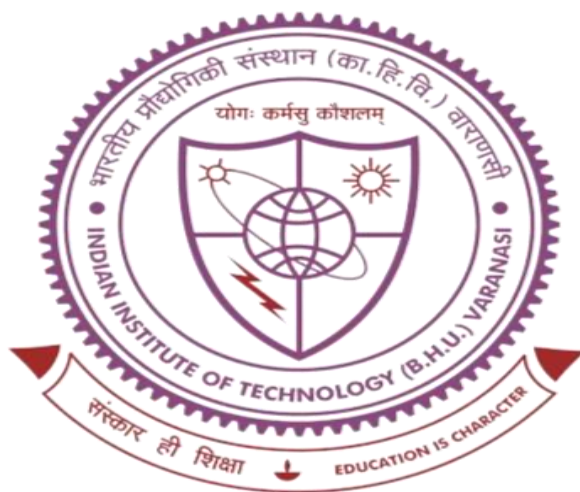


SYNTHESIS AND CHARACTERIZATION OF METAL DOPED PHOTOCATALYST FOR DYE DEGRADATION FROM WASTEWATER



Thesis submitted in partial fulfilment for the Award of Degree

DOCTOR OF PHILOSOPHY

by

SHAKTI PRIYADARSHAN

DEPARTMENT OF CHEMICAL ENGINEERING & TECHNOLOGY

INDIAN INSTITUTE OF TECHNOLOGY

(BANARAS HINDU UNIVERSITY)

VARANASI - 221 005

Roll no: 18041010

2024

Dedication

To one and all

ACKNOWLEDGEMENT

I take this opportunity to express my sincere sense of gratitude and indebtedness to my esteemed supervisor Prof. Vijay Laxmi Yadav, Professor, Department of Chemical Engineering & Technology, who helped enormously and always inspired me by her indispensable guidance and encouragement during the whole long research work. She has always supported and strengthened me in many direct and indirect ways. Her meticulous and valuable reviews, constructive criticism and tireless review of the manuscript has immensely helped me to improve the work.

I also would like to thank my RPEC members, Prof. Dhanesh Tiwari (Professor, Department of Chemistry, IIT (BHU), Varanasi) and Dr. Jyoti Prasad Chakraborty (Associate Professor, Department of Chemical Engineering and Technology, IIT (BHU), Varanasi), for providing me guidance and support along the way.

I owe my thanks to Prof M. K. Mondal, Head of the Department of Chemical Engineering for encouraging and providing all facilities to carry out my research work.

I would like to thank Central Instrumentation Facility (CIF) for providing technical support.

I am very thankful to all technical and nontechnical staff of Department of Chemical Engineering & Technology, Indian Institute of Technology (Banaras Hindu University).

I am thankful to Mr. Shyam Sunder Rao, Dr. Shubham Mishra, Dr. Kanhaiya Lal Maurya and Mr. Himanshu Tiwari for co-operation and motivation during thesis work. I am grateful to all my lab-mates Mr. Brijesh Kumar Yadav, Mr. Devendra Kumar Gond and Ms. Vandna for their adherence.

I would like to express my most heartfelt and cordial thanks to Mr. Parmanand Maurya, Mr. Ravi Saini, Mr Bhanu Pratap, Mr Ashish Gautam, Ms. Mona Vishwakarma and whole department of Chemical Engineering and Technology.


I gratefully acknowledge the Ministry of Education, India, (MoE, India) for granting financial support and Indian Institute of Technology, BHU, Varanasi, India for providing a laboratory facility to carry out the research work.

I am very thankful to Mr. Raj Kumar and late Umesh Pratap for their assistance during my research work.

CERTIFICATE

It is certified that the work contained in the thesis entitled “**Synthesis and characterization of metal doped photocatalyst for dye degradation from wastewater**” submitted by Shakti Priyadarshan has been carried out under my supervision and this work has not been submitted elsewhere for any 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.

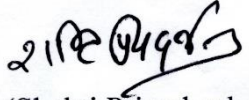

24/7/24
Prof. V. L. Yadav
प्रध्यापक / Professor
रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग
(Supervisor)
Dept. of Chemical Engg. & Tech.
Department of Chemical Eng.
Indian Institute of Technology
काशी हिन्दू विश्वविद्यालय
Banaras Hindu University
वाराणसी / Varanasi-221005
IIT (BHU),
Varanasi-221005, India

Declaration by the candidate

I, **Shakti Priyadarshan**, certify that the work embodied in this Ph.D. thesis is my bonafide work carried out by me under the supervision of Prof. Vijay Laxmi Yadav from July 2018 to July 2023 at the Department of Chemical Engineering & Technology, Indian Institute of Technology (BHU), Varanasi, India. The matter embodied in this Ph.D. thesis has not been submitted for award of any other degree/diploma. I declare that I have faithfully acknowledged and given credit to the research workers whenever their work has been cited in the text and the body of the thesis. I further declare that I have not wilfully lifted some other work, paragraph, text, data, results etc., reported dissertation, thesis etc., or available at websites and included them in this Ph.D. thesis and cited as my work.

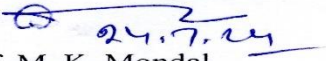
Date.....

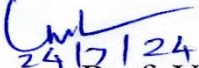
Place: IIT (BHU), Varanasi


(Shakti Priyadarshan)

Certificate from the Supervisor

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


Prof. M. K. Mondal
(Head of the Department)
Department of Chemical Eng.
and Tech.,
IIT (BHU),
Varanasi-221005, India
विभागाध्यक्ष / Head
रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग
Deptt. of Chemical Engg. & Tech.
भारतीय प्रौद्योगिकी संस्थान / Indian Institute of Technology
काशी हिन्दू विश्वविद्यालय / Banaras Hindu University
वाराणसी / Varanasi-221005


24/7/24
Prof. V. L. Yadav
प्रध्यापक / Professor
(Supervisor)
रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग
Deptt. of Chemical Engg. & Tech.
भारतीय प्रौद्योगिकी संस्थान
Department of Chemical Eng.
Indian Institute of Technology
काशी हिन्दू विश्वविद्यालय
Banaras Hindu University
वाराणसी / Varanasi-221005
IIT (BHU),
Varanasi-221005, India

COPYRIGHT TRANSFER CERTIFICATE

Title of the thesis:

Synthesis and characterization of metal doped photocatalyst for dye degradation from wastewater

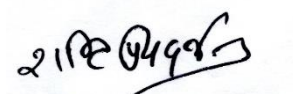
Name of the candidate: **Shakti Priyadarshan**

Copyright Certificate

The undersigned hereby assigns to the Indian Institute of Technology (BHU), Varanasi, all rights under copyright that may exist in and for the above thesis submitted for the award of Ph.D. degree.

Date:

Place: IIT (BHU), Varanasi


(Shakti Priyadarshan)

Note: However, the author may reproduce or authorize others to reproduce material(s) 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.

CONTENTS

Acknowledgment	(ii)
Certificate by the supervisor	(iii) & (iv)
Copyright transfer certificate	(v)
Contents	(vi)
List of Figures	(ix)
List of Tables	(xi)
Nomenclatures	(xii)
Preface	(xv)

CHAPTER 1: INTRODUCTION

1.	Motivation and problem statement	1
2	Problems caused by the industrial dye effluents	7
3	Dye	8
3.1	Types of dye	9
3.1.1	Basic dyes (Cationic dye)	10
3.1.2	Methylene blue	11
3.1.3	Rhodamine blue	12
3.1.4	Anionic dyes	13
3.1.5	Acid blue 113	13
3.1.6	Toxicity of dyes	14
3.1.7	Consumption of dye effluents	15
3.2	Nanotechnology towards environmental remediation	16
3.3	Metal oxide nanoparticles	16
3.3.1	g-C ₃ N ₄ nanomaterial photocatalyst	18
3.3.2	Metal oxide-g-C ₃ N ₄ nanocomposite photocatalysts	28
3.4	Semiconductor Photocatalysis	32
3.4.1	Heterogeneous photocatalysis towards removal of water contaminant	33
3.5	Different theories of photocatalysis	36
3.5.1	·OH free radical theory	36
3.5.2	The direct oxidation theory	36
3.6	Literature survey of g-C ₃ N ₄ based photocatalyst	37
3.7	Aims and objectives of this thesis	39

CHAPTER 2: Preparation and application

1	Introduction	46
2	Setting up and determining elements: making g-C ₃ N ₄	58
	2.1 Templating methods	59
	2.2 Template-free methods	60
	2.3 Sol-gel methods	61
	2.4 Exfoliation method	61
	2.5 Supramolecular preorganization method	63
3	Effect of synthesis parameters	64
	3.1 Pyrolysis temperature	65
	3.2 Heating rate	65
	3.3 Solvent	66
	3.4 Precursor	66
4	Modification	67
	4.1 Non-metal heteroatoms doping	68
	4.2 Metal doping	73
	4.2.1 Alkali metal	76
	4.2.2 Transition metal	77
5	Incorporation of g-C ₃ N ₄ with other materials	77
	5.1 Morphology modulation	78
	5.2 Molecular doping	79
	5.3 Defect engineering	80
6	Environmental applications	80
	6.1 Photo-catalyst	81
	6.2 Water splitting	81
	6.3 NO _x removal	82
	6.4 CO ₂ conversion	83
	6.5 Treatment of emerging contaminants in wastewater	79
	6.6 Fenton-like catalysts	85
	6.7 Adsorbents	86
	6.8 Membrane materials	87
	6.9 Disinfectants	88
7	Mechanism of g-C ₃ N ₄	88

CHAPTER 3 Synthesis of metal doped g-C₃N₄ and characterization techniques

1	Materials	87
2	Synthesis of g-C ₃ N ₄	96
3	Synthesis of metal doped g-C ₃ N ₄	97
4	Optimization of synthesis temperature and time	97
5	Characterization techniques	
	5.1 X-ray Diffraction technique	98
	5.1.1 Applications	100
	5.2 Fourier Transform Infrared Spectroscopy	
	5.2.1 Introduction	101
	5.2.2 Experimental setup	102

5.3	Scanning Electron Microscopy	
5.3.1	Principles of scanning electron microscope	104
5.4	Energy dispersive X-ray spectroscopy	
5.4.1	Applications	105
5.5	UV-vis Diffuse Reflectance spectroscopy	
6	Photocatalytic reactor	107

CHAPTER 4: Degradation by iron-doped g-C₃N₄

1	Introduction	100
2	Experimental	110
3	Characterization	111
3.1	XRD	111
3.2	FTIR analysis	112
3.3	EDX	114
3.4	BET	114
4	Effect of some operating parameters	118
5	Degradation kinetics	119

CHAPTER 5: Summary and future scope

1	Summary of the work	113
2	Future scope	114

References	115
-------------------	-----

Appendix

A: List of conferences	158
-------------------------------	-----

B: List of research publications	159
---	-----

List of figures

Figure no.	Figure caption	Pg no.
Figure 1.1	Worldwide consumption of water	7
Figure 1.2	Classification of dyes based on chemical constitution	11
Figure 1.3	Structure of Rhodamine blue and Methylene blue dye	13
Figure 1.4	Structure of Acid blue 113	15
Figure 1.5	g-C ₃ N ₄ exhibits several surface functions	23
Figure 1.6	Carbon nitride nanocompounds: kinds and applications	24
Figure 1.7	Schematic representation of the photocatalytic degradation	37
Figure 2.1	Preparation of g-C ₃ N ₄ by pyrolysis of melon and thiocyanate	48
Figure 2.2	The scheme of soft templating method and hard templating method	51
Figure 2.3	Supramolecular Preassembly Method for g-C ₃ N ₄ Synthesis The synthesis of g-C ₃ N ₄ involves two approaches	53
Figure 2.4	The structural transformation of the precursors varies with changes in pyrolysis temperature	54
Figure 2.5	Common modification methods of g-C ₃ N ₄	59
Figure 2.6	Potential sites for non-metal doping in the monolayer structure of g-C ₃ N ₄	63
Figure 2.7	Spatial charge-separation mechanisms for four different types of semiconductor heterojunctions	73
Figure 2.8	Fundamental mechanism of heterogeneous photocatalysis	85
Figure 2.9	The structural model of Cu, Pb, and Zn adsorption on C ₃ N ₄	86
Figure 3.1	Steps of synthesis & degradation with g-C ₃ N ₄	88
Figure 3.2	Optimization of synthesis parameters	89
Figure 3.3	Rigaku X-ray diffractometer	90
Figure 3.4	Broker Tensor 27 FTIR spectrometer	93
Figure 3.5	Block diagram of an FTIR spectrometer	93

Figure 3.6	Schematic diagram of a scanning electron microscope	95
Figure 3.7	UV- Vis Diffuse Reflectance Spectrophotometer	98
Figure 3.8	Schematic image of the reactor setup for photodegradation	99
Figure 4.1	Formation of (a) pure g-C ₃ N ₄ and (b) Change in structure after metal introduction	102
Figure 4.2	XRD pattern of g-C ₃ N ₄ doped with metal and (inset) g-C ₃ N ₄	103
Figure 4.3	FTIR spectrum of g-C ₃ N ₄ /Fe, g-C ₃ N ₄ /Co and g-C ₃ N ₄ /Ni	105
Figure 4.4	EDX spectrum of graphitic carbon nitride doped with (a) Ni (b) Co (c) Fe and (d) undoped	106
Figure 4.5	BET results: Adsorption-desorption isotherm at 77.36 K of (a) g-C ₃ N ₄ and (b) g-C ₃ N ₄ /Fe; pore surface area of (c) g-C ₃ N ₄ and (d) g-C ₃ N ₄ /Fe	106
Figure 4.6	Dye degradation with time	107
Figure 4.7	Effect of different parameters on g-C ₃ N ₄ /Fe	110
Figure 4.8	Rate order of iron doped g-C ₃ N ₄ and undoped g-C ₃ N ₄	112

List of tables

Table no.	Table caption	Page no.
Table 1.1	The various methods of synthesizing carbon nitride nanocompounds	28
Table 1.2	The various methods of characterization and their functions	33
Table 2.1	Role of non-metal doping in improving the photocatalytic activity of g-C ₃ N ₄	61
Table 2.2	Role of metal doping in improving the photocatalytic activity of g-C ₃ N ₄	67
Table 4.1	Percent removal for different catalyst	109

List of Abbreviations and Symbols

Abbreviation	Nomenclature
0D	Zero dimensional
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
AB 113	Acid blue 113
AS	Artemia Salina
BET	Brunauer-Emmett-Teller
BG or E_g	Band gap, eV
BJH	Barrett-Joyner-Halenda
BOD	Biological oxygen demand, mg/L
BSE	Backscattered electrons
CB	Conduction band, eV
CL	Cathodoluminescence
COD	Chemical oxygen demand, mg/L
COFs	Covalent organic frameworks
CR	Congo red
CVD	Chemical vapor deposition
DDW	Double distilled water
E_{CB}	Energy of conduction band
E_e	Energy of electron
E_{VB}	Energy of valance band
EBSD or DBSE	Diffacted backscattered electrons
ECs	Emerging contaminants
EDS or EDX	Energy Dispersive X-ray Spectroscopy
Et(OH)	Ethyl alcohol
FTIR	Fourier transform infrared spectroscopy
g-C ₃ N ₄	Graphitic carbon nitride
GO	Graphene oxide
HOMO	Highest occupied molecular orbital

IR	Infrared
JCPDS	Joint Committee on Powder Diffraction Standards
LUMO	Lowest unoccupied molecular orbital
M ₁ and M ₂	Mirror 1 and Mirror 2
MB	Methylene blue
MEE	Material Evaluation and Engineering
MOFs	Metal-organic framework
MW	Molecular weight
NO _x	Oxides of nitrogen
NP(s)	Nanoparticle(s)
PEI	Polyethyleneimine
PMS	Peroxomonosulfate
PPCPs	Pharmaceuticals and personal care products
Ppm	Parts per million
RB5	Reactive black 5
RhB	Rhodamine blue
RO4	Reactive Orange 4
SEM	Scanning electron microscope
TC	Tetracycline hydrochloride
TEM	Transmission electron microscope
TOC	Total organic carbon
TGA	Thermogravimetry analysis
UV	Ultra violet
VB	Valance band
VL	Visible light
Wt	weight
XRD	X-ray diffraction
X	Absolute electronegativity
Lx	lux
λ	Wavelength, nm
ν	Frequency, Hz
D	Interplaner spacing
θ	Diffraction angle

N	Order of diffraction
A	Absorption coefficient

Preface

Industrialization has improved the living style and economic prospects of the people as well as the country. In the meantime, the toxic pollutants e.g., dyes, phenolic derivatives etc are discharged to the ecosystem by various industries like paint, paper, textile, automobile etc. The carcinogenic, mutagenic and teratogenic properties of the pollutants make researchers to explore cost-effective and eco-friendly way for the degradation or removal of such pollutants. In this direction, the advanced oxidation process especially photocatalysis is preferred as an effective tool for the mineralization of toxic compounds.

Light used in photocatalyst is generally ultraviolet light which is in less fraction of solar light while visible light present in solar light is 7-10 times that of ultra violet light present. We have used graphitic carbon nitride to degrade to toxic dye.

The activity of used photocatalyst can be further elevated by different methods, metal doping is one of these methods. Different transition metals are doped in graphitic carbon nitride

The present thesis is categorized into 5 chapters.

Chapter 1 deals with the current situation of water toxicity, different type of dyes and literature review in this field and objectives of this thesis.

Chapter 2 contains the different synthesis method, application of graphitic carbon nitride and mechanism of the photocatalysis.

Chapter 3 is materials and methods, optimization of different synthesis parameter of photocatalyst, doping with few different metal and comparison with pure photocatalyst.

Chapter 4 deals with the characterization photocatalyst with best result and effect of parameters.

While chapter 5 is having conclusion part.