

***Citrullus Lanatus* Peel Extract Templated Synthesis of ZnO/MnO₂ Nanocomposites for Electrochemical Lead Detection and Quantification in Aqueous Solution**



Sartu Mohammed Ahmed

A Thesis Submitted to Department of Applied Chemistry

College of Applied Natural Science

**Presented in Partial Fulfillment of the Requirements for the Degree of Master
of Science in Chemistry (Analytical Chemistry)**

Office of Graduate Studies

Adama Science and Technology University

September, 2024

Adama, Ethiopia

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Sartu Mohammed Ahmed

Advisor: Defaru Negera (Ph.D)

Co-Advisor: Eneyew Tilahun (M.Sc)

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DECLARATION

I hereby declare that this Master Thesis entitled “***Citrullus Lanatus Peel Extract Templated Synthesis of ZnO/MnO₂ Nanocomposites for Electrochemical Lead Detection and Quantification in Aqueous Solution***” is my original work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

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We, the advisor(s) of this thesis, hereby certify that we have read the revised version of the thesis entitled “***Citrullus Lanatus* Peel Extract Templated Synthesis of ZnO/MnO₂ Nanocomposites for Electrochemical Lead Detection and Quantification in Aqueous Solution**” prepared by Sartu Mohammed Ahmed under our guidance submitted in partial fulfillment of the requirements for the degree of Master of Science Degree in Chemistry (Analytical Chemistry). Therefore, we recommend the submission of a revised version of the thesis to the department following the applicable procedures.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic absorption spectroscopy
ASV	Anodic stripping voltammetry
BCPE	Bare carbon paste electrode
BET	Brunauer-Emmett-Teller
BWE	Bare working electrode
CNT	Carbon nano tube
CV	Cyclic voltammetry
DPV	Differential pulse voltammetry
EIS	Electrochemical impedance spectroscopy
E_{pc}	Cathodic peak potential
E_{pa}	Anodic peak potential
E_g	Band gap
FAAS	Flame atomic absorption spectroscopy
FT-IR	Fourier transform infrared
GCD	Galvanostatic charge-discharge
GFAAS	Graphite furnace atomic absorption spectroscopy
GO	Graphene oxide
HMI	Heavy metal ion
HTM	Heavy toxic metal
ICP-MS	Inductively coupled plasma mass spectrometry
I_p	Peak current

I _{pa}	Anodic peak current
I _{pc}	Cathodic peak current
JCPDS	Joint committee on powder diffraction standard
LOD	Limit of detection
LOQ	Limit of quantification
MCPE	Modified carbon paste working electrode
MGCE	Modified glassy carbon electrode
MO	Metal oxide
MWE	Modified working electrode
NCs	Nanocomposites
NPs	Nanoparticles
PVA	Poly vinyl alcohol
QD	Quantum dot
SEM-EDX	Scanning electron microscopy-Energy dispersive X-ray
SWASV	Square wave anodic stripping voltammetry
SWV	Square wave voltammetry
TEM/HRTEM	Transmission electron microscopy/high resolution transmission electron microscopy
TGA/DTA	Thermo-gravimetric Analysis/Differential Thermal Analysis
UV-Vis	Ultraviolet visible
UV-Vis DRS	Ultraviolet Visible Diffuse Reflectance Spectroscopy

WE	Working electrode
WHO	World health organization
WWTP	Wastewater treatment plant
XRD	X-ray diffraction

ABSTRACT

Contamination of water by heavy toxic metals poses significant health risks, with lead being particularly harmful due to its severe impact on human health and ecosystems. Due to this, accurate detection and quantification of lead are crucial for ensuring safe drinking water and preventing lead poisoning. Among various detection methods, electrochemical techniques have gained prominence approach because of enhanced sensitivity, selectivity, and rapid response, particularly when electrode surfaces are modified with nanoparticles (NPs) and nanocomposites (NCs). This study explores the green synthesis of ZnO, MnO₂, and ZnO/MnO₂ NCs with different ratios using *Citrullus lanatus* peel extracts. Comprehensive characterization was performed using TGA/DTA, XRD, FTIR, SEM-EDX, UV-Vis DRS, BET, CV, and EIS. Qualitative phytochemical analysis of *Citrullus lanatus* peel extract revealed the presence of various bioactive compounds. XRD analysis confirmed the formation of NPs and NCs, revealing a crystallite size of 17.05, 22.6, 15.6, 17.33, and 17.4 nm for ZnO, α -MnO₂, and ZnO/ α -MnO₂ NCs at ratios of 1:1, 1:2, and 2:1, respectively. FTIR confirmed the presence of functional groups responsible for reduction and stabilization during biosynthesis. SEM-EDX analysis showed spherical nanoparticles within the nanometer range and successful formation of stable and pure NPs and NCs. UV-Vis DRS confirmed the formation of NPs and NCs, with ZnO showing a sharp absorbance around 366 nm and α -MnO₂ absorbing over the visible range, resulting in band gaps of 3.00 and 1.36 eV, respectively. ZnO/ α -MnO₂ NCs showed absorption edges around 380 nm, 450 nm, and 375 nm, with band gap values of 2.43, 2.35, and 2.29 eV for ratios of 1:1, 1:2, and 2:1, respectively. The specific surface area, pore size, and pore volume were determined using BET, indicating a higher surface area for the 1:2 ratios. Electrochemical characterization using CV and EIS showed enhanced electrode performance with ZnO/ α -MnO₂ NCs modified working electrode (MWE). Lead detection and quantification were performed in an acidic environment (0.1M HCl) using chronoamperometry at -1.1 V for 240 s, with further optimization using square wave anodic stripping voltammetry (SWASV). The study found that ZnO detected approximately 0.112 ppm of Pb²⁺, while α -MnO₂ detected around 0.150 ppm. Among the NCs, 1:2 ZnO/ α -MnO₂ MWE detected 0.171 ppm of Pb²⁺. Under these optimized conditions, Pb²⁺ quantification was conducted with the ZnO/ α -MnO₂(1:2) MWE across concentrations ranging from 0.074 to 0.016 ppm, yielding a calibration curve with a correlation coefficient (R^2) of 0.93577. The LOD for Pb²⁺ was determined to be 0.008 ppm. The NCs exhibit excellent sensitivity in lead detection and quantification, making it promising for accurately monitoring toxic heavy metals in water.

Keywords: ZnO/ α -MnO₂ nanocomposites, *Citrullus lanatus*, Modified working electrode and lead detection.

1. INTRODUCTION

1.1 Background of the Study

Wastewater contaminants refer to various substances and pollutants in water that pose risks to human health and the environment. There are two types of water pollution: point-source pollution and non-point-source pollution. Point sources, such as smokestacks, drainage tubes, industrial waste, municipal wastewater treatment plants (WWTPs), factories, and power plants, contribute to water pollution. Non-point sources include thunderstorms, runoff, oils, grease, animal wastes, pesticides, and fertilizers (Akhtar et al., 2021). Contaminants from domestic sewage can enter surface water through direct or indirect discharge or treated effluents from WWTPs. Domestic sewage contains organic matter, nutrients, pharmaceuticals, and personal care products (El-sayed, 2020). Storm water runoff contains pollutants, which can affect the quality of surface water, seepage water and ground water. These contaminants can originate from heavy metals such as lead, zinc, copper, cadmium, polycyclic aromatic hydrocarbons, mineral oil hydrocarbons and readily soluble salts in runoff which are partly regarded as hazardous to water (Müller et al., 2020). Agricultural practices can introduce metals, pesticides, fertilizers, pathogens, nutrients, and salts that influence surface water. Industrial wastewater often contains heavy metals, chemicals, and organic compounds, which can be harmful if discharged untreated (Chowdhary et al., 2020).

Heavy toxic metals (HTM) can contaminate water sources, posing significant health risks to humans (Kumar et al., 2019). These metals include lead, arsenic, selenium, mercury, cadmium, copper, zinc, nickel and chromium, among other (Sonone et al., 2021). Among the various HTMs, lead is a heavy, soft, malleable, bluish-grey metal that causes severe illnesses to humans and other living organisms within the natural ecosystem. Wastewater containing lead can originate from various sources, such as mining operations, industrial processes, and plumbing systems with lead fixtures or pipes. Because lead is poisonous and can have negative effects on the environment and human health, its presence in water leads to serious health-related problems (Ghorbani et al., 2020). Furthermore, recent reports confirm that lead does not have any biological role for living organisms, especially humans; instead, it causes complicated and fatal health problems, even leading to death. Consequently, its presence in various sources such as food, water, construction materials, cosmetics, and others, necessitates systematic removal, detection, and quantification processes for human well-being. Particularly, its presence in water bodies is very serious and requires an immediate solution (Naseri et al., 2023).

Detecting and quantifying lead accurately is crucial for ensuring safe drinking water and preventing lead poisoning. Various methods have been developed for lead detection and quantification, each with its advantages and limitations including, graphite furnace atomic absorption spectrometry (GFAAS)(Butcher, 2023). atomic absorption spectrometry (AAS) (Inobeme et al., 2023), Flame atomic absorption spectrometry (FAAS) (Jagirani et al., 2021), inductively coupled plasma mass spectrometry (ICP-MS) (Chen et al., 2021), and UV-Vis spectroscopy (Firdaus et al., 2023). Nevertheless, these methods are expensive, time-consuming, and unsuitable for on-site analysis. Thus, it is important to develop a simple, rapid, and cost-effective method for Pb^{2+} ion detection and quantification. Among these methods, electrochemical techniques have gained prominence due to their sensitivity, selectivity, and rapid response, essentially when the electrode surface is modified to improve the sensitivity and selectivity (Inobeme et al., 2023; Shirsat & Hianik, 2023). Nanoparticles (NPs) and nanocomposites (NCs) are integrated onto electrode surface to significantly enhance their response due to their unique properties, such as high surface area, quantum size effects, and enhanced catalytic activities. The high surface area of NPs and NCs increases the number of active sites available for interactions, improving sensitivity and detection limits. Additionally, their small size allows for better penetration and interaction with analytes, leading to more accurate and faster responses (Hassan et al., 2021).

Many NPs and NCs are synthesized using various physical and chemical methods. However, the high cost and toxicity associated with these techniques have led to the development of a more cost-effective, reliable, and eco-friendly green synthesis method. This green method utilizes different parts of plants, making it the most preferred approach for synthesizing nanomaterials. Specifically, for lead detection, these green synthesized NPs and NCs have shown promising results, offering a safer and more environmentally benign option compared to chemical methods. Green synthesis of several promising NPs and NCs have been extensively investigated for lead metal detection and quantification such as Au NPs (Huynh et al., 2022), Ag NPs (Ahmed et al., 2020), CuO/PANI (Slimane Ben Ali et al., 2023), TbFeO₃/CuO NCs (Mahmoudi-Moghaddam et al., 2022), Au/TCODS/BN NCs (Lalmalsawmi et al., 2021), Ag/ChS NCs (Sarikokba et al., 2024) etc. However, instead of using green parts of plants, the use of various sections of fruit and vegetable wastes has been found to be too green method and economically as well was environmentally friendly.

Watermelon, scientifically known as *Citrullus lanatus*, belongs to Cucurbitaceae Family under Genus Citrullus. It is grown almost all over the world including Africa, Asia, the United States and Russia. It is mainly composed of water, which is about 6% sugar and 92% water by weight (Harith et al., 2018). The skin of the *Citrullus lanatus* contains flavonoids, glycosides, alkaloids, tannins, saponins, polysaccharides, and phenols (Fadillah et al., 2021). *Citrullus lanatus* peel extract also contains cucurbitacins, triterpenoid compounds that give the extract its characteristic bitter taste. Cucurbitacins have been extensively researched for their potential therapeutic properties (Feyisayo & Durojaye, 2018). The phenolic compounds present in the peel extract can remove heavy metals and organic pollutants from wastewater through adsorption mechanisms (Yuan et al., 2023). The polysaccharides in the extract act as coagulants or flocculants, aiding in the aggregation and removal of suspended particles (Popoola et al., 2022). Bioactive substances in the peel extract can effectively regulate the shape and growth of NCs. Besides its traditional medicinal uses and as a food source, the peel of the plant can also be used for the synthesis of stable NPs and NCs due to its abundant bioactive ingredients (Ogundare et al., 2021).

Recently, several studies have been conducted on chemical and biological synthesis of ZnO/MnO₂ NCs for the desired applications. However, till currently, none previous reports described synthesis of ZnO/MnO₂ NCs using *Citrullus lanatus* peel extract as a high surface area catalytic modified working electrode (MWE) for the electrochemical lead detection and quantification. As a result, the research was exploring the application of *Citrullus lanatus* peel extract as a template for the formation of stable ZnO/MnO₂ NCs within various compositions for the electrochemical lead detection and quantification, the proposed research will fill a major gap. This could potentially result in the development of highly selective and sensitive MWE for the detection and quantification of lead ion in aqueous solutions.

1.2 Statement of the Problem

Lead is a heavy metal that is extremely toxic and dangerous to both human and environmental health. Lead exposure remains a widespread problem worldwide despite efforts to control it, especially in regions with aging infrastructure, industrial activity, and lead-based products. Lead exposure can happen by eating or drinking contaminated food or water, or by inhaling contaminated dust particles and aerosols. Lead poisoning in humans damages the kidneys, liver, heart, brain, skeleton and the nervous system. In children, chronic exposure to low levels of lead may decrease their intelligence capacity (Kamel et al., 2024).

Previously, traditional analytical techniques for detecting and quantifying lead includes; ICP-MS, AAS, X-ray fluorescence, ion chromatography, and UV-Vis spectroscopy were explored intensively. Nevertheless, despite their high sensitivity, precision, and versatility in terms of their ability to trace various metal ions, these techniques had several limitations, such as complex analytical processing, time-consuming and tedious sample preparations, costly equipment and their inapplicability for onsite applications (Inobeme et al., 2023). In contrast to traditional techniques, electrochemical methods have gained considerable interest due to their relative ease of operation, rapid response, cost-effective fabrication, low-cost instrumentation at high accuracy and precision, and wide linearity of sample concentrations (Tüzün & Atun, 2023). The use of electrochemical methods in the presence of bare electrode for lead detection and quantification poses significant challenges due to the need for sensitive and selective detection methods.

In recent years, the use of green synthesized NCs as a high surface area catalytic working electrode has emerged as a promising approach to enhance the detection and quantification performance of the bare working electrode (BWE). However, the green synthesis of NCs to modify the BWE with desirable properties remains a key issue (Munonde & Nomngongo, 2021). One potential solution to this challenge is the utilization of *Citrullus Lanatus* peel extract as a natural and eco-friendly template for the synthesis of ZnO/MnO₂ NCs. Since the modification of WE using high surface area NCs result in the formation of smooth and homogenous MWE having high electron transfer kinetics, enhanced charge transfer behavior, and improved electrochemical properties in general. This in turn results for the simple systematic detection and quantification of Pb²⁺ present in water with improved specific sensitivity, selectivity and stability. Therefore, the target of this thesis work was focused on the synthesis of ZnO/MnO₂ NCs and their single NPs in the presence of *Citrullus lanatus* peel extract within various volume ratios for the lead detection and then quantification via square wave anodic stripping voltammetry (SWASV). The study were also focused on the effect of composition variation on the fabrication of green alternative catalytic MWE for both detection and quantification of Pb²⁺ ions considering various parameters that could affect the lead detection and quantification process.

1.3 Objectives of the Study

1.3.1 General Objective

- ✚ To synthesize and characterize ZnO/MnO₂ NCs and their respective single oxide NPs in the presence of *Citrullus lanatus* peel extract for the electrochemical detection and quantification of lead ions in aqueous solution.

1.3.2 Specific Objectives

- ✚ To synthesize ZnO, MnO₂ NPs and ZnO/MnO₂ NCs within various composition ratios using *Citrullus lanatus* peel extract as a template.
- ✚ To characterize synthesized ZnO and MnO₂ NPs and ZnO/MnO₂ NCs using TGA/DTA, XRD, UV-Vis DRS, SEM-EDX, FTIR, BET, CV and EIS
- ✚ To prepare MWE using green synthesized ZnO and MnO₂ NPs and ZnO/MnO₂ NCs.
- ✚ To optimize the experimental parameters, such as accumulation time, deposition potential and analyte concentration.

1.4 Significance of the Study

The findings of this research contribute to the advancement of nanotechnology and hold promise for the development of improved high surface area catalytic MWE for the electrochemical detection as well as quantification of lead contaminants in aqueous solutions. This research is essential for monitoring environmental and public health. Organizations that monitor the environment, water treatment plants, and regulatory bodies in charge of ensuring water quality will all be benefited from this research. By incorporating this technology into their current monitoring systems, industries involved in water treatment and wastewater management can achieve real-time detection and take prompt action to mitigate lead pollution. Furthermore, researchers in the fields of analytical chemistry, environmental science, and materials engineering will gain valuable insights into the design and optimization of NCs for enhanced electrochemical performance, leading to broader applications in environmental monitoring and heavy metal detection.

1.5 Scope of the Study

The scope of the study involves collection, preparation, and extraction of aqueous templating agent from *Citrullus lanatus* peel. Then latter, both ZnO and MnO₂ NPs were synthesized within the volume ratios of 1:1 using extract of *Citrullus lanatus* followed by the green synthesis of ZnO/MnO₂ NCs with in the compositions of 1:2, 1:1, and 2:1. Synthesized NPs and NCs were then characterized via TGA/DTA, XRD, FTIR, SEM-EDX, UV-Vis DRS, BET, CV and EIS techniques. At the end, MWE were fabricated using the synthesized NPs and NCs techniques for lead detection and quantification.

2. LITERATURE REVIEW

2.1 Nanoparticles

NPs are extremely small particles, ranging in size from 1 to 100 nanometers. Very interesting features of NPs are tiny size, large surface area, high reactivity, catalytic behavior, and ease of separation. Additionally, they provide a vast number of active sites for interaction with different pollutants and impurities. Furthermore, NPs enable the control of permeability and fouling resistance in a variety of structures and relevant functionalities (Shameem et al., 2021). By adding the proper functional groups at the appropriate times, the performance of the NPs could be improved. Their high electrical density at their edges makes the attachment possible (Saleh et al., 2019). NPs can be divided into metal based, metal-oxide based (MO), and carbon based NPs. MO NPs have gained significant attention due to their unique chemical and physical properties, such as high surface area, tunable electronic structure, and remarkable catalytic activity. These characteristics make them highly suitable for various applications. Specifically, their ability to undergo redox reactions and interact with biological molecules has made them invaluable in the modification of electrodes in the electrochemical techniques. Currently, the modification of electrodes with MO NPs has drawn great attention in the field of industrial, environmental, and food analysis owing to their attractive performance because they offer high sensitivity, selectivity, and stability for detecting and quantifying a wide range of analytes (Dhiman & Kondal, 2021).

2.1.1 Zinc Oxide Nanoparticles

In materials science, ZnO is classified as a n-type metal oxide semiconductor II-VI, with a covalence that lies between that of ionic and covalent semiconductors. Its high bond energy (60 meV), wide energy band (3.37 eV), and strong mechanical and thermal stability at room temperature make it a desirable candidate for use in laser technology, optoelectronics, and electronics. ZnO NPs exhibit excellent semiconducting properties, high catalytic activity, and strong UV absorption capabilities. It can be used as a sensor, converter, energy generator, and photocatalyst due to its piezoelectric and pyroelectric properties. Although the mineral displays a yellow to red color, pure ZnO without the presence of natural contaminants is colorless due to its large band gap. Its low toxicity, biocompatibility, and biodegradability make it a material of interest for biomedicine and pro-ecological systems. Its hardness, rigidity, and piezoelectric constant make it an important material in the ceramics industry. Considering these benefits, a number of recent review papers have detailed advancements in the development and use of diverse ZnO nanostructures with distinct morphologies (Rafique et al., 2022).

ZnO is a fascinating material with a unique crystal structure that plays a crucial role in its properties and applications. ZnO can crystallize in three different forms, as shown in Figure 1: hexagonal wurtzite, cubic zinc blende, and rock salt. Hexagonal wurtzite of ZnO is the most thermodynamically stable material under normal condition. The unit cell consists of two interpenetrating triangular lattice structures, forming a three-dimensional network. Each Zn atom is surrounded tetrahedrally by four oxygen atoms, and each oxygen atom is coordinated to two zinc atoms, corresponding to sp^3 covalent bonding. However, it is possible to stabilize 12 cubic zinc blende by growing ZnO on cubic substrates. ZnO in the rock-salt framework would only occur at relatively high pressure (Özgür et al., 2018).

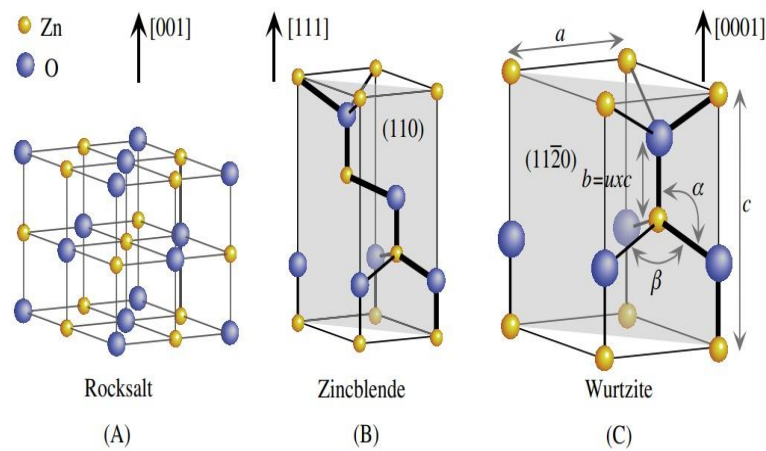


Figure 1 Stick and ball representation of ZnO crystal structures (Özgür et al., 2018).

2.1.2 Green Synthesis of Zinc Oxide Nanoparticles

Table 1 Green synthesis of ZnO NPs using various sources.

Plant(Part extracted)	System	Morphology	Activity carried out	Reference
<i>Acanthus sennii</i>	ZnO NPs	Spherical	Sensing of ascorbic acid (AA) and degradation of acid orange 88 (AO88) dye.	(Bekele et al., 2022a)
<i>Allium cepa</i> (<i>A. cepa</i>) peel extract	ZnO NPs	Spherical	Cu (II) removal	(Canbaz et al., 2023)

<i>Musa acuminata</i> peel extract	ZnO NPs	Hexagonal	Degradation of methylene blue	(F. H. Abdullah et al., 2020)
<i>Rosmarinus officinalis</i>	ZnO NPs	Spherical	Photocatalytic degradation of dyes	(Saad Algarni et al., 2022)
<i>Carica</i> Papaya seed extract.	ZnO NPs	spherical	Sensing activities of silymarin	(Sharma et al., 2018)
<i>Centella asiatica</i> plant extract	NiO, CuO, and ZnO NPs	Hexagonal	Photocatalysis and sensor	(Alam et al., 2021)
<i>Ficus benghalensis</i> extracts	ZnO NPs	Spherical	Cr (VI) removal	(Irshad et al., 2024)
<i>Sphagneticola trilobata</i> Lin	ZnO NPs	Spherical	Adsorption of Chromium metal	(Shaik et al., 2020)
<i>Eucalyptus</i> spp. leaves	ZnO NPs	Spherical	CR (VI) and MG dyes removal	(Chauhan et al., 2020)
<i>Shorea robusta</i> (Sal) Leave extract	ZnO NPs	Spherical	Adsorption study of Pb ²⁺ and Cd ²⁺	(Chandra Joshi & Singh, 2020)
<i>Zingiber zerumbet</i> Smith and <i>Zingiber aromaticum</i>	ZnO NPs	Spherical	Absorbtion of Pb ²⁺ ions	(Azizi et al., 2017)
<i>Ocimum tenuiflorum</i> leaves	ZnO NPs	Spherical	Adsorption of Cd ²⁺ and Pb ²⁺ from solutions	(Elsamra et al., 2023)

2.1.3 Manganese Oxide Nanoparticles

MnO₂, is type of magnetic transition metal, is getting attention among researchers in the field of nanotechnology due to its low toxicity. MnO₂ is a p-type semiconductor with a narrow energy bandgap (1.44 eV). MnO₂ NPs can form a variety of nanostructures, including MnO, MnO₂, Mn₂O₃, and Mn₃O₄. They have multiple oxidation numbers (+2, +3, +4). Because MnO₂ can form several polymorphs, such as α -, β -, γ - and δ - MnO₂, it has many useful applications. It has a dark brown to black color and is insoluble in water. MnO₂ NPs have a high stability, high surface area, robustness and excellent catalytic activity due to their crystal structure, which makes them promising materials for a variety of applications (Baral et al., 2021).

MnO₂ exists in different polymorphs, but they all have the same fundamental MnO₆ structure that is connected in a different way. MnO₂ NPs can be distinguished from one another according to structural linkages. The manganese and oxygen atoms in MnO₂ NPs are bonded together in a distorted octahedral coordination, which is characteristic of the tetragonal rutile crystal type. The manganese atoms occupy the octahedral sites within the oxygen framework; whereas the oxygen atoms are form a close-packed arrangement. As illustrated in Fig.2 numerous crystal types of MnO₂ have been reported, including one-dimensional chain or tunnel structure like α -MnO₂(hollandite), β -MnO₂(pyrolusite), and γ -MnO₂(nsutite), a laminar or layered two-dimensional structure like δ -MnO₂(birnessite), and a three-dimensional structure like λ -MnO₂(akhtenskite) (Dawadi et al., 2020).

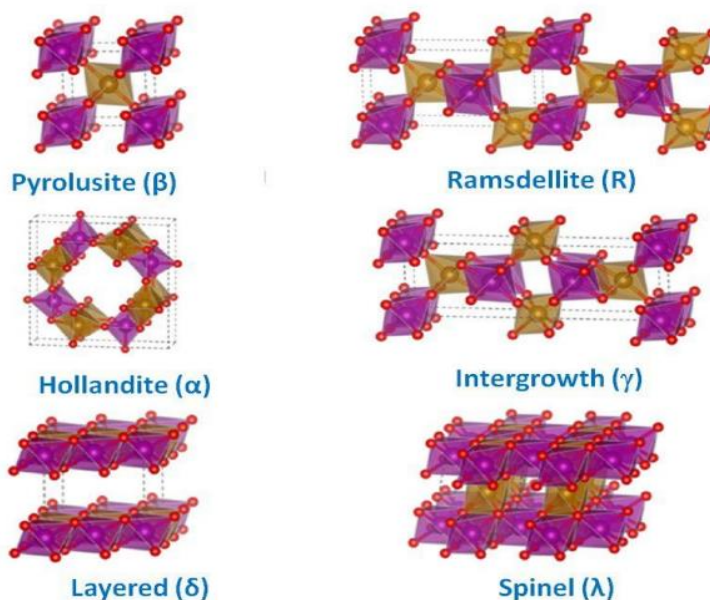


Figure 2 The polymorphs of MnO₂ with well-defined crystalline phases (Kitchaev et al., 2016).

2.1.4 Green Synthesis of Manganese Oxide Nanoparticles

Table 2 Green synthesis of MnO₂ NPs using various sources.

Plant (Part extracted)	System	Morphology	Activity carried out	Reference
<i>Punica granatum</i> plant extract	MnO ₂ NPs	Spherical	Adsorption of Co ²⁺ , Ni ²⁺ , and Cu ²⁺ ions	(Ali & Abdul Kareem, 2024)
<i>Populus nigra</i> (leaf extract)	MnO ₂ NPs		Adsorption of nortriptyline antidepressant and celestine blue dye.	(Akpomie & Conradie, 2023)
<i>Acacia nilotica</i> seed extract	MnO ₂ NPs loaded on the surface of biochar	Cross-linked structure	Methyl Orange removal from aqueous solutions	(Taha & Daffalla, 2023)
<i>Ficus retusa</i> (mulberry family) leaf extract	α -MnO ₂ NPs	Spherical	Adsorption of anionic dyes	(Srivastava & Choubey, 2021)
<i>Ficus benjamina</i> leave extract	MnO ₂ NPs	Spherical	Adsorption of malachite green	(Hasan et al., 2023)
Mango leave	δ -MnO ₂ NPs	Spherical	Dye removal	(Ghosh et al., 2023)
Buffelgrass, <i>Cenchrus ciliaris</i> (L.)	MnO ₂ NPs	Hexagonal	Removal of Ni ²⁺ ions	(Kiruba et al., 2022)
<i>Saraca asoca</i> leaf extract	MnO ₂ NPs	Stacked cubes	Evaluation of invitro anticancer activity	(Majani et al., 2023)
Extract of Aloe vera	MnO ₂ NPs	Spherical	Antibacterial Activity	(Joshi et al., 2020)

2.2 Nanocomposites

NCs represent a cutting-edge class of materials that have gained significant attention in recent years. NCs are multiphase solids in which one of the phases has dimensions of 1, 2, or all 3 less than 100 nm. NPs, nanofibers, and nano-clays are examples of nanomaterials found in NCs. Nanoscale material dimensions result in phase interface interactions, which are crucial for improving the material's properties. The NCs material, which is made up of metallic, non-metallic, and polymeric materials through a particular process, offers additional advantage of retaining primary features to overcome defects and express of some new characteristics (Omanovi et al., 2019). A high surface-to-volume ratio, improved thermal stability, enhanced electrical conductivity, superior barrier properties (effectively preventing the permeation of gases, liquids, or solutes), and exceptional mechanical strength are just a few of the unique and enhanced properties of the NCs (Hassan et al., 2021).

Several NCs synthesis techniques have been used, including chemical, physical reduction, and microwave-assisted synthesis (Chaudhary et al., 2021). However, there are several problems associated with the implementation of these processes in the biological environment due to the use of toxic materials as reducing agents. To address this, an emerging technique is the use of a green technology approach to NCs synthesis. Non-toxic and natural agents such as fungi, bacteria, and plant extracts have been used in this approach to act as stabilizing, capping, and reducing agents in the process of NCs fabrication (Singh, 2022).

Table 3 Green synthesis of NCs using various sources.

Plant (part extracted)	System	Activity carried out	Efficiency	Reference
<i>Psidium guajava</i> leaf extract	Ag/ChS NCs	Detection of Pb ²⁺	LOD of 1.97 µg/L.	(Sarikokba et al., 2024)
<i>Mangifera indica</i>	Polypyrrole/ZnO NCs	Removal of Cu ²⁺ , Pb ²⁺ and Cd ²⁺ ions from Wastewater	Adsorptive removal of 1.96, 1.68, and 1.17 mg/g, respectively.	(Joshi et al., 2021)
<i>Ocimum basilicum</i> plant	MnO ₂ /waste eggshell NCs	Adsorption studies of crystal violet dye	Maximum adsorption of 149.25 mg/g	(Moeen et al., 2022)

<i>Citrullus lanatus</i>	Ferrocenyl-modified MnO ₂ /carbon-based NCs	Storage application	Good performance	(Teimuri-Mofrad et al., 2022)
Pomegranate juice (from fruit seed) and wheat extract	graphene/MnO ₂ quantum dot NCs	Detection of Cr ⁶⁺ and Ni ²⁺	(LOD) of 0.33 mgL ⁻¹ for Cr ⁶⁺ and 0.38 mgL ⁻¹ for Ni ²⁺	(Babaei et al., 2022)
Aloe vera and <i>Matricaria recutita</i> extracts	TiO ₂ /MnO ₂ NCs	Removal of Hg ²⁺	80% Hg ²⁺ removal	(Druzian et al., 2023)
<i>Andrographis paniculata</i> leaf extract	Fe ₃ O ₄ /ZnO NCs	Removal of Cd ²⁺ , Pb ²⁺ , and Cr ⁴⁺	99.81%, 99.76% and 98.1% adsorptive degradation efficiency respectively.	(Manojkumar et al., 2023)
<i>Leek</i> leaf	Fe ₂ O ₃ /MnO ₂ (core/shell) NCs	To remove Pb ²⁺ , Cr ⁴⁺ , Ni ²⁺ and Cd ²⁺ from aqueous solutions	Adsorption rate ranging between (84-99) %	(Hayder & Shanani, 2024)

2.2.1 ZnO/MnO₂ Nanocomposites

Anantha et al. (2021) synthesized ZnO/MnO₂ NCs using a single-step hydrothermal process. The chemical and structural features of the ZnO/MnO₂ NCs were characterized using SEM-EDX, XRD, TGA/DTA, and BET analyses. CV measurements revealed that the ZnO/MnO₂-modified carbon paste electrode (MCPE) exhibited significant electrocatalytic enhancement compared to the bare carbon paste electrode (BCPE) for dopamine detection, showing a remarkable 44.50% increase in dopamine oxidation current. The obtained CV studies correlated well with the results from EIS and Tafel analyses. This superior performance was attributed to the MCPE's larger electroactive surface area, excellent sensitivity, stability, reproducibility, and low limit of detection (LOD = 5.0 µM within

the potential range of 0.2 to 0.6 V vs. saturated calomel electrode (SCE)). The redox peak current for MCPE showed good linearity with a correlation coefficient ($R^2 = 0.9996$), indicating a diffusion-controlled process with controlled electron transfer reactions (Anantha et al., 2021). Dubey et al. (2022) synthesized a highly selective electrochemical sensor for detecting 2,4-dichlorophenol (2,4-DCP) in water using a ZnO/ α -MnO₂ hybrid 1D nanostructure. This nanostructure was developed through a facile ultrasound-induced co-precipitation method, combining ZnO nanoparticles and α -MnO₂ nanowires. Comprehensive characterization via XRD, FTIR, SEM, TEM, and EDX confirmed the successful synthesis of the ZnO/ α -MnO₂ hybrid. Impedance analysis showed a linear calibration curve with a regression coefficient ($R^2 = 0.99$) over the concentration range of 1 mM to 0.01 nM. The sensor exhibited remarkable sensitivity (0.45 k Ω /nM/mm²) and LOD of 2 nM, along with stability and reproducibility over 90 days. The equivalent Randles circuit model demonstrated effective electron transfer kinetics. The sensor was highly selective toward 2,4-DCP even in the presence of other organic compounds and maintained performance across varying conditions such as temperature and pH (Dubey et al., 2022). Furthermore, Gupta et al. (2023) hydrothermally synthesized nanostructured MnO₂ to produce ZnO/MnO₂ NCs with weight ratios of 3:7, 5:5, and 7:3. The resulting materials were characterized using XRD, FT-IR, and SEM-EDX. Electrochemical performance was evaluated through CV, GCD, and EIS. Among the NCs, ZnO/MnO₂ (5:5) exhibited the highest specific capacitance of 277.5 F/g at a current density of 0.3 A/g and an energy density of 24.66 Wh/kg at a power density of 49.06 KW/kg, indicating its potential as a promising material for super capacitor devices. These MnO₂ nanostructures combined with ZnO at a 5:5 ratio showed superior stability and specific capacitance compared to other ratios. Specific capacitance values for different ratios were recorded as 27.3, 163.7, 277.5, and 139.7 F/g at 0.3 A/g. The corresponding energy densities were 2.42, 14.54, 24.66, and 12.41 Wh/kg, while power densities were 43.68, 38.77, 49.06, and 48.59 KW/kg, respectively. This highlights the potential of ZnO/MnO₂ NCs for enhancing the performance of super capacitors (Gupta et al., 2023).

El-Moslamy et al. (2024) synthesized ZnO/MnO₂ NCs through a bio-fabrication process using the intracellular extract of *Streptomyces coelicolor* strain E72 as a reducing/capping agent. The NCs, with particle sizes ranging from 6 to 18 nm, were characterized using FTIR, XRD, SEM, TEM, TGA, and EDS analyses. The production process was scaled up by 31.25 times in a 70-L bioreactor, resulting in a significant increase in yield. The ZnO/MnO₂ NCs exhibited potent antimicrobial efficacy against multidrug-resistant human pathogens, such as *Salmonella paratyphi* and *Candida albicans*, making them suitable for applications in pharmaceuticals, cosmetics, wound dressings, and burn treatments due to their powerful antimicrobial properties. The NCs antimicrobial efficiency was

caused by its suppression of pathogen motility, biofilm formation, and development (EL-Moslami, Rezk, et al., 2024). This highlights the potential of bio-fabricated ZnO/MnO₂ NCs for various biomedical applications. Joudi et al. (2024) synthesized ZnO/MnO₂ NCs via a simple hydrothermal process and tested their photocatalytic activity for dye degradation. The structural and optical properties of ZnO, MnO₂, and ZnO/MnO₂ NCs were confirmed using XRD, SEM, UV-Vis DRS, and PL analyses. The ZnO/MnO₂ NCs demonstrated significantly higher photocatalytic activity for Methyl Orange degradation compared to pure ZnO or MnO₂. This enhanced performance was attributed to their increased surface area, efficient sunlight absorption, and improved charge carrier separation. The impact of the ZnO/MnO₂ molar ratio on structural, optical, and photocatalytic properties was investigated. It was found that increasing the amount of MnO₂ led to reduced charge carrier recombination and enhanced charge separation. Specifically, ZnO/MnO₂ NCs containing 10 mg of MnO₂ demonstrated the highest activity, achieving a degradation efficiency of 94.12% after 2 hours of sunlight irradiation, suggesting that optimizing the composition of ZnO/MnO₂ NCs can significantly enhance their photocatalytic performance (Joudi & Naceur, 2024).

2.3 Sources of Wastewater

Wastewater originates from diverse sources such as residential, commercial, and industrial activities (Akhtar et al., 2021). Surface and groundwater can also contribute to wastewater systems, increasing overall volume. The characteristics of wastewater depend on its source: domestic wastewater (from households and businesses) typically contains contaminants like organic matter, grease, detergents, and suspended solids. In contrast, industrial wastewater may contain toxic chemicals, heavy metals, dyes, organic wastes, and varying sediment loads, often at elevated temperatures or with acidic/basic pH levels. Storm-water runoff from streets and parking lots during rainstorms (storm wastewater) may introduce oil, fuel residues, insecticides, herbicides, and additional sediments (El-sayed, 2020). Numerous strategies have been developed to mitigate the discharge and environmental impacts of wastewater pollutants (Rashid et al., 2021).

According to a study conducted in China, the pie chart in Figure 3 provides valuable insight into the distribution of wastewater sources in China, highlighting the need for targeted strategies to manage and treat wastewater from different sectors effectively. The study analyzed the wastewater composition from various sectors and found that industry effluents accounted for the largest share, representing approximately 41% of the total wastewater generated. Heavy metals from agricultural activities (fertilizers and pesticides) followed closely behind, comprising around 30% of the pie chart. Leakages, animal waste as well as sewage and wastewater are the other contributors to water pollution (Antwi et al., 2021).

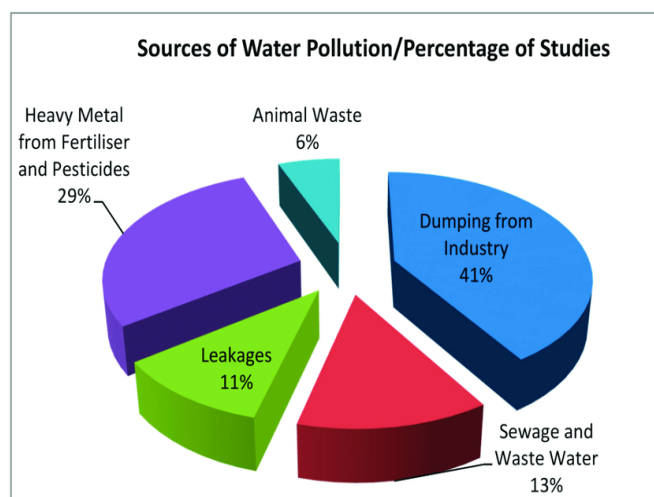


Figure 3 Sources of Water Pollution/Percentage of Studies (Antwi et al., 2021).

2.3.1 Sources of Heavy Toxic Metals in Water

HTM pose a significant threat to water sources, accumulating and spreading through natural and human-related pathways (El-sayed, 2020). These metals, characterized by high density and toxicity even at low concentrations, include copper (Cu), cadmium (Cd), chromium (Cr), zinc (Zn), nickel (Ni), mercury (Hg), arsenic (As), and lead (Pb) (Chowdhary et al., 2020). Extensive research highlights their serious impact on water quality (Akhtar et al., 2021). While essential in trace amounts for metabolic functions, higher amount of these metals can endanger human health. Natural and Anthropogenic activities contribute significantly to their entry into aquatic ecosystems. Figure 2 illustrates the diverse sources of contamination responsible for the presence of heavy metals in water bodies (Sonone et al., 2021).

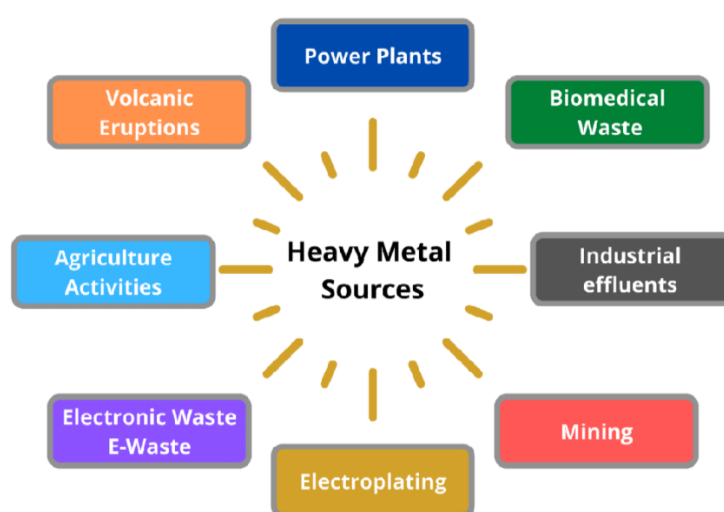


Figure 4 Different sources of contamination heavy metal in water & aquaculture (Sonone et al., 2021).

Natural and anthropogenic activities contribute significantly to the introduction of HTM into water bodies, posing substantial environmental and public health concerns (Raju, 2022). Natural sources such as weathering of rocks, erosion and volcanic eruptions release metals such as arsenic, mercury, chromium, cadmium, and lead into water systems through geological processes (Sonone et al., 2021). Human activities also contribute significantly to HTM contamination. Heavy metals are released into bodies of water by industrial processes, mining operations, improper waste disposal, and agricultural practices (Rashid et al., 2021). Metals such as lead, mercury, and cadmium can be introduced into rivers and lakes by industrial wastewater, while mining activities can introduce metals such as arsenic and copper through mine tailings and runoff (Vareda et al., 2019). Heavy metal contamination can also be caused by agricultural runoff, including the use of fertilizers and pesticides (Akhtar et al., 2021). These heavy toxic metals endanger ecosystems and human health.

2.4 Detection and Quantification of Heavy Toxic Metals

Detecting and quantifying HTM is vital for assessing environmental contamination and protecting public health. Traditional techniques like AAS, ICP-MS, GFAAS, UV-Vis spectroscopy, and X-ray fluorescence provide sensitive and accurate measurements of trace metals (Tüzün & Atun, 2023). However, these methods have limitations, including extensive sample preparation, cleanup, pre-concentration processes, and expensive instrumentation. In recent years, novel detection technologies have been developed to improve monitoring capabilities. Biosensors use biological elements such as plants, enzymes or antibodies for rapid and selective detection. Nanomaterial-based sensors exploit the unique properties of nanomaterials to enhance sensitivity. The choice of detection technique depends on factors like LOD, sensitivity, regulatory standards, concentration range, cost, and potential interference from other matrix components (Shirsat & Hianik, 2023).

2.4.1 AAS

AAS is a widely used method for detecting HTM due to its sensitivity and precision. It operates by measuring the absorption of light by HTM at specific wavelengths, which excites electrons within the atoms. This technique is founded on the principle that ions or atoms absorb light at characteristic wavelengths, leading to electron excitation when exposed to these wavelengths. The absorbed light's quantity is then measured, enabling the determination of the element's concentration in the sample, as described by the Beer-Lambert law, which states that the amount of absorbed light is directly proportional to the concentration of the element. AAS has numerous advantages, including high accuracy, ease of operation, cost-effectiveness, and high sensitivity, detection at low concentration making it a reliable choice for HTM detection. It also minimizes interference from other elements, further enhancing its reliability. Despite some limitations, such as the need for extensive sample

preparation and potential interference in complex matrices, its benefits significantly outweigh these drawbacks, maintaining its widespread application in environmental and industrial monitoring of HTM (Inobeme et al., 2023). Tibebe et al. (2022) highlighted these aspects, emphasizing the technique's effectiveness in providing accurate measurements of metal concentrations in various samples. The concentration of selected heavy metals was analyzed in honey samples. They digested 1 g of honey using a hot plate with 9 ml of HNO_3 and 3 ml of H_2O_2 . The concentrations of heavy metals in the digested samples were measured using a flame atomic absorption spectrometer. The study found concentrations of Zn ranging from 1.97 to 2.04 $\mu\text{g/g}$, Cu from 1.93 to 2 $\mu\text{g/g}$, Mn from 0.83 to 1.01 $\mu\text{g/g}$, Cr from 0.25 to 0.45 $\mu\text{g/g}$, and Cd from 0.025 to 0.031 $\mu\text{g/g}$, while Pb was undetected. These levels were below the World Health Organization's permitted limits, indicating the honey is safe for consumption (Tibebe et al., 2022).

2.4.2 ICP-MS

ICP-MS is another widely utilized spectroscopic technique for detecting HTM. It measures the emission of light from HMIs when excited by an electric discharge in argon plasma. This method uses a quadrupole mass spectrometer to rapidly and continuously determine the mass of various elements, allowing for detection at extremely low concentrations, even as low as one part per quadrillion. Presently, ICP-MS can identify over seventy different elements, with detection limits in the trillion ranges and a linear range extending up to nine orders of magnitude. ICP-MS has several advantages in HTM quantification, making it a prevalent tool in metal analysis. It is renowned for its high sensitivity, precision, and speed. Unlike AAS, which measures only one element at a time, ICP-MS can simultaneously detect and quantify multiple elements. However, it also introduces potential interferences from argon plasma and contamination from cones and glassware. Despite these challenges, ICP-MS stands out for its continuous sample analysis capability, offering uninterrupted detection of analytes. One major concern with ICP-MS is dealing with these interferences, which can complicate the analysis (Inobeme et al., 2023). Chen et al. (2021) developed a novel thiol-grafted magnetic polymer (MPPs-SH) through a "click reaction" between 1,2-ethanedithiol and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{poly}(\text{ethylene glycol dimethacrylate-co-glycidyl methacrylate})$. The resulting MPPs-SH exhibited a high sulfur content (5.4 wt%) and possessed a large specific surface area ($156.8 \text{ m}^2\text{g}^{-1}$). It demonstrated significant adsorption capacities of 254, 64.2, and 56.6 mgg^{-1} for mercury, cadmium, and lead ions, respectively. The researchers developed a method combining magnetic solid-phase extraction with ICP-MS for quantifying trace levels of mercury, cadmium, and lead in environmental water samples. Optimization of extraction conditions, pH, sample volume, sorbent amount, adsorption/desorption time, and elution volume, was conducted. Under optimal conditions, the

method achieved extraction of the three heavy metal ions from 150 mL aqueous solution within 10 minutes, followed by elution using 0.2 molL⁻¹ HNO₃ containing 2% thiourea in 5 minutes. The method demonstrated low LOD (0.21, 0.82, and 2.9 ngL⁻¹) for Hg²⁺, Cd²⁺, and Pb²⁺, respectively (Chen et al., 2021).

2.4.3 UV-Vis spectroscopy

UV-Vis spectroscopy is a widely used technique for detecting HTM in solution. It involves illuminating the sample with electromagnetic radiation across the UV-Vis and near-infrared regions of the spectrum and measuring the absorption of UV-Vis light by heavy metal ions (HMI) in solution. The transmitted light is recorded using a detector, producing the UV spectrum of the sample. Concentrations of specific analytes in aqueous media are determined by measuring absorbance at particular wavelengths, which is then calculated using Beer's law. The absorbance is directly proportional to the analyte concentration, and the UV-Vis device's linearity can be influenced by parameters such as signal-to-noise ratio, instrument resolution, stray light interferences, and molecular and ionic interactions at high concentrations. UV-Vis spectroscopy is particularly effective in quantifying transition metal ions and highly conjugated compounds in solution. It determines the molar absorptivity of various HTMs, which allows for concentration calculations based on a calibration curve. The relationship between metal ion concentrations and absorptivity intensity is typically linear, enabling precise quantification (Inobeme et al., 2023). UV-Vis spectroscopy is highly sensitive and capable of detecting HMIs at very low concentrations. It offers significant advantages such as flexibility, ease of use, and minimal training requirements due to the simplicity of the generated data. This non-destructive technique allows for subsequent analysis of the sample and is relatively cost-effective compared to other spectroscopic instruments. However, it also has limitations. Interferences from other species in the matrix that absorb radiation can affect accuracy, and measurement errors may occur due to light scattering by solid particles in the sample solution. Numerous studies have documented the reliable use of UV-Vis spectroscopy for HTM detection, demonstrating its effectiveness in producing consistent and accurate results (Barzegarzadeh et al., 2023).

Firdaus et al. (2023) introduced a novel method for the simultaneous determination of Cr³⁺ and Cr⁶⁺ ions using Au NPs as a colorimetric agent, coupled with smartphone-based detection and validation by UV-Vis spectrometry. They used a small amount of Au NPs (1 mM) due to its high selectivity and sensitivity towards Cr³⁺ and Cr⁶⁺ ions. The peak absorbance of Au NPs shifted from 520 nm to 630 nm for Cr³⁺ and to 370 nm for Cr⁶⁺. These shifts were linearly proportional to Cr concentration, with linear relationships observed at specific absorbance ratios. The UV-Vis spectrometer's detection

limits were 0.051 ppm for Cr^{3+} and 0.035 ppm for Cr^{6+} , while the smartphone-based method showed a 22% improvement in detection limits. The method was tested on drinking and tap water samples, demonstrating satisfactory accuracy ($< 2.0\%$) and precision ($< 5.0\%$) (Firdaus et al., 2023).

2.4.4 Electrochemical Techniques

The electrochemical approach for detecting HTMs has gained significant attention due to its rapid detection capabilities, operational simplicity, cost-effectiveness, and suitability for on-site field applications. Several electrochemical techniques are employed for HTM detection and quantification, including potentiometry, square wave voltammetry (SWV), cyclic voltammetry (CV), differential pulse voltammetry (DPV), electrochemical impedance spectroscopy (EIS), and anodic stripping voltammetry (ASV). These methods offer various advantages in terms of sensitivity, selectivity, and adaptability to diverse analytical settings (Shirsat & Hianik, 2023). CV is commonly used technique for detecting HMIs. It involves applying a potential ramp to an electrode immersed in a solution containing HMIs, and the resulting current is measured. This provides valuable insights into the electrochemical behavior and redox properties of the HMIs. SWV is known for its sensitivity and specificity in detecting HMIs. This technique applies a series of square-wave potential pulses to an electrode in a solution containing HMIs. The subsequent current measurement reveals detailed information about the electrochemical behavior of the HMIs (Inobeme et al., 2023; Shirsat & Hianik, 2023). ASV is a highly sensitive method for detecting HMIs in aqueous solutions. The instruments used in ASV are portable and relatively affordable. ASV operates through a two-step process: first, analytes are deposited onto the electrode surface, and then they are oxidized into the underlying electrolyte. The rate of metal deposition on the electrode is influenced by factors such as concentration, electrode area, and solution diffusion parameters. The subsequent stripping step is crucial for detection, as it generates the signal by measuring the oxidation potential of each analyte, which corresponds to the current produced during oxidation. ASV can detect HMIs at very low concentrations and is capable of determining multiple elements simultaneously. This method is valued for its high efficiency in quantifying HMIs. SWASV further enhances ASV by introducing a square wave modulation on the potential during the stripping process. This modulation enhances sensitivity and precision by distinctly separating oxidation peaks from background interference. SWASV's ability to achieve superior detection limits and accuracy, especially in complex sample matrices, underscores its advancement over conventional ASV methods, making it a preferred choice for demanding trace metal analyses (Tüzün & Atun, 2023).

However, electrochemical methods come with certain limitations, such as higher LOD and lower sensitivity compared to other techniques. Enhancing these methods often involves coupling them

with different bio-sensing electrodes and modifying electrode materials to improve sensitivity and LOD. These electrochemical techniques, with their unique strengths and limitations, provide versatile and powerful tools for the detection and quantification of HMIs (Shirsat & Hianik, 2023).

Various researchers have used SWASV for detecting various HMIs. In the development of ultrasensitive and selective sensors for HMIs, significant attention has been directed towards the fabrication of titania-modified carbon paste electrodes endowed with electrochemical sensing capabilities. The study focus into the straightforward preparation of modified electrodes and their application in quantifying trace amounts of hazardous Hg^{2+} , Cu^{2+} and Pb^{2+} ions using SWASV (Tüzün & Atun, 2023). The titania NPs were characterized using various techniques such as size analyzer, XRD, and FTIR to determine their chemical properties. The results highlighted the uniform distribution of titania NPs within the graphite matrix of the electrode, predominantly in crystalline anatase form with an average particle size of 85 nm. The fabricated sensor demonstrated outstanding performance in detecting Hg^{2+} , Cu^{2+} , and Pb^{2+} ions, achieving impressively low LOD of 15.26, 0.56, and 1.65 nM, respectively. Furthermore, simultaneous measurements in ternary solutions revealed heightened sensitivity towards Hg^{2+} and Pb^{2+} ions, with LOD further reduced to 8.32 and 0.25 nM, respectively. These findings underscore the promising potential of titania-modified carbon paste electrodes in sensor applications for accurately determining hazardous HMIs, leveraging the advanced capabilities of SWASV for enhanced sensitivity and selectivity in trace metal analysis.

2.5 Nanocomposites for Heavy Toxic Metal Detection and Quantification

NCs have gained significant attention recently due to their synergistic effects, which enhance the detection of HTM and improve sensing properties. Researchers globally are actively focused on developing and optimizing NCs materials for HTM detection. Various NCs materials, including graphene oxide (GO), carbon nanotubes (CNTs), and MO based NCs, are being explored to detect a wide range of HMIs (Shirsat & Hianik, 2023).

Mohammed et al. (2024) synthesized NCs by integrating nickel tungstate (NiWO_4) with multi-walled carbon nanotubes (MWCNTs), which was then used to modify a carbon paste electrode. Advanced characterization techniques, including XRD, SEM, TGA, and FTIR, were employed to thoroughly analyze the NCs. The electrochemical behavior of Cd^{2+} at the modified electrode interface was investigated using CV, DPV, and LSV. The $\text{NiWO}_4/\text{MWCNTs}$ NCs demonstrated exceptional properties, including high sensitivity, enhanced selectivity, and strong adsorption capacity for cadmium ions. Under optimized experimental conditions, a calibration curve was constructed by measuring the DPV responses for a series of standard Cd^{2+} solutions within the concentration range

of 50–450 μM . The peak current of Cd^{2+} exhibited a linear relationship with a regression coefficient ($R^2 = 0.989$). The LOD and LOQ for Cd^{2+} were determined from the calibration curves to be 0.12 μM and 0.42 μM , respectively (Mohammed et al., 2024).

Fort et al. (2024) developed an electrode by integrating unprocessed natural clay (nc) within a chitosan (Chi) matrix on a glassy carbon electrode (GCE), resulting in the nc-Chi/GCE modified electrode for the detection of heavy metals such as Zn^{2+} , Cd^{2+} , Pb^{2+} , and Cu^{2+} , both individually and simultaneously. The electrochemical properties of the modified electrode were assessed using EIS and SWASV. EIS results showed that the clay matrix significantly decreased the charge transfer resistance (R_{ct}) compared to the bare GCE, demonstrating the conductive nature of the clay and its efficiency in promoting electron transfer. Notably, the anodic stripping peak current for Pb^{2+} at -0.48 V vs. Ag/AgCl, KCl was 35.5 times higher than that of the bare GCE, emphasizing the substantial enhancement provided by the clay matrix, which improved electron transfer and enabled the detection of low Pb^{2+} concentrations. Optimization of SWASV parameters, including amplitude, frequency, deposition potential, and accumulation time, was carried out using the nc-Chi/GCE electrode in the presence of 90 nM Pb^{2+} . The electrode exhibited outstanding electrochemical performance, successfully detecting all four heavy metals at low concentrations. Sensitivity and detection limits (LOD) were determined through calibration curves, with LOD values of 4.3 nM for Pb^{2+} , 19.1 nM for Cd^{2+} , 43.5 nM for Zn^{2+} , and 57.3 nM for Cu^{2+} . This high sensitivity is attributed to the synergistic effect of the clay's large active surface area and high porosity, which provides significant interaction with heavy metal ions (Fort et al., 2024).

Luyen et al. (2024) synthesized a ZnO-electrochemically reduced graphene oxide (ZnO/ErGO) NCs and utilized it to modify a glassy carbon electrode (GCE) for the electrochemical detection of Pb^{2+} and Cd^{2+} . They found that the ZnO/ErGO-modified GCE (ZnO/ErGO-GCE) had a significantly larger surface area of 0.130 cm^2 compared to the bare GCE's 0.083 cm^2 . The charge transfer resistance also decreased substantially from 3212 Ω for the bare GCE to 924 Ω for the ZnO/ErGO-GCE, indicating a faster electron transfer rate for the modified electrode. The ZnO/ErGO-GCE exhibited superior electrochemical performance in detecting Pb^{2+} and Cd^{2+} compared to ErGO-GCE and the bare GCE. The peak current showed a linear relationship with Cd^{2+} and Pb^{2+} concentrations in the 2.5–200 μM range. The detection limits for Cd^{2+} and Pb^{2+} were 1.69 ppb and 0.45 ppb, respectively. The modified electrode exhibited a low detection limit, wide linear detection range, high stability, suitable reproducibility, accuracy, and good recovery, making it a promising candidate for manufacturing electrochemical sensors (Luyen et al., 2024).

2.5.1 Nanocomposites Based Lead Detection and Quantification

Lead ion is a HTM that poses serious environmental and health risks, despite its widespread industrial use. The World Health Organization has set a stringent limit of 0.01 mgL^{-1} for Pb^{2+} in drinking water (Kamel et al., 2024).

Sarikokba et al. (2024) fabricated a highly efficient NCs material on GCE (Ag/ChS/GC) for the trace detection of Pb^{2+} using DPV. The Ag/ChS was obtained using 3-trimethoxyoctylsilane grafted chitosan (ChS) and in situ decorated with Ag NPs. The Ag/ChS NCs were synthesized using natural phytochemicals from *Psidium guajava* leaf extract. The electrochemical response of Ag/ChS/GC NCs was significantly increased compared to the bare glassy carbon electrode using the standard probe $\text{Fe}(\text{CN})_6^{3-/4-}$ (100.0 mmol/L acetate buffer at pH 4.5). DPV studies showed that the optimum pH, deposition potential, and deposition time were 4.5, - 0.9 V, and 180 seconds, respectively, for the detection of Pb^{2+} . Under optimized conditions, trace-level detection of Pb^{2+} was achieved using DPV measurements. A reasonably good linear response was obtained ($y \text{ (}\mu\text{A)} = 0.0368 \text{ }\mu\text{g/L} + 3.5742$) with a correlation coefficient ($R^2 = 0.981$) over a wide concentration range of Pb^{2+} from 5.0 to 80.0 $\mu\text{g/L}$ employing (Ag/ChS/GC). The LOD was 1.97 $\mu\text{g/L}$. The stability of the fabricated electrode was confirmed with repeated operations, and their %RSD was found to be less than 5%, indicating reasonably high stability. Recovery studies using spiked Pb^{2+} in both water samples showed good recovery of the analyte (95.52 - 96.06% for spring water and 92.95 - 102.57% for groundwater) (Sarikokba et al., 2024).

Ghafoor et al. (2023) synthesized a cobalt-derived metal-organic framework (MOF), ZIF-67 and incorporated onto the surface of GO using a simple sonication method. ZIF-67/GO, NCs was characterized by various techniques including FTIR, XRD, SEM, and Raman spectroscopy. The ZIF-67/GO NCs was then used by drop-casting it onto GCE. This platform was employed for the individual and simultaneous detection of HMIs (Hg^{2+} , Zn^{2+} , Pb^{2+} , and Cr^{3+}). The estimated LOD for these ions were 2, 1, 5, and 0.6 nM, respectively, which are below the permissible limits set by the World Health Organization. CV of the synthesized ZIF-67/GO NCs showed an enhanced redox response, reduced resistance as measured by EIS, and significant DPV response for each metal ion. While ZIF-67 and GO individually display higher resistivity and lower conductivity, their incorporation resulted in a significant decrease in resistance at the electrode/electrolyte interface. This indicates a synergistic relationship between ZIF-67 and GO, establishing strong chemistry between the two components and making the NCs an ideal candidate for HMI detection with excellent electrochemical capability (Ghafoor et al., 2023).

Kamel et al. (2024) Synthesized zinc/iron layered double hydroxide (LDH) and polyaniline (PANI) (Zn-Fe LDH/PANI) as a model LDH/conductive polymer NCs, representing a promising class of economical multifunctional materials. The NCs electrochemical properties were investigated for the detection of HMIs in water, focusing on lead as a model heavy metal. Zn-Fe LDH/PANI NCs was utilized as modifiers for a carbon paste electrode. The NCs was characterized using XRD, SEM, and FTIR. The electrochemical redox reactions of lead Pb^{2+} ions at the modified electrode interface were studied using CV and DPV. The study established a linear relationship for Pb^{2+} ions in the concentration range of 1-80 μ M, with a LOD of 167.8 nM and a LOQ of 559.4 nM. Additionally, the cost-effectiveness of using this material for lead removal was compared with conventional methods such as ICP-MS or AAS for monitoring heavy metal removal during adsorption processes. Cost analysis revealed that the final overall cost of the modified electrode is estimated as less than 1% of the total cost required to conduct the same adsorption study using a typical ICP-MS or AAS equipment. This shows that this NCs can be regarded as a cheap and multifunctional composite that may find numerous applications in portable onsite pollutant detection in water streams using disposable electrodes (Kamel et al., 2024).

Zhou (2024) synthesized NCs of MWCNTs decorated with ZnO NPs using an in-situ hydrothermal method and applied as a modified electrode for SWV detection of dissolved HMIs. The MWCNT/ZnO NCs exhibited a high specific surface area of 53 m^2/g and enhanced charge transfer conductivity up to 26 S/cm. SWV demonstrated broad linear detection ranges: Cu^{2+} from 1-800 ppb, Pb^{2+} from 5-1000 ppb, and Hg^{2+} from 1-900 ppb, with low LOD of 0.8, 1.2 and 0.7 ppb, respectively. The NCs showed 3-5X higher sensitivity compared to an unmodified screen-printed carbon electrode, highlighting performance improvements achieved through the tailored hybrid interface. Selectivity tests revealed distinct and well-resolved oxidation peaks for each metal ion target, unaffected by high concentrations of Mn^{2+} , Co^{2+} , and Fe^{3+} interferents (Zhou, 2024).

3. MATERIALS AND METHODS

3.1 Chemicals and Reagents

During this work, numerous chemicals and reagents were used, such as distilled water, hydrated zinc acetate (99.7%, Sigma-Aldrich, India), potassium permanganate (99%, Sigma Aldrich, India), sodium hydroxide (97%, Sigma Aldrich, Germany), ethanol (>97%, Fmd, Ethiopia), hydrochloric acid (37%, Alpha Chemika, India), potassium hydroxide (>85.0% sigma Aldrich, Mumbai, India), polyvinyl alcohol (98%, Thermo Fisher Scientific India Pvt. Ltd.) and lead acetate trihydrate (99%, GIDC, India).

3.2 Equipment and Instruments

Knife, grinder, analytical balance, spatula, pipette beakers, volumetric flasks, measuring cylinders, funnels, whatman no1 filter paper, water bath, autoclave, centrifuge (80-2B), aluminum foil, magnetic stirrer, pH meter, bare magnet, centrifuge tube, test tube, brown bottle, ceramic crucible, refrigerator, nickel foam (>99.99%, thickness 1.6mm, Korea), potentiostat (Model CHI604E, Inc. Austin, USA), Pt-wire counter electrode, Ag/AgCl reference electrode, pH meter, TGA/DTA (DTG-60H detector, Shimadzu, Japan), XRD (XRD-7000, Shimadzu, Japan), UV-Vis DRS (UV-Vis1800-double beam spectrophotometer, Shimadzu, Japan), SEM-EDX (SEM S-4700/EDS JEOL-2010, Tokyo, Japan), FT-IR (FT/IR-6600typeA, Jasco, Tokyo, Japan), BET (NOVA 4200 Quantachrome Instruments, Boynton Beach, USA) were equipment and instruments used throughout the work.

3.3 *Citrullus Lanatus* Peel Collection and Extraction

Initially, the healthy normal fruit of *Citrullus lanatus* was collected from agricultural research center (Debreziet). The fruit was then surface cleaned several times with distilled water to avoid any surface impurities. The peel and the internal section of the fruit were separated carefully using a knife. The separated peel was sub-divided into smaller pieces and allowed under shadow dry until all the moisture content was completely removed. The dried peel of the fruit was then ground using plant grinding machine to obtained fine powder. The peel powder was then packed within aluminum foil for further use.

For the aqueous extraction, 50 gram of peel powder was added to 1000 mL of distilled water. The extraction was performed at 50°C for 1 hr. afterward; the formed suspension was allowed to cool to room temperature followed by filtering. The filtrate was then placed in a red colored glass container and stored in a refrigerator at 4°C for further procedures (Jha et al., 2022). The graphical peel extraction procedure is depicted in Figure 5.

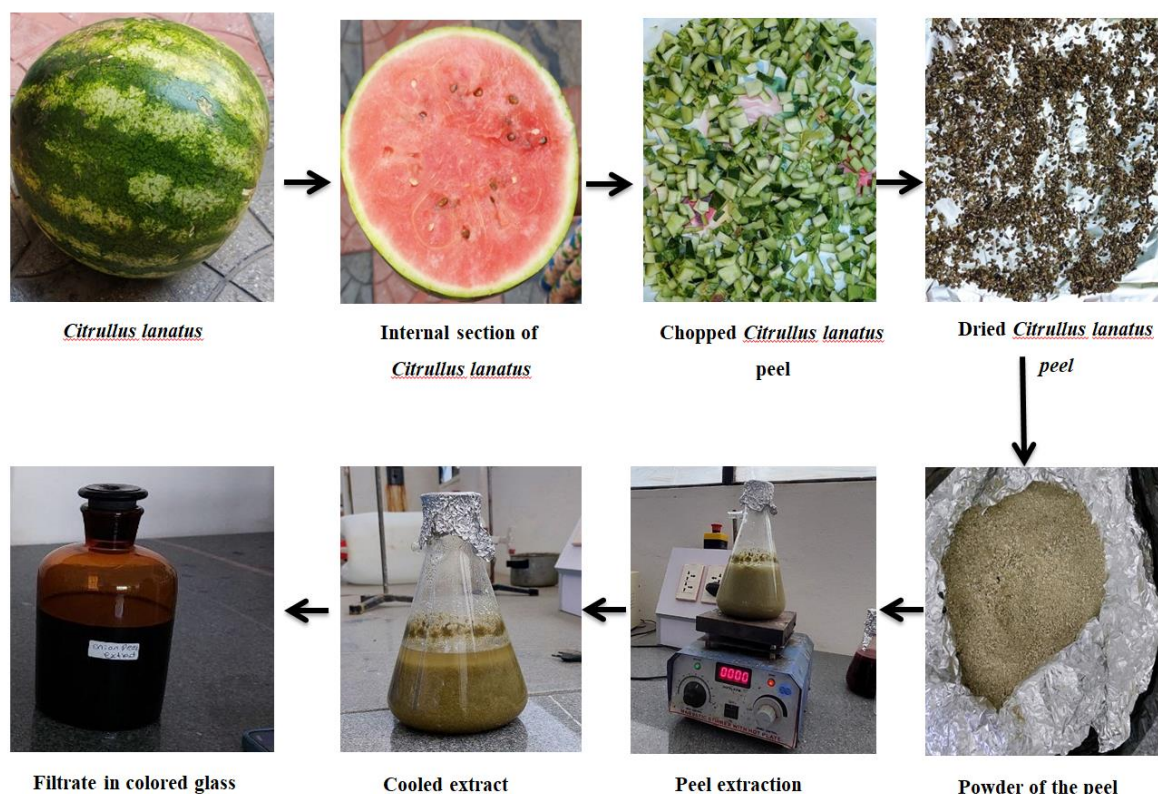


Figure 5 General process for the collection and preparation of *Citrullus lanatus* peel extract.

3.4 Phytochemical Test of *Citrullus Lanatus* Peel Extract

In order to practically confirm the presence/absence of bioactive ingredients such as flavonoids, phenols, alkaloids etc... within the *Citrullus lanatus* peel extract; before using for the synthesis of the targeted NPs and NCs as stabilizing/capping and reducing agent, certain phytochemical investigations were carried out. The presence of these phytochemicals indicates the extract's potential effectiveness in stabilizing, reducing and capping agents.

i. Test for Tannins (Ferric Chloride Test)

5 mL of aqueous peel extract was dissolved in 5 mL of distilled water and three drops of 1% ferric chloride solution were added to confirm the presence of tannins (Shaikh & Patil, 2020).

ii. Test for Flavonoids

The presence of flavonoids in the peel extract was checked through an alkaline reagent test by using 5 mL of aqueous peel extract treated with three drops of NaOH solution (Garg et al., 2019).

iii. Test for Alkaloids (Wagner's test)

The presence of alkaloids in the peel extract checked through Wagner's test by using the aqueous peel extract of 2 mL suspension dissolved in 2 mL of Wagner's reagent (Iodine in Potassium Iodide) in the test tube (Suja Associate Professor & Suja, 2018).

iv. Test for Terpenoids (Salkowski test)

The presence of terpenoids in the peel extract was checked through chloroform by using 4 mL of extract followed by the addition of 3 mL of chloroform. Then, 3 mL of concentrated sulfuric acid (H_2SO_4) was carefully added to form a layer (Balasundram et al., 2006).

v. Test for Steroids

The presence of steroids in the peel extract was checked through Salkowski test by using 2 mL of chloroform and concentrated H_2SO_4 added to the 5 mL aqueous peel extract (Yaseen et al., 2017).

vi. Test for Glycoside

The presence of glycoside in the peel extract was checked through salkowski test by using 2 mL of concentrated H_2SO_4 added to 5 mL of aqueous peel extract (Suja Associate Professor & Suja, 2018).

vii. Test for Reducing Sugar

The presence of reducing sugar in the peel extract was checked through the benedict test by using 3 mL of aqueous peel extract taken into a test tube then 3 mL Benedict reagent was added drop by drop and heated for 5min (Sk et al., 2024).

viii. Test for Phenols

The presence of the phenolic functional group in the peel extract was checked by using 5 mL of aqueous peel extract taken into a test tube and 5 drop of 3% of FeCl_3 added in to an extract drop by drop (Yaseen et al., 2017).

ix. Test for Saponins

The presence of saponins in the peel extract was checked through a frothing test by using 3 mL of aqueous peel extract dissolved in 5 mL of distilled water and the mixture was shaken vigorously (Bano & Deora, 2019).

3.5 Synthesis of ZnO and MnO_2 Nanoparticles

For comparison purpose, ZnO and MnO_2 NPs were synthesized in the presence of *Citrullus lanatus* peel extract. The biosynthesis of ZnO NPs followed the previous literature with slight modification (Al-Tameemi et al., 2023). Briefly, 0.5M of 100 mL of $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ precursor and 100 mL of the peel extract (1:1) were mixed and stirred for 4 hrs at room temperature. Upon completion of the reaction time, the pH of the solution was adjusted to be 11 using 1M NaOH. The formed suspension was then stirred for an additional 20 minutes to ensure the homogenization of the base and then refrigerated overnight. The resulting suspension was centrifuged 3 times at 1500 rpm, followed by washing using absolute ethanol and distilled water at each step. The precipitates were collected in a ceramic dish and dried at 80°C until all the moisture contents were removed. The dried ZnO sample

then allowed for thermal stability analysis in order to identify the calcination temperature. Figure 6 illustrating the graphical synthesis procedure of ZnO sample.

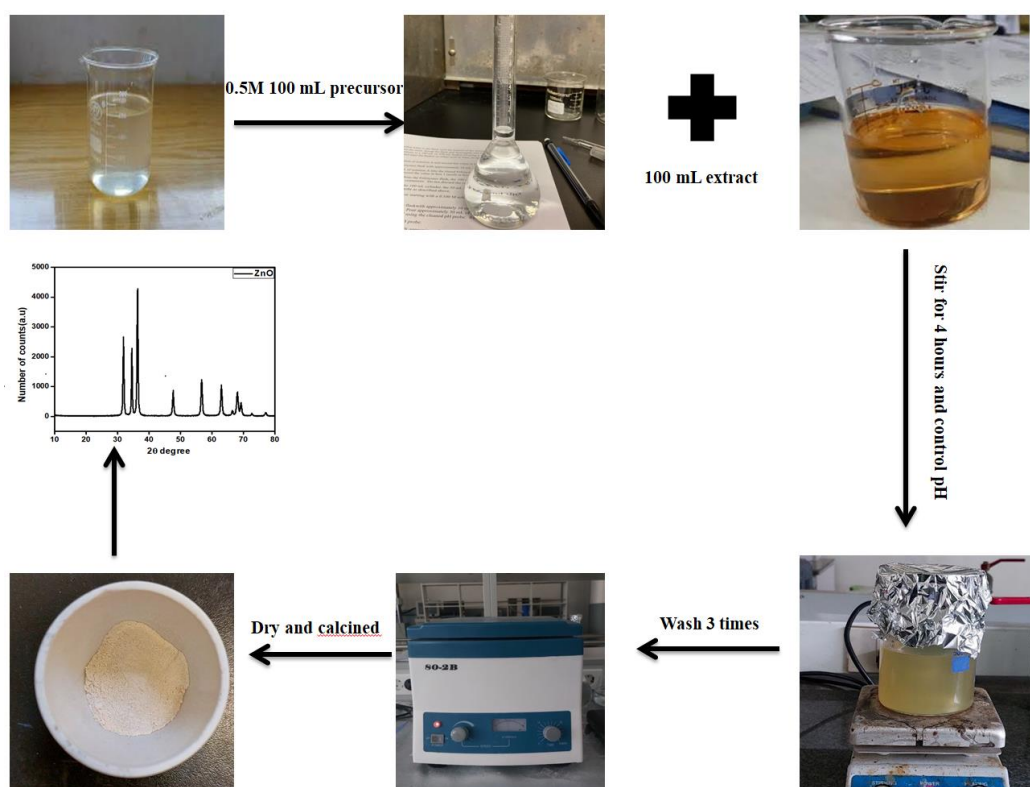


Figure 6 Biosynthesis process of ZnO NPs.

The biosynthesis of MnO_2 NPs followed the previous literature with slight modification (Joshi et al., 2020). Briefly, 100 mL of aqueous peel extract was added to 0.5M 100 mL of KMnO_4 salt. The mixture was stirred for about 4 hrs at room temperature. After the reaction was completed, the pH of the suspension was adjusted to 11 by adding 1M NaOH , followed by an additional 20 minutes of stirring. The suspension was then refrigerated overnight. The formed suspension was separated by centrifugation three times at 1500 rpm using ethanol absolute and distilled water at each step. The material was dried in an oven at 80°C until all moisture was removed, and then further calcined in a muffle furnace based on TGA/DTA data obtained. Figure 7 illustrates the entire process of MnO_2 NPs synthesis.

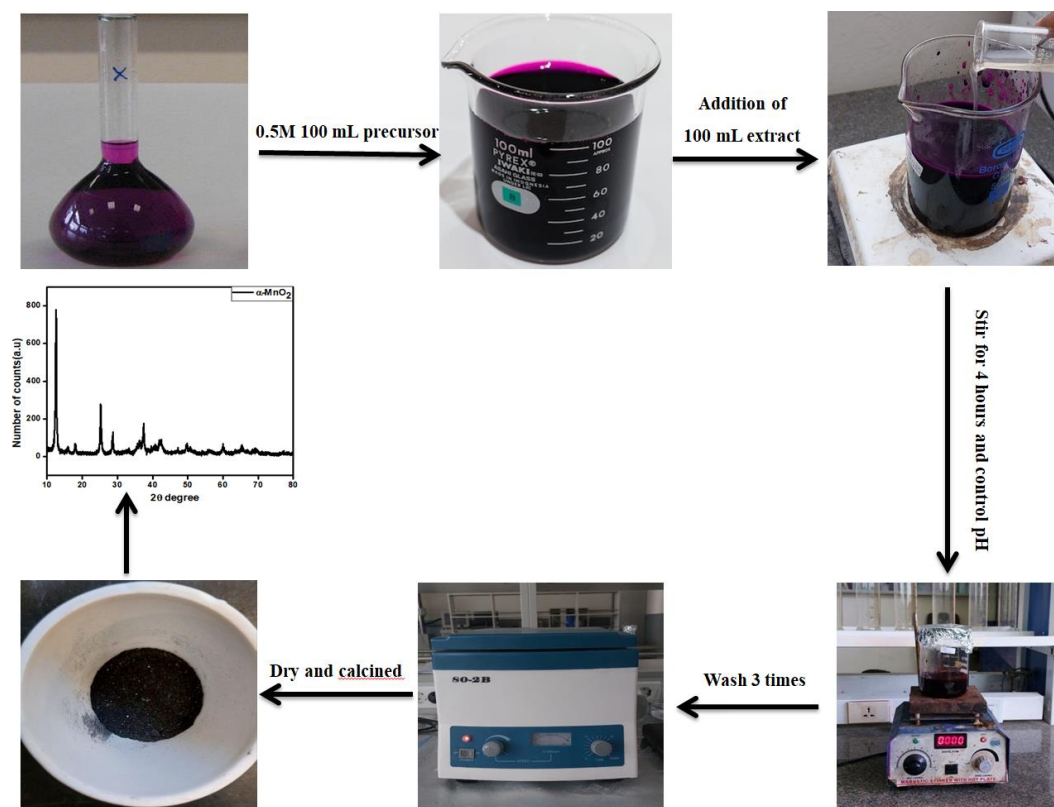


Figure 7 Biosynthesis process of MnO_2 NPs.

3.6 Synthesis of ZnO/MnO_2 Nanocomposites

In the biosynthesis of ZnO/MnO_2 NCs, the procedure was adopted from the literature with minor modifications (Dessie et al., 2021). Briefly, 0.5M of 80 mL of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was mixed with 0.5M of 80 mL KMnO_4 (1:1). The formed solution was continuously mixed in a beaker on a controlled hot plate at 80°C and a pH of 8. After 15 minutes later, 20 mL of extract was added drop wise. The reaction mixture was stirred for 4 hrs. The suspension was left overnight and the precipitate was centrifuged at 1500 rpm for 15 minutes, followed by washing with ethanol and distilled water three times. Then, the collected sample were further dried by using an oven at 80°C and grinded to a fine powder. The grinded ZnO/MnO_2 sample was then calcined based on the TGA/DTA data obtained. The procedure is depicted in Figure 8.

The synthesis of ZnO/MnO_2 NCs with 1:2 and 2:1 ratios of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ to KMnO_4 was performed with modified volumes of KMnO_4 . For the 1:2 ratio, 0.5 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was prepared in 80 mL of distilled water, and 0.5 M solution of KMnO_4 was prepared using 160 mL. For the 2:1 ratio, the same 80 mL of 0.5 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution was used with 40 mL of 0.5 M KMnO_4 solution. These solutions were combined and stirred at 80°C maintaining a pH of 8. After 15 minutes, 20 mL of extract was added drop-wise, and the mixture was

stirred for 4 hrs. The mixture was left overnight, and the precipitate was centrifuged at 1500 rpm for 15 minutes, followed by washing with ethanol and distilled water three times. The precipitate was dried at 80°C and ground into a fine powder. Finally, the powder was calcined based on TGA/DTA data obtained.

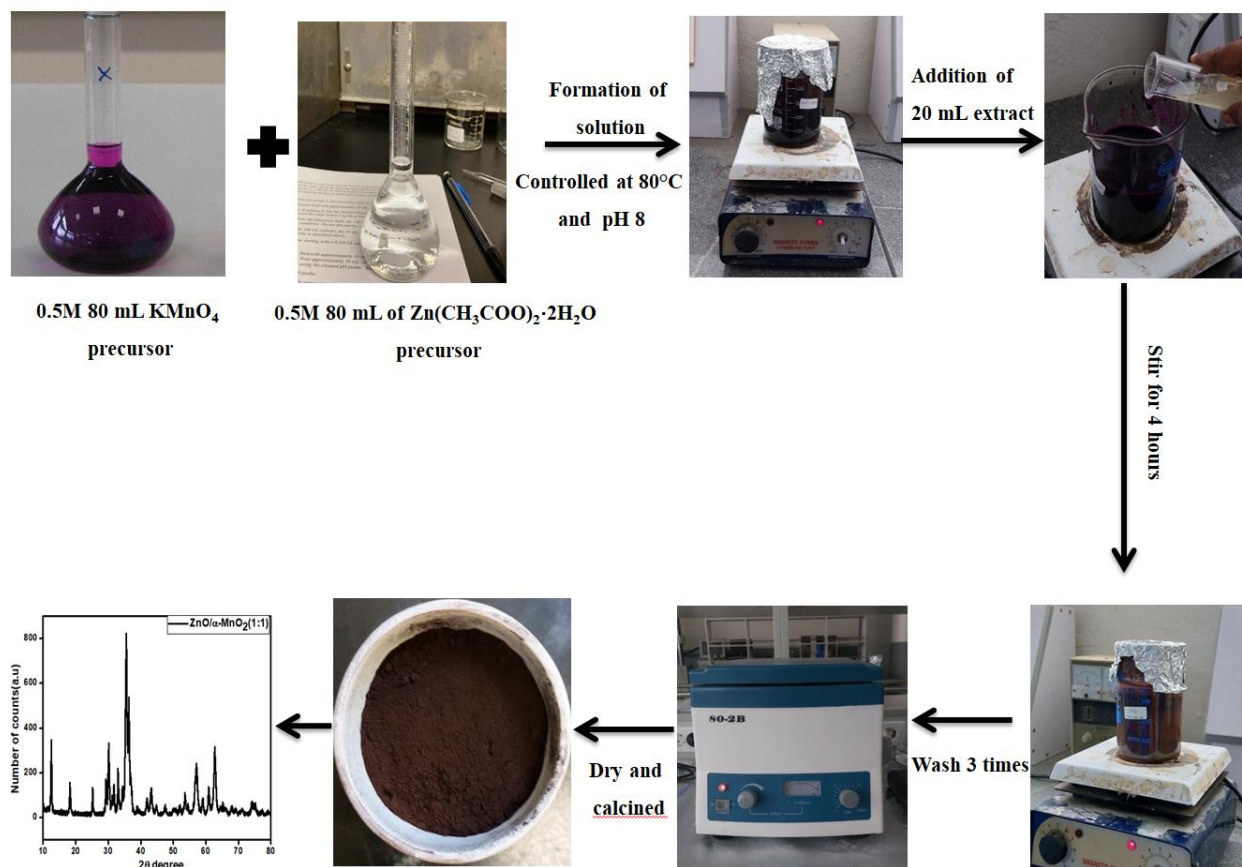


Figure 8 Schematic diagram of the synthesis procedure of biosynthesized of $\text{ZnO}/\text{MnO}_2(1:1)$ NCs.

3.7 Characterization Techniques

The formation of pure and stable ZnO and MnO_2 NPs as well as ZnO/MnO_2 NCs was achieved through a series of analyses including TGA/DTA, XRD, SEM-EDX, FTIR, UV-Vis DRS and BET. These techniques were employed to provide comprehensive surface characterization, functional group analysis, and detailed insights into the structural and optical properties of the NCs (Bekele et al., 2022; Gupta et al., 2023; Issa & Hanan, 2022).

3.8 Working Electrode Preparation

In this study, the preparation of MWE was done by taking a $1 \times 1 \text{ cm}^2$ bare nickel foam. The prepared bare nickel foam was then cleaned by washing with 1M HCl, DH_2O , and absolute ethanol. The cleaned bare nickel foam was then allowed for shadow dry. Then, from each of the green synthesized NPs and NCs, 4 mg was taken and poured in to a 10 mL glass vial followed by addition of 200 μL

polyvinyl alcohol (PVA) and 200 μL of DH_2O . The mixed components was then stirred for 30 minutes and soaked for 24 hrs to ensure proper homogenization. For the preparation of stable MWE, from each of the individually soaked sample, 10 drops was casted on the surface of the cleaned dry nickel foam and allowed for shadow drying, ensuring even adherence and distribution. The prepared MWE with the sample was left to dry and then used for further electrochemical analysis (Dhandapani et al., 2024; Khan et al., 2023; LI et al., 2023).

3.9 Electrochemical Characterization Techniques

CV and EIS were employed to characterize the BWE and MWE electrodes using a potentiostat (Ivium). A conventional three-electrode system was utilized, with the MWE serving as the working electrode, platinum as the counter electrode, and Ag/AgCl as the reference electrode, all immersed in a 1M KOH solution. CV scans were performed over a potential range of 0.0 to +0.7 V with scan rates varying from 10 to 110 mV/s. EIS measurements for the bare as well as MWE covered a frequency range from 100 kHz to 0.2512 Hz at a scan rate of 50 mV/s. These techniques were applied to assess the electrochemical properties of the materials (Bekele et al., 2022; Dhandapani et al., 2024).

3.10 Lead Detection and Quantification

Chronoamperometry and SWASV were conducted using potentiostat connected to a personal computer. The SWASV measurements followed the preconcentration steps. Initially, a 0.1 M HCl solution (pH 3.25) as transferred into the voltammetric cell and a known amount of Pb^{2+} was spiked into it. The MWE were immersed into the cell containing the electrolyte and Pb^{2+} ions were deposited on their surface using chronoamperometry by applying negative potential vs Ag/AgCl for a specified duration. Subsequently, a rest period (2 s) was allowed for the solution to be stabilized. Then the anodic stripping step was conducted by scanning in the positive potential direction from -1.4 V to 0 V vs. Ag/AgCl. Following these steps, various optimization parameters such as scanning potential, scanning time, and analyte concentration were the basic parameters, which were considered (Ghafoor et al., 2023; Vijayalakshmi et al., 2024; Zhou, 2024).

4. RESULTS AND DISCUSSION

4.1 Phytochemical Analysis of Peel Extract

The qualitative phytochemical analysis of *Citrullus lanatus* peel extract reveals the presence of various bioactive compounds. *Citrullus lanatus* peel extract was prepared by aqueous extraction of the dried and grounded plant as the first step in the biosynthesis of NPs and NCs. Table 4 and Figure 9 summarizes the results obtained from the analysis. The qualitative phytochemical analysis of the peel extracts reveals the presence of tannins, alkaloids, terpenoids, steroids, glycoside, reducing sugars, phenols and saponins, which all have the potential to play a significant role in the formation of NPs and NCs (Ogundare et al., 2021). Therefore, these bioactive compounds can act as reducing agents (that reduce the metal ions to form NPs), stabilizers/capping agents, influencing the size, shape, stability, and surface properties of synthesized NPs and NCs. The color changes were indicative of the presence of phytochemicals in the peel extract. Additionally, variations in color changes may also be observed depending on the specific test being performed. The exact color change (Intensity) can vary depending on the concentration and types of phyto-constituents present in the extract, and can also be influenced by other compounds present in the peel extract (Sk et al., 2024).

Table 4 Phytochemical test results of the peel extract.

No.	Phytoconstituents	Chemical test/Reagent	Results	Colors observed
1	Tannins	Ferric Chloride Test	+	Brownish-Orange
2	Flavonoids	Alkaline Reagent Test	-	White (Expected Color Yellow)
3	Alkaloids	Wagner`s Test	+	Brownish-Orange precipitate
4	Terpenoids	Salkowski Test	+	Reddish-Brown layer
5	Steroids	Salkowski Test	+	White-Yellowish layer
6	Glycoside	Salkowski Test	+	Reddish-Black
7	Reducing sugars	Benedict`s Test	+	Brown-Green
8	Phenols	Ferric Chloride Test	+	Brownish-Orange
9	Saponins	Frothing Test	+	Stable Persistent Froth

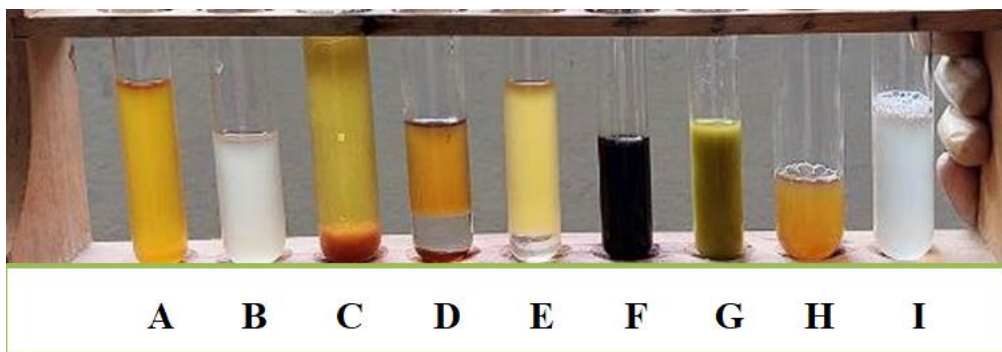


Figure 9 Phytochemical test colors observed when the extract is tested for A) Tannins, B) Flavonoids, C) Alkaloids, D) Terpenoids, E) Steroids, F) Glycoside, G) Reducing sugars, H) Phenols, I) Saponins.

4.2 TGA/DTA Analysis

The TGA/DTA analysis was conducted to study the thermal stability and decomposition behavior of the NPs and NCs as well as to determine their calcination temperature. TGA curve shows mass loss of the sample whereas the DTA curve indicates the energy gain or loss during the process. Figure 10 illustrates the TGA/DTA curve of uncalcinated ZnO NPs, MnO₂ NPs and ZnO/MnO₂(1:1) NCs, which were scanned at the rate of 15 °C/min in the range of 27-800°C under nitrogen atmosphere. The TGA/DTA analysis was conducted by taking about 9.5 mg of ZnO, MnO₂, and ZnO/MnO₂ (1:1) NCs, respectively.

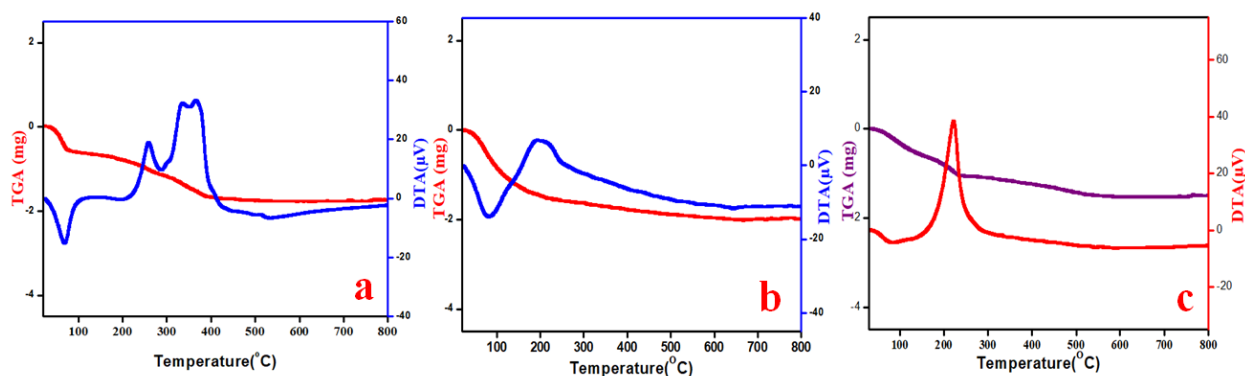


Figure 10 TGA/DTA graphs of uncalcinated ZnO NPs, MnO₂ NPs and ZnO/MnO₂ (1:1) NCs.

The TGA curve of ZnO illustrated in Figure 10 (a) exhibits weight loss in three distinct steps. The first weight loss of 5.74% up to 75°C is attributed to the evaporation of solvent and surface-adsorbed moisture on the ZnO NPs. The second weight loss of 17.42% occurring between 75°C and 395°C indicates the process of carbonization, likely due to the presence of fruit-derived components and other surface adsorbates. The final weight loss of 18.35% between 395°C and 509°C corresponds to the crystallization of the prepared nanomaterial during the heating process. The DTA curve of ZnO

shows an endothermic peak at $-15.26 \mu\text{V}$, corresponding to the loss of physically adsorbed water. As the temperature increases, a significant thermal event with an exothermic peak of $18.79 \mu\text{V}$ suggests the decomposition of organic residues or other surface adsorbate. Another prominent exothermic peak at $32.12 \mu\text{V}$ indicates a major decomposition process, likely associated with the carbonization. Additionally, an exothermic peak at $33.15 \mu\text{V}$ might indicate further decomposition processes or structural changes within the ZnO material. The TGA analysis reveals a total weight loss of 18.35% for ZnO NPs. As depicted from the TGA/DTA graph, no further weight loss is observed starting at 510°C , confirming that the green-synthesized ZnO NPs are thermally stable. Thus, 510°C is a suitable calcination temperature for the formation of stable ZnO NPs (Tadesse Ayanie et al., 2024).

Figure 10(b) also depicts the TGA/DTA curve of MnO_2 NPs showing two distinct weight loss steps. The first weight loss of 16.07% occurs between $27\text{--}216^\circ\text{C}$ and is attributed to the evaporation of surface water and water present in the lattice structured MnO_2 NPs, corresponding to an endothermic peak at $13.92(\mu\text{V})$ on the DTA curve. The second weight loss of 20.45% occurs from $216\text{--}557^\circ\text{C}$, due to the loss of residual organic content, corresponding to an exothermic peak at $6.71 \mu\text{V}$, possibly indicating a phase change. The DTA peaks highlight the thermal events, with the endothermic peak at $13.92 \mu\text{V}$ related to the loss of physically adsorbed water molecules and the exothermic peak at $6.71 \mu\text{V}$ suggesting a phase change. The temperature above which the weight loss becomes constant, 510°C , is used as the calcination temperature for the synthesized MnO_2 NPs to ensure the removal of residual organic content and achieve phase stabilization (Taranu et al., 2022).

TGA/DTA of $\text{ZnO/MnO}_2(1:1)$ NCs is performed to determine its stability as depicted in Figure 10 (c). The NCs experienced a weight loss of 10.95% from $27\text{--}234^\circ\text{C}$, resulted from the loss of surface adsorbed water and related moisture. The second weight loss of 15.59%, in the temperature range of $234\text{--}514^\circ\text{C}$ is attributed to the process of carbonization as indicated by exothermic DTA peaks at $38.25 \mu\text{V}$. $\text{ZnO/MnO}_2 (1:1)$ NCs was thermally stable at a temperature above 514°C . The DTA curve displayed an exothermic peak at $38.25\mu\text{V}$, suggesting a synergistic effect where the interaction between ZnO and MnO_2 enhances the thermal decomposition process. Thus, the NCs showed total weight loss of 15.590 % and the TGA/DTA analysis confirmed that temperatures above 510°C are suitable for calcination (EL-Moslamy, Abd-Elhamid, et al., 2024).

4.3 XRD Analysis

The crystal phase and average crystalline size of green ZnO, α -MnO₂ NPs and each of the various ratios of ZnO/ α -MnO₂ were verified by XRD pattern (R. Wang et al., 2019). Figure 11 shows the XRD pattern of ZnO, α -MnO₂ NPs and each of the various ratios of ZnO/ α -MnO₂ NCs. The analysis was carried out in the range of 10-80° 2 θ values at room temperature using CuK α .

The XRD of ZnO NPs showed sharp peaks at 2 θ value of $\approx$ 31.7°, 34.40°, 36.2°, 47.62°, 56.66°, 62.94°, 66.37°, 67.96° and 69.09° with their corresponding miller indices value of (100), (002), (101), (102), (110), (103), (200), (112) and (201), respectively. The analyzed diffraction peaks agreed with the JCPDS card number of 00-036-1451; which showed hexagonal (wurtzite) ZnO structure (Ismardi et al., 2024). Narrow and prominent diffraction peaks suggest that the product's particles have a well-defined crystalline structure (Geetha et al., 2024). No additional characteristics peaks were observed other than ZnO which is indicative of full conversion of the Zn precursor into ZnO NPs. The peaks displayed perfectly matched the standard XRD pattern of ZnO (Zincite) with entry number [96-901-1663] from match! 3 phase identification software, as shown in Figure 29 of the Appendix. According to Scherer's equation, the calculated average crystallite size of ZnO NPs was found to be 17.05 nm, which is presented in Table 5. This XRD analysis proves that *Citrullus lanatus* peel are effective reducing agent for the synthesis of ZnO NPs. The average crystallite size of the synthesized NPs and NCs were calculated using Debye Scherrer's equation (Equation 1),

$$D = k\lambda/\beta\cos\theta \dots\dots\dots 1$$

Where D is the average crystallite size (nm), K is the Shape factor (0.94), λ is the X-ray wavelength of CuK α radiation (0.154056 nm), β is the full-width at half maximum (FWHM) of the particular peak, and θ is the Bragg's angle in degree.

Figure 11 also contained the XRD spectra of α -MnO₂ NPs that shows intense and narrow peaks at 2 θ values of $\approx$ 12.59°, 18.7°, 25.27°, 28.84° and 37.43° with their corresponding miller indices value of (110), (200), (220), (310), and (211), respectively by comparing to standard diffraction data from JCPDS-00-044-0141 with pure tetragonal crystalline phase structure of α -MnO₂ and lattice parameters containing a=9.7847 Å and c=2.8630 Å (Gupta et al., 2023). The d-spacing calculated for plane (110) was 7.02 nm. The crystallite size of α -MnO₂ was 22.6 nm, calculated using the Debye Scherrer formula. Thus, the XRD pattern demonstrates the successful synthesis of α -MnO₂ phase. No other characteristics peak from impurities is observed. The peaks displayed perfectly matched the

standard XRD pattern of MnO_2 with entry number [96-901-6668] from match! 3 phase identification software, as shown in Figure 29 of the Appendix.

Furthermore, Figure 11 shows the XRD spectra for the three different ratios of synthesized $\text{ZnO}/\alpha\text{-MnO}_2$ NCs. For the $\text{ZnO}/\alpha\text{-MnO}_2(1:1)$ NCs, diffraction peaks are observed at 2θ values of $\approx 12.59^\circ$, 18.7° , 25.27° , 28.84° , 36.57° , 41.7° , 42.1° , 56.3° and 60.2° with their corresponding miller indices values of (110), (200), (220), (310), (400), (420), (301), (600) and (521) crystal planes of $\alpha\text{-MnO}_2$ (JCPDS-00-044-0141). Additionally, ZnO diffraction peaks are noted at 31.7° , 34.40° , 36.2° and 62.94° with their corresponding miller indices values of (100), (002), (101) and (103) crystal planes of ZnO (JCPDS-00-036-1451). For the $\text{ZnO}/\alpha\text{-MnO}_2(1:2)$ NCs, diffraction peaks are observed at 2θ values of $\approx 18.7^\circ$, 28.84° , 36.57° , 39.03° , 56.3° , 60.2° and 65.1° with their corresponding miller indices values of (200), (310), (400), (330), (600), (521) and (002) crystal planes of $\alpha\text{-MnO}_2$ (JCPDS-00-044-0141). The ZnO diffraction peaks appear at 31.7° and 34.40° , corresponding to the miller indices values of (100) and (002) crystal planes of ZnO (JCPDS-00-036-1451). For the $\text{ZnO}/\alpha\text{-MnO}_2(2:1)$ NCs, diffraction peaks are observed at 2θ values of $\approx 18.7^\circ$, 28.84° , 36.57° , 39.03° , 42.1° , 56.3° , 60.2° and 65.1° , corresponding to the miller indices values of (200), (310), (400), (330), (301), (600), (521) and (002) crystal planes of $\alpha\text{-MnO}_2$ (JCPDS-00-044-0141), and ZnO diffraction peaks are noted at 31.7° , 34.40° , 36.2° and 62.94° , corresponding to the miller indices values of (100), (002), (101) and (103) crystal planes of ZnO (JCPDS card number of 00-036-1451). All peaks of $\text{ZnO}/\alpha\text{-MnO}_2$ NCs were indexed without any anomaly.

The calculated average crystallite size of synthesized $\text{ZnO}/\alpha\text{-MnO}_2$ NCs was found to be 15.6, 17.33, and 17.4 nm for the ratio of 1:1, 1:2, 2:1, respectively, and the overall crystallite size and d-spacing is summarized in Table 5. The calculated average crystallite size gives supporting evidence for the $\text{ZnO}/\alpha\text{-MnO}_2$ NCs is in nano-scale. The $\text{ZnO}/\alpha\text{-MnO}_2(1:1)$ NCs have small average crystalline size as compared to the counterpart ratios. This might be contributed due to the presence of an equal volume of capping /reducing agent with salt precursors and this results more homogenization between the mixed two components (M. Abdullah et al., 2021). Furthermore, the XRD spectra of $\text{ZnO}/\alpha\text{-MnO}_2(1:2)$ and $\text{ZnO}/\alpha\text{-MnO}_2(2:1)$ NCs showed sharp and intense peaks, which indicates the material has more crystalline size nature. The peaks displayed perfectly matched the standard XRD pattern of $\text{Mn}_2\text{O}_4\text{Zn}$ (Hetaerolite) with entry number [96-901-2843] from match! 3 phase identification software as depicted in Figure 29 of the Appendix and are in good agreement with the literature. The additional peaks and/or peak disappearances are due to variation in the composition (ratio) and orientation of crystallites in the sample.

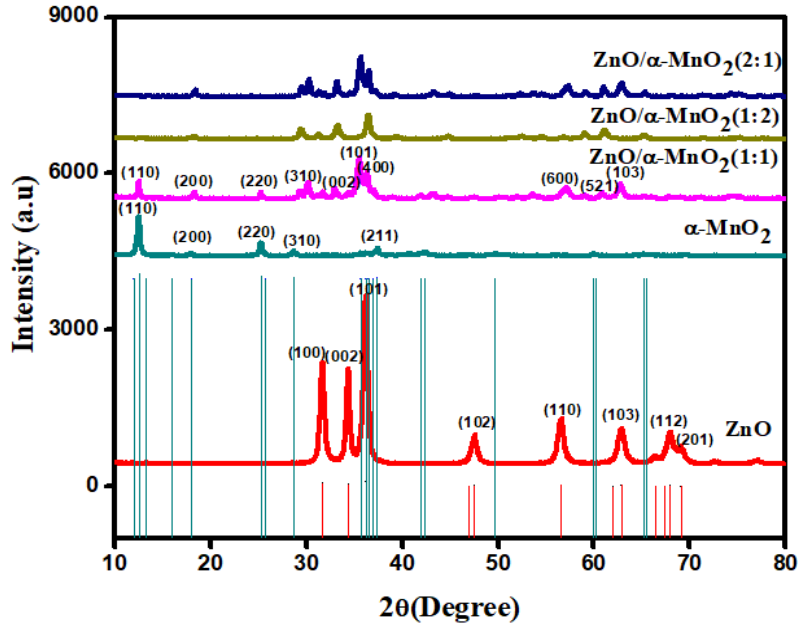


Figure 11 XRD spectra of ZnO, α -MnO₂ NPs and ZnO/ α -MnO₂ NCs with different ratios.

Table 5 XRD data used for calculations of d-spacing and average crystallite size of synthesized S.no.

ZnO NPs						
2θ(°)	θ(°)	FWMH(β) (°)	FWMH(β) (radian)	d-spacing (nm)	hkl value	Crystallite size (nm)
36.2132	18.1066	0.52130	0.0090937	0.239392	101	16.04
31.7367	15.86835	0.51890	0.0090519	0.210616	100	15.92
34.4055	17.20275	0.43340	0.007560	0.227813	002	19.20
Average value(nm)						17.05
α-MnO₂ NPs						
2θ(°)	θ(°)	FWMH(β) (°)	FWMH(β) (radian)	d-spacing (nm)	hkl value	Crystallite size (nm)
12.5975	6.29875	0.34770	0.0060654	7.020887	110	23.26
25.2732	12.6366	0.34000	0.0059311	3.521013	220	23.96
37.4316	18.7158	0.38170	0.0066585	2.400567	211	22.00
Average value(nm)						22.6
1:1 ZnO/α-MnO₂						
2θ(°)	θ(°)	FWMH(β) (°)	FWMH(β) (radian)	d-spacing (nm)	hkl value	Crystallite size (nm)

35.5562	17.7781	0.55040	0.0096014	2.522767	101	15.1672
36.3367	18.1683	0.51520	0.0089873	2.470356	101	16.2375
30.1712	15.0856	0.47090	0.0082145	2.959635	310	17.5120
Average value(nm)						15.6
1:2 ZnO/α-MnO₂						
2θ(°)	θ(°)	FWMH(β) (°)	FWMH(β) (radian)	d-spacing (nm)	hkl value	Crystallite size (nm)
36.4766	18.23831	0.47740	0.0083279	2.461194	101	17.595
33.2955	16.64775	0.52380	0.0091374	2.688709	002	16.122
29.5049	14.75245	0.46680	0.0081430	3.024937	310	17.617
Average value(nm)						17.33
2:1 ZnO/α-MnO₂						
2θ(°)	θ(°)	FWMH(β) (°)	FWMH(β) (radian)	d-spacing (nm)	hkl value	Crystallite size (nm)
35.6802	17.8401	0.51680	0.0090152	2.514284	101	16.184
36.4952	18.2476	0.44090	0.0076912	2.459984	101	18.9921
30.3097	15.1548	0.44360	0.0077383	2.946435	310	18.5637
Average value(nm)						17.4

4.4 FT-IR Analysis

FT-IR measurements were carried out to identify the major functional groups in the *Citrullus lanatus* peel, green synthesized ZnO NPs, α -MnO₂ NPs and ZnO/ α -MnO₂ (1:1) NCs using the peel extract. That was to identify the possible involvement of the peel extract in the synthesis and stabilization of NPs and NCs. FTIR analysis was conducted within the spectrum range of 4000-400 cm⁻¹. Figure 12 shows the functional group of ZnO NPs, α -MnO₂ NPs and ZnO/ α -MnO₂ (1:1) NCs.

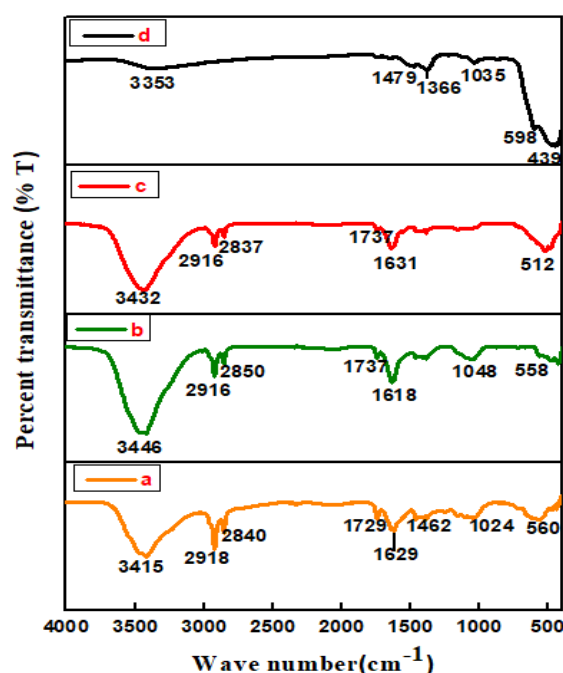


Figure 12 FTIR spectra of (a) peel powder, (b) ZnO, (c) α -MnO₂ NPs and (d) ZnO/ α -MnO₂(1:1) NCs.

Figure 12(a) shows the FTIR spectrum of *Citrullus lanatus* peel, with a strong peak at 3415 cm⁻¹ corresponding to O-H stretching vibrations of -OH groups. A peak at 2915 and 2840 cm⁻¹ indicates the C-H stretching of methyl and methoxy groups. The peak at 1729 cm⁻¹ corresponds to C=O stretching of carboxylic acid or esters, and the peak at 1629 cm⁻¹ corresponds to O-H bending vibrations or adsorbed water (Tamil Elakkiya et al., 2021). Peaks at 1462, 1024, and 567 cm⁻¹ are due to C-H and C-O bending and stretching vibrations. This spectrum suggests an abundance of carboxylic and hydroxyl groups that act as proton donors for binding cations (Lakshmipathy & Sarada, 2016). Figure 12(b) shows the FTIR spectrum of synthesized ZnO, with a broad peak at 3446 cm⁻¹ for O-H stretching vibrations, possibly from ketones, alcohols, carboxylic acids, or adsorbed water. Peaks at 2916 and 2850 cm⁻¹ are related to C-H stretching and bending of alkanes and aldehydes, originating from plant phytochemicals that reduce metal ions into NPs. The peak at 1737 cm⁻¹ is associated with C=O stretching and the peak at 1629 cm⁻¹ corresponds to O-H bending or adsorbed water. The peak at 1048 cm⁻¹ suggests Zn-O stretching, possibly overlapping with C-O stretching, and the peak at 558 cm⁻¹ confirms Zn-O bond formation (Almaary et al., 2023). Figure 12(c) displays the FTIR spectrum of α -MnO₂ NPs, with a broad band at 3432 cm⁻¹ for O-H stretching and adsorbed H₂O molecules. Peaks at 2916 and 2837 cm⁻¹ indicate C-H stretching and bending, while the peak at 1737 cm⁻¹ corresponds to C=O stretching. The peak at 1631 cm⁻¹ is due to O-H bending vibration combined with Mn atoms, indicating adsorbed H₂O on the surface of α -MnO₂, and

the peak at 512 cm^{-1} confirms Mn-O stretching vibration, justifying $\alpha\text{-MnO}_2$ formation (Taranu et al., 2022). Figure 12(d) shows the FTIR spectrum of ZnO/ $\alpha\text{-MnO}_2$ NCs, with a broad peak at 3353 cm^{-1} for O-H stretching vibrations of adsorbed water molecules. Peaks at 1479 and 1366 cm^{-1} correspond to C-H bending possibly from methyl or methylene groups. The band at 439 cm^{-1} is due to Zn-O stretching, while bands at 1035 and 598 cm^{-1} correspond to O-Mn-O lattice vibrations, confirming MnO_2 in the NCs (EL-Moslamy, Abd-Elhamid, et al., 2024; EL-Moslamy, Rezk, et al., 2024). The presence of Zn-O and Mn-O stretching vibrations confirms the successful formation of the NCs.

4.5 SEM-EDX Analysis

The surface morphology and the elemental composition of the green-synthesized ZnO NPs, $\alpha\text{-MnO}_2$ NPs and ZnO/ $\alpha\text{-MnO}_2$ (1:1) NCs were determined by using a SEM-EDX technique. In this study, SEM was utilized to determine the surface morphology of stabilized biogenic NPs and NCs, such as their shape, size, and size distribution at 10.0 kv magnification which were dependent on the ratio of precursors used under the same reaction conditions. The SEM-EDX results of ZnO and $\alpha\text{-MnO}_2$ NPs and ZnO/ $\alpha\text{-MnO}_2$ (1:1) NCs are analyzed as shown in Figure 13.

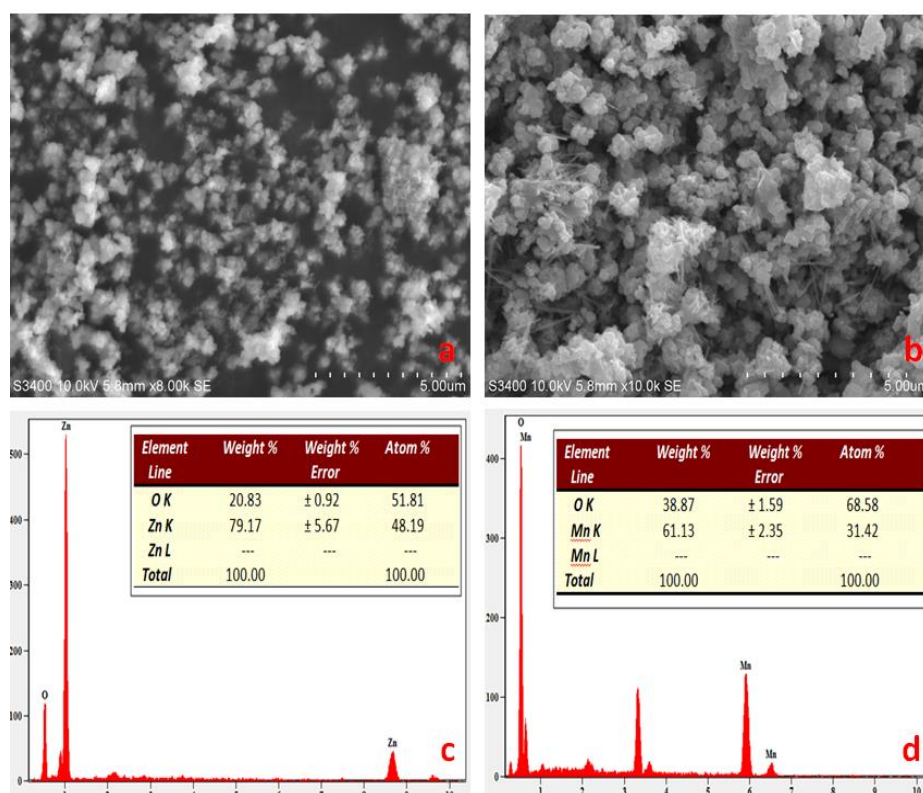


Figure 13 (a-b) SEM image of ZnO, $\alpha\text{-MnO}_2$ and (c-d) EDX mapping of ZnO, $\alpha\text{-MnO}_2$ NPs.

Figure 13(a) presents the topographical structure of ZnO NPs, showing spherical morphology with a particle size in nm range. It reveals a uniform surface morphology across all sections, with no signs

of aggregation or agglomeration. This consistency is likely attributed to the optimized extract used during the synthesis process, which appears to play a crucial role in achieving such uniformity. The ZnO NPs exhibit a relatively uniform size distribution, indicating a high level of control over the synthesis process. The consistent spherical shape and nanoscale dimensions highlight the effective capping action of the biomolecules present in the extract. These biomolecules facilitate uniform growth and nucleation during synthesis, preventing excessive particle growth and ensuring the size reduction observed (M. Abdullah et al., 2021). These results suggest that the *Citrullus lanatus* peel extract functions as both a reducing and a capping agent in the synthesis of ZnO NPs. The formation of the ZnO NPs is further confirmed by the elemental composition data shown in Figure 13(c). The EDX spectrum confirms the presence of zinc and oxygen signals, with weight percentages of 79.17% for zinc and 20.83% for oxygen. The atomic percentages are 48.19% for zinc and 51.81% for oxygen. These findings validate the successful formation of stable and pure ZnO NPs, with minimal error margins, indicating precise elemental quantification (Acharya et al., 2021).

The α -MnO₂ NPs, as shown in Figure 13(b), exhibit spherical shapes with nano-needle-like structures with a particle size in nm range. The SEM displays a homogeneous and well-dispersed distribution of the NPs on the surface, with no signs of aggregation. This uniform morphology and distribution suggest effective nucleation and growth control during the synthesis process (Dubey et al., 2022). The consistent spherical shape of the α -MnO₂ NPs further indicates the efficiency of the synthesis method. Elemental compositions confirmed by EDX analysis of the α -MnO₂ NPs in Figure 13(d) reveal prominent peaks for Mn and O. Specifically, the weight percentages are 61.13% for Mn and 38.87% for O. In terms of atomic percentages, Mn constitutes 31.42%, and O makes up 68.58%, which aligns with the stoichiometric expectations for α -MnO₂ (Gupta et al., 2023).

The SEM-EDX results of ZnO/ α -MnO₂(1:1), ZnO/ α -MnO₂(1:2) and ZnO/ α -MnO₂(2:1) NCs are displayed as shown in Figure 14. It is clearly shown in these Figures that all the synthesized NCs were in the nm range. Figure 14(a) of ZnO/ α -MnO₂(1:1) reveals that the particles are well-dispersed which suggests efficient nucleation during the synthesis process. This efficiency is attributed to the equal amounts of the precursor salt solutions and the use of an optimized extract, ensuring a homogenous distribution of spherical NPs (M. Abdullah et al., 2021). The successful integration of ZnO and α -MnO₂ into the NCs is evident from the EDX proportion, which highlights a mixture of spherical nanoparticles distributed uniformly across the sample. Figure 14(b) depicts a relatively more clustered structure. This suggests a higher content of α -MnO₂, which may lead to increased particle aggregation, thereby increasing the active sites. Figure 14(c) presents more dispersed and

less aggregated morphology. This can be attributed to a higher ZnO content, resulting in a more spread-out distribution. Baral et al. (2021) have shown that the presence of MnO_2 influences aggregation behavior due to its surface chemistry and morphology. Additionally, the electrostatic and magnetic interactions in $\alpha\text{-MnO}_2$ further contribute to this aggregation phenomena (Baral et al., 2021). Elemental analysis through EDX, shown in Figure 14(d), confirms the presence of Zn, Mn and O elements, validating the formation of the $\text{ZnO}/\alpha\text{-MnO}_2$ NCs. The atomic percentages were 20.16% for Zn, 18.08% for Mn, and 61.76% for O, indicating a mixed oxide NCs. These results confirm the successful synthesis of $\text{ZnO}/\alpha\text{-MnO}_2$ NCs with a balanced integration of both oxides, further validating the effectiveness of the synthesis method employed (Gupta et al., 2024).

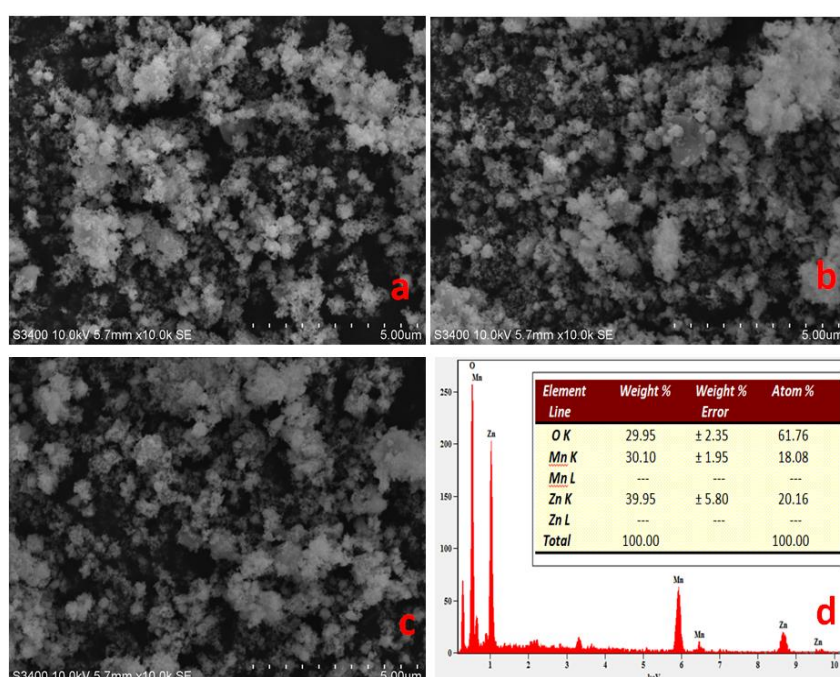


Figure 14 (a-c) SEM image of $\text{ZnO}/\alpha\text{-MnO}_2(1:1)$, $\text{ZnO}/\alpha\text{-MnO}_2(1:2)$ and $\text{ZnO}/\alpha\text{-MnO}_2(2:1)$ NCs (d) EDX mapping of $\text{ZnO}/\alpha\text{-MnO}_2(1:1)$ NCs.

4.6 UV-Vis DRS Analysis

The optical light absorption and bandgap energy of the green ZnO, $\alpha\text{-MnO}_2$ NPs and each ratio of $\text{ZnO}/\alpha\text{-MnO}_2$ NCs were examined by the UV-Vis DRS technique. Figure 15 illustrates the UV-Vis DRS of all samples recorded in the range of 320-800 nm. The observed peaks in Figure 15 (b) and (d) are attributed to the energy band gap (E_g) of NPs and NCs, corresponding to electron transitions from a lower to higher energy states. E_g was evaluated using the Tauc formula, as specified in Equation 2. The band gap value were obtained by extrapolating the linear region of the plot of $(ah\nu)^2$ against $h\nu$ (often referred to as a Tauc's plot) to zero (Aghabeygi & Khademi-Shamami, 2018).

$$(\alpha h\nu) = k (h\nu - E_g)^n \dots\dots\dots 2$$

Where α is the absorbance coefficient, k is the absorption constant for a direct transition, $h\nu$ is the absorption energy, E_g is the band gap energy and n denotes the type of transition which assumes the value $\frac{1}{2}$ for indirect allowed one and $n=2$ for direct allowed transition.

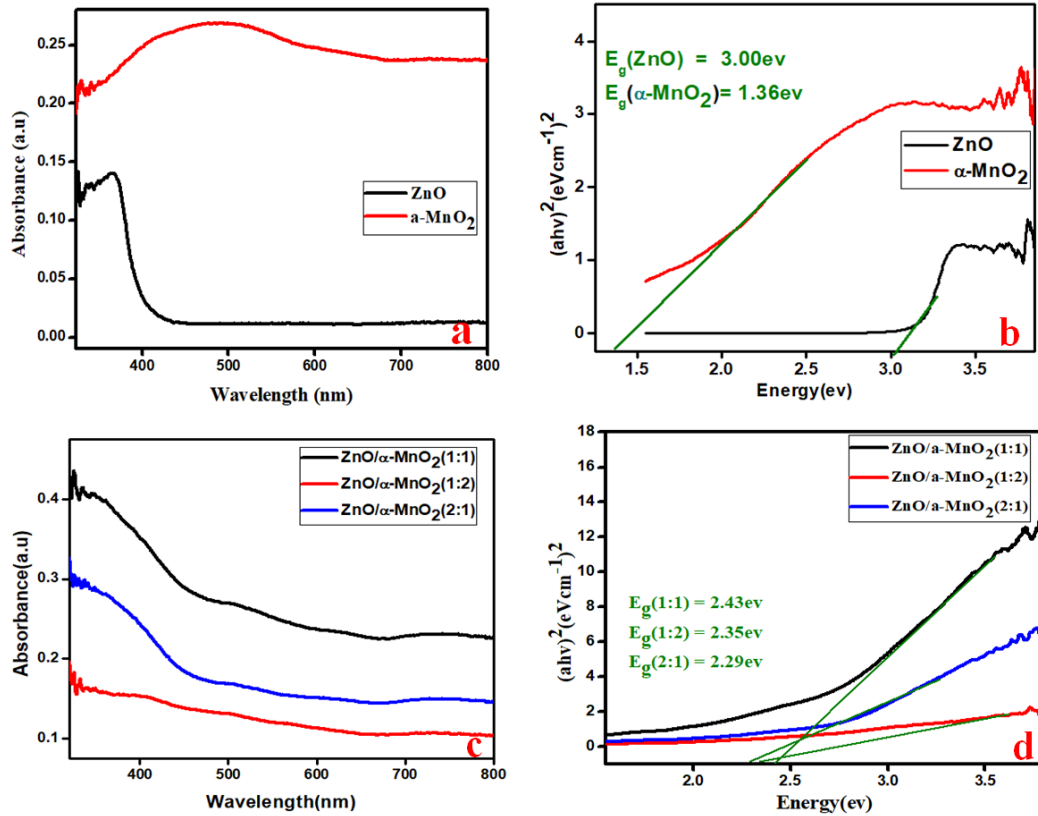


Figure 15 (a) Absorbance of ZnO and $\alpha\text{-MnO}_2$, (b) Tauc plot of ZnO and $\alpha\text{-MnO}_2$, (c) Absorbance of ZnO/ $\alpha\text{-MnO}_2$ NCs at different ratios, (d) Tauc plot of ZnO/ $\alpha\text{-MnO}_2$ NCs at different ratios.

Figure 15 (a) shows the UV-Vis DRS spectra of ZnO and $\alpha\text{-MnO}_2$ NPs. ZnO shows a sharp absorbance around 366 nm indicating a fundamental absorption edge, while $\alpha\text{-MnO}_2$ has a more gradual increase in absorbance over visible wavelength range and can absorb visible light. The absorption in the visible light range is caused by the d to d transitions of Mn ions in $\alpha\text{-MnO}_2$ (Taranu et al., 2022). Tauc formula was employed to calculate the E_g of ZnO and $\alpha\text{-MnO}_2$ materials, which had the respective values of 3.00 eV and 1.36 eV respectively as shown in Figure 15(b). This suggests that ZnO is a wide band gap semiconductor, it only responds to the UV region while $\alpha\text{-MnO}_2$ has a narrower band gap. Studies by Dubey et al. (2022) shows the band gap of synthesized ZnO NPs, $\alpha\text{-MnO}_2$ NPs and ZnO/ $\alpha\text{-MnO}_2$ NCs was calculated as 3.1, 1.9, and 2.52 eV, respectively. These values correlate with our findings (Dubey et al., 2022).

Figure 15 (c) shows the UV-Vis DRS absorption spectra of ZnO/ α -MnO₂ NCs with different ratios. All NCs show enhanced absorption across a broader range than pure ZnO, indicating that combining ZnO with α -MnO₂ affects the optical properties, likely due to the formation of hetero-junctions or changes in the electronic structure. Higher absorbance typically correlates with higher concentration of absorbing species or more significant light-matter interactions. ZnO/ α -MnO₂ NCs shows sharp absorption in the UV region and high reflectance in the visible region. The ZnO/ α -MnO₂ NCs exhibit varying absorption properties based on their ratios: ZnO/ α -MnO₂(1:1) NCs shows an absorption edge around 380 nm with extended absorption into the visible region combining the optical properties of both ZnO and α -MnO₂ to cover the UV and visible regions; ZnO/ α -MnO₂(1:2) NCs starts absorbing notably at around 450 nm, significantly enhancing visible light absorption due to the higher proportion of α -MnO₂ which narrows the band gap; and ZnO/ α -MnO₂(2:1) NCs has an absorption edge around 375 nm with extended absorption into the visible region, primarily reflecting ZnO's properties but still benefiting from α -MnO₂.

The Tauc plot in Figure 15 (d) indicates the E_g of ZnO/ α -MnO₂ NCs, which were estimated to be 2.43, 2.35, and 2.29 eV with the ratios of precursor salts of (1:1), (1:2), and (2:1), respectively. The ZnO/ α -MnO₂(1:1) NCs shows a lower E_g compared to ZnO NPs due to the introduction of α -MnO₂. The NCs enhances the visible light absorption. The ZnO/ α -MnO₂(1:2) NCs have a slightly lower E_g , enhancing visible light absorption. It suggests that the α -MnO₂ component increasingly dominates the electronic properties of the NCs, possibly by narrowing the band gap through increased interface interaction between ZnO and α -MnO₂. The ZnO/ α -MnO₂(2:1) NCs with the lowest E_g among the three NCs. This could indicate that even a relatively high ZnO content does not completely dominate the optical properties, and the α -MnO₂ has a substantial influence. The observed variation in E_g may be due to incorporation of Mn ions into ZnO which can facilitate charge transfer of electron-hole (e^- - h^+) pairs, enhancing the flow of electrons to the conduction band. This charge transfer can reduce the band gap energy by providing additional energy states within the band structure (Selvi et al., 2021). There is inverse relationship between crystallite size and band gap energy of the NCs. This relationship often arises because smaller crystallites have a larger surface area-to-volume ratio, which can lead to quantum confinement effects, where the movement of electrons and holes within the nanomaterial is restricted and changes in the electronic structure, typically resulting in widening of band gap energy (Manikandan et al., 2023).

4.7 BET Analysis

The specific surface area, pore size, and pore volume of ZnO, α -MnO₂ NPs, and ZnO/ α -MnO₂ NCs with different ratios were determined using the BET nitrogen gas (N₂) adsorption/desorption method. Table 6 presents the surface area, pore volume, and pore diameter of these materials, illustrating the changes in these properties based on the composition of the NCs. The table highlights how interactions between ZnO and α -MnO₂ can influence the structural characteristics of the NCs.

The large surface area of the NCs indicated higher loading of an analyte. A larger pore size enhanced the surface area available for analyte immobilization, thereby facilitating stronger binding. These features lead to improved sensing capabilities and higher sensitivity due to more active sites for target-analyte interaction (Manikandan et al., 2023). Large surface area and mesoporous structure promote electrochemical activity by minimizing ion routes, increasing the area of contact, enabling electrolyte flow via the pores, and enhancing electrochemical activity (Verma et al., 2024). According to the International Union of Pure and Applied Chemistry classification, materials that have a pore size diameter of < 2.0 nm is categorized as microporous, in the range between 2.0 and 50.0 nm as mesoporous, and > 50.0 nm as macroporous (Mangalam et al., 2019). Pores that are very close to the boundary between micro and mesoporous can sometimes be considered in either category. For all single and binary nanomaterials the average pore size distribution is in the range of 1-2 nm. Therefore, the materials have micro-mesoporous size distribution properties.

Table 6 Surface area, pore volume and pore size of synthesized S.no.

S.no	Surface area(m ² /g)	Pore volume(cm ³ /g)	NLDFT average Pore diameter(nm)
ZnO	509	0.1690	1.324
α -MnO ₂	521	0.1603	1.324
(1:1)ZnO/ α -MnO ₂	512.47	0.2104	1.448
(1:2)ZnO/ α -MnO ₂	525.48	0.2148	1.324
(2:1)ZnO/ α -MnO ₂	488.22	0.1806	1.448

ZnO and α -MnO₂ along with their various NCs show significant differences in properties. ZnO has a surface area of 509 m²/g and a pore volume of 0.1690 cm³/g; with a non-local density functional theory (NLDFT) of 1.324 nm. In contrast, α -MnO₂ has a slightly higher surface area of 521 m²/g and

a comparable pore radius, but it has a slightly lower pore volume of 0.1603 cm³/g. The NCs created by varying the ZnO to α -MnO₂ ratios exhibit significant variations in their properties. Specifically, the (1:1) and (2:1) NCs show an increase in the average pore radius to 1.448 nm, while the (1:2) NCs maintain the same average pore size as the NPs. The increased pore size may be attributed to interactions between ZnO and α -MnO₂, which could lead to a more open pore structure or changes in the pore network. Additionally, the (1:2) ZnO/ α -MnO₂ NCs show an increase in pore volume, reaching the highest value of 0.2148 cm³/g, indicating a greater void space within the material. This increased pore volume could enhance the material's capacity for adsorption applications. The surface area of the NCs also varies, with the (1:2) ratio exhibiting the highest surface area at 525.48 m²/g; likely due to a synergistic effect between the two components that enhances surface exposure. The interaction between the NPs in the NCs can create a material with a larger surface area by forming numerous small pores or an interconnected pore network. These changes contribute to a greater total pore volume, providing more active sites for detection processes and facilitating improved ion transport, which enhances the overall sensitivity and efficiency of lead detection (Verma et al., 2024). Comparing these physical properties with XRD crystallite sizes indicates that the crystallite size does not directly correlate with surface area, pore volume and pore size. Instead, it is influenced by particle aggregation and interaction between ZnO and α -MnO₂. Notably, the surface area increases with higher α -MnO₂ content.

4.8 Electrochemical Characterization of NPs and NCs

4.8.1 CV

Electrochemical characterization of ZnO and α -MnO₂ NPs and each of the ZnO/ α -MnO₂ NCs based MWE was performed using a three electrode electrochemical workstation in the presence of 1M KOH electrolyte solution in the potential range between 0.0V and +0.7V at different scan rates. A clear and defined redox peaks are observed for all modified NPs and NCs based electrodes. Fig. 16 displays the CV voltammogram for different MWEs utilizing single NPs and NCs of ZnO and α -MnO₂.

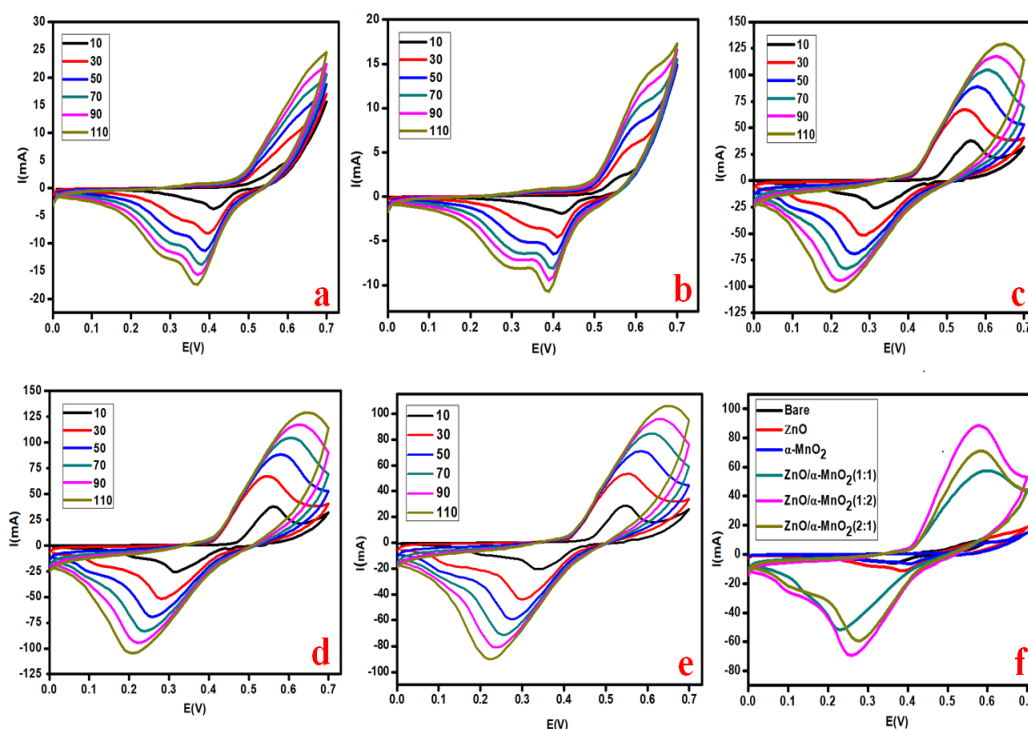


Figure 16 CV of (a) ZnO, (b) α -MnO₂, (c) ZnO/ α -MnO₂(1:1), (d) ZnO/ α -MnO₂(1:2) and (e) ZnO/ α -MnO₂(2:1) NCs at scan rate of 10-110 mV/s and (f) ZnO, α -MnO₂ and ZnO/ α -MnO₂ NCs at 50 mV/s in the presence of the bare electrode.

The CV curves for ZnO NPs in Figure 16 (a), at scan rates of 10, 30, 50, 70, 90, and 110 mV/s, exhibit clear redox peaks, with peak currents increasing as scan rates rise, indicating strong electrochemical activity; the oxidation peak current reaches ~20 mA at 110 mV/s. In contrast, Figure 16 (b) shows α -MnO₂ NPs with distinct but generally lower redox peak currents, peak oxidation current ~15 mA at 110 mV/s. The 1:1 ZnO/ α -MnO₂ NCs in Figure 16 (c) displays significantly higher currents (oxidation peak current ~80 mA at 110 mV/s) due to synergistic effects. Figure 16 (d) shows that the 1:2 ZnO/ α -MnO₂ NCs exhibit even higher currents, with a oxidation peak current of ~125 mA at 110 mV/s. Figure 16 (e) of 2:1 ZnO/ α -MnO₂ NCs present high current values, slightly lower than the 1:2 NCs, with a peak oxidation current ~100 mA at 110 mV/s. There is an increase in peak current for the NCs when compared with the NPs, which indicates an excellent redox reaction on the electrode. A moderate scan rate (50 mV/s) was taken for obtaining a comprehensive understanding of the electrochemical behavior of the MWE. Comparative analysis in Figure 16 (f) at 50 mV/s reveals that BWE has the lowest current, due to its limited redox reaction in its surface which result from a slow mass transfer. The modifications with ZnO, α -MnO₂, and ZnO/ α -MnO₂ NCs improve performance of BWE due to better mass transfer and diffusion rates. The 1:2 NCs shows a peak shift to the left, indicating the need of small potential for the ions to be deposited on

the surface of the MWE. Such a condition might be due to accelerated transfer of electrons (increased conductivity) and large surface area of the (1:2)ZnO/ α -MnO₂, resulting in great current response.

The CV analysis of ZnO, α -MnO₂, ZnO/ α -MnO₂(1:1), ZnO/ α -MnO₂(1:2) and ZnO/ α -MnO₂(2:1) NCs reveals significant differences in their electrochemical performance, as indicated by the ipa and ipc versus square root of the scan rate (mV/s)^{1/2} plots as depicted in Figure 17. The electrochemical behavior of these materials, including NPs and NCs with different ratio, ranges from moderate to strong, with some exhibiting enhanced activity due to synergistic effects. Generally, the peak currents show a linear relationship with the square root of the scan rate, suggesting that the redox reactions at the electrode surfaces are diffusion-controlled (Jjagwe et al., 2024). Among all 1:2 shows a significant increase in ipa and substantial decrease in ipc which shows very high sensitivity and strong electrochemical activity (capable of detecting very low concentrations with high precision).

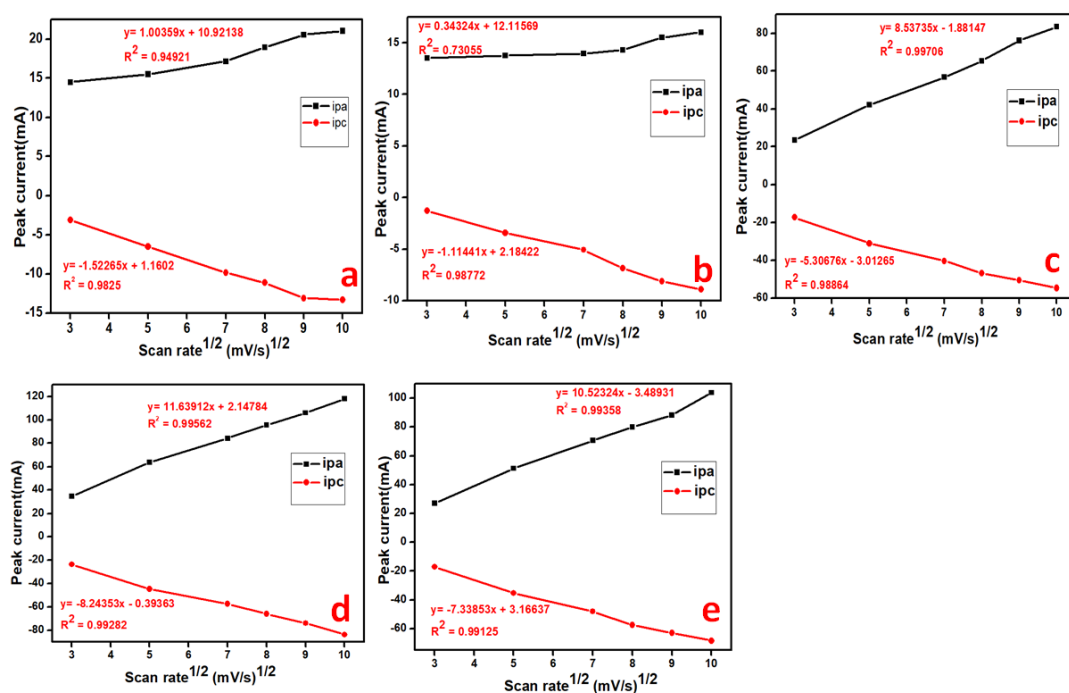


Figure 17 Calibration plot for the redox peak current vs square root of scan rate of (a) ZnO, (b) α -MnO₂, (c) ZnO/ α -MnO₂(1:1), (d) ZnO/ α -MnO₂(1:2) and (e) ZnO/ α -MnO₂(2:1) NCs.

Figure 18 (a - e) displays the plots of ipa and ipc versus the scan rate (mV/s) of ZnO, α -MnO₂, ZnO/ α -MnO₂(1:1), ZnO/ α -MnO₂(1:2) and ZnO/ α -MnO₂(2:1) NCs. ZnO exhibits a moderate ipa slope of 0.07078 with a high R^2 value of 0.97793, while its ipc slope is -0.10287 with R^2 of 0.90824,

suggesting a stable but moderate electrochemical response. In contrast, α -MnO₂ shows a lower ipa slope of 0.02564 ($R^2 = 0.87677$) and ipc slope of -0.07726 ($R^2 = 0.97477$), indicating a weaker but consistent electrochemical behavior. The ZnO/ α -MnO₂(1:1) NCs demonstrates a significantly higher ipa slope of 0.58737 ($R^2 = 0.9653$) and ipc slope of -0.35949 ($R^2 = 0.92022$), suggesting enhanced electrochemical activity due to synergistic effects. The ZnO/ α -MnO₂(1:2) NCs further improves with ipa slope of 0.7935 ($R^2 = 0.94195$) and ipc slope of -0.56527 ($R^2 = 0.95314$), indicating superior electrochemical performance. Finally, the ZnO/ α -MnO₂(2:1) NCs shows a high ipa slope of 0.72126 ($R^2 = 0.95275$) and ipc slope of -0.4984 ($R^2 = 0.92873$), demonstrating a strong electrochemical response. The NCs, particularly with higher proportions of α -MnO₂, exhibit significantly improved electrochemical properties compared to the NPs, likely due to enhanced electron transport and catalytic activity from the synergistic interactions between ZnO and α -MnO₂. These results suggest that the electro-catalytic behavior is a surface-controlled electrochemical process, meaning that the activities predominantly take place on the surface of the MWE (Jjagwe et al., 2024).

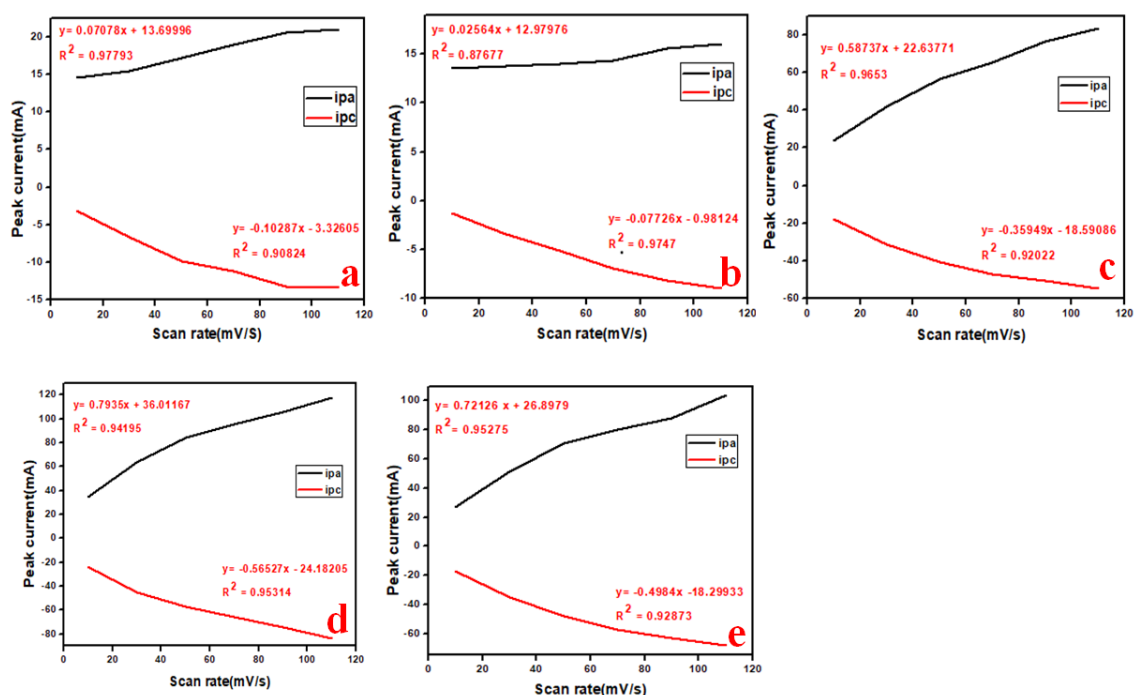


Figure 18 Calibration plot for the redox peak current vs scan rate of (a) ZnO, (b) α -MnO₂, (c) ZnO/ α -MnO₂(1:1), (d) ZnO/ α -MnO₂(1:2) and (e) ZnO/ α -MnO₂(2:1) NCs

It is further supported by the results of electrodes surface area. Since the effective surface areas of the electrode is a main factor which affects the electrochemical based system. The electrochemically active area (A) of the electrodes was calculated according to the Randles-Sevcik (Equation 3).

$$I_p = 2.691 \times 10^5 \times n^{3/2} \times A \times D^{1/2} \times C \times v^{1/2} \dots\dots\dots 3$$

Where I_p is the peak current (μA); n is the number of electrons exchanged ($n=1$); A is the surface area of the electrochemically active electrode (cm^2); D is the diffusion coefficient ($1.9 \times 10^{-5} cm^2 s^{-1}$); C is the concentration of KOH ($mol cm^{-3}$); v is the potential sweep rate (mVs^{-1}). The calculation reveals that the surface area of ZnO, α -MnO₂, (1:1), (1:2) and (2:1)ZnO/ α -MnO₂ are 5.74cm², 7.65cm², 9.56cm², 38.26cm², 28.69cm², respectively. From this result the higher surface area provides enough electrode/electrolyte interfaces for adsorption of ions on the surface of the electrode (Jjagwe et al., 2024).

4.8.2 EIS

EIS analysis provides a fundamental understanding of the electrode/electrolyte interface behavior, charge transfer resistance and ionic diffusion in different recorded frequencies. The electrochemical characterization of BWE, ZnO, α -MnO₂, ZnO/ α -MnO₂ NCs MWE was performed using EIS in 1M KOH electrolyte solution, as represented by nyquist plot in Figure 19. The nyquist plot revealed distinct electrochemical behaviors for different ratios providing insight into their charge transfer and ion diffusion properties. The absence of a semicircular curve (linear start) in the high frequency regions shows a low charge transfer resistance, suggesting the MWE had greater conductivity (Baral et al., 2021; Raj et al., 2023). The linear region in the low frequency indicates Warburg impedance, associated with ion-diffusion controlled process. The Warburg impedance suggests good ion transport within electrode material. The uplift at the end of the curve signifies the dominance of Warburg impedance. This is advantageous as it implies that the electrodes have good conductor behavior and fast ion transport, which is beneficial for high performance electrochemical system (Fall et al., 2021; Lameche et al., 2023).

BWE exhibit the highest impedance, whereas ZnO shows significant impedance but lower than BWE showing a better conductivity. α -MnO₂ shows lower impedance than ZnO indicating a better charge transport contributed due to its enhanced magnetic behavior. The NCs show a lower impedance values indicating enhanced charge transfer properties and improved catalytic properties due to their enhanced surface area that allows for the easily transfer of charge as compared to the single NPs based MWE. Furthermore, among the three ratios of NCs, the ZnO/ α -MnO₂ (1:2) NCs based MWE has lower impedance due to α -MnO₂ effect, indicating enhanced electrical properties. The presence of α -MnO₂ reduces the impedance and facilitates an electron transfer (Ghafoor et al., 2023). The uplift at the end of (1:1) and (1:2) ZnO/ α -MnO₂ NCs indicates an efficient ion diffusion, contributing to their enhanced electrochemical performance. Generally, ZnO/ α -MnO₂(1:2) MWE demonstrates superior electrochemical properties, characterized by low impedance, efficient ion transport, and enhanced conductivity. This enhancement is attributed to the optimized size and high surface area,

which improve charge transfer kinetics by maximizing active sites and facilitating efficient ion and electron exchange. The increased surface area reduces impedance and enhances conductivity, making the (1:2) ratio particularly effective for lead detection and quantification, as supported by CV results (Hamid et al., 2021).

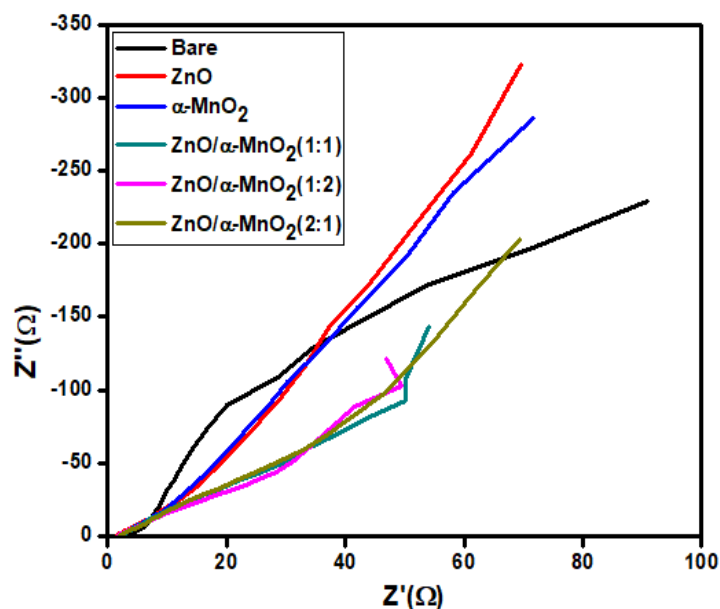


Figure 19 EIS curves for bare, ZnO, α -MnO₂ and ZnO/ α -MnO₂ NCs with different ratios of 1:1, 1:2, and 2:1, respectively in the presence of 1M KOH electrolyte.

4.9 Lead Detection and Quantification

4.9.1 Lead Detection

Figure 20 presents the chronoamperometry curves for the blank, ZnO, α -MnO₂, and ZnO/ α -MnO₂ NCs with ratios of 1:1, 1:2, and 2:1. The BWE shows no reduction peaks in a blank solution, indicating no electrochemical activity in the absence of Pb. Upon the addition of 0.171 ppm Pb²⁺ to a 0.1M HCl solution (pH=3.25), a cathodic peak was observed, corresponding to the reduction of Pb²⁺ ions to Pb metal on the MWE. At acidic pH, lead ions are less likely to form insoluble precipitates compared to neutral or basic conditions, making it easier to deposit lead onto the electrode surface (Mohammed et al., 2024). The ZnO MWE exhibits a significant increase in current, attributed to the semiconducting properties of ZnO that facilitate electron transfer (Ma et al., 2020). Similarly, the α -MnO₂ MWE shows a comparable current response due to its high surface area and redox properties, enhancing its electrochemical activity (Devi et al., 2023; Umeshbabu et al., 2022). The ZnO/ α -MnO₂ NCs exhibit the highest current responses, indicating a synergistic enhancement of electrochemical performance. Among these, the ZnO/ α -MnO₂(1:1) NCs shows a substantial current response, suggesting effective interaction between ZnO and α -MnO₂, which improves electron transfer. The ZnO/ α -MnO₂(1:2) NCs exhibits the highest current response among all samples, likely due to the

increased α -MnO₂ content providing more active sites for redox reactions. Although the ZnO/ α -MnO₂(2:1) MWE also shows a significant current response, it is slightly lower than the 1:2 ratio, suggesting that an optimal ratio of ZnO to α -MnO₂ exists for maximizing electrochemical performance, and excess ZnO may not proportionally enhance the activity.

Preconcentration (Deposition): $\text{Pb}^{2+}(\text{solution}) + 2\text{e}^- \rightarrow \text{Pb}(\text{deposited on MWE})$

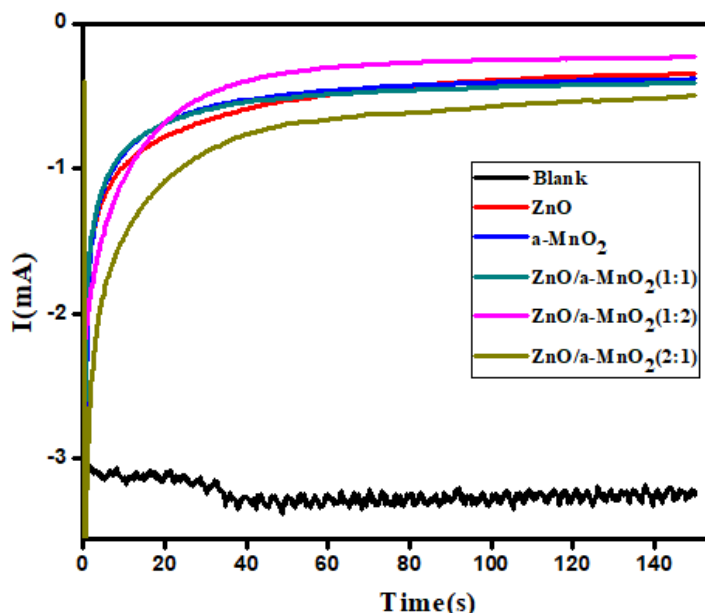


Figure 20 Chronoamperometry responses of blank, ZnO, α -MnO₂, and ZnO/ α -MnO₂ NCs based MWE with different ratios at applied potential of -0.4 V in the absence/presence of 0.171 ppm Pb²⁺ in 0.1M HCl electrolyte solution.

4.9.2 Lead Quantification

SWASV was used for quantification of Pb²⁺. It involves stripping step where the analyte is oxidized, producing a current peak that is proportional to analyte concentration. The Figure 21 shows SWASV voltammogram for determining Pb²⁺ using ZnO, α -MnO₂ and ZnO/ α -MnO₂ NCs with different ratio. The position of the peak potential indicates the potential at which lead is being detected. The specific potential at which current peak occurs corresponds to the oxidation of lead from the electrode surface back to the solution as Pb²⁺. Potential is applied from -1.7 to 0.2V. The peaks are observed in a range of -0.4 to -0.35 V for different modified electrodes.

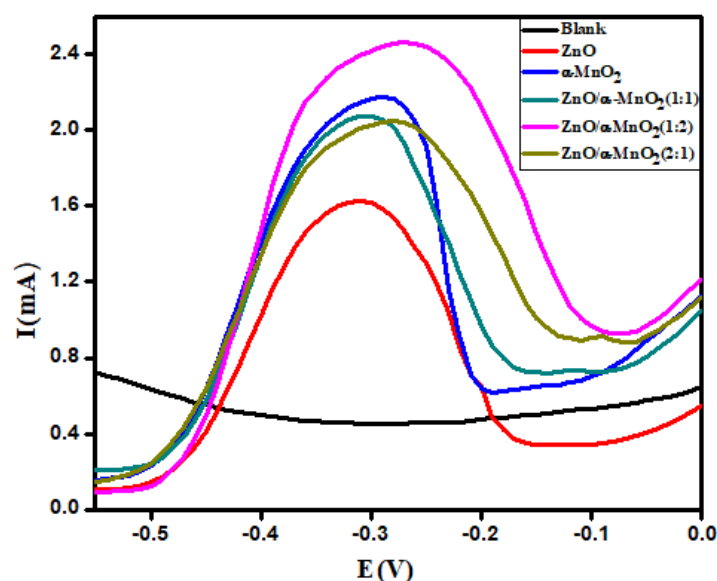


Figure 21 SWASV of 0.171 ppm Pb^{2+} in 0.1M HCl electrolyte based of blank, ZnO, $\alpha\text{-MnO}_2$, and ZnO/ $\alpha\text{-MnO}_2$ NCs based MWE with different ratios.

The peak current is an indicator of the sensitivity of the electrode towards Pb^{2+} quantification. Higher peak current indicates higher sensitivity. The detection of Pb^{2+} ions in a 0.1M HCl electrolyte was evaluated using different electrode materials, including ZnO, $\alpha\text{-MnO}_2$, and ZnO/ $\alpha\text{-MnO}_2$ NCs in various ratios. ZnO MWE exhibited the lowest sensitivity, detecting approximately 0.112 ppm of Pb^{2+} , likely due to its relatively lower surface area and catalytic activity. In contrast, the $\alpha\text{-MnO}_2$ electrode showed better performance, detecting around 0.150 ppm of Pb^{2+} , suggesting enhanced electrochemical properties. The ZnO/ $\alpha\text{-MnO}_2$ (1:1) NCs detected approximately 0.144 ppm, while the ZnO/ $\alpha\text{-MnO}_2$ (2:1) configuration detected around 0.141 ppm, both demonstrating intermediate sensitivities. Notably, the ZnO/ $\alpha\text{-MnO}_2$ (1:2) MWE exhibited the highest sensitivity, detecting the full 0.171 ppm of Pb^{2+} , indicating an optimal combination of ZnO and $\alpha\text{-MnO}_2$ in this ratio. The excellent conductivity was provided by an increase in surface area and charge transfer resulting in great current response. The mechanism for the oxidation of Pb^{2+} from the MWE surface can take place as follows;

Stripping step (Quantification): Pb (deposited on MWE) $\rightarrow \text{Pb}^{2+}$ (solution) + 2e^-

4.10 Optimization of Experimental Conditions for Lead Analysis

ZnO/ $\alpha\text{-MnO}_2$ (1:2) NCs MWE was employed for the efficient electrochemical detection and quantification of Pb^{2+} in aqueous solutions. To establish the optimal experimental conditions, key parameters including accumulation time, deposition potential, and analyte concentration were systematically evaluated using a 0.171 ppm Pb^{2+} solution, prepared from lead acetate trihydrate in

0.1M HCl at pH 3.5. These parameters play a critical role in the effectiveness of Pb deposition on the MWE and its subsequent stripping. The results indicated that optimizing both accumulation potential and time significantly increases the amount of Pb^{2+} deposited on the electrode, leading to higher stripping peak currents, improved sensitivity, and lower LOD.

4.10.1 Effect of Accumulation Time on Lead Detection

Figure 22 exhibits an initial spike in current followed by a gradual stabilization, indicating the achievement of a steady-state current for each applied time interval. The steady-state current increases with longer applied time, suggesting continued progression and accumulation of Pb over time (Tabti et al., 2022). For instance, at 240 s, the steady-state current reaches approximately 12 mA, whereas at 5 s, it is close to -1 mA. This pattern implies that the electrochemical reduction reaction continues to progress, accumulating Pb over longer durations and leading to higher steady-state currents. The initial spike followed by stabilization indicates the kinetics of the reduction reaction, where longer durations result in higher accumulation of the reduced Pb (Vijayalakshmi et al., 2024).

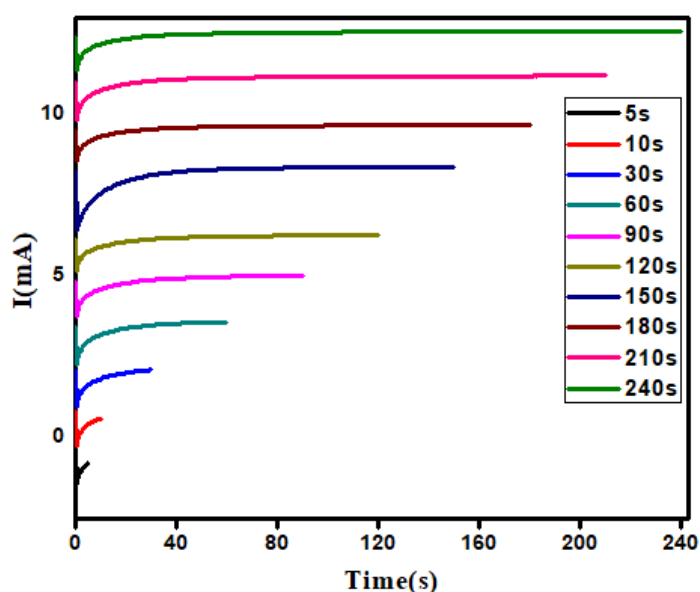


Figure 22 Chronoamperometric responses showing the current (I) over time (s) at different accumulation times (5 to 240 s) in a 0.1M HCl electrolyte with an applied potential of -1.1 V.

4.10.2 Effect of Accumulation Time on Lead Quantification

Figure 23 illustrates the SWASV response of $\text{ZnO}/\alpha\text{-MnO}_2(1:2)$ MWE in a solution containing 0.171 ppm Pb^{2+} in a 0.1M HCl electrolyte, with accumulation times varying from 5 to 240 s. The graph displays the current (I) as a function of potential (E), with peaks corresponding to the stripping of lead from the electrode surface. The accumulation time significantly affects the quantification of

Pb^{2+} as illustrated in Table 7. As the deposition time increases, the peak current rises due to more analyte accumulating on the electrode surface, continuing until saturation occurs. This saturation corresponds to the maximum coverage of the MWE surface with Pb (Hamid et al., 2021). This trend is evident in the current values at different accumulation times, with the peak current reaching 2.43 mA at 150 s, indicating improved sensitivity as more Pb^{2+} are adsorbed onto the electrode surface. However, at longer accumulation times, the current intensity does not significantly increase and may even decrease due to evolution of hydrogen which causes electrode fouling, limited available active sites, and interference of HMI adsorption, as shown by declines in stripping peak currents (Jjagwe et al., 2024). An accumulation time of 210 s exhibits high electrochemical properties, making the oxidation process more efficient, but it may require a higher potential, which is not recommended. Therefore, an accumulation time of 150 s was chosen as it represents an optimal balance between achieving a high peak current for better sensitivity and avoiding excessive electrode saturation. For the lowest concentrations of Pb^{2+} , a longer accumulation time at the MWE is recommended (Baghayeri et al., 2019).

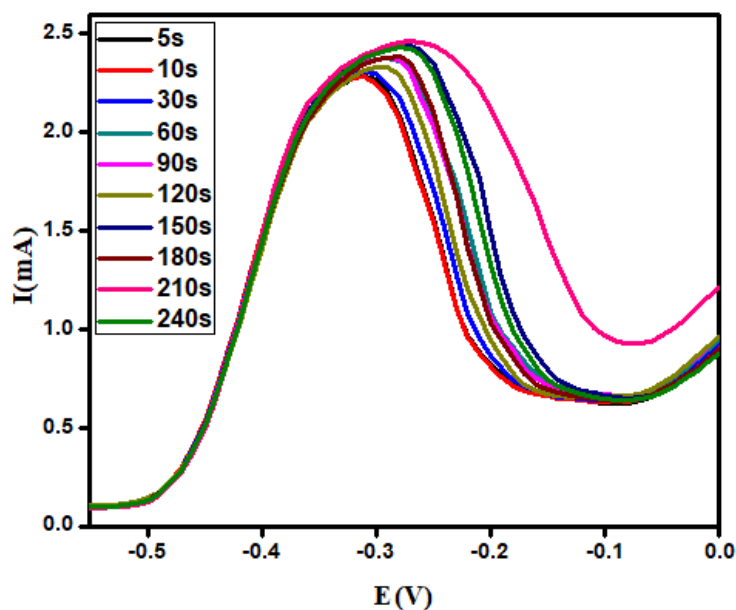


Figure 23 SWASV of 0.171 ppm Pb^{2+} in 0.1M HCl electrolyte at varied accumulation time and at constant potential of -0.5V.

Table 7 Quantification of Pb across various accumulation times (s).

Accumulation time(s)	Pb quantified (ppm)
5	0.158
10	0.158
30	0.159
60	0.164
90	0.164
120	0.161
150	0.168
180	0.167
210	0.171
240	0.168

4.10.3 Effect of Accumulation Potential on Lead Detection

In Figure 24, the current exhibits an initial spike at each applied potential, followed by a gradual stabilization to a steady-state value. As the applied potential becomes more negative, the magnitude of the current increases, reflecting enhanced reduction activity. However, at more negative voltages, particularly at -1.3, -1.5, and -1.7 V, the current fluctuations suggest potential instability, likely due to mass transport limitations or surface reaction dynamics becoming more pronounced. In contrast, the relatively stable currents observed at -0.9 and -1.1 V indicate that these potentials offer a good balance between significant reduction activity and system stability, with -1.1 V standing out as an optimal voltage. Although -1.1 V shows minimal fluctuations, indicating efficient and stable electrochemical performance, slight instabilities are still present. The steady-state currents at different voltages suggest that the process is diffusion-controlled, with the diffusion of electro-active species to the electrode surface determining the current magnitude (Rebey et al., 2022). Additionally, the stabilization indicates that the rate of Pb^{2+} reduction is balanced by the mass transport of Pb^{2+} ions to the MWE, with decreasing current reflecting the progressive coverage of the electrode surface by deposited Pb, thereby making ion diffusion the limiting factor for further deposition.

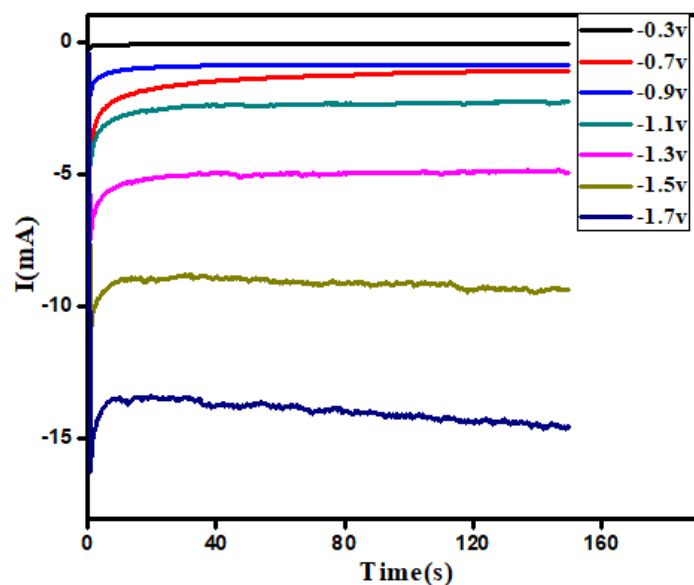


Figure 24 Chronoamperometric responses showing the current (I) over time (s) at different applied potentials (-0.3 to -1.7 V) in a 0.1M HCl electrolyte with an accumulation time of 240 s.

4.10.4 Effect of Accumulation Potential on Lead Quantification

In the accumulation step, the amount of potential applied on ZnO/ α -MnO₂(1:2) MWE has a significant role in the accumulation of Pb²⁺. Figure 25 shows the current response at specified accumulation potentials ranging from -0.4V to -0.1V with a deposition time of 150s and the effects were observed by depositing a solution containing 0.171 ppm of Pb²⁺. The effect of accumulation potential was studied between -0.1V to -1.7V. The peak current varies significantly with different accumulation potentials. At more positive potentials (-0.1V to -0.7V), the current gradually increases significantly around -0.5V, indicating fast reaction kinetics and strong electrocatalytic activity between the electrode surface and Pb ions. This results in an increase in both current and quantified amount, as depicted in Table 8 (Hamid et al., 2021). From -0.7 to -1.1V, there is a decrease in peak current intensity compared to -0.5V. This decrease was due to the hydrogen evolution and formation of bubbles at electrode surface which prevent the oxidation of lead, reducing the current signal (Sarikokba et al., 2024). At more negative potential (-1.3V to -1.7V) the current increases signifying greater electrochemical activity, these higher potentials necessitate greater energy input. Choosing a potential of -0.5V provides a balance between sufficient electrochemical activity and moderate energy consumption.

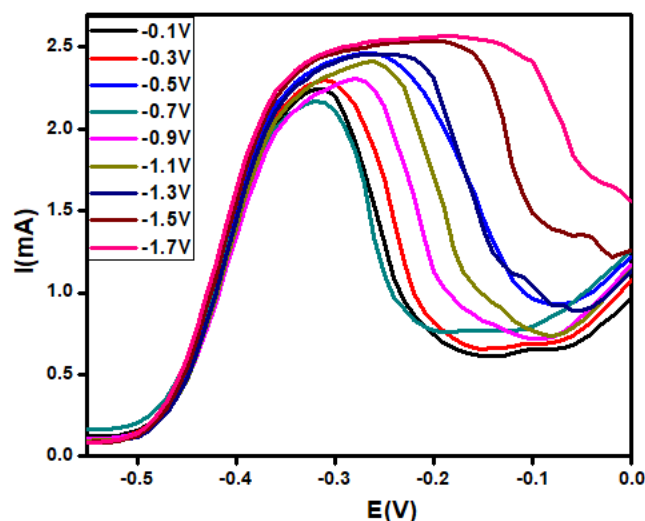


Figure 25 SWASV of 0.171ppm Pb²⁺ in 0.1M HCl electrolyte at varied accumulation potential and at 150s accumulation time.

Table 8 Quantification of Pb across various accumulation potentials (V).

Accumulation potential (V)	Pb quantified (ppm)
-0.1	0.150
-0.3	0.153
-0.5	0.164
-0.7	0.144
-0.9	0.154
-1.1	0.161
-1.3	0.165
-1.5	0.168
-1.7	0.171

4.10.5 Effect of Analyte Concentration on Lead Detection

In Figure 26, each curve shows an initial spike in current followed by a gradual stabilization, indicative of the establishment of a steady-state current for each concentration. The steady-state current increases with higher Pb concentrations. At the highest concentration, the steady-state current reaches approximately 7.39 mA, whereas at the lowest concentration, it is around -0.45 mA. This direct relationship between Pb concentration and current response suggests that higher concentrations result in higher steady-state currents, indicating the MWE's capability to effectively detect changes in Pb concentration. The more active surface area of the MWE facilitates interaction with more Pb²⁺ ions, enhancing the current response.

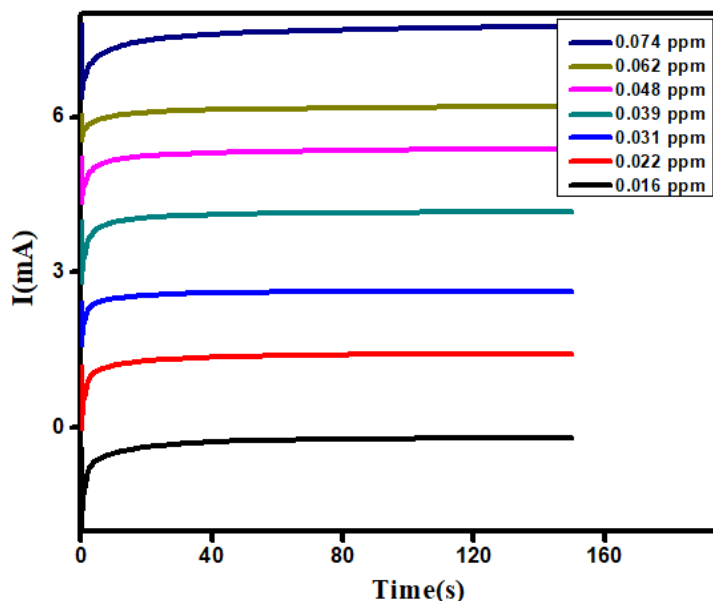


Figure 26 Chronoamperometric response showing the current (I) versus time (s) at different concentration levels (0.074 to 0.016 ppm) in a 0.1M HCl electrolyte, recorded at an accumulation potential of -1.1 V with an accumulation time of 240 s.

4.10.6 Effect of Analyte Concentration on Lead Quantification

The effect of analyte concentration on the anodic peak response of Pb^{2+} ions was studied using SWASV with the $\text{ZnO}/\alpha\text{-MnO}_2(1:2)$ MWE across a concentration range of 0.074 to 0.016 ppm, as shown in Figure 27. Generally, increasing the concentration results in a higher current response because more Pb^{2+} ions are available for reduction and subsequent oxidation. This trend aligns with Faraday's law of electrolysis, which states that the current is directly proportional to the number of moles of analytes being oxidized or reduced (Tüzün & Atun, 2023). More analyte leads to more charge transfer and consequently, a higher current (Lameche et al., 2023). Specifically, as the current increases, the detected ppm increases as depicted in Table 9. The peak shifts observed are likely due to the varying concentrations of Pb^{2+} ions. Additionally, the interaction between the Pb^{2+} ions and the electrode material can influence the electron transfer kinetics, causing a shift in peak potentials (Cotolan et al., 2020).

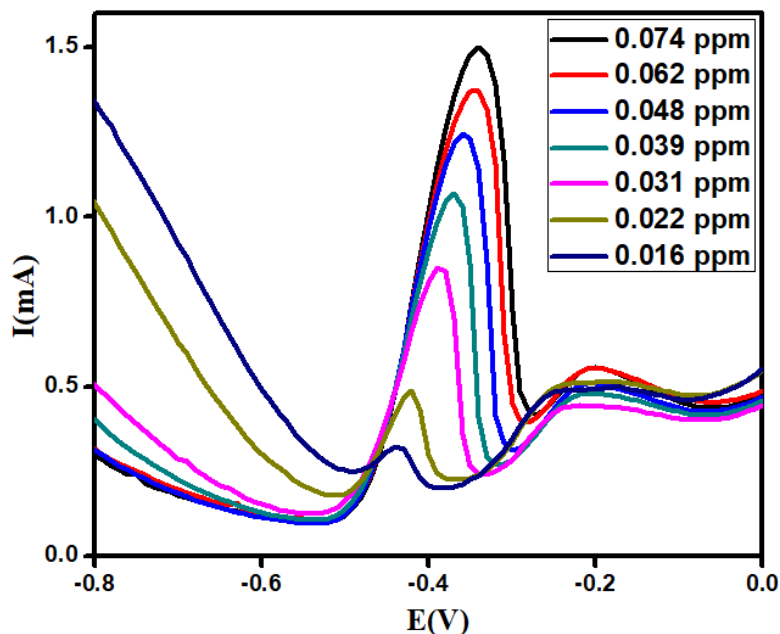


Figure 27 SWASV of Pb^{2+} over a concentration range of 0.074 to 0.016 ppm, with an accumulation time of 150s and a constant potential of -0.5V, in a 0.1M HCl electrolyte solution.

Table 9 Quantification of Pb across various concentrations range (ppm).

Concentration range(ppm)	Pb quantified(ppm)
0.074	0.068
0.062	0.062
0.048	0.053
0.039	0.046
0.031	0.032
0.022	0.017
0.016	0.008

After optimizing the experimental conditions, the quantification of Pb^{2+} was carried out using the SWASV method with a (1:2)ZnO/ α -MnO₂ MWE. The current peak displayed a linear relationship with the Pb^{2+} concentration, as shown in Figure 28, which illustrates SWASV responses for Pb^{2+} concentrations ranging from 0.074 to 0.016 ppm. A calibration plot was generated based on the peak, exhibiting a linear fit described by the equation $y = 19.77597x + 0.14077$, where x is the lead concentration (ppm) and y is the current (mA), with a correlation coefficient of $R^2 = 0.93577$. This calibration curve is used to calculate the LOD, which pertains to the lowest amount of analyte that can be reliably detected. The LOD was found to be 0.008 ppm for Pb^{2+} , according to $\text{LOD} = 3\sigma/K$ (σ is the standard deviation of the 7 measurements and K is the slope of the calibration curve,

respectively) (Tüzün & Atun, 2023). The comparison of (1:2)ZnO/ α -MnO₂ MWE with other modified electrodes for Pb²⁺ detection was shown in Table 10. It can be seen that this method has the comparable linear range and detection limit for the Pb²⁺ detection.

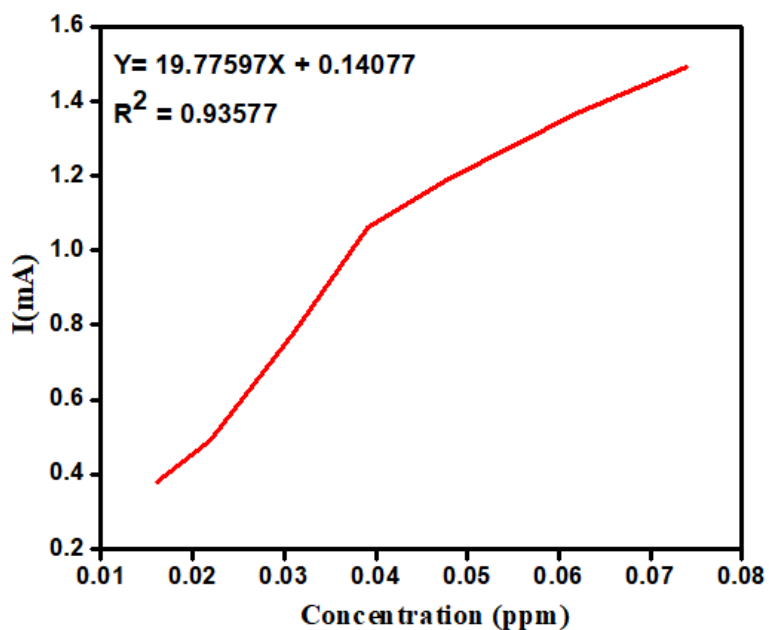


Figure 28 Calibration plot for anodic peak current of Pb²⁺ ranging from 0.074-0.016 ppm using ZnO/ α -MnO₂(1:2) MWE.

Table 10 Comparison of proposed NCs with other studies for the detection of Pb²⁺ ions.

Electrode	Technique	Linear range(ppm)	LOD (ppm)	References
pg- C ₃ N ₄ /CoMn ₂ O ₄ /GCE	SWASV	0.04144 - 0.91168 (optimized at pH= 5, -0.9 V and 180 s)	0.0000014	(Y. Wang et al., 2021)
ZnO/L-cys/GCE	SWASV	0.01 - 0.14 (Optimized at pH=4.5, -1 V and 240 s)	0.000397	(Oliveira et al., 2020)
DTB-RGO/GCE	SWASV	0.0001 - 1 (optimized at pH=4, -1.2 V and 600 s)	0.00008	(Li et al., 2020)
Fe ₂ O ₃ / ZnO/ITO	SWASV	0.04144 - 0.24864 (optimized at -1.1 V and 120 s)	0.002072	(Hamid et al., 2021)
rGO/g-C ₃ N ₄ /GCE	SWASV	0.00000207 - 0.2072 (optimized at pH= 5.5, -1.0V and 600 s)	0.0022170 4	(Fu et al., 2020)
Ag NPs/ChS/GC	DPV	0.005 - 0.08 (optimized at pH=4.5, -0.9 V and 180 s)	0.00197	(Sarikokba et al., 2024)
Zn-Fe LDH/PANI/CPE	DPV	0.2072 - 16.576 (optimized at -1.1V and 150 s)	0.03476	(Kamel et al., 2024)
ZnO/ α -MnO ₂ /NIF	SWASV	0.016 - 0.074 (optimized at -0.5 V and 150 s)	0.008	This study

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

ZnO/MnO₂ NCs and their individual NPs were synthesized using *Citrullus lanatus* peel extract as a natural, eco-friendly template. The qualitative phytochemical analysis of the peel extract revealed the presence of various bioactive compounds, which played a crucial role in the synthesis process. The NPs and NCs were characterized using XRD, FTIR, SEM-EDX, UV-Vis DRS, and BET analysis, revealed well-defined crystallinity, the presence of functional groups, morphological structure, optical properties, and enhanced surface area (for only (1:2)ZnO/ α -MnO₂ NCs). Incorporating the ZnO/MnO₂ NCs into a BWE resulted in a MWE with significantly enhanced electrochemical properties, including superior electron transfer kinetics and improved charge transfer behavior compared to the individual NPs. CV and EIS demonstrated that the ZnO/ α -MnO₂(1:2) NCs MWE exhibited the lowest impedance and the best electron transfer kinetics. This enhancement is attributed to the high content of α -MnO₂ and its large surface area, which collectively improve the electrode's electrical properties. Lead deposition was performed in an acidic environment at -1.1 V for 240 seconds, followed by SWASV for quantification. Among the different NCs based MWEs, the ZnO/ α -MnO₂(1:2) NCs based MWE demonstrated the highest current response, indicating a synergistic enhancement in electrochemical performance due to the increased α -MnO₂ content, which provides more active sites for redox reactions. This ratio was able to detect lead at a concentration of 0.171 ppm, showing the highest sensitivity, while the other ratios, ZnO/ α -MnO₂(1:1) and ZnO/ α -MnO₂(2:1) exhibited intermediate sensitivities. Optimization of the experimental conditions, including accumulation time, deposition potential, and analyte concentration, was conducted using a 0.171 ppm Pb²⁺ solution at pH of 3.5. The optimal conditions for Pb²⁺ detection and quantification were found to be 150 s of accumulation time and -0.5V depositions potential. These optimized parameters resulted in increased stripping peak currents and enhanced sensitivity. Under these optimized conditions, Pb²⁺ quantification was conducted with the ZnO/ α -MnO₂(1:2) MWE across concentrations ranging from 0.074 to 0.016 ppm, yielding a calibration curve with a correlation coefficient (R^2) of 0.93577. The LOD for Pb²⁺ was determined to be 0.008 ppm. These findings demonstrate that the NCs exhibit excellent sensitivity for lead detection and quantification, making them promising candidates for the accurate monitoring of HTM in water.

5.2 Recommendations

The synthesis of ZnO/MnO₂ NCs using *Citrullus lanatus* peel extract as a natural and eco-friendly template has shown significant promise in enhancing the electrochemical properties of MWE for Pb²⁺ detection and quantification. Among the different ratios tested, the ZnO/ α -MnO₂(1:2) NCs demonstrated the highest sensitivity, detecting Pb²⁺ at concentrations as low as 0.008 ppm. This underscores the potential of biogenic materials in fabricating advanced MWEs. Future research should explore several key areas to enhance the findings of the current study.

- Although the ZnO/ α -MnO₂(1:2) NCs exhibited optimal performance, further investigation into the introduction of other MO, could potentially improve sensitivity and selectivity for Pb²⁺ and other HTM.
- While this study primarily focused on the detection of Pb²⁺, expanding the research to other heavy metals or contaminants in water, using similar modified NCs based MWE, could significantly broaden the environmental impact.
- Investigating their long-term stability and potential for regeneration would be essential for practical applications. Studies on how environmental factors such as pH and temperature affect their performance could also be valuable.
- Future research could involve applying the optimized ZnO/ α -MnO₂(1:2) NCs in real-world water samples. Field testing and comparison with standard detection methods will be crucial to validate their effectiveness and robustness in diverse environmental conditions.

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APPENDIX

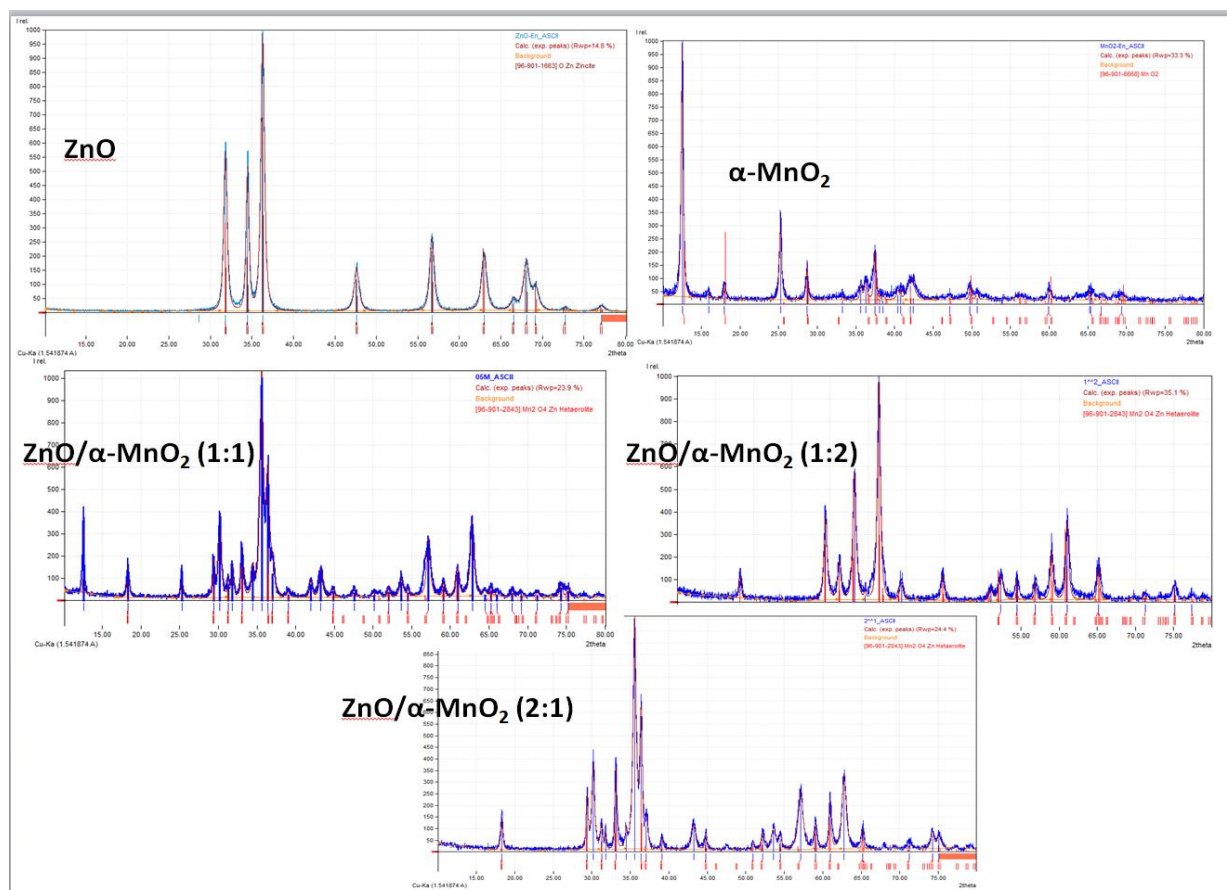


Figure 29 References from match! 3 phase identification software.