



I would like to dedicate this dissertation to Lord Krishna.



‘IT’S BETTER TO LIVE YOUR OWN DESTINY
IMPERFECTLY THAN TO LIVE AN IMITATION
OF SOMEBODY ELSE’S LIFE WITH
PERFECTION ’



“Bhagwat Geeta 3.35”

CERTIFICATE

It is certified that the work contained in the thesis titled “**STUDIES ON ULTRASOUND ASSISTED REMOVAL OF DYE FROM WASTEWATER BY N-RGO SUPPORTED DOPED BIFEO₃ PHOTOCATALYST**” by **TARUN KUMAR DIXIT** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. Degree.

Sweta

(Co-Supervisor)

Department of Chemical Engineering
& Technology,
Indian Institute of Technology
(Banaras Hindu University),
Varanasi 221005
India

A.S.K. Sinha

(Supervisor)

Department of Chemical Engineering
& Technology,
Indian Institute of Technology
(Banaras Hindu University),
Varanasi 221005
India

DECLARATION BY THE CANDIDATE

I, *Tarun Kumar Dixit*, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of *Prof. A.S.K. Sinha* from Dec-2013 to Jan-2021, at the *Department of Chemical Engineering & Technology*, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

Date:

Place: Varanasi

(Tarun Kumar Dixit)

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

Sweta

(Co-Supervisor)

Assistant professor
Department of Chemical Engineering & Technology,
Indian Institute of Technology (Banaras Hindu University),
Varanasi 221005, India

A.S.K. Sinha

(Supervisor)

Professor,
Department of Chemical Engineering & Technology,
Indian Institute of Technology (Banaras Hindu University),
Varanasi 221005, India

V.L Yadav

(Head of Department)

Professor,
Department of Chemical Engineering & Technology, Indian
Institute of Technology (Banaras Hindu University),
Varanasi 221005, India

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: *STUDIES ON ULTRASOUND ASSISTED REMOVAL OF DYE FROM WASTEWATER BY N-RGO SUPPORTED DOPED BIFEO₃ PHOTOCATALYST.*

Name of the Student: Tarun Kumar Dixit

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the "*Doctor of Philosophy*".

Date:

Place: Varanasi

(Tarun Kumar Dixit)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated.

Acknowledgement

First and foremost, I would like to thank my supervisor, Dr A.S.K. Sinha, Professor, Department of Chemical Engineering & Technology, IIT (BHU) for his unparalleled guidance, expertise, encouragement and wisdom to improve my research, academic writing and presentation skills throughout my PhD. Throughout the ups and downs, he remained focused and determined, two characteristics which have definitely rubbed off on me. He will remain a lifelong mentor.

I would also like to thank my co-supervisor, Dr. Sweta, Department of Chemical Engineering & Technology, IIT (BHU) for her guidance, prompt inspirations, timely suggestions with kindness enthusiasm and dynamism have enable me to complete my thesis.

I would also like to thank Dr. R.K. Mandal, Professor, Department of Metallurgical Engineering, IIT (BHU) and Dr. R. S. Singh, Professor, Department of Chemical Engineering for the forever enthusiastic & forward-thinking and giving valuable suggestions during my research progress evaluation committee meetings. They also taught me about the ups and downs of reviewers, which I'll never forget.

I express my sincere thanks to Dr. V.L Yadav, Head & Professor, Department of Chemical Engineering & Technology for his great help. Special thanks to past and present convenor, Departmental post graduate committee (DPGC), Dr. Ravi P. Jaiswal, Prof. V.L. Yadav, Prof. R.S. Singh, Prof. H. L. Pramanik, and Dr Manoj Kumar and Dr. Bhawna Verma, Department of Chemical Engineering & Technology, for encouraging me and providing necessary

guidelines about my project during the course of my work. I also would like to show my gratitude to IIT (BHU) for its financial support during the entire period of my candidature.

Mr. Rajeev Ranjan, Mr. Arvind Singh, Mr. Ankit Kumar, and Mr. Zahoor Alam was five of the best PhD students could have. Sometimes it's really beneficial to have somebody who can give you a quick answer, rather than search for it for hours. Definitely a friend for life, and despite me moving away from the group, I'm sure our paths will cross again soon.

I would appreciate Mr. Bhuneshwar Sharma, Mr. Arjun Prasad, Mr. Umesh Pratap, Mr. Shailendra Kumar Upadhyay & Mr. Rajiv Nayan Pandey, Technical staff, sophisticated instrumentation laboratory and Mr. Arvind Kumar, Mr. Ankit Kumar & Mr. Varun Kumar from Computer Lab for their assistance on the experimental issues with their expertise in characterization, providing me valuable help, support during characterizations & the course of work. And say thanks for their wishes and love.

The people who made my PhD actually fun in moments kept me sane and helped with work during the later hours; Dr. Balendu Shehar, Dr. Pawan Kumar Dr. Mahendra Ram, Dr. Munna Kumar, Dr. Mithilesh Rai, Dr. Dilip Kumar, Dr. Suverna Trivedi, Anuj Prajapati, Vivek Patel, Arun Gautam, Pavan Kumar Gupta, Rohan Bajpai and all the rest of you guys for our friendship and thank you for all the pleasant lunches together and the nice breaks.

I wish to thank all of the M. Tech, PhD and Post-doctoral students within the department of Chemical Engineering Department who have come and gone during this project for all their support, humour, food, and memorable times. Thanks to all my friends in the department, Institute, around BHU and throughout my entire life.

Special thanks for the people that more than everyone else have contributed to the success of my PhD: my family. This journey would never have been steady and strong without the emotional support of my parents, my brother and sister and my wife, who motivated and supported me throughout the PhD life span with utmost love and care. I am forever indebted to the understanding they have shown and for standing by me through every thick and thin. Last, but the most important, I would like to thank *lord Jagannath* who is my ultimate well-wisher and friend.

Date:

Place: Varanasi

(Tarun Kumar Dixit)

Contents

	Page No.
Contents	viii
List of figures	xiv
List of tables	xviii
List of abbreviations	xx
Preface	xi
Chapter-1 Introduction	1-14
1.1 General introduction	3
1.2 Advanced oxidation processes (AOPs)	4
1.3 Photocatalysis: Basic principle and its type	6
1.3.1 Homogeneous photocatalysis	6
1.3.1.1 UV/Hydrogen peroxide (UV/H ₂ O ₂)	7
1.3.1.2 UV/Ozone (UV/O ₃)	7
1.3.1.3 UV/Ozone/Hydrogen peroxide (UV/O ₃ /H ₂ O ₂)	8
1.3.1.4 Photo-Fenton system (UV/F ²⁺ / H ₂ O ₂)	8
1.3.2 Heterogeneous Photocatalysis	9
1.4 Sonolysis	10
1.5 Objectives	14

Chapter-2 Literature reviews	15-44
2.1 Photocatalytic degradation of water pollutants: Fundamentals	17
2.1.1 Key parameters that affect dye degradation	21
2.1.1.1 Effect of catalyst concentration	21
2.1.1.2 Effect of concentration of water pollutants	21
2.1.1.3 Adsorption of pollutants on the surface of photocatalyst	22
2.1.1.4 Dissolve oxygen	22
2.1.1.5 Light intensity	23
2.1.1.6 Effect of pH	23
2.2 Semiconductor properties for photocatalysis	24
2.2.1 Energy gap	25
2.2.2 Electro-hole pair recombination	25
2.3 Bismuth ferrite (BiFeO ₃): A perovskite material	26
2.4 Modification of BFO to improve photocatalytic efficiency	27
2.4.1 Rare earth doping	27
2.4.2 Surface modification	29
2.4.3 Heterojunction with other materials	30
2.5 Graphene and its derivatives	35
2.5.1 Graphene based heterojunctions	37
2.6 Sonophotocatalytic process: Ultrasound assisted photocatalysis	41
Chapter-3 Experimental	47-63
3.1 Synthesis of supports	49
3.1.1 Graphene oxide (GO)	49

3.1.2	Reduced graphene oxide	49
3.1.3	Nitrogen doped reduced graphene oxide	50
3.2	Synthesis of photocatalysts	50
3.2.1	Bismuth ferrite (BFO)	50
3.2.2	Gadolinium doped bismuth ferrite (BGFO)	50
3.3	Synthesis of heterojunctions	51
3.3.1	rGO supported bismuth ferrite (BFO/rGO)	51
3.3.2	N-rGO supported bismuth ferrite (BFO/N-rGO)	51
3.3.3	N-rGO supported gadolinium doped bismuth ferrite (BGFO/N-rGO)	51
3.4	Experimental setup and activity measurements	52
3.5	Contamination source: Rhodamine B	53
3.6	Materials	54
3.7	Characterization tools	54
3.7.1	X-ray diffraction (XRD)	56
3.7.2	Fourier transform infrared spectroscopy (FTIR)	57
3.7.3	Diffused reflectance spectroscopy (DRS)	58
3.7.4	Photoluminescence spectroscopy (PL)	58
3.7.5	Scanning electron microscope (SEM)	59
3.7.6	Energy dispersive X-ray (EDX)	59
3.7.7	Transmission electron microscope (TEM) and selected area electron diffraction (SAED)	59
3.7.8	X-ray photoelectron spectroscopy (XPS)	60

3.7.9	Electrochemical impedance spectroscopy (EIS)	61
3.7.10	Mott-Schottky (MS)	62
3.7.11	Brunauer–Emmett–Teller (BET) surface area	62
Chapter-4 Result and discussion		65-134
4.1	Selection of suitable graphene oxide-based support for bismuth ferrite in photocatalytic degradation process	68
4.1.1	XRD studies	69
4.1.2	FTIR studies	71
4.1.3	UV-DRS analysis	74
4.1.4	TEM analysis	77
4.1.5	XPS studies	78
4.1.6	Photoluminescence studies	85
4.1.7	Electrochemical impedance spectroscopy (EIS) Studies	86
4.1.8	Mott-Schottky analysis	87
4.1.9	Photocatalytic performance	89
4.1.9.1	Effect of catalyst concentration	89
4.1.9.2	Effect of dye concentration	90
4.1.9.3	Effect of pH	91
4.1.9.4	Photocatalytic degradation kinetics	92
4.1.9.5	Reactive species in photocatalytic degradation of RhB	94
4.1.9.6	Plausible mechanism of degradation of RhB	95
4.1.9.7	Stability of photocatalyst	97
4.1.10	Summary	98

4.2 Synergistic effect of N-rGO supported Gd-doped bismuth ferrite on photocatalytic degradation of Rhodamine B	99
4.2.1 XRD studies	99
4.2.2 FTIR studies	101
4.2.3 Diffused reflectance spectroscopy and Photoluminescence spectroscopy studies	103
4.2.4 Morphological analysis	106
4.2.5 XPS studies	108
4.2.6 BET surface area analysis	113
4.2.7 Electrochemical impedance spectroscopy and Mott-Schottky analysis	114
4.2.8 Photocatalytic performance	117
4.2.8.1 Activity and kinetic studies	117
4.2.8.2 Effect of reactive species in degradation process and plausible mechanism	118
4.2.9 Stability of the catalyst	121
4.2.10 Summary	122
4.3 Sono-photocatalytic degradation of Rhodamine B over N-rGO supported Gd-doped bismuth ferrite heterojunction.	124
4.3.1 Sonophotocatalytic performances	124
4.3.1.1 Effect of catalyst loading	124
4.3.1.2 Effect of dye concentration	125
4.3.1.3 Effect of pH	126

4.3.1.4	Effect of ultrasonic power	128
4.3.1.5	Sonophotocatalytic activity	129
4.3.1.6	Plausible mechanism of sono-photocatalytic degradation	131
	of RhB	
4.3.2	Summary	134
Chapter-5	Conclusions and future scopes	135-136
5.1	Conclusions	137
5.2	Future scopes	139
References		141

List of Figures

<u>Fig. No.</u>	<u>Caption of the Figure</u>	<u>Page No.</u>
1.1	Bubble growth and implosion phenomena.	11
1.2	Reaction zones in cavitation process.	12
2.1	Microscopic phenomena of photocatalytic process.	17
2.2	Band edge positions of some semiconductors.	24
3.1	Experimental setup.	52
3.2	A diagrammatic representation of (a) Photocatalytic process; (b) Sonophotocatalytic process.	53
3.3	Chemical structure of Rhodamine B (RhB).	54
4.1.1	XRD patterns of GO, rGO, and N-rGO.	69
4.1.2	XRD patterns of BFO, BFO/rGO, and BFO/N-rGO; Inset shows the enlarge version around 2-theta equal to 51 degrees.	70
4.1.3	FTIR Spectra of GO, rGO, and N-rGO.	71
4.1.4	FTIR Spectra of BFO, BFO/rGO, and BFO/N-rGO.	72
4.1.5	DRS of BFO, BFO/rGO, and BFO/N-rGO.	75
4.1.6	Tauc's Plot of BFO, BFO/rGO, and BFO/N-rGO.	76
4.1.7	TEM images of (a) BFO, (b) BFO/rGO, and (c) BFO/N-rGO; HR-TEM of (d) BFO, (e) BFO/rGO, and (f) BFO/N-rGO.	77
4.1.8	XPS spectra of C 1s (a) rGO, (b) NrGO, (c) BFO/rGO, (d) BFO/N-rGO.	78
4.1.9	XPS spectrum of N1s (a) NrGO (b) BFO/N-rGO.	79

4.1.10	XPS spectra of O 1s (a) rGO, (b) NrGO, (c) BFO, (d) BFO/rGO, (e) BFO/N-rGO.	81
4.1.11	XPS spectra of Bi 4f in (a) BFO, (b) BFO/rGO, (c) BFO/N-rGO; Fe 2p in (d) BFO, (e) BFO/rGO, (f) BFO/N-rGO.	82
4.1.12	PL Spectra of BFO, BFO/rGO and BFO/N-rGO.	85
4.1.13	Nyquist plot of BFO, BFO/rGO and BFO/N-rGO.	86
4.1.14	Mott-Schottky plot of BFO, BFO/rGO and BFO/N-rGO.	87
4.1.15	Effect of catalyst loading.	89
4.1.16	Effect of dye concentration (Catalyst loading 120 mg.L ⁻¹ , pH=4.3).	90
4.1.17	Effect of pH on photocatalytic degradation of RhB.	92
4.1.18	(a)Photocatalytic activity of different materials for the degradation of RhB dye; (b) Reaction kinetics.	93
4.1.19	Reactive trapping experiment for photocatalytic degradation of RhB.	95
4.1.20	Reusability test.	97
4.2.1	XRD patterns of N-rGO, BFO, BGFO, and BGFO/N-rGO (enlarge sections around at 2-theta of 31 and 51 degree).	100
4.2.2	FTIR Spectra of BFO, BGFO, BGFO/N-rGO, and N-rGO (enlarge sections between 510-700 cm ⁻¹ and 1000-1800 cm ⁻¹).	101
4.2.3	(a) DRS absorbance, (b) Tauc's Plot, (c) PL Spectra of BFO, BGFO and BGFO/N-rGO.	104

4.2.4	SEM image of (a) BFO, (b) BGFO, and (c) BGFO/N-rGO; TEM image of (d) BFO, (e) BGFO, and (f) BGFO/N-rGO.	106
4.2.5	EDX of (a) BFO, (b) BGFO, and (c) BGFO/N-rGO.	107
4.2.6	Survey spectra of BFO, BGFO, and BGFO/N-rGO.	108
4.2.7	XPS spectra of N1s in (a) NrGO, (b) BGFO/N-rGO; XPS spectra of O 1s in (c) NrGO, (d) BFO, (e) BGFO, (f) BGFO/N- rGO.	109
4.2.8	XPS spectra of Bi 4f in (a) BFO, (b) BGFO, (c) BGFO/N-rGO.	111
4.2.9	XPS spectra of Gd 3d in (a) BGFO, (b) BGFO/N-rGO.	112
4.2.10	XPS spectra of Fe 2p in (a) BFO, (b) BGFO, and (c) BGFO/N- rGO.	112
4.2.11	Nitrogen adsorption- desorption isotherm of BFO, BGFO, and BGFO/N-rGO.	114
4.2.12	Nyquist plots of BFO, BGFO, and BGFO/N-rGO; (b) Mott- Schottky Plots.	116
4.2.13	(a) Photocatalytic activity (Catalyst loading =120 mg.L-1, pH =4.3); (b) Reaction kinetics	117
4.2.14	Reactive trapping experiment for photocatalytic degradation of RhB.	119
4.2.15	(a) Schematic illustration of photocatalytic degradation of RhB; (b) Magnified illustration of multiple charge transfer occurring in photocatalytic process.	121

4.2.16	(a) The reusability of BGFO/N-rGO composite; (b)XRD spectra of BGFO/N-rGO before and after experiment.	122
4.3.1	Effect of catalyst loading.	125
4.3.2	Effect of RhB concentration.	126
4.3.3	Effect of pH on (a) Photocatalytic degradation; (b) Sono-photocatalytic degradation.	127
4.3.4	Comparative study of rate constant vs. pH between photocatalytic and sono-photocatalytic process.	128
4.3.5	(a)Effect of ultrasonic power density in sono-photocatalytic degradation of RhB. (b) Reaction kinetic plot.	129
4.3.6	(a) Sono-, photo- and sono-photocatalytic degradation of RhB, and (b) corresponding rate constant.	130

List of tables

<u>Table No.</u>	<u>Caption of the table</u>	<u>Page No.</u>
2.1	Rare-earth metal doping in BFO for water pollutants.	28
2.2	BiFeO ₃ based heterojunctions for wastewater treatment.	32
2.3	Graphene-based composites for degradation of water pollutants.	38
2.4	Sonophotocatalytic processes for wastewater treatment.	43
3.1	Instruments used in present study.	55
4.1.1	Observed functional groups by FTIR Spectroscopy	73
4.1.2	Band gap, average crystallite size and particle size of BFO, BFO/rGO, and BFO/N-rGO.	76
4.1.3	Binding energy of C 1s and O 1s electrons in rGO, N-rGO, BFO, BFO/rGO, and BFO/N-rGO.	80
4.1.4	Binding energy of Bi ⁺³ and Fe ⁺³ electrons in BFO, BFO/rGO, and BFO/N-rGO.	84
4.1.5	Flat band positions and carrier concentrations for BFO, BFO/rGO, and BFO/N-rGO.	88
4.1.6	Rate constant (k, g ⁻¹ h ⁻¹) for BFO, BFO/rGO, and BFO/N-rGO.	94
4.2.1	Observed functional groups by FTIR Spectroscopy.	102
4.2.2	Bandgap, surface area, average crystallite size and particle size of BFO, BGFO, and BGFO/N-rGO.	105

4.2.3	Binding energies of O1s and N 1s.	110
4.2.4	Binding energies of Bi 4f, Fe 2p, and Gd 3d.	113
4.2.5	Flat band positions, carrier concentrations of BFO, BGFO, and BGFO/N-rGO.	116
4.2.6	Rate constants of BFO, BGFO, and BGFO/N-rGO.	118
4.3.1	Rate constants and synergy index.	131

List of abbreviations

<u>Abbreviation</u>	<u>Full name</u>
BOD	Biological oxygen demand
AOPs	Advanced oxidation processes
DO	Dissolve oxygen
CB	Conduction band
VB	Valance band
BFO	Bismuth ferrite
BGFO	Gd-doped bismuth ferrite
GO	Graphene oxide
rGO	Reduced graphene oxide
N-rGO	Nitrogen doped graphene oxide
RhB	Rhodamine B
MB	Methylene blue
MO	Methyl orange
TH	Tetracycline hydrochloride
BPA	Bisphenol A
1-4 BQ	1-4 benzoquinone
TBA	Tert-butyl alcohol
PD	Potassium dichromate
AO	Ammonium oxalate

Preface

Water pollution is one of the major concerns for human beings due to directly or indirectly discharge of pollutants into water bodies (namely rivers, groundwater, lakes, and oceans). This affects not only plants and organisms living in these waters but also all-natural biomes and biodiversity. Nowadays, advanced oxidation processes (AOPs) have been used to treat wastewater. AOPs are environmentally friendly processes. These AOPs unlike other processes, they not only transfer the pollutants into harmless end product but also mineralize into innocuous substances such as water and carbon dioxide. The process in which light and catalyst are used, known as photocatalytic process. Similarly, when ultrasound and catalyst are used to treat pollutants known as sonocatalysis. Lately, a combination of ultrasound and light in the presence of a suitable catalyst is used to treat water pollutants known as sonophotocatalytic process.

Several photocatalysts have been investigated for AOPs. For decades, there has been emerging interest in ABO_3 -type perovskite structure. Among perovskites, $BiFeO_3$ is one of the most studied photocatalysts for advanced oxidation processes (bandgap ~ 2.2 eV), and it depicts both ferromagnetic and ferroelectric properties at room temperature. Present thesis reports preparation, characterization, and evaluation of photocatalytic properties of graphene-based material supported doped bismuth ferrite heterostructure for the potential applications in sonocatalytic, photocatalytic and sonophotocatalytic degradation of RhB (a pollutant in wastewater). The thesis is divided into five chapters as follows:

Chapter 1 of the dissertation describes the general introduction of advanced oxidation process, ultrasonication.

Chapter 2 includes a brief introduction and reviews of photocatalytic and sonophotocatalytic processes for wastewater treatment. It also includes photocatalyst BiFeO₃ properties, synthesis, and its challenges in using. It also includes different modification methods of BiFeO₃. Finally, the photocatalytic activity and kinetics studies of pollutant degradation are presented.

Chapter 3 is an experimental section that includes synthesis of supports (graphene oxide and nitrogen-doped graphene oxide), bismuth ferrite, and doped bismuth ferrite. Experimental setup and characterization used in the present study are also described in this chapter.

Chapter 4 includes the result and discussion of the present study. This chapter is divided into three sections as given below:

Section-I: Selection of suitable graphene oxide-based support for bismuth ferrite in photocatalytic degradation process.

Section-II: Synergistic effect of N-rGO supported Gd-doped bismuth ferrite on photocatalytic degradation of Rhodamine B.

Section-III: Sono-photocatalytic degradation of Rhodamine B over N-rGO supported Gd-doped bismuth ferrite heterojunction.

Chapter 5 includes conclusions and suggests possible future work.