

*This thesis is dedicated to my
beloved parents, sister and my respected supervisors for their
constant inspiration, whole hearted cooperation and proper
valuable guidance*

DECLARATION

I declare that the thesis entitled ***“EXTENSIVE INVESTIGATION OF NANOMATERIALS OF ZINC AND IRON METAL OXIDES AND THEIR APPLICATIONS IN BIOLOGICAL AND CHEMICAL SCIENCES”*** has been prepared by me for the Degree of Doctor of Philosophy (Ph.D.) under the supervision of Dr. Mahendra Nath Roy, FRSC (London), (Principal Supervisor), Professor of Chemistry, University of North Bengal and Dr. Suranjan Sikdar (Co-Supervisor), Associate Professor of Chemistry, Ghani Khan Choudhury Institute of Engineering & Technology (GKCIET). No part of this thesis has formed the basis for the award of any other degree or diploma, in this or any other Institution or University.

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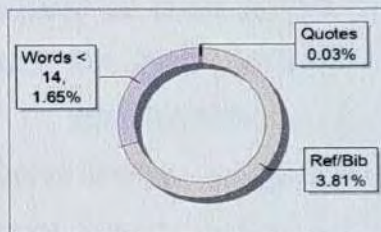
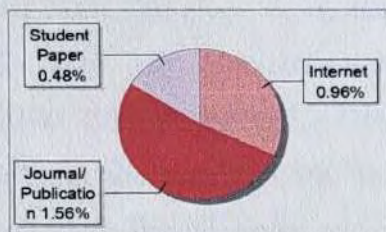
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Behind every success, there must be a beautiful adventure and an unforgettable journey. I would want to offer my sincere gratitude to everyone who has helped me on this amazing journey.

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PREFACE

The research work in the thesis titled with “*EXTENSIVE INVESTIGATION OF NANOMATERIALS OF ZINC AND IRON METAL OXIDES AND THEIR APPLICATIONS IN BIOLOGICAL AND CHEMICAL SCIENCES*” was initiated for about five years ago under supervision of Prof. (Dr.) Mahendra Nath Roy, Professor of Department of Chemistry, University of North Bengal and under co-supervision of Dr. Suranjan Sikdar, Associate Professor of Department of Chemistry, Ghani Khan Choudhury Institute of Engineering and Technology (GKCIET).

The focus of the newly growing field of nanochemistry belongs to the chemical and material sciences deals with the development of novel techniques for producing nanoscale materials. Due in large part to its very small size, nanoscale objects exhibit unique material properties, which attract researchers to the field. Chemical, physical and materials science as well as biological, engineering and medical applications all use nanochemistry. The goal of this study is to synthesize inorganic metal oxide-based nanomaterials using environmentally friendly green and chemical synthesis processes and to investigate the chemical and biological applications of these materials.

Throughout the course of my research, I had the honour of attending a number of national and international conferences and seminars. These events provided me with a wealth of knowledge and inspiration to do my own research work and I was even fortunate enough to publish the thesis-related works in reputable international journals.

Every time the study reported was based on the findings of the other investigators, appropriate acknowledgement has been made in accordance with standard procedure for reporting scientific observation. I am responsible for any oversights and mistakes that may have occurred unintentionally despite taking measures.

I hope that I would face more difficulties in life so that I could apply the information I have acquired from my field of work in the future.

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	plot at 66 minute for at different temperatures ($[\text{CuI } 1] = 4 \text{ mM}$, $[\text{PDS}] = 3 \text{ mM}$, $\text{pH} = 5$). Figure 7: First order kinetics of (a) catalyst's dose variation, (c) PDS concentration variation, (e) pH variation, (g) temperature variation and zero order kinetics of (b) catalyst's dose variation, (d) PDS concentration variation, (f) pH variation, (h) temperature variation. Figure 8: (a) Role of scavenger methanol (MeOH) on MB degradation by CuI 1 ($[\text{CuI } 1] = 4 \text{ mM}$, $[\text{PDS}] = 3 \text{ mM}$, $\text{pH} = 5$, temperature = 298.15 K, $[\text{MeOH}] = 12.5 \text{ }\mu\text{L/mL}$). (b) degradation (%) of MB by CuI 1 ($[\text{CuI } 1] = 4 \text{ mM}$, $[\text{PDS}] = 3 \text{ mM}$, $\text{pH} = 5$, temperature = 298.15 K, $[\text{MeOH}] = 12.5 \text{ }\mu\text{L/mL}$) (c) Role of scavenger isopropanol (IPA) on MB degradation by CuI 1 ($[\text{CuI } 1] = 4 \text{ mM}$, $[\text{PDS}] = 3 \text{ mM}$, $\text{pH} = 5$, temperature = 298.15 K, $[\text{IPA}] = 25 \text{ }\mu\text{L/mL}$). (d) degradation (%) of MB by CuI 1 ($[\text{CuI } 1] = 4 \text{ mM}$, $[\text{PDS}] = 3 \text{ mM}$, $\text{pH} = 5$, temperature = 298.15 K, $[\text{IPA}] = 25 \text{ }\mu\text{L/mL}$). Figure 9: Absorbance of CuI 1 at 652 nm in presence of 100 μM TMB at different pH. Figure 10: Various kinetics model of oxidase mimicking activity of CuI 1 nanozyme in presence of TMB (a) Michaelis Menten, (b) Line weaver burk, (c) Eadie-Hofstee, (d) Hanes-Woolf. Figure S1: (a) XRD spectra and (b) SEM image of pure Iron Oxide Nanoparticles. Figure S2: EDAX spectra of (a) CuI 1, (b) CuI 2 and (c) CuI 3; Elemental mapping of (d) CuI 1 (Cu = Blue, Fe = Red, O = Green), (e) CuI 2 (Cu = Blue, Fe = Green, O =	
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	Red) and (f) CuI 3 (Cu = Blue, Fe = Green, O = Red). Figure S3: Degradation of MB dye in presence of only MB + PDS, only MB + 4mM CuI 1, only MB + 4mM CuI 2 and only MB + 4mM CuI 3. Figure S4: Plot of $\ln K$ vs $1/T$. Figure S5: (a) Role of scavenger parabenzoquinone (PBQ) on MB degradation by CuI 1 ([CuI 1] = 4 mM, [PDS] = 3 mM, pH = 5, temperature = 298.15 K, [PBQ] = 1 mM). (b) degradation (%) of MB by CuI 1 ([CuI 1] = 4 mM, [PDS] = 3 mM, pH = 5, temperature = 298.15 K, [PBQ] = 1 mM). (c) Role of scavenger sodium azide (NaN_3) on MB degradation by CuI 1 ([CuI 1] = 4 mM, [PDS] = 3 mM, pH = 5, temperature = 298.15 K, [NaN_3] = 1 mM). (d) degradation (%) of MB by CuI 1 ([CuI 1] = 4 mM, [PDS] = 3 mM, pH = 5, temperature = 298.15 K, [NaN_3] = 1 mM). Figure S6: The possible degradation mechanism via PDS activation of CuI 1. Figure S7: Time dependent uv absorption spectra of 150 μM TMB in presence of 100 $\mu\text{g/mL}$ (a) IONP, (b) CuI 1, (c) CuI 2, (d) CuI 3, (e) oxidase like activity of nanomaterials during TMB oxidation after 14 minutes. Figure S8: Effect of various concentrations of scavengers on oxidase mimicking activity of CuI 1 (a) IPA, (b) NaN_3, (c) PBQ, (d) AA.	
Chapter VII	Figure 1: XRD pattern of IZ 1, IZ 2, IZ 3 and IZ 4. Figure 2: (a)-(d) SEM images of IZ 1, IZ 2, IZ 3 and IZ 4; (e)-(h) EDS spectra of IZ 1, IZ 2, IZ 3 and IZ 4.	204-212

	Figure 3: HRSEM image of (a) IZ 1, (b) IZ 2, (c) IZ 3 and (d) IZ 4. Figure 4: IR spectra of IZ 1, IZ 2, IZ 3 and IZ 4. Figure 5: Antibacterial activities of all nanocomposites for different (gram-positive and gram-negative) bacterial strains. Figure 6: Antibacterial activities of IZ 3 at different concentrations against different (both gram-positive and gram-negative) bacterial strains. Figure 7: Probable mechanism of action of antibacterial activity of the applied nanoparticles. Figure 8: Radar plot for comparative effect of IZ 1, IZ 2, IZ 3 and IZ 4 against (a) ABTS, (b) DPPH, (c) superoxide and (d) nitric oxide free radicals (scale bar represents the IC₅₀ value in µg/mL) Figure 9: Wheat seed germination percentage as influenced by several kinds of ZnFe₂O₄/ZnO nanocomposites. The vertical bar above the column represents the standard deviation (n=3). Different letters (a, b, c, etc.) indicated that they are statistically different at $p \leq 0.05$ following Tukey's HSD test. Figure 10: Phenotypic appearance (A) and growth attributes (B) of treated and control and treated wheat seedlings. The vertical bar above the column represents the standard deviation (n=20). * symbol indicated that they are statistically significant from their respective control at 95% confidence level as observed through two-tailed t-test.	
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	Figure 11: Different biochemical attributes of IZ 1 treated and control wheat seedlings. Figure 12: Probable mechanism of action of the applied nanomaterials on wheat seed germination and seedling growth. Figure S1: Zone of inhibition (mm) IZ 3 against different bacterial strain at different concentration.	
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LIST OF SCHEMES

CHAPTERS	SCHEMES	PAGE NO.
Chapter IV	Scheme 1: IONP/ MINP1/ MINP2/ MINP3 catalyzed oxidation of TMB	113
Chapter V	Scheme S1: Formation mechanism of nanomaterials by PGP extract (alkaloids and flavonoids compounds).	150
Chapter VI	Scheme S1: Nanozyme catalyzed oxidation of TMB.	186

LIST OF SYMBOLS AND ABBREVIATIONS

TERMS	FULL FORMS
cm	centimeter
nm	nanometer
M	molar
mM	milli molar
μM	micro molar
hr	hour
min	minute
s	second
°C	degree celsius
eV	electron volt
rpm	revolution per minute
g	gram
mL	millilitre
K	Kelvin
MB	Methylene Blue
KJ	Kilojoule
AOPs	Advanced Oxidation Processes
IONPs	Iron Oxide Nanoparticles

EG	Ethylene Glycol
UV-vis	Ultraviolet-visible
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
µg	microgram
PDS	peroxodisulfate
PMS	peroxomonosulfate
HSA	Human Serum Albumin
DNA	Deoxyribonucleic Acid
mA	milliampere
KBr	Potassium Bromide
EDX	Energy Dispersive X-ray analysis
DLS	Dynamic Light Scattering
PDI	polydispersity index
NPs	nanoparticles

LIST OF APPENDICES

APPENDIX A	List of Publications
APPENDIX B	List of Seminars/Conferences Attended

APPENDIX A

LIST OF PUBLICATIONS

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1. Green Synthesis of Iron Oxide Nanoparticles to Explore Cytotoxic Behaviour and to Diminish Environmental Pollution by a Novel Contrivance



Journal of Chemical, Biological and Physical Sciences, 2021, 11(1),
147-170

(Included in the Thesis)

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2. Green synthesis and characterization of heterostructure MnO-FeO nanocomposites to study the effect on oxidase enzyme mimicking, HSA binding interaction and cytotoxicity



ELSEVIER

Chemical Physics Letters, 2021, 1225, 129093

(Included in the Thesis)

-
3. Synthesis and characterization of $\text{Mo}_x\text{Fe}_{1-x}\text{O}$ nanocomposites for the ultra-fast degradation of methylene blue via a Fenton-like process: a green approach



New Journal of Chemistry, 2022, 46, 18055-18068

(Included in the Thesis)

-
4. Green synthesized copper assisted iron oxide nanozyme for the efficient elimination of industrial pollutant via peroxodisulfate activation.



ELSEVIER

Journal of Molecular Structure, 2023, 1283, 135267

(Included in the Thesis)

5. Rational Synthesis and Characterization of Temperature Switching $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ Nanocomposite Used for Anti-bacterial, Anti-oxidant and Seed Germination Properties



New Journal of Chemistry (Accepted)

(Included in the Thesis)

6. Synthesis of β -cyclodextrin grafted rhombohedral-CuO antioxidant nanozyme for detection of dopamine and hexavalent chromium through off-on strategy of peroxidase mimicking activity



ELSEVIER

Microchemical Journal, 2022, 179, 107514

7. Subsistence of diverse interactions of some biologically important molecules in aqueous ionic liquid solutions at various temperatures by experimental and theoretical investigation



ELSEVIER

Journal of Molecular Structure, 2022, 1257, 132571

- 8. Cyclic oligosaccharides as controlled release complexes with food additives (TZ) for reducing hazardous effects**



ELSEVIER

Journal of Molecular Liquids, 2022, 348, 118429

- 9. Synergetic effects of green synthesized CeO₂ nanorod-like catalyst for degradation of organic pollutants to reduce water pollution**



ELSEVIER

Environmental Nanotechnology, Monitoring & Management, 2021, 16, 100539

- 10. Green Synthesis of Cu²⁺ doped ZnO nanoparticles to investigate their Structural, Optical, Morphological properties and Antifungal activities**



Journal of Chemical, Biological and Physical Sciences, 2020, 11(1), 066-081

- 11. Intrinsic Light-Activated Oxidase Mimicking Activity of Conductive Polyaniline Nanofibers: A Class of Metal-Free Nanozyme**



ACS
Chemistry for Life®

ACS Applied Biomaterials, 2022, 5(12), 5518-5531

- 12. β -Cyclodextrin-Stabilized Biosynthesis Nanozyme for Dual Enzyme Mimicking and Fenton Reaction with a High Potential Anticancer Agent**



ACS Omega, 2022, 7(5), 4457-4470

- 13. Probing the Molecular Assembly of a Metabolizer Drug with β -Cyclodextrin and Its Binding with CT-DNA in Augmenting Antibacterial Activity and Photostability by Physicochemical and Computational Methodologies**



ACS Omega, 2022, 7(30), 26211-26225

- 14. Assemble multi-enzyme mimic tandem $\text{Mn}_3\text{O}_4@ \text{g-C}_3\text{N}_4$ for augment ROS elimination and label free detection**



ELSEVIER

Chemical Engineering Journal, 2023, 463, 142355

- 15. β -cyclodextrin Grafted Green Synthesis of Heterojunction $\text{CeO}_2@ \text{ZrO}_2$ Nanocomposite with Highly Efficient Photocatalytic, Fenton and Photo-Fenton Process for Waste Water Treatment**



Journal of Chemical, Biological and Physical Sciences, 2021, 11(4), 427-444

- 16. Assembled Bisphenol A with cyclic oligosaccharide as the controlled release complex to reduce risky effects**



Environmental Science and Pollution Research, 2023, 30, 43300-43319

- 17. A combined physicochemical and computational investigation of the inclusion behaviour of 3-(1-Naphthyl)-D-alanine Hydrochloride insights into β -Cyclodextrin**



ELSEVIER

Journal of Molecular Liquids, 2023, 378, 121583

- 18. Investigation of molecular interactions insight into some biologically active amino acids and aqueous solutions of an anti-malarial drug by physicochemical and theoretical approach**



ELSEVIER

Journal of Molecular Liquids, 2021, 341, 116933

- 19. Exploring inclusion complex of an anti-cancer drug (6-MP) with β -cyclodextrin and its binding with CT-DNA for innovative applications in anti-bacterial activity and photostability optimized by computational study**



RSC Advances, 2022, 12, 30936

- 20. High Visual Colorimetric Determination of F⁻ Ions by Exploiting the Inhibition of Oxidase Mimicking Activity of FeMnO₄@GQD Nanocomposite**



WILEY

Chemistry Select, 2022, 7, e202201186

- 21. Synthesis, Characterization and Visible Light Induced Photo-Degradation of Acid Orange II Dye in Aqueous Medium using a Novel Synthesized Al₂MoZnO₇ Nanocomposite**



Journal of Advanced Chemical Sciences (JACS), 2020, 6(2), 676-681

- 22. Phase variation of manganese oxide in the MnO@ZnO nanocomposite with calcination temperature and its effect on structural and biological activities**

SPRINGER NATURE

Scientific Reports, 2023, 13, 21542

- 23. Label-Free Detection of Epinephrine Using Flower-like Biomimetic CuS Antioxidant Nanozymes**



Inorganic Chemistry, 2023, 62(29), 11291–11303

- 24. Study about Encapsulation of Vitamin C into β -Cyclodextrin: An Approach towards Advancement and Regulatory Release (Book Chapter)**

Research Aspects in Biological Science, 2022, 7, 156–174

APPENDIX B

LIST OF SEMINARS/CONFERENCES ATTENDED

Sl. No.	Seminar/Conference	Date/Year	Organizer and Venue	Role
(1)	National Conference on "Environmental Determinism, Diverse Pollutions, Sources, and Controlling Management through Sciences and Humanities"	March 22-23, 2021	Alipurduar University	Oral Presentation
(2)	National Seminar on "Frontiers in Chemistry-2020"	March 5, 2020	Department of Chemistry, University of North Bengal	Poster Presentation
(3)	International Seminar on Frontiers in Chemistry 2023 & Prof. C. N. R. Rao Endowment Lecture	March 13-15, 2023	Department of Chemistry, University of North Bengal & CRSI North Bengal Local Chapter	Oral Presentation
(4)	International Seminar on 'International Year of the Periodic Table of Chemical Elements-2019'	November 22-23, 2019	Department of Chemistry, University of North Bengal	Poster Presentation

(5)	Virtual International Conference on Emerging Research Trends in Chemical Sciences (ERTCS-2020)	July 24-26, 2020	PG Department of Chemistry, Govt. Post Graduate College Rajouri	Poster Presentation
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