 12.6 nm and 16.2 nm. In Co-Precipitation Method, this approach involves the reaction of manganese salts with alkaline solutions, leading to the formation of MnO NPs. For example, MnO NPs were synthesized using manganese acetate and sodium hydroxide, achieving nanoparticles with size of about 18.35 nm and high crystallinity.[45] However, the process often requires post-synthesis purification to remove by-products. Thus, cost-effective and ecologically benign technologies for Manganese oxide NPs synthesis are urgently required. Figure 1 shows the various chemical methods used for the synthesis of MnO NPs.

Physical Method

The primary physical approaches are laser ablation, mechanical milling, sputtering, lithography evaporation/condensation and electrospinning.[35] Physical synthesis methods have the benefit of avoiding solvent contamination in the generated thin films and ensuring uniform MnO NPs distribution as compared to chemical approaches. The advantages and disadvantages of this method are shown in Table 1. Physical synthesis of NPs using a tube furnace at atmospheric pressure has some drawbacks, such as the fact that the tube furnace takes up a lot of space, consumes a lot of energy while raising the ambient temperature around the source material, and takes a long time to achieve thermal stability. Furthermore, a typical tube boiler takes more than a few kilowatts of power and several tens of minutes of preheating time to achieve a steady operating temperature.[46,47] Laser ablation of metallic bulk materials in solution could be used to synthesize manganese nanoparticles. One significant advantage of laser ablation approach over other ways for producing metal colloids is the absence of chemical reagents in solutions. Manganese oxide nanoparticles in the Mn_3O_4 phase were synthesized using the laser ablation of solids in liquids technique (LASL).[48] The experiments were carried out by ablating a manganese (Mn) target immersed in deionized water as the liquid medium, with a pulsed Nd:YAG laser with a wavelength of 1064 nm. The effect of ablation time on the formation of these oxides was studied as an important parameter, which determines the final composition of the obtained products. The results showed that the nanoparticles are well crystalized and have an approximate size between 7 and 11 nm. This approach can produce pure and uncontaminated metal colloids for future uses.[49] Figure 1 shows the various physical methods that can be used for the synthesis of MnO NPs.

Biological Method

The biological approach to MnO NPs manufacturing includes the use of organisms (bacteria, yeast, and fungi) and plant extracts as reducing agents for metal ions[50–52] as shown in Figure 2. Synthesized monodispersed orthorhombic MnO_2 with Bacillus sp., a heavy metal resistant bacterium.[10] The MnO_2 produced was intracellular and recoverable. Plant-based NP synthesis is extremely cost effective, making it an economically viable and valuable alternative for large-scale NP production.[53] Biomolecules such as flavonoids, proteins, tannins, phenols, and terpenoids have been shown to be effective reducing and stabilizing agents for MnO NP production. Plants rich in antioxidants can also be employed to make the NPs. The antioxidant polyphenols in the plant act as reducing and stabilizing agents.[54,55] A plant extract from Kalopanaxpictus and Yucca gloriosa with curcumin was utilized to create NPs of size 19.2 and 80 nm, respectively, at room temperature, without utilizing the catalyst or other costly materials.[56,57] Green synthesis of MnO NPs using plant extracts as the source of electron generation for manganese salt reduction has certain advantages over microbe-based synthesis in that it does not require cell culture upkeep and can be scaled up for large-scale production.[53] The advantages and disadvantages of the biological method of synthesis are summarized in Table 1. The synthesis of MnO NPs utilizing a plant extract of Moringa oleifera is shown in Figure 2.

The following equations indicate the probable mechanism involved in MnO NPs synthesis.

$$Mn^{2+} + \text{plant extract} \rightarrow [\text{Mn/plant extract}]^{2+}$$
$$[\text{Mn/plant extract}]^{2+} \rightarrow \text{heat } [Mn(OH)_2\text{/plant extract}]$$
$$[Mn(OH)_2\text{/plant extract}] \text{ (Incubation)} \rightarrow \text{MnO NPs}$$

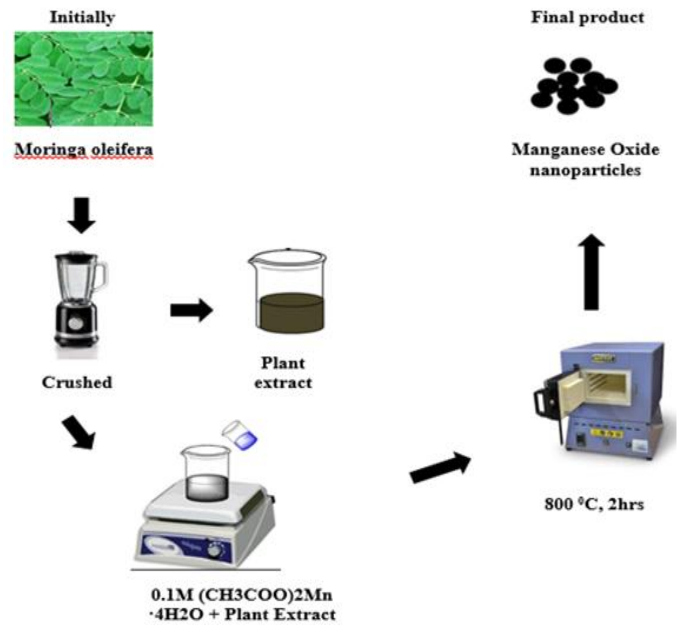

Figure 2. The green synthesis of MnO NPs

EFFECTS OF EXPERIMENTAL PARAMETERS ON MnO NPs SYNTHESIS

The biosynthesis of nanoparticles is influenced by several factors that significantly affect their characteristics and properties.[58] To obtain nanoparticles with the desired size, shape, composition, stability, and other attributes, these factors must be carefully monitored and optimized. The following are parameters impacting nanoparticle synthesis include temperature, pH, type of plant extracts and concentrations, and reaction time.[58]

Effect of pH

pH is a significant element influencing MnO NPs creation using green technology methods. Researchers revealed that the pH of the solution medium affects the size and texture of the synthesized MnO NPs.[59,60] As a result, changing the pH of the solution media can affect the size of the nanoparticles. A solution medium with pH values ranging from 7 to 9 has been identified as the ideal setting for the creation of nanoparticles from *Aeromonas hydrophila* extract.[61]

Table 1. Advantages and disadvantages of different methods of MnO NPs synthesis[59,62-68]

Method	Advantages	Disadvantages	References
Chemical	It enhances large production	Generation of non-ecofriendly products, it is energy intensive processes, use of toxic solvents as reducing and stabilizing agent	62–64
Physical	Control crystallinity, shape and production of MnO NPs with uniform, controlled size and high purity are achievable	Require high capital cost and consume large energy	65,66
Biological	This method is cost effective, non-toxic use of materials and simple	Using microorganisms is not attractive due to the requirements of aseptic cultivation and increased production cost at industrial scale	59,67,68

Effect of Temperature

Temperature is another significant element that influences MnO NPs production via all three processes. Physical procedures demand higher temperatures (>350°C), while chemical approaches require lower temperatures.[61] MnO NPs synthesis utilizing green technology often requires temperatures below 100°C or ambient temperature. The temperature of the reaction medium determines the type of nanoparticle generated.[69] The effect of temperature on the green synthesis of MnO_2 NPs was studied by varying the temperature conditions of the mixture from 75°C to 95°C.[70] The result shows that higher temperature conditions (up to 90 °C) favors the formation of MnO_2 NPs. A further increase in temperature supports the agglomeration of nanoparticles leading to decreased absorbance values. Generally, higher temperatures result in faster reaction rates but may also promote particle aggregation or undesired growth. Thus, controlling the temperature is important to achieve nanoparticles with the desired properties.[71].

Effect of Time

The duration of incubation of the reaction medium has a significant impact on the quality and kind of MnO NPs synthesized utilizing green technology.[72] Similarly, the properties of the synthesized nanoparticles changed over time and were heavily influenced by the synthesis method, light exposure, and storage conditions, among other factors.[73,74] Variations in time can occur in a variety of ways, including particle aggregation caused by long-term storage; particles that shrink or expand during long-term storage; shelf life, and so on, all of which affect their potential.[75]

Effect of type of plant extracts and concentrations

Secondary metabolites found in several living systems, including plants, operate as reducing and stabilizing agents in the creation of MnO NPs. However, the content of these metabolites changes according to the kind of plant, plant portion, and extraction method.[76] Similarly, various microbes produce different internal and extracellular enzymes in varied amounts, which influence nanoparticle production.[77] To achieve the best conditions for green synthesis of MnO NPs, the volume of plant extract must be proportional to the quantity of manganese precursor employed.[78] The yield of MnO NPs depends heavily on the volume of extract utilized for synthesis.[79] According to the findings, the volume and kind of extract utilized in nanoparticle manufacturing have a significant impact on their morphological qualities and biological activities.[80]

CHARACTERIZATION OF MnO NPs

UV-visible (UV-Vis) spectroscopy

UV-visible spectroscopy is a type of molecular spectroscopy that operates using the Bouguer Lambert Beer law. In conjunction with electromagnetic waves, this approach measures Plasmon resonance and total oscillations of the electron conduction band. It is also used to assess fluid absorption as well as other materials.[81] When a light beam passes through a solution, some of it may be absorbed while the remainder is transmitted through it. Transmittance is the ratio of light entering a sample to light exiting it at a certain wavelength. Absorbance is the negative logarithm of transmittance.[82] MnO NPs exhibited UV-Visible absorption spectra ranging from 284 to 400 nm due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.[14,83,84] Furthermore, distinct absorption peaks of MnO NPs suggested that the shape and size of manufactured nanoparticles varied depending on the synthesis process.[85,86] Metal nanoparticles' absorption spectra move towards longer wavelengths as particle size rises.[86,87] Findings on the uses and application of UV as characterization tools in green synthesis of MnO NPs are summarized in Table 2 and 3.

FTIR spectrophotometer

The FTIR analysis is used to identify organic, inorganic, and polymeric compounds by scanning the samples with infrared light. Changes in the typical pattern of absorption bands plainly show a change in material composition. FTIR is useful for identifying and characterizing unknown compounds, detecting impurities, locating additives, and determining decomposition and oxidation.[82] Infrared radiation (10,000 – 100 cm^{-1}) is transmitted through the sample, with some being absorbed and some going through. The absorbed radiation is transformed by the sample into vibrational or rotational energy. The detector produces a signal ranging from 4000 to 400 cm^{-1}, representing the sample's molecular fingerprint. Each molecule has a distinct fingerprint, making FTIR an invaluable tool for chemical identification.[88] MnO NPs are identified by conspicuous peaks such as O-H, C=O, C-O, C-N, C-H, and C≡C as shown in Table 3.

Scanning Tunnelling Microscopy (STM)

This tool produces surface pictures with atomic-scale lateral resolution. A fine probe with a tip scans the conducting sample's surface using a piezoelectric crystal, and the resulting tunnelling current is measured. Quantum tunnelling is the working principle of STM. The surface topography is determined by graphing the tip's height as a function of its lateral position over the sample.[82] STM can be employed in air, vacuum, liquid, or gas at a variety of temperature ranges. The procedure might be difficult because the tip must be sharp and the surfaces clean. Carbon nanotube tips are employed for STM.[89] It is a potentially useful technique for characterizing nanoparticles. The growth of MnO NPs is monitored using STM. Previous studies on the use of STM as a characterization technique is shown in Table 2.

Atomic Force Microscopy (AFM)

AFM is a powerful and adaptable microscopy technique for studying samples at the nanoscale.[90] It captures an image in three dimensions and gives several types of surface measurements to fulfil the needs of scientists. AFM can produce images at atomic resolution with angstrom scale resolution height information while requiring minimal sample preparation. In nanotechnology, it may be used to detect surface roughness and visualize surface texture on a wide range of materials. It is also a non-destructive approach with excellent three-dimensional spatial resolution.[82] Previous studies on the use of

AFM as a characterization technique is shown in Table 2.

Transmission electron microscopy (TEM)

TEM is regarded as the most effective electron microscopy technique for determining the morphological identities of MnO NPs and other metal nanoparticles.[91] In the TEM technique, an electron beam is delivered through the sample, interacts with it, and the transmitted electrons are used to generate a picture by magnifying and focusing them with an objective lens.[82] The upgraded version of TEM with better resolution, which permits imaging of a sample's crystallographic structure at the atomic level. Unlike traditional microscopy, which uses absorption to form images, high resolution transmission electron microscopy creates images by interference in the image plane.[82] Previous studies on the use of TEM are shown in Table 2.

Scanning electron microscopy (SEM)

SEM is used to characterize the morphology of MnO NPs. SEM is a popular approach for imaging surfaces at high resolution, and it can also be used to characterize nanoscale materials. SEM images using electrons in the same way as a light microscope does with visible light.[92] It is limited in some morphological analyses because it provides insufficient information about the true population and average size distribution.[93] SEM has been shown to harm several nanopolymers. As a result, for effective morphological examination by SEM, the NPs must be able to sustain vacuum pressure.[94] Another disadvantage of this technology is that it is quite expensive and slow. Other studies demonstrating the morphological characterization of biosynthesized MnO NPs using SEM are provided in Table 3.

Dynamic Light Scattering (DLS)

DLS is often referred to as quasi-elastic light scattering. It is a widely used approach for determining the size of MnO NPs in colloidal solutions in the nano- and submicrometer ranges.[92] The MnO NPs in a colloidal solution are in constant Brownian motion. DLS monitors light scattering as a function of time and, when paired with the Stokes-Einstein assumption, is used to calculate the NP hydrodynamic diameter (the diameter of the NP and the solvent molecules that diffuse at the same rate as the colloid) in solution. To minimize multiple scattering, DLS requires a relatively low NP concentration.[95] Previous studies on the use of DLS as a characterization technique is shown in Table 2

Energy dispersive X-ray spectrometry (EDX)

This technique provides an overall map of the sample by analyzing near-surface components and estimating elemental proportions at various places. EDX is used to qualitatively and quantitatively determine the elemental composition of MnO NPs and other metal nanoparticles. X-rays are produced when an EDX electron beam bombards MnO NPs.[96] The emitted X-rays are analyzed both qualitatively and quantitatively. For quantitative analysis, the intensities of peaks are used to determine the concentration of individual elements in MnO NPs, but for qualitative analysis, the positions of each X-ray peak on the EDX spectrum are used to identify them. EDX is used in combination with SEM. An electron beam with an energy of 10-20 keV impacts the conducting sample's surface, causing X-rays to be emitted from the material. The energy of the emitted X-rays is determined by the substance under study.[82] Previous studies on the use of EDX as a characterization technique is shown in Table 2.

X-Ray diffractometer (XRD).

XRD can provide crystallographic information as well as phase purity.[97] The average crystallite size of MnO NPs is determined using the Debye-Scherrer formula.[98]

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the average crystal size, λ is the X-ray wavelength, k is Scherrer constant and β is the full width at half maximum. a-MnO_2 exhibits XRD peaks at 2θ = 12.7°, 18.0°, 28.6°, 37.5°, 41.9°, and 49.7°.[99] The intensity of the peak grows as the synthesis temperature and synthesis time of the NPs increase, indicating that the NPs' crystallinity increases with temperature and reaction time and corresponds to standard values. Similarly, altering the reacting species ratio can promote crystallinity.[100] Previous studies on the use of XRD as a characterization technique is shown in Table 2. Furthermore, other techniques adopted for the characterization of biosynthesis MnO NPs are documented in Table 2.

Applications of MnO NPs

MnO NPs synthesized using plant extracts have been reported to exhibit numerous applications in many fields. Some applications of MnO NPs are discussed below as shown in Figure 3.

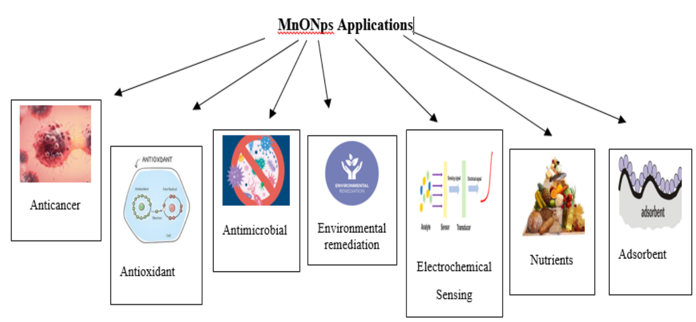

Figure 3. The various applications of MnO NPs

Table 2. Characterization techniques for synthesized MnO NPs[82,101-116]

Techniques	Purpose	Reference
Centrifugation	To separate the synthesized NPs from reaction solution.	101
Transmission electron microscopy (TEM)	Get High Resolution Pictures than a light microscope. Used to study the structure and presence of NPs.	101,102
Scanning electron microscope (SEM)	Get a three-dimensional appearance 3D based on the interaction of the electron beam with the specimen surface.	103
Scanning tunnelling microscopy (STM)	To study the local electronic structure of metal NPs as well as the structure and presence of NPs.	104
Ultraviolet-visible spectroscopy (UV-Vis)	Used for the optical study of the materials and to determine the synthesis of NPs.	101,105
Fourier transform infrared spectroscopy (FTIR)	To study the surface chemistry of metal NPs. Used for the identification of organic, inorganic, and polymeric materials utilizing infrared light for scanning the samples. Used to identify functional groups in the material.	82,106
X-ray diffraction (XRD)	Used for characterization of nanopowders of any sizes. Provide useful information and also help correlate microscopic observations with the bulk sample.	107,108
X-ray photoelectron spectroscopy (XPS)	Used to identify the elemental composition and chemical states of the elements present at the surface of a material.	109
Dynamic light scattering (DLS)	Used to measure the size of particle analyze complex colloidal systems.	101,110
Energy dispersive X-ray spectrometry (EDX)	Used to identify the elemental composition of a sample.	111,112
Atomic force microscopy (AFM)	Analyze complex colloidal systems obtains information by touching the sample's surface with a probe used to obtain high-resolution images. To study the size, shape, and surface roughness of metal NPs.	103,113
Dynamic light scattering (DLS)	Measure the hydrodynamic diameter of nanoparticles in solution.	114,115
Thermogravimetric analysis (TGA)	Study the thermal stability and decomposition of metal NPs.	116

Table 3. SPR bands, and functional groups, characterization techniques of biosynthesized MnO NPs from some plant sources[11,13-16,26,54,56,70,117-121]

Plants/Organisms names	Salt	SPR peak (nm)	Functional group prediction (cm^{-1})	Techniques	Shape	Size (nm)	Application	Ref.
Lemon methanolic extract	$Mn(OAc)_2.4H_2O$	360	OH 3650 C=O 1625 C-O 1026 C=C 1574 Mn-O 901	UV-VIS, FTIR, SEM, and HRTEM	-	50	Antibacterial and Antifungal	13
Kalopanax pictus leaf extract	$KMnO_4$		OH 3000 C=O 1623 C-O 1089 Mn-O 518	UV-VIS, XPS, FTIR, TEM, and EDX	Spherical	1–60	Dye degradation Electrochemical	15
clove, i.e., *Syzygium aromaticum* aqueous extract	$Mn(OAc)_2$	270	OH 3393 C=O 1707 C-O 1220 Mn-O 827	UV-VIS, XRD, FTIR, TGA, FESEM, DLS and TEM	-	4	Electrochemical	11
Phyllanthus amarus leaf extract	$Mn(OAc)_2.4H_2O$	360	OH 3433 C=O 1625 C-O 1021 C=C 1355 Mn-O 580	UV-VIS, XPS, FTIR, TGA, SEM, and TEM	Nanorod	40–50	Fluorescence studies	16

Abutilin indicum	$MnSO_4.H_2O$		OH 3250 C=O 1650 C-O 1060 C-H 2970 Mn-O 580	FTIR, UV-VIS, XRD, EDX and STM	Spherical	80	Photocatalytic and antibacterial	26
Ananas comosus (L.) peel extract	$KMnO_4$	-	OH 3450 C-H 2335 C-N 1384 Mn-O 626	FTIR, XPS, DLS and SEM	Spherical	10–34	Nutritional supplements	117
Dittrichia graveolens (L.) extract	$Mn(OAc)_2$	284	OH 3420 C=O 1650 C-O 1030 C=C 2917 Mn-O 798	UV-VIS, XRD, FTIR, and FESEM	Spherical	38	Dye degradation	14
Yucca gloriosa leaf extract	$Mn(OAc)_2$	410	OH 3400 C=O 1648 C-O 1050 C=C 2920 Mn-O 650	UV-VIS, XRD, FTIR, FESEM, TEM	Spherical	80	Dye degradation	56
Ocimum basilicum L leaves extract	$MnCl_2.4H_2O$	329	OH 3200 C=O 1550 C-O 1028 C-H 2900 N-H 1380 Mn-O 522	UV-Vis, XRD, FTIR, SEM and TEM	Spherical	6.5	Photocatalytic	70
Conocarpus erectus L leaves extract	$MnCl_2$	265	OH 3421 C=O 1638 C-C 1558 Mn-O 671	UV-VIS, XRD, FTIR, EDX, SEM, and AFM	Spherical	80	Nanofertilizer	118
Euphorbia heterophylla Leaves Extract	$MnCl_2.4H_2O$	-	OH 3245 C=O 1610 C-N 1071 Mn-O 559	XRD, FESEM, HRTEM, FTIR	Irregular shaped	13.5	-	119
Aloe vera	$KMnO_4$	-	OH 3378 C=O 1633 C-C 1060 C=C 1383 Mn-O 545	FTIR, XRD and FESEM	Spherical	22, 18 and 16	Antibacterial	120
Gardenia resinifera Leaf extract	$Mn(OAc)_2$	362	OH 3770 C-H 2924 C-N 1435 C≡C 2376 Mn-O 524	UV-VIS, XRD, FTIR, PSA, SEM, EDAX and HRTEM	Spherical	17-32	Antimicrobial activity	121
Bryophyllum pinnatum	$KMnO_4$		OH 3426 C-H 2924 C-O 1034 C=O 1618 Mn-O 524	UV-VIS, XRD, FTIR, SEM	Spherical	4-18	Magnetic property	122
Extracts of orange's juice	$KMnO_4$	-	-	TEM, XRD, TGA, BET	-	7.25	Electrochemical	54

Antibacterial

Green nanoparticles have demonstrated promising antibacterial efficacy against a variety of gram-negative and gram-positive bacteria. However, the mechanisms underlying growth inhibition and bactericidal effects are unclear. Notably, nanoparticle features such as form, size, and surface area, among others, have a significant impact on how they destroy bacterial cells. Manjula et al created manganese oxide nanoparticles using *Gardenia resinifera* leaf extract.[121] The scanning electron microscopy, or SEM, revealed the roughly spherical shape of manganese oxide with a size of around 17-32 nm. The antibacterial activity of synthesized MnO_2 nanoparticles was investigated using the agar well diffusion method. The concrete results indicate that Serratiam arcescens was the most sensitive microorganism with a maximum zone of inhibition (29 mm), followed by Pseudomonas aeruginosa (28 mm). In another study, the synthesis of manganese oxide via a green method using Lemon methanolic extract was reported.[13] The MnO NPs exhibited the strongest antibacterial activity against S. aureus zone of inhibition (18 mm) and E. coli zone of inhibition (19 mm) and it showed moderate activity against S. bacillus zone of inhibition (17 mm). Therefore, the presence of an inhibition zone clearly indicates that the antibacterial activity of synthesized manganese nanoparticles against S. aureus is extremely superior to the standard drug, Chloramphenicol and nearly similar activity against E. coli bacteria.[122]

Dye Degradation

The paper and textile industries drain a vast volume of environmental contaminants, including carcinogenic natural and nondegradable colors. Photocatalytic techniques have received a lot of interest recently due to their ability to degrade dyes efficiently.[123–125] One study investigated the dye degradation activity of MnO_2 NPs to decompose Acid Orange.[56] In their study, MnO_2 NPs were also generated greenly utilizing Y. gloriosa extract. The photocatalytic activities of MnO_2 NPs for dye degradation were investigated with Acid Orange as an organic contaminant, and the results were promising. Time investigation of Acid Orange degradation revealed faster dye breakdown. The dye degradation activity of MnO_2 NPs was investigated using Congo Red and Safranin O dyes. MnO_2 NPs were also created utilizing a green technique involving K. pictus plant extracts.[15] MnO_2 nanoparticles were discovered to destroy two dyes: Congo red and Safranin O. Congo red and safranin O exhibited absorption maxima at 496 and 518 nm, respectively. Time course examination of Congo red degradation at absorption maxima revealed that biologically synthesized MnO_2 nanoparticles have a higher decolorization potential. Congo red was completely degraded in 8 minutes by biologically synthesized MnO_2 nanoparticles. The decolorization capacity of biologically synthesized MnO_2 nanoparticles for degrading safranin O was found to be almost same. The total degradation of safranin O was achieved within 10 to 15 minutes.

Electrochemical Application

Supercapacitors or electrochemical capacitors are energy storage devices that may provide tremendous power while also delivering energy in a short amount of time, unlike batteries. These devices are necessary for high-power supply applications such as electric/hybrid automobiles, backup memories, digital products, aeroplane emergency doors, micro-devices, mobile gadgets, and next-generation portable electronics. This is due to their low cost, low maintenance requirements, safety, short charging times, and high cycle life.[126] The use of synthesized MnO NPs in electrochemical sensing was investigated.[54] Green synthesized MnO NPs using orange peel extract were used to investigate the electrochemical characteristics and discharge performance of J-MnO_2 and P-MnO_2 NPs for possible usage as cathodes in lithium-ion batteries.[52] Galvanostatic charge-discharge investigations were carried out. The results showed that (OPMnO_2) has a greater surface area and lower K content than that made with orange juice extract (OJ-MnO_2). Higher surface area and reduced K content in OP-MnO_2 have a positive impact on its electrochemical characteristics. OP-MnO_2 has twice the capacitance of OJ-MnO_2 at a current density of 0.5 a per gram.

Magnetic Property

The magnetic characteristics of MnO nanoparticles was investigated.[126] SQUID analysis was used in their study to demonstrate the superparamagnetic behavior of MnO NPs. The SQUID results revealed MnO NPs' super-paramagnetic behavior, unlike Ullah et al.[121] study that used Bryophyllum pinnatum aqueous leaf extract as a reducing and capping agent to synthesize bio-molecule capped α-MnO_2 nanoparticles and study their magnetic properties. The study found that the α-MnO_2 nanoparticles exhibit modest ferromagnetic behavior at ambient temperature. At ground state, α-MnO_2 is antiferromagnetic due to its symmetric Mn-O-Mn bonds.[122] Biswas et al.[127] developed Mn-incorporated ZnS nanorods. The Mn-incorporated ZnS Nano-rods exhibited intense orange luminescence at approximately 585 nm. Lower Mn concentrations showed six-line hyperfine splitting in the Electron Paramagnetic Resonance (EPR) spectra, while higher Mn concentrations produced broad Lorentzian-shaped EPR spectra due to Mn-Mn cluster formation. Mn concentrations were ascribed to the Mn-Mn dipole interaction. The isolated Mn^{2+} ion and Mn cluster were also discovered using EPR.[127] EPR results indicate the presence of magnetic dipole interaction in Mn-incorporated ZnS nanorods with greater Mn concentrations. $Mn_xZn_{1-x}S$ NPs with favorable emission characteristics could be used in emissive devices.[127]

Fluorescence Property

MnO_2 nanorods were synthesized employing Phyllanthus amarus plant extract for its fluorescence activity. The fluorescence emission intensity of green synthesized MnO NPs at 518 nm was attributed to d-d transitions in Mn^{3+} ions.[16] The fluorescence emission observed in this situation may be owing to defects in the self-assembly of as-prepared Mn NPs. The d-d transitions in the associated Mn^{3+} ions can be strong due to static Jahn-Tellar distortion.[128] As a result, these could find useful applications in fluorescence-emitting materials.[16]

Nutritional Supplements

Manganese oxide nanoparticles was created from Ananas comosus (L.) peel and used them as dietary supplements for freshwater prawn Macrobrachium rosenbergii.[117] Manganese oxide nanoparticles were given to *M. rosenbergii* for 90 days. The study found that prawns fed a diet supplemented with Manganese oxide NPs had improved growth performance, digestive enzyme activities, muscle biochemical compositions, and total protein levels.[117] In addition, Manganese oxide NP supplementation greatly improved the activity of the antioxidant defense system and metabolic activities such as superoxide dismutase, catalase, glutamic oxaloacetate transaminase, and glutamic pyruvate transaminase. The study concluded that green synthesized Mn_2O_4 NPs were effective and safe as diet supplements for freshwater prawn Macrobrachium rosenbergii. According to this study, it could be used as a diet supplement for other aquatic species because it promotes prawn growth and an antioxidant defense system.[117]

CONCLUSION

The application of manganese oxide nanoparticles in the medicinal, energy storage devices, textiles, Dye degradation, water treatment, fluorescence-emitting materials and Nutritional supplement has garnered a great deal of interest, with a focus on development of more of eco-friendly, nontoxic, and environmentally benign methods using green biotechnology tools for production manganese oxide nanoparticles. This paper provides an overview of the green synthesis of manganese oxide NPs. This review provides insight to the potential of various natural extracts as replacements for physical and chemical methods of synthesizing nanoparticles, eliminating the need for additional capping agents or typical industrial surfactants that are challenging to remove post NPs synthesis and poses a threat to the environment. The recent characterization techniques used in examining the identities of manganese oxide nanoparticles were described in detail. To improve the green approach to synthesis, characterization and applications of manganese oxide nanoparticles more research should be carried out to provide more information regarding various factors that influence green synthesis of manganese oxide nanoparticles and the different techniques that can be used for characterization of the synthesized manganese oxide nanoparticles for its more efficient future applications in different industries.

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