

**SINGLE-STEP SYNTHESIS OF rGO AND ZnO/rGO
COMPOSITE USING NON-TOXIC PRECURSORS:
INVESTIGATING A BROAD RANGE OF
APPLICATIONS.**

*Thesis submitted to the
University of Calicut
For the award of the Degree of*

**DOCTOR OF PHILOSOPHY IN
PHYSICS**

Under the Faculty of Science

By

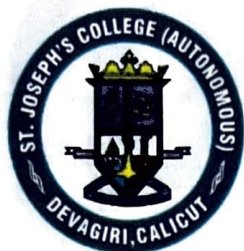
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**Under the Guidance of
Dr. MERIL MATHEW**



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CERTIFICATE

This is to certify that the Ph.D. thesis entitled **“Single-Step Synthesis of rGO and ZnO/rGO Composite Using Non-Toxic Precursors: Investigating a Broad Range of Applications.”** submitted to the University of Calicut for the award of the degree of Doctor of Philosophy in Physics is the record of the original work done by **Ms. Rehma S Philip**, under my supervision and guidance at the Department of Physics, St. Joseph's College (Autonomous) Devagiri, Calicut, Kerala and that no part of this thesis has been published earlier for the award of any other degree or diploma.

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DECLARATION

I hereby declare that the work presented in the thesis entitled “**Single-Step Synthesis of rGO and ZnO/rGO Composite Using Non-Toxic Precursors: Investigating a Broad Range of Applications.**” is based on the original work done by me under the guidance of **Dr. Meril Mathew, Professor, Department of Physics, St. Joseph’s College (Autonomous) Devagiri, Calicut, Kerala** and has not been included in any other thesis submitted previously for the award of any degree. The contents of the thesis have undergone plagiarism check using **iThenticate** software at **C.H.M.K. Library, University of Calicut**, and the similarity index was found within the permissible limit. I also declare that the thesis is free from AI generated contents.

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Symbols and Abbreviations

$\bullet\text{O}_2^-$	-	<i>Superoxide Anions</i>
$\bullet\text{OH}$	-	<i>Hydroxyl Radicals</i>
BQ	-	<i>Benzoquinone</i>
BET	-	<i>Brunauer-Emmett-Teller</i>
C_0	-	<i>Initial Dye Concentration</i>
Cr(III)	-	<i>Trivalent Chromium</i>
Cr(VI)	-	<i>Hexavalent Chromium</i>
C_t	-	<i>Dye Concentration At Time T</i>
CV	-	<i>Cyclic Voltammetry</i>
CVD	-	<i>Chemical Vapour Deposition</i>
e^-	-	<i>Electron</i>
ED-LC	-	<i>Electric Double-Layer Capacitive</i>
EDX	-	<i>Energy Dispersive X-Ray Analyzer</i>
FE-SEM	-	<i>Field Emission Scanning Electron Microscopy</i>
FT-IR	-	<i>Fourier-Transform Infrared Spectroscopy</i>
GCD	-	<i>Galvanostatic Charge Discharge</i>
h^+	-	<i>Hole</i>
HEK	-	<i>Human Embryonic Kidney Cell Line</i>
HP-LC	-	<i>High-Performance Liquid Chromatography (HPLC)</i>
HR-TEM	-	<i>High Resolution Transmission Electron Microscopy</i>
ICP-OES	-	<i>Inductively Coupled Plasma Optical Emission Spectroscopy</i>
IR	-	<i>Infra Red</i>
K_1	-	<i>Pseudo-First-Order Rate Constant</i>
K_2	-	<i>Pseudo-Second-Order Rate Constant</i>
LC-MS	-	<i>Liquid Chromatography- Mass Spectroscopy</i>
MB	-	<i>Methylene Blue</i>
MIC	-	<i>Minimum Inhibitory Concentration</i>
OFX	-	<i>Ofloxacin</i>
Pb	-	<i>Lead</i>
PFO	-	<i>Pseudo First Order</i>
PL	-	<i>Photoluminescence</i>
PSO	-	<i>Pseudo Second Order</i>
q_e	-	<i>Amount Of Pollutant Adsorbed At Equilibrium</i>
q_t	-	<i>Amount Of Pollutant Adsorbed At Time T</i>
R^2	-	<i>Linear Regression Coefficients</i>
rGO	-	<i>Reduced Graphene Oxide</i>
RhB	-	<i>Rhodamine B</i>
ROS	-	<i>Reactive Oxygen Species</i>
RPM	-	<i>Rotation Per Minute</i>
TA	-	<i>Terephthalic Acid</i>

<i>TGA</i>	-	<i>Thermogravimetric Analysis</i>
<i>UV</i>	-	<i>Ultra Violet</i>
<i>UV-Vis</i>	-	<i>Ultra Violet – Visible Spectroscopy</i>
<i>WHO</i>	-	<i>World Health Organization</i>
<i>XPS</i>	-	<i>X-Ray Photoelectron Spectroscopy</i>
<i>XRD</i>	-	<i>X-Ray Diffraction</i>
<i>ZnO</i>	-	<i>Zinc Oxide</i>
<i>ZOI</i>	-	<i>Zone Of Inhibition</i>
λ	-	<i>Wavelength</i>

SINGLE-STEP SYNTHESIS OF rGO AND ZnO/rGO COMPOSITE USING NON-TOXIC PRECURSORS: INVESTIGATING A BROAD RANGE OF APPLICATIONS.

Abstract

ZnO/reduced graphene oxide (rGO) composites are widely recognized for their exceptional multifunctionality. This thesis aims to contribute toward establishing a reliable and sustainable method for synthesizing rGO and ZnO/rGO composites in alignment with the United Nations Sustainable Development Goals (SDGs). We introduce a novel, rapid, and environmentally friendly single-step method for synthesizing ZnO/rGO nanocomposites through the pyrolysis of sucrose and zinc acetate. Unlike conventional methods, this approach is distinguished by its environmental sustainability, as it avoids the use of toxic chemicals and generates no harmful byproducts. This method advances the development of sustainable technologies by providing a green alternative for the cost-effective production of rGO/ZnO composites from inexpensive precursors. To the best of our knowledge, this is the first report of a single-step, rapid synthesis of rGO/ZnO composites via pyrolysis of table sugar and zinc acetate. The streamlined procedure enables bulk production in minutes, making it highly suitable for scalable, industrial applications.

In addition to the synthesis, this work investigates the multifunctional capabilities of ZnO/rGO composites, translating scientific innovation into practical, real-world applications. The material demonstrated excellent performance in heavy-metal removal from Cr(VI)- and Pb(II)-contaminated water, as well as in the photocatalytic degradation of organic pollutants such as methylene blue, rhodamine B, and the antibiotic ofloxacin, highlighting its strong potential for wastewater purification. It also demonstrates significant antibacterial activity against both Gram-positive and Gram-negative bacteria, highlighting its promise for biomedical and disinfection applications. Preliminary electrochemical studies further indicate its suitability for energy-storage devices such as supercapacitors. Overall, this work integrates green chemistry, environmental remediation, public health, and clean energy solutions, thereby contributing meaningfully to multiple global sustainability goals. This method not only simplifies the synthesis process but also represents a sustainable

and energy-efficient approach, making a meaningful contribution to the advancement of green nanomaterial synthesis.

Key words: ZnO/rGO composite, novel single-step synthesis, heavy metal adsorption, antibacterial, photocatalysis, energy storage.



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SINGLE-STEP SYNTHESIS OF rGO AND ZnO/rGO COMPOSITE USING NON-TOXIC PRECURSORS: INVESTIGATING A BROAD RANGE OF APPLICATIONS.

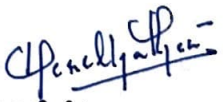
സംഗ്രഹം

പലതരം പ്രയോഗങ്ങൾക്കായി ഉപയോഗപ്പെടുത്താൻ കഴിയുന്നതിനാൽ ZnO/rGO സംയുക്തം ഇതിനകം വളരെയേറെ ശ്രദ്ധ നേടിയിട്ടുണ്ട്. rGOയും ZnO/rGO സംയുക്തങ്ങളും പരിസ്ഥിതി സൗഹൃദവുമായ രീതിയിൽ നിർമ്മിക്കുന്നതിന് ഒരു മാർഗം വികസിപ്പിക്കുക എന്നതാണ് ഈ പ്രബന്ധത്തിന്റെ പ്രധാന ലക്ഷ്യം. ഇത് ഐക്യരാഷ്ട്രസഭയുടെ സുസ്ഥിര വികസനലക്ഷ്യങ്ങളുമായി (SDGs) പൊരുത്തപ്പെടുന്നതാണ്. ഈ പഠനത്തിൽ, സ്യൂക്രോസും (ടേബിൾഷുഗർ) സിങ്ക് അസറ്റേറ്റും പൈറോളിസിസ് വഴി ഒരു ഘട്ടത്തിൽ ZnO/rGO നാനോ സംയുക്തങ്ങൾ നിർമ്മിക്കുന്ന ഒരു പുതിയതും വേഗതയേറിയതും പരിസ്ഥിതി സൗഹൃദവുമായ രീതിയാണ് അവതരിപ്പിക്കുന്നത്. പരമ്പരാഗത രീതികളുമായി താരതമ്യം ചെയ്യുമ്പോൾ, ഈ മാർഗം വിഷപദാർത്ഥങ്ങൾ ഒന്നും ഉപയോഗിക്കാത്തതും ഹാനികരമായ ഉപോൽപ്പന്നങ്ങൾ ഉണ്ടാകാത്തതുമാണ്. കുറഞ്ഞ ചെലവിലുള്ള ആരംഭവസ്തുക്കൾ ഉപയോഗിച്ച് ZnO/rGO സംയുക്തങ്ങൾ ചെലവുകുറഞ്ഞ രീതിയിൽ നിർമ്മിക്കാൻ കഴിയുന്നതിലൂടെ, ഇത് സുസ്ഥിര സാങ്കേതികവിദ്യകളുടെ വികസനത്തിന് സഹായകരമാണ്. ഞങ്ങളുടെ അറിവനുസരിച്ച്, ടേബിൾഷുഗറും സിങ്ക് അസറ്റേറ്റും ഉപയോഗിച്ച് ZnO/rGO സംയുക്തങ്ങൾ ഒരൊറ്റ ഘട്ടത്തിൽ വേഗത്തിൽ നിർമ്മിക്കുന്ന ആദ്യ റിപ്പോർട്ട് ഇതാണ്. ഈ ലളിതമായ നടപടിക്രമം മിനിറ്റുകൾക്കുള്ളിൽ വലിയ അളവിൽ ഉൽപ്പാദനം സാധ്യമാക്കുന്നതിനാൽ, വ്യാവസായികതലത്തിൽ ഉപയോഗിക്കാൻ ഇത് ഏറെ അനുയോജ്യമാണ്.

നിർമ്മാണരീതി വികസിപ്പിക്കുന്നതിനോടൊപ്പം തന്നെ ഇതിന്റെ വിവിധ പ്രായോഗിക ഉപയോഗങ്ങളും ഈ പഠനം പരിശോധിക്കുന്നു. Pb,Cr തുടങ്ങിയ ഘനലോഹങ്ങളാൽ മലിനമായ ജലത്തിൽ നിന്നും അവ നീക്കം ചെയ്ത ജലം ശുദ്ധീകരിക്കാൻ ഇത് പര്യാപ്തമാണ്. ഇതിനോടൊപ്പം ഈ സംയുക്തം വളരെ കാര്യക്ഷമമായ Photocatalyst ആണ്. ഇതിന് മെഥലിൻ ബ്ലൂ, റോഡമിൻ B എന്നീ വർണ്ണങ്ങളെയും ഫ്ലൂറോക്സാസിൻ പോലുള്ള ആന്റിബയോട്ടിക്കുകളേയും വിഘടിപ്പിക്കാൻ കഴിവുണ്ട്. ഇതിനാൽ ഇത് മലിന ജല ശുദ്ധീകരണത്തിന് വളരെ അനുയോജ്യമാണെന്ന് തെളിയുന്നു. കൂടാതെ ഗ്രാം-പോസിറ്റീവ്, ഗ്രാം-നെഗറ്റീവ് എന്നീ ബാക്ടീരിയകളെതിരെ ശക്തമായ ആന്റിബാക്ടീരിയൽ പ്രവർത്തനവും ഇത് കാണിക്കുന്നു. അതിനാൽ മെഡിക്കൽ മേഖലയിലും അണുനാശക ആവശ്യങ്ങൾക്കുമായി ഉപയോഗസാധ്യതയുണ്ട്. പ്രാരംഭ ഇലക്ട്രോകെമിക്കൽ പഠനങ്ങൾ സൂപ്പർകാപ്പാസിറ്ററുകൾ പോലുള്ള ഊർജ്ജ സംഭരണ ഉപകരണങ്ങൾക്ക് ഇത് അനുയോജ്യമാണെന്നും സൂചിപ്പിക്കുന്നു. മൊത്തത്തിൽ, ഈ ഗവേഷണം ഹരിതരസതന്ത്രം, പരിസ്ഥിതി ശുദ്ധീകരണം, പൊതുജനാരോഗ്യം, ശുദ്ധ ഊർജ്ജ പരിഹാരങ്ങൾ എന്നിവയെ ഒരുമിപ്പിക്കുന്നു. ഇതിലൂടെ ആഗോള സുസ്ഥിര വികസന ലക്ഷ്യങ്ങൾക്ക് ഗണ്യമായ സംഭാവന നൽകുന്നു. ഈ രീതി നിർമ്മാണ പ്രക്രിയ ലളിതമാക്കുന്നതോടൊപ്പം സുസ്ഥിരവും ഊർജ്ജക്ഷമവുമായ ഒരുസമീപനം അവതരിപ്പിക്കുന്നു, ഹരിത നാനോമെറ്റീരിയൽ നിർമ്മാണരംഗത്തെ പുരോഗതിക്ക് ഇത് ഒരു പ്രധാന സംഭാവനയാണ്.

പ്രധാന പദങ്ങൾ: ZnO/rGO സംയുക്തം, നവീന ഒറ്റഘട്ട നിർമ്മാണം, ഘനലോഹ മലിനീകരണ നീക്കം, ആന്റി ബാക്ടീരിയൽ, ഫോട്ടോ കാറ്റലിസിസ്, ഊർജ്ജ സംഭരണം


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Preface

The research focuses on the synthesis of reduced graphene oxide (rGO) and ZnO/rGO composites through a single-step, environmentally friendly process, aligning with the principles of the United Nations Sustainable Development Goals (SDGs). Conventional synthetic routes for rGO are typically complex, hazardous, and resource-intensive, involving toxic chemicals, lengthy reaction times, and multiple processing stages that generate harmful by-products. The fabrication of ZnO/rGO composites is even more challenging, as it generally requires the separate synthesis of GO or rGO followed by additional steps to incorporate zinc precursors.

In this context, the present study introduces a novel, rapid, and scalable one-step synthesis route for the fabrication of ZnO/rGO composites using inexpensive, non-toxic, and readily available materials. The process involves the simultaneous pyrolysis of sucrose to form rGO and the thermal decomposition of zinc acetate to yield ZnO nanoparticles, resulting in the formation of the ZnO/rGO nanocomposite. Beyond the synthesis aspect, this study aims to bridge the gap between scientific innovation and practical application by exploring the multifunctional potential of the synthesized ZnO/rGO composites. The synthesized composites exhibit excellent heavy-metal adsorption and strong photocatalytic performance, demonstrating potential for water purification. They also show significant antibacterial activity against both Gram-positive and Gram-negative bacteria, indicating suitability for biomedical applications. Preliminary electrochemical studies further reveal promising behaviour for energy storage, particularly in supercapacitor electrodes.

To the best of our knowledge, this is the first report on the single-step, rapid synthesis of rGO/ZnO composites via the pyrolysis of table sugar and zinc acetate. This method not only simplifies the synthesis process but also represents a sustainable and energy-efficient strategy, making a meaningful contribution to the advancement of green nanomaterial synthesis.

The thesis, entitled “**Single-Step Synthesis of rGO and ZnO/rGO Composite Using Non-Toxic Precursors: Investigating a Broad Range of Applications.**”, is organized into eight chapters:

Chapter 1 provides a comprehensive literature review of the materials under study, reduced graphene oxide (rGO) and zinc oxide (ZnO). The chapter outlines their

fundamental properties, synthesis techniques, and associated challenges. The chapter highlights limitations of conventional ZnO/rGO fabrication routes and emphasizes the need for sustainable, green, and scalable synthesis approaches. The section concludes with the motivation for developing a single-step, industrially scalable process for synthesizing ZnO/rGO composites.

Chapter 2 is divided into two sections. The first details the single-step, green, and scalable synthesis of rGO from sucrose, including optimization of reaction parameters and characterization results confirming its formation. The second section describes the single-step synthesis of ZnO/rGO composites by extending the same green approach. It includes the optimization of reaction parameters such as time, temperature, and selection of a suitable zinc precursor, along with a detailed description of the process sequence. It also includes the results of the comprehensive characterization of the prepared composites.

Chapter 3 investigates the heavy metal adsorption efficiency of the ZnO/rGO composite. After a general overview of heavy metal pollution and associated health risks, the chapter presents detailed studies on the removal of chromium [Cr(VI)] and lead [Pb(II)] from aqueous solutions. In the first section, the adsorptive removal of Cr(VI) is examined by evaluating the effects of key parameters such as initial pH, contact time, adsorbent dosage, and light irradiation. Post-adsorption characterization using EDX and XPS is included to confirm the adsorption. The second section focuses on the removal of Pb(II) ions using the ZnO/rGO composite. The effects of initial concentration, solution pH, contact time, and light irradiation are thoroughly analysed. Post-adsorbent characterization results are also presented to further validate the Pb(II) removal mechanism.

Chapter 4 investigates the antibacterial activity of rGO, ZnO, and ZnO/rGO composites (ZG-10, ZG-40, ZG-60, and ZG-100) against both Gram-positive and Gram-negative bacterial strains. The antibacterial efficacy was assessed using the agar disc diffusion method. Minimum inhibitory concentration (MIC) and cytotoxicity analyses were also performed on the samples.

Chapter 5 discusses the photocatalytic performance of ZnO/rGO composites. The degradation of methylene blue (MB) dye was used as the primary evaluation method, along with scavenger tests to elucidate the degradation mechanism. Additional

studies on Rhodamine B and the antibiotic ofloxacin further confirm the photocatalytic efficiency of the composite.

Chapter 6 evaluates the electrochemical behaviour of rGO, ZnO/rGO (ZG-50), and ZnO (ZG-100) for supercapacitor applications. Cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) analyses demonstrate that the ZnO/rGO composite shows considerable promise as an electrode material for energy storage devices.

Chapter 7 summarizes the overall research findings, integrating the results of synthesis, characterization, and application studies.

Chapter 8 outlines future research prospects and discusses potential industrial applications of the ZnO/rGO composite synthesized through the rapid, green, and scalable single-step method, with emphasis on sustainable water treatment, biomedical uses, and energy storage technologies.

A comprehensive bibliography is provided at the end of each chapter.

CHAPTER I

Introduction, Materials and Methods

1.1. Introduction

Carbon is one of the most abundant and versatile elements on Earth, existing in several allotropes. The common allotropes are graphite, diamond, fullerenes, carbon nanotubes, and graphene, each possessing unique and remarkable properties [1]. Among these, graphene has emerged as the most extensively studied allotrope, often referred to as a “wonder material” or “material of the future” because of its extraordinary properties [2,3].

The discovery of graphene has revolutionized scientific research and technological development. Graphene is a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice. Owing to its extraordinary physical, chemical, and mechanical properties, it has attracted immense interest from both academia and industry. Graphene possesses high electrical and thermal conductivity, superior mechanical strength, excellent optical transparency, and an exceptionally large specific surface area. Such properties make graphene one of the most fascinating and widely investigated nanomaterials of the 21st century [1,2,4,5].

In 2004, Andre Giem and Konstantin Novoselov successfully isolated monolayer graphene from bulk graphite using the mechanical exfoliation (Scotch tape) method. They received the Nobel Prize in Physics in 2010 for this groundbreaking work [1,6]. Their work marked the first theoretical and experimental comparison of the intrinsic properties of graphene, laying the foundation for a new era in material science [7]. In their article, “The Rise of Graphene,” they noted that “only the very tip of the iceberg has been uncovered so far” emphasizing the vast potential of graphene-based research that followed [8]. Since then, research in material science has increasingly focused on the synthesis, modification, and diverse applications of graphene and its derivatives [3,5,7].

The structure of graphene consists of two-dimensional honeycomb lattice of carbon atoms bonded through sp^2 hybridization, forming strong σ - bonds and delocalized π -bonds in a configuration similar to benzene ring [9,10]. This arrangement

gives rise to its unique electronic structure, characterized by zero band gap, and allows it to behave as a semimetal with high carrier mobility [7]. The schematic representation of graphene's atomic structure is shown in Fig. 1.1.

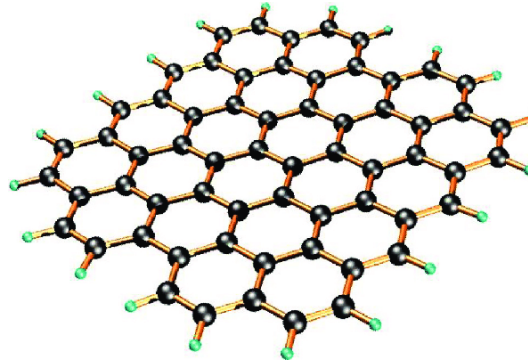


Fig. 1.1: Structure of graphene [11].

Graphene possesses outstanding properties that make it one of the most remarkable materials ever discovered. It is thermodynamically stable and possesses exceptional mechanical, thermal, and electronic characteristics. Graphene is known for its ultra-high specific surface area of approximately $2630 \text{ m}^2 \text{ g}^{-1}$, superior carrier mobility in the range of $(2\text{--}3) \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and excellent thermal ($\sim 5000\text{--}6000 \text{ W m}^{-1} \text{ K}^{-1}$) and electrical ($\sim 10^6 \text{ S cm}^{-1}$) conductivity. It also demonstrates outstanding mechanical strength, nearly 200 times stronger than steel. The Young's modulus is about 1 TPa, making it one of the strongest materials ever tested [1,2,5,6,9,10].

The electrons in graphene behave as massless Dirac fermions, capable of moving at speeds close to that of light, which leads to its extraordinary charge transport behaviour [6,12]. Furthermore, graphene is optically transparent, with an optical transparency of approximately 97.7%, and can withstand an extremely high current density of 10^8 A cm^{-2} [2]. Its chemical inertness and thermal stability make it highly suitable for applications under harsh environmental conditions. These exceptional attributes have earned graphene the title “substance of the future.” [3]. Moreover, the properties of graphene can be tuned and enhanced through several modification strategies, such as heteroatom doping that introduces structural defects and active sites, broadening its range of potential applications [1,6]. The properties of graphene are summarised in Table 1.1.

Parameter	Value
Charge carrier mobility	200,000 cm ² /Vs
Thermal conductivity	5000W/mK
Transparency	97.4%
Specific surface area	2630 m ² /g
Young's modulus	1Tpa
Bandgap	Zero
Electrical conductivity	10 ⁶ S/cm

Table 1.1: Properties of graphene.

Owing to these outstanding features, graphene has found applications across a wide range of scientific and technological fields. The global graphene market is commonly categorized into six major sectors: electronics, automotive, aerospace and defence, medical and healthcare, energy, and others—the latter including industries such as inks, coatings, water purification, and textiles [7]. Continuous research efforts are focused on expanding the potential uses of graphene and integrating it into commercial products to improve the living standards of mankind.

The global graphene market size is valued at approximately USD 419 million in 2024 and is projected to reach around USD 1.78 billion by 2030 [13]. This rapid growth is driven by the rising demand for it in the automotive and aerospace sectors, the increasing need for advanced energy storage systems, and extensive research and development activities. With its exceptional versatility, graphene and its related materials are expected to play a crucial role in addressing contemporary challenges such as the energy crisis and environmental pollution [6,10].

1.2 Synthesis methods of graphene

Graphene exhibits extraordinary properties and has found applications in nearly all fields of science and technology. However, the production of single-layer, defect-free graphene remains a significant challenge. Numerous synthesis techniques have been developed to obtain graphene and its derivatives since Geim and Novoselov first demonstrated a method to isolate graphene in 2004. Over the past two decades, research has advanced rapidly, enabling the large-scale production of graphene through various

methods. Broadly, these synthesis techniques are categorized into two main approaches: top-down (destructive) and bottom-up (constructive) methods.

The top-down approach involves producing graphene by “breaking down” bulk carbon materials such as graphite. This process includes the structural exfoliation or destruction of the parent material, which leads to the separation of individual graphene sheets. The common top-down methods include mechanical exfoliation, chemical exfoliation, ball milling, arc discharge, and chemical synthesis. In contrast, the bottom-up method refers to the preparation/construction of graphene from atomized carbon-based precursors through chemical reactions or deposition processes. This approach enables the formation of graphene sheets directly from atomic or molecular carbon sources. The methods under this category include chemical vapor deposition, epitaxial growth, and pyrolysis [5,12,14]. Fig. 1.2 illustrates the various methods that fall under this classification.

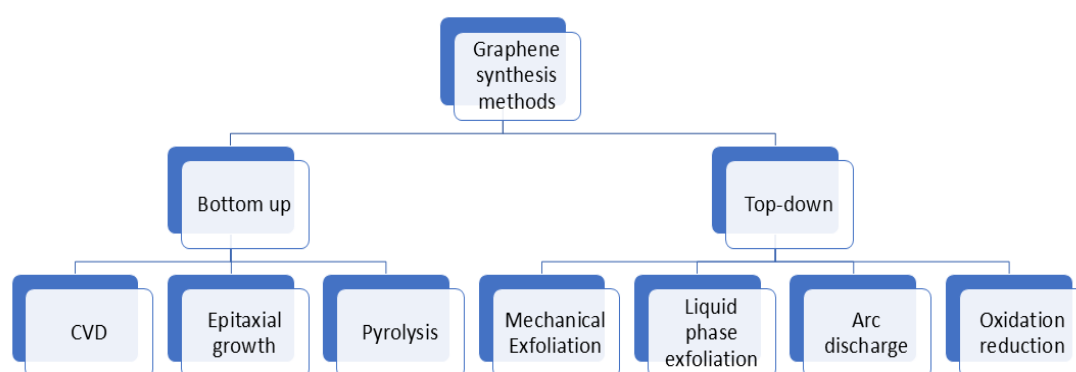


Fig. 1.2: Synthesis methods of graphene.

Although numerous techniques for the synthesis have been developed, only a few can produce high-quality and high-purity graphene [3,12]. Most of the methods are complex, involve lengthy procedures, and are not cost-effective. The properties of graphene are strongly dependent on the number of layers and the presence of structural defects. The techniques such as micro-mechanical exfoliation, CVD, epitaxial growth, arc discharge, and laser or electron beam irradiation, are capable of yielding relatively perfect graphene. However, these methods typically require sophisticated equipment, precisely controlled synthesis environments, and lengthy processing times, resulting in

low yield and high production costs [5,14]. Consequently, most of these methods are suitable primarily for small-scale production.

The following sections discuss some of the widely adopted graphene synthesis methods.

1.2.1 Chemical Vapour Deposition (CVD)

Chemical Vapor Deposition is one of the most widely used and reliable methods for producing high-quality graphene. This technique enables the synthesis of single-layer and few-layer graphene with a large surface area and excellent structural uniformity. The graphene produced by this method is highly suitable for transparent conductive films, solar cells, and semiconductor technologies [15].

CVD is a bottom-up technique that involves the thermal decomposition of hydrocarbon gases such as methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), or hexane (C_6H_{14}) on a metal catalyst substrate such as copper or nickel under an inert atmosphere at elevated temperatures, typically around 1000°C . At this temperature, hydrocarbons decompose into carbon and hydrogen atoms, the carbon atoms diffuse and deposit on the metal substrate surface, eventually forming a continuous graphene layer with high structural integrity and surface area [5,10].

The typical CVD setup includes a furnace for heating, a temperature controller, a vacuum pump, and a pressure gauge to maintain the desired temperature and pressure. It also includes gas flow controllers to regulate precursor gas flow rates, and a reaction chamber where the synthesis takes place [10]. The quality of the resulting graphene is strongly influenced by the controlled deposition of precursor gases, which depends on key parameters such as temperature, gas flow rate, and chamber pressure [15].

The CVD method offers excellent control over graphene thickness and quality, making it ideal for applications in electronics, transparent conductive films, sensors, and energy storage devices. However, the process also presents several challenges. It is time-consuming, requires high energy input, and depends on sophisticated instrumentation. The production cost of CVD-grown graphene is relatively high, and transferring the graphene film from the growth substrate to a target substrate remains a

major difficulty. Additionally, the process demands large quantities of high-purity gases, and maintaining the equipment is complex and expensive [6,12].

1.2.2 Epitaxial growth

The epitaxial growth method is another highly effective bottom-up approach for synthesizing high-quality, large-area graphene. By this technique, graphene is formed through the thermal decomposition of a silicon carbide (SiC) wafer under controlled temperature and pressure. In this technique, single-crystal SiC is heated to very high temperatures, usually between 1200 °C and 1600 °C, in an ultra-high vacuum or inert gas atmosphere. At these temperatures, silicon atoms from the SiC surface sublime, leaving behind the excess carbon atoms, which subsequently rearrange to form graphene layers on the substrate [5,16,17].

The graphene produced by epitaxial growth exhibits excellent structural integrity, uniformity, and low defect density, making it suitable for electronic and optoelectronic applications [14,18]. However, this technique is energy-intensive, requiring high processing temperatures, sophisticated instrumentation, and expensive single-crystal SiC substrates. This increases the production costs and limits scalability for industrial applications [17].

1.2.3 Exfoliation-Based Synthesis of Graphene

Graphite is the oldest known allotrope of carbon. It is composed of stacked layers of sp^2 -hybridized carbon atoms arranged in hexagonal rings. Within each sheet, the carbon atoms are bonded by strong covalent bonds, while the graphene layers are held together by weak van der Waals forces. Due to this weak interlayer bonding, graphite lacks mechanical strength and structural integrity, limiting its direct application in advanced technologies [2]. When these layers are separated into individual graphene sheets, the resulting material exhibits remarkable mechanical, electrical, and thermal properties, as discussed earlier.

Several methods have been developed to produce graphene or graphene-like materials directly from graphite, including exfoliation, arc discharge, and oxidation–reduction techniques. Among these, exfoliation methods are considered simple and effective top-down approaches for graphene synthesis. Depending on the mechanism

used to separate the graphene layers, exfoliation can be classified into mechanical, liquid-phase, and electrochemical types [15].

1.2.3.1 Mechanical Exfoliation

Mechanical exfoliation, also known as the Scotch tape method or peeling-off technique, is one of the earliest and most direct methods used to obtain graphene flakes [10]. In this approach, layers of graphene are mechanically peeled from highly oriented graphite crystals by applying sufficient force to overcome the van der Waals attraction between adjacent layers [17]. The method gained attention when Andre Geim and Konstantin Novoselov successfully isolated monolayer graphene in 2004 using adhesive tape.

The mechanically exfoliated graphene exhibits high structural quality, although the process is time-consuming and yields only a very small quantity (typically less than 0.5 g per day). The resulting flakes vary in size and thickness. Moreover, the process lacks precision and scalability. Therefore, this technique is mainly used for fundamental studies of the intrinsic properties of graphene, rather than for commercial production [15]. Variations such as sonication or high-shear mixing have been employed to improve exfoliation, but they still produce low yields and non-uniform graphene flakes.

1.2.3.2 Liquid-Phase Exfoliation (LPE)

In liquid-phase exfoliation, surfactants or intercalating agents are used to enable the separation of graphene sheets from graphite. These agents insert themselves between the layers, thus increasing the interlayer spacing. This intercalation results in reducing the van der Waals force of attraction between the layers. The process typically involves two stages [17]:

1. Intercalation – chemical agents are inserted between graphite layers, expanding the material.
2. Exfoliation – agitation by suitable methods, such as sonication, disperses the layers into individual graphene sheets.

The resulting dispersion contains single- to few-layer graphene flakes. It is further separated based on size and layer number using centrifugation or filtration [15]. Although LPE is low-cost, scalable, and suitable for large-scale production, it often

involves hazardous or corrosive intercalating agents. Furthermore, this method results in graphene with moderate quality and high defects.

1.2.3.3 Electrochemical Exfoliation

The electrochemical exfoliation method employs electrically assisted expansion and exfoliation to produce graphene. In this method, graphite acts as the electrode material. When a direct current (DC) is applied, it is exfoliated into few-layer graphene in the presence of a conductive electrolyte. The applied potential drives ions from the electrolyte into the graphite structure, facilitating their separation by weakening the van der Waals forces between adjacent layers. As a result, a suspension of mono- and few-layer graphene flakes is produced [10,15].

Various forms of graphite, including foils, rods, plates, or powders, can be used as electrodes [10]. The electrolyte composition plays a crucial role in this technique, as it significantly affects the size, thickness, and electrical properties of the resulting graphene [15].

The main advantage of this method is that it can produce large quantities of mono- and few-layer graphene. However, the graphene flakes produced through this method often exhibit irregular shapes and lower structural quality [17]. Despite this, electrochemical exfoliation remains attractive due to its simplicity, scalability, and cost-effectiveness.

1.2.4 Arc discharge

The arc discharge method is another technique employed for the synthesis of graphene from high-purity graphite electrodes. This method comes under the category of the top-down approach. In this process, the carbon nanostructures such as graphene, carbon nanotubes (CNTs), fullerenes, and multi-layer graphene are produced through a high-temperature plasma-assisted reaction [19,20].

In this method, a chamber filled with an inert gas, such as helium or argon, at low pressure serves as the reaction environment. Two graphite electrodes are kept a few millimetres apart, and a high direct current is applied between them. The resulting high current flows from the anode to the cathode, which creates an intense plasma zone, with extremely high temperatures ($>1700\text{ }^{\circ}\text{C}$). Under these conditions, carbon atoms from

the anode vaporize and subsequently condense to form various carbon nanomaterials, including graphene flakes, multi-layer graphene, CNTs, and fullerenes, and these are deposited on the cathode and chamber walls [21].

The quality and morphology of the carbon nanostructures produced via arc discharge depend on several parameters, including the purity of graphite, electrode spacing, type and pressure of the inert gas, applied current density, and cooling rate [19]. This method is significant for being a chemical-free process that yields graphene with good crystallinity [22].

However, the arc discharge technique also presents significant limitations. The process offers limited control over the types of carbon nanomaterials produced, often resulting in a mixture of graphene, CNTs, and fullerenes, which complicates separation and purification. Moreover, it requires a controlled environment, high energy input, and typically results in a low yield of graphene [21]. Consequently, the method is not suitable for large-scale or commercial graphene production.

1.2.5 Biomass-Derived Graphene (Flash Joule Heating Method)

Biomass wastes such as wheat straw, sawdust, and agricultural residues are rich in carbon. Hence, they can be considered as promising precursors for the sustainable production of graphene. One of the most effective techniques for converting these carbon-rich materials into graphene is the Flash Joule Heating (FJH) method. In this process, a high electric current is passed through the biomass material. The high electrical resistance of the biomass causes a swift rise in temperature, which leads to the rapid phase transformation and the conversion of carbon atoms into graphene. This approach offers substantial environmental and economic benefits. It achieves up to a 50% reduction in production costs and reduces carbon emissions and freshwater consumption by more than 90% compared with conventional synthesis methods [6].

1.2.6 Chemical Methods

Graphene is widely recognized as a remarkable material with outstanding electrical, mechanical, and thermal properties. However, pristine graphene also possesses several inherent limitations that restrict its broader applicability. The major drawbacks are summarized below [2,7,14,17,23,24,25]

1. High production cost: Most of the methods that come under the bottom-up approach require sophisticated instruments and high energy input.
2. Defect formation: The top-down methods are more cost-effective, although they often introduce defects during synthesis, compromising the structural quality of graphene.
3. Low yield: Most of the top-down and bottom-up synthesis methods result in lower production quantities, hindering scalability.
4. Hydrophobic nature: Graphene is hydrophobic in nature, which restricts its use in water-based applications.
5. Poor dispersibility: Pristine graphene disperses poorly in aqueous media, limiting its processability.
6. Agglomeration tendency: The strong π - π stacking between graphene layers results in rapid agglomeration, reducing surface area and deteriorating its superior properties.
7. Difficulty in composite formation: Graphene exhibits poor affinity toward solvents. The tendency of graphene sheets to coagulate in liquid media complicates the preparation of graphene-based composites through solution processing.
8. Zero band gap: The absence of a band gap in graphene limits its use in semiconducting and optoelectronic applications.

The graphene-like structure produced from the oxidation-reduction method eliminates most of the limitations of pure graphene. The low cost and suitability for large-scale production make it one of the most effective strategies and preferred routes for producing graphene-like materials. The graphene-like structure obtained through this method is termed reduced graphene oxide (rGO). It is the chemically modified form of graphene produced by the extensive oxidation of graphite. The process involves three steps: oxidation of graphite to graphite oxide, exfoliation of graphite oxide into graphene oxide (GO), and finally, reduction of GO to produce rGO [25].

Graphene oxide is the starting material for the synthesis of rGO. However, the synthesis of GO involves the chemical oxidation and exfoliation of graphite using strong oxidizing agents. This process introduces oxygen-containing functional groups (such as hydroxyl, epoxy, and carboxyl groups) onto the graphene sheets, significantly altering their physical and chemical properties. The presence of abundant functional

groups makes GO hydrophilic and easily dispersible in water and other polar solvents [23,26].

Several chemical oxidation methods have been developed for the preparation of GO since the 1800s. The widely known methods are the Brodie, Staudenmaier, Hofmann, and Hummer's methods, along with their various modifications. These methods use strong acids (H_2SO_4 , HNO_3 , etc.) and alkali metal compounds (KClO_3 , KMnO_4 , NaNO_3) to oxidise graphite [24]. Over time, each new method has been refined to minimize the limitations of the preceding one by improving safety, efficiency, and yield. The following sections provide a brief discussion of these major chemical routes for GO synthesis.

1.2.6.1 Brodie's oxidation method (Fuming HNO_3 and KClO_3)

The Brodie method was introduced in 1859 by Benjamin C. Brodie, which is recognized as the first method for synthesizing graphite oxide from graphite. At that time, Brodie referred to the oxidized product composed of carbon, oxygen, and hydrogen as "graphon," a term later identified as graphite oxide [7].

In this process, graphite powder is oxidized by treating it with potassium chlorate (KClO_3) and fuming nitric acid (HNO_3) at around 60 °C for three to four days. This oxidation significantly increases the oxygen content and mass of graphite, and the resulting product is subjected to repeated oxidation and washing cycles to remove residual acids and salts. After the cleaning steps, the material is collected and vacuum-dried to get the final product.

Despite having historical importance, the Brodie method suffers from several drawbacks. It is a slow reaction, produces toxic gases, and yields graphite oxide of lower quality. Although it marked a significant milestone in graphene-related research, it is unsuitable for GO production [24,26,27].

1.2.6.2 Staudenmaier method (Fuming HNO_3 , concentrated H_2SO_4 acid and KClO_3)

The Staudenmaier method (1898) is an improved version of Brodie's method. Staudenmaier refined the process by introducing concentrated sulfuric acid (H_2SO_4) along with concentrated nitric acid (HNO_3) and by adding potassium chlorate (KClO_3) in successive portions rather than all at once as used in Brodie's method [7,28]. In this

modified approach, the mixed acids act as strong oxidizing agents, while KClO_3 assists in the oxidation of graphite [29]. During the process, graphite flakes are dispersed in the acid mixture, and KClO_3 is gradually added in portions under controlled temperature conditions. The step-by-step addition of KCl_3 prevents sudden temperature rise or explosion. The oxidation process typically lasts for around four days [28]. After completion, the reaction mixture is quickly cooled by adding DI water and dilute HCl and is repeatedly washed to remove salts and acids remaining in the product [29]. Following purification, the graphite oxide is vacuum-dried at a higher temperature, which causes exfoliation into layers [26].

In this method, the degree of oxidation and uniformity of the resulting graphite oxide were improved by the stepwise addition of KClO_3 [24]. Although this method has significant advancement over Brodie's method by achieving higher oxidation levels and better control over oxygen content, it still requires a long reaction time and involves safety hazards. During the reaction, toxic chlorine gas evolves, and the reaction proceeds at risk of explosion [24,29]. Because of its hazardous nature and long processing time, it is rarely used today.

1.2.6.3 Hummer's method (Concentrated H_2SO_4 acid, KMnO_4 and NaNO_3)

Hummers and Offman reported a highly effective method for producing GO from graphite flakes in 1958 [28]. In this method, hazardous reagents used in earlier approaches (fuming nitric acid and potassium chlorate) were replaced with the safer and more efficient combination of acids and alkali metal oxide. Concentrated sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3), and potassium permanganate (KMnO_4) were used as oxidizing agents in this approach [23,28,30].

In this process, in the first step, graphite powder and sodium nitrate are added to concentrated sulfuric acid in an ice bath. After that, Potassium permanganate is added gradually to it. The gradual addition controls the reaction rate and the ice bath prevents overheating. Water is slowly added after proper mixing and stirring which results in a large exothermic reaction. At this stage, the temperature rises to around 98 °C. Once the oxidation is complete, hydrogen peroxide and water are poured into the mixture to remove residual manganese species (MnO_4^- and MnO_2). Following this, multiple washing cycles eliminate impurities. The resulting graphite oxide is then exfoliated to

produce graphene oxide. The GO produced by this method possesses a high density of oxygen-containing functional groups [26,31,32].

Unlike earlier methods that required several days for the oxidation of graphite, the Hummers method achieves effective oxidation in a significantly shorter time. The substitution of KClO_3 with KMnO_4 improves safety by eliminating the formation of explosive ClO_2 gas, while using NaNO_3 eliminates the acid vapor generation [28]. This method efficiently yields GO with a sheet-like morphology and abundant oxygenated functional groups.

However, despite its efficiency, the Hummer's method has several drawbacks [27,33].

1. Emission of toxic gases such as NO_2 and N_2O_4
2. Evolution of the reaction under explosive conditions
3. Use of large volumes of strong acids (approximately 2.3 L for every 100 g of graphite)
4. Low yield
5. Residual nitrate in the product

To address these drawbacks, several modified versions of the Hummers method have been developed to enhance safety, yield, and environmental sustainability [27]. The key modification involves eliminating NaNO_3 from the reaction mixture [34]. Other refinements are adding a pre-oxidation step prior to KMnO_4 treatment, increasing the amount of KMnO_4 , and substituting KMnO_4 with K_2FeO_4 [33]. By these changes, the oxidation efficiency of the graphite is improved while minimizing toxic gas emissions and enhancing the overall safety and performance.

1.3 Graphene oxide (GO)

GO is a chemically modified form of graphene that contains abundant oxygen-containing functional groups such as hydroxyl, epoxy, carbonyl, and carboxyl groups distributed across its basal planes and edges [2,8,35]. These functional groups are introduced during the oxidation of graphite, and the resultant GO exhibits unique physicochemical properties. The presence of these groups enhances its colloidal stability. Further, the mechanical, electrical, and optical properties of GO can be tuned by controlling the degree of oxidation [3,28]. The hydrophilic nature of the oxygen functionalities makes GO highly dispersible in water and other polar solvents through

hydrogen bonding interactions [2,27]. This superior dispersibility facilitates the formation of uniform thin films of GO on various substrates [27] and enables the synthesis of GO-based composites for a wide range of applications [28].

Several structural models have been proposed for GO. The models of Hofmann, Ruess, Scholz–Boehm, Nakajima–Matsuo, Lerf–Klinowski, and Szabó tried to describe the structure of GO. Among these, the Lerf–Klinowski model is the most widely accepted model due to its strong experimental support from solid-state nuclear magnetic resonance (NMR) and XRD studies. According to this model, GO consists of hydroxyl and epoxy groups randomly distributed across the basal planes, and carboxyl and carbonyl groups are located at the sheet edges [4,36]. The schematic representation of the Lerf–Klinowski structure is shown in Fig. 1.3 [37].

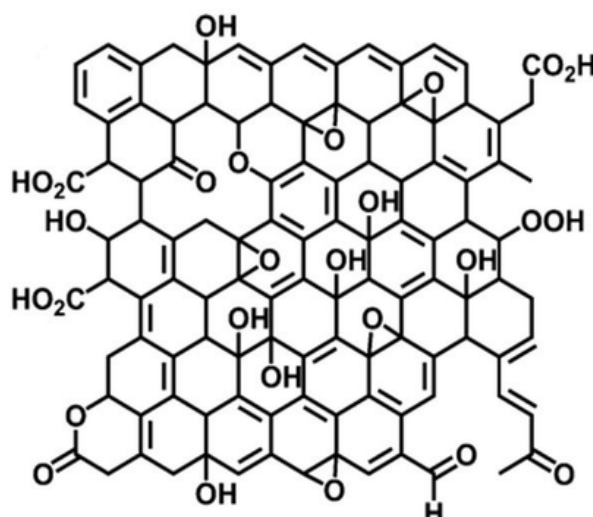


Fig. 1.3: Lerf-Klinowski model of graphene oxide.

Although GO is structurally similar to graphene, its properties differ significantly from those of graphene. The abundant oxygen functional groups present on the surface of GO interrupt the extended π -conjugation within the hexagonal carbon network. This disruption reduces the delocalization of π -electrons, making GO electrically insulating or semiconducting which depends on the degree of oxidation [8,28]. Moreover, the strong oxidation process during synthesis introduces lattice defects, which also lead to a decrease in the electrical conductivity of GO [27]. Thus, the properties of GO are strongly governed by its oxidation level and chemical composition. It can be tuned by the addition or removal of oxygen groups, which adjust the balance between sp^2 and sp^3 carbon atoms in the material [38,39].

Owing to its unique characteristics, such as a high density of oxygen functionalities, large surface area, and excellent dispersibility, GO has found applications in diverse fields. It is extensively used in water purification and filtration, and in biomedical applications like drug delivery and tissue engineering. Furthermore, its excellent solution processability enables easy incorporation into various composite materials, enhancing their performance and expanding their practical applications [27,28,29,35,40].

1.4 Reduced graphene oxide (rGO)

GO has attracted considerable attention as it is the starting material for the large-scale synthesis of graphene. The graphene-like material obtained by reducing GO is known as reduced graphene oxide. It exhibits properties similar to pristine graphene and possesses unique features that make it suitable for specialized applications [23,27].

As discussed earlier, GO has a structure analogous to graphene but contains numerous lattice defects and oxygen-containing functional groups present on both the basal plane and sheet edges [3,28]. The pristine graphene is composed entirely of sp^2 -hybridized carbon atoms [2,4] while GO contains a mixture of sp^2 and sp^3 hybridized carbons. The sp^3 hybridized carbons are found due to the presence of oxygen functionalities and structural distortions [17]. The disruption of the sp^2 conjugated network imparts an insulating nature to GO, while the abundance of oxygen-containing functional groups gives it a highly hydrophilic character. [28,29,35].

The properties of GO can be tailored by controlled chemical modifications. The removal of the oxygen-containing functional groups from GO partially restores the electronic and structural characteristics of graphene [35,41]. This removal process is generally termed as reduction methods. The resulting material after reduction, known as rGO (reduced graphene oxide), is a graphene-like structure and represents an important and versatile member of the graphene family.

rGO exhibits mechanical, electronic, thermal, and optical properties comparable to those of pristine graphene [3]. This is because rGO possesses a graphene-like basal plane with some structural defects and is partially decorated with oxygen-containing functional groups [23,42]. The major difference between GO and rGO lies in the extent of these oxygen functionalities, a factor that greatly influences their overall properties.

rGO is particularly known for its enhanced electrical conductivity. The removal of oxygen functional groups during the reduction process partially restores the π -conjugated network, facilitating efficient charge transport [8]. Additionally, rGO retains a certain degree of hydrophilicity due to the incomplete removal of oxygen functionalities during the reduction process [43]. The structural comparison between GO and rGO is illustrated in Fig. 1.4.

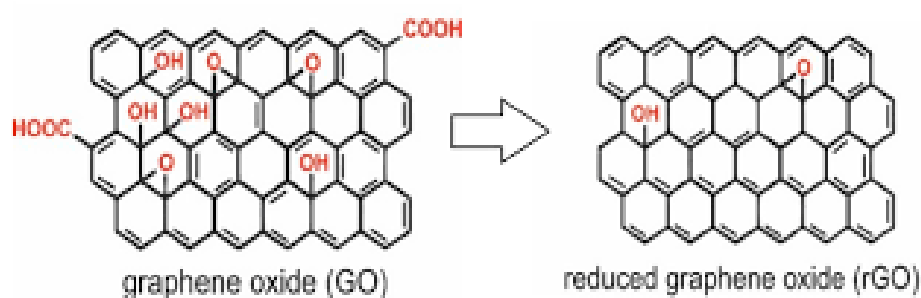


Fig. 1.4: Image illustrating GO and rGO [44].

The rGO can be achieved from GO through various reduction techniques. This process involves the removal of oxygen-containing functional groups from the GO sheets, leading to the partial restoration of sp^2 hybridized carbon bonds [43]. The reduction process involves several approaches, including chemical, thermal, photo-assisted, hydrothermal or solvothermal, and green reduction methods [2,25,35,36].

Chemical reduction is one of the most widely employed and effective approaches, utilizing organic and inorganic reducing agents for the removal of oxygen functionalities from the GO surface. Commonly used reducing agents are sodium borohydride, hydrazine hydrate, hydroiodic acid, urea, ascorbic acid, and amino acids [2,23]. Additionally, catalysts such as aluminium and zinc, as well as organic solvents like dimethylformamide (DMF) and alcohols (methanol, ethanol, isopropanol, benzyl alcohol), have also been reported to effectively reduce GO to rGO [35]. However, many of these reagents are toxic and environmentally hazardous.

Thermal reduction is another approach that offers a cleaner and more efficient alternative. In this method, graphite oxide is rapidly annealed at elevated temperatures (200 to 1000°C), resulting in the decomposition of oxygen functionalities into gases

such as CO, CO₂, and H₂O. This also promotes exfoliation of the graphite oxide to graphene layers [23]. The reduction level can be tuned by controlling temperature, time, and atmosphere (e.g., hydrogen, argon, ammonia, or vacuum) [3]. This approach is more environmentally friendly than the chemical reduction method.

Feature	Graphene Oxide (GO)	Reduced Graphene Oxide (rGO)
Oxygen Content	heavily functionalized with oxygen-containing groups (–OH, –COOH, –C=O, epoxy)	Partially restored graphene with significantly reduced oxygen functional groups
Carbon to oxygen ratio (C/O)	Low C/O ratio	Higher C/O ratio compared to GO
Electrical Conductivity	Insulator/Semiconductor (Poor)	Much higher electrical conductivity due to restoration of sp ² carbon network (closer to graphene)
Hydrophilicity/Hydrophobicity	Hydrophilic	Hydrophobic
Surface Area	Lower than rGO	Higher than GO
Chemical reactivity	Highly reactive surface	Lower chemical reactivity than GO
Thermal stability	Lower thermal stability due to oxygen groups	Higher thermal stability
Preparation method	Chemical oxidation of graphite	Reduction of GO

Table 1.2: Comparison between GO and rGO

In photo-assisted reduction, light sources of different wavelengths are used to remove oxygen functionalities from the GO surface. Techniques using microwaves and lasers are particularly helpful, as they provide rapid, localized, and uniform heating, enabling efficient reduction of GO [23].

Recently, green reduction methods have gained attention as sustainable alternatives. Natural reducing agents derived from plants—such as eucalyptus leaf extract, green tea, starch, rose water, pomegranate juice, and sugarcane bagasse extract, etc., have demonstrated reducing capabilities. The rGO obtained through such eco-friendly routes is biocompatible and particularly suitable for biomedical applications [35].

The structural features of rGO and GO are nearly the same, with the difference of removed oxygen-containing functional groups and partial restoration of sp² hybridized carbons. The structure of GO contains abundant oxygen functional groups, making it highly hydrophilic. In the reduction process, the removal of the most of these groups occurred, resulting in rGO with areas of hydrophilic and hydrophobic areas. The percentage of sp² hybridized carbon atoms is higher in rGO than in GO [2]. A detailed comparison between GO and rGO is summarized in Table 1.2.

1.5 Graphene /graphene like materials from biomass or biomass derived materials

Another promising route for synthesizing graphene and graphene-like materials involves the use of biomass. Biomass resources are abundant, carbon-rich, inexpensive, and readily available in large quantities, making them attractive sustainable precursors. Recent studies have demonstrated the production of graphene and related graphene nanostructures from hydrocarbon-rich materials such as sugarcane bagasse, table sugar, glycine, natural oils, and various forms of vegetation waste [45,46,47,48,49,50]. The synthesis of graphene and graphene-like materials from biomass has gained significant attention, as it enables the conversion of waste into value-added products [51,52].

High-temperature graphitization is another method used for the synthesis of graphene from biomass. During this process, organic compounds undergo thermal decomposition at high temperatures either in ambient conditions, vacuum, or an inert atmosphere. This reaction leads to changes in the chemical composition of the biomass, forming graphene-like structures. The procedure involves heating of biomass, which results in dehydration, degradation, and ultimately graphitization of the organic compounds. Reports from literature indicate that nearly any carbon-rich material can be converted into graphene or graphene-like materials by optimizing the synthesis parameters [53].

A wide range of biomass sources have been reported for graphene production, particularly agricultural wastes such as sugarcane bagasse, rice husk, coffee grounds, spent tea leaves, elephant grass, camphor leaves, neem leaves, wheat straw, coconut shells, peanut shells, wood charcoal, and lignin-based biomass. In addition to these, several other carbon-rich materials—including honey, rice grains, palm oil, chitosan, newspaper, dog faeces, soybeans, hemp, and insects—have also been used to produce graphene or graphene-like materials [52,54,55,56,57].

Among these biomass sources, several carbon-rich materials have been successfully converted into graphene or graphene-like structures through simple direct pyrolysis. S. Saqib Shams et al. reported a scalable, eco-friendly one-step pyrolysis method to obtain few-layer graphene (FLG) from dead camphor leaves (*Cinnamomum camphora*). In their process, dried leaves were heated to 1200 °C at a rate of 10 °C/min under a nitrogen atmosphere and subsequently cooled to room temperature, enabling the isolation of FLG from the pyrolytic residue [58].

Amrita Roy et al. synthesized few-layer multifunctional graphene from dried green tea leaves, tannic acid, and alginic acid using a controlled pyrolysis technique. Pyrolysis was carried out at different temperatures, followed by detailed characterization to optimize graphitization conditions. They found that heating at 1100 °C for 3 h under continuous nitrogen flow produced well-graphitized material, which exhibited high capacitance when evaluated for supercapacitor applications [59].

In another report, Thirunavukkarasu Somanathan and group prepared GO from sugarcane bagasse via oxidation under muffle-furnace conditions. They mixed sugarcane bagasse powder with ferrocene and heated it at 300 °C for 10 min under atmospheric conditions. This approach offers a rapid and efficient route for synthesizing GO from agricultural waste [45].

R. Tamilselvi et al. in their work prepared rGO from coconut-based agricultural wastes (coconut shell and coir) through direct carbonization in a muffle furnace using ferrocene as a catalytic oxidant. They optimized the reaction conditions and yielded rGO and studied its performance as an electrode material for supercapacitors [60].

Ayesha Hashmi and co-workers produced GO at relatively low temperatures using agricultural wastes such as orange peel, rice bran, and sugarcane bagasse, as well as their tricomposite mixture. By heating the biomass–ferrocene mixture at 300 °C for 15 min in a muffle furnace, they demonstrated a simple, green, single-step route for GO synthesis [61].

Yan-Jia Liou synthesized graphene sheets from wood-char powders through direct carbonation at 300 °C, followed by catalytic pyrolysis at temperatures between 700 °C and 1400 °C under vacuum. This process effectively converted wood waste into graphene powders [62].

Depending on the nature and composition of the organic precursor, various multistep processes have been reported for synthesizing graphene from carbon-rich materials. Pyrolysis combined with solvothermal treatment, salt activation, post-exfoliation, and other auxiliary methods is among them to obtain graphene or its derivatives from biomass-derived carbonaceous compounds [55].

Zhaofeng Wang and co-workers proposed a large-scale and controllable method for producing graphene quantum dots (GQDs) from rice husk biomass via thermal pyrolysis followed by hydrothermal treatment to remove silica. In their process, rice husk powder was first pyrolyzed at 700 °C for 2 h in a nitrogen atmosphere, then hydrothermally reacted with excess NaOH at 900 °C for 2 h. The resulting GQDs were highly water-dispersible, exhibited bright and tunable photoluminescence, and demonstrated excellent biocompatibility, making them suitable for biomedical applications [63].

Zhongxin Sun and colleagues synthesized vertically aligned graphene nanosheet arrays using a simple and eco-friendly hydrothermal carbonization process followed by KOH activation, employing spruce bark waste as the carbon precursor. The dried spruce bark underwent hydrothermal treatment at 180 °C for 12 h, after which the product was mixed with KOH and calcined at 800–1000 °C under nitrogen. After purification, the obtained graphene exhibited a 3D interconnected architecture, ultrahigh specific surface area, and hierarchical porosity, resulting in impressive electrochemical energy-storage capability when used as a supercapacitor electrode material [64].

Ganesh K. Parshetti and co-workers reported a novel approach to producing porous graphene-like nanosheets from the lignocellulosic fibres of oil palm empty fruit bunches (EFB) through thermal graphitization for efficient CO₂ capture. The dried biomass was first hydrothermally treated at 250 °C for 20 min, then cleaned and pyrolyzed in nitrogen atmosphere at 1000 °C for 2 h at a heating rate of 2 °C/min. This process yielded ultra-microporous graphene nanosheets derived entirely from waste EFB [65].

Aumber Abbas and team developed a sustainable strategy for synthesizing graphene quantum dots from biowaste using pyrolysis followed by a solvothermal reaction, and examined their performance as highly selective chemical sensors. In their work, spent tea leaves were dried and pyrolyzed at 500 °C for 3 h, producing biochar that was subsequently reacted hydrothermally with potassium monopersulfate (Oxone) and DMF to prepare GQDs. They demonstrated that the GQDs exhibit strong and tunable fluorescence. Also evaluated its efficiency as an effective probe for Fe³⁺ detection and achieved a detection limit as low as 0.29 μM [66].

Graphene synthesis from biomass offers a sustainable route for converting low-value waste materials into high-value carbon nanostructures. Despite these advantages, the approach faces some drawbacks. The inherent structural complexity, variable composition, and presence of inorganic impurities in biomass precursors result in graphene with defects, heterogeneous morphology, and poor purity.

Considering this, sucrose stands out as an attractive carbon precursor for producing graphene or graphene-like materials. Sucrose is a simple disaccharide composed of glucose and fructose, with the chemical formula C₁₂H₂₂O₁₁, composed of only carbon, hydrogen, and oxygen. Unlike natural biomass, it does not contain minerals, ash, or other inorganic impurities. It is stable under normal conditions and undergoes thermal decomposition at relatively lower temperatures, where hydrogen and oxygen are released as volatile species, leaving behind a carbon-rich residue. Under controlled reaction atmospheres, sucrose can be converted into high-quality graphene or graphene-like carbon materials. Several studies have demonstrated the successful formation of graphitic layers or few-layer graphene from sucrose, making it a promising candidate for producing graphene-like materials.

A. Bayat and group synthesized photoluminescent single-layer graphene quantum dots (SLGQDs) using glucose dissolved in deionized water as the precursor through a hydrothermal process carried out in a Teflon-lined stainless-steel autoclave at 200 °C for 8 h. Atomic force microscopy confirmed that the resulting quantum dots were single-layered, while transmission electron microscopy revealed an average lateral size of approximately 8 nm [67].

Eduardo Ruiz-Hitzky and colleagues reported the preparation of graphene-like carbon materials from sucrose and gelatin assembled within silica-based porous solids, without the use of reducing agents. These materials exhibited conductive behaviour arising from the formation of sp^2 carbon networks [68].

Fuping Pan and co-workers developed nitrogen-doped graphene (NG) through one-step pyrolysis of sugar in the presence of urea, demonstrating its excellent performance as a metal-free electrocatalyst for the oxygen reduction reaction (ORR). A homogeneous mixture of crystalline sugar and urea was heated to 1000 °C at 3.5 °C/min under Ar flow and held for 1 h before natural cooling. The resulting NG exhibited low nitrogen doping, high graphitization, enhanced conductivity, and a high surface area, all contributing to its superior ORR activity and long-term stability in alkaline media [69].

In another report, Yanyan Zhu and coworkers introduced a fast synthesis method for 3D graphene frameworks (GFs) using sugars with the aid of molten salts for high-performance, nonenzymatic hydrogen peroxide electrochemical sensing. In their study, the sugars used included glucose, sucrose, fructose, lactose, and maltose. Each sugar was ground together with Na_2CO_3 and then subjected to rapid pyrolysis at 1000 °C for 2 minutes under a nitrogen atmosphere. This molten-salt-assisted process enabled a scalable approach for synthesizing GFs from sugars, with molten Na_2CO_3 acting as a structural template [70].

Pallellappa Chithaiah et al. reported a green and facile strategy for the large-scale production of rGO and nitrogen-doped rGO (N-rGO) through direct thermal decomposition of sucrose and glycine at 475 °C in approximately 7 min. Their method is environmentally benign, avoiding the use of hazardous chemicals, metal catalysts, or

solvents, while enabling rapid and efficient synthesis of high-quality graphene-like nanosheets [47].

1.6 The method followed in this work

In summary, producing graphene or graphene-like materials is challenging and involves several limitations. Methods capable of yielding high-quality, nearly defect-free graphene require sophisticated instrumentation, precise control of synthesis conditions, vacuum environments, and high energy input. Because of these operational requirements, these techniques are costly, and some are suitable only for small-scale production [52,54].

rGO has emerged as a practical alternative to pristine graphene, as it retains many graphene-like properties and possesses unique characteristics suited for specific applications. The common approach for producing rGO is by the chemical oxidation of graphite using Hummer's method and their later modifications. These methods use strong, corrosive acids and alkali metal compounds to convert graphite into oxidized forms. These traditional methods face several challenges: they use highly toxic and corrosive chemicals, release hazardous gases during the reaction, and often require extended processing under harsh, exothermic conditions that can even become explosive. In addition, handling of toxic reagents and managing harmful by-products present significant risks to both human health and the environment [24,36,71,72].

These challenges underscore the need to develop an economically viable and environmentally friendly alternative method to produce rGO. The synthesis of graphene-like structures from green materials using simpler protocols is particularly appealing due to its cost-effectiveness, rapid processing, non-toxicity, biocompatibility, and scalability. Recent research has made some progress in this direction. In this study, rGO was synthesised from sucrose in a muffled atmosphere without harmful chemical reagents or catalysts. This method allows the production of a large quantity of rGO in a few minutes by a single step, making it highly promising. It also does not produce toxic gases or hazardous by-products, further emphasising its potential as a safer and sustainable way to produce rGO.

1.7 Zinc oxide (ZnO)

In this study, ZnO was chosen as the metal oxide component. ZnO is an inorganic, white, odourless compound that naturally occurs as the mineral zincite [73,74]. In the molecule, the Zn^{2+} and O^{2-} ions are held together by strong ionic bonds due to their large electronegativity difference (3.44 for oxygen and 1.65 for zinc) [75]. It is one of the most widely investigated n-type direct bandgap semiconductors. Its native n-type conductivity is identified to arise from the intrinsic defects such as oxygen vacancies and zinc interstitials [76,77].

ZnO shows excellent optical transparency, strong luminescence, and a wide direct bandgap of 3.1–3.37 eV. It exhibits high exciton binding energy of approximately 60 meV at room temperature [77,78]. It is a low-cost, non-toxic, and biocompatible material that is abundant and stable under chemical, thermal, and photochemical conditions. Furthermore, ZnO exhibits high charge-carrier mobility, favourable thermal and electrical properties, and pronounced surface reactivity [79,80,81].

ZnO mainly occurs in two common crystal structures: hexagonal wurtzite and cubic zinc blende. Among these, the hexagonal wurtzite form is the most stable under ambient conditions. It is due to its tetrahedral coordination, where each Zn atom bonds with four O atoms. A third polymorph, the rock-salt structure, is also possible, but only under extreme pressures of around 10 GPa [75,80].

ZnO is eminent for its unique mechanical, optical, electrical, and physicochemical properties, which enable its widespread use across physics, chemistry, and materials science. It finds diverse applications in optoelectronics [82], photocatalysis [83], antibacterial [84], and energy storage [85]. ZnO also plays an important role in medicine, the rubber and plastics industry, sensors, paints, batteries, solar cells, agriculture, electronics, ceramics, and cosmetics [73,86,87,88].

As a wide bandgap metal oxide semiconductor, ZnO predominantly absorbs ultraviolet (UV) radiation, making it highly suitable for UV-shielding applications. Consequently, it is widely used in sunscreens, cosmetics, UV-protective coatings, and paints. It is also incorporated into textiles and polymer-based films to produce UV-absorbing packaging materials and protective fabrics for food and medical applications.

[75,89,90,91]. As an n-type semiconductor with high electrochemical stability, high breakdown voltage, and strong electric field tolerance, ZnO is used in high-power electronic devices and field-emission technologies. Its wide bandgap also makes it suitable for short-wavelength optoelectronic devices such as UV and blue light emitters [80].

The bandgap of ZnO is highly size-dependent. When the material is reduced from the bulk to the nanoscale, its optical and physicochemical properties change significantly due to the quantum confinement effect. This size-dependent bandgap modulation makes ZnO nanostructures valuable in solar cells, laser diodes, photodetectors, sensors, and bio-imaging applications [75].

ZnO is also widely recognized for its potential in water remediation. It is an efficient photocatalyst owing to its electronic structure, light-responsive nature, and favourable charge-transport properties. When exposed to light with energy equal to or greater than its bandgap, electrons are excited to the conduction band, leaving behind holes in the valence band. These photogenerated charge carriers interact with adsorbed water and oxygen molecules on the ZnO surface to produce reactive oxygen species (ROS), which subsequently degrade organic pollutants into harmless end products such as CO₂ and water [79,92,93].

In addition to photocatalysis, ZnO also found effective as an adsorbent in pollution-remediation applications. Its high surface area, chemical stability, surface polarity, and ability to form composites enhance its adsorption performance. Physical adsorption, chemical adsorption, and redox reactions facilitated by photogenerated electron-hole pairs are the commonly reported adsorption mechanisms of ZnO [75,94].

ZnO is a non-toxic, biocompatible material with inherent antibacterial and antimicrobial properties. Thus, it is valuable in biomedical applications. The reported antibacterial mechanism of ZnO includes the sharp edges of ZnO nanoparticles and the release of Zn²⁺ ions, which disrupt and inhibit bacterial cell functions. Furthermore, the ability to generate ROS also contributes to its antimicrobial activity by inducing oxidative stress in microbial cells [84,95,96].

ZnO is widely used as an additive to enhance heat-transfer efficiency in various materials owing to its high thermal conductivity and excellent thermal stability [97,98]. It is reported to be incorporated with nanofluids (advanced heat transport fluids) to improve their heat-transfer performance in heat-exchanger systems. For instance, in solar-thermal collectors, ZnO-based nanofluids help to maximize solar-energy absorption and overall thermal efficiency [99]. Additionally, ZnO nanostructures have been employed as effective heat-spreader materials in LED thermal-management applications, enabling efficient dissipation of heat and improved device performance [100].

In the electronics industry, ZnO's wide bandgap, high transparency, high electron mobility, strong room-temperature luminescence, and semiconducting behaviour make it a promising candidate for transparent conducting electrodes, heat-protective windows, thin-film transistors, light-emitting diodes, sensors, UV detectors, etc. [101,102,103,104,105].

In photovoltaics, ZnO is widely employed as an electron-transport layer or photoactive layer because of its high electron mobility, optical transparency, and low cost [101]. It is used in perovskite, dye-sensitized, organic, and heterojunction solar cells, often in nanostructured forms—such as nanowires, nanoparticles, or thin films—to enhance device performance [106,107].

ZnO is also utilized in photocatalytic water splitting to generate hydrogen and oxygen due to its low cost, non-toxicity, and UV-responsive semiconductor nature. Although its efficiency is limited by its wide bandgap and rapid charge recombination, various strategies such as doping, defect engineering, and composite formation are being explored to improve its performance [108,109].

ZnO also exhibits strong piezoelectric properties, which arise from its non-centrosymmetric hexagonal wurtzite structure. Under mechanical stress, the atoms become polarized, generating an electrical potential. This makes ZnO highly attractive for piezoelectric sensors, nanogenerators, energy harvesting devices, and biomedical implants [110,111,112,113,114].

Furthermore, ZnO is a promising material for pseudocapacitors, where energy is stored through fast and reversible Faradaic reactions [115]. Although pure ZnO has limitations such as low conductivity and moderate cycling stability, significant improvements have been achieved through doping, nano-structuring, and forming composites [116,117,118].

ZnO is also widely utilized in the agricultural sector. ZnO nanoparticles have been reported to enhance plant growth and overall plant health by improving nutrient uptake, photosynthetic efficiency, and enzymatic activity. They can also regulate carbon and nitrogen metabolism, promote the production of secondary metabolites, and strengthen the antioxidant defence system in plants. Additionally, ZnO nanoparticles have shown potential to increase crop yield and stress tolerance, and several studies indicate that they may also function as effective biocontrol agents against plant diseases [119,120,121].

ZnO is also widely used as an additive in conventional materials such as paints, plastics, ceramics, glass, cement, rubber, and pharmaceutical ointments. It functions as a UV absorber in sunscreens, a vulcanization activator in rubber, an opacifying pigment in paints, and an antibacterial component in medicinal formulations.

1.8 Synthesis Methods of ZnO

The properties of ZnO highly depend on its morphology, particle size, crystallinity, particle distribution, and surface characteristics. These features depend largely on the synthesis method and the processing parameters, such as the choice of precursors, reaction time, temperature, and substrate. ZnO can be synthesized in a wide variety of nanostructured forms such as nanoparticles, nanorods, nanotubes, nanobelts, tetrapods, rings, bowls, hemispheres, disks, flowers, and nanosheets, and so on. Each morphology exhibits distinct characteristics that make it suitable for specific applications [122]. Moreover, the properties of ZnO can also be tailored through surface functionalization and doping [75].

Various physical, chemical, and biological methods are used for the synthesis of ZnO [123]. Examples of methods that come under physical methods are plasma arc, sputtering, physical vapor deposition, thermal evaporation, ball milling, electric arc

deposition, and laser ablation. These techniques rely on physical forces to generate nanostructures from bulk materials or smaller molecular units. Although effective, they often require sophisticated equipment, controlled environments, and high operational costs [123,124].

Chemical methods for synthesizing ZnO nanoparticles involve chemical reactions. These methods fall into three main categories: solid-phase, liquid-phase (commonly referred to as wet-chemical methods), and vapour-phase. Among these, liquid-phase methods are the most widely used ones because of their simplicity, versatility, and scalability. Techniques such as chemical precipitation, sol–gel processing, hydrothermal or solvothermal reactions, and microemulsion methods fall under this category. These approaches generally require lower energy input, use simple and inexpensive chemicals, rely on basic laboratory equipment, and are cost-effective, making them suited for large-scale industrial production of ZnO nanoparticles [123,124].

Biological routes demonstrated an environmentally friendly alternative for ZnO synthesis and are described as green methods. These approaches use plant extracts, proteins, or microorganisms for the synthesis of ZnO nanoparticles without toxic chemicals or energy-intensive procedures. These methods are capable of producing high-quality ZnO with excellent biocompatibility [123,124,125].

1.9 Limitations of ZnO

Despite its remarkable optical, electrical, and physicochemical properties, pristine ZnO exhibits several inherent limitations that restrict its effectiveness in advanced applications. One major constraint is its wide band gap (~ 3.2 eV), which allows light absorption primarily in the ultraviolet region of the solar spectrum. This significantly limits its visible light activity, thus reducing its efficiency in photocatalysis, solar energy conversion, and photoelectrochemical processes [108,126]. In addition, pristine ZnO suffers from rapid recombination of photogenerated electrons and holes, resulting in poor charge separation and consequently low photocatalytic and photoelectrochemical performance [127,128,129].

ZnO is an n-type semiconductor with relatively low intrinsic conductivity [130,131], which limits its use in applications requiring fast charge transport, such as supercapacitors, electrocatalysis, and high-performance electronic devices. Another major constraint of ZnO is the poor stability against photo corrosion during prolonged illumination, especially in aqueous environments [80,108,132]. This leads to structural degradation, reduced chemical stability, and diminished long-term activity.

Moreover, ZnO nanoparticles tend to agglomerate due to strong van der Waals forces and high surface energy [133,134]. This agglomeration reduces the effective surface area and the available active sites. These limitations can be effectively addressed by the incorporation of rGO with ZnO, enhancing the performance through their complementary and synergistic properties.

1.10 ZnO/rGO composite

ZnO and rGO are two high-performing materials that are widely explored across numerous advanced technologies. When combined and forming ZnO/rGO composite, their individual properties complement and show remarkable synergistic effects. The composite formation enhances the intrinsic properties of both components and broadens the functional versatility of the resulting material. Consequently, ZnO/rGO composites have received significant research attention and have demonstrated superior performance in adsorption [135], photocatalysis [136], energy storage [137], sensing [138], batteries [139], electrocatalyst [140], piezoelectric material [141], microwave absorbent [142], electrochemical and biosensor [143,144], antibacterial and anticancer [145,146], photocatalytic water splitting [147], solar cells [148], and optical applications [149].

Incorporation of rGO with ZnO effectively overcomes the inherent limitations of pristine ZnO. The presence of rGO improves the photocatalytic and sensing capabilities of ZnO by enhancing the electrical conductivity and increasing the surface area. It also stabilizes the structural integrity of the material. These improvements arise from several reinforcing mechanisms of enhanced charge separation, extended visible-light absorption, efficient electron transport pathways, and improved dispersion of ZnO nanoparticles.

One of the most significant advantages of ZnO/rGO composite lies in its enhanced performance in light-driven applications. The presence of rGO reduces the effective band gap of ZnO, enabling greater visible-light absorption and improved photo-generation of charge carriers [150,151]. In the composite, rGO acts as an efficient electron scavenger and transporter due to its excellent electrical conductivity. It extracts photogenerated electrons from ZnO at the point of generation and transfers them rapidly through its conductive network. This significantly improves the charge-separation efficiency and thus reduces the electron–hole recombination rate [152,153,154,155]. This mechanism greatly enhances photocatalytic, photoelectrochemical, and sensor performances.

In addition, rGO in the composite structure contributes a large two-dimensional surface area, which improves the number of active sites for adsorption, catalysis, and sensing processes that primarily occur on the surface [156,157]. Moreover, in the composite, ZnO nanoparticles are grown on or anchored to the surface of rGO sheets, present as embedded or intercalated between them [158,159]. These ZnO particles act as spacers that prevent the restacking of rGO sheets caused by van der Waals forces, which further enhances the surface area of the composite material [42]. Similarly, rGO prevents ZnO nanoparticles from agglomerating, ensuring that ZnO remains highly dispersed throughout the composite. This dispersion improves reactivity, accessibility, and overall material performance [160].

The conductive rGO network also improves the electrical properties of the composite, making ZnO/rGO favourable for the electrochemical energy-storage applications such as supercapacitors, batteries, and electrocatalytic systems [161]. Furthermore, the presence of rGO also improves the structural stability of ZnO by reducing photocorrosion and maintaining integrity during prolonged illumination [162]. The flexibility and mechanical strength of rGO contribute to better durability and long-term performance. Moreover, the oxygen-containing functional groups on rGO introduce additional binding and adsorption sites for metal ions and organic contaminants [163,164].

Overall, ZnO/rGO composites represent a promising class of multifunctional materials with enhanced performance across a wide range of technological applications. Their superior efficiency compared to the individual components makes them highly

attractive for next-generation energy, environmental, optical, and sensing technologies. Recent research on ZnO/rGO composites and their various applications is summarised in Table 1.3.

No.	Composite	Synthesis	application	Ref.
1	self-assembled Hollow-Sphere ZnO/rGO Nanocomposite	low temperature (95 °C) chemical solution reaction	Anode Materials for Lithium-Ion Batteries	139
3	ZnO-RGO nanocomposite	wet chemical reaction	selective detection of Cd ²⁺ ions	165
4	N-doped ZnO–rGO films	electrochemical synthesis	Photo-electrocatalytic degradation of antibiotics	166
5	ZnO/rGO composite	hydrothermal method	Photodegradation MB	167
6	ZnO/rGO composite	ultrasonication method	gas sensor and supercapacitor	168
7	RuO ₂ /ZnO@rGO composite	Sol-gel and hydrothermal	electrocatalysts for alkaline seawater electrolysis and solar-light degradation of organic pollutants	140
8	Flexible PVDF/ZnO/rGO composite	spin-coating.	piezoelectric nanogenerators	141
9	ZnO/rGO composite	facile One-Step method	Pb ²⁺ removal	135
10	of ZnO-RGO nanocomposites	green process using garlic cloves extract.	anticancer efficacy	146
11	Cr doped ZnO@rGO nanocomposites	Sol-Gel and hydrothermal methods	Super capacitor	169

12	AgNPs-ZnO/rGO composites	hydrothermal methods, and Hummer's method	Photocatalytic hydrogen production and antibacterial activity against E. coli	170
13	ZnO@rGO nanocomposites	biotemplate assisted microwave technique	enzyme free electrochemical detection of urea and glucose	143
14	ZnO/rGO nanocomposites	hydrothermal method	photocatalytic degradation of 2-naphthol	171
15	rGO@ZnO Nanocomposites	Wet chemical method	Esterification of Acetic Acid	172
16	Al-doped ZnO/rGO nanocomposites	green approach using pomegranate peel extract	anticancer and photocatalytic activities	173
17	ZnO/ZnO nanocrystal-modified rGO foam	hydrothermal and freeze-drying processes	wide-frequency microwave absorption	142
18	ZnO/rGO nanocomposites	co-precipitation method	A non-enzymatic electrochemical sensor for effective detection of urea	174
19	ZnO/rGO composite	hydrothermal synthesis	Photocatalytic degradation of an organophosphorus pesticide	175
20	ZnO/RGO composite	hydrothermal method.	non-contact respiratory sensor	138
21	zinc oxide coated on rGO	green synthesized	Adsorption of cationic basic fuchsin dye	176

	nanocomposite (ZnO-rGO NC)			
22	ZnO-RGO-PPy	Hydrothermal	water-borne epoxy nanocomposite coating with anticorrosive reinforcement	177
23	GO-ZnO mediated Ocimum basilicum leaves extract nanocomposite	Green synthesis	antioxidant, antibacterial, antidiabetic and photocatalytic activity	145
24	PANI-ZnO-rGO nanocomposite	chemical oxidative polymerization and probe sonication	biosensor for L- arginine detection	144
25	ZnO/rGO NCs	hydrothermal method	photocatalytic degradation of dyes	178
26	RGO-ZnO) nanocomposites	green Benedict's route	water splitting applications and photocatalytic activity	147
27	Mg-doped ZnO/rGO	sol-gel procedure	acetic acid sensing	179
28	ZnO/RGO composite	solution combustion method	Photocatalytic degradation	153
29	Reduced graphene oxide/ZnO nanocomposites	one-step solid-state preparation	photo-sensing and photoelectrical gas sensing	180
30	ZnO/RGO composites	hydrothermal method	microwave absorption	181
31	2D/2D ZnO/rGO Nanocomposites	Microwave assisted	Photocatalytic Removal of Tetracycline	182

32	ZnO decorated rGO composite	hydrothermal method	catalytic ozonation	183
33	ZnO/rGO aerogel	Sol-gel method	selective NO ₂ detection at room temperature	184
34	rGO/ZnO nanofibers	electrospinning	gas sensors for detecting NO and NO ₂	185
35	ZnO/rGO nanosheets	chemical precipitation and hydrothermal method	ethylene glycol gas sensor	186
36	Highly Conducting rGO in ZnO Nanostructure	Sol-gel	Heterojunction solar cell	148
37	phytochemical enriched ZnO grafted on few- layered graphene sheets	Green chemistry	degradation of medical effluents	187

Table 1.3: Recent research on ZnO/rGO composites and their various applications.

1.11 Synthesis methods of ZnO/rGO composite

Various synthesis methods have been developed for preparing ZnO/rGO composites. In most cases, the fabrication process involves two or more steps, where either rGO or its precursor GO is combined with ZnO or a suitable zinc-containing precursor [156]. The composite is typically synthesized using wet-chemical routes such as hydrothermal or solvothermal treatment, microwave-assisted methods, sol-gel processes, co-precipitation, or electrochemical techniques. During these syntheses, ZnO nucleates, grows, and anchors onto the oxygen-containing functional groups and defect sites present on GO/rGO, forming a stable hybrid structure. These methods account for more than 80% of the reported fabrication techniques [150].

The formation of ZnO/rGO composites can generally be categorized into two approaches. In the in-situ method, ZnO nanoparticles are directly grown on the carbonaceous framework, establishing strong interfacial contact and uniform dispersion. In contrast, the ex-situ method involves synthesizing ZnO nanoparticles separately, followed by their attachment onto pre-prepared rGO sheets. The literature review indicates that in-situ growth is the most common and effective strategy for achieving well-anchored ZnO/rGO nanocomposite structures [150].

1.11.1. Hydrothermal or solvothermal method

Hydrothermal and solvothermal methods operate on the same fundamental principle, with the naming convention depending solely on the solvent used. When water is the solvent, the process is referred to as hydrothermal, whereas the use of organic solvents designates it as solvothermal [188]. This technique is one of the most widely employed approaches for synthesizing ZnO/rGO composites. In this method, the reaction takes place in a sealed system under temperatures above the boiling point of the solvent and at pressures greater than one bar [156].

In the procedure, zinc salt is mixed with GO/rGO in water or an organic solvent. During mixing, the zinc precursor initially forms an intermediate $\text{Zn(OH)}_2 \cdot n\text{H}_2\text{O}$ species with the solvent. Upon heating for prolonged durations (commonly 8–20 hours) at elevated temperatures (120–300 °C) and pressure, this intermediate decomposes to form ZnO. The ZnO nucleates and grows on the graphene sheets and yields the ZnO/rGO composite [150]. When GO is used as the starting material, hydrothermal conditions promote the simultaneous reduction of GO to rGO during composite formation, resulting in in situ formation of the composite.

Changing the reaction parameters, such as the type of precursor, concentration, reaction temperature, and pressure can tune the particle size, morphology, and overall characteristics of the ZnO/rGO composite.

For example, Sugianto et al. [189] synthesized a ZnO/rGO composite using the hydrothermal method for electrochemical sensing applications. In their work, $\text{Zn(NO}_3)_2$ and GO were used as the starting materials. The synthesis involved multiple steps, outlined as follows.

1. Synthesis of GO using the modified Hummers method.
2. Preparation of uniform GO suspension in water by ultrasonication for 1 hour.
3. $\text{Zn}(\text{NO}_3)_2$ and hydrazine hydrate (10 mL) were added to the GO suspension, followed by ultrasonication for 30 minutes.
4. The mixture was transferred to a Teflon-lined autoclave and heated at 160 °C for 2 hours.
5. The resulting solid was collected by centrifugation at 4000 rpm for 15 minutes and subsequently dried at 110 °C for 3 hours.

This procedure demonstrates that the hydrothermal approach for the synthesis of ZnO/rGO is a relatively slow multi-step process. It requires multiple instruments such as an autoclave, centrifuge, sonicator, furnace, and magnetic stirrer, making it an equipment-intensive method. While the example described uses a zinc salt as the precursor, several studies have reported the use of pre-synthesized ZnO nanoparticles during the hydrothermal treatment [178,190]. Incorporating pre-synthesized ZnO adds an additional preparation step, making the overall process even more time-consuming.

1.11.2. Co-precipitation method

The co-precipitation method is another synthesis process, widely employed for the fabrication of composite nanomaterials. In this method, two or more components precipitate simultaneously from the same solution [191]. It is a well-established, simple, and fast approach for synthesizing nanocomposites at low temperatures in liquid media. For the synthesis of ZnO/rGO composites, zinc ions are precipitated in the presence of GO/rGO, and the subsequent calcination step results in the formation and anchoring of ZnO nanoparticles onto the graphene sheets.

In a typical ZnO/rGO composite preparation, the synthesis begins with mixing a zinc salt precursor with GO or rGO by ultrasonic treatment. When zinc salts dissolve in water, the zinc ions exist as hydrated species. This mixture undergoes condensation when the pH of the solution is increased by adding a precipitating agent such as NaOH or NH_4OH . The introduction of the precipitating agent leads to the formation of zinc hydroxide ($\text{Zn}(\text{OH})_2$), which precipitates onto the GO/rGO surface. The subsequent heating or calcination transforms $\text{Zn}(\text{OH})_2$ into ZnO, producing a well-dispersed ZnO/rGO hybrid material with enhanced structural, optical, and electronic properties [150].

For example, Osama Usman et al. [192] synthesized rGO–ZnO hybrids using a one-pot co-precipitation method and evaluated their antibacterial activity. The synthesis involved several steps:

1. $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was mixed with polyvinylpyrrolidone (PVP) in acetic acid and stirred for 30 minutes to form the Zn–PVP complex.
2. GO was then added to this mixture and sonicated for 24 hours.
3. NaOH was added dropwise to this suspension kept at 80 °C under vigorous stirring to induce co-precipitation.
4. The resulting precipitate was collected by centrifugation at 7500 rpm and subsequently underwent cleaning process.
5. Finally, the product was dried overnight at 150 °C and ground into a fine powder.

This procedure demonstrates that the co-precipitation approach, although relatively simple, still involves multiple steps and is time-consuming. Moreover, the rapid nature of co-precipitation causes nucleation and growth to occur simultaneously, making it difficult to control particle size and morphology. In addition to this, high-temperature thermal treatment is typically required to obtain the final crystalline ZnO/rGO composite.

1.11.3. Sol-gel method

The sol–gel method is another versatile low-temperature chemical route for synthesizing nanomaterials and their composites. In this method, the liquid sol containing dispersed precursor species was converted to a solid gel network through hydrolysis and condensation reactions. This multi-step process begins with the hydrolysis of metal precursors to produce metal hydroxide species, followed by their condensation into a three-dimensional gel structure [156]. This method has several advantages. It offers precise control over composition, enables the synthesis of nanoparticles at relatively low temperatures, and allows for tuning the morphology and particle size [150].

The sol-gel method is one of the widely used synthesis methods for the ZnO/rGO composite. The method typically begins with the preparation of a colloidal sol by dissolving a zinc precursor (such as zinc acetate) in a suitable solvent along with

GO/rGO. The mixture then undergoes condensation to form a gel in which the zinc-based species become anchored onto the graphene sheets. This follows drying and calcination that convert the intermediate species into ZnO nanoparticles, resulting in a composite where ZnO is uniformly distributed over the rGO surface [193].

For example, Fahad A. Alharthi and co-workers [172] synthesized an rGO/ZnO composite via the sol–gel method and evaluated its efficiency in the esterification of acetic acid. The synthesis procedure they followed is outlined below:

1. Synthesis of Graphene oxide powder by modified Hummers' method.
2. Preparation of uniform GO dispersion in water using ultrasonication for 30 minutes.
3. Slow addition of aqueous solution containing zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, to the GO dispersion with stirring.
4. Dropwise addition of this mixture into a hot 1 M KOH solution.
5. The resulting mixture was then stirred for 3 hours at 100 °C, followed by ultrasonication for 2 hours.
6. The final solid product was collected by centrifugation and subsequently washed repeatedly with water and methanol to remove the impurities.

1.11.4. Microwave assisted method

Microwave-assisted synthesis is a fast, effective, and energy-efficient method for preparing ZnO/rGO composites. It offers notable advantages over other chemical methods. In this process, the reaction mixture is heated with microwave irradiation, which produces rapid and uniform heating throughout the mixture. This method promotes accelerated reaction rates, controlled nucleation, and uniform dispersion of ZnO nanoparticles on rGO sheets [150,194].

In a typical microwave-assisted procedure, zinc salts are dissolved in a suitable solvent and mixed with GO or rGO. The mixture then undergoes vigorous stirring or ultrasonication to ensure uniform dispersion. A precipitating or reducing agent such as NaOH, urea, or ammonia is then added to initiate ZnO nucleation. Upon exposure to microwave irradiation, rapid and uniform heating accelerates the decomposition of the zinc precursor, promoting the in-situ growth of ZnO nanoparticles on the graphene

sheets [118]. When GO is used, the strong microwave field simultaneously reduces GO to rGO, producing the ZnO/rGO composite [195].

For example, Tian Lv et al. synthesized ZnO/rGO composites using a microwave-assisted method and evaluated their photocatalytic performance toward methylene blue degradation [195]. The procedure involved:

1. Preparation of GO using modified Hummers' method.
2. Dispersion of GO into a $\text{Zn}(\text{NO}_3)_2$ solution, followed by 30 minutes of ultrasonication to achieve uniform mixing.
3. Addition of a dilute NaOH solution dropwise to adjust the pH to 10–11.
4. Microwave irradiation of the mixture in a microwave system at 100 °C for 30 minutes.
5. Collection of the resulting ZnO/rGO composite.
6. Washing steps followed by drying in a vacuum oven at 60 °C for 24 hours.

The advantages of the microwave-assisted synthesis method include enhanced distribution of ZnO across the rGO framework, improved ZnO crystallinity, smaller and more uniform particle sizes, and significantly shorter reaction times. This method eliminates the need for high-temperature calcination. The homogeneous heating reduces the agglomeration of nanoparticles, resulting in a uniform composite [196]. However, the method still requires initial GO preparation and subsequent incorporation steps, making it a multi-stage process overall.

A review of the reported synthesis methods for ZnO/rGO composites shows that most techniques involve multi-step, time-consuming procedures. These approaches typically require several preparation, purification, and thermal treatment stages, making the overall process lengthy and equipment-intensive. Additional reports describing these various synthesis strategies are summarized in Table 1.4.

From the literature review, it is evident that ZnO/rGO composites are exceptional functional materials with broad applicability across numerous advanced fields. However, most reported synthesis routes for ZnO/rGO composites involve multistep, time-consuming procedures. In nearly all studies, the rGO component is prepared through chemical methods such as Hummers' method or its modified versions. As discussed in Section 1.2.6, this approach involves hazardous reagents, generates

toxic gases, requires strict temperature control due to its exothermic and potentially explosive nature, and often involves lengthy and difficult product-recovery steps. Consequently, the synthesis procedures of ZnO/rGO composite are laborious and environmentally unfavourable. These challenges highlight the growing need for simpler, safer, and more scalable synthesis methods for the efficient fabrication of ZnO/rGO composites.

Sl. No	Method of Synthesis	Brief Description (Precursors, T°, Time, etc.)	Application Studied	Ref.
1	Green hydrothermal (bio-assisted)	Step 1: preparation of GO powder Step 2: GO+ Zn(CH ₃ COO) ₂ + leaf extract; hydrothermal ~200 °C, 8hrs Step 3: ZnO/rGO composite (vacuum oven, 120°C, 24h)	Photocatalytic degradation (organic pollutants)	197
2	Wet chemical synthesis	Step 1: Preparation of GO-modified Hummer method step 2: GO to rGO using ascorbic acid Step 3: rGO + ZnO precursors mixed chemically; 4 h in an oil bath maintained at 80°C	electrochemical detection	198
4	Chemical solution mixing	Step 1: GO (Hummer's method) Step 2: GO reduction to rGO Step3: preparation of ZnO by green method Step 4: ZnO nanoparticles + rGO by solution mixing.	Electrochemical energy storage	199
5	Solution combustion method	Step 1: synthesis of GO Step 2: synthesis of precursor solution	Photocatalysis	153

		<p>(DI water + zinc nitrate + glycine + citric acid + GO)</p> <p>Step 3: heating precursor solution 80 °C until a viscous solution was formed.</p> <p>Step 4: heating till transformed into a gel and ignited by the heating up to 250 °C.</p>		
6	UV-assisted reduction	<p>Step 1: preparation of GO by hummers method</p> <p>Step 2: sonication of GO + ZnO (commercial) + ethanol mixture</p> <p>Step 3: irradiation of UV-light with the main wavelength at 365 nm for about 7 h under continuous magnetic stirring.</p>	Photocatalysis	200
7	Microwave-assisted synthesis	<p>Step 1: synthesis of GO by Hummers method</p> <p>Step 2: probe sonication of Zinc acetate + GO in DI water</p> <p>Step 3: NaOH solution was added to this.</p> <p>Step 4: The solution irradiated with microwave for 20 minutes.</p>	non-enzymatic glucose sensing and supercapacitor applications	118
8	ultrasonication method	<p>Step 1: Preparation of ZnO by coprecipitation method</p> <p>step 2: GO by modified Hummer's method</p> <p>Step 3: preparation of ZnO@rGO nanohybrids using ultrasonication method</p>	gas sensor and supercapacitor	168

9	Chemical solution mixing	<p>Step 1: Preparation of Carica papaya leaf extract</p> <p>Step 2: zinc acetate dihydrate + leaf extract, adjust the pH at 12, heating at 80 °C for 4 h.</p> <p>Step 3: drying at 50 °C for 6 hours</p> <p>Step 4: synthesis of GO-modified Hummer's method</p> <p>Step 5: reduction of GO to rGO by chemical method</p> <p>Step 6: rGO-ZnO nanocomposite by sequential sonication and mixing process</p>	Adsorption of cationic basic fuchsin dye	176
10	One-pot hydrothermal	<p>Step 1: GO preparation</p> <p>Step 2: GO+ Zn(NO₃)₂ + NaOH hydrothermal heating at 180–200 °C</p> <p>Step 3: Calcination</p>	Cr(VI) adsorption and reduction	201
11	hydrothermal method	<p>Step 1: Preparation of rGO by improved Hummers method</p> <p>step 2: GO to rGO → thermal reduction in a furnace at 400 °C for 5 h.</p> <p>step 3: preparation of ZnO via hydrothermal method at 150 °C for 12 h.</p> <p>step 4: drying at 120 °C for 2 h.</p> <p>step 5: ZnO–rGO nanocomposite by hydrothermal method at 180 °C for 24 h.</p> <p>step 6: dried at 120 °C for 12 h</p>	photocatalytic degradation of dyes	178

12	Wet chemical synthesis	Step 1: GO synthesis Step 2: thermal reduction of GO to rGO Step 3: ZnO nanoflakes by hydrothermal reaction Step 4: ZnO collected, and calcinated at 300 °C for 30 min Step 5: dispersion (rGO + DMF)+ ZnO flakes → sonicated for 1hr Step 6: reacted at 100 °C for 3 h	solar-assisted supercapacitor applications	202
13	Green + hydrothermal	Step 1: ZnO synthesized using date-syrup extract Step 2: synthesis of GO Step 3: reduction of GO to rGO Step 4: rGO + ZnO via hydrothermal method	MB dye photocatalysis	190

Table 1.4: Summary of synthesis routes and key processing steps for ZnO/rGO composites reported in recent studies.

1.12 Research Gap and Motivation

rGO has outstanding properties and is found applicable across various fields of science and technology. However, the synthesis methods widely used are often time-consuming, involve multi-step processes, require toxic chemicals, and evolve under explosive conditions. In addition to this, these methods produce toxic gases, risking human health and the environment. Therefore, extensive research is ongoing to develop greener and sustainable approaches for rGO synthesis.

As we discussed already, ZnO is another promising material with a wide range of applications. The incorporation of rGO with ZnO improves the properties of the resultant ZnO/rGO composite material, making it highly valuable. ZnO/rGO composites have drawn significant scientific and technological attention due to their outstanding multifunctional properties. However, the methods exist for the synthesis of

ZnO/rGO composite suffer from many limitations that hinder their scalability. These methods are usually multi-step process that requires the separate preparation of GO or rGO, and an additional step to incorporate ZnO nanoparticles. Moreover, these procedures are often time-consuming, energy-intensive, utilize hazardous reagents, and produce by-products. The complexity of these processes hinders their viability for industrial-scale production. Therefore, there is a need to develop methods that align with the increasing global emphasis on green, environmentally responsible material synthesis.

From the literature review, it was recognized that there remains a clear research gap in developing a simple, rapid, and eco-friendly method that can produce ZnO/rGO composite using safe, cost-effective, and widely available precursors. Motivated by these limitations, the present work aims to establish a sustainable, single-step synthesis route that minimizes chemical usage, reduces environmental impact, and supports the principles of the United Nations Sustainable Development Goals (SDGs), particularly “responsible consumption and production.” Based on this, the objectives of the proposed work are framed and are given below.

1.13 Objectives of the work

1. To synthesize rGO using an environmentally friendly method employing non-toxic precursors.
2. To develop a green and sustainable method for synthesizing ZnO/rGO composites.
3. To study the heavy metal adsorption efficiency of the synthesized ZnO/rGO composite in various metal-ion-contaminated solutions.
4. To investigate the antibacterial activity of the synthesized rGO, ZnO, and ZnO/rGO composites against various bacterial strains.
5. To evaluate the photocatalytic efficiency of the synthesized ZnO/rGO composite for the degradation of various dyes/antibiotics.
6. To examine the electrochemical applicability of the synthesized rGO, ZnO, and ZnO/rGO composites for potential energy-storage applications.

1.14 References

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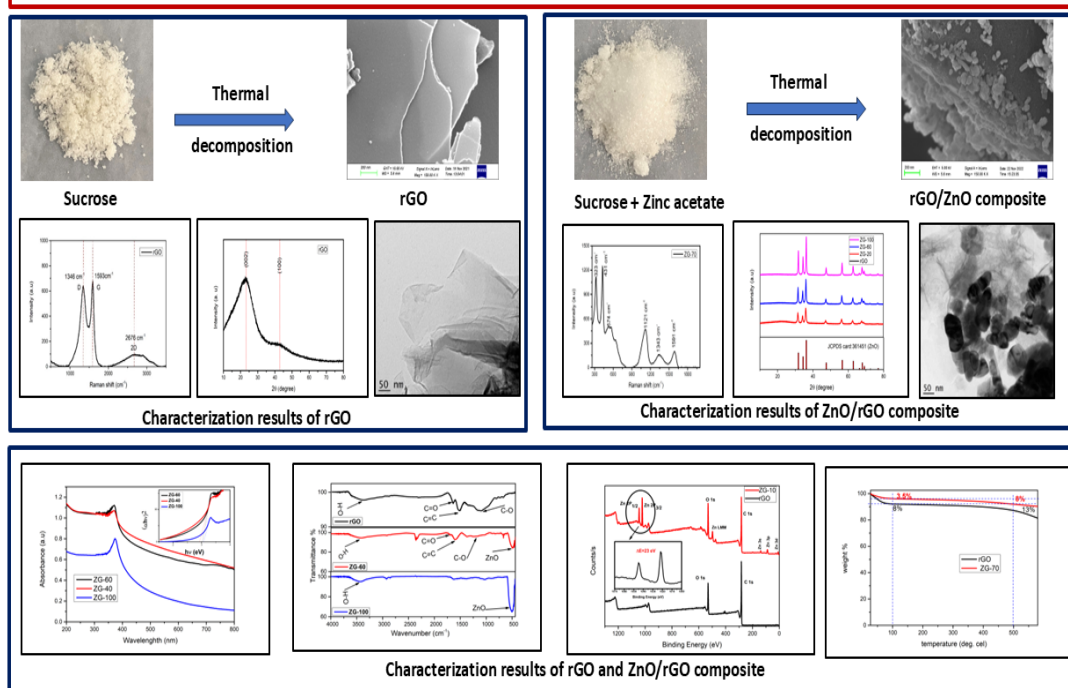
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Chapter II

Novel Single-Step Synthesis of rGO and ZnO/rGO Composites from Non-Toxic Precursors and Their Physicochemical Characterization.

Abstract

Synthesis of rGO and ZnO/rGO Composite via a Simple One-Step Pyrolysis Method Using Sucrose and Zinc Acetate



In this study, we employed a single-step, rapid-heating method to synthesise rGO and ZnO/rGO composites using readily available and affordable materials, sucrose and zinc acetate. This single-step synthesis involves the pyrolysis of sucrose to produce rGO, simultaneously with the decomposition of zinc acetate to produce the ZnO/rGO nanocomposite. Unlike conventional methods, this approach is distinguished by its environmental sustainability. This method is cost-effective and industrially scalable, enabling the rapid production of large quantities of ZnO/rGO composite within minutes. The use of low-cost precursors, a simple synthesis procedure, energy efficiency, and scalability make this approach significant. Our group is the first to report single-step synthesis of ZnO/rGO composite in a few minutes via the pyrolysis of table sugar and zinc acetate. By adopting this method, we successfully produced rGO and its nanocomposite with ZnO without the use of hazardous substances, harmful gas

emissions, or the harsh conditions typically associated with traditional rGO production methods. The structural and morphological characteristics of the synthesised samples were extensively analysed to confirm the formation of rGO and ZnO/rGO composites. Characterisation techniques included X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), Fourier-transform infrared spectroscopy (FT-IR), and UV-visible spectroscopy. These analyses verified the successful synthesis of rGO and ZnO/rGO composites through the single-step heating process. This method advances the development of sustainable technologies by providing a green alternative for the cost-effective production of ZnO/rGO composites from inexpensive precursors.

2.1 Synthesis of rGO

2.1.1 Introduction

As discussed in Chapter 1, rGO is a versatile material known for its outstanding electrical, mechanical, and thermal properties [1]. Because of the unique characteristics, rGO has found applications across a broad spectrum of scientific and technological domains [2-9]. The chemical route is the most widely used method for large-scale rGO production. This conventional approach involves two major steps: the oxidation of graphite to produce GO, followed by its reduction to obtain rGO [10].

The commonly used process sequence for the preparation of rGO involves a number of chemical routes beginning with the oxidation and exfoliation of graphite through various methods. The chemical methods for graphite oxidation include the Brodie, Staudenmaier, Hofmann, Hummers, and their variations. These approaches generally rely on strong acids (such as H_2SO_4 and HNO_3) combined with powerful oxidizing agents (like KMnO_4 , KClO_3 , and NaNO_3) to induce oxidation [11-13].

Despite their effectiveness, these traditional chemical methods suffer from major limitations. They require toxic and hazardous reagents, often release harmful gases, and involve highly exothermic reactions that can be potentially explosive [11-13]. Furthermore, the safe disposal of the resulting hazardous by-products as well as the safe handling of toxic gases poses significant environmental challenges and increases the overall production cost, especially at industrial scales [14].

Following oxidation, the resulting GO must be reduced to remove a substantial portion of its oxygen-containing functional groups. This step partially restores the conjugated sp^2 carbon structure characteristic of graphene, yielding rGO [10]. This reduction step can be achieved through various methods, including thermal, chemical, microwave-assisted, photo-induced, hydrothermal, and solvothermal techniques [15-18].

In conclusion, the conventional production of rGO is a complex, multistep, costly, and time-consuming process. It poses significant environmental and safety risks due to the use of toxic chemicals and the generation of hazardous by-products, making it less suitable for sustainable, large-scale applications.

The challenges associated with the conventional methods of rGO production emphasise the need to develop an economically viable and environmentally friendly alternative method to produce rGO. The synthesis of graphene-like structures from green materials with simpler protocols is particularly attractive due to their cost-effectiveness, rapid processing, non-toxicity, biological compatibility, and the ability to produce in large quantities. Recent studies have demonstrated progress in this direction, with the successful synthesis of graphene-like structures from hydrocarbon-rich compounds such as sugarcane bagasse, table sugar, glycine, vegetable oils, and various types of biomass waste [19-22].

This first portion of this chapter presents a novel, rapid, and environmentally friendly approach for the synthesis of rGO. This method avoids the use of toxic chemicals and generates no harmful byproducts associated with conventional rGO production methods. Sucrose was used as the sole precursor material, and the pyrolysis of sucrose produced rGO. The process enables bulk production within minutes, making it suitable for industrial-scale applications. The prepared rGO was characterized through comprehensive analyses, including XRD, Raman spectroscopy, FT-IR, FE-SEM, EDX, HR-TEM, UV-visible spectroscopy and, XPS. All the analyses also confirmed the formation of layered sheet-like structure of rGO. This simple and cost-effective method offers an industrially scalable approach for producing rGO. The following sections describe the synthesis of rGO from sucrose and provide the results of comprehensive characterisation techniques that validate its successful formation.

2.1.2 Experimental section

2.1.2.1 Materials required

Reduced graphene oxide was synthesised through the pyrolytic reduction of a low-cost and widely available precursor—table sugar [sucrose, 99% purity, Nice Chemicals, India]. Sucrose, a carbon-rich disaccharide composed of one glucose and one fructose unit, served as the carbon source. Its molecular structure is shown in Fig. 2.1, highlighting its abundance of carbon atoms suitable for graphitisation. The sucrose was used as received, without any further purification.

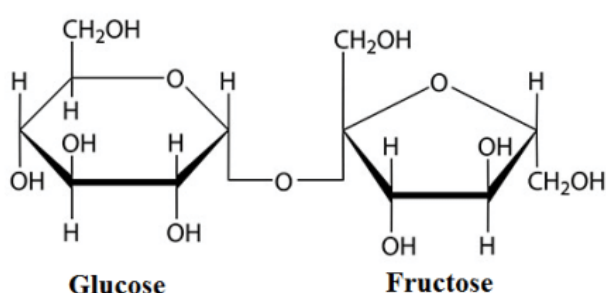


Fig. 2.1: Structural representations of sucrose: Haworth-type structure [23].

2.1.2.2 Synthesis of rGO

rGO was synthesised via a single-step pyrolysis method using sucrose as the carbon precursor. Specifically, 2 g of sucrose was placed in a 100 mL borosilicate beaker and heated in a preheated muffle furnace at temperatures ranging from 400°C to 550 °C for a few minutes. After pyrolysis, a black, foamlike, carbonaceous material formed in the beaker. This material was collected and ground into a fine powder using an agate mortar. The thermal decomposition and dehydration of sucrose during this process led to the formation of reduced graphene oxide.

2.1.3. Results and discussions

2.1.3.1 Optimization of reaction conditions

2.1.3.1.1 Reaction temperature

To determine the optimal pyrolysis temperature, rGO samples were prepared at various temperatures within the temperature window of 400°C to 550°C as per the

literature review [21]. The results of these analyses, which guided the selection of the optimal synthesis temperature, are discussed in the following section.

2.1.3.1.1.1 XRD analysis of rGO prepared at different temperatures

X-ray diffraction is a widely used technique for determining the structural characteristics of the material. It provides valuable information about crystal structure, lattice parameters, and crystallite size. It is a non-destructive technique commonly employed to characterise the material under investigation [24]. By analysing the diffraction peaks in the XRD spectrum, one can infer whether the material is crystalline or amorphous, and whether the structure is in the nanoscale or microscale range.

When an X-ray beam is incident on a crystalline material, the periodic arrangement of atoms in the crystal lattice causes the incident X-rays to undergo diffraction. The diffracted X-ray waves originating from successive lattice planes (Miller planes) interfere constructively under certain conditions. This constructive interference results in characteristic diffraction pattern, known as the X-ray diffraction (XRD) spectrum or diffractogram. This constructive interference follows Bragg's law, given by:

$$n\lambda = 2d\sin(\theta) \quad (2.1)$$

where n is the order of diffraction, λ is the wavelength of the incident X-rays, d is the interplanar spacing, and θ is the angle of incidence (and reflection) relative to the crystal planes.

The resulting XRD pattern is unique to each crystalline phase, effectively serving as a "fingerprint" for material identification. For a mixture of phases, XRD allows both qualitative and, to some extent, quantitative analysis of the different crystalline components present [25-26].

XRD was employed to analyse the samples synthesised at 400 °C, 475 °C, and 550 °C, in comparison with pristine graphite powder. The rGO samples were labelled according to their respective synthesis temperatures (i.e., 400 °C, 475 °C, and 550 °C). It was recorded using a Rigaku Miniflex 600 diffractometer (Japan) at a scan rate of 5°/min. The diffraction data over the 2θ range of 10° to 50° are presented in Fig. 2.2a. Compared to graphite, all rGO samples exhibited broad, low-intensity peaks in the 20°–25° range, corresponding to the (002) reflection. This broadening and reduced intensity

suggest the formation of poorly ordered, amorphous graphene sheets with low stacking order [27-28].

The XRD pattern of rGO samples synthesised at 400 °C, 475 °C, and 550 °C over an extended 2θ range of 10° to 80° are shown in Fig. 2.2b. All samples displayed a characteristic rGO peak around 23°, which corresponds to the (002) plane of rGO [27-28]. Additionally, a smaller but distinct peak near 43° was observed in the samples prepared at higher temperatures (475 °C and 550 °C). This peak corresponds to the (100) plane and is associated with in-plane structural ordering and turbostratic disorder, which are typical features of reduced graphene oxide [29].

The similarity in XRD patterns for the samples synthesised at 475 °C and 550 °C suggests comparable structural features. Hence, 475 °C was chosen as the optimal pyrolysis temperature due to its lower energy.

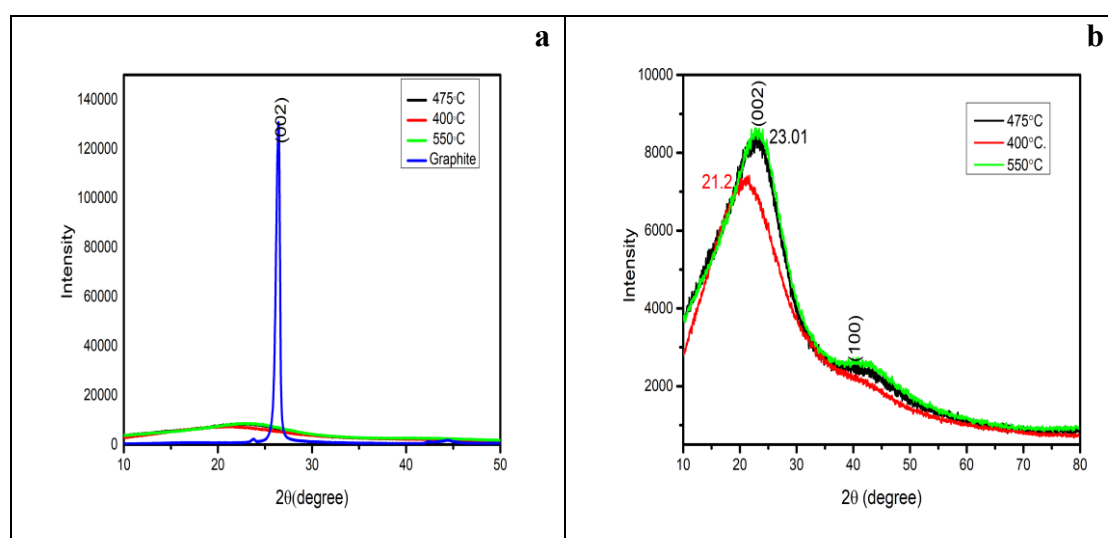


Fig. 2.2: a). Comparison of XRD patterns of rGO prepared by heating sucrose at temperatures 400 °C, 475 °C, and 550 °C with pristine Graphite powder, b) XRD patterns of rGO prepared by heating sucrose at temperatures 400 °C, 475 °C, and 550 °C.

Furthermore, the effect of pyrolysis duration was evaluated based on the visual appearance of the products. A minimum heating time of 7 minutes yields a spongy, fluffy structure characteristic of few-layered nanostructures. In contrast, prolonged heating resulted in denser, less voluminous materials. This reduction in volume and yield at longer durations is attributed to the progressive oxidation of carbon into CO₂, which escapes from the sample during extended heating.

Fig. 2.3 shows the initial sucrose precursor alongside the physical appearance of the product obtained after pyrolysis at 475 °C for 7 minutes.

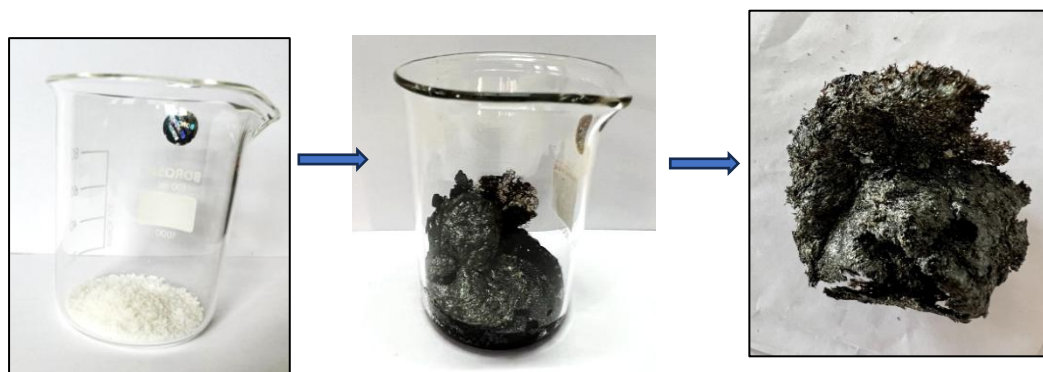


Fig. 2.3: Optical images of the sucrose precursor and the resulting products after pyrolysis at 475 °C for 7 minutes.

2.1.3.1.1.2 Raman analysis of rGO prepared at different temperatures

Raman spectroscopy is a powerful, non-destructive technique used to characterise materials by probing their molecular vibrations through inelastic scattering of light. It provides valuable insights into the chemical structure, composition, and properties of a material [30]. In this study, Raman spectra were recorded using a confocal Raman microscope (WITec ALPHA300 RA). Raman spectroscopy is particularly well-suited for characterising rGO, as it reveals information about structural disorder, defect density, and the degree of graphitisation [31].

The Raman spectra of rGO typically exhibit three key bands: the D band ($\sim 1350\text{ cm}^{-1}$), associated with structural defects and disorder; the G band ($\sim 1580\text{ cm}^{-1}$), corresponding to the E_{2g} vibrational mode of sp^2 -hybridised carbon atoms; and the 2D band ($\sim 2700\text{ cm}^{-1}$), a second-order overtone of the D band, which is sensitive to the number of graphene layers and their stacking order [32-34].

Fig. 2.4 presents the Raman spectra of rGO samples synthesised at pyrolysis temperatures of 400 °C, 425 °C, 475 °C, 525 °C, and 550 °C. All samples exhibit prominent D and G bands, confirming the formation of rGO from sucrose-derived carbon. Notably, the 2D band is clearly visible only in the sample prepared at 475 °C, suggesting a more ordered graphitic structure with well-aligned sp^2 carbon domains

[34-35]. The intensity and clarity of the 2D band are strongly influenced by the layer number and orientation of graphene sheets.

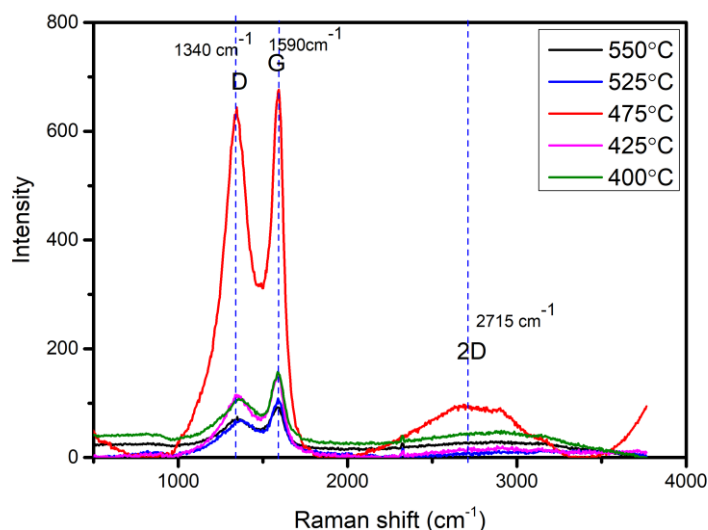


Fig. 2.4: Raman spectra of rGO produced by heating sucrose at different temperatures

The sample synthesised at 475 °C showed the most well-defined D and G bands, along with a distinct 2D band—indicating a relatively high-quality rGO structure. This result validates the selection of 475 °C, as determined from XRD analysis, as the optimal pyrolysis temperature for rGO synthesis. Therefore, the sample prepared by heating sucrose at 475 °C for 7 minutes was selected for further synthesis and detailed characterization.

These findings are consistent with earlier work by Pallelappa Chithaiah et al. [21]

2.1.3.2 Characterization of rGO

The successful formation of rGO via a simple, single-step pyrolytic method was confirmed through a comprehensive set of characterisation techniques. These include XPS, Raman analysis, XRD, FE-SEM, EDX, HR-TEM, FT-IR, and UV–visible spectroscopy. The sample synthesised from sucrose at 475 °C for 7 minutes is referred to as “rGO” in the subsequent sections. The results from these analyses, conducted on this standard rGO sample, are presented and discussed in the following sections.

2.1.3.2.1 Elemental analysis by XPS

X-ray photoelectron spectroscopy (XPS, Thermo Scientific) is a surface-sensitive analytical technique used to determine the elemental composition and chemical bonding states of constituent elements [36]. This technique involves irradiating the material with X-rays and measuring the kinetic energy of the emitted photoelectrons. By calculating the difference between the photon energy and the kinetic energy of the ejected electrons, the binding energies of electrons can be determined. A plot of photoelectron intensity versus binding energy allows for the identification and quantification of elements, as well as insights into their chemical states—even at trace levels. In addition, subtle shifts in the binding energy of an element in the same oxidation state can provide valuable information about changes in its local chemical environment [37].

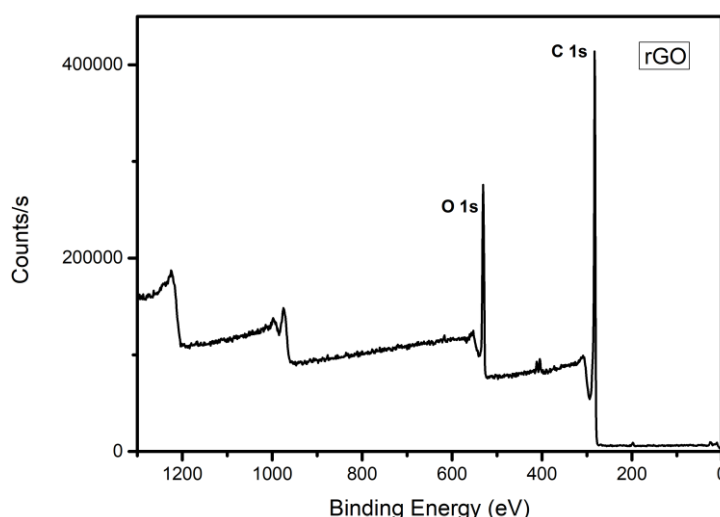


Fig. 2.5: a) XPS survey spectra of rGO.

Fig. 2.5a shows the XPS survey spectrum of the synthesised rGO. Two prominent peaks are observed: one corresponding to the C 1s state at approximately 285 eV, and another to the O 1s state at around 534 eV. Quantitative analysis of the XPS data revealed that the rGO sample contains 82.7% carbon and 17.3% oxygen, suggesting the formation of carbon-rich graphene-like structures.

To gain deeper insight into the chemical bonding environment, high-resolution XPS spectra of the C 1s and O 1s regions of rGO were analysed. Fig. 2.5b displays the

deconvoluted C 1s core-level spectrum of the rGO sample. The C 1s spectrum exhibits an asymmetric peak with a long tail extending towards higher binding energies in the range of 282eV to 295eV. This tail portion of the C1s peak is attributed to various oxygen linkages to carbon atoms, indicating the presence of various oxygen-containing functional groups attached to the carbon sheets [38].

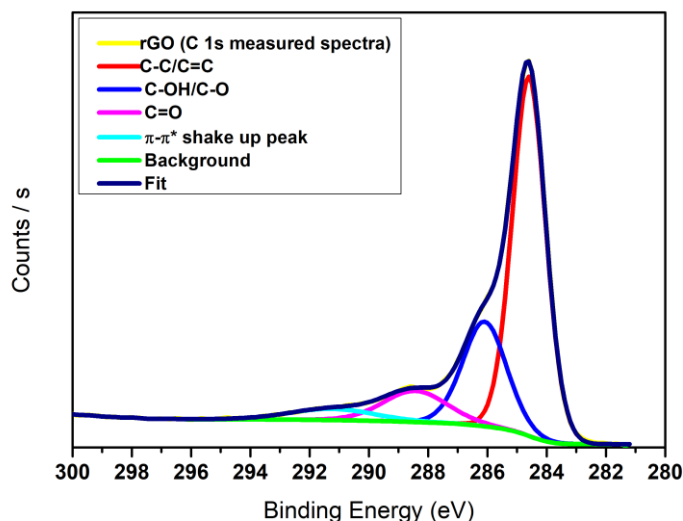


Fig. 2.5: b) Deconvoluted C 1s spectra of rGO

The C 1s peak was deconvoluted into four distinct components, each corresponding to different carbon bonding states. The most intense peak, located at 284.6 eV, is attributed to unoxidized sp^2 - and sp^3 -hybridised carbon atoms—representative of the graphitic domains in rGO. A second, prominent peak at 286.09 eV corresponds to carbon atoms bonded to hydroxyl (C–OH) or epoxide (C–O) groups on the basal plane of rGO. Additionally, peaks observed at 288.43 eV were identified as C=O bonds in the carbonyl and carboxyl groups of the samples [39-40]. The less intense but significant peak around 291 eV is originated from the aromaticity of rGO, indicated by the π - π^* shake-up satellite peak. This peak results from the π - π^* transition of highly localised electrons present in the graphitic and aromatic systems, confirming the aromatic hexagonal structure of graphene [41-42].

Similarly, Fig. 2.5c shows the high-resolution O 1s core-level spectrum of rGO, which was deconvoluted into three distinct peaks corresponding to different oxygen-containing functional groups. The peak at 531.67 eV is assigned to carbonyl groups

(C=O), representing oxygen double-bonded to aromatic carbon. The peak at 533.56 eV corresponds to ether or epoxide groups (C–O), indicating oxygen singly bonded to carbon. The third peak, observed at 535.56 eV, is attributed to hydroxyl groups (C–OH), in which oxygen is singly bonded to carbon [39].

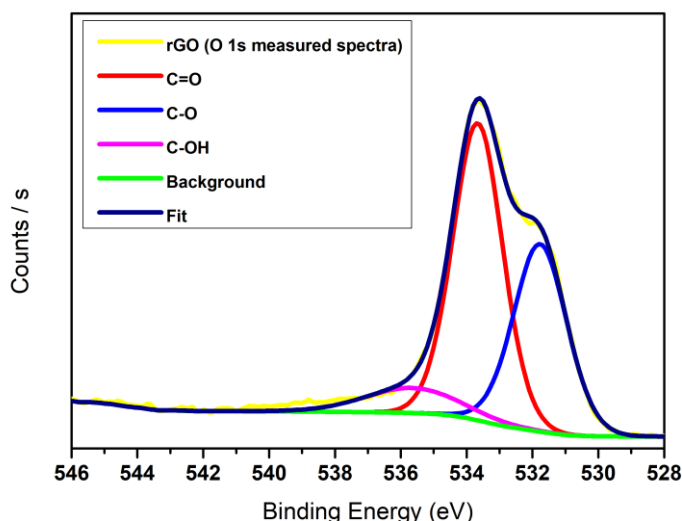


Fig. 2.5: c) Deconvoluted O 1s spectra of rGO

This detailed XPS analysis further confirms the successful formation of rGO from the sucrose-derived carbon structure.

2.1.3.2.2 Structural analysis by Raman spectroscopy

The Raman spectra provided strong evidence confirming that the sucrose-derived carbon structure is rGO. Fig. 2.6 shows the Raman spectra of rGO. The spectra of rGO exhibit two prominent peaks, the D band and the G band, both of which are widely recognised fingerprints of graphene-based materials [32]. Additionally, a significant peak, the 2D band, corresponding to the second-order mode of the D band, is visible in the Raman spectra of rGO sheets [33].

The D band, observed at 1346 cm^{-1} , arises due to structural imperfections or defects induced by hydroxyl, epoxide, carboxyl groups, etc., as well as the vacancies on the hexagonal honeycomb carbon basal plane of graphene. This band, also referred to as the "defect band," represents sp^3 carbon atoms and is a result of the breathing mode of K-point phonons of A_{1g} symmetry. On the other hand, the G-band at 1593 cm^{-1} , known as the graphitic band, is characteristic of all highly oriented non-defective sp^2

hybridised carbon networks. It is generated by the first-order scattering of the E_{2g} phonons on the graphite structure [43-44].

The presence of a broad and less intense peak at 2676 cm^{-1} corresponds to the first overtone of the D band, known as the 2D band. This peak arises from a two-phonon intervalley double-resonance mechanism [45]. Its appearance is associated with the presence of graphitic domains. The intensity and shape of the 2D band are sensitive to the number of graphene layers and their stacking order [34-35]. The 2D peak serves as further confirmation of the formation of a graphitic structure resulting from the pyrolysis of sucrose [46].

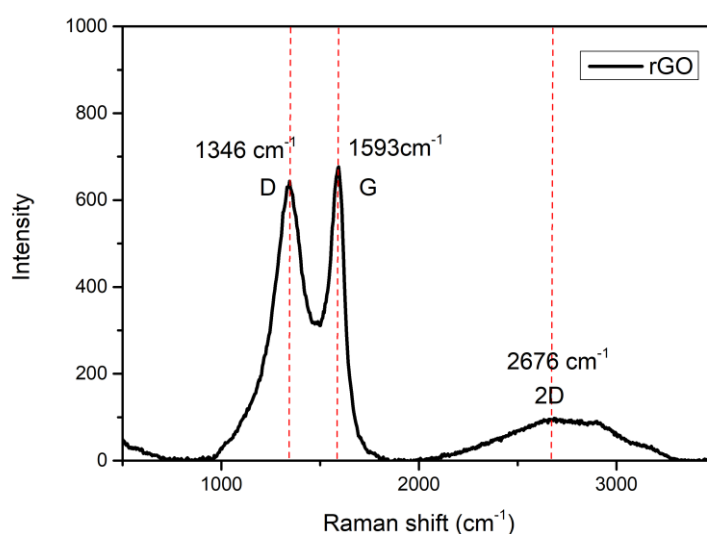


Fig. 2.6: Raman spectra of rGO

2.1.3.2.3 Structural analysis by XRD

The XRD pattern of sucrose-derived rGO is presented in Fig. 2.7, confirming the successful synthesis of rGO via a single-step pyrolysis method using sucrose as the carbon precursor. The diffraction pattern displays a broad and relatively weak peak centred at $2\theta \approx 23^\circ$, corresponding to the (002) crystallographic plane [28]. This peak is indicative of the graphitic nature of rGO and suggests the presence of few-layered graphene sheets [27]. The broadness of this peak reflects the disordered, partially amorphous structure of rGO.

Additionally, a smaller but distinct shoulder peak around $2\theta \approx 43^\circ$ is observed, which corresponds to the (100) plane. This peak is associated with the turbostratic disorder commonly observed in reduced graphene oxide structures, which further supports the formation of rGO [29].

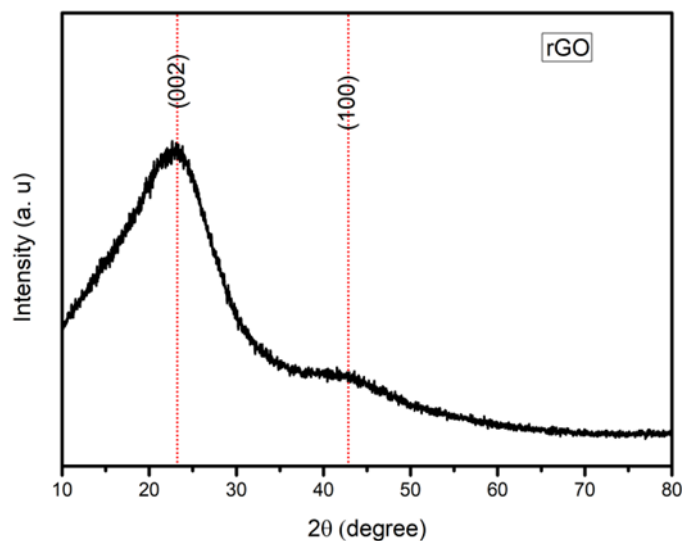


Fig. 2.7: XRD pattern of rGO

The interlayer spacing (d-spacing) of the (002) plane in rGO synthesised at 475 °C was calculated using Bragg's Law (Eqn. 2.1) and found to be 0.387 nm.

2.1.3.2.4 Morphological and compositional analysis by FE-SEM and EDX

The surface morphology and microstructure of sucrose-derived rGO were examined using Field Emission Scanning Electron Microscopy (FESEM, ZEISS GeminiSEM 300). FESEM is a high-resolution imaging technique that uses a focused beam of electrons to scan the surface of a sample, enabling the visualisation of surface features at the micro- and nanoscale. This analysis provides valuable insights into the texture, porosity, and structural features of the synthesised rGO.

To complement the morphological analysis, the elemental composition of the rGO samples was investigated using EDS integrated with the FESEM system. EDS analysis enabled the identification and quantification of the elemental composition of the rGO.

Fig. 2.8a shows the FE-SEM image of rGO, which portrays its layered 2D planar morphology. These layers appear to be free of voids or cracks and exhibit dimensions spanning several micrometres in length and breadth. Fig. 2.8b provides a magnified FE-SEM image of rGO that further emphasises the layered nature of rGO.

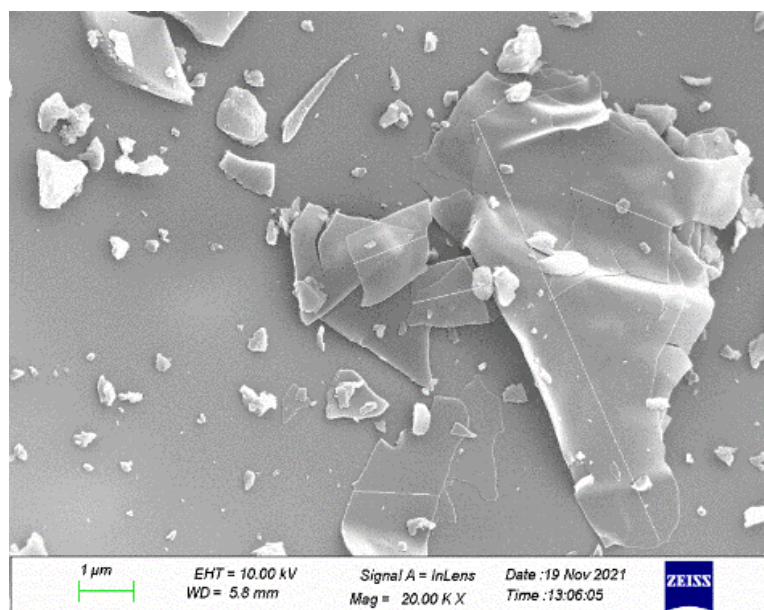


Fig. 2.8: a) FE-SEM image of rGO.

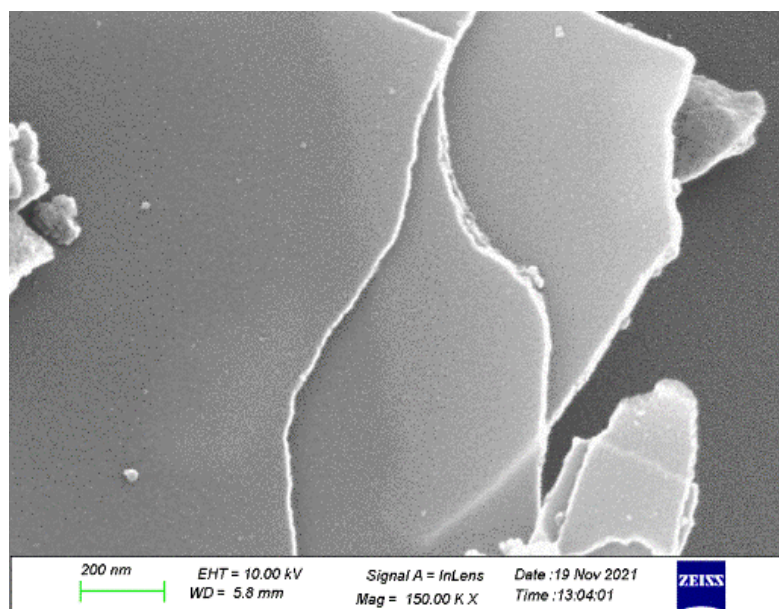


Fig. 2.8: b) Magnified FE-SEM image of rGO.

The composition of rGO was analysed by EDS spectra, which is shown in Fig. 8c. It demonstrates that the rGO comprises carbon and oxygen; the absence of any additional peak indicates that no impurity elements were present.

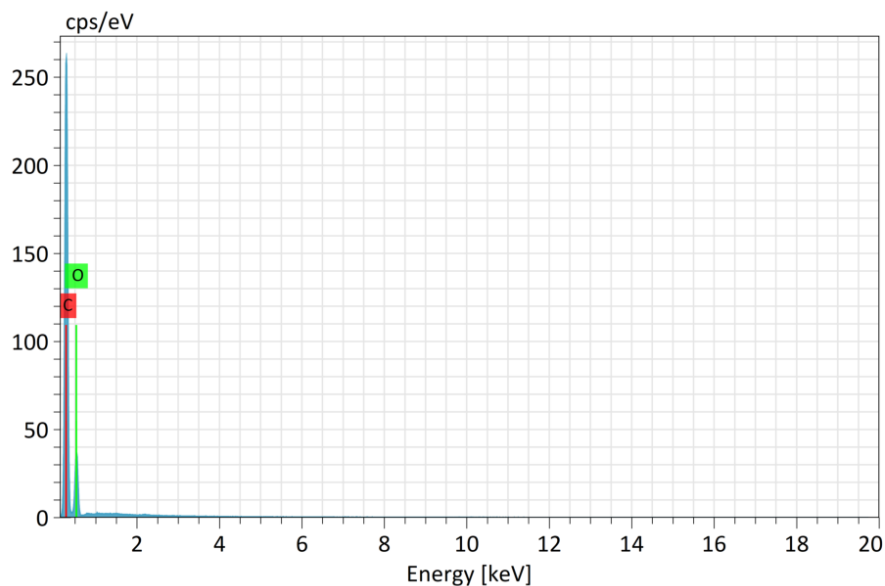


Fig. 2.8: c) The EDX spectra of rGO

The elemental mapping of rGO, presented in Fig. 2.8d, reveals a uniform distribution of the constituent elements, confirming the well-formed and homogeneous structure of the rGO sheets.

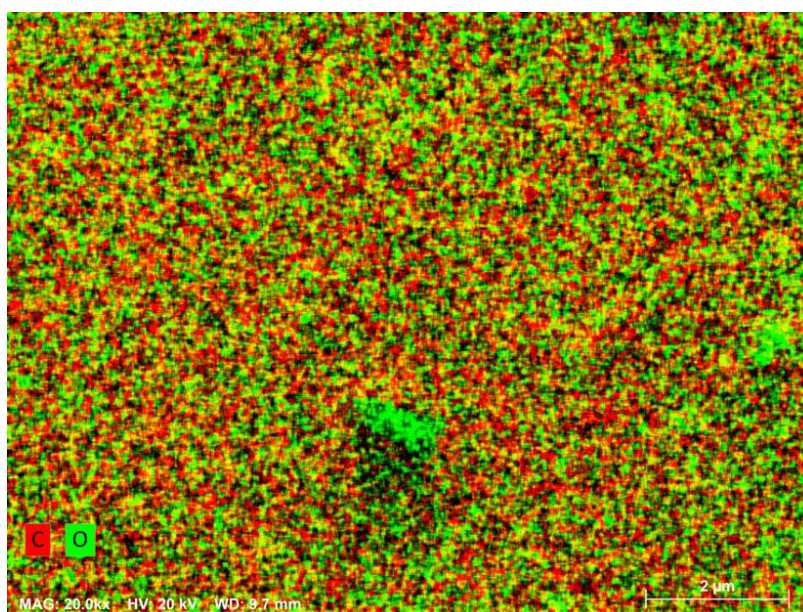


Fig. 2.8: d) Elemental mapping of rGO

2.1.3.2.5 Morphological analysis using HR-TEM.

High-Resolution Transmission Electron Microscopy (HRTEM, JEOL JEM-2100, Japan) was employed for a detailed structural investigation of the sucrose-derived rGO. HRTEM provides ultra-high-resolution imaging by transmitting a beam of

electrons through a thin specimen, enabling visualisation of the material at the atomic scale. This method allows direct observation of lattice fringes, providing insights into the crystallinity of the material. In this study, HRTEM imaging was used to further examine the morphological characteristics and nanoscale features of the prepared rGO sample.

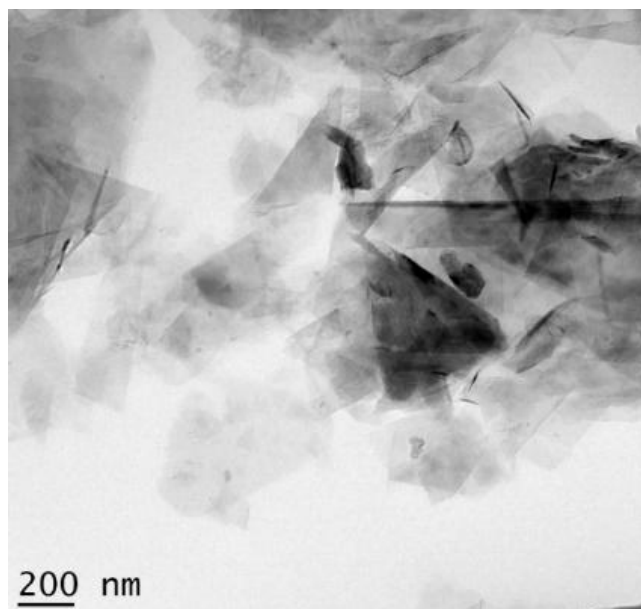


Fig. 2.9: a) TEM image of rGO

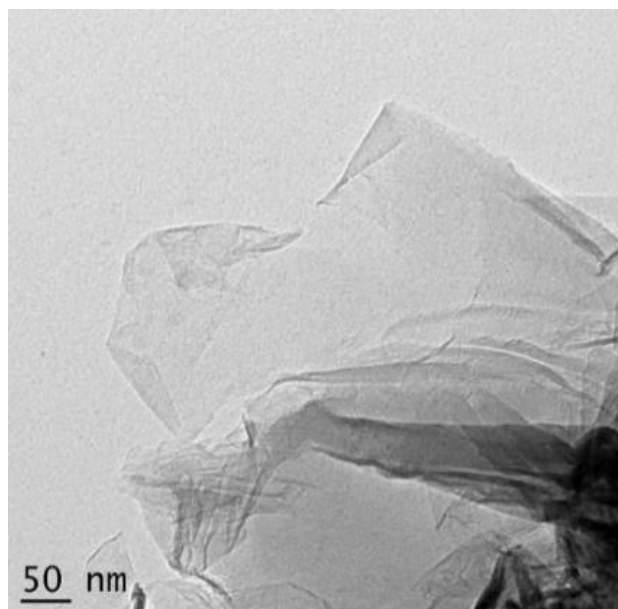


Fig. 2.9: b) Magnified TEM image of rGO

HR-TEM images of rGO at different magnifications are shown in Figures 2.9a and 2.9b. These images reveal that the sucrose-derived rGO mainly consists of few-

layered domains. The rGO exhibits a characteristic sheet-like structure with a curled and wrinkled morphology. The darker regions observed in the images are attributed to the folding and stacking of the rGO sheets.

The HR-TEM allows atomistic scale imaging, which can provide the crystallographic structure of the samples. Fig. 2.9c illustrates the HR-TEM image of rGO, demonstrating a lattice distance of 0.386 nm corresponding to the most prominent plane (002), consistent with the results from the XRD spattern of rGO [47].

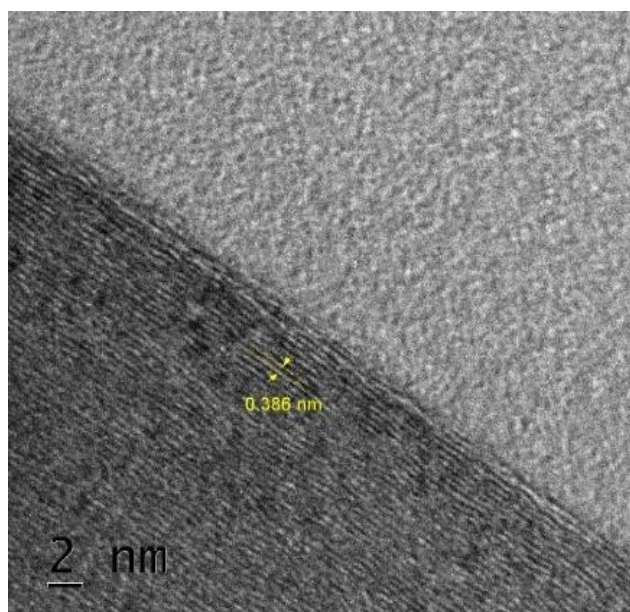


Fig. 2.9: c) HR-TEM image of rGO showing lattice fringes.

The TEM elemental mapping for the rGO (Fig. 2.10a, 2.10(b-c)) was analysed to verify the spatial distribution of elements. The mapping images reveal a uniform distribution of the constituent elements, confirming the well-formed and homogeneous structure of the rGO sheets.

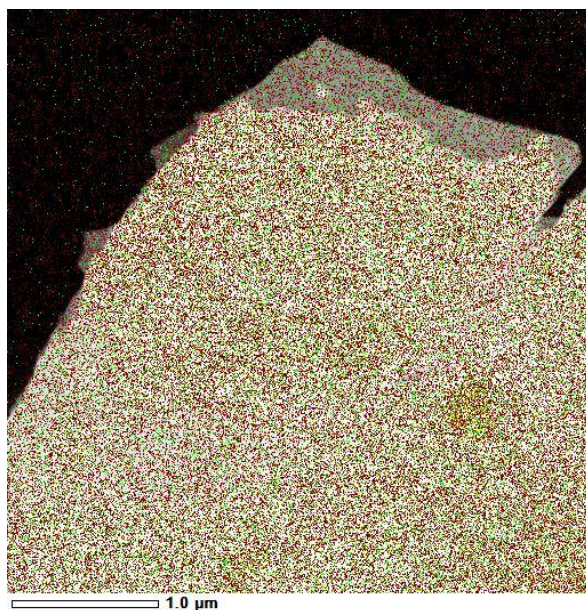


Fig. 2.10: a) Elemental TEM mapping of rGO

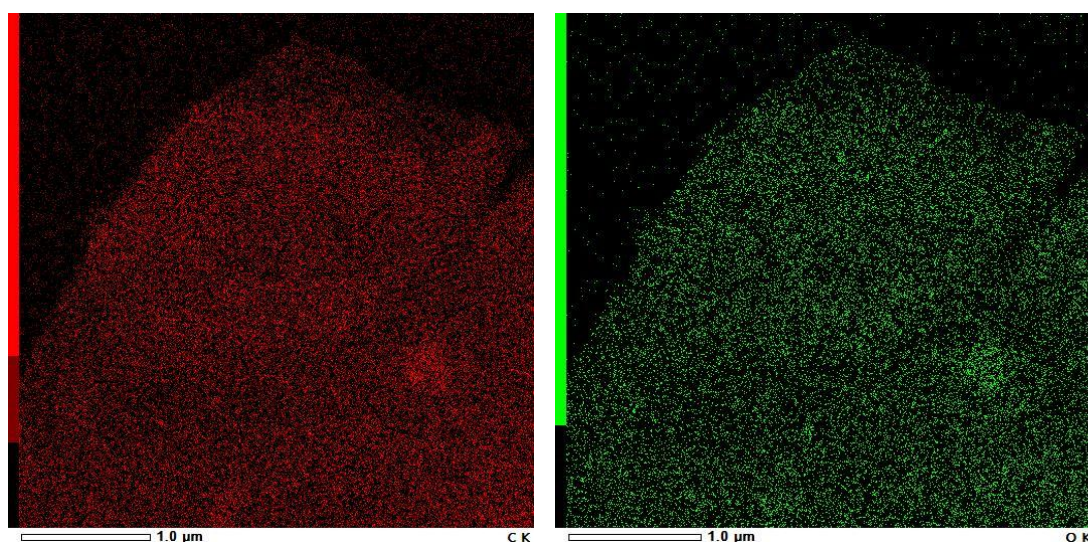


Fig. 2.10: b, c) Elemental mapping of rGO (carbon (red) and oxygen (green)).

2.1.3.2.6 Characterization using FT-IR spectroscopy

Fourier-Transform Infrared spectroscopy was conducted using a Thermo Scientific Nicolet iS5 instrument in the range of $4000\text{--}400\text{ cm}^{-1}$ to investigate the functional groups present in the samples. This technique was used to identify the specific chemical bonds and functional groups present in the materials. This analysis was performed on rGO to gain insights into its structural characteristics. The corresponding spectrum is illustrated in Fig. 2.11. The broad absorbance band in the range $3650\text{--}3000\text{ cm}^{-1}$ is assigned to the stretching vibrations of hydroxyl groups of

adsorbed water molecules in the samples [48-49]. A band in the range 1800 cm^{-1} to 650 cm^{-1} in the spectra corresponds to oxygen and carbonic functional groups, confirming the oxidised graphitic structure in rGO. In this spectral region, the absorbance peak at 1675 cm^{-1} corresponds to the stretching vibration of the C=O bond. Additionally, the band centred around 1157 cm^{-1} in the $1200\text{--}1006\text{ cm}^{-1}$ range was attributed to various C-O containing groups such as alkoxy, carboxy, and epoxy groups on the rGO surface. The featured band at 1564 cm^{-1} , which corresponds to the stretching of the C=C bond, indicates the presence of unoxidized sp^2 bonds in the graphene backbone, suggesting a honeycomb-like graphene structure [19, 32].

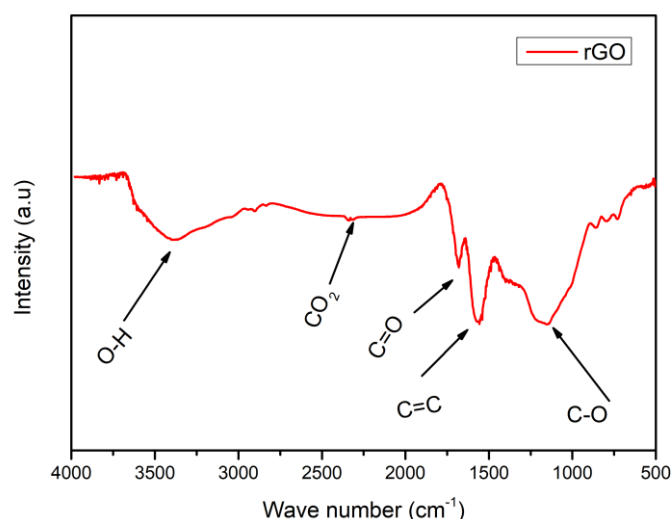


Fig. 2.11: FT-IR spectra of rGO.

2.1.3.2.7 Characterization using UV-visible spectroscopy

UV-visible spectroscopy (Shimadzu UV-1800 spectrophotometer) was employed to provide further confirmation of the formation of rGO. Fig. 2.12 displays the optical absorbance spectrum of rGO in the wavelength range of 200–800 nm. The UV-visible spectrum shows a characteristic shoulder peak around 270 nm [50]. This shoulder peak indicates the $\pi\text{--}\pi^*$ transition of aromatic C-C bonding, which is a characteristic feature of rGO. The presence of this shoulder peak signifies the presence of sp^2 -hybridized carbon bonds [51-52]. The presence of this peak further supports the successful formation of reduced graphene oxide.

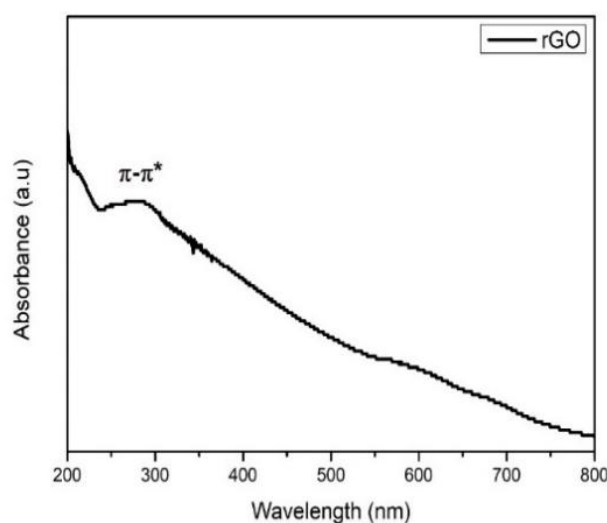


Fig. 2.12: UV-visible absorbance spectra of rGO.

In summary, the sucrose-derived rGO was characterised using various analytical techniques, including XPS, Raman spectroscopy, XRD, FE-SEM, HR-TEM, FT-IR, and UV–visible spectroscopy. The results from all these analyses confirmed the successful formation of rGO from sucrose via the pyrolysis method.

2.2 Synthesis of ZnO/rGO composite

2.2.1 Introduction

After confirming the successful synthesis of rGO from sucrose, we extended this simple, single-step pyrolytic method to prepare metal oxide–rGO composites. ZnO was selected as the metal oxide of interest. As discussed in Chapter 1, ZnO is a highly promising material known for its outstanding mechanical, optical, and physicochemical properties [53]. Owing to its non-toxicity, abundance, low cost, and excellent chemical, thermal, and photosensitivity [54], ZnO finds widespread applications across physics, chemistry, and materials science [55-58]. It is the most extensively studied *n*-type semiconductor, typically crystallizing in the hexagonal wurtzite structure. ZnO exhibits a wide direct bandgap of approximately 3.37 eV and a high exciton binding energy of around 60 meV at room temperature [59].

When combined with rGO, the functional performance of ZnO is significantly enhanced. This synergy expands its utility in areas such as heavy-metal adsorption,

photocatalysis, antimicrobial activity, energy storage, sensing, and optoelectronic devices [48,60-64].

Conventionally, the synthesis of ZnO/rGO composites is a multistep process and can proceed via either in-situ or ex-situ methods [65]. In the in-situ approach, ZnO nanoparticles nucleate and grow directly on the defect sites of the carbonaceous material, often simultaneously with the reduction of GO to rGO. In contrast, the ex-situ method involves combining pre-synthesized ZnO with GO or rGO [66].

The synthesis of ZnO/rGO composites typically involves the use of either rGO or its precursor, GO, along with ZnO or a suitable zinc-containing salt. Most reported methods for synthesizing ZnO/rGO composites involve a first step of preparing GO (usually through oxidation of graphite), followed by its incorporation with a zinc salt and subsequent treatment via solvothermal, hydrothermal, sol-gel, microwave, or co-precipitation methods [65]. In many cases, ZnO nucleation and anchoring occur on the oxygen-containing functional groups of GO, while GO is simultaneously reduced to rGO [66]. A detailed explanation of various ZnO/rGO synthesis methods is included in Chapter 1. These conventional approaches, however, are time-consuming, often require additional reagents, involve multiple synthesis steps, and rely on hazardous and toxic chemicals—especially for the preparation of GO/rGO. Therefore, developing a single-step, rapid, cost-effective approach for synthesising ZnO/rGO composites is of significant interest.

The second part of this chapter presents a novel, rapid, and environmentally friendly method for synthesizing ZnO/rGO composites. In this method, both rGO and ZnO are synthesized and integrated simultaneously through a rapid pyrolysis process using non-toxic, cost-effective precursors—sucrose and zinc acetate. The use of low-cost precursors, a simple synthesis procedure, energy efficiency, and scalability make this approach significant. As per the literature, our group is the first to report single-step synthesis of ZnO/rGO composite in a few minutes via the pyrolysis of table sugar and zinc acetate. By adopting this method, we successfully produced rGO and its nanocomposite with ZnO without the use of hazardous substances, harmful gas emissions, or the harsh conditions typically associated with traditional rGO production methods. The structural and morphological characteristics of the synthesized samples were extensively analysed to confirm the formation of ZnO/rGO composites.

Characterization techniques included XRD, Raman spectroscopy, XPS, FE-SEM, HR-TEM, FT-IR, and UV-visible spectroscopy. These analyses verified the successful synthesis of rGO and ZnO/rGO composites through the single-step heating process. This method is not only scalable and energy-efficient but also enables the production of ZnO/rGO composites within minutes, offering a viable and sustainable alternative to conventional synthesis routes. The following sections detail the synthesis of ZnO/rGO using sucrose and zinc acetate, along with the results of comprehensive characterisation techniques that confirm its successful formation.

2.2.2 Experimental section

2.2.2.1 Materials required

The synthesis of ZnO/rGO composites was carried out using only two low-cost and readily available precursors: sucrose (99%, Nice Chemicals, India) and zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, analytical grade, 98.5%, Nice Chemicals, India). Both the chemicals were used without further purification.

2.2.2.2 Synthesis of ZnO/rGO composites

ZnO/rGO composites were synthesised following a similar approach to that used for rGO preparation, with experimental trials conducted using sucrose and various zinc salts as precursor materials. The preparation parameters, such as heating time, zinc precursor type, and precursor form, were systematically optimised to identify the most suitable synthesis conditions. In these experiments, 1.2 g of sucrose and 0.2 g of zinc salt were mixed in a 100 mL borosilicate beaker. The mixture was then subjected to pyrolysis in a preheated muffle furnace maintained at 475 °C, the temperature optimised for rGO synthesis from sucrose. Different pyrolysis durations of 5, 7, 10, 15, and 60 minutes were investigated. Zinc nitrate and zinc acetate were used as zinc precursors, and both granular and paste forms of the precursors were trialled. The resulting carbonaceous structures were collected, ground to a fine powder in an agate mortar, and subsequently analysed for further characterisation [67].

2.2.3 Results and discussions

2.2.3.1 Optimization of reaction conditions

2.2.3.1.1 Reaction time

The composites were fabricated by heating a mixture of sucrose and a zinc precursor in a preheated muffle furnace maintained at 475 °C. In the initial trials, zinc nitrate was used as the zinc source at a weight ratio of 10% zinc nitrate to 90% sucrose. To examine the thermal decomposition behaviour of the zinc salt and identify the optimal heating duration for ZnO/rGO formation, the mixtures were subjected to pyrolysis for 5, 7, 10, 15, and 60 minutes.

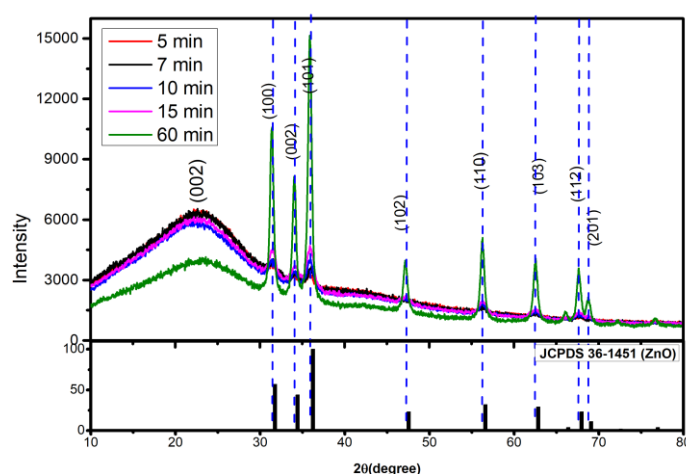


Fig. 2.13: XRD patterns of ZnO/rGO composites (10% zinc nitrate, 90% sucrose) prepared by heating a mixture of sucrose and zinc nitrate at 475 °C for different reaction durations.

The corresponding XRD patterns of the samples are shown in Fig. 2.13. All spectra display sharp, well-defined diffraction peaks alongside a broad, low-intensity peak. The prominent peaks at 2θ values of 31.77°, 34.42°, 36.25°, 47.53°, 56.60°, 62.86°, and 67.96° correspond to the (100), (002), (101), (102), (110), (103), (112), and (201) crystallographic planes of the hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451) [68]. The broad peak around 23° is attributed to the (002) plane of rGO [28]. These results confirm that even a short heating time of 5 minutes is sufficient to produce crystalline ZnO, with crystallinity improving as the heating duration increases.

Additionally, the physical appearance of the resulting products revealed that shorter heating durations produced a spongy and fluffier structure- a crucial indication of few-layered nanostructure- while longer heating periods yielded denser and less voluminous, hard material. The reduction in volume and yield for prolonged durations is attributed to the oxidation of carbon to CO_2 , which escapes the sample during extended heating.

Based on both structural and morphological observations, a heating duration of 7 minutes was found to provide an optimal balance between material integrity and crystallinity, and was therefore adopted for further synthesis of ZnO/rGO composites.

2.2.3.1.2 Zinc precursor

Next, we investigated the effect of different zinc precursors on the synthesis of ZnO/rGO composites. Zinc nitrate and zinc acetate were employed as zinc sources, each mixed with sucrose at a fixed weight ratio of 10% zinc precursor to 90% sucrose. Both mixtures were processed under identical conditions—heated in a preheated muffle furnace at 475°C for 7 minutes. The resulting XRD patterns are presented in Fig. 2.14.

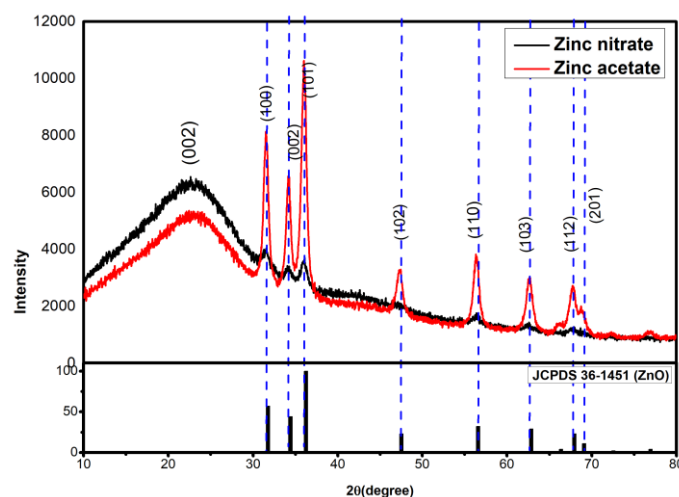


Fig. 2.14: XRD patterns of ZnO/rGO composites synthesised with 10 wt% zinc precursor (zinc nitrate or zinc acetate) and 90 wt% sucrose, heated at 475°C for 7 minutes, showing the effect of precursor type on crystallinity.

The analysis revealed that, under the same experimental conditions, the sample synthesised with zinc acetate exhibited sharper, more intense diffraction peaks

corresponding to ZnO than the sample prepared with zinc nitrate. The enhanced peak sharpness and intensity indicate a higher degree of crystallinity in the ZnO phase when zinc acetate is used as the precursor.

These findings suggest that zinc acetate promotes more efficient and rapid crystallisation of ZnO during the pyrolytic process. Thus, zinc acetate was selected as the preferred zinc precursor for the subsequent synthesis of ZnO/rGO composites.

2.2.3.1.3 Process sequence

In the experiments conducted thus far, granular precursors were used for the synthesis of ZnO/rGO composites. This section presents a comparative study between two synthesis sequences: one using the precursors in their original powder (granular) form, and the other using a paste formed by adding a few drops of water to the same precursor mixture. The expectation behind using the aqueous form was that it might promote a more uniform dispersion of ZnO within the rGO sheets. To maintain consistency, both approaches were subjected to identical synthesis conditions: a reaction temperature of 475 °C, a reaction time of 7 minutes, and zinc acetate as the zinc precursor.

The XRD patterns of the resulting composites are presented in Fig. 2.15. The results demonstrate that the sample synthesised from granular precursors exhibited sharper and more intense diffraction peaks, indicating a higher degree of crystallinity in the ZnO phase. In contrast, the sample derived from the paste precursor showed reduced crystallinity.

Furthermore, a marked difference in the physical appearance of the two products was observed. The sample synthesised from the aqueous paste precursor appeared dense and compact, lacking the characteristic spongy morphology associated with few-layered rGO structures. This observation suggests that the aqueous precursor may have suppressed the formation of well-defined rGO layers.

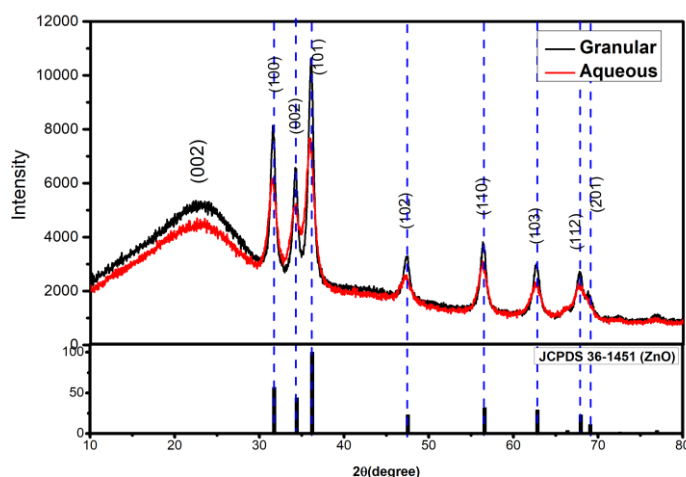


Fig. 2.15: XRD patterns of ZnO/rGO composites synthesised using 10 wt% zinc acetate and 90 wt% sucrose under different processing sequences: (i) precursors in powder form and (ii) precursors mixed into a paste with a few drops of water. All samples were heated at 475 °C for 7 minutes.

Based on these findings, granular precursors were selected for the subsequent synthesis of ZnO/rGO composites.

2.2.3.1.4 Synthesis of ZnO/rGO composites prepared with the optimal conditions

The optimisation results revealed that combining granular zinc acetate with sucrose, heated for 7 min at 475°C, produced fluffier and crystalline ZnO/rGO composite materials. Fig. 2.16 presents the optical images of the ZnO/rGO composite synthesised under these optimal conditions, using a precursor composition of 10% zinc acetate and 90% sucrose by weight. The ZnO/rGO composite with different ZnO:rGO loading was prepared by changing the sucrose and zinc acetate precursor ratios. Different quantities of zinc salts were taken with sucrose and heated in a preheated muffle furnace. The quantities of zinc acetate taken were 0gm (corresponding to rGO), 0.2gm, 0.4gm, 0.6gm, 0.8gm, 1gm, 1.2gm, 1.4gm, 1.6gm, 1.8gm and 2gm, with the total weight of both precursors kept constant at 2gm. The composites were labelled ZG-10, ZG-20, ZG-30, ZG-40, ZG-50, ZG-60, ZG-70, ZG-80, ZG-90, and ZG-100; the digit value represents the percentage of zinc acetate used to prepare the corresponding sample. After the heating, the resulting ZnO/rGO composites were collected from the beaker and finely ground into homogeneous powders for further analysis.

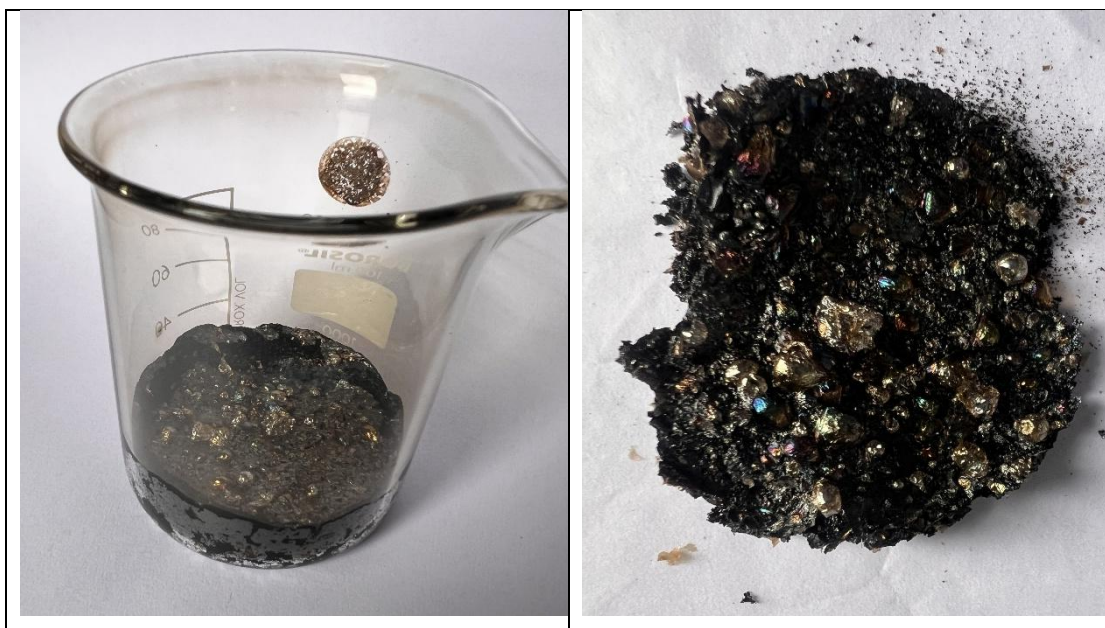


Fig. 2.16: a,b) Optical images of ZnO/rGO composite prepared from sucrose and zinc acetate at a heating temperature of 475°C and heating time of 7min.

2.2.3.2 Characterization of ZnO/rGO composites

The characterization of ZnO/rGO composite synthesised by a simple single-step pyrolytic method with optimised conditions was demonstrated with XRD, XPS, Raman spectroscopy, FE-SEM, EDX, HR-TEM, FT-IR and, UV-visible spectroscopy. The results of the analysis techniques are discussed in the following sections.

2.2.3.2.1 Elemental analysis by XPS

X-ray Photoelectron Spectroscopy was employed to investigate the elemental composition, chemical bonding, and electronic states of the constituent elements in the ZnO/rGO composite. Fig. 2.17a presents the full-scan (survey) spectra of rGO and the ZnO/rGO composite sample ZG-10. The rGO spectrum exhibits two prominent peaks attributed to C 1s at ~285 eV and O 1s at ~534 eV. In the case of ZG-10, the survey spectrum reveals additional peaks corresponding to Zn 2p, Zn 3s, Zn 3p, and Zn 3d core levels, as well as a Zn LMM Auger peak, confirming the presence of ZnO in the composite [69-70]. The Zn 2p region shows a characteristic spin-orbit doublet, with Zn 2p_{3/2} at ~1021.6 eV and Zn 2p_{1/2} at ~1044.54 eV, exhibiting an energy separation (ΔE) of ~23 eV. This splitting is indicative of Zn in the +2-oxidation state [32,69,71], and the Zn 2p_{3/2} binding energy further confirms the formation of ZnO with a hexagonal wurtzite crystal structure [72]. Quantitative XPS analysis revealed that rGO contains 82.7% carbon and 17.3% oxygen, while the ZG-10 composite contains 76.38% carbon,

20.37% oxygen, and 3.25% zinc. These results confirm the successful synthesis of rGO and the incorporation of ZnO into the rGO matrix.

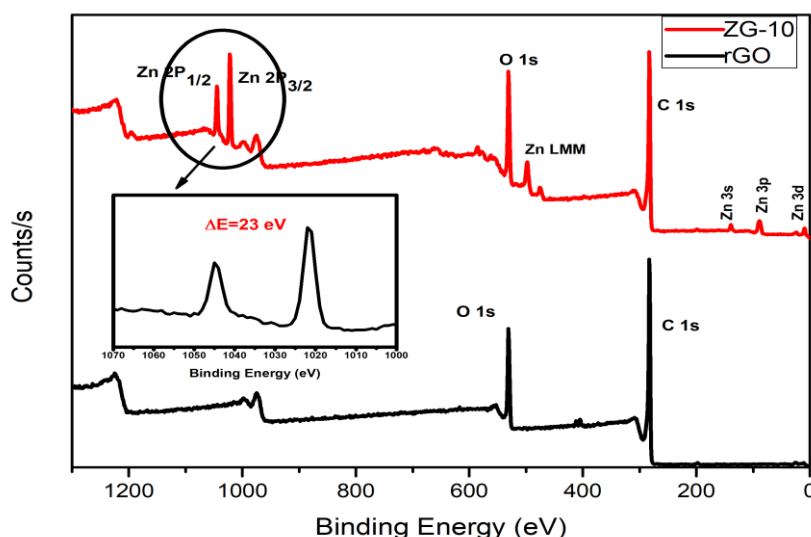


Fig. 2.17: a) XPS survey spectra of rGO and ZnO/rGO composite ZG-10.

To get more details, high-resolution spectra of C 1s, O 1s states for rGO and C 1s, O 1s and, Zn 2p states for ZG-10 were analysed. Fig. 2.17b represents the stacked C1s core-level spectra for rGO and ZG-10. In both spectra, an asymmetric peak with a long tail towards higher binding energy within the range of 282eV to 295eV was observed. This tail portion of the C1s peak is attributed to various oxygen linkages to carbon atoms, indicating the presence of different oxygen-containing functional groups bound to carbon sheets [38].

The C 1s peak of rGO and ZG-10 was deconvoluted into four different components (Fig. 2.17b), and the state of carbon corresponding to each peak was identified. In both samples, the peak at 284.6 eV was attributed to unoxidized carbon with sp^2 and sp^3 hybridization. This is the most intense peak in both rGO and ZG-10 spectra, indicating the graphitic structure. The second strong peak in the spectra, observed at 286.09 eV for rGO and 286.04 eV for ZG-10, was assigned to hydroxyl (C-OH) or epoxide (C-O) groups present in the rGO basal plane. Additionally, peaks at 288.43 eV for rGO and 288.12 eV for ZG-10 were identified as C=O bonds in the carbonyl and carboxyl groups of the samples [39-40]. The slight shift in peak positions observed could be attributed to the interaction between rGO and ZnO, which alters the

electronic environment of the rGO in the composite. The less intense but significant peak around 291 eV in both samples originated from the aromaticity of rGO, indicated by the π - π^* shake-up satellite peak. This peak resulted from the π - π^* transition of highly localised electrons present in the graphitic and aromatic systems, confirming the aromatic hexagonal structure of graphene [41-42].

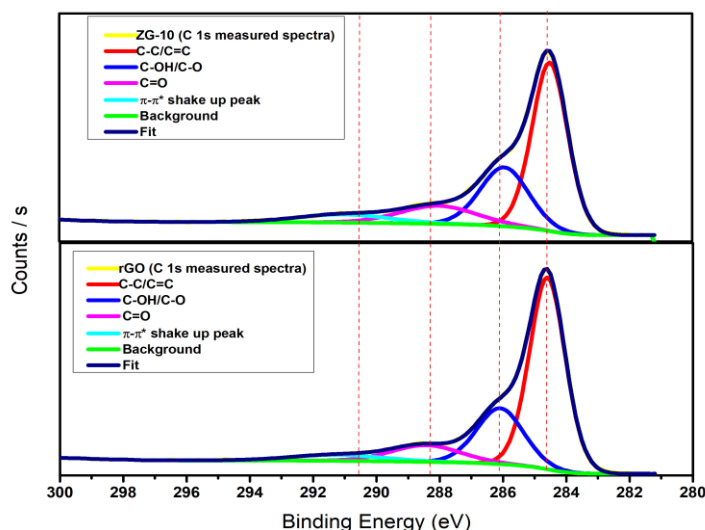


Fig. 2.17: b) C 1s spectra of rGO and ZnO/rGO composite ZG-10.

Similarly, Fig. 2.17c depicts the O1s core-level spectra of rGO and ZG-10, which were deconvoluted into three peaks representing C=O (from the oxygen double bond to aromatic carbon), C-O (from the oxygen single bond to carbon), and C-OH (from the carbon single bond to the hydroxyl group). Their binding energies are 531.67, 533.56, and 535.56 eV for rGO and 531.53, 533.42, and 534.78 eV for ZG-10, respectively [39]. The O 1s region of ZG-10 also displays peaks attributed to lattice oxygen in the hexagonal wurtzite structure of ZnO, the oxygen vacancies and, the adsorbed oxygen [71]. However, the characteristic binding energy feature of O 1s in ZnO typically falls within the range of 530 eV to 532 eV [73], which overlaps with the binding energy range of oxygen-carbon bonding as in rGO. Consequently, it cannot distinguish between the O 1s curves corresponding to different forms of oxygen-carbon and oxygen-zinc binding energies. The slight shift observed in the binding energies of O1s in ZG-10 and rGO spectra may be attributed to this overlap between the oxygen-carbon and oxygen-zinc binding energies.

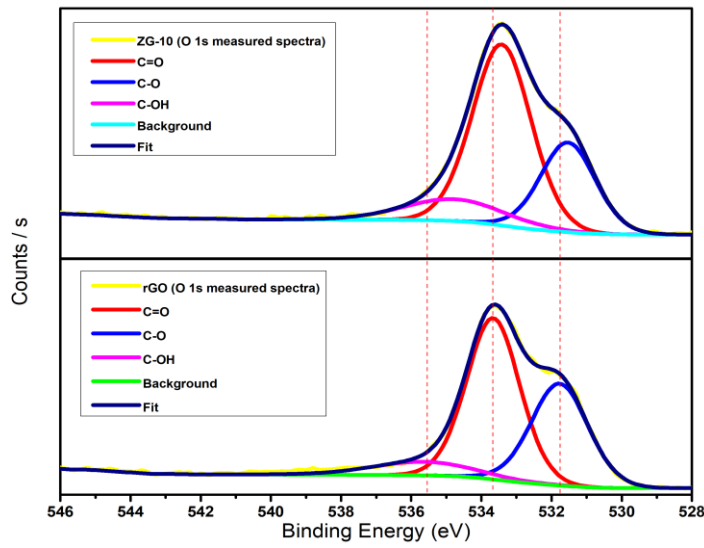


Fig. 2.17: c) O 1s spectra of rGO and ZnO/rGO composite ZG-10.

2.2.3.2.2 Raman analysis

The Raman spectrum of the ZnO/rGO composite sample ZG-70 is shown in Fig. 2.18. The spectrum clearly displays characteristic peaks for both rGO and ZnO, confirming the successful formation of the composite. The peaks observed at 323 cm^{-1} , 431 cm^{-1} , 574 cm^{-1} , and 1121 cm^{-1} correspond to the E_2 (low), E_2 (high), E_1 (LO), and A_1 (LO)– E_1 (LO) vibrational modes of ZnO, respectively [63,74]. In addition, two prominent bands at 1343 cm^{-1} and 1591 cm^{-1} are observed, corresponding to the D and G bands of rGO. The D band arises due to structural defects and disorder (sp^3 carbon), while the G band is associated with the in-plane vibration of sp^2 -bonded carbon atoms [43-44]. The presence of these distinctive peaks confirms the successful integration of ZnO nanoparticles within the rGO matrix and validates the formation of the ZnO/rGO composite.

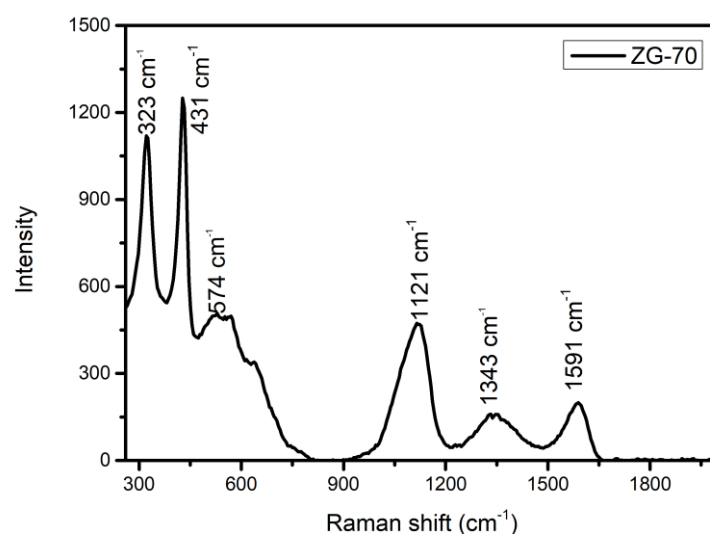


Fig. 2.18: Raman spectra of ZnO/rGO composite ZG-70.

2.2.3.2.3 Structural analysis by XRD

The XRD spectra of ZnO/rGO composite samples, ZG-10, ZG-20, ZG-60, ZG-70, and pure ZnO (ZG-100) are displayed in Fig. 2.19, all plotted on the same intensity scale for comparison. The diffractograms exhibit a series of sharp and intense peaks at 2θ values of 31.77° , 34.42° , 36.25° , 47.53° , 56.60° , 62.86° , and 67.96° , corresponding to the (100), (002), (101), (102), (110), (103), (112), and (201) crystallographic planes, respectively. These diffraction peaks are in good agreement with the JCPDS card number 36-1451, thereby confirming the formation of a hexagonal wurtzite ZnO crystal structure [68,75,76].

The XRD patterns of the ZnO/rGO composite samples (ZG-10, ZG-20, ZG-60, and ZG-70) exhibit characteristic diffraction peaks corresponding to both rGO and ZnO, confirming the successful formation of the composite material. A progressive decrease in the intensity of the rGO (002) peak is observed with increasing ZnO content, as clearly illustrated in the magnified XRD region between 10° and 30° (Fig. 2.20a). This reduction can be attributed to three key factors: (i) the intercalation and growth of ZnO nanoparticles between the rGO layers, which disrupts the regular stacking order and thereby reduces the crystallinity of rGO—as further supported by FE-SEM observations (Section 2.2.3.2.4); (ii) the decreasing proportion of rGO relative to ZnO as the composite transitions from pristine rGO to ZG-100; and (iii) the dominance of

the highly crystalline ZnO phase, which may overshadow the relatively broad and weak rGO signals. Additionally, the increasing ZnO content, as indicated by the sample labels, correlates with a corresponding decrease in the rGO peak intensity. The absence of any additional peaks or unidentified peaks affirms the high purity of the synthesised composites. The distinct XRD patterns provide valuable insights into the crystalline characteristics of the ZnO/rGO composite, supporting the efficacy of the synthesis method.

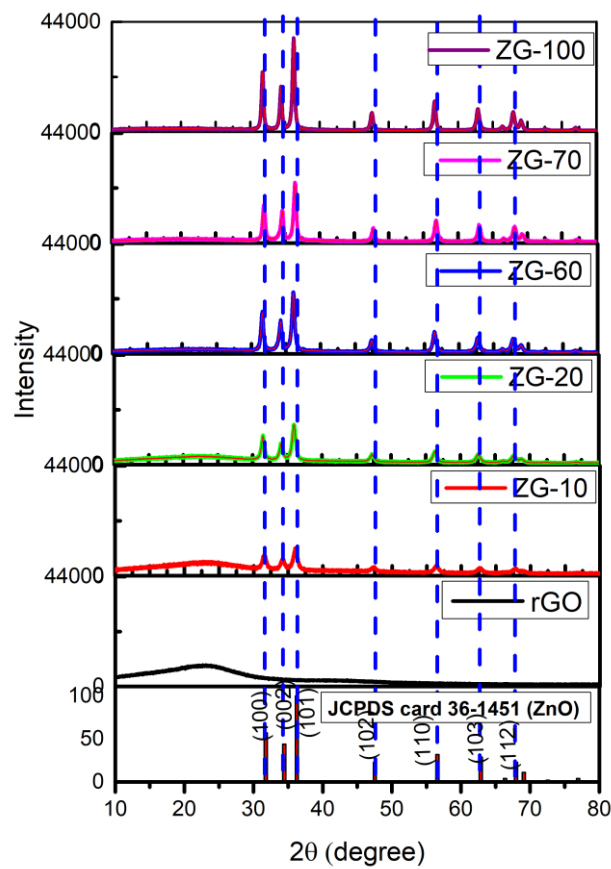


Fig. 2.19: XRD pattern of ZnO/rGO composites ZG-10, ZG-20, ZG-60, ZG-70 and pure ZnO (ZG-100).

Furthermore, the crystallite size (D) of ZnO nanoparticles in the composite was calculated using the Scherrer equation (Eqn. 2.2).

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2.2)$$

Where K is the Scherrer constant 0.94, λ is the wavelength of X-rays used (0.154 nm), β is full width at half maximum of prominent XRD peaks of ZnO and θ is the Bragg angle [32]. Table 2.1 lists the lattice constant and crystallite size for various samples corresponding to the (101) plane of ZnO at 36.26° .

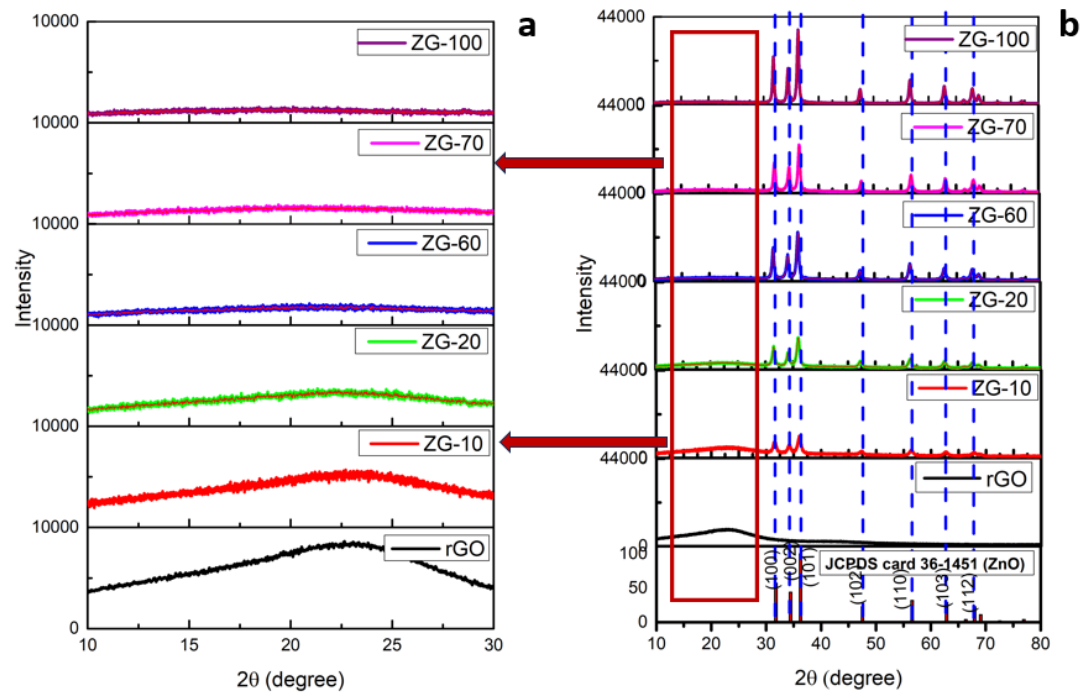


Fig. 2.20: a) XRD patterns of rGO in the range 10° - 30° . b) XRD pattern of rGO, ZnO/rGO composites ZG-10, ZG-20, ZG-60, ZG-70 and pure ZnO.

Sample	Crystallite size (nm)	a = b	c
ZG-10	12.26	3.26	5.23
ZG-20	14.80	3.26	5.23
ZG-60	19.15	3.26	5.22
ZG-70	20.36	3.25	5.20
ZG-100	23.63	3.25	5.21

Table 2.1: Crystallite size and unit cell parameters of ZG-10, ZG-20, ZG-60, ZG-70 and ZG-100.

The results indicate that the unit cell parameters of ZnO remain largely unaffected by the variation in rGO content within the composite, suggesting that the

incorporation of rGO does not induce significant lattice distortion in the ZnO phase. However, a clear trend is observed in the crystallite size, which increases progressively from ZG-10 to ZG-100. This suggests that the presence of rGO influences the nucleation and growth behaviour of ZnO during the thermal synthesis, with lower rGO content led to the formation of larger ZnO crystallites.

2.2.3.2.4 Morphological and compositional analysis by FE-SEM and EDX

The surface morphology of the composite samples ZG-40, ZG-70 and ZG-100 was investigated by using FESEM imaging. The elemental composition was investigated using Energy-Dispersive X-ray Spectroscopy (EDS) equipped with FE-SEM.

The FE-SEM image of the ZnO/rGO composite ZG-40 and ZG-70 (Fig. 2.21a and 2.21b) reveals the distribution of ZnO nanoparticles on the surface and as intercalated and embedded between the layers of rGO sheets. The large surface area of rGO facilitates the effective anchoring of ZnO nanoparticles. Moreover, the composite image also illustrates the layered morphology of rGO.

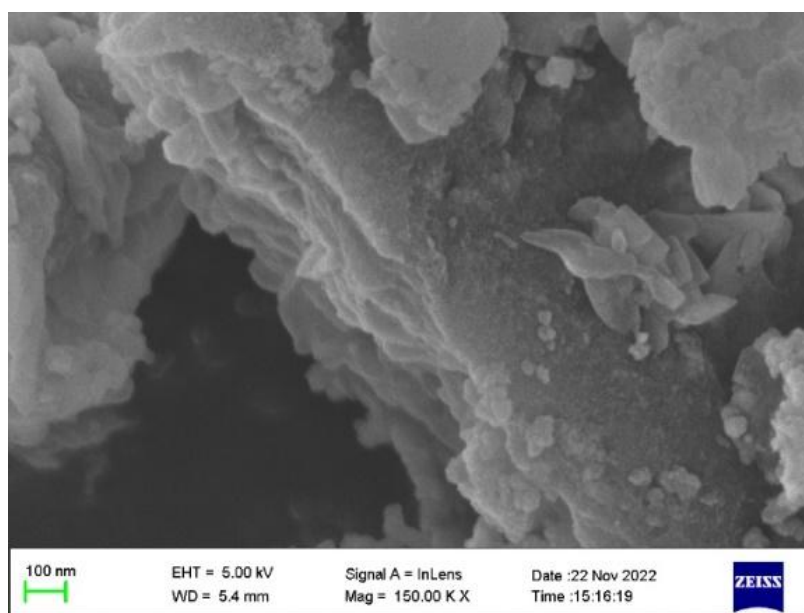


Fig. 2.21: (a) FE-SEM image of ZG-40 showing the sheet-like morphology of rGO with embedded ZnO nanoparticles.

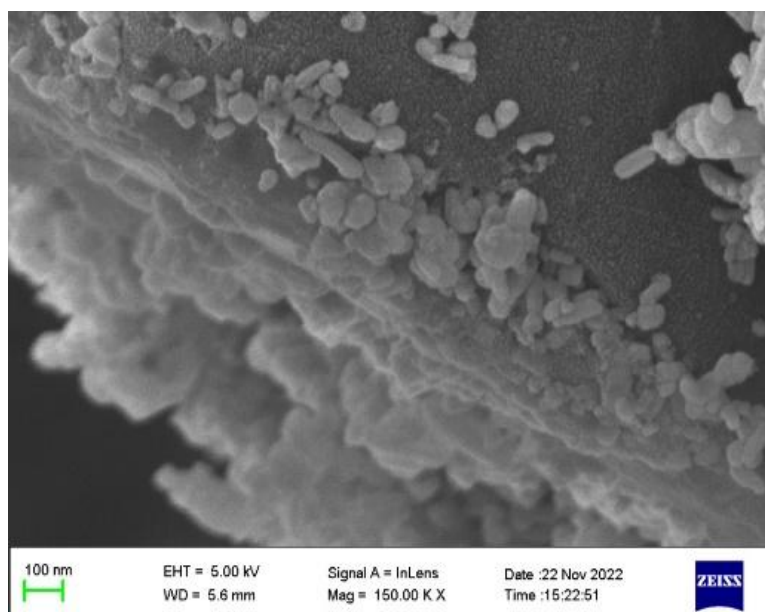


Fig. 2.21: b) FE-SEM image of ZG-70 showing the sheet-like morphology of rGO with a higher density of embedded ZnO nanoparticles.

The morphology of pristine ZnO (ZG-100) is presented in Fig. 2.21c. The image displays the distribution of ZnO grown in nano size.

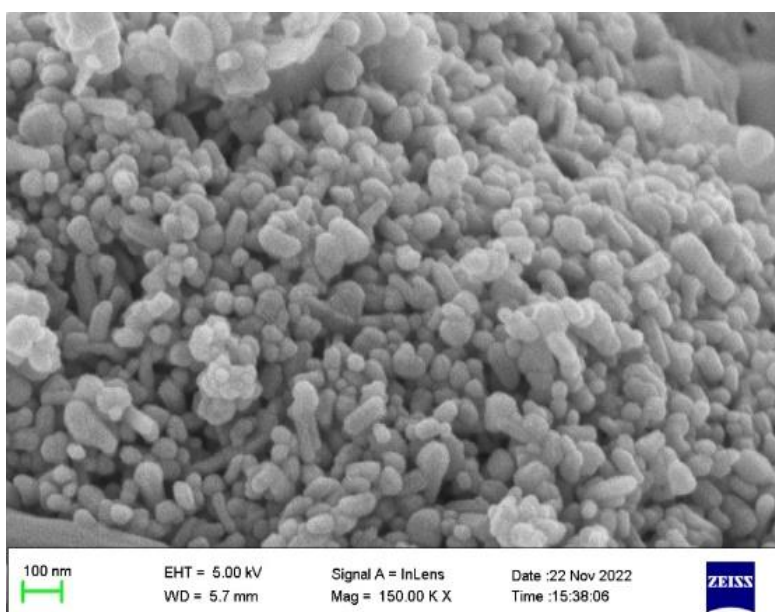


Fig. 2.21: c) FE-SEM image of ZG-100.

The atomic composition of the samples was also analysed. Table 2.2 displays the atomic percentage of rGO, ZG-40, ZG-70 and, ZG-100 obtained from the EDX spectral analysis. The table indicates that rGO comprises 77% carbon and 23% oxygen. In the EDX data of the ZnO/rGO composite, an additional peak corresponding to zinc

is observed along with carbon and oxygen. The percentage composition of ZG-40 is 77.38% carbon, 15.88% oxygen, and 6.74% zinc. In the case of ZG-100, the material is composed of 57.63% zinc and 42.37% oxygen. This comprehensive analysis sheds light on the structural features and elemental composition of the synthesised materials.

Elements	Samples			
	rGO	ZG- 40	ZG-70	ZG-100
Carbon (%)	76.91	77.38	56.51	0
Oxygen (%)	23.09	15.88	29.46	42.37
Zinc (%)	0	6.74	14.02	57.63

Table 2.2: The atomic composition of rGO, ZG-40 and ZG-70 measured by EDX spectrum analysis.

The EDX spectra obtained from various points on the ZG-40 sample were analysed to confirm the successful formation of the composite. Figures 2.22a, 2.22b, and 2.22c show the FE-SEM images of ZG-40 at different scanning areas where EDX analysis was conducted. Table 2.3 presents the comprehensive EDX data collected from multiple regions of the composite surface, including a white powdery area, a dark sheet-like region, and a zone containing both features.

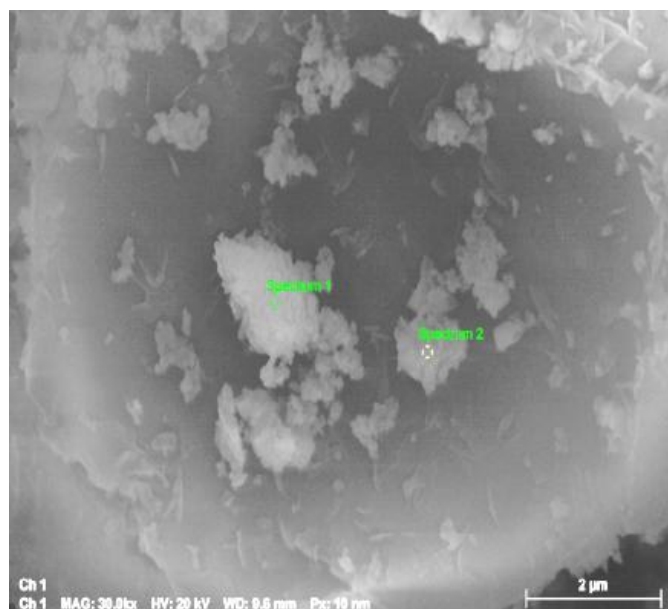


Fig. 2.22: a) FE-SEM image showing the white powdery spot of ZG-40 selected for EDX scanning.

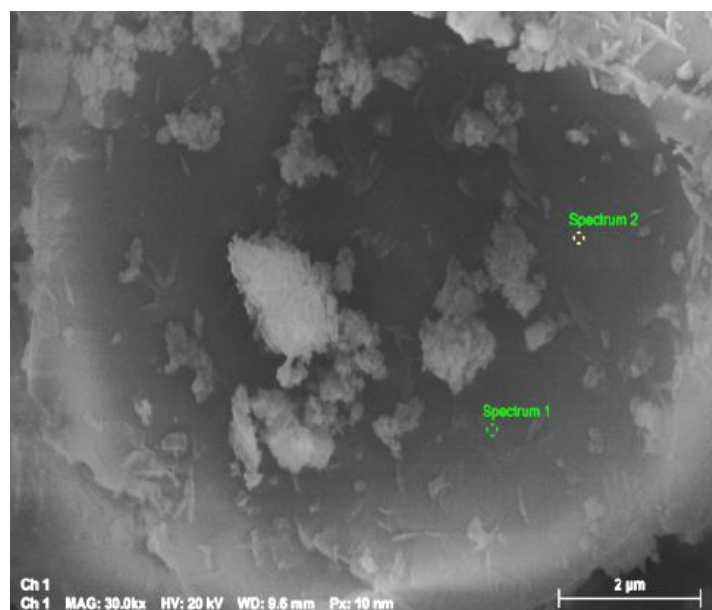


Fig. 2.22: b) FE-SEM image showing the dark sheet like area of ZG-40 selected for EDX scanning.

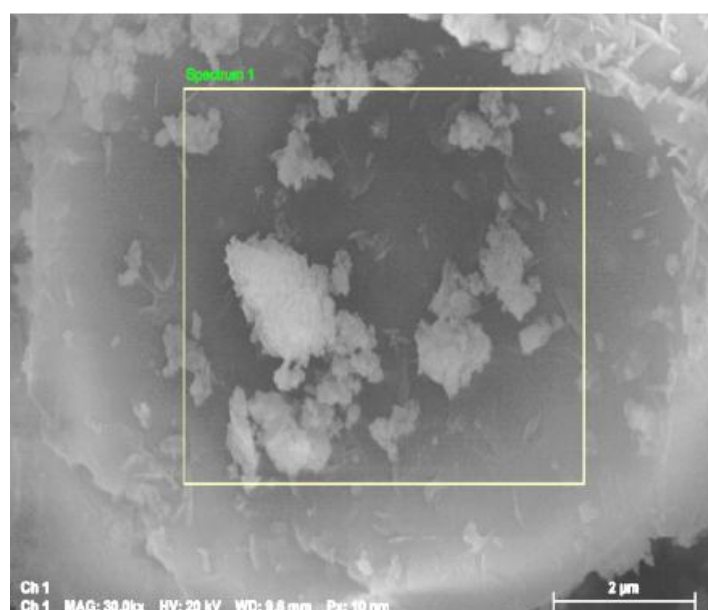


Fig. 2.22: c) FE-SEM image showing the area including powdery and dark sheet dark sheet like area of ZG-40 selected for EDX scanning.

Despite the visual differences among these regions, the elemental composition remained consistently similar across all scanned areas. This uniformity indicates that the ZG-40 composite possesses a homogenous structure rather than displaying distinct agglomerations of ZnO and rGO. The consistent elemental distribution confirms the successful synthesis of a well-integrated ZnO/rGO composite, in which ZnO

nanoparticles are evenly dispersed throughout the rGO matrix. Such uniform dispersion enhances interfacial interactions between the components, thereby improving the composite's overall properties.

Sample ZG-40	EDX from white powdery spot	EDX from dark sheet like area	EDX from area containing both powdery and dark sheet like area
C (%)	75.13	79.84	77.38
O (%)	19.65	14.56	15.88
Zn (%)	5.22	5.6	6.74

Table 2.3: Images taken from various part of the composite ZG-40 and the corresponding EDX data

2.2.3.2.5 Morphological analysis using HR-TEM.

HRTEM imaging was used to further investigate the morphological characteristics of the ZnO/rGO composite sample. The HR-TEM images of composite ZG-60 at different magnifications are illustrated in Fig. 2.23a and 2.23b. The images clearly illustrate the composite formation, showing the distribution of ZnO nanoparticles on the rGO sheets. This dispersion plays a vital role in enhancing the surface area and improving the interaction between ZnO and rGO, which directly influences the physical and chemical properties of the composite.

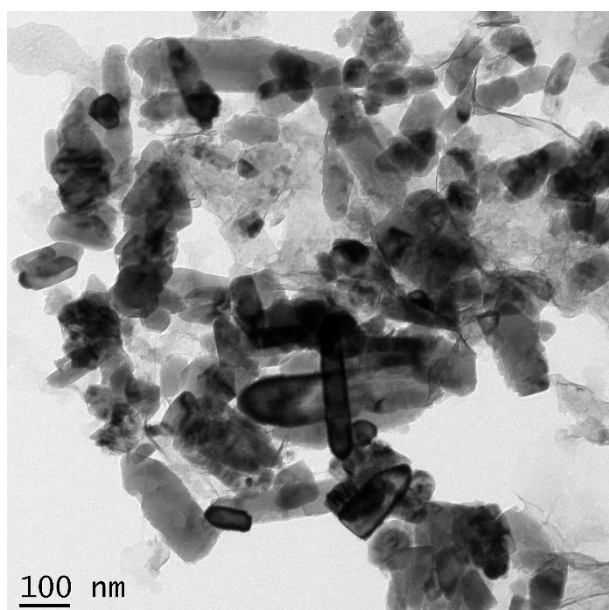


Fig. 2.23: a) TEM images of ZG-60.

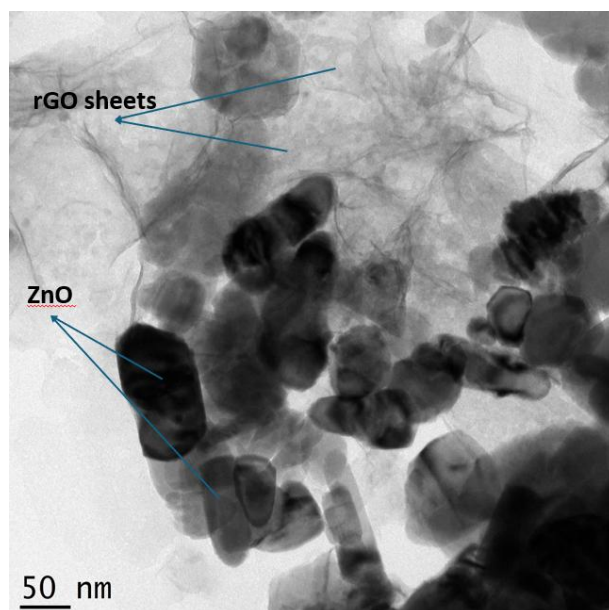


Fig. 2.23: b) TEM images of ZG-60 at higher magnification.

The atomistic-scale image of ZG-60 in Fig. 2.23c displays the planes corresponding to (100) and (002) with interplanar spacings of 0.249 nm and 0.286 nm, respectively. These planes represent the most prominent planes of ZnO, same as the results from the XRD analysis.

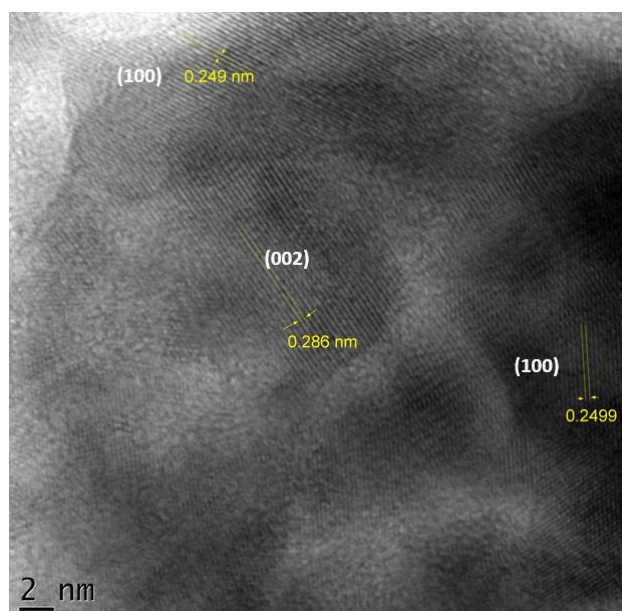


Fig. 2.23: c) HR-TEM image of ZG-60 showing lattice fringes of ZnO.

The TEM elemental mapping for the composite ZG-60 (Fig. 2.24, 2.25) was analysed to study the spatial distribution of the constituent elements. The results

indicate that the elements C, O, and Zn in ZG-60 are uniformly dispersed throughout the samples.

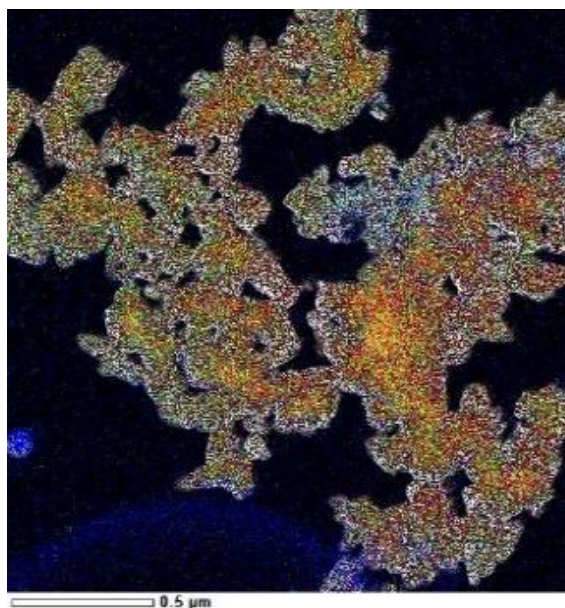


Fig. 2.24: Elemental TEM mapping of ZG-60.

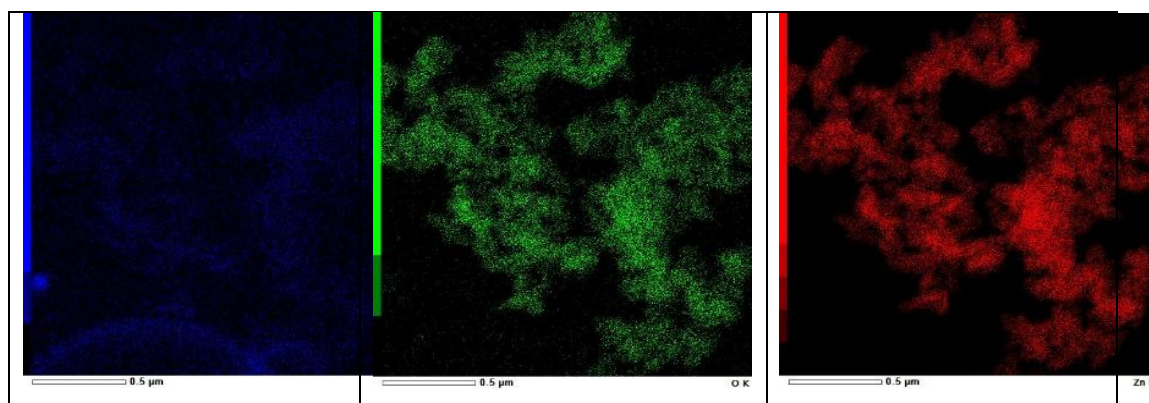


Fig. 2.25: Elemental mapping of ZG-60 (carbon (blue), oxygen (green) and zinc (red)).

2.2.3.2.6 Characterization using FT-IR spectroscopy

The FT-IR spectra of rGO, the ZnO/rGO composite (ZG-60), and pure ZnO (ZG-100) are presented in Fig. 2.26. This analysis was conducted to identify the specific chemical bonds and functional groups present in the materials. A broad absorbance band in the range of $3650\text{--}3000\text{ cm}^{-1}$ is observed in all samples, which is attributed to the O–H stretching vibrations of hydroxyl groups from adsorbed water molecules [48–49]. The absorbance peak at 1675 cm^{-1} corresponds to the stretching vibrations of the C=O bond, present in both rGO and ZG-60. Additionally, a broad band centred around 1157 cm^{-1} in the range of $1200\text{--}1006\text{ cm}^{-1}$ is attributed to C–O containing functional

groups such as alkoxy, carboxy, and epoxy groups on the rGO surface. The featured band at 1564 cm^{-1} , which corresponds to the stretching of the C=C bond, indicates the presence of unoxidized sp² bonds constituting the graphene backbone, suggesting a honeycomb-like graphene structure [19,32].

Moreover, both ZG-60 and ZG-100 samples exhibit a characteristic peak at 496 cm^{-1} , corresponding to Zn–O–Zn stretching vibrations, confirming the formation of ZnO in these samples [77-78]. The simultaneous presence of ZnO-specific peaks and rGO-related functional group bands in the FT-IR spectrum of ZG-60 confirms the successful synthesis of the ZnO/rGO composite.

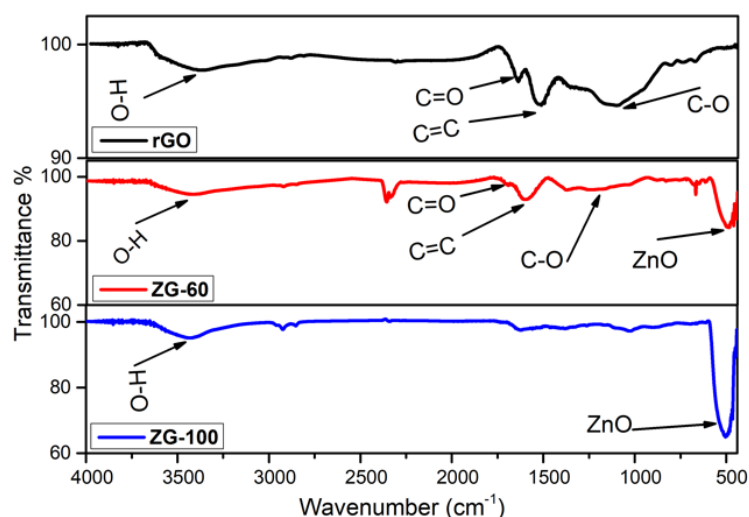


Fig. 2.26: FT-IR spectra of rGO, ZG-100 and ZG-60.

2.2.3.2.7 Characterization using UV-visible spectroscopy

Fig. 2.27 displays the UV-visible spectrum of ZnO/rGO composites (ZG-40, ZG-60) and pure ZnO (ZG-100). The pure ZnO and the composites exhibit a characteristic absorption peak around 374 nm, indicating the formation of ZnO in all the samples [79]. Notably, the presence of rGO significantly enhances the light absorption capacity of the composite in the spectral region. The formation of the composites results in an increase in the fraction of absorbable light. The alterations in the absorbance suggest modifications in the electronic structure of the composite, which is often influenced by the interactions and synergistic effects between the components (rGO and ZnO) in the composite material [80].

The band gaps of ZG-40, ZG-60 and, ZG-100 were determined using the tau plot method, where a graph was plotted between $(\alpha h\nu)^2$ (where α is the absorption coefficient per unit length and $h\nu$ is the photon energy) vs. photon energy. The linear portion of the graph was extrapolated to $\alpha=0$ to obtain the band gap values. For ZG-100, ZG-60, and ZG-40, the calculated band gap values were 3.07 eV, 3.02 eV, and 2.92 eV, respectively, in agreement with reported values [81]. The incorporation of rGO with ZnO in composite samples led to a shift in the band gap of ZnO to a lower energy range. This reduction in the band gap is attributed to the formation of a strong Zn-O-C bond between ZnO and rGO in the composites [51,82]. The narrowing of the band gap in these heterostructures enhances their light absorption capacity compared to pure ZnO. The enhanced light-absorption capacity of the composite samples, particularly in the visible range, is highly advantageous for their effectiveness in visible-light photocatalytic processes.

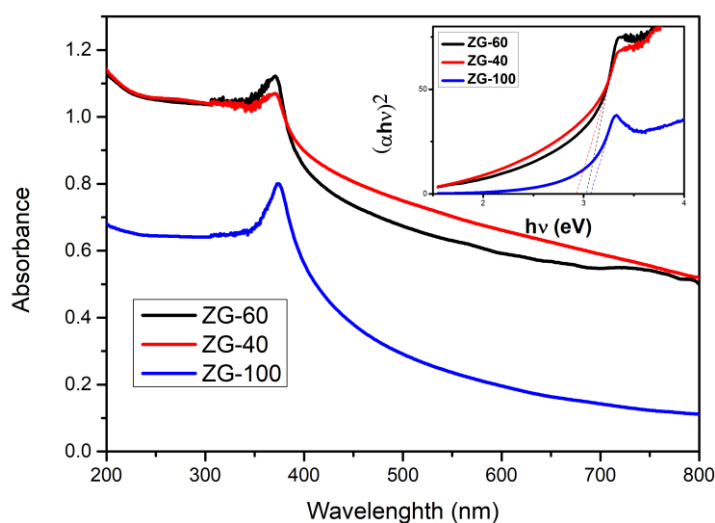


Fig. 2.27: UV-visible absorbance spectra of ZnO/rGO composites ZG-40, ZG-60 and ZG-100, inset illustrates the corresponding Tauc plot.

2.2.3.2.8 Thermal stability analysis.

The thermal stability of rGO and ZnO/rGO composite was investigated using thermogravimetric analysis (Hitachi STA7200) in a Nitrogen atmosphere. The powder ZG-70 was chosen as the model composite sample for the study, and the TG curves for rGO and ZG-70 are depicted in Fig. 2.28. These analyses were conducted in a nitrogen atmosphere, with a heating rate of 10°C/min at a temperature range of 27°C to 580°C.

The figure shows that both rGO and ZG-70 exhibit notable thermal stability, with only minor weight loss up to 580°C. Specifically, there was an initial mass loss of 3.5% for ZG-70 and 8% for rGO up to 100°C. This initial weight loss is primarily attributed to the removal of adsorbed moisture and of some hydroxyl groups that adsorbed in the samples. Between 100°C and 500°C, ZG-70 and rGO experienced a slight weight loss: 4.5% for ZG-70 and 5% for rGO. This loss is primarily due to the decomposition of liable functional groups, such as hydroxyl, epoxy, and carboxylate groups, in rGO, and the evaporation of remaining water molecules [83]. Notably, after reaching a temperature of 500°C, a substantial residue remains in both samples. ZG-70 retains 92% of its initial weight, while rGO retains 87%. This high residue percentage indicates the exceptional thermal stability of the prepared samples, even at elevated temperatures.

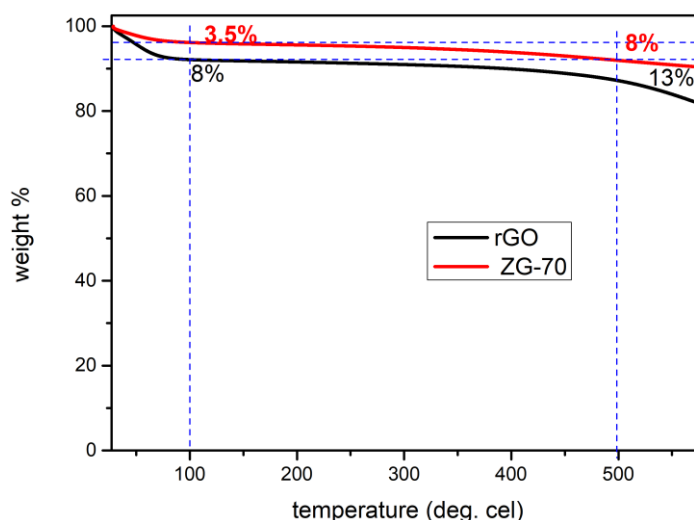


Fig. 2.28: TGA graph of rGO and ZG-70.

2.3 Conclusions

This chapter presents a novel, single-step method for synthesising ZnO/rGO nanocomposites using two low-cost reagents. To the best of our knowledge, this is the first report demonstrating the successful formation of ZnO/rGO composites using these inexpensive materials in a single-step process. The approach is environmentally friendly, avoiding the use of toxic chemicals commonly employed in traditional methods for rGO synthesis. The ZnO/rGO nanocomposite is prepared using a rapid single-step synthesis involving the pyrolytic reduction of the carbon-rich compound sucrose along with zinc acetate. This method is industrially scalable, as it enables large-

scale production within minutes at low cost. The synthesis approach offers a safer and more sustainable alternative for producing rGO-based materials. The major conclusions of this chapter are pointed out below.

- Reduced graphene oxide (rGO) was successfully synthesised through the thermal decomposition of sucrose in a preheated muffle furnace at 475 °C for 7 minutes.
- X-ray photoelectron spectroscopy (XPS) of rGO revealed distinct C 1s and O 1s peaks, and high-resolution spectra provided insights into the chemical environments of carbon and oxygen atoms.
- Raman spectroscopy of sucrose-derived rGO showed prominent D, G, and 2D bands, confirming the successful formation of reduced graphene oxide.
- X-ray diffraction (XRD) analysis displayed a broad peak at approximately 23°, corresponding to the (002) plane of rGO, indicative of a partially ordered graphitic structure.
- Field Emission Scanning Electron Microscopy (FE-SEM) images demonstrated the layered morphology of rGO, highlighting the sheet-like structure.
- Energy Dispersive Spectroscopy (EDS), integrated with FE-SEM, was employed for elemental composition analysis of the samples.
- Transmission Electron Microscopy (TEM) images further confirmed the sheet-like morphology of rGO.
- Fourier Transform Infrared Spectroscopy (FTIR) analysis identified various oxygen-containing functional groups on the carbon basal plane of rGO.
- UV–Visible spectroscopy exhibited characteristic absorption features of rGO, corroborating its successful synthesis.
- The ZnO/rGO composites were successfully synthesised using a sustainable, one-step thermal decomposition method employing sucrose and zinc acetate as precursors.

- XPS confirmed the successful formation of ZnO/rGO composites, with distinct C 1s, O 1s, and Zn 2p peaks indicating the presence of their respective elements and bonding states.
- Raman spectroscopy of the ZnO/rGO composites revealed characteristic vibrational modes of ZnO (E_2 , $E_2(\text{High})$, $E_1(\text{LO})$, and $A_1(\text{LO})$ - $E_1(\text{LO})$) as well as the D and G bands of rGO, confirming the presence of both components.
- XRD patterns displayed well-defined peaks consistent with the hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451), along with the broad (002) peak of rGO, confirming the crystalline nature and phase purity of the composites.
- FE-SEM imaging illustrated the intercalation of ZnO nanostructures within the rGO matrix, confirming successful composite formation with uniform distribution.
- TEM images further confirmed the homogeneous dispersion of ZnO nanoparticles embedded on the rGO sheets, supporting the morphological integration of both components.
- FTIR analysis revealed oxygen-containing functional groups on the rGO basal plane and the characteristic Zn–O–Zn stretching vibrations, indicating successful chemical integration of ZnO and rGO.
- UV–Visible spectroscopy of the composites showed absorption features corresponding to ZnO, confirming its presence; additionally, a redshift in the absorbance edge suggested a narrowing of the band gap upon rGO incorporation.
- The incorporation of rGO into ZnO resulted in a decrease in the optical band gap, which is favourable for enhancing photocatalytic and optoelectronic properties.
- Thermogravimetric Analysis (TGA) demonstrated the high thermal stability of both rGO and ZnO/rGO composites, indicating their potential for high-temperature applications.

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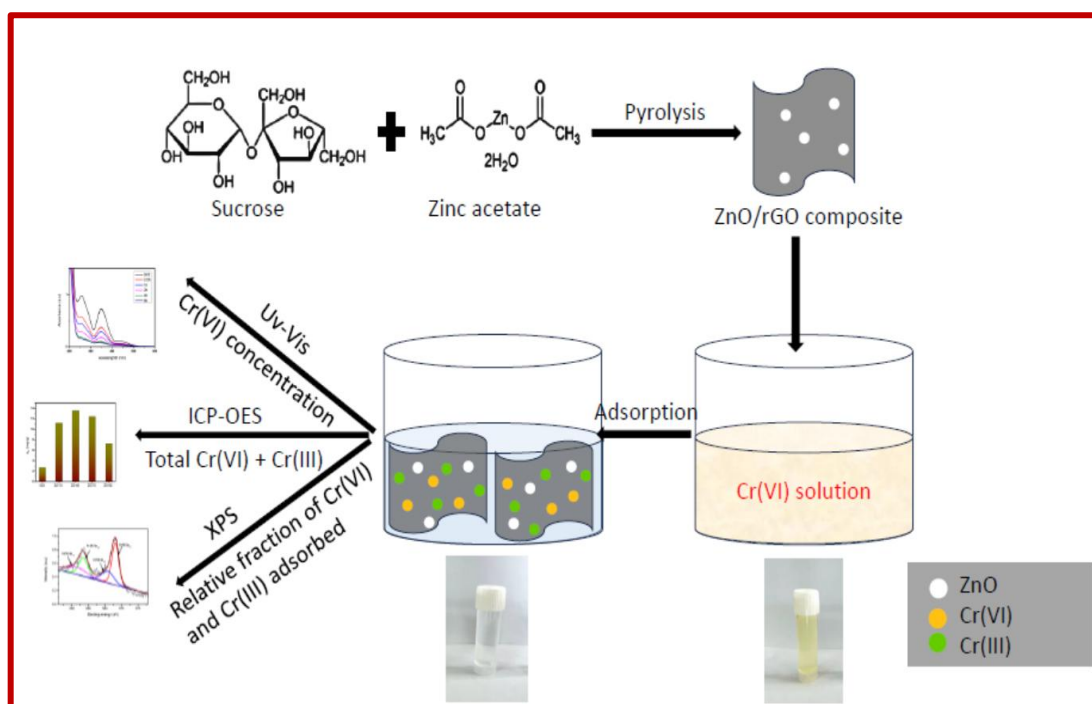
Chapter III

Heavy Metal Removal Using ZnO/rGO Composite: An Effective Strategy for Environmental Remediation

Abstract

The contamination of water by heavy metals from various industrial effluents is a significant factor contributing to the scarcity of clean water worldwide. To address this issue, there is a need to develop low-cost adsorbents to remove heavy metals from contaminated water. Reduced graphene oxide (rGO)- based composites are efficient adsorbents for heavy metals. In this work, a green, rapid single-step heating process was used to prepare both rGO and rGO/ZnO composite materials, avoiding the use of any toxic reagents. The composite material is studied for its efficiency in removing heavy metals chromium (Cr^{6+}) and lead (Pb^{2+}).

Hexavalent chromium (Cr^{6+})

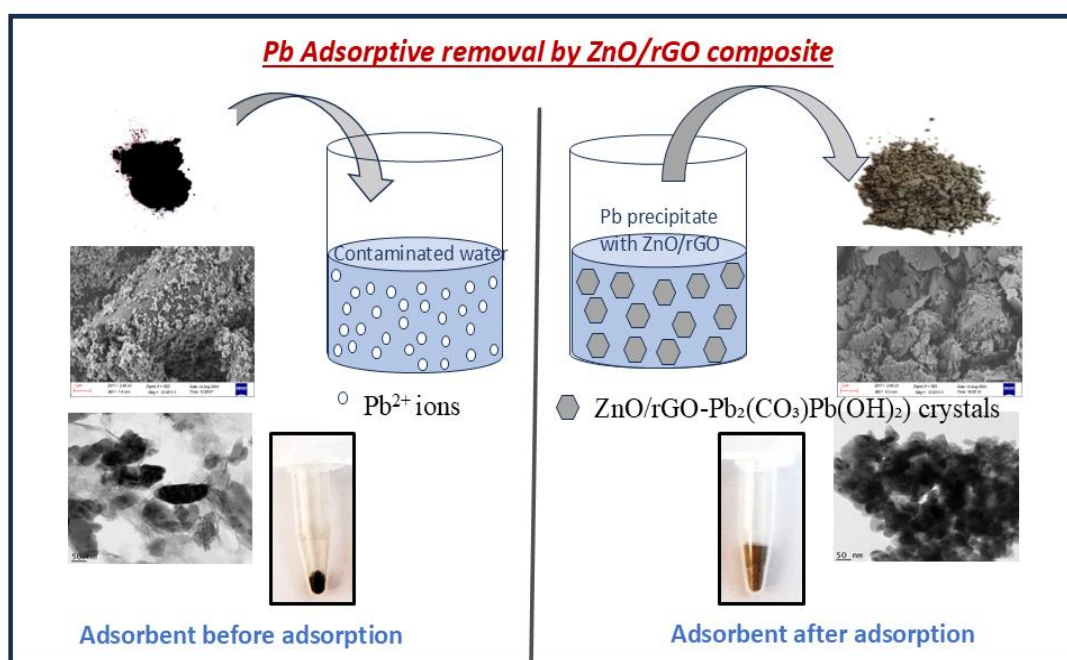


Summary of the overall findings on Cr^{6+} removal from contaminated water using the ZnO/rGO composite

The rGO/ZnO composite synthesized from Sucrose and Zinc acetate demonstrates the ability to adsorb hexavalent chromium ($\text{Cr}(\text{VI})$) from contaminated water.

Adsorption experiments were conducted by varying the adsorbent, contact time, initial pH, and initial Cr(VI) concentration. The composite demonstrated an adsorption efficiency nearly five times higher than that of pure rGO. Kinetic data were analysed with pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. The Langmuir and the Freundlich isotherm models were also studied. The Cr(VI) adsorption mechanism involves electrostatic interactions, complexation, pore filling, and reduction, as confirmed by zeta potential measurements, BET surface area analysis, EDX, and XPS analysis. The influence of light on adsorption was also examined, revealing a photosensitive contribution of ZnO to the adsorption–reduction process. These studies suggest that rGO/ZnO composite has the potential as a cost-effective and efficient adsorbent for removing Cr(VI) contaminants from industrial effluent.

Lead (Pb^{2+})



Summary of the overall findings on Pb removal from contaminated water using the ZnO/rGO composite.

Anthropogenic lead pollution is a critical environmental issue that endangers water and soil quality, posing significant risks to ecosystems and human health. Controlling the bioavailability of this toxic metal is essential for mitigating its impact. The second part of this study explores the immobilization of Pb^{2+} ions from contaminated solutions using a ZnO/rGO composite, synthesized through a green single-step method. The

adsorption process was analysed by monitoring changes in Pb^{2+} concentration in the contaminated solution and examining mineralogical transformations in the spent adsorbent. XRD analysis confirmed the formation of lead carbonate hydroxide (hydrocerussite, $\text{Pb}_2(\text{CO}_3)\text{Pb}(\text{OH})_2$) as a secondary phase, demonstrating an adsorption-precipitation mechanism of lead removal. The composite exhibited an exceptional Pb adsorption efficiency of 1400 mg/g, evidenced by significant changes in the volume and colour of the post-adsorbent. This high efficiency not only ensures effective lead removal but also reduces waste disposal costs. These findings highlight the potential of ZnO/rGO composites as a promising and cost-effective adsorbent for Pb^{2+} removal from wastewater across a wide range of initial concentrations, offering an environmentally sustainable solution to mitigate lead pollution.

3.1 Introduction

Water is often referred to as the elixir of life, as its availability is indispensable for the survival of all living organisms. According to the United States Geological Survey, approximately 71% of the Earth's surface is water. Despite this abundance, only 2.5% of the Earth's water constitutes freshwater. The distribution of this freshwater is further limited, with 68.7% stored in ice glaciers and icecaps, 30.1% as underground water, and a mere 2.5% available in surface and other freshwater sources [1]. Therefore, the conservation of this precious and limited resource is of utmost importance for the continuation of life on our planet. A critical global challenge today is the growing scarcity of fresh water. Numerous natural and anthropogenic activities contribute to the pollution of water sources [2]. Both organic and inorganic pollutants, including dyes [3], heavy metals [4], pharmaceuticals [5], microbials [6], pesticides [7] etc., pose significant threats to water quality.

Heavy metal pollution presents a significant and growing threat to environmental and public health worldwide. The extensive use of heavy metals such as chromium (Cr), lead (Pb), copper (Cu), arsenic (As), cadmium (Cd), cobalt (Co), nickel (Ni), and mercury (Hg) across various industrial sectors has led to the continuous release of toxic effluents into the environment [8,9]. Lead, for example, primarily arises from industries such as paint manufacturing, electroplating, coal combustion, mining, battery production, and pesticide formulation [10-13]. Cadmium pollution similarly originates from fossil fuel combustion, smelting operations, electroplating, and the use

of fertilizers and pesticides [14]. A notable disease caused by prolonged cadmium exposure is Itai-itai disease, first identified in Japan; the term translates to "it hurts—it hurts," referring to the intense pain experienced by those affected [15]. The un-treated or poorly treated wastewater from these industries contaminates soil and ground-surface water sources, which are the life-maintaining factor of millions of living beings of flora and fauna. Irrigation of crops with such contaminated water severely impacts agricultural productivity by reducing plant growth, inhibiting photosynthesis, and lowering crop yields [16]. Moreover, heavy metals accumulate in various plant tissues, entering the food chain and eventually being ingested by humans and animals. Therefore, the treatment of heavy metal polluted water is essential to ensure a healthy and sustainable ecosystem, as well as to address the global challenge of freshwater scarcity. The World Health Organisation (WHO) have recommended the tolerable level of heavy metals in drinking water, with recommended maximum concentrations (mg/L) as follows: As – 0.01, Pb – 0.01, Cd – 0.005, Cr – 0.05, Hg – 0.001, Ni – 0.07, and Mn – 0.01 [17].

Water scarcity due to heavy metal pollution has gained wide interest in research due to the harmful implications of these inorganic pollutants on the living organisms. The heavy metals have density five times higher than water, referred to as heavy metals, and the pollution due to heavy metals gets wide attention because they are non-degradable, persistent, and tend to bioaccumulate in ecosystems [12,13,18]. The primary concern regarding heavy metal pollution is that it cannot be degraded or destroyed [19].

Although certain heavy metals are essential in trace amounts for maintaining biological functions, excessive exposure can lead to toxicity [20,21]. Even at low concentrations, these metals can cause irreversible damage to vital organs such as the liver, kidneys, and brain, and may impair the nervous and reproductive systems [22]. Furthermore, heavy metals are known to be mutagenic and carcinogenic [13,23,24], posing serious risks to both human and environmental health. Once released, they enter the food chain, persist in the environment, and disrupt metabolic and cellular functions in exposed organisms.

The removal of these toxic elements from industrial effluents is critical to safeguarding ecosystems and human health. Several methods have been adopted for

heavy metal remediation from wastewater, including ion exchange, membrane filtration, chemical reduction, reverse osmosis, chemical precipitation, coagulation and, so on [11, 22, 25-28]. However, these approaches often suffer from several drawbacks, such as high operational and maintenance costs, limited removal efficiency, significant energy and chemical requirements [29], and the generation of secondary pollutants in the form of toxic sludge [2]. Therefore, there is a pressing need to develop environmentally friendly, cost-effective, and sustainable technologies for the remediation of heavy metal pollution.

Adsorption has been getting significant attention due to its operational simplicity, rapid processing, low energy and cost requirements, and high efficiency. Moreover, it is well-suited for large-scale applications and does not require sophisticated instrumentation [30-34]. The adsorbent materials can be easily separated from the treated water through simple sedimentation, further enhancing the practicality of the method. Adsorption is particularly effective for removing contaminants by binding them to a solid surface, making it one of the most promising techniques for addressing heavy metal pollution in water.

As a surface phenomenon, adsorption involves the adsorption of pollutants onto the surface of a solid material (the adsorbent). It is considered one of the most efficient, adaptable, and scalable approaches for heavy metal removal. However, to meet growing environmental demands, there is a continued need to develop adsorbents that are not only highly efficient but also cost-effective, sustainable, and environmentally friendly. An ideal adsorbent should combine high adsorption capacity, chemical stability, low cost, and minimal environmental impact.

Various classes of materials have been explored as potential adsorbents for heavy metal remediation, including carbon-based materials, polymer-based materials, magnetic nanomaterials, bio-adsorbents, mineral adsorbents, metal-organic frameworks (MOFs), metal oxides, zeolites, and nanoclays. These materials have demonstrated the ability to remove a wide range of heavy metal contaminants efficiently [18, 24, 31, 33, 35-41].

Nanomaterials have attracted considerable interest as effective adsorbents in combating heavy metal pollution. This is attributed to their small particle size, expansive surface area, porosity, and abundance of active adsorption sites—all of which

contribute to their superior adsorption capacities [42]. Among them, metal oxide nanomaterials stand out for their notable advantages, including non-toxicity, economic viability, ample surface-active sites, ease of synthesis and surface modification, and wide availability [16, 43]. These features make metal oxide-based nanomaterials highly promising for water treatment applications.

Nano metal oxides have demonstrated excellent performance in removing heavy metals, even at low concentrations, which is a vital benefit of adsorption over other technologies. The predominant mechanism by which heavy metals are adsorbed onto metal oxides and their composites is pore filling, where the metal ions occupy the mesopores and micropores of the adsorbent [16]. Another adsorption mechanism involves redox reactions between the metal oxide and specific multivalent heavy metals, occurring at the surface of the adsorbent [16]. A notable example is the reduction of hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)) during interaction with the adsorbent surface [36, 44,45].

Ion exchange is another important mechanism in the adsorption of heavy metals. For example, magnesium oxide (MgO) can undergo ion exchange with Pb^{2+} ions, wherein magnesium ions in the adsorbent are replaced by lead ions, leading to the formation of lead oxide (PbO) [46]. In some cases, surface precipitation can also significantly contribute to heavy metal removal. In this process, heavy metal ions form sparingly soluble secondary solid phases that precipitate and adhere to the surface of the adsorbent [47-49]. A representative example is the removal of Pb^{2+} using calcium carbonate (CaCO_3), where the lead ions react to form lead carbonate hydroxide [$\text{Pb}_2(\text{CO}_3)\text{Pb}(\text{OH})_2$], commonly known as hydrocerussite [50]. This precipitate firmly attaches to the adsorbent surface, facilitating effective and stable lead immobilization.

Metal oxide-based nanomaterials have emerged as highly efficient adsorbents for the removal of heavy metals from contaminated water. A wide variety of configurations—such as pure metal oxides, metal–metal oxide nanocomposites, polymer-supported metal oxides, metal oxide–metal oxide hybrids, and carbon-based metal oxide nanohybrids—have been extensively explored [43]. These structural and compositional modifications significantly enhance the adsorption performance of metal oxides, making them more effective in remediating heavy metal pollution in water.

Among various metal oxides, ZnO stands out as a highly effective adsorbent for heavy metal removal. It is one of the most widely studied metal oxides due to its favourable physicochemical properties, including biocompatibility, affordability, long-term chemical stability, and favourable surface characteristics [51]. It is also non-toxic and possesses strong antibacterial activity, making it especially suitable for water purification [25]. Furthermore, its ability to generate photoinduced electron–hole pairs under light irradiation [52-53] enables redox-based interactions, which are particularly beneficial for the removal of redox-sensitive species such as Cr(VI).

Beyond its role in heavy-metal adsorption, ZnO exhibits excellent antimicrobial, antifouling, and photocatalytic properties. These multifunctional characteristics enable ZnO not only to adsorb toxic metal ions but also to degrade organic pollutants and inactivate microbial pathogens, making it a highly versatile material for comprehensive water treatment applications [20].

Kovo G. Akpomie et al. reviewed the adsorption mechanisms of radionuclides and heavy metals onto ZnO nanoparticles. They identified complexation, precipitation, ion exchange, and electrostatic interactions as the primary mechanisms involved, with complexation being the most dominant. According to their findings, ZnO NPs exhibited adsorption capacities for a wide range of metal and radionuclide ions, including Pb(II), Hg(II), Co(II), As(III), Cr(III), Ba(II), Zn(II), Se(IV), V(V), La(III), and U(VI). The reported adsorption capacities of ZnO NPs synthesized via different methods ranged from 0.30 to 1500 mg/g. Their comprehensive analysis highlights the significant potential of ZnO nanoparticles as efficient adsorbents for the decontamination of wastewater contaminated with heavy metals and radionuclides [25].

Similarly, in another review, Vikas Dhiman et al. systematically analysed the performance of various ZnO-based nano-adsorbents for heavy-metal removal from wastewater. Their study included pristine ZnO nanoparticles, doped ZnO nanostructures, ZnO nanocomposites, and surface-functionalized ZnO materials. The review compared the maximum adsorption capacities of these materials for several heavy metal ions, including Cd^{2+} , Hg^{2+} , As^{3+} , Pb^{2+} , Cr^{6+} , Ni^{2+} , Co^{2+} , and Cu^{2+} . The authors concluded that ZnO-based nano adsorbents demonstrate effective and versatile adsorption capabilities, making them promising candidates for treating heavy metal-contaminated water [20].

The literature suggests that ZnO nanoparticles possess notable heavy metal adsorption capabilities. However, many studies report that bare ZnO often exhibits lower efficiency compared to its modified materials. To enhance its adsorption performance, ZnO is frequently incorporated with or surface-functionalized using various materials such as carbon derivatives, biochar, other metal oxides, metals, chitosan, and polymers [54]. Among these, carbon-based materials have emerged as the most effective modifiers, significantly improving ZnO's adsorption capacity.

One major limitation of using pristine ZnO nanoparticles as adsorbents lies in their post-adsorption separation. Due to their nanoscale size and hydrophilic nature, ZnO nanoparticles tend to remain highly dispersed in aqueous media, forming cloudy suspensions that hinder efficient recovery. To overcome this issue, ZnO can be integrated with support materials that possess a large surface area and lower hydrophilicity, like rGO. These materials not only provide a platform for anchoring ZnO nanoparticles but also improve adsorption efficiency and facilitate easier separation after treatment.

rGO has a one- or few-layered structure with a high surface area, making it ideal for adsorption applications [55,56]. The surface of rGO is rich with functional groups, which serve as active sites for adsorption and enhance its versatility [57]. These functional groups also improve their dispersibility in liquids, facilitate composite formation with other materials, and allow for chemical modifications. These unique properties make rGO an attractive material for diverse applications in science and technology. Due to their high surface area and oxygen-containing functional groups, graphene oxide (GO) and rGO are widely employed as adsorbents [18, 58, 59].

Several studies have reported enhanced adsorption efficiency of ZnO through incorporation with GO or rGO. Naveen Chandra Joshi et al. investigated the adsorption of toxic Pb^{2+} and Cr^{6+} ions using a ZnO/rGO composite, reporting maximum adsorption capacities of 16.261 mg/g for Pb^{2+} and 10.718 mg/g for Cr^{6+} [60]. In another study, Siti Zu Nurain Ahmada et al. evaluated the adsorptive removal of Pb^{2+} using a ZnO/GO composite and found a remarkably high maximum adsorption capacity of 909.09 mg/g [18].

Haixia He et al. developed a novel ZnO-functionalized rGO composite for efficient adsorption and reduction of Cr(VI). Their results demonstrated a Cr(VI)

removal efficiency of up to 99%, with a maximum adsorption capacity of 68.97 mg/g achieved within 3 hours [61]. Similarly, Moeng Geluk Motitswe et al. applied a reduced graphene oxide–zinc oxide nanocomposite for the removal of Pb^{2+} and Cd^{2+} from contaminated water, achieving near-complete removal (~100%) with corresponding adsorption capacities of 19.99 mg/g and 49.99 mg/g, respectively [62].

Taiba Naseem et al. conducted adsorption and kinetics studies of Cr(VI) using both GO and rGO-ZnO nanocomposites. The maximum adsorption capacities were calculated as 19.49 mg/g for GO and 25.45 mg/g for the rGO-ZnO nanocomposite, highlighting the improvement in performance due to rGO incorporation [63]. In another notable study, Dibya Ranjan Rout et al. investigated Cr(VI) adsorption using a ZnO-decorated graphene composite and reported enhanced chemical adsorption with a maximum uptake of 232.58 mg/g [64].

This chapter presents a systematic investigation into the removal of heavy metals using a ZnO/rGO composite synthesized via a single-step green method, employing zinc acetate and sucrose as precursors. The study focuses on two model contaminants: hexavalent chromium (Cr^{6+}), a common anionic heavy metal, and divalent lead (Pb^{2+}), a cationic heavy metal, in aqueous solutions.

The removal of Cr(VI) was evaluated both qualitatively and quantitatively using UV–Visible spectroscopy and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), respectively. ICP-OES analysis quantifies the concentration of heavy metals in the tested sample, expressed in mg/L. A series of adsorption experiments was conducted to optimize the adsorbent, which has maximum removal efficiency. Also studied the effects of various operating parameters, such as initial pH, initial concentration, and contact time, on the treatment of a Cr(VI)-contaminated solution. The ICP-OES data were used to investigate the kinetics and equilibrium studies. Additionally, the adsorbent was examined by the Energy Dispersive X-Ray Analyzer (EDX) and X-Ray Photoelectron Spectrum (XPS) after adsorption to establish the presence of adsorbed chromium over the adsorbent surface. These experiments reveal that rGO/ZnO composite synthesized in a single-step pyrolysis method is a facile, cost-effective, and industrially scalable material for the Cr(VI) contaminant remediation.

The study on Pb^{2+} removal highlights a novel mechanism involving not just adsorption but also the formation of a stable lead-bearing mineral phase—lead carbonate hydroxide ($\text{Pb}_2(\text{CO}_3)\text{Pb}(\text{OH})_2$), also known as hydrocerussite. This work is the first to report such a mechanism using a ZnO/rGO composite. The material exhibited exceptional Pb^{2+} removal efficiency, the highest recorded among ZnO/rGO-based adsorbents to date. Comprehensive analyses using ICP-OES, XRD, FE-SEM, EDX, HR-TEM, and XPS confirmed the surface precipitation and mineralization of Pb^{2+} as hydrocerussite on the composite surface. The influence of factors such as pH, adsorbent dosage, initial concentration, contact time, and, light conditions was systematically examined to understand the adsorption behaviour. These results demonstrate that the ZnO/rGO composite is not only effective at removing Pb^{2+} from highly contaminated water but also offers a sustainable and scalable solution for heavy metal remediation.

3.2 Adsorptive Removal of Hexavalent Chromium Using ZnO/rGO Composite

3.2.1 Introduction

Among the heavy metals, chromium is one of the most abundantly used resources in the production of many household items we use in our daily routine, from newspapers to kitchen utensils. The steel, leather, wood, paper, and paint industries release significant amounts of chromium ions [65,66] into water bodies and soil. These ions are harmful contaminants with mutagenic and carcinogenic properties [67,68], making them a severe global concern requiring immediate attention. A single industry, leather tanning, is responsible for releasing over 600,000 tons of chromium waste into the environment annually in India [69].

In nature, chromium exists in several oxidation states, -2 to +6; among these, trivalent chromium Cr(III) and hexavalent chromium Cr(VI) are two stable states. Cr(III) is a micronutrient essential for human metabolism [21]. However, at higher concentrations, it becomes poisonous and has a negative impact on human health [40]. Cr(VI), on the other hand, is the second stable form of chromium and is 300 times more toxic than Cr(III) [70]. Due to its higher dispersibility and solubility [67,69], Cr(VI) moves through solids and liquids, resulting in widespread poisoning far from the site of discharge. Also, due to this property, it can easily penetrate through cell membranes [71] and cause severe dermatological and internal health problems. Millions of people

were exposed to more than tolerable levels of chromium poisoning through oral, inhalation and, dermal routes [58]. The tolerable chromium levels in drinking and industrial water are 50µg/L and 0.5-270 mg/L, respectively, per the WHO guidelines [72]. The chromium contamination in water from various industrial areas exceeded this limit. The concentration of chromium in regions surrounding leather tanneries in India typically ranges from 2000 to 5000 mg/L [69]. The subsequent toll of the Cr(VI) explosion on human health appears in the form of pulmonary disorders, reproductive and developmental issues, neurological and immunological disorders, skin and stomach ulcers, and liver and kidney damage, all leading to long-term health problems or even death [30,73]. Chromium toxicity in plants results in decreased seed germination, slowed growth, lower yield, inhibited enzymatic activities, weakening of photosynthesis, nutrient imbalances, and genetic mutations [74].

In general, industries that use chromium, such as steel and leather, employ extremely acidic chromium pickling processes; the wastewater from these stages releases high levels of chromium-laden acid effluents to the environment. In the steel industry, to get the characteristic glossy finish, the steel is pickled in a pickling solution that contains dissolved metals, including chromium, in highly acidic conditions [75]. In the tanning process in the leather industry, there is also a stage at which the animal hides are treated in a highly acidic chromium-containing solution [76]. Thus, removing Cr(VI) from industrial wastewater in acidic pH is essential before discharging into the ecosystem.

As discussed in earlier sections, both rGO and the ZnO/rGO composite exhibit significant potential for adsorbing heavy metals. The incorporation of ZnO into rGO has been shown to enhance its adsorption efficiency toward Cr(VI), as reported by Thaiba et al. [63]. N. C. Joshi et al. synthesized a ZnO/rGO material using *Tectona grandis* leaf extract and investigated its ability to remove Pb(II) and Cr(VI) ions from contaminated water. The composite demonstrated adsorption capacities of 16.261 mg/g for Pb(II) and 10.718 mg/g for Cr(VI) [60]. Similarly, Rout et al. evaluated the Cr(VI) adsorption performance of a ZnO–rGO–PEG composite synthesized via an improved Hummers method followed by coupling and calcination [64]. Although the rGO/ZnO composite shows potential for Cr(VI) removal, studies evaluating its adsorption performance remain limited.

The prepared samples were tested for their Cr(VI) removal efficiency from contaminated water. The chromium adsorption experiments were qualitatively evaluated by performing UV-Visible absorbance spectroscopy (Shimadzu 1800) and quantitatively evaluated by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES- perkin Elmer avio200). ICP-OES analysis quantifies the concentration of heavy metals in the tested sample in mg/L. A series of adsorption experiments was conducted to optimize the adsorbent, which has maximum removal efficiency. Also studied the effect of various operating variables such as initial pH, initial concentration, and contact time on the treatment of Cr(VI) ion contaminated solution. The ICP-OES data were used to investigate the kinetics and equilibrium studies. Additionally, the adsorbent was examined by the Energy Dispersive X-Ray Analyzer (EDX) and X-Ray Photoelectron Spectrum (XPS) after adsorption to establish the presence of adsorbed chromium over the adsorbent surface. These experiments reveal that rGO/ZnO composite synthesized in a single-step pyrolysis method is a facile, cost-effective, and industrially scalable material for the Cr(VI) contaminant remediation.

3.2.2 Experimentation

Analytical grade Potassium dichromate ($K_2Cr_2O_7$, 99.5%) was used as Cr(VI) source, and the aqueous solutions of Cr(VI) ions were prepared in de-ionised water. 1M hydrochloric acid (HCl) and 1M Sodium hydroxide (NaOH) were used to adjust the pH of the solution. All chemicals were used without any further purification.

The 50 mg/L hexavalent chromium ion stock solution was freshly prepared by dissolving $K_2Cr_2O_7$ in 1000 mL deionized water in a volumetric flask. The stock solution was then diluted to produce a series of working standard solutions of varying concentrations. The UV-Visible spectrophotometer was initially used to assess the Cr(VI) ion in the solution with rGO/ZnO composite as an adsorbent. A decrease in the Cr(VI) characteristic peak at 350 nm with time indicates the proportional removal of the Cr(VI) ion from the solution. A colour change from bright yellow to colourlessness was observed in the Cr(VI) solution with the progress of time. ICP-OES measurement and the NaOH test provided qualitative and colourimetric confirmation of the adsorbent's ability to remove chromium from the stock solution.

Experiments were carried out to identify the adsorbent with the highest adsorption efficiency. For this, chromium solution of concentration 25 mg/L with an initial pH of 2 was mixed with 2 g/L of one of the adsorbents (ZG-0 to ZG-100) at room temperature. At selected intervals, 3 ml solution was extracted, filtered using Whatman filter paper, and transferred to a UV-Visible spectrophotometer for analysis. After reaching equilibrium, the solution was separated from the adsorbent and collected for NaOH test and ICP-OES analysis. The optimised adsorbent was used for further adsorption experiments. The Cr(VI) in the various stages of adsorption was qualitatively analysed from the absorbance peak of the corresponding UV-Visible spectrum using equation 3.1 [37].

$$\text{Percentage of removal} = \frac{A_0 - A}{A_0} 100 \quad (3.1)$$

Where A_0 and A are the absorbance peak height of Cr(VI) stock solution and solution after adsorption, respectively.

Further, the adsorptive removal of Cr(VI) from the Cr(VI)- contaminated solution by adsorbents was quantitatively confirmed by ICP-OES analysis. The residual concentration of the chromium after contact with various adsorbents, the effect of contact time, and the effect of initial concentration on adsorptive removal were studied by this analytical technique. By comparing the Cr(VI) ion concentration in the solution before and after adsorption, the adsorption efficiency of the samples was determined. The samples' percentage removal and adsorption efficiency were calculated using equations 3.2 and 3.3 [37, 77].

$$\text{Percentage of removal} = \frac{C_0 - C}{C_0} 100 \quad (3.2)$$

$$\text{Adsorption efficiency}(q_e) = \frac{V(C_0 - C)}{m} \quad (3.3)$$

where C_0 is the initial Cr(VI) ion concentration, C is the concentration of Cr(VI) after adsorption, q is the quantity of metal adsorbed over adsorbent in mg/g, m is the adsorbent mass in gram and V is the volume in litre of contaminated water used for experiment.

3.2.2.1 Mathematical modelling (Kinetics and Isotherms)

The effect of contact time and adsorption kinetics was studied using pseudo-first-order (PFO) kinetics, pseudo-second-order kinetics (PSO), and the intraparticle diffusion model (IPD). The experiment was conducted in a solution containing 25 mg/L of Cr(VI) at pH 1.5, using an adsorbent dosage of 2 g/L. 5 ml solution was removed at various time intervals (0.5 h, 1 h, 2 h, 4 h, 6 h, and 24h) and made up to 15 ml using de-ionised water for ICP-OES measurement. The ICP-OES analysis data were fitted to different kinetic models [21, 78].

The non-linear and linear equation of PFO kinetics is given in equations 3.4 and 3.5:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3.4)$$

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (3.5)$$

Where q_e and q_t are the adsorption efficiency at equilibrium and at time t in mg/g (at $t=0$, $q_t=0$ and at $t \rightarrow \infty$, $q_t=q_e$) and k_1 (h^{-1}) denotes the PFO kinetic rate constant.

The equation of PSO can be expressed by the rate equation (3.6) and its corresponding linear form (3.7).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3.6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3.7)$$

Where q_t is the adsorption efficiency at time t in mg/g, q_e is the maximum contaminant that can be loaded on the adsorbent and k_2 (g/mg h): is the PSO rate constant. q_e and k_2 are the constants obtained from the straight line plotted between t vs $\frac{t}{q_t}$.

Another model that describes the adsorption kinetics is the intra particle diffusion model (equation 3.8) which relates the quantity of metal adsorbed to the square root of time.

$$q_t = k t^{\frac{1}{2}} + C \quad (3.2)$$

Where q_t denotes the amount of contaminant adsorbed at time t , k is the rate constant and C is the y-intercept [79].

Cr(VI) adsorption isotherms on the adsorbent were also investigated. The residual amount of chromium adsorbed on the adsorbent was assessed at different Cr(VI) initial concentrations ranging from 5 to 30 mg/L, while keeping the other parameters constant (pH and adsorbent dosage at 1.5 and 2 g/L, respectively).

The results were analysed using Langmuir and the Freundlich isotherm models. The mathematical expressions for the Langmuir isotherm in non-linear and linear forms are given in equations 3.9 and 3.10, respectively. [21, 80, 81].

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3.3)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (3.4)$$

Where C_e (mg/L) is the initial concentration of Cr(VI) solution, q_e (mg/g) is the amount of metal adsorbed per unit mass of adsorbent, q_m (mg/g) and b (L/mg) are Langmuir maximum adsorption capacity and Langmuir adsorption constant. The values of q_m and b can be calculated from the linear plot of $\frac{C_e}{q_e}$ versus C_e . A dimensionless quantity R_L , calculated from the Langmuir parameters, serves as a predictor for the affinity between adsorbate and adsorbent. R_L , the separation factor is expressed as in equation 3.11 [82].

$$R_L = \frac{1}{1 + b C_0} \quad (3.5)$$

where b is the Langmuir constant and C_0 is the initial metal ion concentration

The linear and non-linear form of Freundlich isotherm is shown in equation 3.12 and 13 [21, 80, 81].

$$q_e = k_f C_e^{\frac{1}{n}} \quad (3.12)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (3.13)$$

Where C_e (mg/L) is the initial concentration of Cr(VI) solution, q_e (mg/g) is the amount of metal adsorbed per unit mass of adsorbent, k_f is the Freundlich adsorption constant and n is the Freundlich exponent. Both k_f and n can be determined by analysing the slope and intercept of the linear plot drawn between $\ln q_e$ and $\ln C_e$.

All experiments were carried out in ambient light using a magnetic stirrer with a constant stirring speed of 150 rpm to ensure uniform mixing in the solution.

3.2.3 Results and discussions

3.2.3.1 Cr(VI) adsorption test

UV-Visible spectroscopy assessed the adsorptive removal of Cr(VI) from the contaminated solution. The spectrum exhibited two distinct absorbance bands at 350 nm and 260 nm, corresponding to specific electronic transitions within the molecular structure of chromic acid [83,84]. A decrease in these peak intensities is observed as the concentration of Cr(VI) ions decreases in the solution [85]. Hence, the analysis of Cr(VI) ion removal was carried out by measuring the intensity of the characteristic absorbance peak at 350 nm. The diminishing peak height clearly illustrated a reduction in the concentration of Cr(VI) in the solution. This can also be seen in the colour of the solution, which progressively switches from bright yellow to colourless, indicating the adsorptive removal of Cr(VI) by the adsorbent from the solution. Fig. 3.1 depicts the characteristic absorbance peak of the Cr(VI) stock solution and the variation in the peak after 2 h of reaction with various adsorbents. The reduction in peak height represents the adsorptive removal of Cr(VI) ions. It is lowest for rGO, and a significant reduction in intensity is observed for both peaks at 350 nm and 260 nm in the ZnO/rGO composite samples ZG-20, ZG-30, ZG-40, ZG-50, ZG-60, ZG-70, ZG-80, ZG-90 and ZG-100. Among these composite adsorbents, ZG-40 shows the maximum reduction in intensity, indicating the highest removal efficiency. The absorbance peak intensities showed that when utilizing rGO as the adsorbent, the reduction in peak intensity was only 14%. Conversely, when using ZG-40, the peak corresponding to Cr(VI) ions experienced a substantial decrease from 100% to 35% (65% reduction) within the 2 hours of the experiment. Interestingly, pure ZnO (ZG-100) does not show any adsorption, as the absorbance graph retraces the absorbance of the initial chromium ion stock solution.

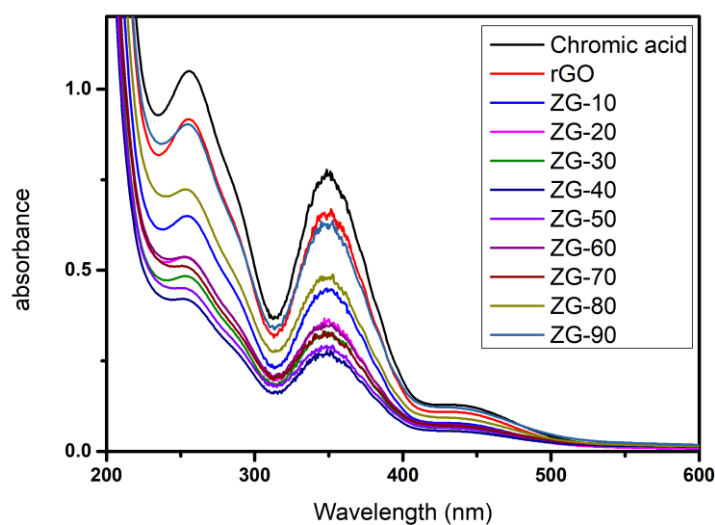


Fig. 3.1: UV–Visible absorbance spectra of Cr(VI) solution after 2 h of adsorption using different adsorbents.

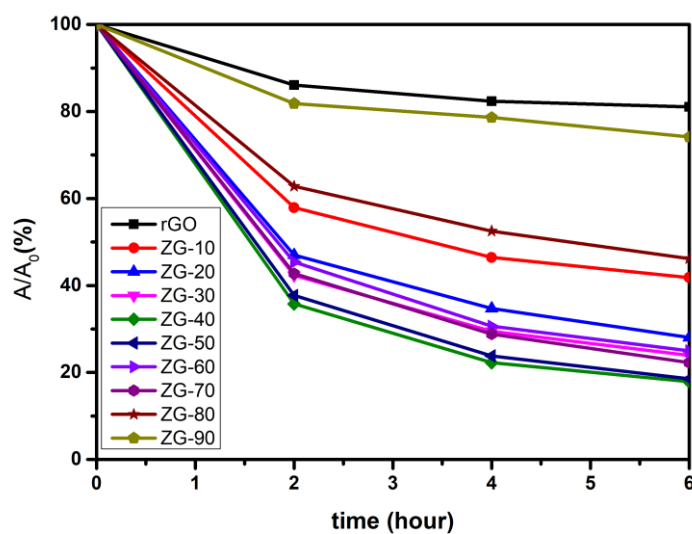


Fig. 3.2: The percentage of Cr(VI) remained after adsorption with various adsorbents with time. (Initial concentration: 25 mg/L, pH:2, dosage: 2g/L)

The experiment was continued for up to 6 h to study the drop in the absorption intensity with the evolution of time. Fig. 3.2 depicts the un-adsorbed fraction of hexavalent chromium (A/A_0 %) vs. time graph for various adsorbents. Pure rGO removed 19 % of Cr(VI), whereas the most efficient adsorbent achieved 83 % removal.

ZG-40, identified as the most effective, exhibited 4.3-fold higher adsorption efficiency than pure rGO.

The transformation of bright yellow Cr(VI) solution to a colourless solution can indicate either the removal of Cr(VI) or the reduction of chromium's oxidation state from Cr(VI) to Cr(III) [86]. If Cr(III) is present in the solution, it can be confirmed by adding excess NaOH to the solution, which will change the colour from colourless to green, indicating the formation of trivalent chromium species Hexahydroxochromate ($[\text{Cr}(\text{OH})_6]^{3-}$) [87, 88]. This reaction is reversible, and the addition of the oxidizing agent H_2O_2 to the green-coloured Cr(III) complex solution turns it back to a bright yellow-coloured solution containing Cr(VI) ions [86].

In this work, the solution obtained after reacting with the adsorbent was tested using NaOH. We added excess NaOH to the colourless supernatant after removing the adsorbent, but no green colouring was observed in the solution. This indicates the absence of Cr(III) in the solution, which confirms the adsorptive removal of Cr(VI) rather than the change in oxidation state from Cr(VI) to Cr(III). Therefore, the NaOH test provides the first evidence that the adsorbent effectively removed the chromium ion from the solution upon interaction with the adsorbent. Fig. 3.3 shows the image of the colour transition in a Cr(VI) solution, from yellow to colourless, and the absence of green colouring upon adding excess NaOH.

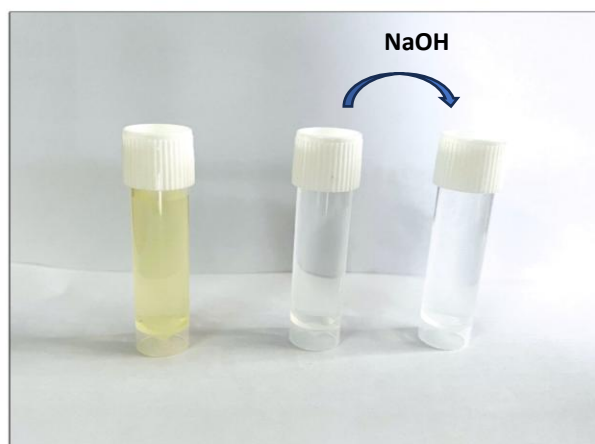


Fig. 3.3: Photographic representation of chromic acid (yellow) and the liquid after adsorption (clear) with adsorbent ZG-40. Demonstration of the absence of Cr(III) with excess NaOH test.

Sl. No	Adsorbent	Concentration of Chromium (mg/L)
1	-	32.26 (stock solution)
2	rGO	26.96
3	ZG-10	9.95
4	ZG-40	5.22
5	ZG-70	7.46
6	ZG-90	17.8

Table 3.1: The concentration of chromium present in the solution after attaining equilibrium adsorption with various adsorbents.

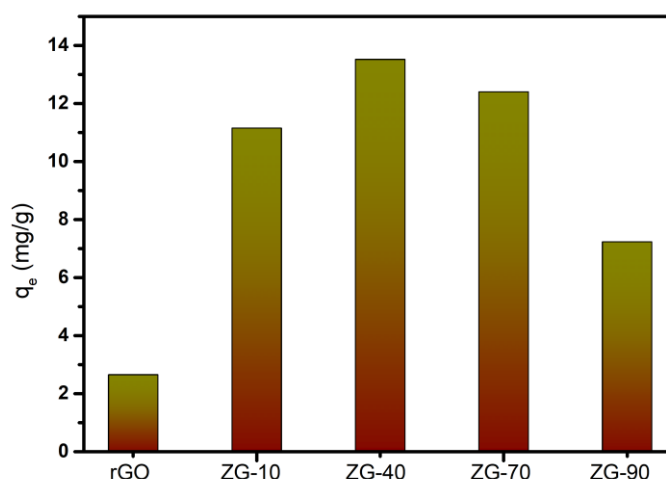


Fig. 3.4: Adsorption efficiency in mg/g of various adsorbents (Initial concentration: 32 mg/L, pH: 2, dosage: 2g/L, adsorption time: 24h).

The effectiveness of different adsorbents in adsorbing and removing chromium from a solution was quantitatively confirmed through ICP-OES measurements. Table 3.1 shows the post-adsorption chromium concentrations of various adsorbents after reaching equilibrium. The results revealed that all tested adsorbents efficiently removed chromium from the solution, but with varying degrees of efficiency. Fig. 3.4 graphically illustrates the chromium adsorption capacities (q_e) of different adsorbents. The adsorption capacities (q_e) calculated using equation 3.3 indicate the chromium adsorption capacity of different adsorbents based on the difference in chromium ion concentration in the solution before and after adsorption. ZG-40 exhibited the

maximum chromium uptake efficiency (q_e - 13.52 mg/g), which is 5.1 times higher than the efficiency of pure rGO (q_e - 2.65 mg/g). Additionally, the results indicated that the incorporation of even a tiny amount of ZnO in rGO (ZG-10) significantly enhanced the adsorption efficiency of rGO from 2.65 to 11.15 mg/g, indicating the existence of a synergistic effect of ZnO in the rGO matrix. Adsorption increased with ZnO loading in the composite up to ZG-40, but declined with further addition of ZnO, as shown in Fig. 3.4.

3.2.3.2 Effect of pH

Industrial effluents containing Cr(VI) are usually acidic in nature [75,76]. The pH of the initial Cr(VI) ion solution plays a crucial role in the adsorption [89]. Several experiments were conducted to determine the effectiveness of the adsorbent in removing Cr(VI) under various acidic pH levels. It was observed that the adsorptive removal of Cr(VI) occurred only at acidic pH levels. Therefore, the impact of pH on the adsorption efficiency of the adsorbent for Cr(VI) was studied at pH levels of 1.5, 2, and 2.5 using UV-Visible spectrum analysis. Fig. 3.5 represents the adsorptive efficiency of ZG-40 at different initial pH; it is observed that the adsorption efficiency improved as the Cr(VI) solution became more acidic. The percentage removal of Cr(VI) ions by the adsorbent was 38% at pH 2.5, 59% at pH 2.0, and 72% at pH 1.5.

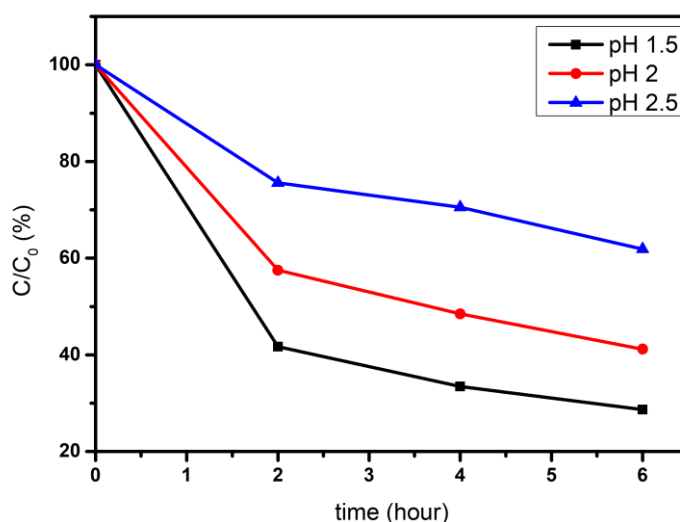


Fig. 3.5: Effect of initial pH of the Cr(VI) solution on adsorption efficiency. (Adsorbent ZG-40, Initial concentration- 25 mg/L, dosage: 2g/L)

The adsorption capacity is affected by the pH level of the solution. The pH impacts both the surface charge of the adsorbent material and the ionic state of Cr(VI) ions within the solution [90]. Cr(VI) ions exist as different anionic species at different pH levels. At acidic pH levels (<4), they exist as hydrogen chromate ions (HCrO_4^-), whereas at higher pH levels, they gradually change to chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions [80]. The adsorption of HCrO_4^- ions is favoured over CrO_4^{2-} ions due to the lower adsorption free energy associated with HCrO_4^- . This promotes superior adsorption for Cr(VI) in acidic medium [91,92]. Additionally, the surface charge of the adsorbent is significantly affected by the pH level of the solution. This has been confirmed by zeta potential measurements conducted on ZG-40 in two different environments: with a neutral pH and an acidic pH of 1.5. Zeta potential measurement is a technique used to understand the surface charge that develops at the interface between a solid surface and a liquid medium. ZG-40 demonstrates a zeta potential of -16.8 mV in the pH of deionized water, but under acidic conditions, it exhibits a zeta potential of +6.8 mV. The positive zeta potential value indicates that the adsorbent's surface is protonated at lower pH levels [93]. This results in a positively charged surface of the adsorbent under acidic pH conditions, which enhances the electrostatic attraction between the anionic Cr(VI) species and the adsorbent. As a result, there is a significant increase in adsorption efficiency. The zeta potential analysis of the sample ZG-40 after adsorption at pH 1.5 yielded a measured value of -1.7 mV, in contrast to the +6.8-mV recorded for ZG-40 before adsorption. This observation suggests that the adsorption process resulted in the deposition of anionic chromium species onto the adsorbent surface, resulting in a reduction of positive surface charge. In contrast, electrostatic repulsion and higher competition with OH^- ions hinder the adsorption of Cr(VI) ions over the adsorbent at higher pH levels [94,95]. Therefore, the acidic pH characteristics of both the adsorbent and the adsorbate are highly advantageous for chromium removal, especially considering that the industrial effluents that contain chromium are typically acidic.

3.2.3.3 Effect of contact time and the adsorption kinetics

The effect of time on adsorption was investigated qualitatively and quantitatively at different intervals (0.5h, 1h, 2h, 4hr and 6hr) by UV-Visible spectrometer and ICP-OES analysis. Fig. 3.6 shows the variation in the UV-Visible peak of chromic acid after contact with the adsorbent ZG-40 for 6h. The results indicate that

adsorption is time-dependent, and the removal efficiency is not linear with time. The adsorption efficiency of Cr(VI) increased rapidly during the primary phase, while a slow secondary phase followed until equilibrium. This trend has been observed in other studies using various adsorbents [21,96].

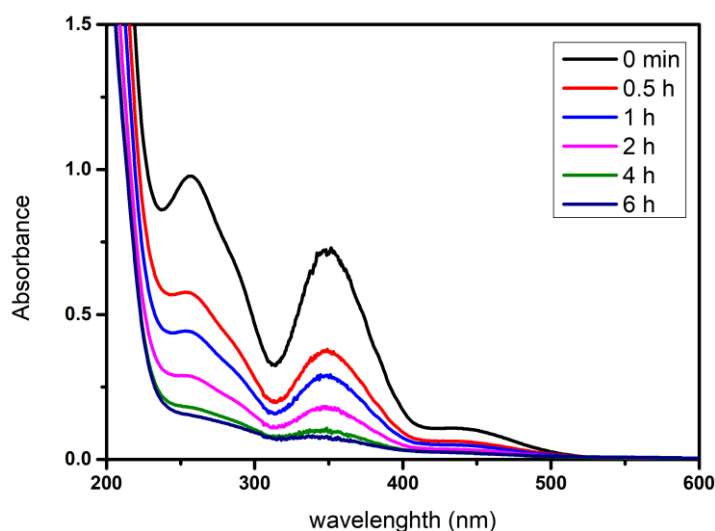


Fig. 3.6: UV- Visible absorbance spectra of Cr(VI) during adsorption with time. (Initial concentration: 25mg/L, pH:1.5, Adsorbent ZG-40, dosage: 2g/L).

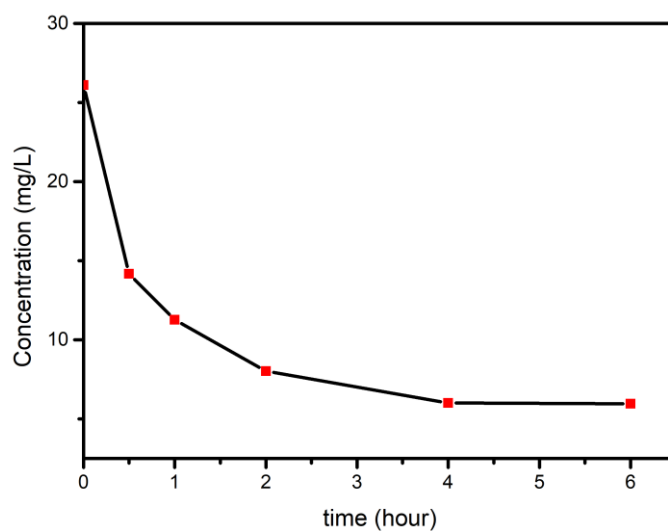


Fig. 3.7: The concentration of chromium remained in the solution during adsorption with time measured by ICP-OES analysis. (Initial concentration: 25mg/L, pH:1.5, Adsorbent ZG-40, dosage: 2g/L).

The chromium concentration at various time intervals was also determined by ICP-OES analysis, and the corresponding graphical representation of data is displayed in Fig. 3.7, demonstrating the rapid and slow phase of adsorption. In the initial 30 min, the ZG-40 composite achieves a removal efficiency of 46%. A subsequent 11% removal follows this in the next 30 min and continues further with a decline in the rate of removal efficiency. The initial rapid adsorption may be related to the empty pores and large adsorption sites available for adsorption [19].

The adsorbent removed 77% of Cr(VI) within 4 h of contact, with only a slight increase to 77.19% after 6 h, indicating that maximum adsorption efficiency was nearly reached within 4 h.

The intraparticle diffusion model, represented by equation 3.8, is a kinetic model used to describe the adsorption kinetics. The experimental data were fitted to the model, depicted in Fig. 3.8, indicating that intraparticle diffusion is the rate-limiting step [78, 97]. It clearly demonstrates the primary rapid adsorption phase and the secondary slow phase. The initial rapid stage is attributed to adsorbate diffusion on the external surface, and the subsequent slower stage indicates gradual sorption, where intra-particle diffusion is the rate-limiting step [98].

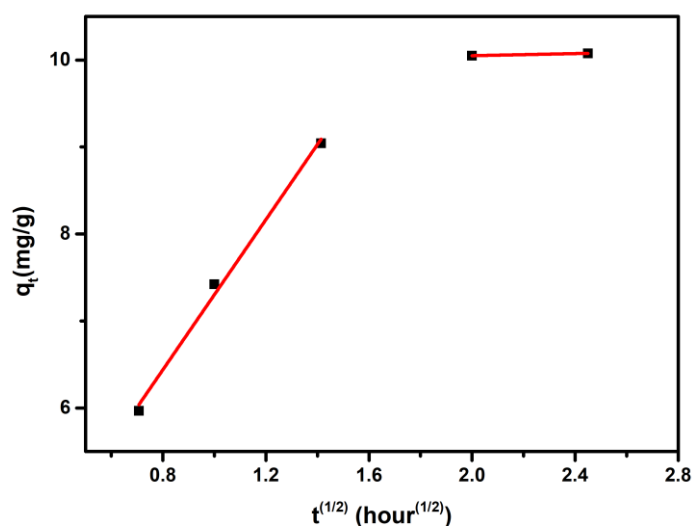


Fig. 3.8: Linearized intraparticle diffusion kinetics for adsorption of Cr(VI). (Initial concentration: 25 mg/L, pH:1.5, Adsorbent ZG-40, dosage: 2g/L)

Pseudo-first-order (PFO) and pseudo-second-order (PSO) models were also used to investigate the kinetics of chromium removal and to understand the adsorption mechanism. The experimental data were fitted to equations 3.5 and 3.7; the corresponding graphs were given in Fig. 3.9 (a and b). On comparison of R^2 values of PFO and PSO fitting, it has been seen that the removal of Cr(VI) by ZG-40 follows the PSO kinetics. This indicates that the adsorption mechanism is controlled by chemisorption, which involves electron sharing between the adsorbent and the adsorbate [79, 90, 99].

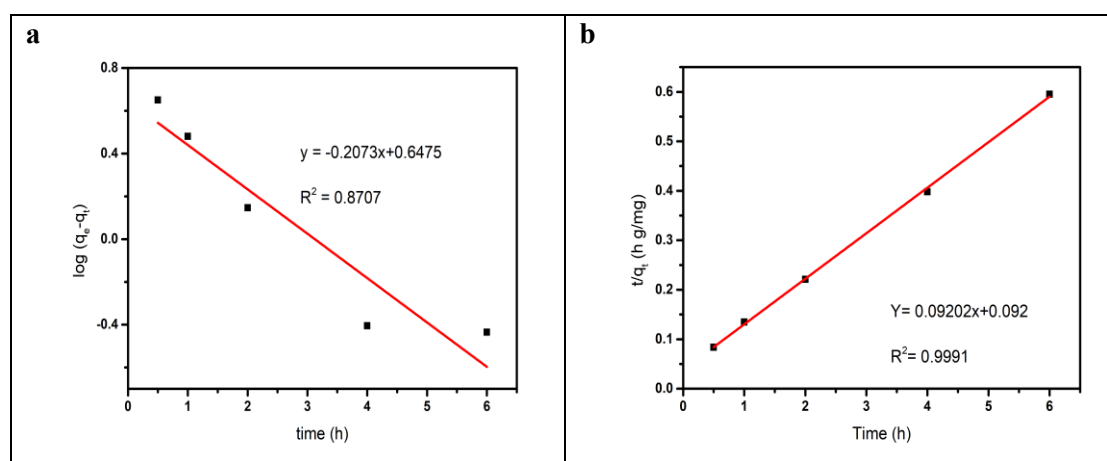


Fig. 3.9: Adsorption data fitted with (a) Pseudo first order kinetics, and (b) pseudo second order kinetics (adsorbent - ZG-40, pH - 1.5; adsorbent dose - 2 g/L, initial concentration 25 mg/L).

3.2.3.4 Adsorption isotherms

The way heavy metals are adsorbed onto an adsorbent is significantly influenced by the functional groups present in the adsorbent. Adsorbents with heterogeneous functional groups involve multiple pathways, rather than a single one, for adsorption to occur [100]. Various isotherm models were used to study the interaction between the adsorbent and adsorbate. This study investigated the two widely used isotherms: the Langmuir and the Freundlich isotherm models. Fig. 3.10 (a and b) illustrates the Langmuir and the Freundlich isotherm models fitted to the experimental data. Both models show a good fit to the experimental data, and similar observations were reported elsewhere [45, 63, 91].

The Langmuir isotherm is based on assumptions like: adsorption occurs evenly in active sites, forming monolayer adsorption; each binding site exhibits equal affinity towards the adsorbate; the adsorbent possesses a fixed number of adsorption sites; the

absence of lateral interactions among the adsorbates once adsorbed [82, 90]. Based on the Langmuir fit (Fig.3.10a), the maximum adsorption efficiency of the ZG-40 adsorbent was determined to be 14.08 mg/g. This value is consistent with the experimental adsorption efficiency and confirms that the prepared adsorbent has a strong adsorption efficiency for hexavalent chromium ions. The Langmuir fitting also yielded the separation factor R_L , represented by equation 3.11. The R_L value indicates the type of adsorption: irreversible ($R_L=0$), favourable ($0 < R_L < 1$), linear ($R_L=1$) and unfavourable ($R_L > 1$). The computed R_L value, obtained from the Langmuir constant (b) and C_0 parameters, is 0.233, indicating favourable adsorption [82, 101].

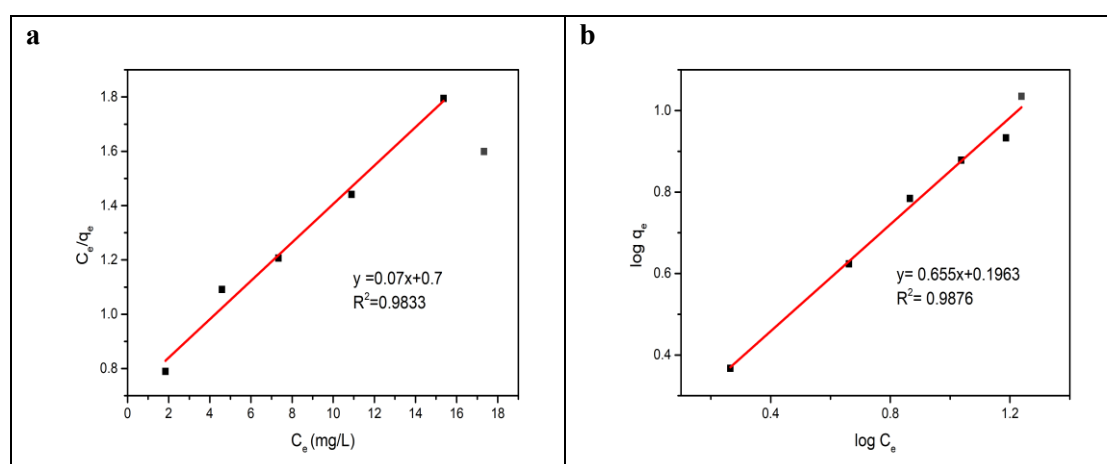


Fig. 3.10: Adsorption data fitted with a) Langmuir isotherm and b) Freundlich isotherm. (Adsorbent - ZG-40, pH - 1.5; adsorbent dose - 2 g/L)

On the other hand, the Freundlich adsorption isotherm model also demonstrated a favourable fit with the experimental data. This model effectively describes the multilayer adsorption of the adsorbate over heterogeneous surfaces [67]. The Freundlich parameter 'n,' calculated from the fit slope, represents the favourability of metal adsorption on the composite surface. For favourable adsorption, the requirement is $n > 1$. The Freundlich parameter n computed from Fig. 3.10 (b) is 1.53, which satisfies the adsorption criteria [102,103].

3.2.3.5 Adsorption mechanism

Carbon and its derivatives have been found to be effective in adsorbing heavy metals. The presence of oxygen functional groups, namely hydroxyl (-OH), carboxyl (-COOH), epoxy (-COC-), and carbonyl (-C=O) groups, is responsible for their notable efficiency in adsorption. These functional groups play a crucial role in the surface chemistry of carbon materials, acting as active sites for the adsorption of heavy metals

[104]. Among carbon derivatives, reduced graphene oxide (rGO) stands out due to its exceptional properties, including a high surface area and abundant oxygen functional groups, which make it an effective adsorbent of heavy metals [105]. When combining ZnO with rGO, the synergistic effect significantly enhances the heavy metal adsorption efficiency of rGO [104].

The Coulombic interaction between the adsorbent and adsorbate, which plays a crucial role in adsorption, is evidenced by the studies on the effect of pH. Further, the available active adsorption sites for adsorption are proportional to the surface area of the adsorbent. BET analysis was used to compare the surface area of the adsorbents rGO and ZG-40. The analysis revealed that the surface area of ZG-40 is $29.418\text{m}^2/\text{g}$, which is much higher than that of rGO ($1.265\text{m}^2/\text{g}$). The enhanced surface area of ZG-40 is one of the critical factors in the superior adsorption efficiency of the composite. Further, the surface area of ZG-40 after adsorption was analysed, and it was found that the surface area was significantly reduced to $8.4926\text{m}^2/\text{g}$. This reduction could be attributed to the adsorption and filling of Cr ions in the pores of the adsorbent.

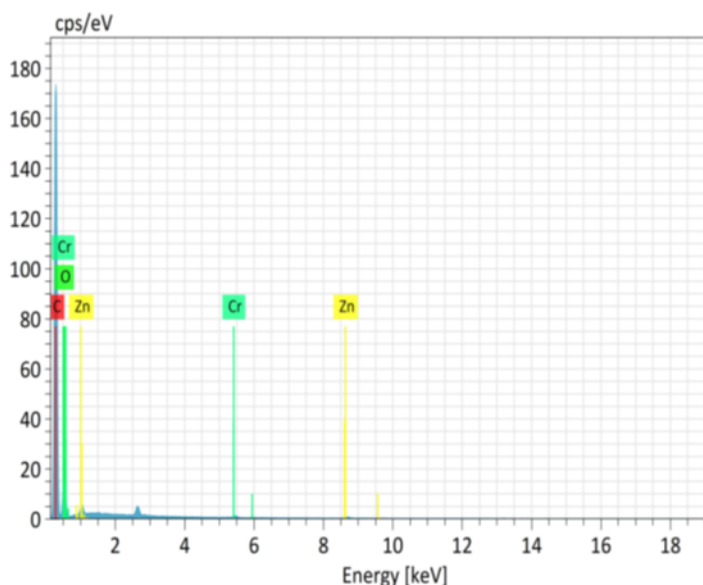


Fig. 3.11: EDX spectra adsorbent ZG-40 after adsorption.

The compositional analysis of the surface of ZG-40 after adsorption was investigated with EDX spectra. After adsorption, the adsorbent was removed from the solution, washed twice with distilled water, collected, and dried, and the EDS spectra of the powder (ZG-40Cr) were recorded. The EDX spectra of the Cr-loaded adsorbent is shown in Fig. 3.11. The peak corresponding to Cr in the EDX spectra of ZG-40Cr

confirmed the chemical modification of the adsorbent surface with Cr(VI) ions during the chromium adsorption experiment.

In addition, XPS spectra of post-adsorbed ZG-40 (ZG-40Cr) were further used to confirm chromium adsorption over the adsorbent. Fig. 3.12 is the XPS spectra corresponding to ZG-40Cr. The two observed asymmetric peaks corresponding to Cr 2P in Fig. 3.12 reveal the presence of adsorbed chromium on the adsorbent [97]. These peaks were deconvoluted into four simple peaks. The peaks at 576.90 eV, 586.64 eV can be attributed to Cr(III) 2p_{3/2} and 2p_{1/2} state, whereas the peaks at 579.43 eV, 589.15 eV correspond to Cr(VI) 2p_{3/2} and Cr 2p_{1/2} state respectively, based on the previously reported values [106]. Surprisingly, the XPS analysis manifests that a part of Cr(VI) was reduced to Cr(III) upon adsorption; 60% of the total Cr bound to ZG-40 accounted for Cr(III). This reveals that the redox reaction is the key mechanism behind the adsorptive removal of Cr by the adsorbent. This is a promising outcome, given that 60% of adsorbed highly toxic Cr(VI) is transformed into less toxic Cr(III) ions.

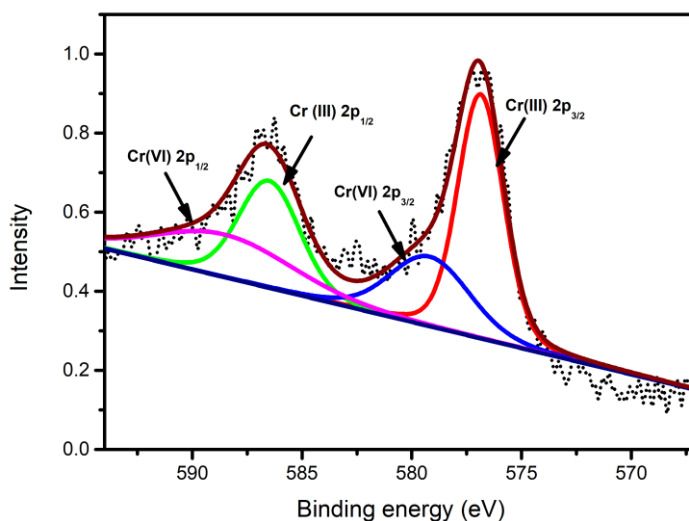
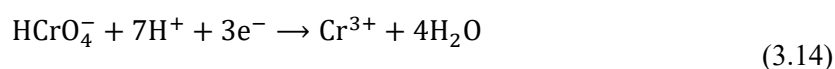


Fig. 3.12: XPS spectra corresponding to Cr 2p of the adsorbent ZG-40 after adsorption.

The Cr(VI) ion was first adsorbed over the adsorbent in acidic pH due to the coulombic interaction between the positively charged adsorbent and the anionic chromium species HCrO_4^- . A significant portion of adsorbed Cr(VI) was further reduced to Cr(III) by utilizing the excess hydrogen ions in the acidic chromium-contaminated solution and the electrons provided by the adsorbent [79]. The remaining Cr(VI)

adsorbed exists as such over the adsorbent. The equation governing the reduction is given in the equation 3.14 [107].

The primary limitation of the adsorption method is the safe disposal of the adsorbent loaded with toxic Cr(VI) species. To address this issue, it has been suggested that adsorption combined with the in situ reduction of Cr(VI) to the less toxic Cr(III) is a promising solution. Therefore, adsorption followed by reduction is the highly preferred strategy for the treatment of pollution due to Cr(VI) heavy metal ions [36,45]. In the present study, there is promise in the fact that a significant portion of the adsorbed Cr(VI) undergoes reduction to Cr(III).



Furthermore, equation 3.14 indicates the role of electron generation in effective adsorption. The oxygen-containing functional groups of rGO, particularly phenolic groups, are typical electron donors for Cr(VI) adsorption [70,95]. Moreover, ZnO is a photoactive substance with high exciton binding energy. The light of suitable wavelength generates photogenerated electron-hole pair [52]; hence, we hypothesised the participation of light-generated e^- in the adsorption process. Thus, the adsorption experiment was repeated in a completely dark situation and under light irradiation (Xenon lamp as the light source) using rGO and ZG-40 as adsorbents. Fig. 3.13 depicts the percentage removal of Cr(VI) by rGO and ZG-40 under dark and light conditions, analysed by UV-Visible spectrophotometer.

The adsorption efficiency of rGO remains the same under both dark and light conditions since it lacks any photoactive components. In contrast, the adsorption efficiency of ZnO/rGO composite enhanced upon light irradiation, demonstrating the photocatalytic contribution. The percentage of Cr(VI) removal achieved by ZG-40 in the absence of light is 55%, while in the presence of light, it increases to 70%. Hence, the active participation of photogenerated charge carriers was evidenced by the improved adsorption efficiency of ZG-40 when exposed to light.

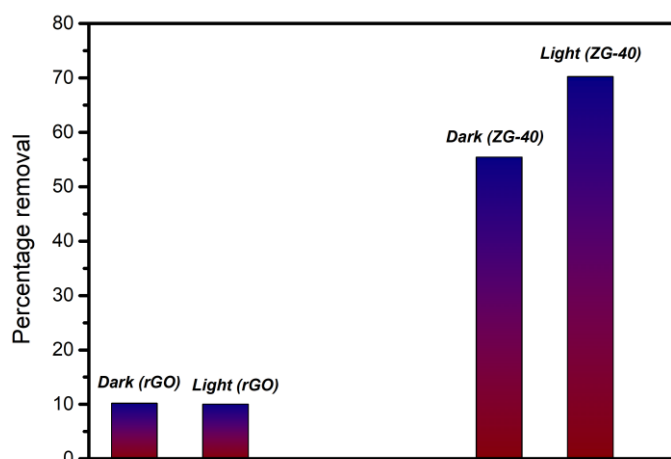


Fig. 3.13: Percentage removal of Cr(VI) by adsorbents rGO and ZG-40 under dark and light conditions (initial pH-1.5, concentration of the Cr(VI) solution-25g/L, adsorbent dose-2g/L, contact time- 1h).

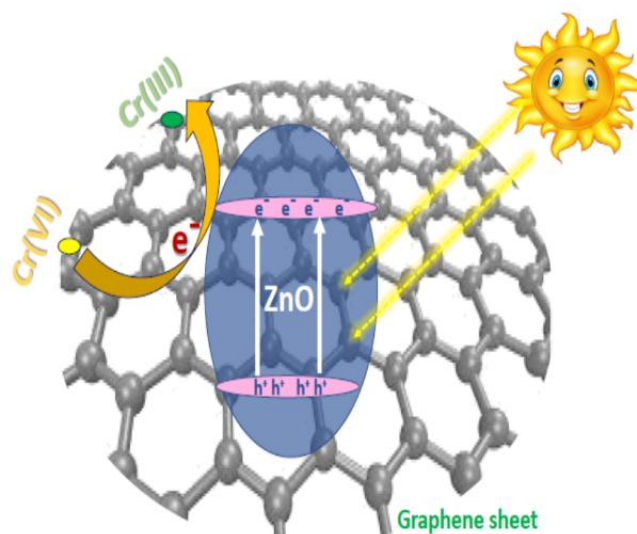
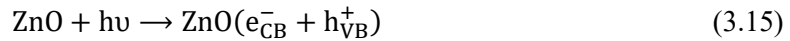


Fig. 3.14: Schematic representation of the photo enhanced Cr(VI) adsorption and reduction.

ZnO is recognized for its photosensitivity. It can absorb a broad spectrum of solar radiation. Upon exposure to photons with energy surpassing the band gap, the electron from the valence band is excited to the conduction band, leaving a hole (h^+) in the valence band as per equation 3.15 [108]. However, ZnO exhibits lower quantum efficiency due to the rapid recombination of photogenerated charge carriers [109].

Furthermore, it possesses insufficient adsorption sites for the adsorption of the adsorbate.



These limitations of ZnO are effectively addressed by incorporating rGO with ZnO to form a composite. rGO is known for its high electron mobility [110], making it a promising material in optoelectronic applications. The high electron mobility of rGO allows for the immediate transportation of the photoelectron generated in ZnO through the rGO sheets, separating the electron from the hole at the point of generation [111,112]. As an electron scavenger, rGO suppresses the recombination rates of photogenerated charge carriers in ZnO [113]. The electrons trapped by the rGO become available for the photoreduction of Cr(VI) as per equation 3.16, thus promoting the availability of electrons in Cr(VI) reduction and adsorption. Furthermore, the abundance of adsorption sites on rGO further enhances the adsorption efficiency. This dual role of rGO, as a facilitator of photoreduction and provider of adsorption sites, contributes to the improved performance of the ZnO-rGO composite's enhanced photocatalytic reduction of Cr(VI) under light irradiation compared to darkness [114]. A schematic representation showing the generation of photoelectrons and the enhancement of Cr(VI) reduction and adsorption over the adsorbent is shown in Fig. 3.14. The trial in both light and dark implies that the adsorbent could be applicable “around the clock”. The interactions governing the Cr(VI) adsorptive removal of Cr(VI) by the adsorbent are summarised as Coulombic interaction, complex formation, pore filling, and reduction [115].

3.3. Efficient Mineralization and Removal of Pb^{2+} from Water Using ZnO/rGO Composites

3.3.1 Introduction

Lead (Pb) has been used by humans since around 7000 BC, primarily because of its ease of extraction, corrosion resistance, and ductility [116]. Archaeologists found the oldest lead artefacts of 6400 BC and 5000 BC, suggesting their use during the Neolithic period, long before the Copper and Bronze Ages [117]. Despite its use, the harmful effects of lead on health and the environment were unknown for millennia. However,

by the second century BC itself, the toxic effects of lead were documented by the Hellenistic physician Nicander of Colophon, who identified the symptoms of acute lead poisoning [116]. A suggestive theory considers lead poisoning as a contributing factor to the decline of the Roman Empire. In ancient Rome, lead was extensively used for water transportation and as a wine preservative. Water was transported through lead pipes, and the wine preservative contains lead acetate (lead sugar), which can sweeten the poor-quality wine. Prolonged exposure to lead caused widespread health issues among Roman emperors and patricians, including reproductive problems, shorter life expectancy, fertility disorders, and lower birth rates. The use of lead has continued to expand over time, finding more applications. The economic and cultural development of the fifteenth century widely used lead-based paints to decorate great cities and cathedrals. Further, the Renaissance saw increased lead usage due to advancements in metallurgy, influenced by alchemy. Physicians of the time began to recognize the dangers of lead poisoning, particularly among professions such as potters, tinsmiths, and painters [116].

Nowadays, the hazardous effect of lead is well known to the scientific and medical community. Thus, anthropogenic activities are highly focused on the word “lead-free”, such as lead-free paint, lead-free batteries, lead-free ceramics, etc., indicating how hazardous lead is and the harmful implications of lead to living organisms. Modern research is very much focused on minimising lead exposure to humanity. Although lead is known for its toxicity, lead continues to be widely used in various industries due to its affordability and availability. It is commonly found in lead-acid batteries, insecticides, fossil fuel combustion, electromagnetic shielding, the energy sector, alloys, construction, and ammunition, etc. [10-13]. The mining, processing, and industrial applications of Pb cannot be avoided entirely to date. Efforts are taking place to reduce lead usage globally; however, various sources of exposure to lead remain, particularly in low- and middle-income countries [118]. Heavy metals, including lead, are non-biodegradable, persistent, and bio-accumulative [12,13,18]. As a result, many regions still suffer from lead contamination, which has accumulated over the decades.

Anthropogenic emissions of lead to the environment rocketed following the introduction of leaded gasoline in the 1920s, peaked in the 1980s, and declined due to the ban after recognising its severe health impacts [117]. The development of the

automobile industry also significantly contributed to anthropogenic lead inputs in the hydrosphere and biosphere. Additionally, lead, often present as an impurity in fossil fuels, is a significant source of atmospheric pollution through fossil fuel combustion. The disposal of coal-based solid waste has also led to lead contamination in the surrounding soil and groundwater [10]. Improper recycling of used lead-acid batteries is another critical source of lead pollution, where it heavily contaminates water bodies and groundwater systems in many regions [119]. Historical and ongoing anthropogenic and geological activities have resulted in significant lead accumulation, affecting ecosystems worldwide. Remarkably, studies have found lead contamination even in the Tibetan Plateau glaciers—one of the most remote and pristine regions on Earth, which serves as a vital water source for millions. Isotopic analyses reveal that lead traces in these glaciers span from the Stone Age (over 36,000 years ago) to as recently as 2015 [117]. The World Health Organization (WHO) estimated that more than one million deaths globally were attributed to lead exposure, with many more individuals suffering from disabilities and diseases [120]. These alarming statistics highlight that lead pollution in water, air, and soil remains a pressing global challenge. Consequently, research continues to focus on reducing lead exposure and mitigating its impacts on human health and the environment.

Human exposure to lead primarily occurs through inhalation of lead-containing dust, consumption of contaminated food and water, and absorption through the skin [121,122]. Even at trace levels, lead poses significant health risks, disrupting metabolic functions and cellular processes [23,123]. It can damage vital organs such as the kidneys, liver, and cause severe harm to the nervous, skeletal, circulatory, enzymatic, endocrine, immune, and reproductive systems [12, 27]. Furthermore, heavy metal accumulation is both mutagenic and carcinogenic [13, 23,24]. The WHO estimated that in 2021, more than 1.5 million deaths globally were attributed to lead exposure, with many more individuals suffering from disabilities and diseases [121]. These alarming statistics highlight that lead pollution in water, air, and soil remains a pressing global challenge. Consequently, research continues to focus on reducing lead exposure and mitigating its impacts on human health and the environment.

Treating water contaminated with Pb is essential for ensuring sustainable ecosystems and addressing the global challenge of freshwater scarcity. Various techniques have been developed for lead removal, including ion exchange, chemical

precipitation, reverse osmosis, and membrane filtration [11, 27, 28]. However, many of these methods require substantial investment and infrastructure. Adsorption using low-cost materials has emerged as a promising alternative for removing heavy metals due to its simplicity in operation, affordability, suitability for large-scale application, and high efficiency [32-34].

As discussed earlier, ZnO and its composites exhibit effective adsorption capabilities for heavy metal removal. Several studies have investigated the removal of lead (Pb) using ZnO-based materials, with reported adsorption capacities widely varying from 25 mg/g to 1120 mg/g [124-129]. For example, Navish Kataria et al. studied Pb(II) and Cd(II) adsorption onto ZnO nanoflowers synthesized by a low-temperature hydrothermal method and found adsorption capacities of 115 mg/g for Pb(II) and 71.5 mg/g for Cd(II) [125]. Similarly, K. Yogesh Kumar prepared hierarchically assembled mesoporous ZnO nanorods via hydrothermal synthesis, which showed capacities of 160.7 mg/g for Pb(II) and 147.25 mg/g for Cd(II) [126]. Manisha Sharma et al. synthesized mesoporous ZnO and TiO₂@ZnO monoliths through a nanocasting process and reported high Pb²⁺ capacities of 790 mg/g and 978 mg/g, respectively, while the corresponding Cd²⁺ capacities were 643 mg/g and 786 mg/g [128]. V. Venkatesham et al. synthesized nanosized, large-surface-area ZnO by a gel combustion method and applied it for Pb²⁺ adsorption [124], while Susan Azizi et al. reported an adsorption capacity of 19.65 mg/g for green-synthesized ZnO nanoparticles [130].

From the literature, it is evident that the incorporation of GO/rGO with ZnO enhances ZnO's performance due to the exceptional surface and structural properties of GO/rGO. However, fewer studies have explored Pb²⁺ removal using ZnO/GO and ZnO/rGO composites. For instance, Siti Zu Nurain Ahmad reported a Pb²⁺ adsorption capacity of 909.09 mg/g using a ZnO/GO composite [18]. Lu Liu et al. synthesized nano-ZnO-loaded graphene oxide electrodes via catalytic pyrolysis of petroleum tar and demonstrated a capacity of 5.60 mg/g for Pb²⁺ removal from seawater [131]. Moeng Geluk Motitswe et al. evaluated the Pb²⁺ removal performance of an ZnO/rGO nanocomposite and reported an adsorption capacity of 242 mg/g, with the mechanism attributed to strong ionic bonding and electrostatic interactions [62]. Similarly, Naveen Chandra Joshi et al. reported a capacity of 16.216 mg/g for a ZnO/rGO composite synthesized via a sonochemical method [60]. The present section is the detailed

evaluation of the lead removal efficiency of the ZnO/rGO composite, which was prepared using a new facile method.

An effective strategy for reducing lead mobility and bioavailability in aquatic environments is the immobilisation of Pb through the formation of insoluble precipitates or mineral phases. This approach has demonstrated significantly higher lead removal efficiency compared to conventional adsorbents. Among the materials studied, phosphate- and carbonate-based minerals are the most commonly investigated for lead immobilisation via mineralisation [132]. However, various other materials can also promote the formation of lead-bearing mineral phases [48,133,134,135,136]. Among the lead-based mineral phases, hydrocerussite is one of the most stable, with the lowest solubility constant [136,137]. In the present study, we also observed lead decontamination by the ZnO/rGO composite, which proceeded via a dissolution-precipitation mechanism leading to the formation of hydrocerussite. To our knowledge, this is the first work demonstrating Pb removal by ZnO/rGO composite through the solidification of dissolved Pb ions in water.

The novelty of this work lies in the efficient immobilisation and removal of Pb^{2+} from contaminated water using a ZnO/rGO composite synthesised via a green, single-step pyrolysis method. This study is the first to demonstrate that Pb^{2+} removal by ZnO/rGO through the formation of a highly stable lead-bearing mineral phase—lead carbonate hydroxide (hydrocerussite). Moreover, the composite exhibits the highest Pb^{2+} removal efficiency reported so far for ZnO/rGO-based materials. Comprehensive analysis using ICP-OES, XRD, FE-SEM, EDX, HR-TEM, and XPS confirmed the effective removal of Pb. Various factors influencing the adsorption process, including pH, initial concentration, contact time, and light conditions, were systematically investigated to better understand the mechanism. The ZnO/rGO composite, synthesised by a simple, low-cost, and sustainable method that shows high removal efficiency, makes these materials a promising candidate for treating lead-contaminated water.

3.3.2 Experimentation

Batch studies were conducted to identify the most efficient adsorbent among composites made with different rGO to ZnO ratios, and to investigate the effects of initial pH, light exposure, contact time, and initial Pb^{2+} concentration on the Pb^{2+} removal efficiency of the ZnO/rGO composite at room temperature. Laboratory grade

lead nitrate was used as Pb^{2+} ion source. A stock solution of Pb^{2+} (2000 mg/L) was prepared by dissolving lead nitrate in deionized water, and working solutions of desired concentrations were prepared by diluting the stock solution. In each experiment, 40 mL of Pb^{2+} solution was taken in a beaker, and the required dosage of adsorbent was added. The mixture was stirred at 350 rpm using a magnetic stirrer. Aliquots were collected, filtered, and analysed at specified intervals for Pb^{2+} concentration using the ICP-OES technique. The powders were tested in a 250 mg/L Pb^{2+} solution to determine the composite with the highest removal efficiency. The influence of pH on Pb^{2+} removal was evaluated by adjusting the solution to pH levels of 2, 7, and 9 using NaOH and HCl. For all other experiments, the lead solutions were used without any pH adjustment. The effect of initial Pb^{2+} concentration was evaluated using synthetic Pb^{2+} solutions with concentrations of 50, 100, 250, 500, 750, 1000, 1500, and 2000 mg/L. The effect of contact time was investigated by adding the adsorbent to a 1500 mg/L Pb^{2+} solution. Aliquots were collected at intervals of 0.5, 1, 2, 4, 8, and 24 hours, and at equilibrium. Furthermore, the effect of light on adsorption was studied under various conditions: in complete darkness, at 35°C while maintaining darkness, under laboratory lighting, and under light irradiation using a xenon lamp.

The percentage removal of Pb^{2+} was calculated using Equation 3.17, and the adsorption capacity (q), representing the amount of Pb^{2+} adsorbed per unit mass of adsorbent (mg/g), was calculated using Equation 3.18 [138].

$$\text{Percentage of removal} = \frac{C_0 - C}{C_0} * 100 \quad (3.17)$$

$$\text{Adsorption efficiency}(q) = \frac{V(C_0 - C)}{m} \quad (3.18)$$

Where C_0 is the initial concentration and C is the final concentration in mg/L, V is the volume of the solution under study in litres, and m is the mass of the adsorbent used in grams. To determine the equilibrium adsorption efficiency (q_e), C is replaced with C_e , the equilibrium concentration.

X-ray diffraction of powder samples after interaction with Pb ions was measured with a Rigaku Miniflex 600 equipped with a Cu X-ray source (working at 40 kV and 15 mA). Diffractograms were recorded in the range between 3° and 80°. The

morphological studies of powder before and after adsorption were analysed by scanning electron microscopy (Hitachi SU6600 Variable Pressure FESEM) and transmission electron microscopy (HR-TEM, Jeol/JEM 2100). The elemental mapping analysis was done with dispersive spectroscopy (Horiba, EMAX, 137 eV) equipped with FE-SEM. The atomic composition was analysed by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, ULVAC-PHI Inc., USA) equipped with micro-focused (100 μm , 15 kV) monochromatic Al-K α X-Ray source ($h\nu = 1486.6 \text{ eV}$).

3.3.3 Result and discussion

3.3.3.1 Optimization of adsorbent

The concentration variations in lead-bearing aqueous solutions during their interaction with the ZnO/rGO composites were monitored through batch experiments. To identify the adsorbent with the highest adsorption efficiency, experiments were performed at an initial lead concentration of 250 mg/L, an adsorbent dosage of 2 g/L, and an interaction time of 2 hours. The results are illustrated in Fig. 3.15.

Among the pristine samples, rGO removed 7.5% of lead, while ZG-100 (ZnO) achieved a removal efficiency of 67.8%. Typically, rGO is known for its high adsorption efficiency, which is attributed to its unique properties, such as a large surface area and oxygenated functional group [18, 58, 59]. In contrast, ZnO generally exhibits lower adsorption efficiency because of the lack of adsorption sites. However, in this study on Pb removal, pure ZnO (ZG-100) exhibited significantly higher removal efficiency than pure rGO, with more than a 9-fold efficiency. A major drawback of ZnO as a lead-removal agent is the difficulty in separating the adsorbent from contaminated water after the adsorption process, especially at low Pb^{2+} concentrations. Its interaction with lead-containing solutions often results in the formation of a colloidal suspension, complicating recovery of the solid particles after adsorption. This limitation is addressed by incorporating materials with limited water dispersion, like rGO. In this study, the integration of rGO with ZnO greatly enhances lead removal efficiency and facilitates the separation of the composite after interaction with lead solutions. Even adding 10% ZnO in rGO (sample ZG-10) showed an increase in efficiency from 7.5 to 36.2% of Pb removal. This result indicates that ZnO plays the primary role in lead removal, with rGO as a supportive component in the composite. TEM images of the ZnO/rGO composite (Fig. 2.21 a,b) demonstrate that ZnO nanoparticles are embedded

and trapped within the rGO sheets. The layered, sheet-like structure of rGO, combined with its numerous defects and adsorption sites, allows ZnO nanoparticles to bind effectively to the rGO sheets. The composite sample ZG-60 was found to be the most efficient adsorbent, removing over 84% of lead from the contaminated solution in 2 hours with 1g/L adsorbent. This represents a nearly 12-fold improvement in removal efficiency compared to pure rGO. When rGO forms a composite with ZnO, the overall efficiency of the composite is enhanced due to increased surface area, improved surface charge, and synergistic interactions.

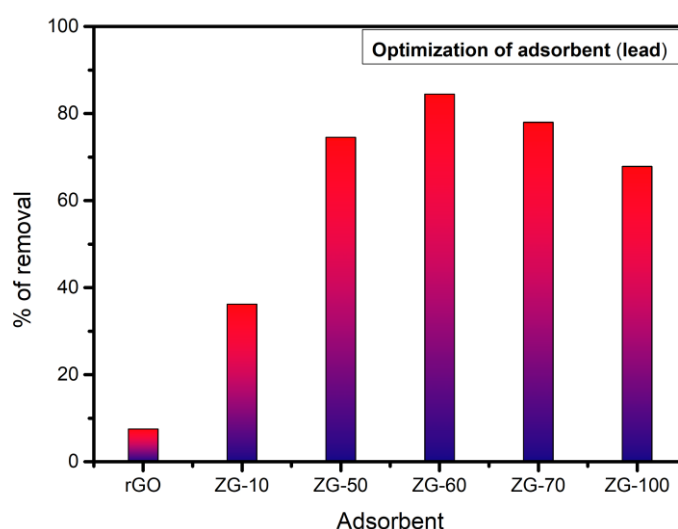


Fig. 3.15: Optimization study to identify the adsorbent with maximum Pb^{2+} removal efficiency (initial Pb^{2+} concentration: 250 mg/L; reaction time: 2 h; adsorbent dosage: 2 g/L)

3.3.3.2 Effect of time

Time is a critical factor influencing the adsorption rate during the sorption process. Fig. 3.16 shows the change in Pb^{2+} concentration in the contaminated solution upon interaction with ZG-60 over time. A rapid increase in removal efficiency was observed during the initial stages, followed by a gradual slowdown as time elapsed. Within the first 30 minutes, the ZG-60 composite removed 64.23% of Pb^{2+} , and a removal efficiency of 97.56% was achieved after 4 hours. A measurement taken after 12 hours confirmed the complete removal of Pb^{2+} from the solution. The rapid initial uptake is attributed to the abundant availability of active adsorption sites on the

composite surface. As these sites become occupied over time, the number of available sites decreases, leading to a reduced adsorption rate. This behaviour is reported and indicates that the adsorption rate strongly depends on the number of unoccupied sites on the composite surface [56,138].

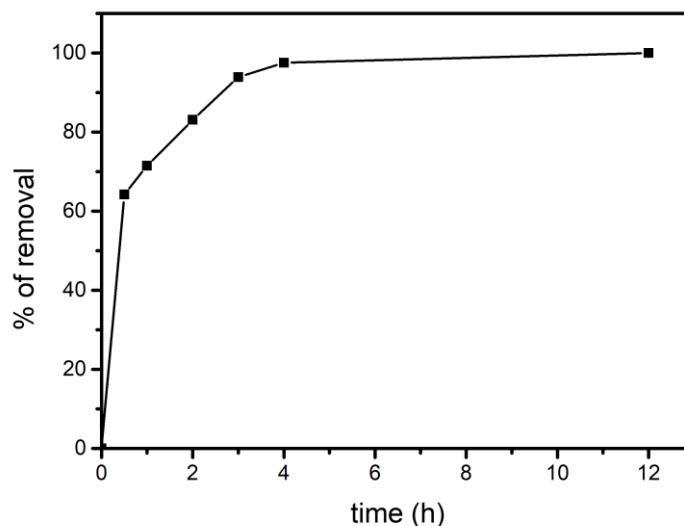


Fig. 3.16: Effect of interaction time on the adsorption of Pb^{2+} (adsorbent ZG-60, initial Pb ion concentration: 250 mg/L; adsorbent dosage: 2g/L)

3.3.3.3 Effect of pH

The effect of pH on the adsorption-precipitation reaction of Pb^{2+} ions onto the ZnO/rGO composite (ZG-60) was studied. Fig. 3.17 illustrates the percentage of lead removal at various pH levels. The composite effectively removed lead across all pH ranges, with more than 80% of removal efficiency. For the given initial lead concentration, dosage, and contact time, the composite ZG-60 removed 100% Pb ions from the Pb-contaminated solution at basic pH. At neutral pH, the removal efficiency was 93.5%, while at acidic pH, it dropped to 81%. This indicates that lower pH levels reduce lead removal efficiency.

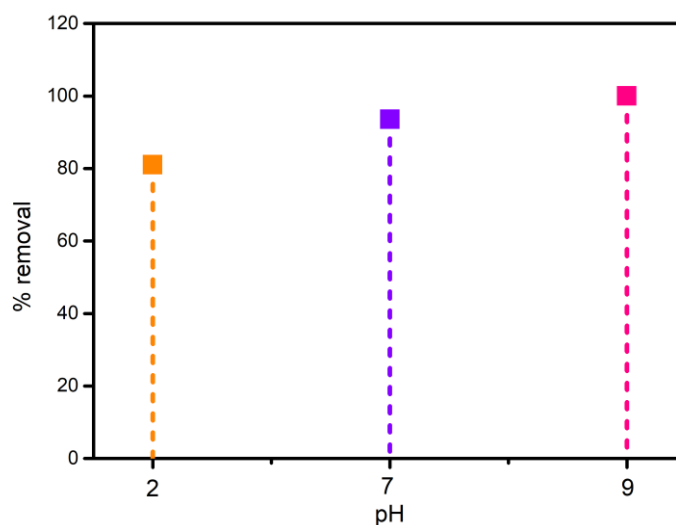


Fig. 3.17: Effect of initial pH of the Pb^{2+} solution on adsorption efficiency (adsorbent ZG-60, initial Pb ion concentration: 250 mg/L; reaction time: 3h; adsorbent dosage: 2g/L).

The pH of the solution significantly influences the heavy metal removal efficiency of the adsorbent, as it affects both the surface functional groups of the composite and the speciation of metal ions in solution [48,139]. In acidic media, the surface becomes positively charged due to protonation, which hinders the adsorption of positively charged Pb^{2+} ions. The high concentration of H^+ ions leads to competitive adsorption, where protons compete with Pb^{2+} for active sites, resulting in slightly lower removal efficiency under acidic conditions [140,141]. Additionally, at lower pH levels, surface functional groups such as $-\text{OH}$, $-\text{COO}^-$, and $-\text{O}^-$ undergo protonation, further reducing their availability for binding with Pb^{2+} [139]. In contrast, under basic conditions, the abundance of OH^- ions increases the negative surface charge density of the adsorbent, enhancing electrostatic attraction between the negatively charged ZG-60 surface and Pb^{2+} ions. This electrostatic (Coulombic) interaction promotes more effective lead adsorption at higher pH values [141,142]. Zeta potential measurements confirm this pH-dependent variation in surface charge: ZG-60 exhibits a surface charge of -80.35 mV at basic pH, -47.3 mV at neutral pH, and $+12.46$ mV at acidic pH. These results align with the observed pH-dependent removal behaviour. In summary, the ZG-60 composite demonstrates consistently high Pb^{2+} removal efficiency across the entire pH range, maintaining over 80% efficiency, with enhanced performance under basic

conditions due to the increased negative surface charge that promotes stronger adsorption of lead ions.

3.3.3.4 Concentration study

A series of equilibrium experiments was performed using a 2 g/L dosage of ZG-60, which was identified as the most effective adsorbent. Even at very high initial Pb^{2+} concentrations, the Pb^{2+} ions in the solution at equilibrium are measured to zero, demonstrating the exceptional removal efficiency of the composite. Therefore, the adsorbent dosage was reduced to 1 g/L in all subsequent experiments.

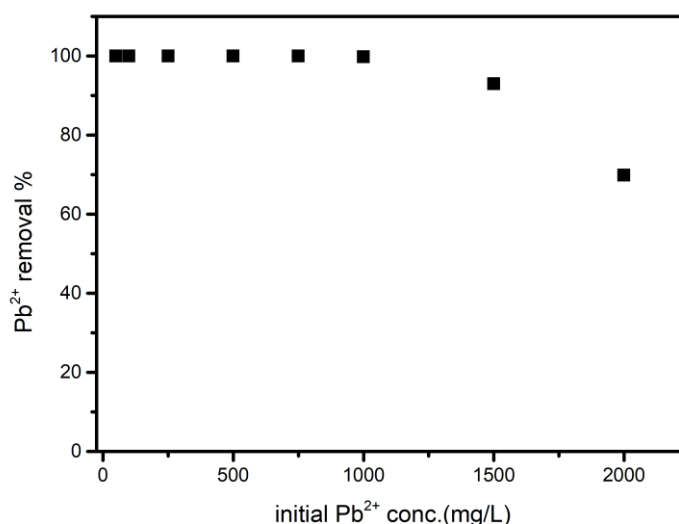


Fig. 3.18: Percentage removal of Pb^{2+} by the ZG-60 at various initial concentrations Pb^{2+} contaminated solutions.

The removal efficiency (expressed as a percentage) of ZG-60 was then evaluated for Pb^{2+} solutions with initial concentrations ranging from 50 to 2000 mg/L, using Equation 3.17, and is illustrated in Fig. 3.18. For initial Pb^{2+} concentrations of up to 750 mg/L, the final equilibrium concentration after adsorption is zero, demonstrating a removal efficiency of 100%. At an initial Pb^{2+} concentration of 1000 mg/L, 99.76% of the lead was removed, resulting in a residual concentration of only 2.42 mg/L. The removal efficiency of solutions with 1500 mg/L of Pb^{2+} was 93%, yielding a final concentration of 105 mg/L. At the highest tested concentration of 2000 mg/L, the removal efficiency was 69.86%, with a residual Pb^{2+} concentration of 602.7 mg/L. These results demonstrate the exceptional efficiency of ZG-60 in removing Pb^{2+} from

aqueous solutions, achieving nearly complete removal for concentrations up to 1000 mg/L and maintaining significant efficiency even at higher initial concentrations.

Further, the amount of adsorbate the adsorbent can hold is calculated using equation 3.18 and is graphically represented in Fig. 3.19. As shown, the amount of Pb^{2+} adsorbed by ZG-60 (q_e) increases steadily with the initial Pb^{2+} concentration, reaching 1395 mg/g at 1500 mg/L. At the highest tested concentration of 2000 mg/L, q_e slightly increases to 1397.3 mg/g, indicating that the maximum adsorption capacity of ZG-60 is approximately 1.4 g/g. In other words, 1 gram of ZG-60 can extract and retain about 1.4 grams of Pb^{2+} from the solution, meaning the adsorbate mass exceeds that of the adsorbent itself. This suggests that the adsorption mechanism may not be limited to simple surface adsorption alone, as it is unlikely for a conventional adsorbent to hold more than its weight in adsorbate.

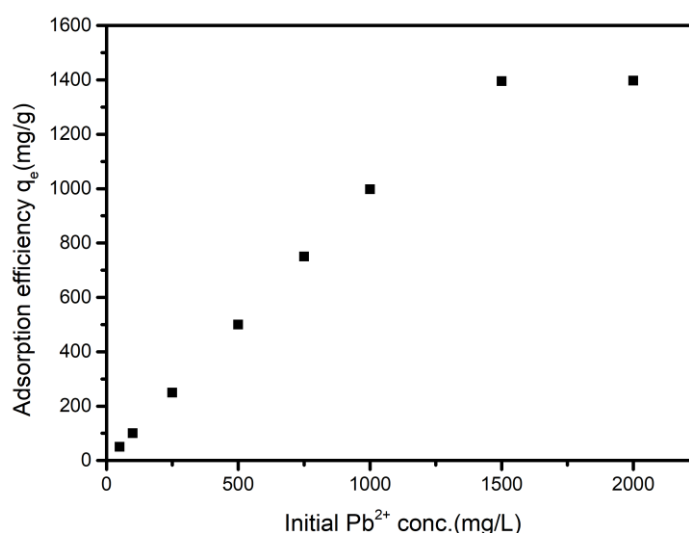


Fig. 3.19: Lead fixation capacity (adsorption efficiency) of ZG-60 under different initial Pb concentrations (initial Pb concentrations: 50, 100, 500, 750, 1000, 1500, and 2000 mg/L, reaction time: equilibrium; adsorbent dosage: 1 g/L).

Interestingly, after reaching equilibrium, the solid material recovered from the Pb^{2+} contaminated solution exhibited a noticeable increase in volume and a distinct colour change. The photographs of ZG-60 before and after adsorption, shown in Fig. 3.20, reveal a significant expansion in volume and a shift in colour from black to grey. These observations suggest the formation of a new secondary lead-containing solid phase upon the interaction of the ZnO/rGO composite with the Pb^{2+} solution. Based on

these results, we hypothesize that the dominant removal mechanism is not limited to surface adsorption but rather a combined adsorption–precipitation process. The exceptionally high q_e value, along with the physical changes in the adsorbent, supports this hypothesis. In this mechanism, Pb^{2+} ions are extracted from the solution and immobilized through the formation of insoluble Pb-bearing precipitates, leading to effective and stable lead removal. The size of this secondary phase depends on the initial lead concentration. The secondary phase is nanosized at low concentrations, whereas at higher concentrations, it grows into larger precipitates.

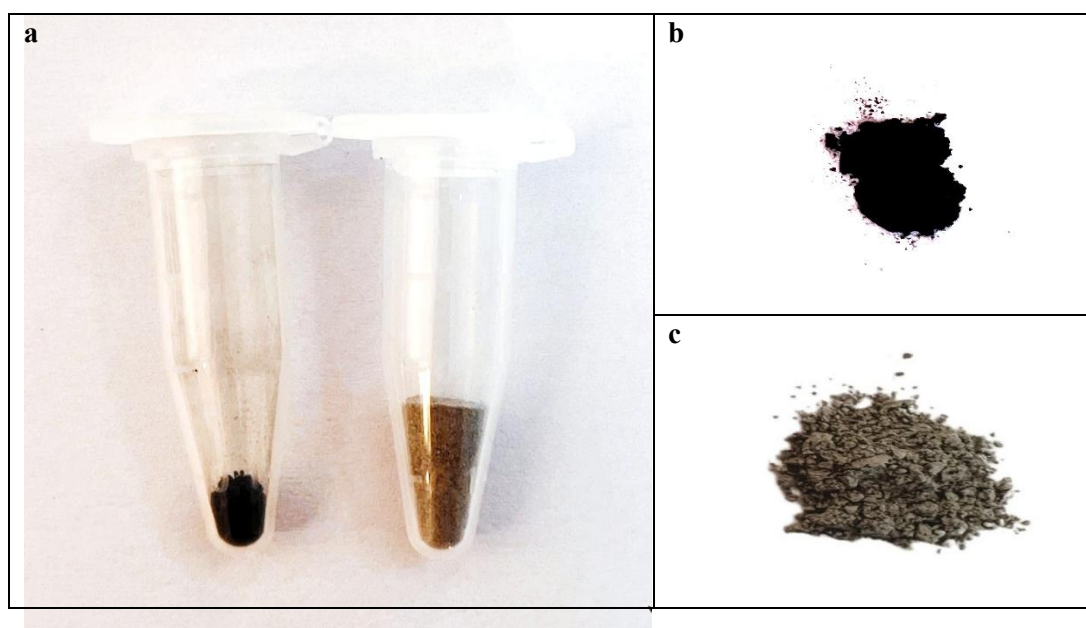


Fig. 3.20: (a) Image showing the volume change of ZG-60 before and after interaction with the lead-bearing solution; (b, c) Images illustrating the colour change of ZG-60 before and after interaction with the lead-bearing solution.

3.3.3.5 Analysis of post adsorbent

The characterization of the post-adsorbent could shed light on the mineralogical changes that occurred during the lead adsorption-precipitation reaction. The structural, morphological, and compositional properties of the solid material collected after the adsorption were analysed using XRD, FE-SEM, EDS, HR-TEM, and XPS techniques.

3.3.3.5.1. Structural analysis by XRD

The XRD analysis provides valuable insights into the crystallization products formed during the lead adsorption by ZnO/rGO composites. The diffraction patterns of ZG-60 before and after adsorption are shown in Fig. 3.21. The XRD spectra of post-

adsorbed ZG-60 displayed characteristic peaks for ZnO, along with additional sharp and intense peaks corresponding to lead carbonate hydroxide ($\text{Pb}_2\text{CO}_3 \cdot \text{Pb}(\text{OH})_2$), commonly known as hydrocerussite. The prominent diffraction peaks for hydrocerussite appear at 19.92° , 20.95° , 24.68° , 27.14° , 34.49° , 40.38° , and 53.83° , as confirmed by the JCPDS database card (13-0131) [47,143, 144]. Hydrocerussite is a lead carbonate mineral known for its high stability under ambient conditions and low solubility in water [145]. The presence of these well-defined peaks strongly supports the adsorption-precipitation mechanism of lead removal, where Pb^{2+} ions are extracted and transformed into a highly crystalline solid phase on the ZnO/rGO composite surface.

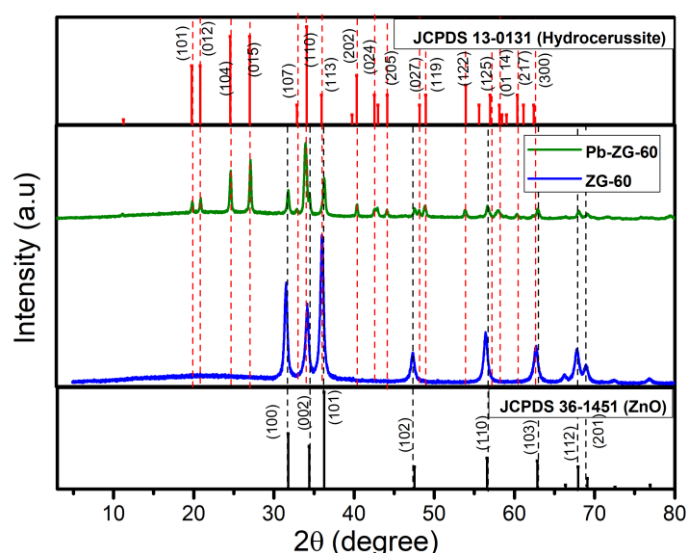


Fig. 3.21: X-ray powder diffraction patterns of ZnO/rGO composite before (ZG-60) and after interaction with Pb-bearing solution (ZG-60-Pb).

To understand more about the lead removal mechanism by ZnO/rGO composite, XRD analysis was performed on post-adsorption samples of rGO, ZG-30, ZG-60, and ZG-100, as shown in Fig. 3. 22. The XRD pattern of rGO does not exhibit peaks corresponding to lead compounds, consistent with its limited lead removal efficiency through a pure adsorption mechanism without precipitation. In contrast, the spectra of ZnO/rGO composites display characteristic peaks for ZnO along with additional peaks attributed to hydrocerussite. These results strongly support the hypothesis that lead removal in this system primarily occurs through adsorption, followed by precipitation

of Pb^{2+} as crystalline hydrocerussite onto the ZnO/rGO composites. ZnO serves as the key reactive component, driving the process and enabling the immobilisation of lead.

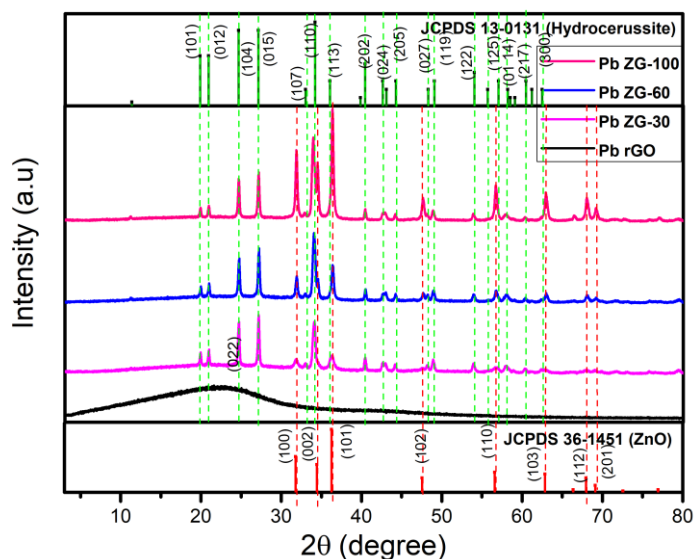


Fig. 3.22: X-ray powder diffraction patterns of ZG-100, ZG-60, ZG-30, and rGO after interaction with Pb-bearing solutions.

Notably, in the spent ZG-100 sample (Pb–ZG-100), the hydrocerussite peaks are relatively weak compared to the prominent ZnO peaks, which can be attributed to the high crystallinity of ZnO and a comparatively lower extent of lead precipitation. On the other hand, the XRD spectra of Pb–ZG-30 and Pb–ZG-60 exhibit much stronger hydrocerussite peaks relative to ZnO, indicating more effective lead immobilization. These results further support the hypothesis that lead removal in this system primarily occurs through adsorption, followed by precipitation of Pb^{2+} as crystalline hydrocerussite onto the ZnO/rGO composites. ZnO serves as the key reactive component driving the process, enabling the immobilization of an amount of lead exceeding its weight. Further details on the lead removal mechanism are discussed in Section 3.3.3.6.

3.3.3.5.2 Morphological analysis by FE-SEM imaging

Fig. 3. 23 presents the morphological analysis of the most efficient adsorbent, ZG-60, after interaction with Pb^{2+} solution. The formation of a distinct hexagonal plate-like solid phase is clearly observed, indicating the development of a new secondary phase. This morphology aligns with the reported structure of hydrocerussite, which

crystallizes in a hexagonal form, thereby confirming that Pb^{2+} removal occurs via precipitation as hydrocerussite facilitated by the ZnO/rGO composite.

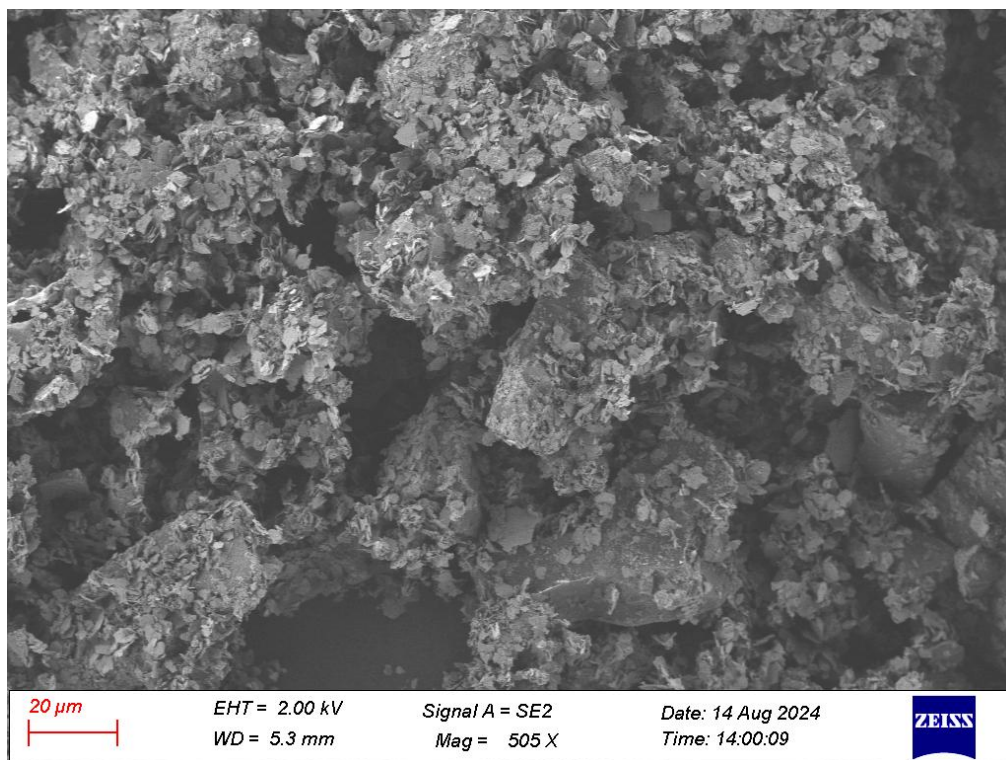


Fig. 3.23: FE-SEM image of ZG-60 after interaction with Pb^{2+} contaminated water in low magnification.

To facilitate comparison, the results of pristine ZG-60 and spent ZG-60 (Pb ZG-60) are displayed side by side. Figures 3.24 (a), (c) and, (e) show FE-SEM images of ZG-60, while Figures 3.24 (b), (d) and, (f) depict Pb ZG-60 at different magnifications. The FE-SEM images of pristine ZG-60 reveal the uniform distribution of nanosized ZnO particles over the rGO sheets. However, after Pb adsorption, Pb ZG-60 undergoes a distinct morphological transformation, demonstrating the formation of hexagonal hydrocerussite crystals with ultrathin thickness, distinctly different from the pristine ZG-60 structure. The precipitation and growth of micrometer-sized hydrocerussite crystals observed in these images strongly support the adsorption-precipitation mechanism of lead removal, which is also confirmed by the quantitative ICP-OES and XRD results. The SEM images further illustrate that after Pb^{2+} adsorption, the adsorbent surface is densely covered with micron-sized hexagonal plate-like structures. This observation aligns well with the adsorption efficiency calculations, which reveal that 1

g of ZG-60 can successfully remove approximately 1.4 g of Pb by forming a solid precipitate.

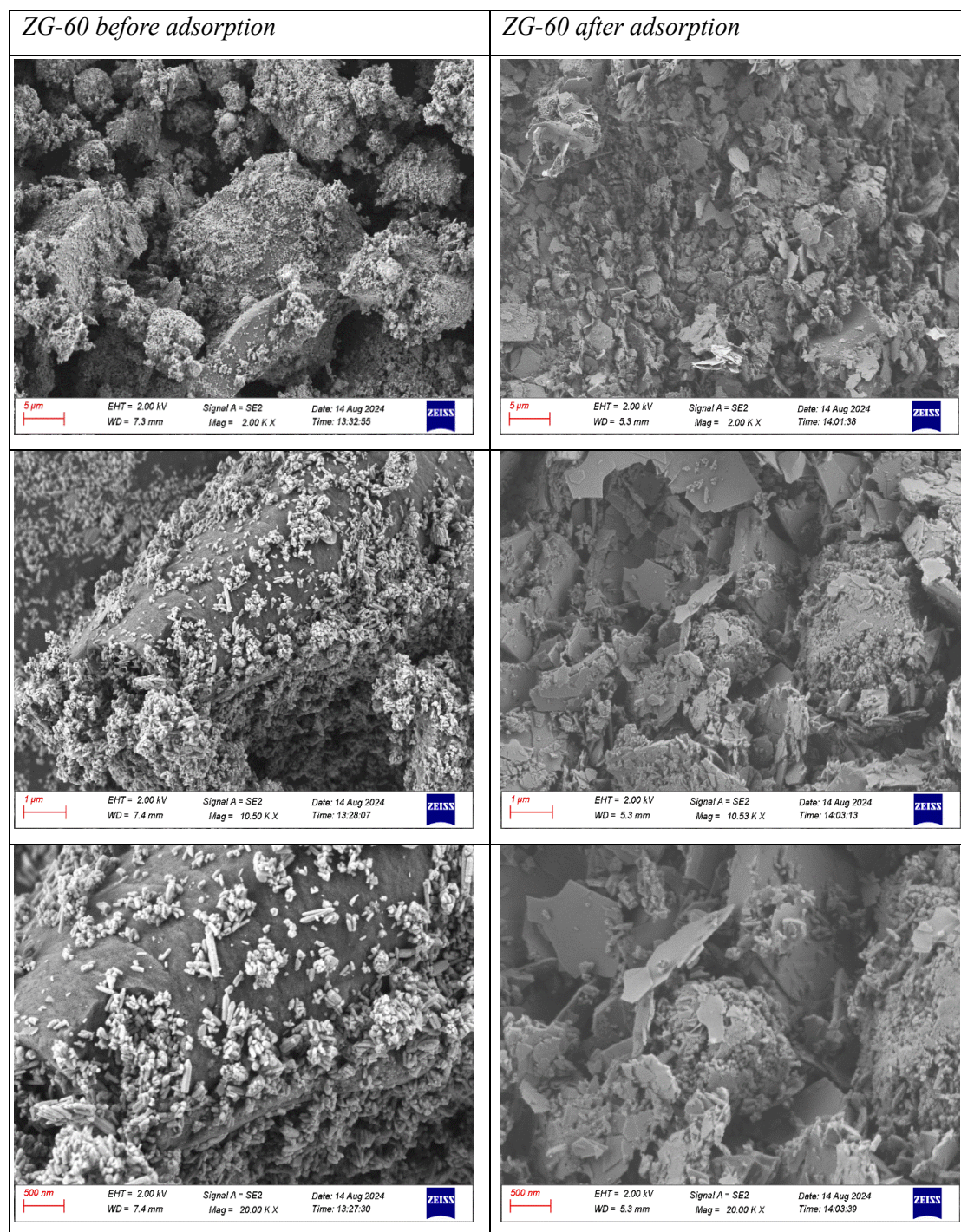


Fig. 3.24: FE-SEM images of ZG-60 (a, c, e) and hydrocerussite-bearing ZG-60 (b, d, f) at different magnifications. For easier comparison, images at the same magnifications for ZG-60 and ZG-60-Pb are placed side by side.

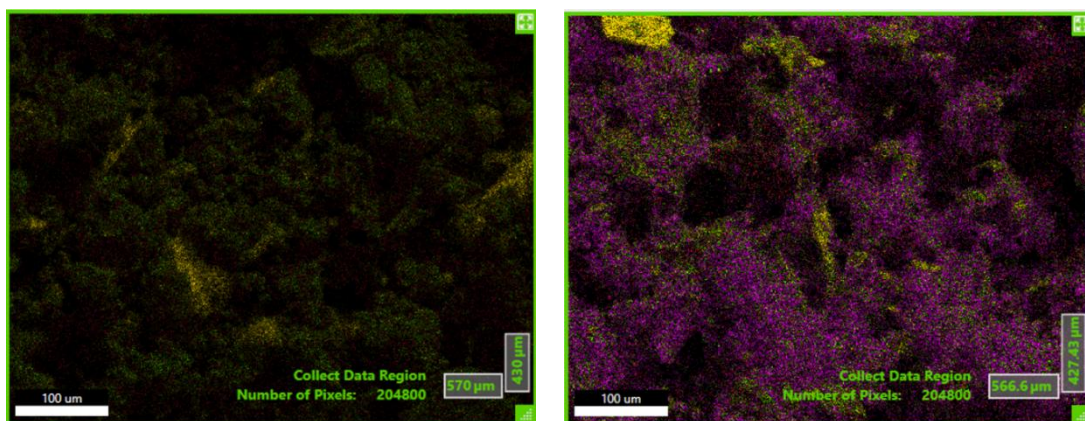


Fig. 3.25: Superimposed elemental mapping images of (a) ZG-60 and (b) ZG-60-Pb, with colours representing Yellow for carbon, Green for oxygen, Red for zinc, and Pink for lead.

Figures 3.25 (a) and (b) display EDS mapping images of ZG-60 and Pb ZG-60, respectively. The mapping image of pristine ZG-60 exhibits a uniform distribution of colours corresponding to carbon, oxygen, and zinc. In contrast, Pb ZG-60 shows a predominant pink colouration corresponding to lead, signifying the bulk formation of Pb-bearing hydrocerussite precipitate. (The yellow colour in the top corner originates from the carbon tape used during the imaging process and is unrelated to the adsorbent composition.)

3.3.3.5.3 Morphological analysis by TEM imaging

Further morphological analysis by TEM of ZG-60 and Pb ZG-60 reveals results consistent with the FE-SEM analysis. Figures 3.26 (a) and (b) depict the TEM images of the ZnO/rGO composite, ZG-60. The images illustrate nanosized ZnO particles trapped and embedded within rGO sheets. The ZnO particles are uniformly dispersed in the rGO sheets, rGO is observed as lighter regions. rGO acts as a scaffold-like structure that supports the ZnO particles. The overall morphology of ZG-60 exhibits a loosely packed structure, with ZnO particles dispersed across the rGO framework.

In contrast, after Pb adsorption, the morphology undergoes a significant transformation. The TEM images of Pb ZG-60 (Figures 3.26 (c) and (d)) reveal a much denser structure with more defined shapes, signifying the formation of a secondary lead-bearing solid structure. The post-adsorption structure transitions into a bulk-like morphology characterised by densely packed crystalline hydrocerussite formations. These hexagonal platelets aggregate, creating a compact and dense structure compared

to the open, dispersed morphology of pristine ZG-60. This structural transition provides direct evidence of the precipitation and growth of hydrocerussite on the adsorbent surface.

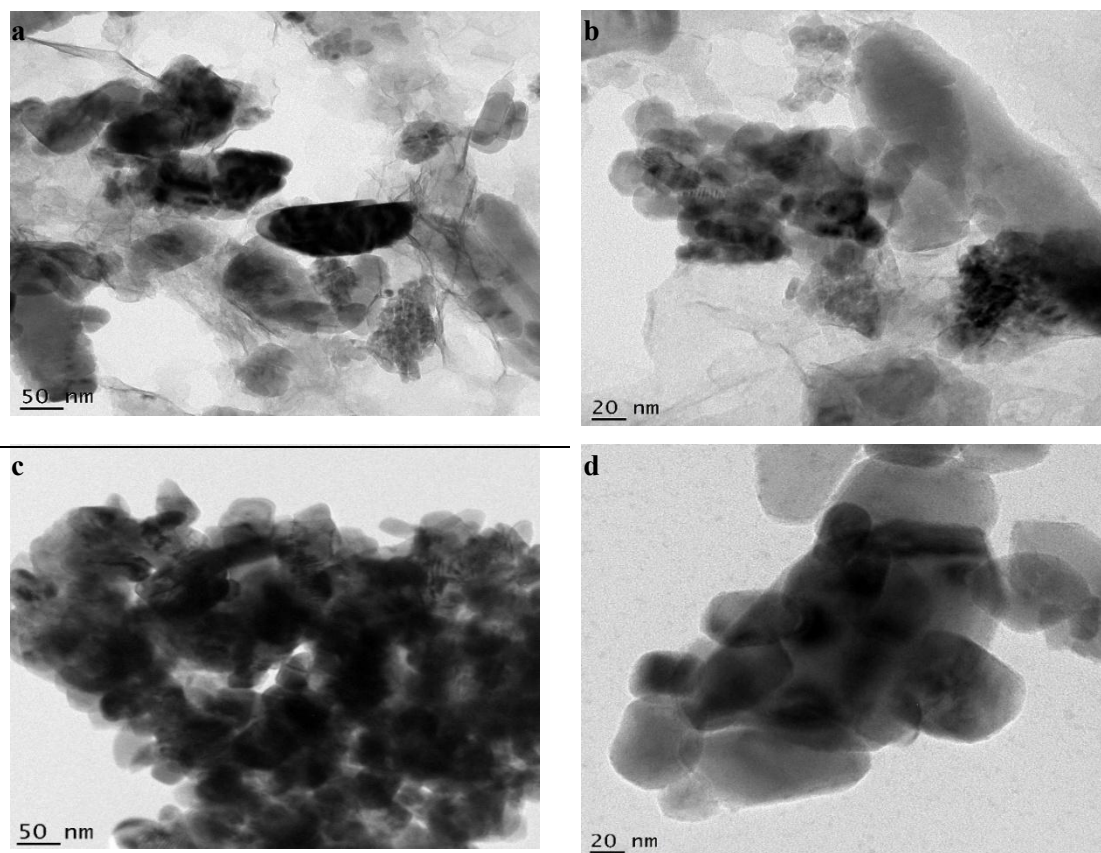


Fig. 3.26: TEM images of (a,b) ZG-60 at different magnifications, (c,d) solid after reaction with lead aqueous solution (ZG-60-Pb) at different magnifications.

3.3.3.5.4 XPS analysis

X-ray Photoelectron Spectroscopy (XPS) was employed to analyse the elemental composition and chemical states of ZG-60 and ZG-60-Pb by measuring electron binding energies. The survey spectrum, depicted in Fig. 3.27, reveals distinct peaks corresponding to carbon (C 1s), oxygen (O 1s), and zinc (Zn 2p) in ZG-60. The C 1s and O 1s peaks are located at 284 eV and 530 eV, respectively. The Zn 2p peak appears as a doublet (Zn 2p_{3/2} and Zn 2p_{1/2}) due to spin-orbit coupling, with binding energies at 1021.42 eV and 1044.03 eV, respectively [146,147]. Additionally, the spectrum displays Zn LMM Auger lines.

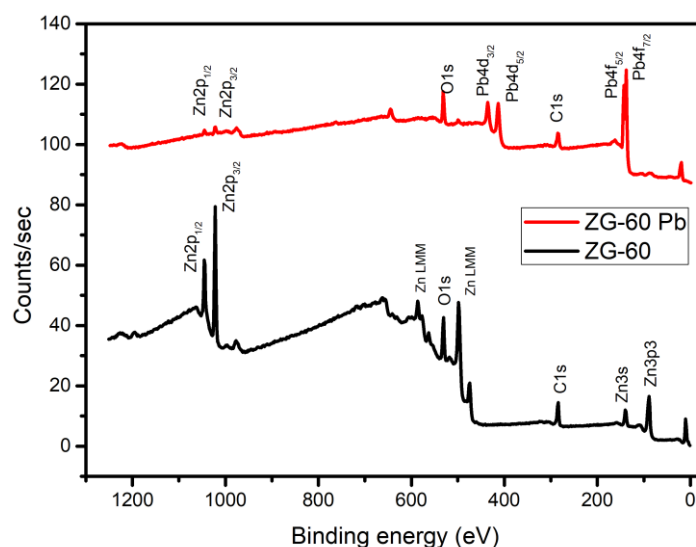


Fig. 3.27: XPS survey spectra of adsorbent before (ZG-60) and after (ZG-60-Pb) reaction with lead aqueous solution.

For ZG-60 Pb, additional peaks corresponding to lead (Pb 4f and Pb 4d) are observed. The Pb 4f peaks appear as a doublet with binding energies at 140.18 eV (Pb 4f_{7/2}) and 141.56 eV (Pb 4f_{5/2}) [47,141], while the Pb 4d peaks are located at 412.96 eV (Pb 4d_{5/2}) and 434.47 eV (Pb 4d_{3/2}) [148]. These new peaks confirm the successful adsorption of Pb onto the composite. Notably, the intensity of Zn-related peaks is weaker in ZG-60 Pb, indicating the substantial presence of Pb in the spent adsorbent. Also, it could suggest the dissolution of Zn ions from the ZnO/rGO composite during interaction with the Pb ion solution. A detailed explanation of Zn²⁺ dissolution during this process is provided in section 3.3.3.6.

3.3.3.5.5 Stability test of post adsorbent bearing Pb mineral

The adsorption process involving surface precipitation reaction was found to be irreversible. To assess the stability of the lead-bearing precipitate under various conditions, a series of tests was conducted. The post-adsorbent was thoroughly dispersed in distilled water, and the solution, after removing solid particles, was analysed for desorbed lead ions. The results were notable, as the lead concentration in the solution fell below the instrument's detection limit, indicating that no desorbed ions were present. To further evaluate stability, the same solution containing the post-adsorbent was magnetically stirred for 3 hours at 500 rpm at room temperature. Testing the solution again for desorbed Pb ions revealed no detectable lead ions, indicating the

strong stability of the precipitated lead compound. The test was repeated under more stringent conditions by stirring the solution for an additional 3 hours at 50°C. Even under these conditions, the lead concentration remained undetectable. These results confirm that the lead precipitate formed on the ZnO/rGO composite surface is highly stable, ensuring both effective lead removal and safe immobilization. This demonstrates the potential of the process for reliable lead extraction and environmentally secure disposal from contaminated solutions.

3.3.3.6 Proposed mechanism of lead removal

The mechanism of Pb removal by the ZnO/rGO composite (ZG-60) was investigated by monitoring the changes in concentration of Pb and Zn ions in a solution of high initial Pb concentration of 1500mg/L upon interacting with a relatively low adsorbent dosage of 1g/L over time. Fig. 3.28 illustrates the variation in lead concentration in the lead-bearing solution during its interaction with the adsorbent ZG-60 along with the corresponding release of zinc ions into the solution. The trends reveal a notable inverse relationship: as Pb is progressively removed from the solution, Zn ions are concurrently released. This inverse relationship suggests that the mechanism of lead removal involves an ion exchange process where Zn^{2+} ions from the ZG-60 composite are released into the solution as Pb^{2+} ions are taken up.

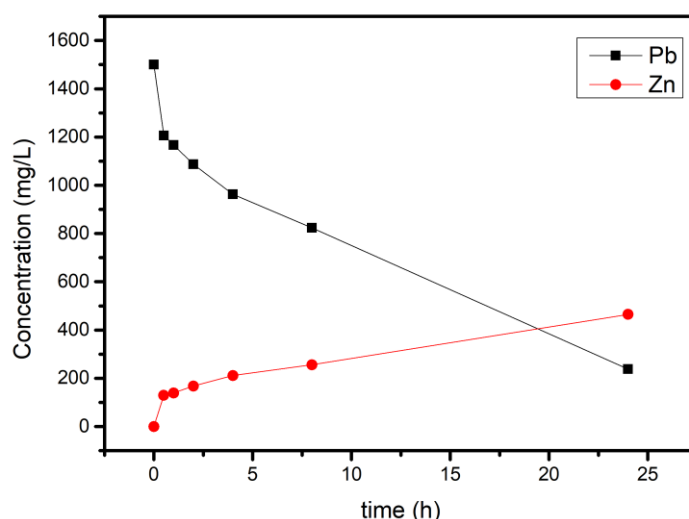


Fig. 3.28: The Pb and Zn concentration changes in the aqueous solution over time during lead removal study (adsorbent: ZG-60, initial Pb ion concentration: 1500 mg/L; adsorbent dosage: 1g/L; without pH adjustment).

During the initial 30 minutes, the Pb concentration exhibits a sharp decline, indicating rapid adsorption. This is followed by a more gradual decrease, suggesting a slower removal phase. A similar but opposite trend is observed for Zn, where the concentration increases at the beginning and then stabilises at a slower rate. These observations strongly suggest an ion exchange process where Pb^{2+} ions replace Zn^{2+} ions on the surface of the ZG-60 adsorbent. The displaced Zn^{2+} ions are released into the solution, while Pb^{2+} ions become immobilised, forming a solid phase on the composite surface. Notably, the amount of Zn^{2+} released into the solution is relatively low compared to the total Pb^{2+} removed, indicating that only a small fraction of ZnO participates in the ion exchange process.

A control experiment was performed to confirm that the release of Zn ions is specifically triggered by the presence of Pb^{2+} and not due to spontaneous leaching. ZG-60 was stirred in deionised water under identical conditions (same adsorbent dose, contact time, and stirring speed) for 30 minutes, 1 hour, and 4 hours. The supernatant was then analysed for Zn content. In all cases, Zn concentrations were below the detection limit of the instrument, indicating that the composite does not spontaneously release Zn^{2+} ions in the absence of Pb^{2+} . This strongly affirms that Zn release in the presence of Pb is due to a reactive ion exchange process rather than leaching, pointing towards the dissolution-precipitation mechanism of lead removal.

Similar observations have been reported in the literature, where the dissolution–precipitation mechanism plays a key role in Pb removal. For example, in ball-milled serpentine used as an adsorbent, Mg^{2+} is replaced by Pb^{2+} , followed by subsequent precipitation of hydrocerussite, effectively immobilizing Pb [47]. Similarly, in nitrogen-doped magnesium oxide-modified biochar, the ion exchange between Mg^{2+} and Pb^{2+} initiates hydrocerussite formation [48]. In another study using MgO@ZnO@BC (biomass carbon), Pb^{2+} is fixed through ion exchange with Mg^{2+} and Zn^{2+} released from the MgO and ZnO phases, which triggers the formation of lead carbonate minerals [49]. Other studies have also reported the dissolution–precipitation mechanism as a key pathway in Pb immobilization [41, 50, 149].

Our proposed mechanism for lead (Pb^{2+}) removal by the ZG-60 composite involves a combination of adsorption, ion exchange, and subsequent precipitation. As revealed by TEM imaging, ZnO nanostructures are uniformly dispersed and highly

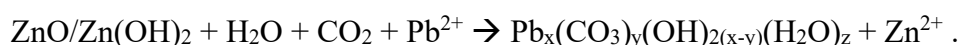
exposed across the surface of the rGO sheets, offering abundant active sites for interaction. This structural arrangement plays a critical role in the initial stage of the removal process. At the initial stage of the adsorption process, the high surface availability of ZnO facilitates a rapid ion exchange, where Pb^{2+} ions from the solution replace Zn^{2+} ions at the surface of the composite. This exchange occurs primarily within the first few atomic layers of the ZnO lattice. The displaced Zn^{2+} ions are released into the solution, while the Pb^{2+} ions nucleate on the surface of the composite to form a new solid Pb-bearing phase. Over time, these nucleated Pb phases—identified as hydrocerussite—undergo crystallization and continue to grow by incorporating additional Pb^{2+} directly from the solution. This growth does not involve further ion exchange but rather a precipitation process, which contributes significantly to the continued reduction of Pb^{2+} concentration in the solution. As the surface becomes progressively coated with hydrocerussite, the accessibility of ZnO sites decreases, and the ion exchange rate slows down. Eventually, a saturation point is reached where further Zn dissolution is minimal.

As shown in Fig. 3.28, the concentration of Zn^{2+} released into the solution is relatively low compared to the total amount of Pb^{2+} removed, suggesting that only a minor portion of ZnO is involved in the ion exchange process. This discrepancy confirms that most of the Pb^{2+} is immobilized through the precipitation and growth of hydrocerussite rather than solely via Zn^{2+} substitution. FE-SEM (Fig. 3. 24 b,d,f) and TEM (Fig. 3.26 c,d) images clearly show the formation of microcrystals covering the surface of the composite after adsorption, which is identified as hydrocerussite based on XRD analysis. This two-step process—initial ion exchange followed by surface nucleation and crystal growth—proves highly effective. A large quantity of the highly toxic Pb^{2+} is removed from the solution, while only a small amount of the less toxic Zn^{2+} is introduced. This not only ensures efficient contaminant removal but also minimizes secondary pollution.

The efficiency of this mechanism is reflected in the exceptionally high adsorption capacity. The adsorption efficiency calculated from the data shown in Fig. 3.28, the ZG-60 composite achieves a maximum Pb^{2+} uptake of approximately 1400 mg/g at an initial concentration of 1500 mg/L, which exceeds the weight of the adsorbent itself. Similar trends are observed in the concentration studies (Fig. 3.19), where the adsorption capacity plateaus at around 1400 mg/g at the initial Pb

concentrations of 1500 mg/L and 2000 mg/L. These results suggest that the high adsorption capacity is not due to surface exchange alone but to the subsequent growth of Pb-bearing precipitates, which effectively utilize the excess Pb^{2+} in solution. The volume increase and distinct colour change of the adsorbent after Pb removal visually support this transformation. In summary, Pb^{2+} removal occurs via a synergistic mechanism involving surface ion exchange and the formation of stable Pb precipitate hydrocerussite, making ZG-60 a promising material for treating lead-contaminated water.

Several studies have reported that adsorbents containing carbonate (e.g., calcite, aragonite, marble) and sulphate phases (e.g., gypsum, anhydrite) promote Pb removal through the formation of corresponding precipitates such as cerussite/hydrocerussite (lead carbonate/lead carbonate hydroxide) and anglesite (lead sulphate) [132,149, 150]. In these cases, the carbonate and sulphate groups are inherent to the adsorbent structure, and the dominant removal mechanism is identified as dissolution–precipitation. However, similar mechanisms have also been observed in adsorbents lacking carbonate and sulphate groups. For example, Min Chen et al. reported the use of serpentine mineral as an adsorbent and suggested that lead carbonate precipitation occurs even in the presence of very dilute atmospheric CO_2 . They explained that CO_2 from the air–water interface dissolves to form H_2CO_3 , which dissociates into HCO_3^- and CO_3^{2-} . At the solid–liquid interface, unstable lead hydroxide converts into more stable basic lead carbonate in the presence of this dissolved CO_2 [47]. In another study, Hongru Shang et al. investigated Pb sorption using nitrogen-doped magnesium oxide-modified biochar. They proposed a combined mechanism involving ion exchange, precipitation, and additional interactions between Pb^{2+} and surface functional groups. They experimentally demonstrated that the carbonate (CO_3^{2-}) involved in hydrocerussite precipitation originated from atmospheric CO_2 . Their proposed reaction mechanism aligns closely with our observations of hydrocerussite formation. Based on their findings, we formulated a reaction that reflects the conditions of our system:



This reaction represents a combined ion exchange and precipitation mechanism [48].

Other studies have also highlighted the key role of atmospheric CO_2 in promoting lead immobilization via carbonate precipitation [133,149].

Moreover, ZnO has been reported to exhibit carbon fixation capabilities, which may also play a role in carbonate formation [151]. In addition, carbon originating from sucrose-derived rGO and residual impurity carbon could further contribute to the formation of carbonates.

3.3.3.7 Effect of Light on Pb removal.

As reported in our previous studies, the ZnO/rGO composite used in this work exhibits high photoactivity under visible light, demonstrating effective dye degradation [146]. Further, in the Cr(VI) removal, visible light irradiation enhanced the removal performance [44]. Thus, we investigated the effect of light on the Pb removal performance of the most efficient adsorbent, ZG-60. To investigate the influence of light on the adsorption–precipitation mechanism of lead removal, experiments were conducted under three conditions: xenon lamp irradiation, ambient laboratory light, and complete darkness. It is reported that the solution temperature can influence adsorption processes [140]. Higher temperatures increase ion mobility, enhance interaction with active adsorption sites, and reduce the viscosity and density of the solution, thereby improving mass transfer [24]. The light source used in the experiment was a xenon lamp, which emits a spectrum similar to solar light, including radiation in the infrared (IR) region. During the experiment with light irradiation, it was found that the IR component heats the solution and raises the solution temperature to 35°C. To determine whether this IR-induced heating alone accounted for the observed efficiency enhancement upon light irradiation, a control experiment was conducted in complete darkness with the solution maintained at 35 °C. For experimental convenience and to observe the minor changes in lead removal under different light conditions, the Pb²⁺ concentration in the test solution was set to 1500 mg/L, and the reaction time was decreased to 3 hours.

The results in Fig. 3.29 demonstrate that the removal efficiency was highest under light irradiation, followed by laboratory light, and lowest in complete darkness. This clearly indicates a notable enhancement in lead removal under light irradiation. The results also depicted that Pb²⁺ removal efficiency in the “Dark at 35 °C” condition was higher than in room-temperature darkness but significantly lower than under xenon lamp irradiation. This confirms that the observed enhancement in lead removal in light

irradiation is primarily due to the photo response of the ZnO/rGO composite rather than thermal effects.

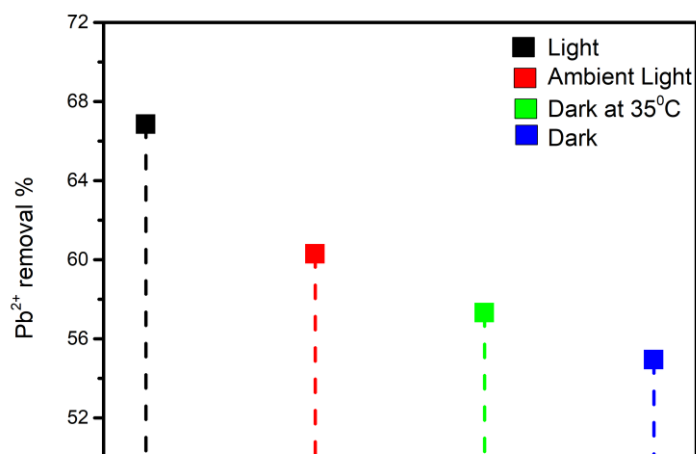


Fig. 3.29. Effect of light on Pb²⁺ removal by ZG-60 under xenon lamp irradiation in comparison with ambient laboratory light, complete darkness, and a solution maintained at 35 °C in the dark. (initial Pb ion concentration: 1500 mg/L; reaction time: 3h; adsorbent dosage: 1g/L)

Based on these findings, it can be inferred that, in the absence of light, lead removal proceeds primarily via chemical interactions between Pb²⁺ ions and Zn²⁺ in the ZnO lattice. The oxygen-containing functional groups (e.g., hydroxyl, phenolic) and defects on the rGO sheets facilitate electron sharing and transfer [49,152]. The slight increase in removal efficiency at elevated temperatures in darkness supports the role of thermally enhanced ion mobility.

However, ZnO is a well-known photoactive semiconductor. Upon light exposure, photogenerated electrons and holes are generated, and Zn²⁺ enters a high-energy excitonic state [53]. These photo-excited species can actively participate in the chemical processes involved in lead removal. Notably, our results indicate that the first stage of lead removal involves ion exchange between Pb²⁺ and Zn²⁺. In the excitonic state, Zn²⁺ is more reactive and may exchange more readily with Pb²⁺, explaining the enhanced removal under light. Additionally, rGO serves as a supporting material by enhancing light absorption, providing a large surface area, and suppressing charge

carrier recombination—further boosting the photoactivity of the composite [109,153,154,155].

Under ambient laboratory light, the intensity and spectral overlap with the absorption range of ZnO are limited yet sufficient to generate a measurable increase in removal efficiency over dark conditions. Under xenon lamp irradiation, the absorbable portion of the spectrum is much broader and more intense, resulting in a significantly greater generation of charge carriers and a larger population of Zn^{2+} in the excitonic state, which further boosts lead removal efficiency.

In conclusion, the ZnO/rGO composite exhibits a substantial enhancement in lead removal under light irradiation due to its photoactive nature. These results underscore the potential of light-assisted adsorption–precipitation strategies and encourage further investigation into the role of photoactivation in heavy metal remediation.

3.4 Conclusions

Heavy metal pollution is a critical environmental issue that endangers water and soil quality, posing significant risks to ecosystems and human health. Contamination of water bodies by heavy metals from various industrial activities is a major contributor to the global scarcity of clean water. To mitigate this issue, the development of low-cost and effective adsorbents for heavy metal removal is essential. Reduced graphene oxide (rGO)-based composites have shown great promise as efficient adsorbents.

In this chapter, we explored the adsorptive removal of hexavalent chromium (Cr(VI)) and lead (Pb) using a ZnO/rGO composite synthesized via a green, single-step method employing zinc acetate and sucrose as precursors. The major conclusions drawn from this study are summarized below.

Chromium

- The Cr(VI) adsorptive removal efficiency of the samples was investigated in batch mode using UV-Visible spectral analysis and the ICP-OES analytical technique, all samples, except pure ZnO, demonstrated measurable Cr(VI) adsorption.
- Among the ZnO/rGO nanocomposites, ZG-40 demonstrated superior adsorption efficiency when exposed to acidic Cr(VI) solutions.

- The adsorption capacity of ZG-40 on Cr(VI) is 13.5 mg/g, which is five times higher than pure rGO.
- Kinetic studies confirmed pseudo-second-order behaviour, indicating chemisorption as the dominant mechanism.
- The kinetic data analysis also fitted well with the intraparticle diffusion model, indicating that intraparticle diffusion is the rate-limiting step.
- Zeta potential analysis showed that the adsorbent surface acquires a positive charge under acidic conditions, promoting electrostatic attraction with anionic Cr(VI) species.
- BET analysis confirmed pore filling during the adsorption process.
- XPS revealed partial reduction of Cr(VI) to Cr(III), with 60% of bound chromium present as Cr(III).
- The overall adsorption mechanism involves electrostatic interaction, surface complexation (chemisorption), pore filling, and partial reduction.
- Light-assisted experiments demonstrated a photocatalytic contribution from ZnO in the adsorption process.
- The ZnO/rGO composite, synthesized via a cost-effective and scalable route, exhibits Cr(VI) removal performance.

Lead (Pb)

- Lead (Pb) pollution poses a severe threat to ecosystems and human health due to its high toxicity and persistence.
- Controlling the bioavailability of Pb is crucial for mitigating its environmental and biological impact.
- This study investigates the immobilisation of Pb²⁺ ions from contaminated water using ZnO/rGO composite.
- Unlike Cr(VI) adsorption, ZnO played a dominant role in Pb²⁺ removal, with rGO significantly enhancing overall efficiency.
- The adsorption process was analysed by monitoring changes in Pb²⁺ concentration in the contaminated water and examining mineralogical transformations in the spent adsorbent.
- Results confirmed an adsorption–precipitation mechanism as the primary pathway for Pb removal.

- The most effective adsorbent, ZG-60, exhibited an exceptional Pb adsorption efficiency of 1400 mg/g (1 gram of ZG-60 can hold 1.4 grams of Pb), evidenced by significant changes in the volume and colour of the post-adsorbent.
- The value indicates that 1 g of the material could accommodate an amount of Pb more than its weight on its surface.
- At a low dosage of 1 g/L, ZG-60 completely removed Pb^{2+} from solutions across a broad concentration range (up to ~1000 mg/L).
- XRD analysis confirmed the formation of lead carbonate hydroxide (hydrocerussite, $\text{Pb}_2(\text{CO}_3)\text{Pb}(\text{OH})_2$) as a secondary phase, demonstrating an adsorption-precipitation mechanism of Pb removal.
- FE-SEM imaging revealed hexagonal, flake-like hydrocerussite structures uniformly covering the adsorbent surface.
- TEM images demonstrated the dense accumulation of precipitate, further supporting the adsorption-precipitation mechanism.
- The composite maintained >80% efficiency across all pH levels, demonstrating its robustness under varying environmental conditions.
- The lead-laden ZnO/rGO composite exhibited high retention capacity, facilitating its safe disposal thereby, reducing the bioavailability of lead.
- Overall, the ZnO/rGO composite demonstrates exceptional potential as a cost-effective, scalable, and highly efficient material for lead remediation in contaminated water.

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Chapter IV

Evaluation of Antibacterial Activity of rGO and rGO/ZnO Composites on Diverse Bacterial Strains

Abstract

Antibacterial agents are essential to maintain the health of living beings. The misuse and overuse of antibiotics have led to the development of resistance against antibiotics in microbes. To address this issue, efficient, cost-effective, and biocompatible alternatives for conventional antibiotics need to be developed. Reduced graphene oxide (rGO), ZnO, and their composite have been identified as being efficient in disinfecting bacterial strains. The antibacterial efficiency of the samples rGO and the composites ZG-10, ZG-40, ZG-60, and ZnO (ZG-100) was evaluated against gram-positive and gram-negative bacterial strains using the agar disc diffusion method. The samples showed remarkable bactericidal activity against all the tested bacterial strains, and their zone of inhibition was comparable to that of conventional antibiotics. Different samples are proven to be effective for different bacterial strains. The sample rGO was found to be more efficient in inhibiting *E. coli* with a zone of inhibition of 19.5 mm, whereas the ZG-10 composite exhibited superior efficiency against *P. aeruginosa* with a zone of inhibition of 20.5 mm. The sample ZG-100 showed high disinfection efficiency against *S. aureus* and *S. enteritidis* with zones of inhibition of 22.8 and 23 mm, respectively. The minimum inhibitory concentration and cytotoxicity of the samples were also tested. From the analysis, the tested samples demonstrate strong antibacterial efficacy and less cytotoxicity, positioning them as a promising material for biomedical applications.

4.1 Introduction

The use of antibiotics to combat bacterial infections is essential for maintaining the health of living organisms. However, the widespread abuse and overuse of antibiotics in human, animal, and plant healthcare have led to the emergence of drug resistance or antibiotic resistance [1,2], posing one of the most severe threats to global health [3,4]. This alarming situation arises as microbes develop resistance to commonly used drugs, limiting the effectiveness of available treatments [5,6]. Consequently, the ineffectiveness of antibiotics against infectious diseases makes it harder to treat the

diseases, resulting in substantial costs to individuals and society in terms of lives and money [3, 7]. Moreover, the bacteria with a code of antibiotic resistance can transfer the resistance to the subsequent generations [8], exacerbating the problem. Each year, the United States faces over 2.8 million antibiotic-resistant infections, leading to 35,000 deaths. Addressing the spread and impact of antibiotic-resistant bacteria in healthcare requires a coordinated global action plan [9]. To address this challenge, extensive research efforts have been directed towards developing alternative bactericides that possess lower cytotoxicity, greater biocompatibility, lower cost, and are effective for bacteria with antibacterial resistance. Nanomaterials that exhibit antibacterial properties are emerging as an alternative to conventional antibiotics [10]. Developing resistance against nanoparticles is difficult, making them promising alternatives to conventional antibacterial materials [8, 11]. Both rGO [3, 4, 12] and ZnO [1,13,14] have exhibited bactericidal properties, positioning them as promising antibacterial agents in various medical applications [14]. The antibacterial properties of ZnO, rGO, and their composite can be utilised in the textile, food industries, and hospitals where there is a need to prevent bacterial growth and transfer [15]. Thus, materials with antibacterial effects can have broad areas of application.

The antibacterial mechanism of rGO remains incompletely understood, but it is anticipated to arise from a combination of its physical properties and attached chemical functionalities [12]. Graphene's sharp edges can disrupt bacterial cell membranes, while its sheet-like structure isolates and hinders bacterial growth and proliferation [4]. Additionally, chemical functionalities like carboxyl, hydroxyl, and epoxy groups on the graphene sheets induce oxidative stress, contributing to bacterial destruction [16].

There are reports on the antibacterial properties of rGO and their various composites prepared through different methods. Shalini Bhatt et al. reported the physical and chemical mechanisms that can cause the antibacterial properties of graphene-based materials, such as cell membrane stress, mechanical wrapping, photo-thermal ablation, and oxidative stress [17]. Zou et al., in their report, compared the antibacterial efficacy of bio-reduced rGO and commercial rGO against *Escherichia coli* (*E. coli*) as a test target. They demonstrated that cell membrane stress and oxidative stress play a role in the antibacterial efficiency of rGO[18]. Active research is being done on the antibacterial properties of graphene and its hybrid composites. Graphene-based polymeric composites are also getting wide attention in various fields, such as

wound bandages and dressings, antimicrobial coatings, drug delivery, food packaging, and water disinfection. Nabira Fatima et al. reviewed on the recent developments for antimicrobial applications of graphene-based polymeric composites [19]. Another review by Srinivasarao Yaragalla et al. focused on the antibacterial properties of graphene and its hybrid composites, their preparation methods, factors affecting the antibacterial activity and the antibacterial applications [20].

In the case of nanosized ZnO, the nano-size gives a unique antibacterial mechanism. ZnO demonstrates antibacterial activity against both gram-positive and gram-negative bacteria [1, 21]. The primary toxicity mechanisms of ZnO involve the leaching of Zn^{2+} ions, the generation of reactive oxygen species (ROS), and the internalisation of ZnO nanoparticles, all contributing to bacterial destruction [22]. ZnO nanomaterials have shown broad-spectrum of antibacterial properties, lasting antibacterial effects, and excellent biocompatibility makes the research focus on ZnO as an alternative bactericide. Shengjie Jiang and group reviewed the current mainstream claims about the antibacterial mechanisms and applications of ZnO [1]. Amna Sirelkhatim published a comprehensive review on the antibacterial activity and toxicity mechanisms of zinc oxide nanoparticles, with a particular emphasis on their bactericidal and bacteriostatic effects [23]. Wei Juene Chong et al. reviewed the multi-therapeutic potential of biodegradable Polylactic acid (PLA) -ZnO nanocomposite biomaterials. The composite exhibits antibacterial properties, tissue engineering viability, and enhanced biocompatibility, making it versatile for various biomedical applications [24].

There are a few reports on the antibacterial properties of the composite formed by combining rGO and ZnO. Rajapaksha et al. studied the antimicrobial performance of the ZnO-rGO nanocomposite against antibiotic-resistant *Staphylococcus aureus*, *Escherichia coli*, and *Salmonella typhimurium* bacteria in contaminated aquatic systems and evidenced that ZnO-rGO composite showed excellent antimicrobial efficacy against these organisms [2]. Sherif Elbasuney et al. reported on the antibacterial properties of nanocomposites based on rGO combined with metal oxides (AgO, NiO, and ZnO), which exhibited antimicrobial activity against pathogenic bacteria and unicellular fungi [25].

Many reviews and reports in the literature discuss the antibacterial effectiveness of graphene, graphene-based composites, ZnO, ZnO-based composites, and rGO/ZnO

composites [1-4,8,11-21, 24-25]. However, to our knowledge, this is the first study to investigate the antibacterial effectiveness of rGO and its composite with ZnO prepared through a single-step thermal decomposition method.

This chapter presents an evaluation of the antibacterial activity of pure rGO and ZnO/rGO composites prepared by a single-step pyrolysis method. The activity was tested against both gram-positive (*Staphylococcus aureus*) and gram-negative bacteria, including *Pseudomonas aeruginosa*, *Salmonella enteritidis*, and *Escherichia coli*, using the disc diffusion method. Additionally, the minimum inhibitory concentration (MIC) needed to inhibit visible bacterial growth was determined through the 96-well plate microdilution method. To assess the biocompatibility of the samples with mammalian cells, the cytotoxicity test was conducted on hEK 293 cells. The results revealed that sucrose-derived rGO and ZnO/rGO composites exhibit promising potential for applications in biomedical fields as versatile materials with effective bactericidal properties.

4.2 Experimental section

4.2.1. Antibacterial Activity Test

Using the agar disc diffusion method, the antibacterial effectiveness of the samples rGO, ZG-10, ZG-40, ZG-60, and ZG-100 was assessed against gram-positive *S. aureus* and gram-negative strains of *S. enteritidis*, *E. coli*, and *P. aeruginosa* bacteria. The bacterial strains were grown on a Mueller Hinton Agar (MHA) agar plate with a 5 mm thickness using Lucia-Bertani broth, a nutrient broth. The filter paper was cut into 8mm diameter discs and soaked with 20 μ g mL⁻¹ samples for drug loading. The filter paper discs were dipped in agar plates containing bacterial strains and incubated for 24 hours; the zone of inhibition (ZOI) for each bacterial colony was measured in millimetres.

4.2.2. Determination of minimum inhibitory concentration (MIC)

The MIC value is the lowest concentration of samples (antimicrobial agent) to prevent the growth of bacterial colonies after a certain interval of time. The MIC values of samples rGO, ZG-10, ZG-40, and ZG-60 were determined by the 96-well plate microdilution method against *S. aureus*, *P. aeruginosa*, *S. enteritidis*, and *E. coli* bacterial strains according to the standard protocols [26].

4.2.3. Cytotoxicity test

Cytotoxicity of samples was tested against the Human embryonic kidney cell line (HEK-293). HEK-293 cell was procured from the National Centre for Cell Sciences, Pune, India and maintained in RPMI-1640 media, supplemented with 10% fetal bovine serum, 100 U mL⁻¹ penicillin and 100 µg mL⁻¹ streptomycin and kept at 37°C in an incubator with 5% CO₂. The cells were passaged at 80-90% confluency, and the medium was changed every third day. Cytotoxicity of the drugs rGO, ZG-10, ZG-40, ZG-60 and ZG-100 were estimated by MTT (3-(4,5-Dimethylthiazol-2-yl)- 2,5-Diphenyltetrazolium Bromide) assay [27]. A 24-well plate was initially seeded with approximately 1x10⁵ mL⁻¹ cells using a complete growth medium (RPMI-1640) and allowed to attach. At 60% confluency, the medium was replaced with fresh medium and varying drug concentrations (0-200 µg mL⁻¹) were introduced to each well. Following a 48-hour incubation period, the medium was replaced once again with a fresh medium. Subsequently, 50 µL of 0.5% MTT solution was added to each well and incubated for 4 hours. The formazan crystals formed were dissolved using dimethyl sulfoxide, and the absorbance was measured at 570 nm using a UV-visible spectrophotometer (Systronics, India) and percentage viability was calculated using the formula;

$$\% \text{ Cell death} = \frac{Ab \text{ of control} - Ab \text{ of sample}}{Ab \text{ of control}} * 100$$

4.3 Results and discussions

4.3.1 Antibacterial activity of rGO, rGO/ZnO composites and ZnO

The development of highly efficient, cost-effective, and less cytotoxic bactericides that can replace conventional antibiotics is a need in the current age. The antibacterial efficacy of samples rGO, ZG-10, ZG-40, ZG-60, and ZG-100 was evaluated against gram-positive bacterial strain *S. aureus* and gram-negative bacterial strains *P. aeruginosa*, *S. enteritidis*, and *E. coli*, using the agar disc diffusion method. The disc diffusion study demonstrated the ability of the sample to destroy bacterial colonies, as indicated by the size of the inhibition zones. It serves as a measure of disinfection effectiveness. An antibiotic, Gentamycin, which is active on both gram-positive and gram-negative bacterial strains, was also analysed under the same conditions as a positive control. The bacterial strains were cultured in a nutrient broth (Luria-Bertani broth) in a Mueller Hinton Agar (MHA) agar plate of 5mm thickness.

Filter paper was cut into discs of approximately 8mm diameter and was wet with various samples of concentration 20 μ g/ml to attain drug loading in the filter paper disc. The filter paper discs were immersed in agar plates cultured with bacterial strains and incubated for 24 hours; the zone of inhibition for each bacterial colony was determined in mm.

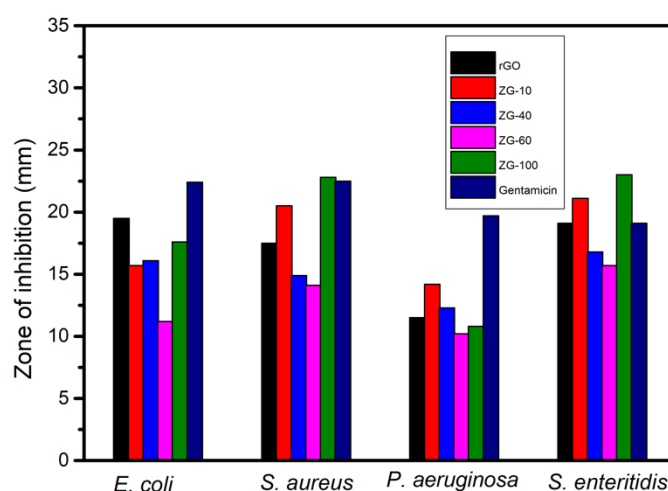


Fig. 4.1: Zone of inhibition of samples rGO, ZG-10, ZG-40, ZG-60, and ZG-100 comparing with antibiotic Gentamicin for bacterial strains *E. coli*, *S. aureus*, *P. aeruginosa* and *S. enteritidis*.

Fig. 4.1 depicts the zone of inhibition (ZOI) of different samples against the tested bacterial strains. It is evident that various samples exhibit distinct efficiencies against different bacterial strains. rGO displays a larger inhibition zone against *E. coli* compared to other disinfectants. However, the composite ZG-10 exhibits superior performance over pure rGO against *P. aeruginosa*, while ZG-100 demonstrates maximum disinfection efficacy against *S. aureus* and *S. enteritidis*. All samples demonstrated promising disinfection capabilities against gram-positive and gram-negative bacterial strains, which is comparable to the disinfection efficiency of the traditional antibiotic Gentamycin. The results reveal that the samples rGO, ZnO, and their composite prepared by the pyrolysis method exhibit high antibacterial efficiency comparable to that of conventional antibiotics. In conclusion, the prepared samples display remarkable antibacterial efficiency and may serve as an effective alternative to conventional antibacterial materials.

The antibacterial activities of rGO [3], ZnO [28], and their derivatives have been studied extensively because they are less toxic, easier to produce, cost-effective, and highly effective against various pathogens [29]. Aside from the other benefits, these drugs can be stored at high temperatures where the organic antimicrobials fail. Furthermore, no by-products are produced by this new generation of drugs. Due to the tolerable cytotoxicity on mammalian cells, rGO, ZnO, and their composite have emerged as a promising alternative to conventional antibiotics [28,29].

4.3.2 Minimum inhibitory concentrations (mg mL⁻¹).

The antibacterial activity of the samples was also evaluated using Minimum Inhibitory Concentration (MIC) values, and is presented in Table 4.1. The MIC value represents the minimum concentration of an antimicrobial agent required to inhibit the visible growth of bacteria in the standardized growth medium. Lower MIC values indicate higher efficacy of the antibacterial agents. The results are consistent with the observations from the zone of inhibition tests.

As indicated in Table 4.1, the minimum concentration required to inhibit *E. coli* with the most efficient disinfectant, rGO, is 0.75 mg mL⁻¹. Similarly, ZG-100 exhibits lower MIC values for both *S. aureus* and *S. enteritidis*, with an MIC of 0.625 mg mL⁻¹. For *P. aeruginosa*, ZG-10 was found to be more effective than any other disinfectant studied, with an MIC value of 1 mg mL⁻¹.

Bacteria	MIC (mg mL ⁻¹)				
	rGO	ZG-10	ZG-40	ZG-60	ZG-100
<i>E. coli</i>	0.75	> 1.25	1.25	> 1.25	1.00
<i>S. aureus</i>	1.00	0.75	1.25	1.25	0.625
<i>P. aeruginosa</i>	1.25	1.00	1.25	> 1.25	1.25
<i>S. enteritidis</i>	0.75	0.625	1.00	> 1.00	0.625

Table 4.1: MIC values of rGO, ZG-10, ZG-40, ZG-60 and ZG-100 on various bacterial strains

4.3.3 Cytotoxic analysis

The cytotoxicity analysis of the samples evaluates the safety and biocompatibility of materials intended for biomedical applications. This test determines if samples that are toxic to microorganisms are also harmful to mammalian cells. The IC_{50} value serves as an indicator of cytotoxicity, quantifying the substance's potential to inhibit biological responses. Specifically, the IC_{50} value represents the concentration of the drug required to reduce cell viability by 50%.

Human Embryonic Kidney cells (HEK293) were employed for the cytotoxic tests, and the IC_{50} values for the tested samples are depicted in Fig. 4.2. Among the samples, rGO demonstrated the least cytotoxicity with an IC_{50} value of $104.38 \mu\text{g mL}^{-1}$. ZG-100 is the second least cytotoxic sample, exhibiting an IC_{50} value of $94.14 \mu\text{g mL}^{-1}$. ZG-10 displayed an IC_{50} value of $91.44 \mu\text{g mL}^{-1}$, while ZG-40 and ZG-60 exhibited further increased cytotoxicity with IC_{50} values of $69.89 \mu\text{g mL}^{-1}$ and $61.99 \mu\text{g mL}^{-1}$, respectively. These results provide insights into the relative cytotoxic effects of the samples on HEK293 cells, indicating their varying impact on mammalian cells.

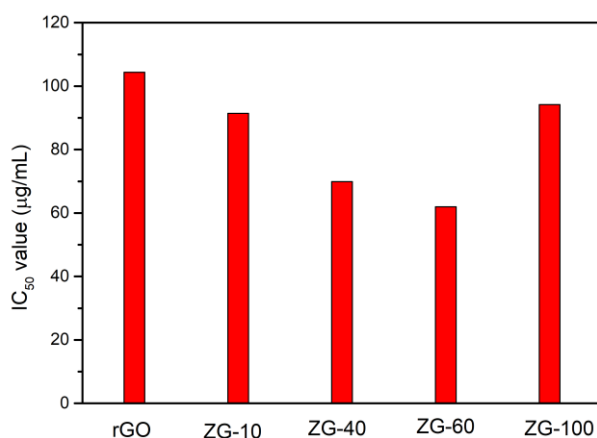


Fig. 4.2: IC_{50} values of samples rGO, ZG-10, ZG-40, ZG-60, and ZG-100 tested on HEK293 cells.

4.4 Mechanism of antibacterial activity

Reduced graphene oxide and ZnO have been identified as highly effective antibacterial agents. Despite the lack of complete knowledge regarding their antibacterial mechanisms, rGO, ZnO, and their composites are being extensively

investigated as promising next-generation antibacterial materials [12,13]. These nanomaterials demonstrate biocompatibility, cost-effectiveness in synthesis, and efficacy against various disease-causing microbes [21,30,31]. Unlike organic antimicrobials, these novel drugs can be stored at high temperatures without degradation and do not generate any by-products. The antimicrobial evaluations of the prepared samples (rGO, ZnO, and rGO/ZnO composites) against different bacterial strains indicate their high efficiency against all tested bacterial strains [32].

The antibacterial mechanism of rGO primarily arises from its exceptional physical and chemical properties. As a 2-dimensional carbon allotrope, rGO possesses a large surface area, with its basal plane decorated with structural imperfections and populated by oxygen-containing functional groups. This unique morphology and associated chemical functional groups contribute to the antimicrobial action of rGO [12,16]. The antibacterial mechanism attributed to its morphology mainly works through the nano-knife and blanket effects. The sharp edges of rGO act as nano-knives, penetrating the bacterial cell walls and inducing leakage of cellular components. Moreover, the sheet-like nature of rGO envelops the bacteria like a blanket, isolating them from the surroundings, thus hindering proliferation and nutrient consumption [3,29]. This effect is particularly noticeable in liquid media. Furthermore, the antibacterial efficiency of rGO is influenced by the lateral dimension of its sheets. Large-sized sheets exhibit increased antibacterial efficacy [12]. The chemical impact of rGO on the antibacterial mechanism is attributed to the oxidative stress generated by the chemical functionalities present on the surface of rGO. The oxygen groups associated with rGO induce oxidative stress in microorganisms, leading to the deactivation of cellular components [3,29]. This combined physical and chemical mechanism contributes to the antibacterial efficacy of rGO, rendering it a promising antibacterial agent for the future.

ZnO has also been recognized as an efficient antibacterial material and has been extensively studied in recent years. The proposed antibacterial mechanisms responsible for the toxicity of ZnO towards bacteria involve several pathways. These include Zn^{2+} leaching, internalization of ZnO nanoparticles, generation of ROS, and loss of cell wall integrity upon contact with ZnO particles [11,23]. One extensively studied antibacterial mechanism of ZnO involves the leaching of zinc ions (Zn^{2+}) into the surrounding medium. Zn^{2+} penetrates the cell membrane, internalizes, and interacts with cell

organelles, leading to bacterial cell dysfunction [1, 15]. The antibacterial activity of ZnO primarily depends on the size and morphology of the ZnO particles [23]. The mode of action varies between nano and micro-sized ZnO particles. Nanosized particles can enter bacterial cells, while micro-sized particles interact with cell walls, causing disintegration through ion diffusion and free radical generation, ultimately entering the cell and disrupting cellular components [11]. The ZnO can initiate antibacterial activity even in the absence of light [1]. The generation of ROS species and Zn^{2+} release is proportional to the size of the ZnO particles [23]. Additionally, the corners and edges of the ZnO surface contribute to membrane injury, with the extent of damage highly dependent on particle morphology and size. Smaller-sized particles with abundant corners and edges, characterized by an abrasive morphology, play a significant role in cellular wall damage. The highly defective surface of ZnO contributes to its toxicity [15,23]. Collectively, these antibacterial mechanisms make ZnO a promising antimicrobial agent against various pathogens.

4.5 Conclusion

The development of highly efficient, cost-effective, and less cytotoxic bactericides that can replace conventional antibiotics is a need in the current age. The antibacterial capabilities of samples rGO, ZG-10, ZG-40, ZG-60, and pure ZnO (ZG-100) are tested against gram-positive *S. aureus* and gram-negative *P. aeruginosa*, *S. enteritidis*, and *E. coli*, using the disc diffusion method. The samples exhibited high antibacterial efficiency against the tested bacterial strains. The highest zone of inhibition of 19.5 mm was observed for *E. coli* with the sample rGO. ZnO (ZG-100) demonstrated the most disinfective properties against *S. aureus* and *S. enteritidis*, with ZOI values of 22.8 mm and 23 mm, respectively. For *P. aeruginosa*, the composite sample ZG-10 displayed the maximum ZOI area at 14.2 mm. The observed zones of inhibition for the samples are comparable to those of conventional antibiotics. The MIC values of the samples against the studied bacterial strains were analysed. The minimum inhibitory concentration required to inhibit *E. coli* by rGO was 0.75 mg mL^{-1} . ZG-100 demonstrated MIC values of 0.625 mg mL^{-1} against both *S. aureus* and *S. enteritidis*. The MIC value of ZG-10 against *P. aeruginosa* was 0.75 mg mL^{-1} . The cytotoxicity of the samples was also tested using HEK293 as test cells, and the IC_{50} values were found to be in the range of 62 to $104 \mu\text{g mL}^{-1}$. In summary, the samples prepared using this method are promising candidates in the biomedical field due to their low cytotoxicity,

cost-effectiveness, ease of production, and high efficacy against various bacterial strains.

4.6 References

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Chapter V

The Study on Efficient Photocatalytic Degradation of Toxic Dyes and Antibiotics Using ZnO/rGO Composite

Abstract

Photocatalytic degradation is an advanced, energy-efficient method for removing organic pollutants such as dyes and antibiotics. This approach harnesses light energy to detoxify pollutants, offering a more efficient, cost-effective, and environmentally friendly alternative to traditional wastewater purification methods. ZnO is a known photoactive material; incorporation of rGO with ZnO enhances the photocatalytic efficiency by many folds. The photocatalytic efficiency of the prepared ZnO/rGO composites was tested to decompose the MB dye aqueous solution. The degradation of MB in the solution following photocatalysis was verified through LC-MS analysis. The complete degradation mechanism was exposed through a series of scavenger tests. The efficacy of ZnO/rGO composite as a photocatalyst was further confirmed by testing on Rhodamine B, a dye, and Ofloxacin, an antibiotic. The studies concluded that the rGO and ZnO/rGO composite prepared via a single-step heating method is both industrially scalable and cost-effective, and can be used as a highly efficient photocatalyst for combating environmental pollution.

5.1 Introduction

One of the most alarming consequences of rapid industrialization is the uncontrolled discharge of harmful pollutants, including heavy metals, fertilizers, pesticides, herbicides, insecticides, dyes, pharmaceutical residues, and oils into natural water bodies. This not only leads to a severe scarcity of freshwater but also disrupts ecological balance and biodiversity. The release of untreated industrial effluents into rivers, lakes, and groundwater systems urgently demands attention in the modern era [1].

Water is universally recognized as the elixir of life. However, the scarcity of clean and safe drinking water has become a major global challenge. There is a direct correlation between growing industrialization and increasing environmental pollution. Urban expansion and industrial growth significantly deteriorate the quality of water

resources. Many industries discharge large volumes of untreated wastewater containing various pollutants into water bodies, contributing to severe water pollution [2].

Over the past five decades, the release of organic dyes, pesticides, and pharmaceutical compounds—such as antibiotics—into aquatic environments has intensified. Water, being a universal solvent, readily dissolves a wide range of contaminants, making purification both complex and costly [1]. The consumption of such contaminated water leads to the spread of waterborne diseases, posing serious health risks to humans and animals alike. Globally, millions of people die each year from illnesses linked to polluted water [3]. Moreover, the ecological impact is profound, as aquatic life is severely affected by the degraded water quality [4].

Synthetic dyes are among the major contributors to water pollution and are extensively used across a wide range of industries, including textiles, plastics, paper, food, rubber, printing, construction, pharmaceuticals, and cosmetics [5,6,7]. These industries collectively generate vast quantities of dye-laden wastewater. Approximately 10,000 synthetic dyes are commercially available worldwide, with an estimated global production of 700,000 tons per year. Alarming, nearly 200,000 tons of these dyes are discharged into the environment annually due to inefficiencies in the dyeing processes [8].

Dyes are generally complex aromatic compounds with metal ions, amine groups, and extended conjugated structures, which render them chemically stable, non-biodegradable, and toxic. These dyes are water-soluble organic compounds that resist degradation and significantly harm aquatic environments [1,9,10]. The presence of dyes in water inhibits sunlight penetration, thereby reducing the rate of photosynthesis and affecting aquatic flora and fauna [11]. Dyes are generally classified into cationic, anionic, and non-ionic types based on their ionic nature [1,12]. Most synthetic dyes are hazardous to human health—they are often carcinogenic, mutagenic, persistent, and non-biodegradable [11,13]. Exposure to these contaminants through ingestion, skin contact, or inhalation can severely impact human health, leading to disorders of the respiratory system, reproductive organs, liver, brain, and central nervous system [10].

In addition to dyes, pharmaceutical contaminants such as antibiotics have emerged as significant environmental threats [14]. These compounds enter water systems through hospital effluents, pharmaceutical industry discharges, and human or

animal excretion. Antibiotics in general persist in aquatic environments due to their low biodegradability and chemical stability, posing serious concerns related to antimicrobial resistance and ecological toxicity [15].

Clean and safe water is a fundamental human necessity, yet approximately 1.2 billion people lack access to safe drinking water, and over 2.6 billion are deprived of basic sanitation services [3]. The unchecked discharge of industrial effluents containing harmful pollutants into natural water bodies significantly contributes to this crisis. Tackling this life-threatening issue requires efficient treatment of wastewater before it is released into the environment.

Numerous treatment technologies have been developed to manage industrial wastewater, including adsorption, ion exchange, chemical coagulation, electrolysis, carbon filtration, biological treatments, membrane filtration, and reverse osmosis (RO). However, these conventional methods often suffer from critical drawbacks such as complex operation, high energy consumption, generation of secondary pollutants, high implementation and operational costs, and issues with post-treatment separation or sludge disposal [2,4].

Among these, adsorption is widely favoured due to its simplicity, cost-effectiveness, and lack of secondary pollutant generation. However, it merely transfers pollutants from one phase to another without degrading them, thus requiring additional disposal steps. Other processes like precipitation, flocculation, and reverse osmosis generate significant secondary waste, necessitating further treatment.

Given these limitations, there is a growing interest in advanced oxidation processes (AOPs)—a group of technologies that rely on the generation of highly reactive oxygen species (ROS) capable of degrading a wide range of organic and inorganic pollutants. AOPs include ozonation, Fenton reactions, electrochemical oxidation, and photocatalysis, either applied individually or in combination [5,16]. Among these, photocatalysis has emerged as one of the most promising technologies for water treatment due to its efficiency, sustainability, and environmental compatibility [17].

Photocatalysis is a light-driven process that utilizes semiconductor materials (photocatalysts) capable of absorbing photon energy and initiating redox reactions to degrade pollutants. Upon exposure to light (typically UV or visible), the photocatalyst

generates electron-hole (e^-h^+) pairs that interact with adsorbed water and oxygen molecules to form ROS such as hydroxyl radicals ($\bullet OH$) and superoxide anions ($\bullet O_2^-$). These ROS are highly reactive and capable of breaking down complex, toxic molecules into simpler, non-toxic, and mineralized products such as CO_2 and H_2O [14, 16,18].

The photocatalytic process involves several key steps [8]:

- Mass transfer of the pollutant from the bulk solution to the catalyst surface.
- Adsorption of the pollutant onto active sites of the photocatalyst.
- Generation of ROS through photon-induced excitation of the photocatalyst.
- Oxidation and degradation of the adsorbed pollutants by ROS.
- Desorption of the degradation byproducts from the catalyst surface.
- Diffusion of the byproducts into the surrounding aqueous medium.

Photocatalysis is advantageous due to its operation under ambient temperature and pressure, its ability to completely mineralize stable organic compounds, and its reliance on renewable light energy, making it highly energy-efficient and sustainable. Additionally, it produces no secondary pollutants [5,14]. In addition to photodegradation, photocatalysis can effectively and simultaneously deactivate microorganisms such as bacteria and viruses, which are major contributors to waterborne pollution. This makes photocatalysts a highly attractive option for comprehensive water treatment [14].

Given these attributes, photocatalysis has garnered significant attention as a next-generation technology for treating industrial wastewater containing dyes, pesticides, phenolic compounds, surfactants, and pharmaceuticals [14]. The byproducts formed after photocatalytic treatment are generally non-toxic and include simple molecules such as carbon dioxide, water, and harmless inorganic ions [1,5,16].

Therefore, the development of photocatalysts capable of efficiently utilizing light, especially visible light, is a key priority in environmental remediation research. Various semiconductor materials have been investigated as photocatalysts, including TiO_2 , ZnO , Fe_2O_3 , SnO_2 , SnS , CeO_2 , ZrO_2 , and WO_3 [7,19,20]. Among these, ZnO and TiO_2 are the most extensively studied due to their chemical stability, non-toxicity, and strong oxidative properties [21,22] .

Compared to TiO_2 , ZnO exhibits several distinct advantages. It possesses a much higher electron mobility ($200\text{--}300\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) than TiO_2 ($0.1\text{--}4\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), enabling faster charge transport and enhanced photocatalytic performance [21]. Additionally, its lower refractive index (~ 2.0) minimizes light scattering and improves photon absorption. Furthermore, the longer lifetime of photoinduced charge carriers, the ability to crystallize at lower temperatures, and the anisotropic growth behaviour of ZnO collectively make it a more favourable photocatalyst than TiO_2 [22].

Among various semiconducting materials studied for photocatalysis, ZnO stands out as one of the most efficient for the degradation of environmental contaminants. It is a direct wide band gap semiconductor ($\sim 3.37\text{ eV}$) active in the near-UV region of the solar spectrum and possesses a high exciton binding energy ($\sim 60\text{ meV}$) [16,23]. ZnO has gained significant attention in photocatalytic applications due to its high photosensitivity, strong redox potential, excellent charge carrier mobility, and robust light-harvesting capability. Additionally, its favourable properties—such as thermal and chemical stability, non-toxicity, and low production cost—further support its widespread use in environmental remediation technologies [7,14,19,22,24].

Compared to other photocatalysts, ZnO can effectively generate hydrogen peroxide (H_2O_2), which plays a significant role in the degradation of organic pollutants [25]. Moreover, ZnO can be synthesized through various simple, scalable, and cost-effective techniques such as the sol–gel method, hydrothermal, solvothermal processes, and chemical deposition [26,27,28]. The production cost is low compared to other semiconductors such as TiO_2 . These low-cost fabrication routes, combined with its excellent photocatalytic properties, make ZnO a highly attractive and promising material for sustainable environmental remediation and green water treatment technologies.

Despite these advantages, ZnO also has inherent limitations that hinder its large-scale practical application. Its wide band gap restricts absorption to only $\sim 5\%$ of the solar spectrum (UV region), leaving the visible ($\sim 43\%$) and IR ($\sim 52\%$) parts untapped. That is, pure ZnO can only utilize 5% of the solar spectra to excite electrons from the valence band to the conduction band. Moreover, ZnO suffers from rapid recombination of photogenerated electron–hole pairs, decreasing their availability for redox reactions, which diminishes its photocatalytic efficiency [7,14,19]. Further, Photo corrosion is

another critical issue that compromises its long-term stability [21,30]. These drawbacks limit its direct application in solar-driven water purification processes.

Several strategies have been developed to enhance the photocatalytic efficiency of ZnO, aiming to overcome its inherent limitations such as wide band gap, rapid electron–hole recombination, and limited visible light absorption. These enhancement methods include metal and non-metal doping, coupling with other semiconductors, forming composites, and integrating with carbon-based materials [19,29, 31,32]. The ultimate goal of these approaches is to achieve efficient solar-light-driven photocatalysis and extend the lifetime of photogenerated charge carriers.

One widely adopted method is doping ZnO with transition metals [7]. This strategy introduces defects and intermediate energy levels into the ZnO lattice, modifying its band structure and extending light absorption into the visible region. Metal ions such as Ag, Mn, Cu, Co, Fe, and Al have been commonly used, resulting in the narrowing of the band gap and improved photocatalytic activity under visible light [8]. These dopants induce intra-band states that reduce the band gap, enabling ZnO to absorb photons of longer wavelengths [21,25].

However, metal doping may sometimes introduce recombination centers, which facilitate the premature recombination of photogenerated electron–hole pairs and diminish photocatalytic efficiency. To address this, non-metal doping (e.g., carbon, nitrogen, sulfur) has gained attention. These dopants introduce states near the valence band and are less likely to cause recombination [21]. Additionally, doping with rare earth ions like La^{3+} , Ce^{3+} , Pr^{3+} , and Nd^{3+} has also been reported to effectively reduce ZnO's band gap and improve its photocatalytic performance [33].

Another widely explored method to enhance the photocatalytic efficiency of ZnO is the construction of heterojunction-based coupled photocatalysts. By coupling ZnO with other semiconducting materials possessing appropriate band gap energies, it is possible to improve light absorption—particularly in the visible range—facilitate more efficient separation of photogenerated charge carriers, and increase the surface area and number of active adsorption sites. These enhancements collectively contribute to higher photocatalytic activity [30,31]. Several semiconductors have been successfully coupled with ZnO, including Bi_2O_3 [34], CdO [35], CuO [36], SiO_2 [37], TiO_2 [38], WO_3 [39], and ZrO_2 [40]. The formation of heterojunctions in these systems

facilitates interfacial charge transfer between the two semiconductors, significantly suppressing the recombination of photogenerated electron-hole pairs and thereby improving photocatalytic efficiency.

However, despite their advantages, the successful design and optimization of coupled photocatalysts depend heavily on the careful selection of semiconductor materials and the synthesis method. Precise control over the band alignment and interfacial contact remains a critical challenge in the development of these systems.

Among the various approaches, hybridizing ZnO with graphene derivatives, especially rGO, is one of the most effective and widely explored strategies [2,22,41]. rGO offers excellent properties such as high electrical conductivity, large surface area, chemical stability, and ease of synthesis (compared to graphene synthesis), making it a versatile co-catalyst and electron acceptor [42].

In ZnO/rGO composites, the rGO sheets serve multiple roles:

- Electron Scavenger
- Conductive Pathway
- Photosensitizer
- Adsorbent

In ZnO/rGO composites, rGO acts as a conductive substrate and electron reservoir, effectively scavenging photogenerated electrons from ZnO. The formation of a heterojunction between ZnO and rGO induces a built-in electric field at the interface due to the difference in their Fermi levels. This promotes the migration of photogenerated electrons from ZnO to rGO, significantly reducing electron-hole recombination [43,44]. The high electron mobility of rGO also facilitates rapid electron transport, further enhancing charge separation [22].

Moreover, the presence of rGO modifies the electronic structure of ZnO, resulting in band gap narrowing. This shift enables the composite to harvest photons in the visible range, thereby improving solar light utilization [43,45]. The synergistic interaction between ZnO and rGO extends light absorption, improves charge carrier dynamics, and enhances the surface reactivity of the catalyst [2].

Beyond its electronic advantages, rGO contributes to improved photocatalytic efficiency by providing a high density of adsorption sites due to its large surface area

and abundant oxygen-containing functional groups [43,46]. This enhances the adsorption of organic pollutants and facilitates their degradation. Additionally, rGO serves as an anchoring platform for ZnO nanoparticles, ensuring better dispersion and increased exposure of active sites to the reactants.

In conclusion, the integration of rGO with ZnO addresses the primary drawbacks of pure ZnO, including limited visible-light response, rapid charge recombination, and low surface activity. The ZnO/rGO composites exhibit improved light absorption, enhanced charge carrier dynamics, and greater surface reactivity, making them highly effective for the photocatalytic degradation of various environmental pollutants under solar irradiation.

ZnO/rGO composites, prepared through various synthesis techniques, have been extensively investigated as efficient photocatalysts for the degradation of a wide range of environmental pollutants, including dyes and antibiotics. Several notable studies have reported on their photocatalytic performance:

- Pham Van Tuan et al. synthesized ZnO/rGO nanorods via a hydrothermal method conducted at 160 °C for 24 hours, varying the rGO content. The composite with 5% rGO achieved complete degradation (100%) of methylene blue (MB) under visible light irradiation within 50 minutes, demonstrating excellent photocatalytic activity [47].
- Hui Lu et al. developed ZnO–rGO composites through a one-step electrodeposition method on an FTO substrate, using lithium perchlorate (LiClO₄) as the supporting electrolyte. Their catalyst exhibited significantly enhanced performance compared to pure ZnO, achieving a 99.1% degradation of MB within 120 minutes [48].
- Asif Nisar et al. prepared ZnO-decorated rGO composites via a chemical reduction technique. Their study on visible-light-driven photocatalytic degradation of MB reported up to ~99% efficiency within 60 minutes, confirming the potential of ZnO–rGO systems for dye removal [49].
- Manman Xie et al. synthesized RGO/ZnO rod-like composites via a high-temperature hydrothermal method using GO/ZnO₂ microspheres as precursors. The resulting composite achieved photodegradation efficiencies exceeding 90% for both methylene blue (MB) and methyl orange (MO) under UV and visible

light irradiation, significantly outperforming pure ZnO₂, ZnO, and GO/ZnO₂ [50].

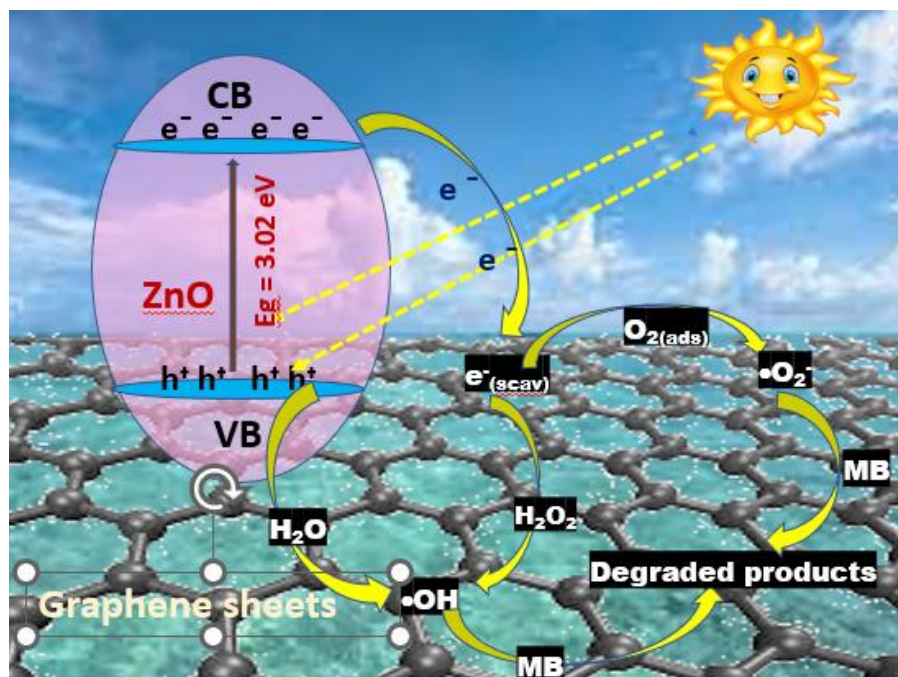
- Poornima Sengunthar et al. fabricated ZnO–rGO nanocomposites and rGO via a hydrothermal method as well as modified Hummer’s method. Their photocatalytic experiments showed more than 85% degradation of methyl orange and rhodamine B under UV irradiation for 2 hours [51].
- Chin Boon Ong et al. successfully decorated ZnO nanoparticles onto rGO nanosheets using a simple sol–gel method. The resulting nanocomposite demonstrated excellent photocatalytic degradation of perfluorooctanoic acid (PFOA) and methyl orange under solar light [52].
- K. V. Ashok Kumar et al. synthesized ZnO quantum dots (QDs) via a precipitation method and ZnO/rGO composites (0.5–2 wt% ZnO) by hydrothermal synthesis. The photocatalytic activity was tested against tetracycline (TC) and hexavalent chromium [Cr(VI)], achieving 68% TC and 84% Cr(VI) abatement under visible light within 120 minutes [53].

The literature extensively supports that ZnO/rGO composites exhibit excellent photocatalytic performance under light irradiation, making them promising candidates for environmental remediation. To evaluate the photocatalytic efficiency of the synthesized ZnO/rGO composite samples, MB was selected as a model organic pollutant. MB is a widely used cationic dye belonging to the thiazine group with the chemical formula: C₁₆H₁₈ClN₃S. It is an aromatic heterocyclic basic dye. It is extensively used in the textile, paint, and plastic industries [5,23]. Its extensive use and subsequent discharge into aquatic systems contribute significantly to water pollution. MB is chemically stable, non-biodegradable, and highly soluble in water, making it a persistent pollutant [2,5].

MB poses serious environmental and health concerns, including toxicity, carcinogenicity, and adverse biological effects such as methemoglobinemia, digestive disorders, nausea, vomiting, and tissue necrosis [5,54]. Given its environmental persistence and harmful nature, it is imperative to develop sustainable and efficient techniques for its degradation [2].

Photocatalytic degradation offers an environmentally friendly pathway for the breakdown of MB into non-toxic end products. The degradation pathway typically

involves an initial N-demethylation of the dye molecule, followed by the cleavage of both central and peripheral aromatic rings, leading to the formation of intermediate compounds. These intermediates are further mineralized into harmless molecules such as H_2O , CO_2 , ammonium ions, and sulfate ions [5]. As the degradation progresses, the deep blue colour of the MB solution gradually fades, ultimately turning colourless, indicating successful decolorization and mineralization. The schematic representation of MB degradation by ZnO/rGO composite is shown below.



Schematic representation of MB degradation by ZnO/rGO composite.

ZnO/rGO composites have demonstrated high efficiency as heterogeneous photocatalysts, capable of utilizing solar energy to disrupt the conjugated structure of dye molecules. To further validate their photocatalytic performance, additional degradation experiments were conducted on two other environmentally persistent pollutants: Rhodamine B (RhB) and the antibiotic Ofloxacin (OFX).

Rhodamine B, a xanthene dye, is widely used in the textile and cosmetic industries and is known for its mutagenic and carcinogenic properties. Although once used as a food colouring additive, it has since been banned due to its toxicity. RhB exhibits high photostability and resistance to environmental degradation, making it a challenging pollutant to remove from aquatic systems. Its persistence poses serious

risks to ecosystems and public health, necessitating effective treatment prior to discharge into natural water bodies [1,55,56].

Ofloxacin, a second-generation fluoroquinolone antibiotic, is extensively used to treat bacterial infections, particularly in the urinary tract [57]. Due to its chemical stability—attributed to robust carbon–fluorine bonds—it persists in the environment and is frequently detected in hospital effluents, urban wastewater, groundwater, and even drinking water. OFX contamination is especially concerning, as even trace concentrations can contribute to the development of antibiotic-resistant bacteria. Conventional wastewater treatment methods are often ineffective at removing such pharmaceuticals, highlighting the need for advanced remediation strategies like photocatalysis [58,59].

In this chapter, the photocatalytic efficiency of the ZnO/rGO composite synthesized via a green, single-step method was systematically investigated. MB was employed as a model organic dye to evaluate the degradation performance of the composites under light irradiation. A series of ZnO/rGO composites with varying ZnO loadings was tested to determine the optimal composition for maximum photocatalytic activity. The degradation kinetics of MB were analysed using the most efficient catalyst, and the extent of degradation was confirmed through LC-MS analysis. To understand the underlying mechanism, reactive species trapping experiments were conducted, which helped identify the key reactive oxygen species involved in the degradation process.

Additionally, the versatility of the composite was validated through its successful application in the degradation of Rhodamine B and the pharmaceutical pollutant Ofloxacin. These investigations confirm that both rGO and ZnO/rGO composites exhibit excellent photocatalytic performance and are promising candidates for environmental remediation. The results highlight the potential of the ZnO/rGO system as a robust, cost-effective, and sustainable photocatalyst for real-world water purification applications.

5.2 Assessment of photocatalytic degradation performance

Photocatalytic studies were conducted using methylene blue, Rhodamine-B, EDTA-Disodium salt, Benzoquinone (BQ), Histidine, and Terephthalic acid. All

chemicals were used without further purification. The ofloxacin solution was prepared by dissolving and diluting commercially available ofloxacin tablets in distilled water.

The photocatalytic degradation efficiency of various samples, namely rGO, ZG-30, ZG-50, ZG-70, ZG-90, and ZG-100, was evaluated against MB under visible light exposure. UV- Visible spectroscopy (Shimadzu-1800) was employed to quantify the photodegradation process. A Xenon flash lamp (Xenon Light Source - 150W, Model-HO-SC-XE150) served as the solar simulator. For the degradation experiments, an aqueous stock solution of MB was prepared at a concentration of 10 mg/L. The photocatalysts were added to the MB solution at a ratio of 1 mg/ml. Before irradiation, the mixture of the MB solution and the photocatalyst was stirred in the dark for 60 minutes to achieve adsorption-desorption equilibrium. Subsequently, the suspension was exposed to the Xenon flash lamp with continuous stirring for 30 minutes to study the degradation of MB in the presence of the photocatalyst under light irradiation. At regular intervals of 15 minutes during irradiation, a portion of the suspension was withdrawn, and the catalyst was separated through centrifugation. The resulting filtrate was then subjected to analysis using a UV- Visible spectrophotometer over a wavelength range of 400 to 800 nm. A decrease in the absorbance peak at 664 nm indicated the degradation of MB based on the established Beer-Lambert law. The photodegradation efficiency was calculated using Equation 5.1 [60]:

$$\text{Photodegradation efficiency (\%)} = \frac{C_0 - C}{C_0} * 100 \quad (5.6)$$

Where C_0 is absorbance peak intensity of the MB stock solution and C is the absorbance peak intensity at various time intervals with photocatalyst.

5.3 Results and Discussion

5.3.1 Photocatalytic performance of ZnO/rGO composites

The photocatalytic degradation efficiencies of different samples, rGO, ZG-30, ZG-50, ZG-70, ZG-90, and ZG-100, were evaluated against MB dye under xenon lamp irradiation at room temperature. Prior to irradiation, the sample-MB suspension was subjected to 60 minutes of dark stirring to achieve adsorption-desorption equilibrium. The light irradiation time-dependent reduction in MB concentration in the test solution with catalyst was monitored by recording the absorbance spectra using a UV-Visible spectrophotometer.

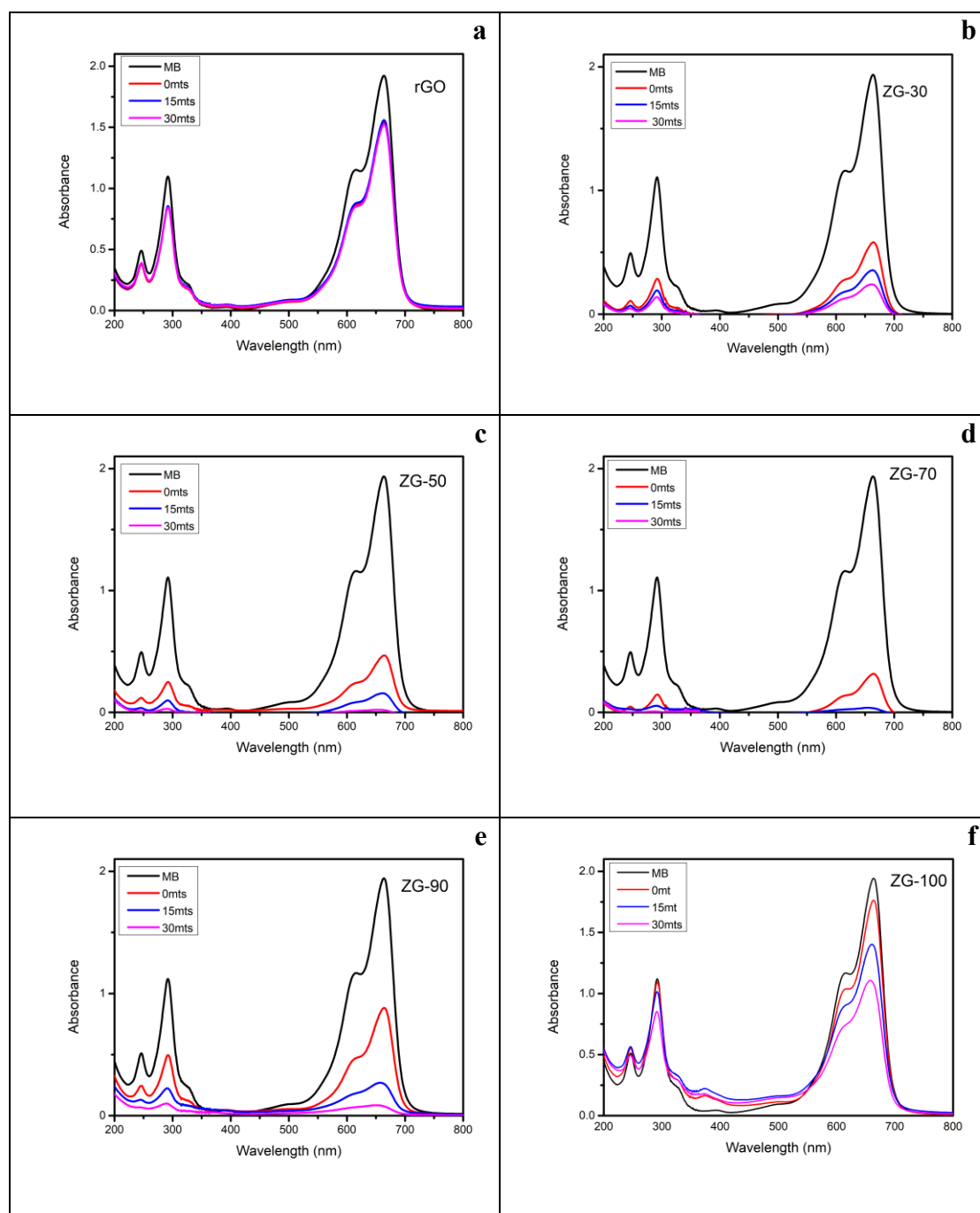


Fig. 5.1: (a-f) UV-visible absorbance spectral changes of MB solutions over time for rGO, ZG-30, ZG-50, ZG-70, ZG-90 and ZG-100 under Xenon irradiation.

Fig. 5.1 (a-f) illustrates the degradation efficiency of various catalysts on the MB dye solution. Each graph displays multiple curves. The curve labelled "MB" in all the graphs corresponds to the UV-visible spectrum of the initial stock solution of MB. The curve marked "0 min" represents the spectrum of the solution after reaching adsorption-desorption equilibrium, following 60 minutes of dark stirring. The

subsequent curves correspond to the MB–catalyst mixtures after different durations of light irradiation.

For rGO, a noticeable initial decrease in MB concentration is observed due to its adsorption onto the surface of rGO. However, once the available adsorption sites become saturated, no further reduction in MB concentration occurs under light irradiation, indicating the absence of photocatalytic activity (Fig. 5.1a). In contrast, pure ZnO (ZG-100) exhibits only a slight reduction in MB intensity during the dark stirring phase, suggesting a limited number of adsorption sites. Upon light irradiation, a further decline in MB concentration is observed, indicating that ZnO facilitates photocatalytic degradation of MB (Fig. 5.1f).

All composite samples (ZG-30, ZG-50, ZG-70, and ZG-90) show improved adsorption and photodegradation efficiency. The more pronounced initial decrease in MB concentration during the dark phase is attributed to enhanced adsorption, indicating a greater number of available adsorption sites in the composite samples. Under light irradiation, significant photodegradation is observed in all composites. The degradation rate is clearly higher than that of pristine ZnO, confirming the beneficial role of rGO in improving overall photocatalytic activity.

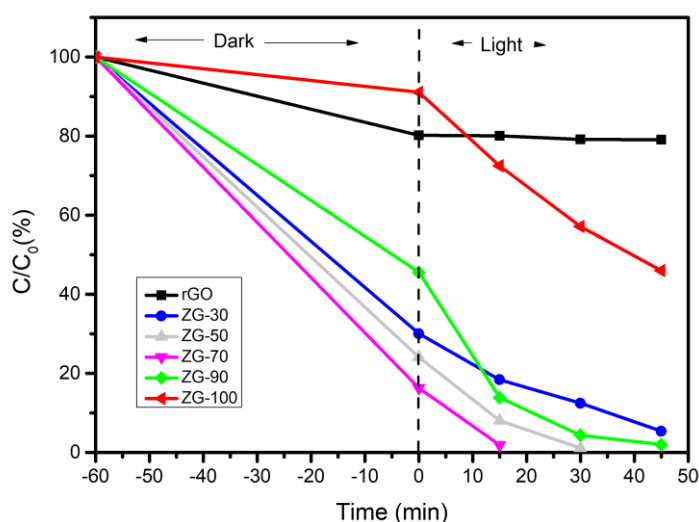


Fig. 5.2: Consolidated MB removal/degradation performance of samples rGO, ZG-30, ZG-50, ZG-70, ZG-90 and ZG-100 (corresponding to figures 10 a-e) with time.

Fig. 5.2 consolidates the MB degradation performance of all tested samples. The curve corresponding to rGO shows an initial reduction in MB concentration during the dark stirring phase. This reduction is attributed to the abundant adsorption sites of rGO, where MB molecules are loaded to their maximum capacity. The stagnant curve during photoirradiation experiments suggests that additional reduction does not take place, indicating that rGO is photochemically inactive. This result is unsurprising, as rGO is a known photochemically inactive material, primarily due to its nearly zero band gap [61].

However, the significant advantage of rGO lies in its ultra-high surface area. This characteristic promotes surface phenomena by offering numerous active surface sites, which serve as crucial reaction centres for photocatalysis. Despite its lack of intrinsic photoactivity, rGO can still play a vital role in catalytic processes due to these active sites, facilitating various surface reactions and adsorption phenomena [29].

In contrast, the curve representing ZG-100 (pure ZnO) in Fig. 5.2 shows minimal initial adsorption during the dark phase, due to the relatively low surface area and fewer active sites. However, upon exposure to xenon lamp irradiation, MB degradation progresses steadily, reaching approximately 46% after 45 minutes. This photodegradation is attributed to the photocatalytic activity of ZnO, which generates electron-hole pairs under light. These charge carriers initiate the formation of ROS, which oxidize and break down MB molecules into smaller fragments. However, the rapid recombination of photogenerated electron and hole pairs, combined with the limited number of adsorption sites, limits the application of ZnO as a highly efficient photocatalyst [41,45].

In the ZnO/rGO composite samples, a combination of the advantageous properties of both components is observed. Focusing first on adsorption, the composites show significantly enhanced MB adsorption compared to the pristine materials, rGO and ZG-100. This improvement is clearly reflected in the “zero-minute” points along the vertical reference line in Fig. 5.2, corresponding to each composite. These results indicate that the composites provide a greater number of active surface sites than either pure rGO or ZnO.

Since adsorption is a surface-driven phenomenon, the surface area of the catalyst plays a crucial role in photocatalysis by providing abundant active sites and facilitating the diffusion of pollutants across the catalytic surface [4]. To evaluate the enhanced adsorption behaviour, the specific surface areas of synthesized rGO and the ZnO/rGO nanocomposite were compared using the Brunauer–Emmett–Teller (BET) method. The analysis revealed that the composite has a specific surface area of 29.418 m²/g, significantly higher than that of pure rGO (1.265 m²/g). This substantial increase in surface area explains the higher initial adsorption of MB by the composite during the dark stirring phase, compared to rGO alone.

Under light irradiation, all ZnO/rGO composite samples degrade MB with varying efficiencies, which is much higher than pristine ZnO. While ZnO is inherently photoactive, its performance is limited by a high electron–hole recombination rate, limited surface adsorption sites, and a wide band gap [41,45]. However, combining rGO with ZnO addresses these limitations, enhancing both adsorption and photodegradation through synergistic interactions. As a result, all ZnO/rGO composites show significantly improved efficiency, compared to pure ZnO, as depicted in Fig. 5.2. This confirms the beneficial role of rGO in boosting the photocatalytic behaviour of ZnO.

	% MB removed/degraded in system with time					
Time (min)	rGO	ZG-30	ZG-50	ZG-70	ZG-90	ZG-100
0 (after 60 min dark stirring)	19.77	69.92	75.86	83.67	54.42	8.89
15	19.93	81.60	91.94	98.09	86.10	27.49
30	20.81	87.54	98.86	100	95.61	42.84
45	20.91571	94.62532	100	100	97.9845	54.01

Table 5.1: The percentage of MB removed/degraded in solution using different ZnO/rGO composite photocatalysts with time.

The photodegradation efficiency of the samples rGO, ZG-30, ZG-50, ZG-70, ZG-90, and ZG-100 for MB removal is summarized in Table 5.1. This table presents

the data depicted in Fig. 5.2 in a more precise and accessible format, providing clearer insight into the adsorption and photodegradation performance of each sample.

Based on the comparative analysis of photocatalytic activity, the ZG-70 composite was identified as the most efficient catalyst, achieving 98% degradation (Table 5.1) of MB within just 15 minutes of light irradiation. Therefore, all further investigations were carried out using the ZG-70 sample.

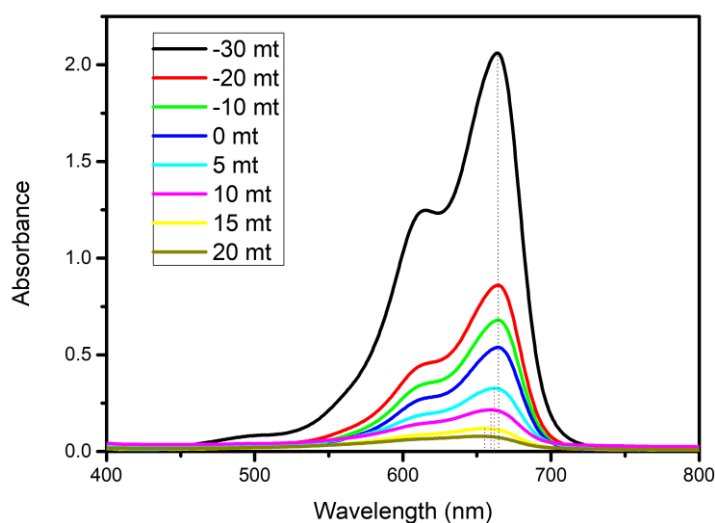


Fig. 5.3: UV–Visible spectra of MB solution during photocatalytic degradation by ZG-70 under xenon lamp irradiation at different irradiation times.

During initial experiments, it was observed that the ZnO/rGO composites exhibited a high adsorption capacity. Notably, a significant reduction in MB absorbance was recorded after 60 minutes of dark stirring, indicating substantial dye adsorption (84%) even before irradiation (Table 5.1). To avoid excessive dye removal during the dark phase and to better distinguish photocatalytic degradation, the dark stirring period was reduced to 30 minutes in subsequent experiments. After this adsorption phase, the samples were exposed to light, and absorbance measurements were taken at 5-minute intervals using a UV–Visible spectrophotometer to monitor the progression of photodegradation. The photodegradation efficiency of ZG-70 was examined in detail. The time-dependent spectra, measured over the wavelength range of 400–800 nm, are shown in Fig. 5.3. Remarkably, even with the reduced dark stirring

period, ZG-70 achieved approximately 97% degradation of MB within just 20 minutes of light exposure.

A closer examination of the spectrum in Fig. 5.3 reveals a gradual shift in the maximum absorbance peak of MB from 664 nm to 649 nm as photodegradation progresses. Fig. 5.4 depicts the rescaled view of Fig. 5.3, highlighting the spectral shift. This spectral shift, known as the hypsochromic shift, is attributed to the N-demethylation of the dimethyl amino group in the MB molecule. This process involves the breakdown of conjugated bonds within the MB structure. The blue shift in the UV–Visible spectra of MB indicates the formation of intermediate byproducts such as Azure A, Azure B, Azure C, and Thionine during the degradation process [62,63]. The hypsochromic effect is a well-documented phenomenon during MB degradation and has been reported in previous studies [64,65].

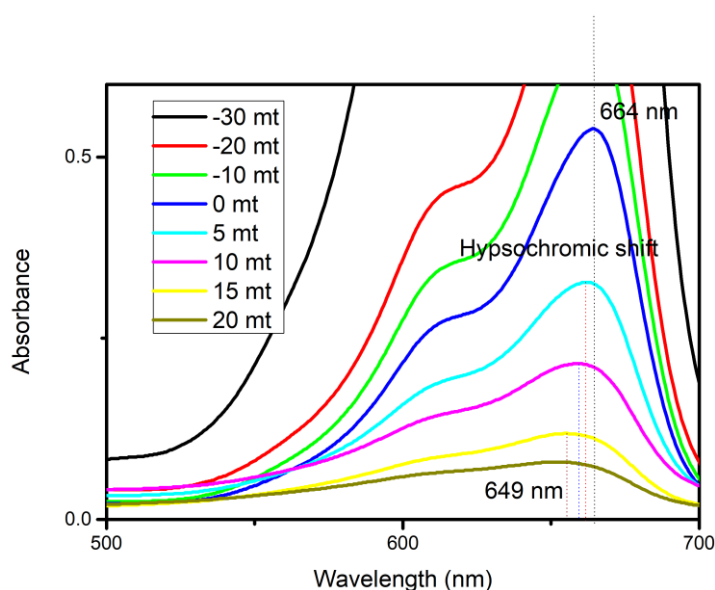


Fig. 5.4: Rescaled view of Fig. 5.3, highlighting the hypsochromic shift in the maximum absorbance peak of methylene blue from 664 nm to 649 nm during photodegradation by ZG-70.

The MB degradation test was repeated in the absence of light using ZG-70 as the photocatalyst to investigate whether the hypsochromic effect is present during adsorption. Stirring the ZG-70-MB suspension in darkness for 240 minutes led to the removal of 98% of MB, a significantly slower rate compared to the 20-minute removal achieved in the presence of light. The corresponding UV-Visible spectrum is presented

in Fig. 5.5. This removal was attributed to MB adsorption onto the catalyst surface. Despite the solution's decolouration, UV-Visible spectral analysis revealed that the peak at 664 nm did not exhibit a blue shift (hypsochromic effect). This observation suggests that decolourisation occurring in the presence of light is a result of photodegradation, whereas decolourisation in the absence of light is primarily due to adsorption of MB onto the catalyst's surface. The results demonstrate that adsorptive removal of methylene blue is achievable even in the absence of light, although it requires a longer duration. Under light irradiation, photodegradation becomes the dominant removal mechanism, proceeding at a much faster rate. This indicates that ZG-70 functions effectively both as an adsorbent and as a photocatalyst.

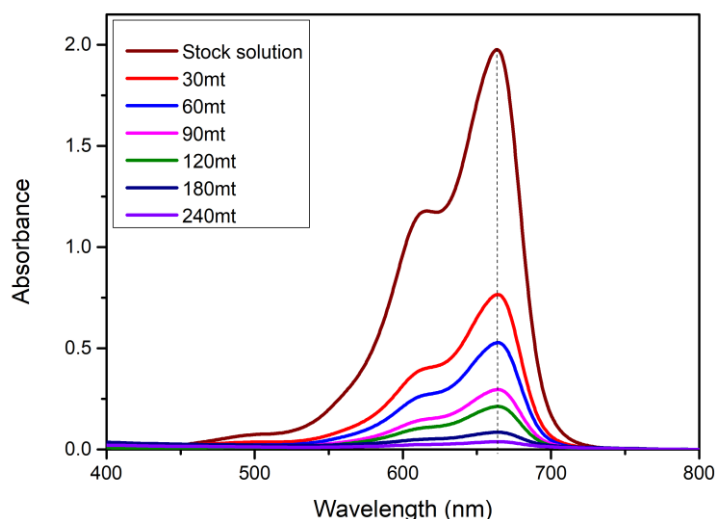


Fig. 5.5: The gradual decrease in UV-Visible spectrum of MB solutions over ZG-70 nanocomposite under dark condition, showing no hypsochromic shift during the adsorption process.

5.3.2 Kinetic studies

The photodegradation kinetics of MB using the photocatalysts were analysed based on the widely accepted Langmuir–Hinshelwood (LH) model for heterogeneous catalysis. The model is described by the following equation (Equation 5.2) [22]:

$$C = C_0 e^{(-kt)} \quad (5.2)$$

Where C is the absorbance of MB at time t , C_0 is the initial absorbance at $t = 0$, and k is the kinetic constant of the degradation process. Rearranging Equation 1 yields its linearised form (Equation 5.3):

$$-\ln\left(\frac{C_0}{C}\right) = kt \quad (5.3)$$

Fig. 5.6 presents the kinetic plots of $-\ln\left(\frac{C_0}{C}\right)$ versus time for both the pristine ZnO sample (ZG-100) and the composite sample (ZG-70). In both cases, the data points exhibit a linear trend, indicating that the degradation of MB follows a pseudo-first-order kinetic behaviour consistent with the Langmuir–Hinshelwood model [2,66].

From the slope of the linear fits, the kinetic rate constants were determined. The rate constant for ZG-70 was found to be 0.0878 min^{-1} , which is approximately 5.6 times higher than that of pure ZnO (ZG-100), which exhibited a rate constant of 0.0156 min^{-1} . This substantial increase highlights the enhanced photocatalytic efficiency of the ZG-70 composite compared to the pristine ZnO.

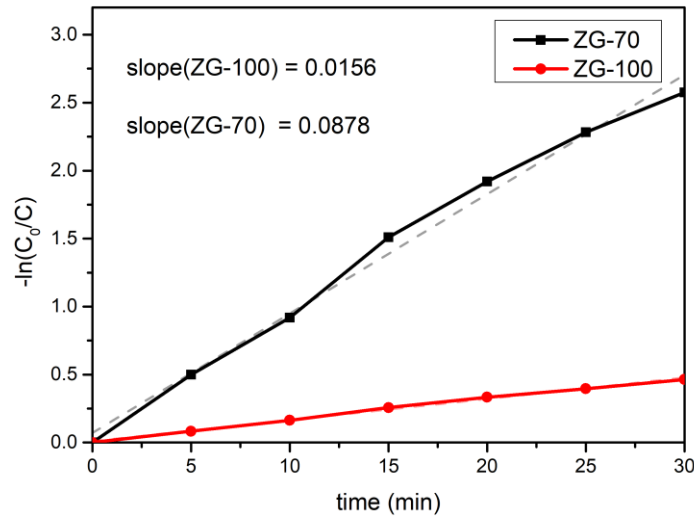


Fig. 5.6: Langmuir -Hinshelwood pseudo-first-order kinetic model for MB photodegradation using ZG-70 and ZG-100 as photocatalyst.

5.3.3 Photodegradation confirmation tests

5.3.3.1 LC-MS

Photocatalysis is an oxidative process in which reactive oxygen species trigger the cleavage of chemical bonds in high-molecular-mass toxicants, converting them into simpler, non-toxic, lower-mass molecules. During the photocatalytic degradation of MB, the aromatic rings in the dye molecule are broken down, ultimately yielding smaller end products such as CO_2 , H_2O , SO_4^{2-} , and NH_4^+ [67].

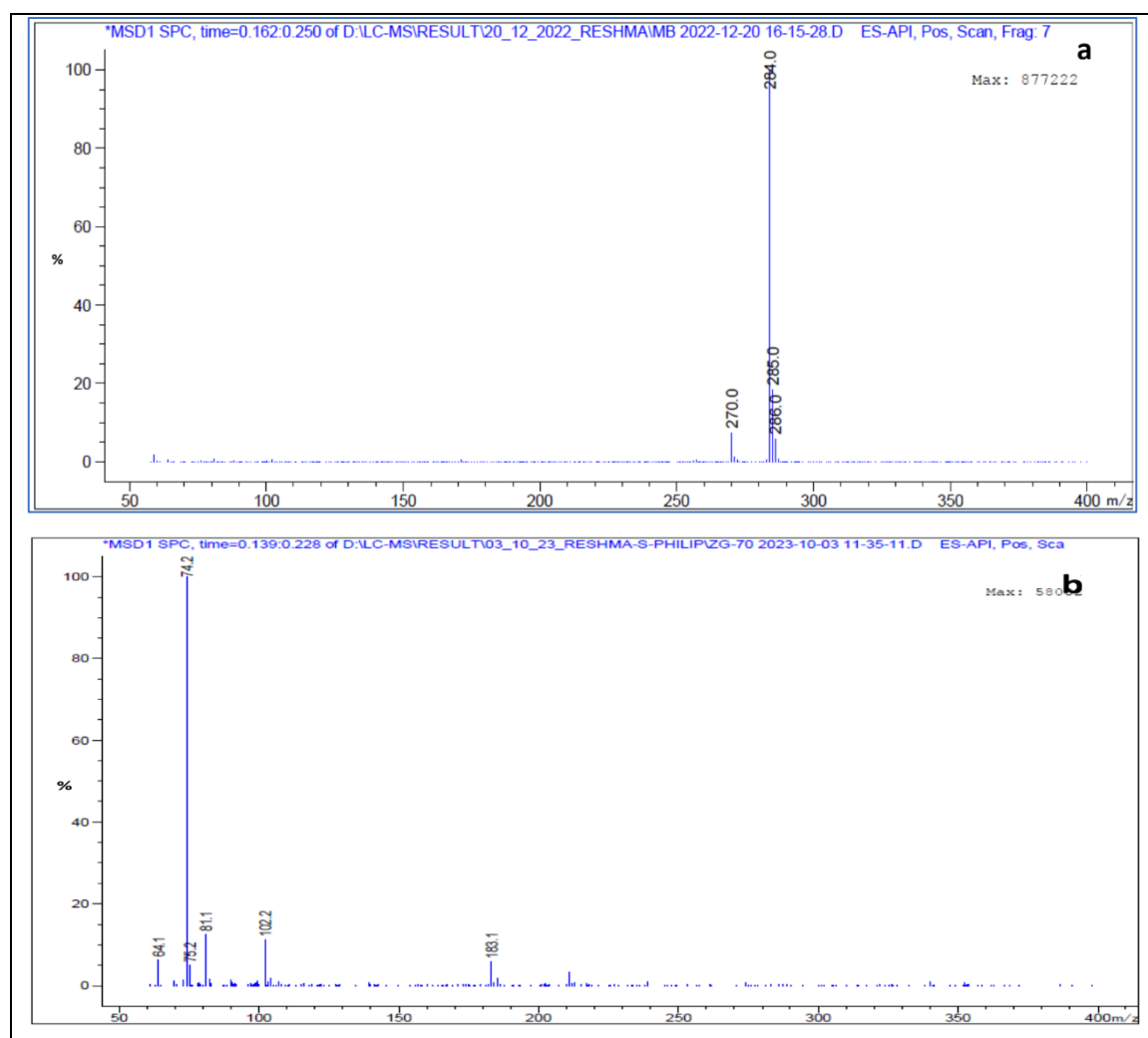


Fig. 5.7: LC-MS spectra of a) MB b) MB after photo reacted with catalyst ZG-70.

The occurrence of MB photodegradation was confirmed through liquid chromatography–mass spectrometry (LC–MS) analysis, which examined the mass spectra of the test solution before and after photocatalytic treatment. Different mass

peaks were observed based on the concentration of compounds present. The LC-MS spectra of the MB solution before and after the photoreaction are depicted in Fig. 5.7(a-b).

Fig. 5.7a shows a prominent peak at m/z value 284, corresponding to the MB dye molecule [68]. In contrast, Fig. 5.7b illustrates the LC-MS spectra of MB after photodegradation with catalyst, the peak corresponding to MB has vanished, while new peaks in the lower mass ranges have emerged. At the m/z value of 183, a small peak is observed, which corresponds to the intermediate formed through the process of demethylation cleavage of MB. Additionally, another minor peak at m/z value 102 is attributed to the presence of carboxylic acid groups. Furthermore, the peaks at much lower m/z values indicate that the MB molecule breaks down into smaller molecules such as carbon dioxide, nitrate, sulphate, and water [69]. The absence of the MB peak and the appearance of lower-mass peaks strongly indicate the decomposition of the MB molecule into simpler molecules due to the photocatalytic process.

5.3.3.2 UV-Vis spectrum of the post adsorbent

To confirm the complete degradation of MB by the photocatalyst during irradiation, the catalyst was separated from the reaction mixture, dried, and then re-dispersed in distilled water, followed by one hour of sonication. After sonication, the catalyst was removed via centrifugation, and the UV-Visible spectra of the remaining solution in the range of 500 nm to 800 nm were recorded. The corresponding spectrum is depicted in Fig. 5.8. This procedure was designed to detect any residual MB molecules that may have remained adsorbed on the catalyst surface. If present, these molecules would be released into the water during sonication, producing a characteristic absorbance peak in the UV-Visible spectrum. The absence of an MB peak in the UV-Visible spectrum of “filtrate after sonicating the used ZG-70 catalyst” as shown in Fig. 5.8, confirms that no residual MB remained adsorbed on the catalyst surface. This indicates that the MB molecules were degraded during the photocatalytic reaction. This result further validates that the removal of MB under light irradiation occurs through photodegradation rather than adsorption.

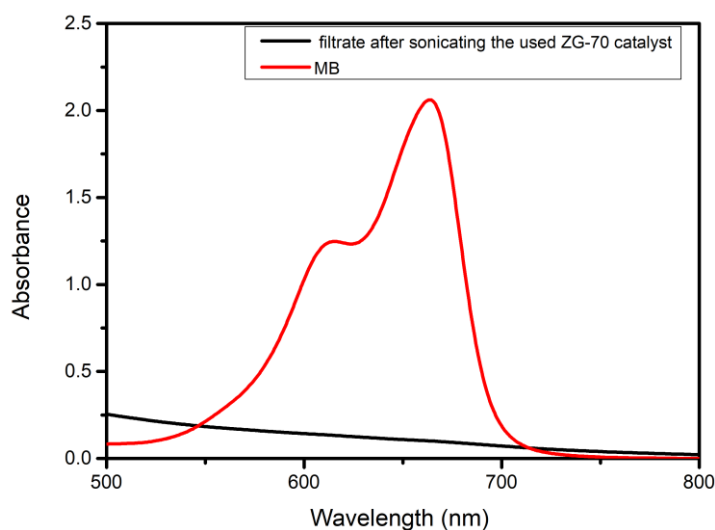


Fig. 5.8: UV– Visible spectrum of the solution obtained after sonication of the recovered photocatalyst following MB degradation, showing the absence of desorbed MB on the catalyst surface.

5.3.4 Mechanism of photodegradation

The photocatalytic degradation of pollutants using any heterogeneous catalyst comprises several key steps: the diffusion of pollutants into the liquid, their adsorption onto the catalyst surface, the generation of photoinduced ROS on the catalyst surface, the subsequent reaction between these ROS and the organic pollutant, and finally, the removal of resulting byproducts from the catalytic surface [8].

The photodegradation process begins with the adsorption of pollutants onto the catalyst surface. Since adsorption is a surface-driven process, a higher surface area improves photocatalytic efficiency by increasing active site availability and aiding pollutant diffusion [4]. As previously discussed, BET analysis confirmed that the ZnO/rGO composite exhibits a significantly greater surface area than pure rGO. This explains the greater initial adsorption of MB by the composite during the dark phase. The enhanced surface area is mainly attributed to the incorporation of rGO into the composite.

In addition to the surface area advantage, the presence of π – π interactions between the aromatic rings of rGO and MB molecules further enhances dye adsorption onto the rGO sheets [22,51]. As ROS generation occurs at the catalyst surface, efficient

adsorption is crucial for effective photodegradation. A photocatalyst that can adsorb more MB molecules enables faster and more efficient degradation.

Furthermore, the surface charge of the catalyst plays a significant role in determining its photocatalytic efficiency. To assess this, zeta potential measurements were performed on rGO and the composite sample ZG-40 to evaluate the surface charge at the interface between the solid catalyst and the liquid medium. The measurements revealed zeta potential values of -18 mV for rGO and -17 mV for composite, indicating that the prepared samples possess anionic surface charges. This negative surface charge promotes the diffusion of the cationic MB dye across the catalyst surface via Coulombic attraction, thereby enhancing adsorption and, subsequently, photocatalytic activity.

Following the discussion on surface properties, the photocatalytic mechanism of the ZnO/rGO composite is examined in detail. A fundamental aspect of photocatalysis is the generation of ROS, which drive the degradation of organic pollutants.

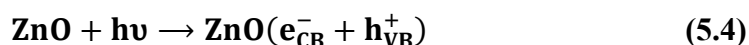
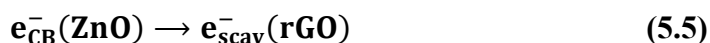
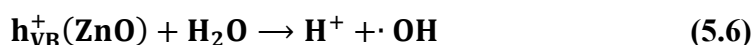
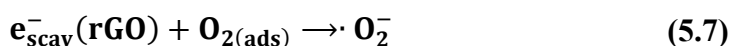
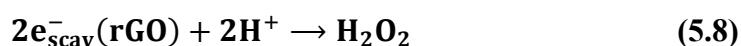
The basic mechanism in ZnO-based photocatalysis begins with the absorption of photons possessing energy equal to or greater than its band gap. This excitation leads to the formation of electron-hole pairs (e^-/h^+), as represented in Equation 5.4. These charge carriers interact with adsorbed water and oxygen molecules on the catalyst surface, generating highly reactive species such as $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$, as shown in Equations 5.6 and 5.7 [16,25,32].

The efficiency of photodegradation is directly linked to the quantity of ROS generated. However, pristine ZnO suffers from major limitations: (1) the rapid recombination of photogenerated e^-/h^+ pairs, which significantly reduces ROS yield, [7,14,19] (2) the wide band gap, which restricts the light absorption to the ultraviolet region [7,19,22,30] and (3) a limited number of adsorption sites, which restricts dye interaction at the surface. These drawbacks reduce its overall photocatalytic efficiency. This is clearly illustrated in Fig. 5.2 (C/C_0 vs. time), where ZG-100 (pure ZnO) shows both poor adsorption after dark stirring (zero-minute mark) and limited photodegradation performance under irradiation.

A promising strategy to enhance photodegradation efficiency is the integration of rGO with ZnO. The incorporation of rGO effectively addresses the key limitations associated with pristine ZnO as a photocatalyst [22,43]. The primary limitation of ZnO as the photocatalyst is the rapid recombination of photogenerated electron-hole pairs. Due to the excellent electrical conductivity and high charge carrier mobility of rGO, it

acts as an electron acceptor and transport medium, scavenging electrons from the ZnO conduction band immediately upon generation. This efficient charge separation significantly suppresses the recombination rate, thereby increasing the lifetime of photogenerated charge carriers [2,31,41,44].

In this composite system, rGO functions as an electron reservoir, while ZnO remains the primary site for ROS generation. The extended lifetime of separated charges enhances the likelihood of interaction with surrounding molecules, boosting the generation of reactive oxygen species. Specifically, photogenerated holes (h^+) in ZnO oxidize water molecules to form $\cdot OH$, while electrons (e^-), transferred to rGO, reduce adsorbed oxygen molecules to form superoxide radicals ($\cdot O_2^-$). These ROS are highly reactive and play a crucial role in the degradation of organic pollutants. The generated ROS further mineralize MB into smaller, non-toxic molecules such as CO_2 , H_2O , and other simple byproducts [29,31]. The detailed mechanism of ROS generation under light irradiation in the ZnO/rGO composite system is summarised in Equations 5.4–5.10.



The second major limitation of ZnO as a photocatalyst is its wide band gap, which confines its light absorption primarily to the ultraviolet region of the solar spectrum. Although the solar spectrum spans a broad range of wavelengths, only a small fraction falls within the UV range, limiting the overall light-harvesting efficiency of ZnO. Despite this, ZnO still exhibits moderate photocatalytic activity, as evidenced by the performance of ZG-100 shown in Fig. 5.2. The incorporation of rGO into ZnO addresses this limitation by narrowing the band gap of the composite material, thereby enhancing its ability to absorb visible light [22,45]. This improved optical response leads to more efficient solar energy utilization, as confirmed by the UV–Visible

spectral analysis discussed in Chapter 2, Section 2.2.3.2.7. As a result, the ZnO/rGO composites exhibit superior solar-to-photocatalytic conversion efficiency, significantly boosting their photocatalytic performance compared to pure ZnO [43].

The third limitation of pure ZnO as a photocatalyst is its low number of adsorption sites. Since adsorption is a surface-dependent process, the catalyst's surface area is a critical factor influencing photocatalytic efficiency. As noted earlier, BET analysis revealed that the ZnO/rGO composite has a significantly larger specific surface area than pure rGO. This increase confirms that composite formation enhances the available surface area and thus increases the number of active sites. Consequently, the composite exhibits greater initial adsorption of MB during the dark stirring phase compared to ZnO alone.

5.3.5 Experimental Validation of ROS Formation

5.3.5.1 ROS scavenging experiments

In photocatalytic systems, scavengers are compounds used to selectively capture reactive oxygen species generated during the reaction, thereby helping to identify the specific species responsible for pollutant degradation. To investigate the generation of active ROS in the ZnO/rGO composite (ZG-70) under light irradiation, a series of ROS trapping experiments was performed. Three scavengers were used: EDTA to trap photogenerated holes (h^+), benzoquinone (BQ) for superoxide radicals ($\bullet O_2^-$), and histidine for hydroxyl radicals ($\bullet OH$) [60,69,70].

Each trapping experiment involved the addition of 1 mL of a 10 mM scavenger solution to the MB–ZG-70 suspension before initiating light irradiation. These scavengers neutralize their respective ROS, reducing their availability for dye degradation and thus decreasing overall photocatalytic efficiency. The extent of this reduction indicates the relative importance of each ROS in the degradation process [45].

As shown in Fig. 5.9, the MB solution without any scavenger exhibited the fastest and highest degradation efficiency. In contrast, the presence of each scavenger led to a noticeable decline in photodegradation performance, confirming the active participation of h^+ , $\bullet O_2^-$, and $\bullet OH$ in the photocatalytic mechanism. Among these, $\bullet OH$ were identified as the dominant species, as evidenced by the most significant inhibition of MB degradation in the presence of histidine.

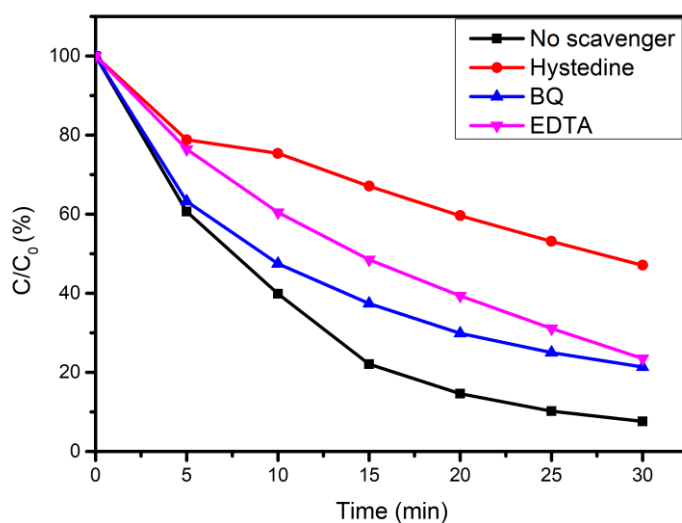


Fig. 5.9: Percentage of photodegradation of MB using the photocatalyst ZG-70 without and with scavengers.

5.3.5.2 Terephthalic acid test

The generation of hydroxyl radicals under light irradiation was further investigated using terephthalic acid (TA) as a probe molecule. TA is a non-fluorescent compound that selectively reacts with $\bullet\text{OH}$ radicals to form 2-hydroxyterephthalic acid (TAOH), a highly fluorescent molecule [60,71]. In this experiment, the ZG-70 photocatalyst was dispersed in a mixed solution containing 0.5 mM TA and 2 mM NaOH. The suspension was stirred in the dark for 10 minutes to establish adsorption-desorption equilibrium before exposure to light.

Following this, the TA-ZG-70 mixture was irradiated using a xenon flash lamp, and photoluminescence (PL) spectra were recorded at 10-minute intervals. Fig. 5.10 presents the PL spectra of TA after removal of the photocatalyst at various irradiation times. A gradual increase in fluorescence intensity at 425 nm (under excitation at 315 nm) was observed, demonstrating the progressive generation of $\bullet\text{OH}$ radical over time with irradiation [60,70].

For comparison, PL spectra of the TA solution collected after dark stirring (0-minute light exposure) were also recorded. As shown in Fig. 5.10, the spectra exhibit negligible fluorescence, confirming that $\bullet\text{OH}$ radicals were not generated in the absence of light. These results clearly demonstrate that hydroxyl radicals are produced only under photoirradiation and that their concentration increases proportionally with irradiation time.

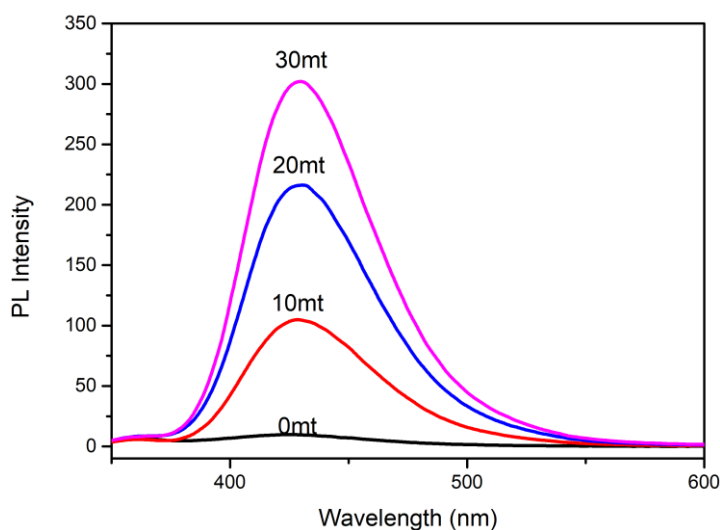


Fig. 5.10: PL spectra of terephthalic acid solution collected after interaction with ZG-70 under xenon lamp irradiation at different irradiation times.

5.4 Evaluation of Photocatalytic Activity Against Other Pollutants

The MB degradation experiments confirmed the excellent photocatalytic efficiency of the ZnO/rGO composite synthesized via a green single-step method. Following this, the photocatalytic performance of the composite was further evaluated for the degradation of another commonly used textile dye, RhB, as well as the pharmaceutical contaminant Ofloxacin, an antibiotic.

5.4.1 Rhodamine B

RhB is a synthetic cationic dye known for its vibrant pink colouration and is extensively used across various industries, including textiles, paper, leather, and cosmetics [55]. Structurally, RhB contains conjugated aromatic rings and amine functional groups, which impart high chemical stability and environmental persistence [56]. In addition to industrial applications, RhB is also employed as a fluorescent tracer dye in microscopy and biomedical research for studying cellular and tissue interactions [72,73].

Despite its wide utility, RhB is classified as a hazardous pollutant. It was once used as a food colouring agent and additive in products such as curry powder and chilli powder. However, due to growing concerns about its safety, it has been banned in food-related applications [1]. Exposure to RhB can cause skin and eye irritation, affect the respiratory tract, and pose serious risks to the reproductive and nervous systems.

Furthermore, RhB has been reported to exhibit carcinogenic and mutagenic properties [1,25,55]. When discharged untreated into water bodies, it poses a significant threat to both aquatic ecosystems and human health [74]. Therefore, the treatment of RhB-contaminated wastewater is of critical importance.

The photocatalytic activity of the synthesized ZnO/rGO composites was further evaluated using RhB as a model dye, following the same experimental procedure employed in the MB degradation studies. An optimization study was conducted to identify the most efficient photocatalyst among the samples ZG-30, ZG-50, ZG-70, ZG-90, and ZG-100. For comparison, rGO was also included in this analysis. The results are presented in Fig. 5.11.

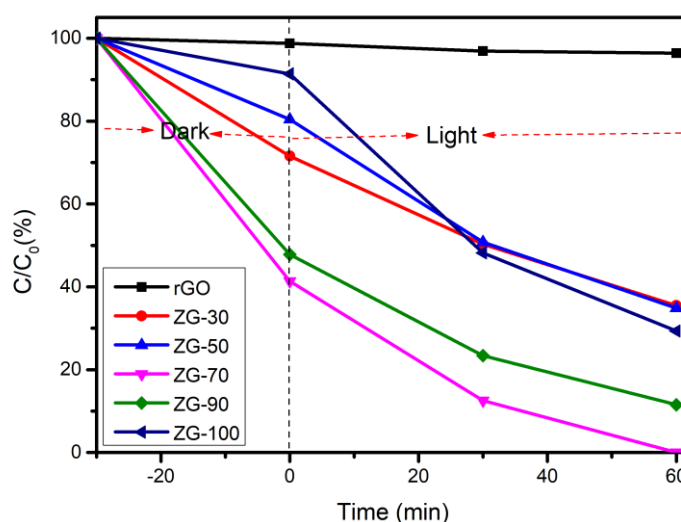


Fig. 5.11: Photocatalytic degradation of RhB using various photocatalysts under different irradiation durations.

The overall trend observed in RhB degradation closely resembles that of MB, except for rGO. Unlike MB, RhB showed poor adsorption on the surface of rGO, likely due to weaker interactions between RhB molecules and the rGO surface. On the other hand, pure ZnO (ZG-100) demonstrated minimal adsorption in the dark phase but showed moderate photocatalytic activity under light irradiation.

In contrast, the ZnO/rGO composites exhibited enhanced performance, with increased dye adsorption during the dark phase and improved photodegradation rates under light exposure. Among the tested samples, ZG-70 again demonstrated the highest

photocatalytic efficiency, confirming its superior performance across different dye pollutants.

Table 5.2 summarizes the percentage of RhB removed or degraded from the solution by different catalysts—rGO, ZG-30, ZG-50, ZG-70, ZG-90, and ZG-100—over time. This tabulation corresponds to the data illustrated in Fig. 5.11, providing a clearer and more detailed comparison. rGO exhibited minimal adsorption capacity, removing only about 3.5% of RhB after 90 minutes (30 minutes dark stirring followed by 60 minutes of light exposure). In contrast to its behaviour with MB, pure ZnO demonstrated slightly higher adsorption efficiency for RhB, removing 8.5% during the dark phase and achieving 70% degradation after light irradiation. The formation of ZnO/rGO composites significantly enhanced both adsorption and photocatalytic degradation. Among them, ZG-70 stands out as the most efficient, adsorbing 59% of RhB during the dark phase and achieving complete degradation after 60 minutes of photoirradiation.

	% RhB removed/degraded in system with time					
Time (min)	rGO	ZG-30	ZG-50	ZG-70	ZG-90	ZG-100
0	1.24908	28.43497	19.61793	58.63336	52.16752	8.59662
30	3.08597	49.74284	49.22851	87.43571	76.63483	51.80015
60	3.60029	64.51139	65.17267	100	88.46436	70.68332

Table 5.2: Time-dependent percentage of RhB removed/degraded in solution using different ZnO/rGO composite catalyst

The RhB solution was treated with the most efficient photocatalyst, ZG-70, under two different conditions—in complete darkness and under light irradiation—to evaluate the respective contributions of adsorption and photocatalysis. The corresponding UV–visible spectral changes are presented in Fig. 5.12.

Fig. 5.12a illustrates the spectral changes during dark stirring. A noticeable decrease in absorbance was observed in the first 15 minutes, indicating rapid adsorption of RhB molecules onto the catalyst surface, facilitated by the availability of abundant active sites. As the adsorption sites became occupied, the rate of adsorption declined

sharply. After 75 minutes, no further decrease in absorbance was observed, suggesting that the adsorption had reached saturation.

In contrast, Fig. 5.12b presents the UV–visible spectral changes of the RhB solution with ZG-70 under xenon lamp irradiation. A significantly greater reduction in absorbance occurred within the first 25 minutes compared to the dark condition, indicating simultaneous adsorption and photodegradation. The photogenerated reactive species degrade the adsorbed RhB molecules on the catalyst's surface, thereby regenerating the active sites and allowing further adsorption–photodegradation cycles. As a result, the absorbance peak corresponding to RhB progressively diminished and completely disappeared after 120 minutes, confirming the efficient photocatalytic degradation by ZG-70 under light exposure.

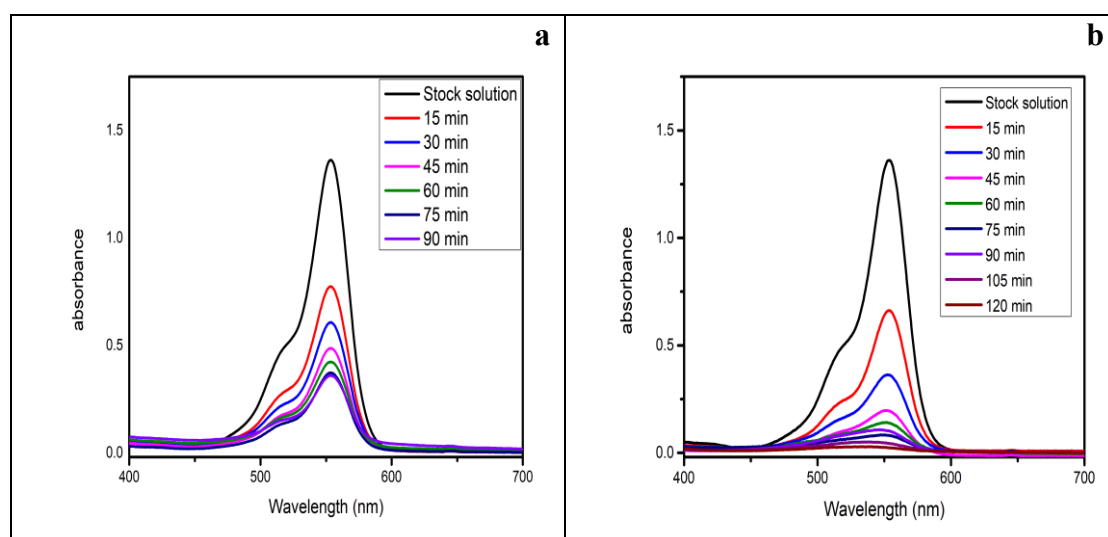


Fig. 5.12: UV–visible absorbance spectra of RhB solution with ZG-70 photocatalyst: (a) in dark stirring, showing minimal change due to adsorption; (b) under light irradiation, demonstrating significant spectral reduction indicating effective photodegradation.

The photodegradation of RhB was further confirmed by high-performance liquid chromatography (HP-LC) analysis conducted before and after the photocatalytic reaction [75]. As shown in Fig. 5.13, the HP-LC chromatogram of the initial RhB stock solution displays a prominent peak corresponding to RhB. However, this characteristic peak is completely absent in the chromatogram recorded after the solution was treated with the ZG-70 photocatalyst under light irradiation for 90 minutes. The disappearance of the RhB peak indicates the effective degradation of the dye, confirming the photocatalytic efficiency of the ZG-70 composite.

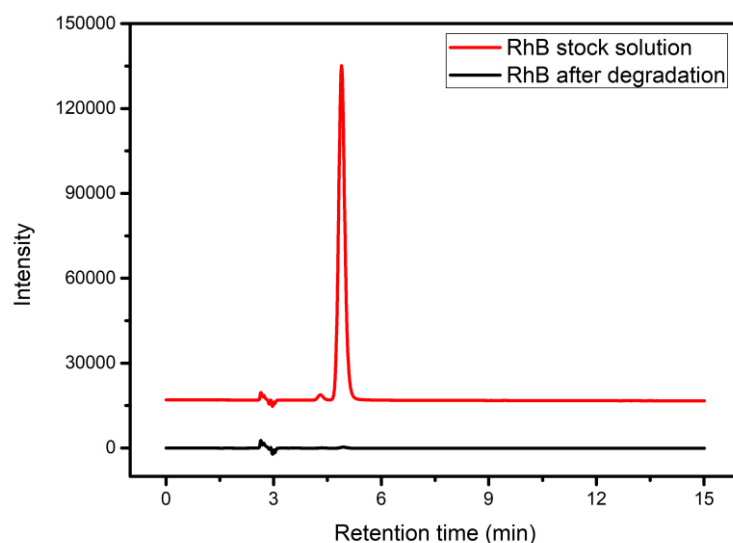


Fig. 5.13: HP-LC chromatogram for RhB dye before and after degradation.

5.4.2 Antibiotic Ofloxacin

The photocatalytic performance of the synthesized ZnO/rGO composite was further assessed for the degradation of Ofloxacin, a widely used second-generation fluoroquinolone antibiotic. It is commonly prescribed to treat bacterial infections such as respiratory, urinary tract, and gastrointestinal illnesses [76]. Due to its extensive use and continuous discharge through pharmaceutical waste, hospital effluents, and human excretion, Ofloxacin is frequently detected in aquatic environments. Its chemical stability and low biodegradability make it resistant to conventional biological and chemical treatment methods [58,59].

The persistence of Ofloxacin in water poses significant environmental and public health risks, even at low concentrations [57]. It can contribute to the development of antibiotic-resistant bacteria, disturb aquatic microbial ecosystems, and potentially harm human and animal health [59]. Its recalcitrant nature categorizes it as an emerging contaminant, underscoring the need for advanced and effective remediation strategies. Advanced photocatalysts, such as ZnO/rGO composites, have shown promise in degrading such complex, persistent molecules under light irradiation, offering a potential pathway for the effective removal of pharmaceutical contaminants from water systems.

Fig. 5.14 presents the photocatalytic degradation efficiencies of various ZnO/rGO composites in the removal of Ofloxacin, a persistent pharmaceutical contaminant. For comparison, the removal efficiency of pristine rGO is also included. Both rGO and pure ZnO exhibited minimal adsorption during the initial dark stirring phase, indicating limited interaction with the Ofloxacin molecules. However, upon forming ZnO/rGO composites, a significant increase in adsorption efficiency was observed. Since photocatalysis is a surface-driven process, enhanced adsorption plays a crucial role in facilitating photodegradation by ensuring effective interaction between the pollutant and the catalyst surface.

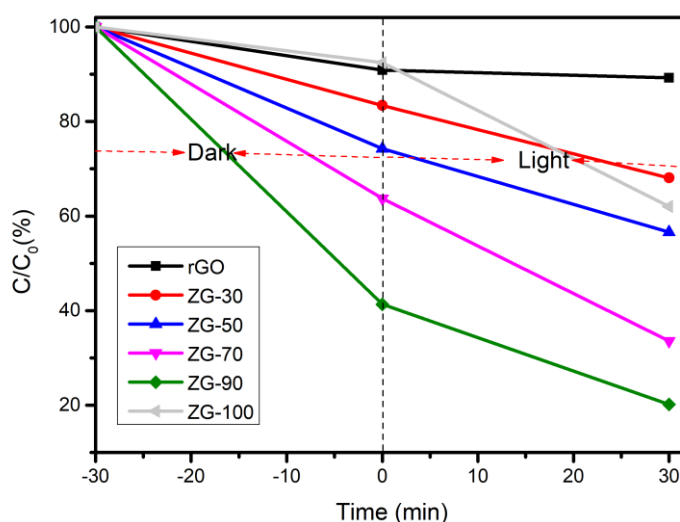


Fig. 5.14: Photocatalytic degradation of antibiotic Ofloxacin using various photocatalysts under different irradiation durations.

Upon light irradiation, ROS are generated, which initiate the degradation of Ofloxacin molecules. Although pure ZnO demonstrates photocatalytic activity, its effectiveness is limited due to its low adsorption capacity, rapid recombination of photogenerated electron-hole pairs, and suboptimal light utilization [7,14,19,45]. These limitations are effectively addressed by incorporating rGO, which enhances surface area, improves charge separation, and extends light absorption [22,43,45]. This synergistic effect is clearly reflected in the superior performance of the ZnO/rGO composites.

Interestingly, unlike in the case of dye degradation, where ZG-70 showed the highest activity, the composite ZG-90 emerged as the most efficient photocatalyst for Ofloxacin degradation, as indicated in Fig. 5.14.

Table 5.3 presents the percentage of Ofloxacin removed or degraded over time using different catalysts, corresponding to the data shown in Fig. 5.14. After 30 minutes of dark stirring, both rGO and ZG-100 showed poor adsorption capacities, removing only about 9% and 7% of Ofloxacin, respectively. During the light irradiation phase, rGO showed a marginal increase in removal to 10.7%, while ZnO exhibited photocatalytic activity, degrading around 38% of the antibiotic. Similar to the trend observed with dye pollutants, incorporating rGO into the ZnO matrix significantly enhanced both adsorption and photodegradation efficiency. Among the composites, ZG-90 showed the best performance, adsorbing 59% of Ofloxacin in the dark phase and degrading 80% after 30 minutes of illumination.

	% Ofloxacin removed/degraded in system with time					
Time (min)	rGO	ZG-30	ZG-50	ZG-70	ZG-90	ZG-100
0	9.14179	16.60448	25.74627	36.28731	58.67537	7.55597
30	10.7276 1	31.90299	43.37687	66.41791	79.85075	37.96642

Table 5.3: The percentage of Ofloxacin removed/degraded in solution using different ZnO/rGO composite catalyst with time.

The Ofloxacin solution was treated with the most efficient photocatalyst, ZG-90, under two different conditions: one stirred in complete darkness and the other exposed to light irradiation. The corresponding UV–visible spectral changes at various time intervals are presented in Fig. 5.15.

Fig. 5.15a shows the spectral evolution under dark conditions. A sharp decrease in absorbance was observed during the first 15 minutes, attributed to the rapid adsorption of Ofloxacin molecules onto the catalyst surface, where abundant active sites were initially available. However, as these sites became saturated, no further significant reduction in Ofloxacin concentration was observed, indicating that adsorption had reached equilibrium.

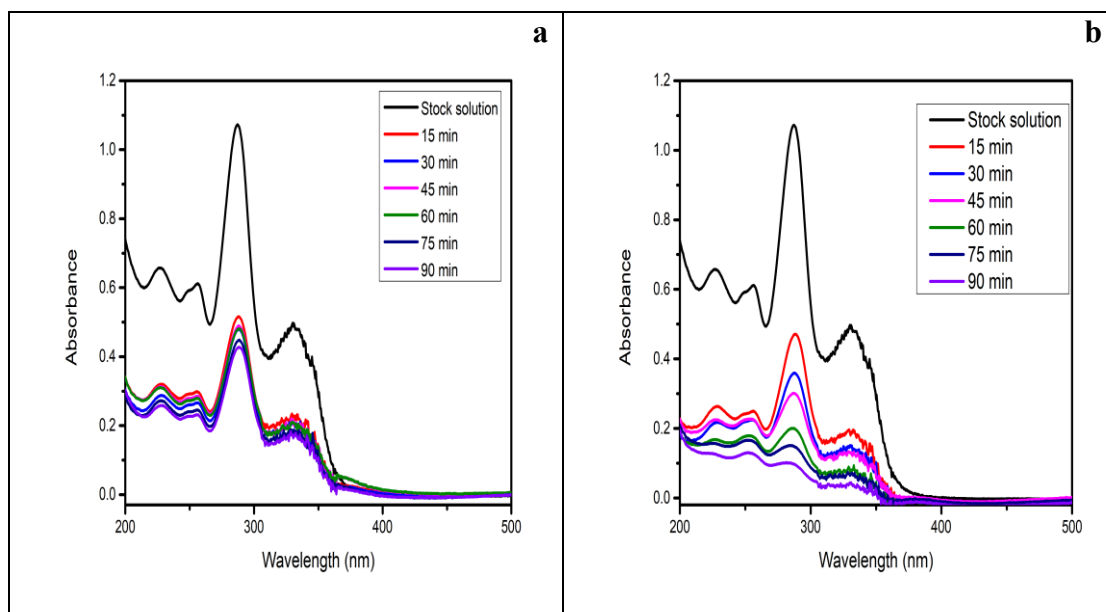


Fig.5.15: UV–visible absorbance spectra of Ofloxacin solution with ZG-90 photocatalyst: (a) in dark stirring, showing minimal change due to adsorption; (b) under light irradiation, demonstrating significant spectral reduction indicating effective photodegradation.

In contrast, Fig. 5.15b depicts the spectral changes under xenon lamp irradiation. A continuous and more pronounced decrease in absorbance was recorded, reflecting the combined effect of adsorption and photocatalytic degradation. The initial decline was rapid due to the immediate degradation of adsorbed Ofloxacin molecules by photogenerated reactive oxygen species. As degradation proceeded, newly vacant active sites became available, allowing further adsorption of remaining pollutant molecules, which were subsequently degraded. This cyclic process resulted in the gradual and efficient breakdown of Ofloxacin in the presence of ZG-90 under light irradiation.

The purification of Ofloxacin-contaminated water using the ZG-70 photocatalyst under 120 minutes of light irradiation was confirmed by HP-LC analysis of the solution before and after photocatalysis. The HP-LC chromatograms of both samples are presented in Fig. 5.16. In the chromatogram of the Ofloxacin stock solution, two prominent peaks corresponding to the parent compound are clearly visible. However, these peaks are absent in the chromatogram of the solution after photocatalytic treatment, indicating the efficient decomposition of the Ofloxacin molecules. This result confirms that the ROS generated during light irradiation

effectively broke down the pharmaceutical compound in the presence of the ZnO/rGO (ZG-70) photocatalyst.

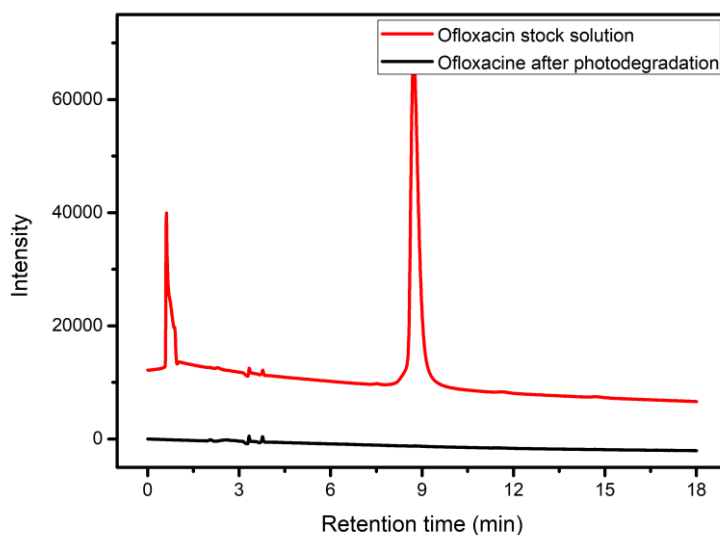


Fig. 5.16: HP-LC chromatogram for antibiotic ofloxacin before and after degradation.

5.5 Conclusions

The experimental results demonstrate that the ZnO/rGO composite, synthesized via a novel single-step pyrolytic method using sucrose and zinc acetate, is a highly efficient photocatalyst capable of degrading both dyes and antibiotics. The key findings from this study are summarized below:

1. rGO exhibits high adsorption capacity for methylene blue (MB) but is photochemically inactive.
2. ZnO shows limited adsorption but gradually degrades MB under light irradiation due to its intrinsic photocatalytic activity.
3. The formation of ZnO/rGO composites significantly enhances both adsorption and photodegradation efficiency.
4. Among all samples, ZG-70 was identified as the most efficient photocatalyst.
5. The incorporation of rGO with ZnO addresses the limitations of pure ZnO by:
 - suppressing electron–hole recombination,

- improving light absorption, and
 - providing abundant active surface sites.
6. ZG-70 at a dosage of 1g/L achieved 98% degradation of MB within just 20 minutes of light irradiation.
 7. A hypsochromic shift (peak shift from 664 nm to 649 nm), associated with N-demethylation, was observed during degradation.
 8. Kinetic studies confirmed that the degradation process follows Langmuir–Hinshelwood pseudo-first-order kinetics.
 9. LC-MS analysis validated the breakdown of MB molecules into low-molecular-weight fragments after photocatalysis.
 10. Scavenger experiments using histidine, benzoquinone, and EDTA confirmed the role of reactive species in the degradation mechanism.
 11. Among the ROS species, $\bullet\text{OH}$ were found to be the most dominant and effective in dye degradation.
 12. The generation of hydroxyl radicals under light irradiation was confirmed using terephthalic acid as a probe molecule.
 13. The photocatalytic performance of ZnO/rGO was also evaluated against other pollutants—Rhodamine B and the antibiotic Ofloxacin—to confirm its broad-spectrum efficacy.
 14. ZG-70 was identified as the most efficient photocatalyst for RhB degradation.
 15. ZG-90 demonstrated superior photocatalytic performance in degrading Ofloxacin.
 16. The complete degradation of Rhodamine B and Ofloxacin was verified through HP-LC analysis, showing the disappearance of their characteristic peaks after photocatalytic treatment.

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Chapter VI

Studies on Electrochemical and Energy Storage Properties of ZnO/rGO Composites for Supercapacitor Devices

Abstract

This chapter presents an evaluation of the electrochemical performance of reduced graphene oxide (rGO), ZnO/rGO composite (ZG-50), and pure ZnO (ZG-100) for supercapacitor applications. The energy storage performance of these materials was analysed using cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) techniques in a three-electrode system. The CV analysis revealed that rGO exhibited typical electric double-layer capacitive (EDLC) behaviour, while the ZG-50 composite showed features of both EDLC and pseudocapacitance, confirming its hybrid charge storage mechanism. The GCD curves further supported this observation, displaying nearly symmetric charge–discharge profiles that indicate good reversibility and electrochemical stability. Among the samples, ZG-50 demonstrated the highest specific capacitance, which can be attributed to the synergistic interaction between ZnO and rGO. The incorporation of ZnO nanoparticles between rGO sheets inhibited sheet restacking, increased porosity, and surface area, and facilitated efficient ion diffusion and electron transport. These findings suggest that ZnO/rGO composites possess electrochemical performance and hold great promise as efficient electrode materials for next-generation supercapacitors.

6.1 Introduction

The world is currently facing a growing energy crisis driven by the rapid depletion of fossil fuels, increasing global energy demand, and growing environmental concerns associated with greenhouse gas emissions. Traditional energy resources such as coal, oil, and natural gas are finite and unsustainable in the long term, contributing significantly to climate change and environmental pollution. To ensure a sustainable and clean energy future, it is essential to adopt alternative strategies such as renewable energy generation, energy-efficient technologies, and advanced energy storage systems [1].

Renewable energy sources such as solar, wind, and tidal energy provide sustainable and environmentally friendly alternatives to fossil fuels [2]. However, the

intermittent nature of these sources poses challenges for a consistent energy supply. Therefore, the development of advanced energy storage technologies has become vital to ensure stable and reliable energy delivery to end-use devices. Effective energy storage systems can address these intermittency issues, enhancing the reliability and efficiency of renewable energy utilization [2,3].

Conventional batteries are widely used for energy storage; however, they suffer from several limitations, including low conversion efficiency, slow charging rates, limited cycle life, and safety concerns. Moreover, batteries typically release energy at a slower rate, resulting in lower power density. In contrast, conventional capacitors deliver high power density but suffer from low energy storage capacity. These limitations have created the need for innovative energy storage devices that combine high energy and high-power capabilities, among which supercapacitors have emerged as a promising alternative [4].

Supercapacitors, also known as ultracapacitors, have emerged as a promising class of energy storage devices that bridge the gap between traditional batteries and conventional capacitors [5]. They offer high energy storage capacity, superior power density, and rapid charge–discharge performance. Additionally, they exhibit long cycle life, high specific capacitance, and excellent operational stability [6,7]. Owing to these unique properties, supercapacitors are increasingly being developed for diverse applications, including portable electronic devices, electric vehicles, and renewable energy systems, where efficient and reliable energy storage is essential [8,9].

6.1.1 Benefits of Supercapacitors

1. **High Power Density:** Supercapacitors can deliver energy at much higher rates than batteries, making them ideal for applications that require quick bursts of power.
2. **Rapid Charging and Discharging:** They can be charged within seconds or minutes, unlike batteries that often require several hours.
3. **Long Cycle Life:** Unlike batteries that degrade their efficiency over repeated charge–discharge cycles due to chemical reactions, supercapacitors can withstand thousands to millions of cycles with minimal loss of performance

4. **Wide Operating Temperature Range:** They operate efficiently under extreme environmental conditions, enhancing their reliability.
5. **Eco-Friendly and Safe:** Supercapacitors are inherently safer than batteries, with lower risks of leakage, overheating, or explosion.
6. **Support for Renewable Energy:** They serve as excellent buffers for intermittent renewable energy sources, stabilizing the power supply and improving overall system efficiency [2,5,6,7,8,10,11].

6.1.2 Working Principle of Supercapacitors

Supercapacitors operate on the same fundamental principle as conventional capacitors—storage of energy through charge separation—but differ in their materials and mechanisms. In a conventional capacitor, two metallic plates are separated by a solid insulating dielectric [3]. The charge is stored electrostatically on the plates, and energy is stored in the electric field of the dielectric.

In contrast, a supercapacitor uses porous electrodes made of high-surface-area materials [12] such as activated carbon, graphene, carbon nanotubes, conducting polymers, or metal oxides [13]. Instead of a solid dielectric, it uses an electrolyte, which may be aqueous, organic, or ionic liquid-based. When a voltage is applied, positive and negative ions in the electrolyte migrate toward the oppositely charged electrodes, forming an electric double layer (EDLC) at the electrode–electrolyte interface. In some supercapacitors, additional energy is stored through fast surface redox reactions, known as pseudocapacitance.

Hence, while conventional capacitors store charge electrostatically, supercapacitors store it electrochemically at the interface between electrode and electrolyte. This mechanism allows them to achieve far higher capacitance and energy storage capacity than traditional capacitors, while maintaining fast charge–discharge performance [9].

6.1.3 Components of a Supercapacitor

A supercapacitor consists mainly of three essential components [8,14]:

- **Electrodes:** The primary energy-storing components, made from high-surface-area materials that enable efficient charge accumulation.

- **Electrolyte:** Provides mobile ions that move between electrodes during charging and discharging. Its composition determines the operating voltage and stability of the device.
- **Separator:** A thin, porous insulating membrane placed between the two electrodes. It allows ion movement but prevents electrical short circuits.

6.1.4 Working of the supercapacitor

During charging, positive ions migrate toward the negatively charged electrode, while negative ions move toward the positively charged electrode, forming a thin double layer of separated charges at each interface [12]. This double layer stores electrical energy without any bulk chemical reactions, enabling rapid charging and high-power output.

When the supercapacitor is discharged, the stored charges are released: ions in the electrolyte return to their original positions, and electrons flow through the external circuit, delivering energy to the connected load.

Unlike batteries, supercapacitors do not depend on slow chemical reactions. As a result, they exhibit rapid charge–discharge behaviour, high power density, and long operational life, making them suitable for modern energy storage applications such as electric vehicles, renewable energy systems, portable electronics, and backup power devices [8].

6.1.5 Types of Supercapacitors

Supercapacitors are a class of advanced energy storage devices that combine the advantages of both batteries and conventional capacitors. They offer high power density, rapid charge–discharge capability, and excellent cycling stability. Based on their energy storage mechanisms, supercapacitors are generally categorized into three main types: Electrical Double-Layer Capacitors (EDLCs), Pseudo capacitors, and Hybrid Capacitors [6,7,10,15].

1. Electrical Double-Layer Capacitors (EDLCs)

EDLCs store energy through electrostatic charge separation at the electrode–electrolyte interface. In this process, no chemical reaction occurs; instead, energy is stored by the accumulation of ions forming an electric double layer at the interface

[4,12,16]. These supercapacitors are characterized by high power density, long cycle life, and moderate energy density [10]. The commonly used electrode materials include activated carbon, graphene, and carbon nanotubes, all of which provide a large surface area for charge accumulation [1,11].

2. Pseudocapacitors

In pseudocapacitors, energy storage occurs through fast and reversible Faradaic (redox) reactions at the electrode surface [4,12,16]. Their cycle life is generally shorter due to the involvement of surface redox reactions. Typical electrode materials that exhibit pseudocapacitance include transition metal oxides (such as RuO_2 , MnO_2 , NiO , V_2O_5 , TiO_2 , etc.) and conducting polymers (such as polyaniline and polypyrrole) [1,6,11].

3. Hybrid Capacitors

Hybrid capacitors are designed to bridge the gap between EDLCs and pseudocapacitors, combining both electrostatic and Faradaic charge storage mechanisms [7,17]. They offer an optimal balance between energy density and power density, with a longer cycle life compared to batteries. Depending on their configuration, hybrid capacitors may use asymmetric electrodes—typically a carbon-based material (for EDLC behaviour) and a redox-active material (for pseudocapacitive behaviour). The commonly employed electrode materials include carbon–metal oxide composites, graphene–polymer composites, and carbon nanotube-based hybrids. These materials enhance both capacitance and stability, resulting in superior overall performance [15].

Although supercapacitors possess lower energy density than batteries, their high power density, fast charge–discharge response, and excellent thermal stability make them highly attractive for various applications. Ongoing research focuses on enhancing their energy storage capability by developing advanced materials such as graphene and its derivatives, conducting polymers, and carbon nanotubes. These advancements aim to reduce the performance gap between supercapacitors and batteries, paving the way for next-generation high-performance energy storage systems.

6.1.6 Types of Electrode Materials for Supercapacitor Applications

The performance of a supercapacitor largely depends on the type of electrode material used, as it determines the charge storage mechanism—whether electrical double-layer capacitance (EDLC), pseudocapacitance, or hybrid behaviour. Based on their composition and properties, electrode materials are generally classified into carbon-based materials, metal oxides, conducting polymers, and composite or hybrid materials [14].

1. Carbon-Based Materials

Carbon-based materials are the most widely used electrodes in supercapacitors, primarily exhibiting EDLC behaviour. In these materials, charge is stored electrostatically through ion accumulation at the electrode–electrolyte interface without involving any chemical reactions [5]. The electrochemical performance of carbon electrodes is strongly influenced by their surface area, pore structure, electrical conductivity, and mechanical strength. Commonly used carbon materials include activated carbon, carbon nanotubes (CNTs), graphene or reduced graphene oxide (rGO), and carbon fibres, all of which offer large surface areas and good electrical conductivity [2,16]. These materials are preferred for their low cost, high stability, and long cycle life.

2. Metal Oxides

Metal oxides represent another important class of electrode materials that store charge through fast and reversible Faradaic (redox) reactions, characteristic of pseudocapacitors. These materials generally offer higher energy density than carbon-based EDLCs due to their redox-active nature [5]. Commonly studied metal oxides include RuO_2 , MnO_2 , NiO , Co_3O_4 , V_2O_5 , and Fe_2O_3 [11].

Among them, RuO_2 exhibits excellent capacitance and electrical conductivity but is limited by high cost and toxicity, restricting their large-scale application. In contrast, Co_3O_4 , MnO_2 , and ZnO are widely explored due to its abundance, low cost, environmental friendliness, and good electrochemical performance, making them a promising alternative for sustainable supercapacitor electrodes [18].

3. Conducting Polymers

Conducting polymers are another extensively studied group of electrode materials for supercapacitors. They store energy through fast and reversible redox reactions, similar to metal oxides, providing higher specific capacitance than EDLCs. Common examples include Polyaniline (PANI), Polypyrrole (PPy), and Polythiophene (PTh) [9].

These materials offer several advantages, such as high capacitance, lightweight nature, and mechanical flexibility, making them suitable for wearable and flexible energy storage devices. However, their major limitation lies in poor cycling stability due to volumetric expansion and contraction during repeated charge–discharge processes, leading to gradual capacity fading over time [5,19].

4. Composite and Hybrid Materials

Composite or hybrid materials are developed to combine the advantages of different types of electrode materials and to balance energy density, power density, and cycling stability [20]. These materials typically integrate the high surface area and conductivity of carbon materials with the redox activity of metal oxides or conducting polymers. Such hybrid systems exhibit both electric double-layer capacitance and Faradaic pseudocapacitance, resulting in improved overall performance—higher energy and power density, enhanced mechanical stability, and longer cycle life [7,17]. Typical hybrid combinations include:

- **Carbon–metal oxide composites**
- **Carbon–conducting polymer composites**
- **Metal oxide–conducting polymer composites**
- **Composites/Hybrid** combining carbon, metal oxide, and polymer components

In addition, asymmetric supercapacitors—which use different electrode materials for the anode and cathode (for instance, rGO–RuO₂ and rGO–PANI)—have been explored to further enhance performance [21]. Despite these advancements, hybrid electrode design still faces challenges, such as achieving uniform dispersion of active materials, optimizing nanostructures for efficient ion diffusion, and ensuring strong interfacial contact between different components.

6.2 Review of Earlier Works

Reduced graphene oxide is considered a highly promising material within the carbon family for supercapacitor applications. Its large surface area, excellent electrical conductivity, thermal stability, environmental friendliness, and low cost make it an attractive electroactive electrode material for energy storage devices [11,12]. Numerous studies have been carried out to evaluate the electrochemical performance of rGO-based supercapacitors, employing various synthesis routes and electrolytes.

Pinku Krishnan et al. prepared rGO via a modified Hummers method followed by chemical reduction and reported that the rGO-based supercapacitor achieved a maximum specific capacitance of 232 F g^{-1} in 6 M KOH, with corresponding energy and power densities of approximately 21 Wh kg^{-1} and 400 W kg^{-1} , respectively [1].

In a study by Fatima Tuz Johra et al., hydrothermally reduced graphene oxide was examined as a supercapacitor electrode, yielding a specific capacitance of 367 F g^{-1} at a current density of 1 A g^{-1} in 1 M H_2SO_4 electrolyte [12].

Subramanian Natarajan et al. synthesized rGO from spent lithium-ion battery graphite and demonstrated its potential as an electrode material for supercapacitors. The prepared rGO exhibited excellent electrochemical behaviour due to its high surface area and mesoporous structure, achieving a specific capacitance of 112 F g^{-1} at a current density of 0.5 A g^{-1} [22].

Rajneesh Kumar Mishra et al. developed a symmetric supercapacitor architecture based on rGO and nitrogen-doped rGO (N-rGO) electrodes, highlighting the role of nitrogen functionalization in enhancing capacitance and cycling performance [2].

In another study, Kalimuthu Vijaya Sankar et al. investigated the electrochemical performance improvement of rGO-based supercapacitors using a redox additive electrolyte. The rGO electrode exhibited a specific capacitance of 500 F g^{-1} and an energy density of 44 Wh kg^{-1} in 1 M KOH + 0.05 M KI electrolyte. In a non-aqueous polymer gel electrolyte (PVA + KOH + KI), it showed a specific capacitance of 298 F g^{-1} at 0.83 A g^{-1} [10].

Xu-Yuan Peng et al. fabricated electrochemically reduced graphene oxide (ErGO) films with controllable size and thickness for supercapacitor electrodes. The

ErGO films delivered a specific capacitance of 128 F g^{-1} and an energy density of 17.8 Wh kg^{-1} within a potential window of 1.0 V in 1.0 M NaNO_3 electrolyte [23].

Sanjaya D. Perera et al. studied the electrochemical behaviour of alkaline deoxygenated graphene oxide and observed energy densities of 20 Wh kg^{-1} and 50 Wh kg^{-1} in LiTFSI and EMITFSI electrolytes, respectively, along with corresponding maximum power densities of 11 kW kg^{-1} and 14.7 kW kg^{-1} [4].

In another work, Bing Zhao et al. synthesized graphene sheets with different reduction levels by thermally reducing graphene oxide at temperatures between 200°C and 900°C . The sample reduced at 200°C exhibited the highest specific capacitance of 260.5 F g^{-1} at a current density of 0.4 A g^{-1} [16].

The incorporation of metal oxides into rGO can significantly enhance its supercapacitive performance, as metal oxides contribute pseudocapacitive behaviour in addition to the electrical double-layer capacitance inherent to carbon-based materials [17]. Among these, rGO/ZnO composites have gained considerable attention due to their environmental friendliness, low cost, corrosion resistance, and superior electrochemical performance [24]. Furthermore, the introduction of ZnO nanoparticles between the rGO layers reduces the strong π - π stacking interactions that typically cause graphene sheet agglomeration. This intercalation effectively prevents sheet restacking, increases the available surface area, and thereby improves the overall specific capacitance of the composite [25].

J. Jayachandiran et al. synthesized ZnO and rGO/ZnO nanocomposites via an ultrasonic-assisted solution process for supercapacitor electrode applications. The rGO/ZnO nanocomposite exhibited a higher specific capacitance of 312 F g^{-1} compared to pure ZnO (200 F g^{-1}), along with excellent cycling stability up to 1000 cycles [6].

Sagolsem Nonganbi Chanu and co-workers fabricated ZnO/rGO nanocomposites through a chemical reduction approach using varying ZnO concentrations, achieving a remarkable specific capacitance of 848 F g^{-1} at a scan rate of 10 mV s^{-1} within a potential window of -0.3 to 0.3 V in 1 M KCl electrolyte [24].

Yuvaraj Haldorai et al. developed a nano ZnO@rGO composite using a one-pot supercritical carbon dioxide process, obtaining a high specific capacitance of 314 F g^{-1} with outstanding cycling stability [26].

Zijiong Li et al. investigated a 3D sandwich-structured ZnO/rGO/ZnO electrode, which achieved a maximum specific capacitance of 275 F g^{-1} at a scan rate of 5 mV s^{-1} in $1.0 \text{ M Na}_2\text{SO}_4$ electrolyte [27].

S. Rai and colleagues synthesized ZnO/rGO nanohybrids through a reduction-based process using non-toxic ascorbic acid. The resulting nanohybrid exhibited a specific capacitance of 345 F g^{-1} , nearly double that of pure rGO (190.5 F g^{-1}) at the same scan rate [25].

M. Sreejesh et al. prepared rGO/ZnO nanocomposites via a microwave-assisted method and demonstrated their potential in both non-enzymatic glucose sensing and supercapacitor applications. The composites exhibited a high capacitance of 635 F g^{-1} and retained excellent cyclic stability over 1000 cycles [28].

Swati Chaudhary et al. synthesized rGO/ZnO nanorod composites via a simple one-step thermal reaction method and achieved a specific capacitance of 472 F g^{-1} , an energy density of 2.62 Wh kg^{-1} , and a power density of 32.24 W kg^{-1} for the rGO:ZnO ratio of 1:2 [7].

Similarly, Mohan Raja et al. investigated the electrochemical properties of ZnO/rGO nanocomposites prepared by a scalable chemical reduction method, reporting a specific capacitance of 280 F g^{-1} , significantly higher than that of the individual components, pure ZnO (125 F g^{-1}) and rGO (137 F g^{-1}) [29].

This collective evidence highlights that integrating ZnO with rGO effectively enhances surface area, charge transfer, and pseudocapacitive contribution, thereby improving the energy storage performance of the composite electrodes.

6.3 Electrochemical analyses

To evaluate the energy storage performance of rGO, ZnO/rGO composite (ZG-50), and pure ZnO (ZG-100), various electrochemical analyses were conducted. Cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements were performed using a three-electrode configuration in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte.

The three-electrode setup consisted of a working electrode (WE), counter electrode (CE), and reference electrode (RE). The working electrode, where the electrochemical reactions occur, was prepared by coating the active material onto a

graphite sheet. A platinum wire served as the counter electrode to complete the electrical circuit and facilitate current flow between the electrodes. The reference electrode, a stable and non-polarizable Ag/AgCl electrode, provided a constant potential reference against which the working electrode's potential was measured.

CV measurements were recorded at scan rates of 5, 25, 50, 75, and 100 mV/s within a potential window of 0 to 500 mV. Similarly, GCD measurements were carried out at current densities of 1, 2, 3, 6, and 10 A/g over the same potential range as that used for CV analysis.

6.3.1 Cyclic Voltammetry (CV)

Cyclic voltammetry is a widely used technique to study the electrochemical behaviour of supercapacitors. In this method, the potential of the working electrode is linearly swept between two predetermined voltage limits and then reversed, while the corresponding current response is recorded [15]. The resulting plot of current versus voltage is known as a cyclic voltammogram.

This technique provides valuable information about the capacitive behaviour, energy storage capability, and electrochemical stability of the material. Additionally, CV helps identify the presence of redox-active species, reveals the nature of charge storage processes (electrostatic or faradaic), and offers insights into the reaction mechanisms and reversibility of the system [15].

The supercapacitance from CV graph is measured using equation 6.1[27,30].

$$C = \frac{\int idV}{mK(V2 - V1)} \quad (6.7)$$

Where $\int idV$ is the area of one complete cycle of CV curve, (V2-V1) is the potential window (V), m is the weight of the active material (g) in the working electrode and K is the scan rate (V/s).

The cyclic voltammogram of rGO recorded at different scan rates of 5, 25, 50, 75, and 100 mV/s within the potential window of 0–0.5 V is shown in Fig. 6.1. The graph depicts the current response corresponding to the applied potential. The obtained curve exhibits a nearly rectangular-shaped hysteresis loop, which is characteristic of electric double-layer capacitance (EDLC) behaviour [5]. This indicates good capacitive

behaviour of rGO. As the scan rate increases, the current response also rises, which is typical of electrochemical capacitors. At lower scan rates, electrolyte ions have sufficient time to diffuse into and interact with the active sites of the electrode material, leading to higher capacitance. However, at higher scan rates, the limited diffusion of charge carriers restricts their access to all active sites, resulting in a reduced charge storage capacity [6,17]. The symmetric shape of the loops further confirms the good reversibility and stability of the charge–discharge process in the system.

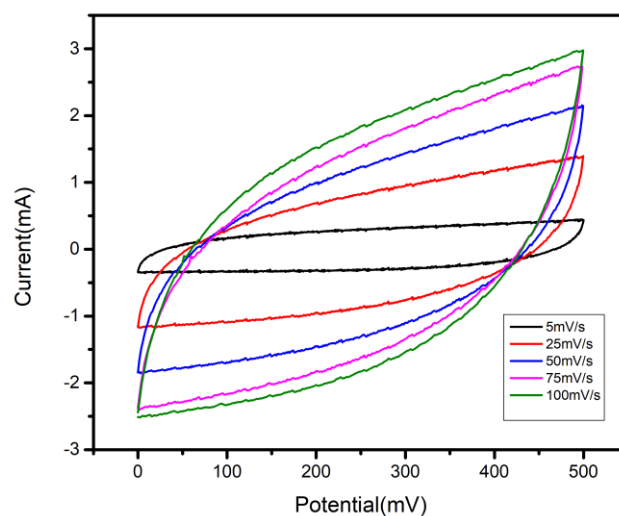


Fig. 6.1: Cyclic Voltammogram of rGO at different scan rates.

Fig. 6.2 shows the cyclic voltammogram of ZG-50 (ZnO/rGO composite) at various scan rates (5–100 mV/s) within the same potential window of 0–0.5 V. The curve also exhibits a nearly rectangular hysteresis loop, though with slight distortions. These inflection points may be attributed to the occurrence of redox reactions contributed by the ZnO component during the potential sweep. As ZG-50 combines both rGO and ZnO, it exhibits hybrid capacitance behaviour, where charge storage arises from both EDLC and faradaic processes [17,28]. Similar to rGO, an increase in scan rate leads to a corresponding increase in current response, consistent with capacitive characteristics. The symmetry of the loops indicates reversible redox behaviour and stable electrochemical performance during repeated charge–discharge cycles.

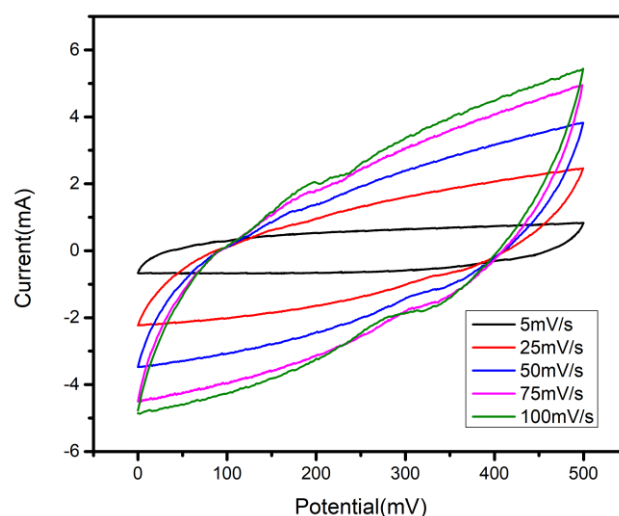


Fig. 6.2: Cyclic Voltammogram of ZG-50 at different scan rates.

Fig. 6.3 presents the cyclic voltammogram of ZG-100 (pure ZnO). The curve shows a distinct distortion with prominent redox peaks, confirming the pseudocapacitive nature of ZnO. With increasing scan rate, the current response also increases, indicating typical supercapacitive behaviour. The overall symmetry of the loop suggests reversible faradaic reactions and stable charge–discharge cycles within the system.

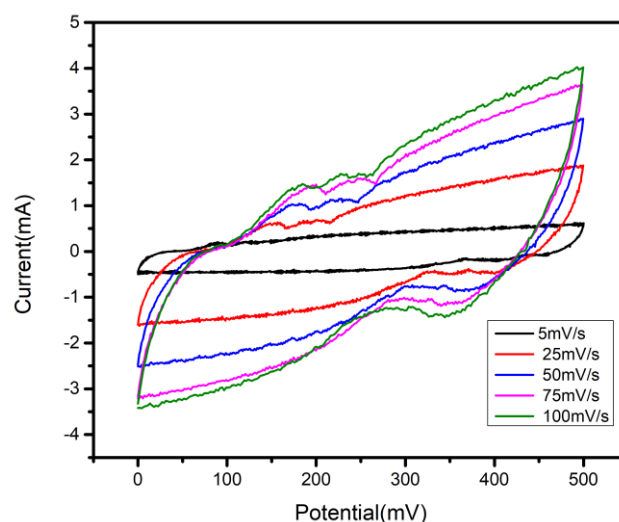


Fig. 6.3: Cyclic Voltammogram of ZG-100 at different scan rates.

As discussed earlier, the area enclosed by the CV loop corresponds to the charge storage capacity and, consequently, the supercapacitance of the material. To compare the capacitive performance, the CV curves of rGO, ZG-50, and ZG-100 recorded at the same scan rate of 100 mV/s and plotted on the same scale are shown in Fig. 6.4. It is evident from the e that the loop area of ZG-50 is significantly larger than that of rGO and ZG-100, indicating that the supercapacitance of the ZG-50 electrode is superior to that of the pristine samples. This enhancement in capacitance can be attributed to the synergistic interaction between rGO and ZnO.

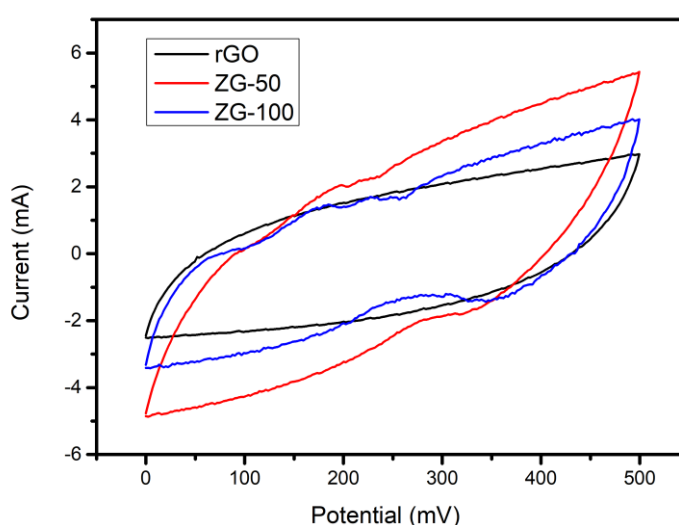


Fig. 6.4: Cyclic Voltammogram of rGO, ZG-50 and ZG-100 at a scan rate of 100mV/s.

The composite formation of rGO with ZnO markedly enhances the charge storage capability of the electrode material. The specific capacitance of ZG-50 is significantly higher than that of pure rGO, primarily due to the increased surface area and improved porosity of the composite. ZnO nanoparticles are intercalated and embedded between the rGO sheets in the composites. This intercalation effectively prevents the restacking of rGO layers, thereby increasing the number of electrochemically active sites available for ion adsorption and charge storage [6].

The increased surface area of the ZnO/rGO composite promotes efficient ion transport and diffusion within the electrode–electrolyte interface, resulting in enhanced charge storage. Additionally, the strong interfacial interaction between ZnO and the conductive rGO network establishes rapid electron transport pathways, reducing internal resistance and improving charge–discharge efficiency [6, 27]. These synergistic

effects—combining the pseudocapacitive contribution of ZnO with the high electrical conductivity of rGO—result in superior electrochemical performance and significantly improved specific capacitance for the ZG-50 composite.

The specific capacitance values of the electrochemical cells fabricated using rGO, ZG-50, and ZG-100 were quantitatively calculated at various scan rates using Equation (6.1), and the corresponding results are presented in Table 6.1. The specific capacitance of the electrochemical system decreases as the scan rate increases, primarily because the higher scan rate provides insufficient time for ions to diffuse deeply into the pores of the electrode material coated on the working electrode, resulting in a reduced charge storage capacity [17].

	Capacitance (F/g)		
scan rate	rGO	ZG-50 capacitance	ZG-100
5	51.4	107.28	68.2
25	31.52	53.96	38.68
50	23.94	40.92	28.872
75	20.14667	34.94667	24.05333
100	17.025	28.43	19.632

Table 6.1: Specific capacitance of rGO, ZG-50 and ZG-100 obtained from CV analysis.

From the table, it is evident that the ZnO/rGO composite sample ZG-50 exhibits the highest charge storage capability compared to the individual samples rGO and ZnO. This enhancement in capacitance can be attributed to the interconnected conductive network of the composite and synergistic interaction between rGO and ZnO [7,11]. The composite structure provides increased surface area, improved charge transfer, and combined EDLC–pseudocapacitive behaviour, thereby boosting the overall electrochemical performance [17,28].

6.3.2 Galvanostatic charge discharge (GCD)

Galvanostatic Charge–Discharge analysis is a technique for evaluating the electrochemical performance of supercapacitors. In this method, a constant current is applied while the corresponding voltage is recorded over time [31]. From the GCD curves, key parameters such as specific capacitance, energy density, and power density

can be determined. The present study performed GCD analysis at various current densities ranging from 1 to 10 A/g within the potential window of 0–0.5 V, and the specific capacitance was calculated using equation (6.2) [32].

$$C = \frac{J\Delta t}{\Delta V} \quad (6.2)$$

Where J is the current density in A/g, Δt is the discharge time and ΔV is the potential window.

Fig. 6.5 presents the GCD curves of rGO at different current densities (1, 2, 3, 6, and 10 A/g). The curves display a linear and symmetric triangular shape, which is characteristic of ideal EDLC-type capacitive behaviour [14]. The symmetry between the charge and discharge curves indicates good reversibility and stable electrochemical performance [17]. A longer discharge time is observed at lower current densities, indicating higher charge storage. Further, specific capacitance and current density are inversely related; higher current densities typically result in lower capacitance values [14]. The linear discharge slope further suggests a constant charge–voltage relationship and the absence of significant faradaic contributions.

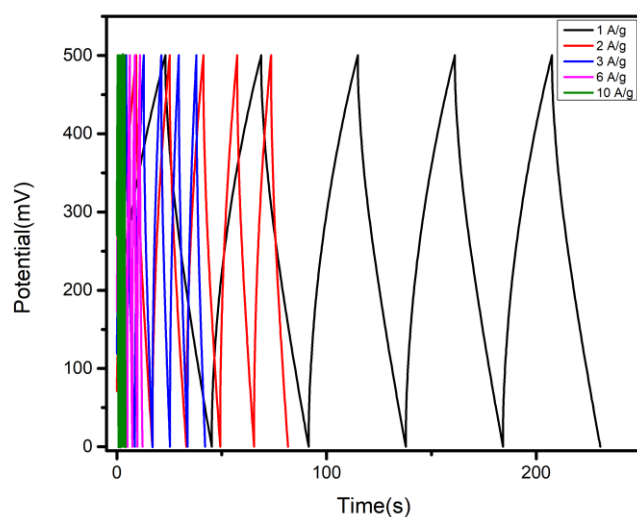


Fig. 6.5: GCD curves of rGO at different current densities 1, 2, 3, 6 and 10 A/g.

The GCD curves of the ZnO/rGO composite (ZG-50) at various current densities (1, 2, 3, 6, and 10 A/g) are shown in Fig. 6.6. The curves exhibit nearly symmetric triangular shapes with slight deviations from linearity, which can be attributed to the pseudocapacitive contribution of ZnO [14,33]. This indicates that the

charge storage process involves both double-layer and faradaic mechanisms, confirming the hybrid nature of the composite electrode. Longer charge–discharge durations observed at lower current densities correspond to enhanced energy storage, while the symmetry of the curves suggests excellent reversibility and stability of the electrochemical reactions [17,29].

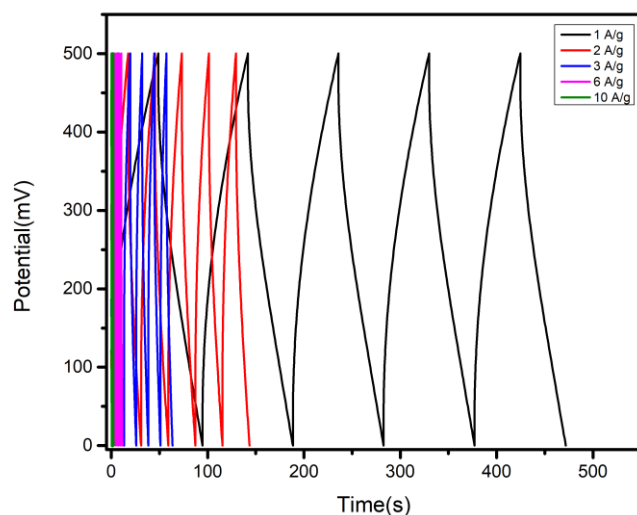


Fig. 6.6: GCD curves of ZG-50 at different current densities 1, 2, 3, 6 and 10 A/g.

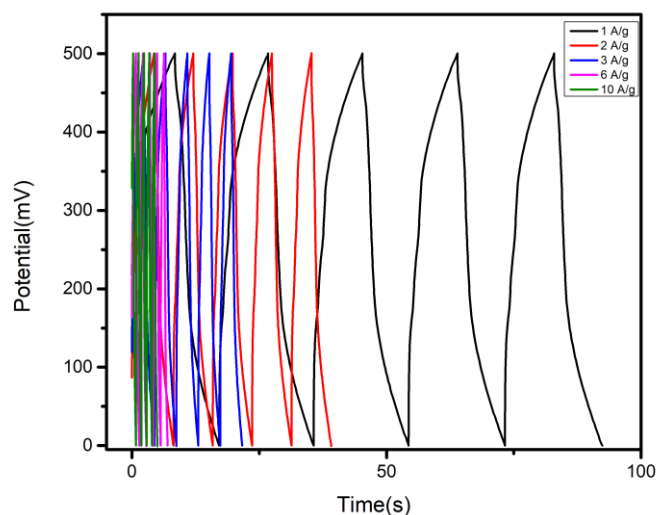


Fig. 6.7: GCD curves of ZG-100 at different current densities 1, 2, 3, 6 and 10 A/g.

Similarly, Fig. 6.7 presents the GCD curves of ZG-100 (ZnO) recorded at various current densities. The curves exhibit significant deviations from linearity,

indicating that the capacitance is not constant and that faradaic reactions contribute to the overall charge storage process [33]. Moreover, with increasing current density, the discharge time decreases, reflecting the characteristic inverse relationship between current density and specific capacitance in electrochemical systems [14].

In all cases, the voltage profiles remain stable throughout the cycles, demonstrating the good electrochemical stability of the electrode materials.

The specific capacitance values obtained from the GCD measurements for rGO, ZG-50, and ZG-100 at various current densities were calculated using equation (6.2) and are summarized in Table 6.2. Among the samples, the composite electrode ZG-50 exhibited the highest specific capacitance, outperforming both pristine rGO and ZnO for all current densities. This enhanced performance is attributed to the synergistic interaction between the conductive rGO network and the pseudocapacitive behaviour of ZnO.

Current density (A/g)	Specific capacitance (F/g)		
	rGO	ZG-50	ZG-100
1	92.86	187.10	37.06
2	64.36	113.16	30.82
3	50.46	75.78	25.98
6	29.28	27.12	16.80
10	16.68	9.36	21.00

Table 6.2: Specific capacitance of rGO, ZG-50 and ZG-100 obtained from GCD analysis.

The formation of the ZnO/rGO composite leads to a pronounced improvement in the charge storage performance of the electrode material. At a current density of 1 A g⁻¹, the specific capacitance of ZG-50 is calculated to 187 F g⁻¹, which is substantially higher than the values obtained for pristine rGO (92.8 F g⁻¹) and ZnO (37 F g⁻¹). This improvement clearly demonstrates the superior electrochemical performance of the composite compared to the individual components.

The superior electrochemical performance of ZG-50 arises from the synergistic interaction between ZnO and rGO. In the composite, ZnO contributes pseudocapacitive charge storage through reversible faradaic reactions, while rGO provides a highly

conductive network that facilitates efficient electron transport. This combined EDLC–pseudocapacitive mechanism leads to a significant increase in the overall specific capacitance of the ZG-50 electrode [17,28].

Moreover, the incorporation of ZnO within the rGO matrix improves the porosity and effective surface area of the electrode material, thereby increasing the number of electrochemically active sites available for ion adsorption and charge storage [6]. The enhanced surface area promotes efficient ion diffusion and transport at the electrode–electrolyte interface, which further contributes to the improved capacitance. In addition, the strong interfacial interaction between ZnO and the conductive rGO framework creates short and efficient electron transport pathways, reducing internal resistance and enhancing charge–discharge efficiency [6,27].

Although the present study was carried out without detailed optimization of critical parameters such as the ZnO-to-rGO composition ratio, choice of electrolyte, operating potential window, electrode thickness, and current density, the ZnO/rGO composite still demonstrates a specific capacitance greater than 100 F g^{-1} . This promising result indicates the strong potential of the composite system. We believe that further enhancement in the capacitance and overall electrochemical performance of ZnO/rGO composites can be achieved through careful optimization of these parameters, which is therefore proposed as future work.

6.4 Conclusion

This chapter explored the electrochemical performance of rGO, ZnO (ZG-100), and ZnO/rGO composite (ZG-50) as electrode materials for supercapacitor applications. The electrochemical analyses using CV and GCD techniques revealed that all the samples exhibit supercapacitive behaviour. The rGO electrode demonstrated typical electric double-layer capacitance (EDLC) behaviour, as evidenced by its nearly rectangular CV curves and linear, symmetric GCD profiles. In contrast, the ZnO electrode showed distinct redox peaks in its CV curve and non-linear GCD response, indicative of pseudocapacitive behaviour associated with reversible faradaic reactions. The ZnO/rGO composite (ZG-50) exhibited hybrid capacitive characteristics that combined both EDLC and pseudocapacitance characteristics.

Among the materials studied, ZG-50 displayed the highest specific capacitance and excellent reversibility, indicating superior charge storage capability. The specific

capacitance obtained from the CV curves at a scan rate of 5 mV s^{-1} was 107 F g^{-1} for ZG-50, significantly higher than that of rGO (51.4 F g^{-1}) and ZnO (68.2 F g^{-1}). A similar trend was observed in GCD analysis, where ZG-50 exhibited a specific capacitance of 187.1 F g^{-1} , outperforming rGO (92.86 F g^{-1}) and ZnO (37.06 F g^{-1}). This enhanced performance for the composite can be attributed to the synergistic interaction between ZnO and rGO, where ZnO nanoparticles intercalate between rGO sheets, preventing sheet restacking, enhancing porosity, and increasing the effective surface area available for ion diffusion and charge accumulation. The improved structural and conductive network facilitates rapid electron and ion transport, resulting in enhanced electrochemical performance.

In summary, the formation of the ZnO/rGO composite significantly improves charge storage capacity compared to pristine rGO and ZnO. The results highlight that the ZG-50 composite is a promising and efficient electrode material for next-generation high-performance supercapacitors.

6.5 References

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Chapter VII

Summary and conclusions

In summary, we developed a simple, single-step rapid pyrolysis method for synthesizing ZnO/rGO composites using low-cost and non-toxic precursors—zinc acetate and sucrose. This approach enables the production of rGO and ZnO/rGO composites on an industrial scale within minutes, providing a fast, efficient, and sustainable green synthesis route. To the best of our knowledge, this is the first report in which both rGO and ZnO are simultaneously produced and integrated into a composite in a single step. This method enables the bulk production of ZnO/rGO composite within a short period, offering a promising approach for scalable and environmentally friendly synthesis.

The present work aligned strongly with several United Nations Sustainable Development Goals (SDGs) by introducing a green, low-cost, and scalable approach for nanomaterial synthesis and demonstrating its applications in environmental and societal well-being. The single-step fabrication of rGO and ZnO/rGO composites using non-toxic, inexpensive, and widely available precursors supports the goal of “Responsible Consumption and Production” by minimizing hazardous chemicals, reducing energy consumption, and promoting sustainable synthesis practices. The demonstrated efficiency of the composite in removing toxic heavy metals and degrading organic pollutants directly contributes to the goal of “Clean Water and Sanitation”, offering a potential solution for water purification and pollution control. Its significant antibacterial activity aligns with “Good Health and Well-Being”, emphasizing the efficiency of the material in biomedical applications. Furthermore, the composite’s promising electrochemical performance for supercapacitor applications supports “Affordable and Clean Energy” by enabling the advancement of sustainable energy storage technologies. Overall, this work integrates green chemistry, environmental remediation, public health, and clean energy solutions, thereby contributing meaningfully to multiple global sustainability goals. The achievements of this thesis can be summarized as follows.

A novel approach for synthesizing ZnO/rGO nanocomposites in a few minutes is demonstrated in this study. The ZnO/rGO nanocomposite was prepared through a rapid

single-step pyrolytic reduction of the carbon-rich compound sucrose with zinc acetate. This method is environmentally friendly and industrially scalable, as it avoids toxic chemicals and is suitable for large-scale production within minutes at a low cost. The formation of rGO and the ZnO/rGO nanocomposite was confirmed through comprehensive analyses, including XRD, Raman spectroscopy, FT-IR, FE-SEM, EDX, HR-TEM, UV–visible spectroscopy, and XPS. The morphological analyses clearly illustrate the layered nature of sucrose-derived rGO, while the spectroscopic analysis confirms aromatic C–C bond formation characteristics in rGO. All the analyses also confirmed the formation of ZnO in all the composite samples. Overall, the synthesis route offers a safer, greener, and highly sustainable alternative for producing rGO-based materials.

Experimental results showed that the synthesized ZnO/rGO composite is a promising, cost-effective, and industrially scalable material for adsorbing various heavy metals. In this study, we specifically investigated the removal of Cr(VI) and Pb²⁺. Notably, the adsorption mechanisms differ significantly between Cr(VI) and Pb²⁺. Cr(VI) removal by the composite involves a combination of electrostatic interactions, surface complexation through chemisorption, pore filling, and the partial reduction of adsorbed Cr(VI) to Cr(III). This process is effective only under acidic conditions, with a maximum adsorption capacity of 13.5 mg/g. Importantly, no secondary phase formation is observed, apart from the chemical reduction of Cr(VI). In contrast, Pb²⁺ removal proceeds through an adsorption–precipitation mechanism. Pb²⁺ ions are extracted from solution, nucleate, and are immobilized as a sparingly soluble solid phase, which subsequently grows into crystalline structures in the presence of excess Pb²⁺. The most efficient sample, ZG-60, achieved an outstanding Pb²⁺ adsorption capacity of 1400 mg/g (1.4 g of Pb per gram of adsorbent) and demonstrated efficiency across all pH ranges. The formation of a secondary lead phase—hydrocerussite [Pb₂(CO₃)Pb(OH)₂] is clearly evidenced by visual changes in the spent adsorbent, and further confirmed through XRD, FE-SEM, and TEM analyses. These findings highlight the superior potential of the ZnO/rGO composite for Pb²⁺ remediation, offering a more effective and sustainable solution for mitigating lead contamination in water.

The ZnO/rGO composite also demonstrated excellent photocatalytic efficiency in degrading various organic pollutants, including dyes and antibiotics. The tested pollutants included methylene blue (MB), Rhodamine B (RhB), and the antibiotic

Ofloxacin. Detailed photocatalytic studies were carried out using MB as the model dye, and all the prepared samples showed significant photocatalytic activity. In the composite, rGO functions as a co-catalyst, improving pollutant adsorption and aiding in the separation of photogenerated charges. Among the tested samples, ZG-70 exhibited the highest activity, achieving 98% degradation of MB within just 20 minutes of light exposure. Scavenger experiments using histidine, benzoquinone (BQ), and EDTA confirmed the involvement of reactive species in the degradation process, with hydroxyl radicals ($\bullet\text{OH}$) identified as the dominant contributors. The generation of $\bullet\text{OH}$ radicals under light irradiation was further verified using terephthalic acid as a probe molecule. To demonstrate the broad-spectrum capability of the material, the photocatalytic performance of the ZnO/rGO composite was also evaluated against RhB and Ofloxacin, confirming its effectiveness in the degradation of diverse organic contaminants.

Furthermore, the efficacy of the samples in disinfecting various bacterial strains was evaluated using the agar disc diffusion method against *S. aureus*, *P. aeruginosa*, *S. enteritidis*, and *E. coli*. All tested samples exhibited high antibacterial efficacy, comparable to conventional antibiotics commonly used to treat infections caused by these pathogens. The minimum inhibitory concentration (MIC) values were also determined, further confirming the potency of the materials against the studied bacterial strains. Cytotoxicity studies were conducted using HEK293 cells, and the IC_{50} values were found to be in the range of 62–104 $\mu\text{g mL}^{-1}$, indicating relatively low toxicity. Overall, the materials synthesized through this method show significant promise for biomedical applications due to their low cytotoxicity, cost-effectiveness, rapid and scalable synthesis, and high antibacterial effectiveness across multiple bacterial strains.

The electrochemical performance of rGO, ZnO (ZG-100), and the ZnO/rGO composite (ZG-50) was evaluated for supercapacitor applications using CV and GCD analyses. All samples exhibited supercapacitive behaviour. The rGO electrode showed characteristic electric double-layer capacitance (EDLC), while the ZnO electrode displayed characteristics of pseudocapacitance. The ZnO/rGO composite (ZG-50) demonstrated a hybrid capacitive behaviour that integrated both EDLC and pseudocapacitive contributions. Among the materials studied, ZG-50 displayed the highest specific capacitance and excellent reversibility, indicating superior charge storage capability. This enhancement can be attributed to the strong synergistic

interaction between ZnO and rGO, where ZnO nanoparticles prevent the restacking of rGO sheets, increase porosity, and expand the electrochemically active surface area. This optimized structure provides efficient pathways for rapid electron and ion transport, greatly improving overall electrochemical behaviour.

This research successfully demonstrated a sustainable, eco-friendly, and industrially scalable method for synthesizing ZnO/rGO nanocomposites, addressing key global challenges related to environmental pollution, healthcare, and the growing energy crisis. Moreover, the versatility and simplicity of the synthesis process also indicate that it can be extended to fabricate other graphene–metal oxide nanocomposites, marking an important advancement toward large-scale green nanotechnology and its practical implementation.

Chapter VIII

Recommendations

- **Synthesis**

Explore the feasibility of this synthesizing method for the preparation of other rGO-based composites integrated with other metal oxides.

- **Energy Storage & Conversion**

Optimize the electrochemical performance of the ZnO/rGO composite by adjusting key parameters such as electrolyte type, potential window, electrode thickness, and current density. Coupling the composite with other metal oxides may further enhance its energy-storage behaviour. These improvements could enable the effective use of ZnO/rGO composites in next-generation high-performance supercapacitors.

- **Water remediation**

The heavy-metal removal efficiency of the composite was evaluated in the laboratory using synthetically prepared contaminated water. However, the adsorption behaviour and underlying mechanisms may vary significantly in real industrial effluents due to the presence of multiple competing heavy-metal ions, salts, and complex matrices. Therefore, further studies are recommended to assess the material's performance using actual industrial wastewater samples to validate its practical applicability.

- **Biomedical Potential**

Conduct detailed and systematic investigations into the biomedical applications of ZnO/rGO composites, including antimicrobial mechanisms, cytotoxicity, and potential therapeutic uses.

- **Industrial Translation**

Advance toward large-scale, cost-effective commercialization of ZnO/rGO composites across environmental, biomedical, and energy applications. The scalability and green nature of the synthesis route strongly align with the United Nations Sustainable Development Goals (SDGs), supporting global efforts in sustainability and technological innovation.

APPENDIX

A) PUBLICATIONS

1. **Philip, Reshma S.**, N. Aparna, and Meril Mathew. "Hexavalent chromium removal using reduced graphene oxide-zinc oxide composite fabricated via simple pyrolysis method." *Applied Surface Science Advances* 19 (2024): 100535. (IF-8.7)
2. **Philip, Reshma S.**, Arunaksharan Narayanankutty, and Meril Mathew. "The antibacterial efficacy of reduced graphene oxide (rGO) and rGO/ZnO composites produced through thermal pyrolysis method against various bacterial strains." *Zeitschrift für Physikalische Chemie* 239.6 (2025): 995-1012. (IF- 3.2)
3. **Philip, Reshma S.**, N. Aparna, and Meril Mathew. "A novel and facile method for the synthesis of rGO/ZnO nanocomposite and its versatile use in water treatment." *Composites Part A: Applied Science and Manufacturing* 189 (2025): 108620. (IF-8.9)
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5. Aparna, N., **Reshma S. Philip**, and Meril Mathew. "Photocatalytic activities of SnS thin films deposited at room temperature." *Applied Surface Science Advances* 13 (2023): 100374.
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7. Aparna, N., **Reshma S. Philip**, and Meril Mathew. "Tailoring the properties of SnS thin films deposited at room temperature by varying the amount of complexing agent for enhanced photocatalytic activity." *Materials Today Sustainability* 27 (2024): 100941.
8. Aparna, N., **Reshma S. Philip**, and Meril Mathew. "SnS thin films deposited at room temperature—efficient and reusable dark catalyst for water remediation at ambient conditions." *Surfaces and Interfaces* 51 (2024): 104537.

9. Aparna, N., **Reshma S. Philip**, and Meril Mathew. "Heavy metal removal from wastewater by SnS thin films deposited by the modified SILAR technique at ambient temperature." *Materials Chemistry and Physics* 341 (2025): 130939.

B) PRESENTATIONS

1. Reshma S Philip, Meril Mathew (2025). "Single-Step Synthesis of rGO and rGO/ZnO Composite Using Common Non-Toxic Precursors: Exploring a Wide Array of Applications" at the international seminar entitled "69th DAE Solid State Physics Symposium 2025" on 19 – 23 December 2025 held at IIT Roorkee organized by Bhabha Atomic Research Centre, Mumbai, India.
2. Reshma S Philip, Aparna N, Meril Mathew (2025). "Adsorptive removal of Lead (Pb) ions from contaminated solution by ZnO/rGO composites" at the international seminar entitled "International Conference on Advanced Materials and Characterization (ICAMC 2025)" on 11–13 Aug 2025 organized by Sathyabama Institute of Science and Technology (Deemed to be University) Chennai.
3. Reshma S Philip, Aparna N, Meril Mathew (2024). "Heavy metal removal from waste water by ZnO/rGO composite" at the international seminar entitled "Advanced Functional Materials and Devices (AFMD 2024)" on 26-29 Feb 2024 organized by Nanotechnology Research centre, SRMIST, Kattankulathur-603203, Chennai.
4. Reshma S Philip, Arunaksharan Narayanankutty, Meril Mathew (2024). "The antibacterial efficacy of rGO and ZnO/rGO composite produced through thermal pyrolysis method against various bacterial stains" at the international seminar entitled "International Conferences on Advances in Functional Materials and Coatings (ICAFMC-2024))" on 14-16 Feb 2024 organized by MES Ponnani College, Ponnani, Malappuram (Dt), Kerala.
5. Reshma S Philip, Aparna N, Meril Mathew (2024). "Photocatalytic degradation of methylene Blue dye using ZnO/rGO composite" at the international seminar entitled "International Conference on Advanced Materials (ICAM 2024)" on 3 - 4 Jan 2024 organized by Departments of Physics & Chemistry, Deva Matha College, Kuravilangad, Kerala

6. Reshma S Philip, Aparna N, Meril Mathew (2023). “Chromium (VI) removal from waste water by ZnO/rGO composite synthesized by simple pyrolysis method” at the international seminar entitled “International Conference on Science and Technology of Advanced Materials (STAM.23)” on 18 – 20 April 2023 organized by Mar Athanasius College (Autonomous) Kothamangala, Kerala.
7. Reshma S Philip, Arunaksharan Narayanankutty, Meril Mathew (2023). “Antibacterial activity of rGO and ZnO/rGO composite synthesized from Sucrose and Zinc acetate” at the international seminar entitled “International Conference on Functional Materials for Advanced Technology – 1 (ICFMAT-1)” on 2 - 4 Jan 2023 organized by Central University of Kerala



Efficient Mineralization and removal of Pb^{2+} from water using ZnO/rGO composite synthesized via a facile One-Step method

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ARTICLE INFO

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ZnO/rGO composite
Water remediation
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removal of Pb^{2+}
Hydrocerussite
Lead carbonate hydroxide

ABSTRACT

Anthropogenic lead (Pb) pollution is a critical environmental issue that endangers water and soil quality, posing significant risks to ecosystems and human health. Controlling the bioavailability of this toxic metal is essential for mitigating its impact. This study investigates the immobilisation of Pb^{2+} ions from contaminated solutions using a ZnO/rGO composite, synthesised via a green, single-step method employing zinc acetate and sucrose as precursors. The adsorption process was analysed by monitoring changes in Pb^{2+} concentration in the contaminated solution and examining mineralogical transformations in the spent adsorbent. The composite, even at a small dosage of 1 g/L, achieved complete removal of lead from contaminated solutions across a wide range of concentrations, from 0 up to nearly 1000 mg/L. The most effective adsorbent, ZG-60, exhibited an exceptional Pb removal capacity, absorbing more lead than its weight; 1 g of ZG-60 can hold 1.4 g of Pb from the contaminated solution. XRD analysis confirmed the formation of lead carbonate hydroxide (hydrocerussite, $\text{Pb}_2(\text{CO}_3)\text{Pb}(\text{OH})_2$) as a secondary phase, demonstrating an adsorption-precipitation mechanism of Pb removal. These findings highlight the potential of ZnO/rGO composites as a promising and cost-effective sorbent for Pb^{2+} removal from contaminated water, offering an environmentally sustainable solution to mitigate lead pollution.

1. Introduction

Lead (Pb) has been used by humans since around 7000 BCE, primarily due to its ease of extraction, corrosion resistance, and ductility. Archaeologists have found the oldest lead artefacts, of dating back to 6400 BCE and 5000 BCE, suggesting their use during the Neolithic period, long before the Copper and Bronze Ages [1]. Today, the harmful effects of lead on health and the environment are well recognised by the scientific and medical communities. Although lead is known for its toxicity, lead continues to be widely used in various industries due to its affordability and availability. It is commonly found in lead-acid batteries, insecticides, fossil fuel combustion, electromagnetic shielding, the energy sector, alloys, construction, and ammunition etc. [2,3,4,5]. The mining, processing and industrial applications of Pb cannot be avoided entirely to date. Efforts are underway to reduce lead usage globally; however, various sources of exposure to lead persist, particularly in low- and middle-income countries [6]. Heavy metals, including lead, are non-biodegradable, persistent, and bio-accumulative [4,5,7]. As a result, many regions still suffer from lead contamination, that has accumulated over the decades.

Human exposure to lead primarily occurs through inhalation of lead-containing dust, consumption of contaminated food and water, and absorption through the skin [8,9]. Even at trace levels, lead poses significant health risks, disrupting metabolic functions and cellular processes [10,11]. It can damage vital organs such as the kidneys, liver and cause severe harm to the nervous, skeletal, circulatory, enzymatic, endocrine, immune, and reproductive systems [4,12]. Furthermore, heavy metal accumulation is both mutagenic and carcinogenic [5,10,13]. The World Health Organization (WHO) has set the recommended maximum permissible level of lead in drinking water at 0.01 mg/L [14]. Additionally, WHO estimated that in 2021, more than 1.5 million deaths globally were attributed to lead exposure, with many more individuals suffering from disabilities and diseases [8]. These alarming statistics highlight that lead pollution in water, air, and soil remains a pressing global challenge. Consequently, research continues to focus on reducing lead exposure and mitigating its impacts on human health and the environment.

Treating water contaminated with Pb^{2+} is essential for ensuring sustainable ecosystems and addressing the global challenge of fresh-water scarcity. Various techniques have been developed for lead

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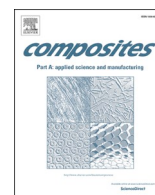
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A novel and facile method for the synthesis of rGO/ZnO nanocomposite and its versatile use in water treatment

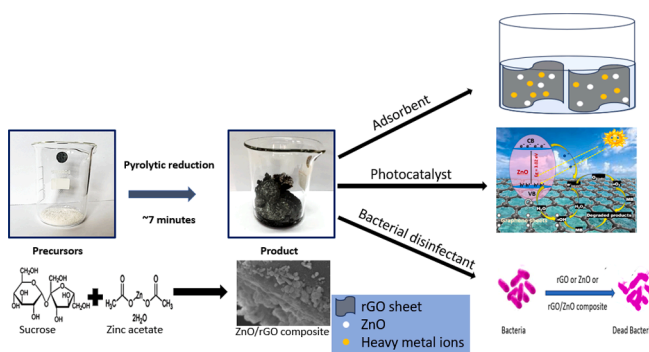
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HIGHLIGHTS

- Novel rapid single-step pyrolytic route for synthesising reduced graphene oxide/ZnO (rGO/ZnO) nanocomposite and rGO.
- Detailed characterization of rGO and rGO/ZnO nanocomposite.
- rGO/ZnO nanocomposite was found to be efficient in the absorptive removal of heavy metals chromium, lead, and cadmium.
- The photocatalytic activity of the rGO/ZnO nanocomposite was studied using methylene blue as a model dye.
- rGO, ZnO and rGO/ZnO nanocomposite exhibited disinfection capabilities against various bacterial strains.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Reduced graphene oxide/ZnO composite
Photocatalyst
Heavy metal adsorbent
Bacterial disinfectant
Water pollution remediation
Green synthesis approach

ABSTRACT

We introduce a novel, rapid, and environmentally friendly method for synthesising reduced graphene oxide (rGO)/ZnO nanocomposite. This single-step synthesis involves the pyrolytic decomposition of sucrose to produce rGO, simultaneously with zinc acetate to produce the rGO/ZnO nanocomposite. Unlike conventional methods, this approach is distinguished by its environmental sustainability, avoiding the use of toxic chemicals and generating no harmful byproducts. This method advances the development of sustainable technologies by providing a green alternative for the cost-effective production of rGO/ZnO composites from inexpensive precursors. The process enables bulk production within minutes, making it suitable for industrial-scale applications. Various characterisation techniques confirmed the successful formation of rGO and rGO/ZnO nanocomposites. The materials were then evaluated for their efficacy as a comprehensive water purification solution, demonstrating effectiveness in heavy metal removal, photodegradation of organic pollutants, and bacterial disinfection.

1. Introduction

Graphene, a one-atom-thick, two-dimensional carbon allotrope, has attracted significant interest from both scientific and industrial communities due to its exceptional properties, including superior charge

transport, thermal conductivity, optical properties, mechanical strength and outstanding specific surface area [1,2,3]. Despite its remarkable potential, the production of single-layered, defect-free graphene remains a challenging process. Techniques such as mechanical exfoliation, chemical vapour deposition, electron or laser beam irradiation, arc

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Meril Mathew*

The antibacterial efficacy of reduced graphene oxide (rGO) and rGO/ZnO composites produced through thermal pyrolysis method against various bacterial strains

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Abstract: Antibacterial agents are essential to maintain the health of living beings. The misuse and overuse of antibiotics have led to the development of resistance against antibiotics in microbes. To address this issue, efficient, cost-effective, and biocompatible alternatives for conventional antibiotics need to be developed. Reduced graphene oxide (rGO), ZnO, and their composite have been identified as being efficient in disinfecting bacterial strains. The synthesis of rGO, ZnO, and their composite is usually a multi-step, time-consuming process that uses harmful reagents and catalysts. In this study, we prepared rGO from sucrose and rGO/ZnO composite from sucrose and zinc acetate by a single-step heating process. The method is green, eco-friendly and only uses commonly available non-hazardous precursors for preparation. The characterisation techniques, XRD, XPS, FE-SEM, and HR-TEM, displayed the formation of rGO and ZnO in the samples. The antibacterial efficiency of the samples rGO, the composites ZG-10, ZG-40, ZG-60 and ZnO (ZG-100) were evaluated against Gram-positive and Gram-negative bacterial strains using the agar disc diffusion method. The samples showed remarkable bactericidal activity against all the tested bacterial strains, and their zone of inhibition was comparable to that of conventional antibiotics. Different samples are proven to be effective for different bacterial strains. The sample rGO was found to be more efficient in

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Hexavalent chromium removal using reduced graphene oxide-zinc oxide composite fabricated via simple pyrolysis method

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ARTICLE INFO

Keywords:

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rGO/ZnO composite
Hexavalent chromium
Adsorptive removal
Kinetics and Isotherm
Photo assisted adsorption

ABSTRACT

The contamination of water by heavy metals from various industrial effluents is a significant factor contributing to the scarcity of clean water worldwide. To address this issue, there is a need to develop low-cost adsorbents to remove heavy metals from contaminated water. Reduced graphene oxide (rGO) based composites are efficient adsorbents of heavy metals. In this study, a green and rapid single-step heating process was utilized to prepare both rGO and rGO/ZnO composite materials, avoiding the use of any toxic reagents. The rGO/ZnO composite synthesized from sucrose and zinc acetate demonstrates a remarkable ability to adsorb hexavalent chromium (Cr(VI)). The Cr adsorption studies were carried out by varying adsorbent, contact time, initial pH, and concentration. The adsorption efficiency of the composite is five times higher than that of pure rGO. The adsorption mechanism of Cr(VI) onto the adsorbent is electrostatic interaction, complexation, pore filling, and reduction, identified through Zeta potential measurement, BET, EDX, and XPS analysis. These studies suggest that rGO/ZnO composite has great potency as a cost-effective and efficient adsorbent for removing Cr(VI) contaminants from industrial effluents.

Introduction

Water is often referred to as the elixir of life, as its availability is indispensable for the survival of all living organisms. According to the United States Geological Survey, approximately 71 % of the Earth's surface is water. Despite this abundance, only 2.5 % of the Earth's water constitutes freshwater. The distribution of this freshwater is further limited, with 68.7 % stored in ice glaciers and icecaps, 30.1 % as underground water, and a mere 2.5 % available in surface and other freshwater sources [1]. Therefore, the conservation of this precious and limited resource is of utmost importance for the continuation of life on our planet. A critical global challenge today is the growing scarcity of fresh water. Numerous natural and anthropogenic activities contribute to the pollution of water sources [2]. Both organic and inorganic pollutants, including dyes [3], heavy metals [4], pharmaceuticals [5], microbials [6], pesticides [7] etc., pose significant threats to water quality.

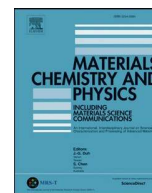
Heavy metal pollution poses a significant and alarming threat to the world today. The widespread use of heavy metals, including chromium, lead, cadmium, cobalt, and mercury, in various industrial sectors leads to the discharge of effluents containing these toxic substances into the environment [8]. These heavy metals have been getting significant

attention due to their extreme toxicity, causing damage to various organs even with minimal exposure [9]. The primary concern regarding heavy metal pollution is that it cannot be degraded or destroyed [10]. Among these heavy metals, chromium is one of the most abundantly used resources in the production of many household items we use in our daily routine, from newspapers to kitchen utensils. The steel, leather, wood, paper, and paint industries release significant amounts of chromium ions [11,12] into water bodies and soil. These ions are harmful contaminants with mutagenic and carcinogenic properties [13,14], making them a severe global concern requiring immediate attention. A single industry, leather tanning, is responsible for releasing over 600,000 tons of chromium waste into the environment annually in India [15].

In nature, chromium exists in several oxidation states, from -2 to $+6$; among these, trivalent chromium Cr(III) and hexavalent chromium Cr(VI) are two stable states. Cr(III) is a micronutrient essential for human metabolism [16]. However, at higher concentrations, it becomes poisonous and has a negative impact on human health [17]. Cr(VI), on the other hand, is the second stable form of chromium and is 300 times more toxic than Cr(III) [18]. Due to its higher dispersibility and solubility [13,15], Cr(VI) move through solids and liquids, resulting in

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Heavy metal removal from wastewater by SnS thin films deposited by the modified SILAR technique at ambient temperature

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HIGHLIGHTS

- Deposition of SnS thin films using a modified SILAR method at room temperature
- Removal of Cr(VI) from wastewater by SnS thin film via adsorption-reduction method
- SnS thin films exhibited high efficiency, reusability, easy recovery and selectivity
- Investigated the impact of various operating variables on chromium removal efficiency
- Highlighted the advantages of thin films over nanoparticles for water remediation

ARTICLE INFO

Keywords:

Heavy metal removal
Tin monosulfide
Thin film
SILAR
Water remediation
Chromium removal

ABSTRACT

This study investigates the effectiveness of tin monosulfide (SnS) thin films in removing heavy metals from wastewater. The SnS thin films were deposited at room temperature using a modified version of the successive ionic layer adsorption and reaction (SILAR) method. The deposited samples were confirmed to be SnS through XRD, XPS, and EDAX analysis. The XRD analysis revealed that the SnS thin films are polycrystalline with an orthorhombic crystal structure. Variations in the number of SILAR cycles resulted in changes in film thickness, crystallinity, crystallite size, and morphology. The SnS thin films were utilized to remove heavy metals from wastewater. UV-visible spectroscopic examination and ICP-OES analysis demonstrated that SnS thin films effectively removed chromium (Cr(VI)) from contaminated water. Under irradiation from a xenon lamp, the SnS thin films eliminated nearly 99 % of Cr(VI) from a 100 ml solution (initial concentration - 25 mg/l, pH - 2.5) within 80 min. Additionally, the SnS thin films removed 97 % of Cr(VI) under ambient light conditions and 94 % in dark conditions. The removal of Cr(VI) by the SnS thin films was identified as an adsorption-reduction process, with XPS analysis of the spent sample confirming the formation of Cr(III). The SnS thin films exhibited high efficiency, easy recovery, and reusability for Cr(VI) removal. The study also investigated the impact of several factors on chromium removal efficiency, including initial pollutant concentration, solution pH and salinity, and speed of magnetic stirring. Furthermore, the selectivity of SnS thin films was demonstrated through their efficiency in removing cadmium and lead. The thin films removed 72 % of cadmium in dark conditions and 82 % under illumination within 40 min. The lead removal rates were 78 % in dark conditions and 99.8 % in illuminated conditions within 40 min. This study highlights the advantages of using thin films for water remediation compared to nanoparticles.

1. Introduction

Water contamination by heavy metals is recognized as one of the most significant environmental issues due to their high toxicity, carcinogenic properties, ability to aggregate, persistence in the environment, and bio accumulative nature [1–7]. Heavy metals are defined as metals

with a density greater than 6 g/cm³ [1]. Although these metals play a vital role in biological metabolism, excessive concentrations can have serious and lethal effects on human health. Due to their mutagenic and carcinogenic characteristics, heavy metals pose a significant risk to both human health and the environment, even at low levels [1,2,8]. Heavy metal ions are non-biodegradable and have a long residence time in the

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Photocatalytic activities of SnS thin films deposited at room temperature

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ARTICLE INFO

Keywords:

Thin film
Photocatalysis
Methylene Blue
Tin Monosulfide

ABSTRACT

Tin monosulfide (SnS) thin films were deposited on glass substrates at room temperature utilising a simple, inexpensive, and modified chemical approach known as Successive Layer Adsorption and Reaction (SLAR). The properties of the films were thoroughly studied using an XRD, SEM, EDAX, and UV-VIS spectrophotometer. It was possible to deposit smooth, homogeneous, and uniform thin films with polycrystalline nature, orthorhombic structure, and UV-VIS absorption. Under visible light irradiation, SnS thin films demonstrated high photocatalytic degradation of Methylene Blue. It showed effective degradation of a common textile dye available in the market as well. Dye degradation was found to be of first order, following the Langmuir-Hinshelwood mechanism. Theoretical band structure calculations suggested that the relative positions of the highest valence band and lowest conduction band were 1.605 eV and -0.085 eV, respectively. The photocatalyst's reusability, the involvement of the hydroxyl radical in photodegradation, and the variation in photocatalytic performance of SnS thin films with dye solution pH and initial dye concentration were all examined. Changes in the cationic precursor's molarity caused changes in the thin film's crystallinity, stoichiometry, and bandgap. Non-stoichiometric films demonstrated higher photocatalytic activity.

Introduction

Water pollution caused by dye-contaminated colored waste water produced by various industries has recently become a major concern all over the world. Despite the fact that these dyes are detrimental to the environment, they are widely used in a variety of industries, including textiles, plastics, paper, paints, medicine, cosmetics, food processing, and so on [1,2]. These industries discharge dye-contaminated effluents into the environment, resulting in aqueous pollution. The textile sector is the largest user of dyes among these industries, and it is estimated that the textile industry alone contributes 17–20% of total water pollution [3,4]. Even at trace quantities, the extremely toxic, possibly carcinogenic, mutagenic, and xenobiotic [3–7] dyes released as industrial effluents into water bodies are hazardous to human health and the ecosystem. Since the extent of water pollution and its negative consequences are worrying, quick action should be taken to clean waste water and detoxify pollutants.

Photocatalysis with heterogeneous semiconductor catalysts has gained popularity in recent years as a highly effective, low-cost, and simple process for converting harmful organic contaminants into non-toxic end products using light [8]. Some of the appealing features of photoreduction utilising heterogeneous catalysts [9] include easy

recovery, reuse, and a reduction in secondary waste production. Photocatalysis for dye degradation addresses not only environmental concerns but also energy concerns because the process uses solar energy, which is naturally abundant, free, and infinite [10,11]. Most prominent photocatalysts, such as TiO₂, ZnO and others, only operate under UV (only 4–5% of the solar spectrum) light irradiation due to their wider bandgap. This results in reduced absorption and thus, a slower rate of photocatalytic reaction [10,12,13]. Industrial waste water treatment necessitates visible light-driven photocatalysts capable of absorbing the majority of the solar spectrum. Visible light accounts for about 43% of incoming solar energy [10,14]. Tin monosulfide (SnS) could be an excellent photocatalyst due to its adequate bandgap corresponding to the visible region. SnS has a high stimulated carrier quantum yield and a low recombination velocity [15,16]. Because of the high mobility of electrons ($2.37 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and holes ($7.35 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in SnS, the separation efficiency of electron-hole pairs (EHPs) is high. SnS also has strong oxidation and thermal stability at normal temperatures [13]. In addition to these photocatalytic capabilities, SnS has many other advantages, such as decreased toxicity, cost effectiveness, abundance of constituent elements and so on [8,10,16]. Despite the fact that SnS meets the majority of the requirements for a scalable photocatalyst for industrial applications, there is very little research on the

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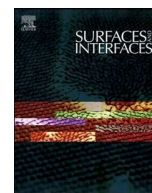
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SnS thin films deposited at room temperature – Efficient and reusable dark catalyst for water remediation at ambient conditions

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ARTICLE INFO

Keywords:

Dark catalysis
Thin film
Tin monosulphide
Round-the-clock catalyst
SILAR

ABSTRACT

This study describes the dark catalytic degradation of cationic, anionic, and commercial dyes by SnS thin films under dark ambient conditions without the assistance of any external stimuli. The thin films were deposited by a modified SILAR (Successive Ionic Layer Adsorption and Reaction) method at room temperature and characterised using XRD, XPS, FESEM, TGA, and UV–visible spectrophotometers. The dark catalytic degradation of methylene blue (MB) dye was investigated using a spectrophotometer and validated by LCMS analysis and an adsorption desorption test. Within 15 min, 48 % of the MB dye (original concentration: 10 mg/l) had been degraded by the catalyst, and by 90 min, the degeneration was almost complete. The ROS (reactive oxygen species) scavenger test and indicator test confirmed the role of the hydroxyl radical in the degradation process. The influence of initial dye concentration, magnetic stirring, and the composition of the catalyst on the degradation efficiency was also studied. The same catalyst was used five times in succession to test its reusability, and it was then structurally and thermally characterised to test its stability. This study emphasises the possible use of SnS thin film as an effective, reliable, and reusable around-the-clock catalyst for the degradation of dye-contaminated waste water without the assistance of light or any chemical additives.

1. Introduction

All living creatures depend on water as a vital resource, and it is critical to the growth of society, the economy, and the creation of energy. Our water resources, including surface, ground, sewage, and drinking water supplies, are under threat from contamination. Dye, medicines, pesticides, heavy metals, bacteria, viruses, and other chemicals are among the principal water contaminants. Environmental harm from water pollution includes sickness, the extinction of species, a tainted food supply, and other issues. Therefore, it is crucial to improve waste water reclamation.

To reduce the risks posed by discharged organic pollutants, a variety of strategies, including advanced oxidation processes (AOPs), physical techniques, and biological treatments, have been developed [1]. Physical approaches, however, convey water contaminants downstream without accomplishing degradation and have significant limitations, including low efficiency, high cost, difficulties in implementation, secondary contamination, regeneration issues, etc. [1,2,3]. Traditional biological procedures often take a long time, involve the employment of microorganisms or enzymes under difficult operating conditions, and

may not be able to degrade current generation dyes that can withstand microbial attack [1,3]. They may also produce sludge as a by-product [2]. AOPs, which utilise highly reactive species produced in situ by photocatalysis, electrochemistry, the Fenton reaction, etc., can be seen as a promising method for treating waste water [1,4,5]. However, the majority of these techniques necessitate external inputs such as light illumination, chemical additives, electricity, and so on [4]. One of the most popular AOPs, photocatalysis, typically consumes a lot of energy and has little to no catalytic activity in the absence of light, making it difficult to operate them continuously around the clock [6]. Additionally, the most commonly utilized photocatalysts, including TiO₂, exhibit low quantum yields as they can absorb only the UV region of the solar spectrum, thus limiting their practical applicability [7].

An alternative that is more practical is the catalytic degradation of organic contaminants without the use of outside inputs [6]. Dark catalysis is an AOP that outperforms others in terms of energy and chemical savings, as well as ease of usage [4]. Without using external energy or chemical reagents, organic pollutants can be transformed into non-toxic or less hazardous compounds in aqueous systems through catalytic degradation carried out in the dark at ambient temperature

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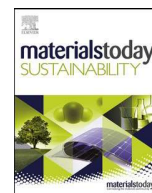
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Tailoring the properties of SnS thin films deposited at room temperature by varying the amount of complexing agent for enhanced photocatalytic activity

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ARTICLE INFO

Keywords:

Tin monosulphide (SnS)
Thin film
Complexing agent
Triethanolamine (TEA)
SILAR
Photocatalysis

ABSTRACT

This work examines how the characteristics and photocatalytic efficacy of modified SILAR-deposited SnS thin films are affected by the addition of a complexing agent. Stannous chloride dihydrate and sodium sulphate were used as tin and sulphur sources, respectively, while triethanolamine (TEA) served as a complexing agent in film deposition. The modified SILAR method facilitated the formation of well-adhesive thin films on the glass substrate at room temperature. The formation of SnS was demonstrated using EDAX and XPS analysis. XRD analysis proved that all the films are polycrystalline in nature with an orthorhombic crystal structure. The presence of chlorine as an involuntary dopant was observed in all the films prepared with TEA. Optical studies employing UV–visible spectroscopy found that all of the films have good visible absorption, with bandgap values ranging from 1.58 eV to 2.2 eV. Even though the films were deposited at room temperature, all films exhibited good thermal stability as per TGA analysis. The introduction of TEA caused improvements in the adhesion of the film to the substrate, a decrease in the band gap, a change in the morphology and composition, and an increase in the crystallinity and crystallite size. Due to their suitable bandgap corresponding to the visible region, SnS thin films exhibited good photocatalytic efficiency in degrading various types of dyes. The SnS thin film catalyst reduced 97% of methylene blue in 90 min at room temperature without using any reducing agent. The LCMS analysis validated the photocatalytic degradation of dye, whereas the UV–visible spectroscopic analysis gave a quantitative measure of the degradation efficiency. The reduction in photodegradation efficiency in the presence of OH radical scavengers confirmed the role of OH radicals in the degradation process. The terephthalic acid test further demonstrated the generation of OH radicals during the dye degradation process. The observed increase in photocatalytic activity of SnS thin films with TEA addition could be due to TEA-induced bandgap reduction, crystallinity increase, and crystallite size increase. The catalyst was reusable, stable, easy to recover after use, and effective against various kinds of dyes. The study emphasizes the use of complexing agents as a useful tool for modifying the characteristics and, consequently, the photocatalytic efficiency of modified SILAR-deposited SnS thin films.

1. Introduction

Tin monosulfide (SnS) has attracted the interest of researchers during the last two decades as a prospective candidate for a variety of technological uses. Chemical stability, constituent element abundance (sulphur 0.042%, tin 0.00022% in the earth's crust), low cost, non-toxicity, and ease of doping [1–10] are some of the general features of SnS that make it appropriate for device manufacturing. Due to desirable properties such as a direct band gap near the optimum value of 1.5 eV, a high absorption coefficient ($>10^4 \text{ cm}^{-1}$), a high quantum efficiency, and

intrinsic p-type conductivity, SnS thin films have been extensively investigated as solar cells, sensors, photodiodes, photocatalysts, FETs, photoelectrochemical cells, lithium-ion batteries, photo detectors, and so on [1,5–23].

SnS thin films can be deposited using a variety of deposition processes, including chemical bath deposition (CBD) [3,24,25], electrodeposition [26,27], successive ionic layer adsorption and reaction (SILAR) [1,3,11,28], spray pyrolysis [29], sputtering [9,30], thermal evaporation [12,22], co-evaporation [23], dip coating [3,10], and others. The properties of the film are strongly influenced by the deposition

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Deposition of SnS thin films on various substrates at room temperature

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ABSTRACT

This study describes a modified SILAR technique for depositing Tin monosulphide (SnS) thin films on diverse substrates, such as glass, ITO coated glass, and OHP sheet, all at room temperature. This simple, less expensive, environmentally friendly, and industrially scalable method allows excellent control over the deposition rate and thickness, as well as many experimental flexibilities. The advantages of depositing films at room temperature include energy efficiency, cost-effectiveness, and suitability for heat-sensitive materials. The deposited SnS thin films underwent comprehensive analysis through XRD, FESEM, EDAX, XPS, TGA, and UV–visible spectroscopy to thoroughly understand their properties. The results showed that the films were polycrystalline, orthorhombic, single-phase, and nearly stoichiometric, with a bandgap value in the visible region. The deposition conditions were optimized to achieve high-quality thin films, and the impact of substrate variations on film characteristics was also investigated. The study showcased the simplicity of doping in the modified SILAR process. Furthermore, the study demonstrated the photocatalytic degradation effectiveness of SnS thin films against the dye Rhodamine B. Various analyses, including UV-visible spectroscopy studies, ROS scavenger tests, ROS indicator tests, and kinetic analysis, were performed. The photodegradation process was effectively described by the Langmuir–Hinshelwood (L-H) mechanism.

1. Introduction

Thin film technology has revolutionized various fields of research in solid-state electronics, physics, and chemistry, owing to its distinctive blend of chemical, mechanical, and physical properties. These two-dimensional materials boast a substantial surface-to-volume ratio and exhibit unique behaviours compared to bulk materials with the same chemical composition [1,2]. The processing of materials into films meets the criterion of microminiaturization and enables easy integration into many types of devices. Thin films find applications in diverse fields such as electronics, optics, space exploration, industrial sectors, defence and more. Their popularity is attributed to their cost-effectiveness, light-weight nature, and other intriguing characteristics [1–3]. Tin monosulfide (SnS) is an orthorhombic double-layer IV–VI compound semiconductor material with lattice parameters $a = 0.439$ nm, $b = 1.1983$ nm, and $c = 0.3984$ nm [4]. Because of their high absorption coefficient, absorption tunable bandgap in the visible region, intrinsic p-type conductivity, and high theoretical conversion efficiency, SnS thin films are emerging as viable PV absorbers [4–6]. In addition to light harvesting, SnS thin films have uses in photocatalysis, photo-electrochemical cells, infrared detectors, and other optoelectronic

systems [6,7]. Tin monosulfide is less toxic, less expensive, and more environmentally friendly, and its basic elements are abundant on Earth [4–6].

The choice of synthesis route significantly influences the characteristics of materials, making fabrication technology a crucial aspect [4]. Researchers are actively seeking easy, cost-effective methods for large-area deposition, adopting green synthesis routes for environmentally friendly pathways, and aiming to achieve phase-pure, uniform, and well-adhesive thin films with specific chemical compositions [4,8,9]. While various techniques have been developed for precise thin film growth, most of these methods are physical in nature. Physical methods often face criticism due to their high cost and size limitations, primarily because they require a vacuum. In contrast, chemical approaches offer the advantages of low-cost, large-area deposition and the ability to achieve ultrathin growth. The literature demonstrates the synthesis of SnS thin films through diverse chemical techniques, including atomic layer deposition [10], SILAR [4,5,6,11,12,13], spray pyrolysis [14], dip coating [13], chemical bath deposition [13], electro-deposition [15], etc. However, many of these chemical methods face challenges related to high substrate temperatures, the use of toxic reactive gases, and so on.

In response to these challenges, we present an affordable, simple, and

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