

Production of nanofibrillated cellulose from agrowaste residues and its application in phosphate removal from wastewater



**Thesis submitted in partial fulfillment for the
Award of degree**

DOCTOR OF PHILOSOPHY

By

Archana Pandey

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

Dedicated
to
My Loving Father
&
My Dear Husband...

CERTIFICATE

It is certified that the work contained in the thesis titled “**Production of nanofibrillated cellulose from agrowaste residues and its application in phosphate removal from wastewater**” by **Ms. Archana Pandey** has been carried out under our 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 the Comprehensive Examination, Candidacy, and SOTA for the award of Ph.D. Degree.


Date: 14.08.2025

Place: Varanasi



(Supervisor)

Prof. Yogesh Chandra Sharma
Department of Chemistry
Indian Institute of Technology (BHU)
Varanasi - 221005



(Co-Supervisor)

Prof. Ajay S. Kalamdhad
Department of Civil Engineering
Indian Institute of Technology Guwahati
Guwahati - 781039

DECLARATION BY THE CANDIDATE

I, "Archana Pandey", certify that the work embodied in this thesis is my bonafide work and carried out by me under the supervision of **Prof. Yogesh Chandra Sharma Indian Institute of Technology (BHU)** and co-supervision of **Prof. Ajay S. Kalamdhad Indian Institute of Technology (Guwahati)** during **July 2021 to July 2025**, 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 credit to the research workers wherever their work has 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 work.

Date: 14.08.2025

Place: Varanasi

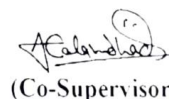

(Archana Pandey)

CERTIFICATE BY THE SUPERVISORS


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


(Supervisor)

Prof. Yogesh Chandra Sharma
Department of Chemistry
Indian Institute of Technology (BHU)
Varanasi - 221005


(Co-Supervisor)

Prof. Ajay S. Kalamdhad
Department of Civil Engineering
Indian Institute of Technology Guwahati
Guwahati - 781039


Head of Department
Department of Chemistry
Indian Institute of Technology (BHU)

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

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **Production of nanofibrillated cellulose from agrowaste residues and its application in phosphate removal from wastewater**

Name of the Student: **Archana Pandey**

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: 14.08.2025

Place: Varanasi


(Archana Pandey)

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

ACKNOWLEDGEMENT

I extend my heartfelt gratitude to my supervisor, **Prof. Yogesh Chandra Sharma (IIT-BHU)**, for his invaluable guidance, unwavering mentorship, and constant encouragement throughout my research journey. My profound thanks to my PhD co-supervisor, **Prof. Ajay S. Kalamdhad (IIT-Guwahati)**, for his enduring support and insight over the course of this work.

I am thankful to the **Head, Prof. Sundaram Singh**, and **former Heads, Prof. Yogesh Chandra Sharma** and **Prof. Dhanesh Tiwari**, for their constant motivation, administrative support, and for fostering an environment conducive to research excellence in the department.

My heartfelt thanks to my RPEC members, **Prof. Sundaram Singh (Dept. of Chemistry)** and **Prof. H. L. Pramanik (Dept. of Chemical Engineering & Technology)**, for their valuable suggestions and constructive feedback, which consistently pushed me to think deeper and improve my work.

I greatly appreciate the technical assistance provided by the **CIF (Departmental) and CIF (Central) facilities**, which played a crucial role in the experimental and analytical aspects of this research. I am also grateful to Ministry of Education for extending financial assistance in form of a **Teaching Assistantship (TAship)**.

I am thankful to all the **teaching and non-teaching staff** of the Department for their cooperation and timely assistance in resolving both academic and administrative matters.

I would like to sincerely thank all my lab mates; **Dr. Siddhi, Dr. Vartika, Dr. Sunita, Surajit, Neeraj, Vishwani, Shirin, Dr. Lokesh, Dr. Poonam, Dipankar, Gaurav and Pragya** for fostering a warm, collaborative, and friendly atmosphere in the laboratory.

A special thanks to my dear friend **Shikha**, whose companionship and ability to bring positivity during stressful times made this journey smoother. I also acknowledge my **batchmates** for their consistent kindness and willingness to extend a helping hand whenever needed.

On a deeply personal note, I am profoundly indebted to the constant cheerleader of my life, my husband, **Dr. Rohit Pandey**, whose unwavering strength, patience, and encouragement have been my constant foundation. To my beloved son, **Shreesay**, your innocence, laughter, and unconditional love have been a constant reminder of life's true joys and have given me the motivation to persevere through challenging situations. To my **parents**, I owe everything, your sacrifices, hard work, and values have shaped me into who I am today, and your unconditional love has been my anchor. To **my brothers and sisters**, for being my stressbusters, mood lifters and source of happiness. To my **in-laws**, I am deeply thankful for your blessings, understanding, and steady emotional support, which have given me strength and peace of mind during this demanding phase of my life.

I bow my head in gratitude to the founder of IIT BHU, **Pandit Madan Mohan Malviya**, the architect of this glorious temple of learning, knowledge and education. Finally, to **Almighty**, for blessing me with good health, incredible people, and a nurturing research environment that has made this journey not only possible but truly fulfilling.

I would also take this opportunity to thank all people who have directly or indirectly supported me along this incredible journey □ I have not travelled the road alone.

Date:

Place: Varanasi



(Archana Pandey)

LIST OF FIGURES

Figure No.	Title	Page No.
CHAPTER 1		
Figure 1.1	Global active phosphate reserves country-wise in billion tonnes.	3
Figure 1.2	Change of phosphate speciation as a function of pH.	6
Figure 1.3	Schematic illustration of phosphorous cycle and anthropogenic phosphorous cycle.	9
Figure 1.4	A global snapshot of ocean dead zones: tracking the spread and severity of low-oxygen areas across the world's coastal waters.	12
Figure 1.5	Common adsorbents used in phosphate adsorption method.	16
Figure 1.6	Characterization techniques used in the analysis of produced NFCs as adsorbent for phosphate removal from wastewaters.	24
CHAPTER 3		
Figure 3.1	Schematic representation of experimental design of nanofibrillated cellulose production.	41
Figure 3.2	FT-IR analysis of synthesized NADES and their individual components.	44
Figure 3.3	¹ H NMR spectra of (a) Glycerol; (b) Xylitol; (c) Citric acid; (d) Tartaric acid; (e) Gly-CA; (f) Xyl-CA; (g) Gly-TA; (h) Xyl-TA.	47
Figure 3.4	(a) FT-IR spectra; (b) XRD analysis; (c) TGA; (d) DTG of NFC samples synthesized using different pretreatment methods.	54
Figure 3.5	Particle size distribution of synthesized NFCs.	56
Figure 3.6	TEM images of (a) NFC/Gly-CA; (b) NFC/Xyl-CA; particle size distribution of (c) NFC/Gly-CA; (d) NFC/Xyl-CA.	57
Figure 3.7	SEM images and EDX of (a & d) untreated biomass; (b & e) NFC/Gly-CA; (c & f) NFC/Xyl-CA respectively.	59
CHAPTER 4		
Figure 4.1	Schematic diagram depicting the fabrication process of CTAB@NFC for removal of phosphate.	66

Figure 4.2	SEM images of; (a) pristine NFC; (b) CTAB@NFC (before adsorption); (c) CTAB@NFC*P (after adsorption).	67
Figure 4.3	EDS spectra and corresponding element distribution content of; (a & b) CTAB@NFC (before and after adsorption) respectively; EDS mapping of C, O, N, Br, P and elemental distribution of CTAB@NFC (after adsorption).	68
Figure 4.4	FTIR spectra of (a) pristine NFC, CTAB, CTAB@NFC (before and after adsorption); (b) XRD patterns of pristine NFC and CTAB@NFC; (c) BET analysis of CTAB@NFC.	70
Figure 4.5	Schematic illustration of the interactions between CTAB and NFC at varying molar concentrations (0.5, 1, 1.5 and 2 mM).	72
Figure 4.6	(a) Pre-screen adsorption studies; (b) effect of adsorbent dose; (c) zeta potential value and; (d) pH_{PZC} value of CTAB@NFC respectively; (e) effect of different pH values; (f) effect of competing anions.	76
Figure 4.7	(a & b) Effect of different contact time on phosphate removal by CTAB@NFC and adsorption kinetics; (c & d) Effect of different initial concentration and adsorption isotherm.	79
Figure 4.8	XPS spectra of CTAB@NFC prior to and post phosphate adsorption: (a) C1s spectra; (b) N1s spectra; (c) P2p spectra; and (d) survey scanning spectra of adsorbents (pre- and post-adsorption); (e) desorption cycles of phosphate on CTAB@NFC.	82
Figure 4.9	Representation of possible adsorption mechanisms for phosphate removal on CTAB@NFC.	83

CHAPTER 5

Figure 5.1	Schematic diagram depicting the fabrication process of Mg doped NFC/BN.	89
Figure 5.2	SEM images of; (a) NFC/BN; (b & c) Mg@NFC/BN (pre and post phosphate adsorption respectively); (d) high resolution SEM micrograph of Mg@NFC/BN; (e & f) EDS spectra and corresponding element distribution content of Mg@NFC/BN, (g) EDS elemental mapping.	91
Figure 5.3	FTIR spectra of (a) NFC, BN, NFC/BN composite, Mg doped NFC/BN (before and after adsorption); (b) XRD patterns of pristine NFC, BN NFC/BN composite and Mg doped NFC/BN.	94

Figure 5.4	(a) Pre-screen adsorption of pristine NFC, BN, NFC/BN composites; (b) effect of different pH values; (c) pH_{PZC} value of Mg@NFC/BN and; (d) effect of adsorbent dose.	99
Figure 5.5	(a) Effect of different contact time and adsorption kinetics; (b) Effect of different initial concentration adsorption isotherm; (c) effect of co-existing anions.	104
Figure 5.6	(a) Linear plot of $\ln(q_e/C_e)$ versus $1/T$; (b) Water-retention property of soil samples.	106
Figure 5.7	(a) XPS spectra of Mg@NFC/BN prior to and post phosphate adsorption; (b) P 2p spectra (post adsorption); (c & d) O 1s spectra (pre and post adsorption); and (e & f) Mg 1s spectra (pre and post adsorption).	108
Figure 5.8	Representation of adsorption mechanisms for phosphate removal on Mg doped NFC/BN.	109

LIST OF TABLES

Table No.	Title	Page No.
CHAPTER 1		
Table 1.1	Total reserves/resources of rock phosphate in India.	4
Table 1.2	Various sources of phosphate pollution and its concentration range found in wastewater.	10
Table 1.3	Advantages and disadvantages of phosphate removal techniques.	13
Table 1.4	A comparative data of properties of cellulose and NFC.	18
CHAPTER 2		
Table 2.1	List of chemical name, formula, molecular weight and manufacturers.	26
Table 2.2	Kinetic and isotherm equations.	35
CHAPTER 3		
Table 3.1	Acid-catalyzed recovery of cellulose and total NFC production from SCB.	50
Table 3.2	A comparison table of feedstock used, production methods, nanocellulose yield and other properties.	60
CHAPTER 4		
Table 4.1	BET specific surface area, average pore diameter, and total pore volume of synthesized CTAB@NFC.	70
Table 4.2	Adsorption kinetic parameters of phosphate removal on CTAB@NFC.	79
Table 4.3	Adsorption isotherm parameters of phosphate removal on CTAB@NFC.	80
CHAPTER 5		
Table 5.1	Properties of bentonite.	86
Table 5.2	Composition of adsorbents prepared with different mass ratios of NFC, BN, and MgCl ₂ .	88
Table 5.3	Kinetic parameters of the phosphate removal onto Mg@NFC/BN.	100

Table 5.4	Isotherm parameters of the phosphate removal onto Mg@NFC/BN at different temperatures.	101
Table 5.5	Thermodynamic parameters of the phosphate removal onto Mg@NFC/BN at different temperatures (298.5 K, 308.5 K and 318.5 K).	105

LISTS OF ABBREVIATIONS

ATP	Adenosine Triphosphate
BET	Brunauer-Emmett-Teller
BN	Bentonite
BSE	Backscattered Electron
C_0	Initial concentration of adsorbate
C_e	Equilibrium concentration of adsorbate
cm	Centimetre
cm^{-1}	Wavenumber
Conc.	Concentration
C_t	Concentration at time (t)
CTAB	Cetyltrimethylammonium bromide
DES	Deep eutectic liquid
DLS	Dynamic Light Scattering
DNA	Deoxyribonucleic acid
DTG	Differential thermogravimetric analysis
EBPR	Enhanced Biological Phosphorus Removal
EDS	Energy Dispersive Spectrometry
FE-SEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared spectroscopy
g	Gram
g/L	Gram per litre
h	Hour
HIU	High intensity ultrasonication
IL	Ionic liquid
K	Kelvin
k_1	Pseudo- first order rate constant
k_2	Pseudo- second order rate constant
K_d	Thermodynamic equilibrium constant
K_F	Freundlich constant
kg	Kilogram
kJ/mol	Kilo joule per mole
kJ/mol/K	Kilo joule per mole per kelvin
K_L	Langmuir constant
M	Molar
m^2/g	meter square per gram
mg	milligram
mg/L	milligram per litre
min	minute
mm	millimetre
MOFs	Metal-Organic Frameworks

mol	mole
NADES	Natural deep eutectic liquid
n_F	Freundlich heterogeneity factor
NFC	Nanofibrillated cellulose
Nm	Nanometre
NMI	National Mineral Index
n_S	Sips heterogeneity factor
PLC	Phosphate loaded composite
pH_{PZC}	Point of zero charge
q_e	Amount of adsorbate adsorbed on per unit gram of adsorbent at equilibrium
q_{cal}	Amount of adsorbate adsorbed on per unit gram of adsorbent at equilibrium (calculated)
Q_0	Langmuir constant
q_t	Amount of adsorbate adsorbed at time t in per unit gram of adsorbent
R	Gas constant (8.314 J mol ⁻¹ K ⁻¹)
R^2	Coefficient of determination
RNA	Ribonucleic acid
rpm	Rotations per minute
SCB	Sugarcane bagasse
SDG	Sustainable Development Goals
SEM	Scanning Electron Microscopy
T	Temperature
t	Time
TEM	Transmission Electron Microscopy
TGA	Thermo-gravimetric Analysis
UNFC	United Nations Framework Classification for Resources
V	Volume
W	Weight
WHO	World Health Organization
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray diffraction
α	initial adsorption rate
β	desorption constant
ΔG^0	Standard free energy change
ΔH^0	Change in standard enthalpy
ΔS^0	Change in standard entropy
θ	Plane angle
θ/s	Plane angle per second
λ	Wavelength

PREFACE

The growing global concern over environmental degradation, resource depletion, and waste management has driven researchers and innovators toward the exploration of sustainable materials and processes. In this context, the concept of utilizing agricultural residues into high-value products has gained significant attention, both in academic research and in industrial innovation. This thesis is a reflection of my own academic curiosity and commitment to environmental stewardship, and it seeks to contribute meaningfully to the field of sustainable biomaterials. The genesis of this research stemmed from an awareness of two intersecting challenges. On one hand, the sugarcane industry generates vast quantities of fibrous residues, which are often underutilized or disposed of in ways that contribute to environmental stress. On the other hand, industrial and agricultural runoff continues to introduce excessive phosphate into water bodies, leading to eutrophication, water quality deterioration, and loss of aquatic biodiversity. These parallel issues inspired me to investigate whether an innovative, green approach to material synthesis could offer a dual solution, valorising waste biomass while providing an efficient material for environmental remediation.

Sugarcane bagasse is an abundant lignocellulosic biomass in many parts of the world, especially in sugar-producing countries like India, Brazil etc. Traditionally, it is used as fuel in mills, composted, or left to decompose. However, its rich cellulose content makes it an excellent precursor for nanofibrillated cellulose production. The production of nanofibrillated cellulose offers numerous advantages: it is renewable, biodegradable, exhibits surface functionalization flexibility due to presence of dense amount of hydroxyl groups, exceptional mechanical strength and high specific surface area. By adopting green approach in its production process, this work aimed to avoid harsh chemicals and excessive energy consumption, aligning with global efforts to minimize environmental impact in biomaterials production.

The journey of this research was shaped by the challenge of bridging two fields; biomass valorisation and water pollution control, into a coherent, scientifically robust framework. My aim was not only to demonstrate that nanofibrillated cellulose can be derived from sugarcane bagasse using environmentally benign methods, but also to evaluate its performance in phosphate removal from wastewater. This required a

multidisciplinary approach, drawing from materials science, environmental engineering, and analytical chemistry.

What makes this research particularly relevant is its alignment with the broader principles of the circular economy. The transformation of sugarcane bagasse; an agricultural residue into a functional nanomaterial for pollutant removal represents a closed-loop strategy where waste is reimagined as a resource. This not only reduces environmental burdens but also offers economic opportunities for agro-industrial regions. Moreover, phosphate removal is an urgent environmental priority, given the scale of eutrophication-driven ecological damage worldwide.

The results presented in this thesis demonstrate that it is possible to produce high-quality nanofibrillated cellulose from sugarcane bagasse through a green processing route and that the biomaterial can be effectively applied for phosphate adsorption from wastewater. Beyond the data and conclusions, this work also reflects the process of persistent inquiry, adaptation, and learning. Scientific research is rarely linear; it is an iterative journey shaped by both setbacks and breakthroughs. The practical challenges encountered from variability in biomass composition to fine-tuning material characterization techniques were as instructive as the successful outcomes. In writing this thesis, my intention has been to not only present the scientific findings, but also to situate them within the urgent global conversation about sustainability, resource efficiency, and environmental protection. The hope is that this work will contribute to a growing body of knowledge on bio-based nanomaterials, inspire further innovations in agricultural waste utilization, and highlight the potential of green chemistry in addressing critical environmental challenges.

This preface, therefore, is not merely an introduction to the work that follows; it is also an invitation to consider the larger implications of scientific research in a world facing complex ecological crises. The intersection of waste management, material science, and water treatment represents a fertile ground for innovation, and the work presented in this thesis is one small step toward a future where industrial by-products are transformed into valuable solutions for environmental sustainability.