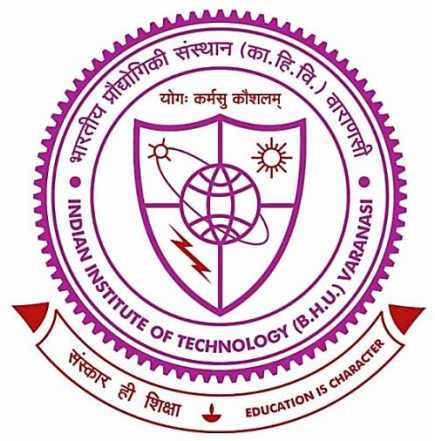
Prussian Blue Nanoparticles Mediated Sensing and Removal of Hazardous Materials



THESIS SUBMITTED FOR THE AWARD OF DEGREE OF

DOCTOR OF PHILOSOPHY

By

Hari Prakash Yadav

"DEPARTMENT OF CHEMISTRY"
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI-221005
INDIA

Roll No. 19051015

2023

CERTIFICATE

It is certified that the work contained in the thesis titled **"Prussian Blue Nanoparticles Mediated Sensing and Removal of Hazardous Materials"** by **Hari Prakash Yadav** has been carried out under my supervision and 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.

Prof. P. C. Pandey
(Supervisor)
Department of Chemistry,
Indian Institute of Technology
(Banaras Hindu University),
Varanasi–221005

DECLARATION BY THE CANDIDATE

I, "**Hari Prakash Yadav"**, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of "**Prof. P. C. Pandey"** from "**July-2019"** to "**Aug-2023**," at the **Department of Chemistry**, **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 willfully 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: 28/8/2023

Place: Varanasi

(Hari Prakash Yadav)

CERTIFICATE BY THE SUPERVISOR

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

Prof. P. C. Pandey
(Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi- 221005

Prof. P. C. Pandey
Department of Chemistry
Indian Institute of Technology (BHU)
Varanasi-221005

Prof. Y. C. Sharma
Head of Department
Department of Chemistry,
Indian Institute of Technology
(Banaras Hindu University),
Varanasi- 221005

विभागाध्यक्ष / HEAD
रसायन विज्ञान विभाग
Department of Chemistry
भारतीय प्रौद्योगिकी संस्थान (का.हि.वि.वि.)
Indian Institute of Technology (B.H.U.)
वाराणसी–२२१००५ / Varanasi-221005

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **Prussian Blue Nanoparticles Mediated Sensing and Removal of Hazardous Materials**

Name of the Student: Hari Prakash Yadav

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**" degree.

Date: 28/8/2023

Place: Varanasi.

(Hari Prakash Yadav)

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

DEDICATED TO MY LOVING PARENTS...

ACKNOWLEDGEMENT

At the top and foremost, I am indebted to thank my greatest teacher of all that is almighty God. I realize that my present, past and future is for a reason. Our culture has taught teachers class is above the God therefore I am grateful to have Gurus in my life. I am deeply indebted to my spiritual Guru and founder of Banaras Hindu University, **Pt. Mahamana Madan Mohan Malviya Ji**, by his visionary thought the nation have eminent personalities.

To begin with, I "**Mr. Hari Prakash Yadav**" would like to express my deep sense of gratitude to my supervisor and academic Guru "**Prof. P. C. Pandey**", for providing me generative, positive supervision and also for his valuable guidance, constant support, critical and motivating comments throughout the course of my research work. Thank you Boss you always bring me on earth with touching sky and making my PhD life so enjoyable and amicable.

I express my heartiest thanks to RPEC members, "**Prof. Y. C. Sharma**", Department of Chemistry, IIT (BHU), Varanasi, "**Prof. Sushant Kumar Shrivastava**", Department of Pharmaceutical engineering and Technology, IIT (BHU), Varanasi and also "Prof. Ram Pyare" and "Dr. Anil Kumar", Department of Ceramic engineering, IIT(BHU), Varanasi for their valuable suggestions, constant guidance and kind encouragement during my research work.

My sincere thanks to the former Heads, "**Prof. Dhanesh Tiwary**" Department of Chemistry, IIT (BHU), Varanasi, the present head "**Prof Y.C. Sharma**" as well as all the faculty members of Department of Chemistry IIT (BHU) for their kind support and for extending all required facilities to carry out my research work smoothly.

I gratefully acknowledge the facilities provided by **CIFC, IIT (BHU)**, Varanasi for doing various characterization of samples.

My special thanks to "**Prof. P.C. Pandey**", "**Prof. Y. C. Sharma**" and **"Prof. Sushant Kumar Shrivastava"**, IIT-BHU who always encouraged me and promoted to next step.

I am extending my thanks to my senior lab members "**Dr. Shwarnima Singh**" **"Dr. Murli Dhar Mitra"**, for the valuable suggestion during my research work, and creating enjoyable lab ambience and good memories which I cherish forever. A lot of thanks to my colleague "**Atul Kumar**", "**Maneesha**", ". For their kindness, help and support "I heartily express the millions of thanks to my affectionate friends "**Dr. Vipin Kumar"**, **"Dr. Ajit Kumar"**, "**Avinash Kumar Chaurasia"**, "**Apurv Solanki"**, "**Vartika Verma"**, "**Sunita Maurya"**, "**Kuldeep Kumar Maurya"**, "**Dr. Ranvijay Pratap"**, and "**Dr. Sujeet Dev Sonkar"** and all my batchmates for their kind co-operation and friendly environment during entire period of my research.

I am thankful and indebted to **DRDO, New Delhi,** and **IIT** (**BHU**) for providing me financial support during my research work.

I would like to express my deepest affection to my wife "**Snehlata Yadav**"**,** Mother-in-Law "**Pramila Yadav**", Father-in-Law "**Ram Belas Yadav**", and my sisters "**Urmila Devi", "Pramila Devi**", and "**Meera Yadav**", for their love, concern, continuous moral support and encouragement which enabled me to perform my liabilities without any reservations.

Devi", "Pramila Devi", and "**Meera Yadav**", for their love, concern, continuous moral support and encouragement which enabled me to perform my liabilities without any reservations.

Finally, my parents, "**Late Smt. Imarti Devi**" and "**Mr. Ram Suresh,**" gave me my name, my life, and everything else in between. I pride myself on having words for everything, but they truly shut me up when it comes down to describing how much I love them and appreciate the effort they have put into giving me the life I have now. They are the reason I did this, the reason I strive to be better. Their pride, for me, is my main goal in life.

At the last but not the least, I thank to all my well-wishers and critics whose names I may have failed to mention here unintentionally. Thanks to all of you for being there for me when times were the toughest.

Date: 28/8/2023

Place: Varanasi

(Hari Prakash Yadav)

List of Figures

List of Table

3-APTMS	: 3-Aminopropyltrimethoxysilane
3-GPTMS	: 3-Glycidoxypropyltrimethoxysilane
EETMS	: 2-(3,4-Epoxycyclohexyl)-ethyltrimethoxysilane
PEI	: Polyethyleneimine
PB	: Prussian Blue
PY	: Prussian yellow
PW	: Prussian white
BG	: Berlin green
PBNPs	: Prussian Blue nanoparticles
PBAs	: Prussian Blue analogues
MHCFs	: Metal hexacyanoferrates
THF-H_2O_2	: Tetrahydrofuran – Hydrogen peroxide
HCl	: Hydrogen Chloride
SPE	: Screen-printed electrode
Ag/AgCl	: Silver/Silver chloride
K_3[Fe (CN)$_6$]	: Potassium ferricyanide
CV	: Cyclic voltammetry
DPV	: Differential pulse voltammetry
I_{pa}	: Anodic current
I_{pc}	: Cathodic current
EIS	: Electrochemical impedance spectroscopy
CPE	: Carbon paste electrode

BE	: Binding energies
TGA	: Thermogravimetric analysis
R_{et}	: Electron-transfer resistance
ppm	: Parts per million
K_d	: Distribution coefficient
Rh B	: Rhodamine B
ICP-MS	: Inductively coupled plasma mass spectroscopy
EDX	: Energy-dispersive X-ray spectroscopy
MSNPs	: Mesoporous silica nanoparticles
MSPs	: Mesoporous silica Particles
TEM	: Transmission electron microscopy
HRSEM	: High Resolution Scanning Electron Microscope
XPS	: X-ray photoelectron spectroscopy
XRD	: X-ray Diffraction
DLS	: Dynamic light scattering
SAED	: Selected area electron diffraction pattern
UV-Vis	: Ultraviolet-Visible
FL Spectroscopy	: Fluorescence Spectroscopy
BET	: Brunauer-Emmett-Teller
CA	: Chemical adsorption
EA	: Electrochemical adsorption
λ	: Wavelength

º	: Angle (degree)
mg	: Milli gram
μM	: Micro molar
nM	: Nanomolar
mM	: Millimolar
sec	: Time (second)
LOD	: Limit of detection

Preface

Selectivity in the sensing process has been a fundamental requirement, and its lack has hampered the practical implementation and subsequent commercialization of numerous chemical sensors. Chemical sensors are devices that consist of a chemically selective layer that is either closely related to or integrated within a physico-chemical transducer. They have received a lot of attention because they provide an inexpensive, portable, and simple to use analytical tool for identifying and quantifying specific analytes in the fields of food technology, medical engineering, environmental engineering, and pollution monitoring. The extensive use of nanoscale material "Prussian blue nanoparticles (PBNP)" in sensing, catalysis, removal, and electrochromic device development is reasonable due to the distinct physical and chemical properties they possess, which has led to an increase in its synthesis protocols. Fabricating these chemical sensors with high catalytic efficiency, selectivity, and sensitivity is one of the present research's primary problems. For the synthesis of Prussian blue (PB), several methods, including chemical and electrochemical processes, are available and frequently address specific restrictions; (i) PBN obtained through chemical synthesis frequently involves instantaneous nucleation and results in the formation of unstable, agglomerated, and large-sized nanoparticles; (ii) PBN made using electrochemical techniques has the drawback of being large-scale producible while having a narrow range of applications; (iii) PBN made using conventional methods limits the dispersibility of these nanomaterials in different solvents; and (iv) PBN made using electrochemical techniques has the (iv) Retaining the PBN's catalytic capability while changing the homogeneous nano-suspension of PBN into a stable heterogeneous nano matrix over solid support. The synthesis of PB frequently fell into

difficulties related to their practical functionality, which led to a methodical search for the control synthetic methodology and its application to solve the issues. As a result, a technique must be developed that can produce stable, less-agglomerated colloidal dispersions of PBNP that have enhanced catalytic properties and intrinsic characteristics, as well as the ability to transform homogeneous nano-suspension into a heterogeneous system that aims for a similar catalytic efficiency. The use of catalytic materials as chemically sensitive layers has accelerated the development of chemical sensor technology, and the role of nanomaterials in this development has received considerable attention. Metal nanotubes, nanocomposites, nanorods, nanostructured polymers, nanoparticles, nanowires, and different allotropes of carbons such as carbon nanotubes, graphene, and others have been shown to improve catalytic efficiency and selectivity during the sensing process. Because they have a higher surface-to-volume ratio than bulk materials, nanoparticles are advantageous and have received particular attention in the field of chemical sensing as a biocatalyst substitute.

Peroxidase enzyme, which is employed in many bioassay kits in healthcare, is one of the potentially studied biocatalysts. The sensitivity of peroxidase activity to environmental conditions drew global scientists' attention to its replacement, and the role of Prussian blue, an artificial peroxidase, has received interest and directed for precise investigations on transition metal hexacyanoferrate. Transition metal hexacyanoferrates are a type of exceptionally stable coordination compound that has been applied in fields such as display technology, solid-state batteries, hydrogen storage, cesium remediation, and sensor fabrication. Prussian blue is the most studied transition metal hexacyanoferrate. It is an inorganic crystalline material that has been employed in numerous analytical applications and extensively researched due to its

electrochemical, magnetic, photophysical, and electrochromic properties. However, because of the non-processability of such crystalline material in different solvents, many potential uses, particularly as a replacement for peroxidase, are constrained. Accordingly, one of the criteria that makes up the focus of the current research programme is the discovery of how to synthesize processable Prussian blue nanoparticles used for sensing and removal of hazardous materials.

The present study describes the synthesis of Prussian blue nanoparticles from a single precursor potassium ferricyanide in the presence of organic reducing agents such as polyethylenimine (PEI), tetrahydrofuran-hydroperoxide (THF-H_2O_2), and 2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane and cyclohexanone. Besides, these protocols have been attempted with variations in PEI, THF-H_2O_2, and EETMS content to switch the nano-dimensions and in turn, to its catalytic performance. PEI, THF-H_2O_2, and EETMS stabilize the nanoparticles via a resultant hydrophobic reaction product and enhance the dispersibility in various solvents (water, methanol, acetone, tetrahydrofuran, dimethyl sulfoxide, etc.). The process was extensively explored for the heterogeneous modulation, as THF-H_2O_2 correspondingly allows the successful incorporation of homogeneous nanodispersion over and within the designated suspension matrix; mesoporous silica nanoparticles (MSNP) i.e., silica (SiO_2) via retaining its catalytic ability.

This work has been organized into three chapters with Summary and Future Projection where the influential role of PEI, THF-H_2O_2, and EETMS has been investigated and discussed from different perspectives in an elementary means. Chapter (I) ‘General Introduction' incorporates with reviews of the present status of the subject, included with the outcome of earlier studies

performed on the PB and its analogues, and validate the reason for embarking upon the current study, along with a precise interpretation of the origin, objectives, and work design to the corresponding research program. Chapter (II) includes the synthetic strategy of three different types of PBNPs by using PEI with HCL, THF-H_2O_2, and EETTMS with cyclohexanone and their characterization by using different instruments. Synthesis of heterogenous PBNP (THF-H_2O_2 mediated) with MSNP that has a very efficient role in the removal process. Chapter (III) includes the preparation of screen-printed electrode, and graphite paste electrodes with PBNP which displayed size-dependent electrochemical and catalytic activity towards arsenic, cesium, and hydrogen peroxide. The as-synthesized homogenous and heterogenous PBNPs have positive approaches toward fluorometric sensing, magnetic movement-based PBNP sensing, and in the removal of cesium.

The contents of the thesis have been published in Chemosensors 2021, 9(9), 253; Frontiers in Enviornmental Science Volume 11 – 2023, doi: 10.3389/fenvs.2023.1230983.