Studies on functionalization, characterization and application of cellulose and its composites

Thesis submitted in partial fulfilment
For the Award of Degree

Doctor of Philosophy

in

Biochemical Engineering

by

Rahul Ranjan

School of Biochemical Engineering
Indian Institute of Technology (BHU) Varanasi
Uttar Pradesh- 221005

Roll No: 19011001 **2024**

Dedicated
to
My Beloved Parents

SCHOOL OF BIOCHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI - 221005

CERTIFICATE

It is certified that the work contained in the thesis titled " **Studies on functionalization, characterization and application of cellulose and its composites** " by **Mr. Rahul Ranjan** 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.

Dr. Prodyut Dhar
(Supervisor)
School of Biochemical Engineering
Indian Institute of Technology
(Banaras Hindu University) Varanasi
Dr. Prodyut Dhar, Ph.D.
Assistant Professor
School of Biochemical Engineering
Indian Institute of Technology (BHU)
Varanasi-221005, U.P., INDIA

DECLARATION BY THE CANDIDATE

I, "**Rahul Ranjan**", certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of "**Dr. Prodyut Dhar**" from July 2019 to May 2024, at the School of Biochemical Engineering, Indian Institute of Technology (Banaras Hindu University), 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 others work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work

CERTIFICATE BY THE SUPERVISOR

Date:

Place: Varanasi **(Mr. Rahul Ranjan)**

CERTIFICATE BY THE SUPERVISOR

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

Dr. Prodyut Dhar, Ph.D.
Assistant Professor
School of Biochemical Engineering
Indian Institute of Technology (BHU)
Varanasi-221005, U.P., INDIA

Dr. Prodyut Dhar
(Supervisor)
School of Biochemical Engineering
Indian Institute of Technology
(Banaras Hindu University) Varanasi

Forwarded
समन्वयक
Coordinator
जैवरासायनिक अभियांत्रिकी स्कूल
School of Biochemical Engg
भारतीय प्रौद्योगिकी संस्थान
Indian Institute of Technology
(बी.एच.यू.) वाराणसी-221005

Prof. Vikash Kumar Dubey
(Coordinator)
School of Biochemical Engineering
Indian Institute of Technology
(Banaras Hindu University) Varanasi

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **Studies on functionalization, characterization and application of cellulose and its composites**

Name of the Student: **Mr. Rahul Ranjan**

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:

Place: Varanasi (Mr. Rahul Ranjan)

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.

ACKNOWLEDGEMENTS

I extend my deepest gratitude to the individuals who have contributed in completion of my research, whether directly or indirectly. Foremost, I am immensely thankful to my esteemed mentor, Dr. Prodyut Dhar, whose invaluable guidance and unwavering support have been instrumental throughout my PhD journey. Their wisdom and encouragement have enabled me to navigate this dissertation successfully, providing both freedom to explore and guidance during moments of uncertainty. I am also indebted to my Doctoral Committee members, Prof. Rajesh Kumar Upadhyay and Dr. Sanjay Kumar, for their insightful feedback and motivation. I wish to place on record the use of the Central Instruments Facility (CIF), IIT (BHU), Central Discovery Centre, and Sophisticated Analytical & Technical Help Institute (SATHI) BHU for conducting the instrumental analysis required for my research work. I thank the School of Biochemical Engineering for providing essential instrumentation for carry out my research work smoothly. Special thanks to the Science Engineering Research Board (SERB), India, for granting me the travel funds to attend the ACS Spring conference. I am also grateful to the technical and non-technical staff of the School of Biochemical Engineering, particularly Mr Dinesh Kumar, Umesh Kumar, Arun Kumar and Usha Yadav, for their cooperation and assistance throughout my doctoral journey. Lastly, I am fortunate to have collaborated with friends Kaustubh and Shubham, whose teamwork and stimulating research discussions have been invaluable. I thank my co-research fellows, especially Rohit, Smruti, Vedang, Ankit and Ram, for their kind and moral support. I also thank my dear friends Manash, Abhay, Preeti, Aditya, Deepak, Diwakar, Satyavarat, Rodhia, Brijendra and Prabhakar for their help and support in

during my doctoral journey. I also want to acknowledge my old supervisor, Dr. Ashish Kumar Singh, for all kinds of support at the initial stage of my doctoral journey. I am incredibly fortunate to have amazing parents whose unwavering support and encouragement, along with their numerous sacrifices, have been instrumental in enabling me to reach this significant milestone in my life. I acknowledge my brothers Rohit and Ronit for their invaluable support and love. I also wish to acknowledge interns Suraj, Angesh, Rishabh, and Muskan for their help in conducting experiments during my doctoral journey. I wish to acknowledge the Maharaj and the canteen staff for providing me with healthy food and snacks during my doctoral journey. At the end I owe it all to the Almighty for being all in all and enabling me to complete the doctoral work.

Date:

Place: Varanasi **(Rahul Ranjan)**

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

LCA	Life cycle assessment
NaOH	Sodium hydroxide
MFC	Microfibrillated cellulose
NC	Nanocellulose
TAPPI	Technical Association of the Pulp and Paper Industry
MCC	Microcrystalline cellulose
NFCs	Nanofibrillated cellulose
CNC	Cellulose nanocrystals
BC	Bacterial cellulose
CNFs	Cellulose nanofibers
CMFs	Cellulose microfibrils
KOH	Potassium hydroxide
MoS_2	Molybdenum disulphide
2D	Two-dimensional
1T	1-Trigonal
2H	2-Hexagonal
3R	3-Rhombohedral
$NaClO_2$	Sodium chlorite
H_2O_2	Hydrogen peroxide
NaOCl	Sodium hypochlorite
Na_2SO_3	Sodium sulphite
E. coli	*Escherichia coli*
S. aureus	*Staphylococcus aureus*
H_2SO_4	Sulphuric acid
H_3PO_4	Phosphoric acid
H_3PO_3	Phosphorous acid
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
HCl	Hydrochloric acid
HPH	High pressure homogenizer
DS	Degree of substitution
DMF	Dimethylformamide

PA	Phosphoric acid
DAHP	di-ammonium hydrogen phosphate
ADP	Ammonium di-hydrogen phosphate
Des	Deep eutectic solvents
ILs	Ionic liquids
DOX	Doxorubicin
CNF-P	Phosphorylated cellulose nanofiber
UPF	UV protection factor
GSM	Grams per square meter
FESEM	Field emission scanning electron microscopy
Q_e	Highest adsorption capacity
C_e	MB/MG concentration
C_0	Initial MB/MG concentration
V	Volume of the MB/MG solution
W	Gram of adsorbent
SB	Sugarcane bagasse
RH	Rice husk
MB	Methylene blue
MG	Malachite green
MOF	Metal-organic frame work
CO	Carbon monoxide
NO_x	Nitrogen oxides
ROS	Reactive oxygen species
CO_2	Carbon dioxide
DRH	Delignified rice husk
DSDSB	Delignified sugarcane bagasse
DDDSB-MoS_2	Delignified sugarcane bagasse-molybdenum di-sulphide
DRH-MoS_2	Delignified rice husk-molybdenum di-sulphide
FTIR	Fourier transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
XRD	X-ray diffraction
SEM	Scanning electron microscope

Mo	Molybdenum
S	Sulphur
O	Oxygen
C	Carbon
PFO	Pseudo first order
PSO	Pseudo second order
CB	Conduction band
VB	Valence band
UV-DRS	UV-Vis diffuse reflectance spectroscopy
C.I	Crystallinity index
PC	Phosphorylated cellulose
VC	Viscose cloths
NMR	Nuclear magnetic resonance spectroscopy
AMT	Ammonium molybdate trihydrate
PC@5.5 %	PC gel with solid content of 5.5 %
PC@4.9 %	PC gel with solid content of 4.9 %
PC@4.3 %	PC gel with solid content of 4.3 %
K	Consistency index
N	Power law index
LVR	Linear viscoelastic region
G'	Storage modulus
G''	Loss modulus
FWHM	Full width at half maximum
K_i	Diffusion rate constant
C_i	Boundary layer thickness
PCMo@0.1%	Phosphorylated cellulose printed structures with 0.1g of AMT
PCMo@0.25%,	Phosphorylated cellulose printed structures with 0.25g of AMT
PCMo@0.5%,	Phosphorylated cellulose printed structures with 0.5g of AMT
PCMo@0.75%,	Phosphorylated cellulose printed structures with 0.75g of AMT
PCMo@1%,	Phosphorylated cellulose printed structures with 1g of AMT
T_{onset}	Onset thermal degradation temperature
T_{max}	50 % weight loss
ΔH	Enthalpy

ΔS	Entropy
ΔG	Gibb's free energy
DRS	Delignified rice straw
RSF-45	Rice straw film produced from gel prepared after 45 min of curing
RSF-60	Rice straw film produced from gel prepared after 60 min of curing
RSF-75	Rice straw film produced from gel prepared after 75 min of curing
RSF-90	Rice straw film produced from gel prepared after 90 min of curing
RS	Rice straw
TGA	Thermogravimetric analysis
APTES	(3-Aminopropyl) triethoxy silane
RSA-45	Rice straw aerogel produced from gel prepared after 45 min of curing
RSA-60	Rice straw aerogel produced from gel prepared after 60 min of curing
RSA-75	Rice straw aerogel produced from gel prepared after 75 min of curing
RSA-90	Rice straw aerogel produced from gel prepared after 90 min of curing
PALCAM	Polymyxin Acriflavin Lithium-chloride Ceftazidine Esculin Mannitol
PDA	Potato Dextrose agar
MRS	De Man, Rogosa and sharpe
XLD	Xylose Lysine Deoxycholate
CFU/g	Colony forming unit per gram
PET	Polyethylene terephthalate
TPA	Terephthalic acid
PU foam	Polyurethane foam
VRBA	Violet red bile agar
SCBF-30	Sugarcane bagasse film produced from gel prepared after 30 min of curing
SCBF-45	Sugarcane bagasse film produced from gel prepared after 45 min of curing

SCBF-60	Sugarcane bagasse film produced from gel prepared after 60 min of curing
SCBF-75	Sugarcane bagasse film produced from gel prepared after 75 min of curing
SCBF-90	Sugarcane bagasse film produced from gel prepared after 90 min of curing
PSCB-30	Phosphorylated sugarcane bagasse aerogel produced from gel prepared after 30 min of curing
PSCB-45	Phosphorylated sugarcane bagasse aerogel produced from gel prepared after 45 min of curing
PSCB-60	Phosphorylated sugarcane bagasse aerogel produced from gel prepared after 60 min of curing
PSCB-75	Phosphorylated sugarcane bagasse aerogel produced from gel prepared after 75 min of curing
DPPH	2,2-Diphenyl-1-picrylhydrazyl
PSCB-G	Phosphorylated sugarcane bagasse foam modified with Gallic acid
CC	Charge content
FD	Fossil depletion
POF	Photochemical ozone formation
TA	Terrestrial acidification

PREFACE

Given the global challenges presented by petroleum-based polymers, as well as the need to combat climate change and dwindling fossil fuel resources, there has been a noticeable push on sustainable technologies and research. These challenges have highlighted a crucial effort to shift away from the conventional dependence on polymers derived from petroleum to sustainable and affordable alternatives that are both eco-friendly and renewable. Development of renewable polymers with scalable processes for commercial utilization is another focus point towards developments in sustainable polymers. In line with the research progress in renewable polymers, there exists sustainable development goals (SDGs) such as clean water and sanitation (SDG6), industry, innovation and infrasturucture (SDG 9), life below water (SDG 14), life on land (SDG 15), climate action (SDG 13), responsible consumption and production (SDG 12), sustainable cities and communities (SDG 11), and affordable and green energy (SDG 8) by United Nations. There has been a strong push to find alternative methods for producing polymers to address environmental concerns. As a result, there has been an intensive attempt to investigate biopolymers as potential solutions. In this field, agricultural biomass and waste offer exciting opportunities to create valuable products while reducing environmental harm. Cellulose is an extremely promising option for biopolymer production due to its remarkable properties such as mechanical strength, crystallinity, hydrophilicity, biodegradable, sustainable, environmentally friendly, non-toxic, affordable, and widely accessible. This thesis focuses on utilising different agro-wastes to extract cellulose, their *in-situ* modification, and phosphorylation *via* green routes for development of value-added products. The present thesis consists of 8 chapters in which chapter 4 to chapter 7 discuss the methodologies performed. The cellulose extraction and phosphorylation have been performed using an industrially viable, scalable, and green approach. The phosphorylated cellulose processed with the sustainable routes were 3D-printing, moulding, solution casting, freeze drying, and spinning to fabricate complex structure, cups and plates, films, aerogels, and threads. This thesis explores various sustainable solutions derived from abundantly available agricultural biomass to value-added products, specifically emphasizing sugarcane bagasse (SB), rice husk (RH), viscose

cloth, and rice straw for addressing urgent environmental challenges and provide practical advancements in different sectors. In chapter 4, the process of delignification of SB and RH is revealed, resulting in the extraction of cellulose that can be used as an effective adsorbent for methylene blue (MB) and malachite green (MG) dyes, respectively. In addition, using molybdenum salt and thiourea treatments, the resulting cellulose is converted into highly effective adsorbents and photocatalysts for removing dyes. These absorbents also demonstrate antibacterial properties against *Escherichia coli* and *Staphylococcus aureus* for scalable and continuous wastewater dye and bacterial decontamination with potential practical applicability. The chapter introduces a unique strategy for the up-conversion of agricultural biomass into value-added bio-adsorbents, which can effectively and economically address the remediation of dyes with simultaneous microbial decontamination from polluted wastewater streams. Chapter 5 demonstrates an important development in sustainable material innovation using viscose cloth for gel production through phosphorylation. The phosphorylated gels exhibit improved properties, including higher water absorption, swelling capacity, and rheological attributes. Additionally, they show significant enhancements in their ability to remediate MB. The addition of MoS_2 salts to PC also showed excellent shear-thinning properties. It facilitated the *in-situ* growth of MoS_2 to introduce photocatalytic and antibacterial properties, enhancing the rate of MB degradation and pathogens removal from wastewater. This chapter provides a green, facile and energy-efficient strategy for fabricating PCs with easy processability through additive manufacturing techniques for producing value-added products, opening up new avenues for high-performance applications including continuous photodegradation and antibacterial properties. Chapter 6 of the thesis explores the process of transforming rice straw waste into useful materials like food packaging films, aerogels, and thermal boxes. The films and aerogel boxes demonstrate remarkable mechanical strength, thermal stability, and flame-retardant properties using phosphorylation, solution casting and freeze-drying techniques. Furthermore, the development of biodegradable cups and aerogel boxes showcases the versatility and environmental friendliness of materials made from rice straw. The rice straws have been processed to form films (heat sealing), cups (anti-fizzing and solvothermal stability) and aerogels properties (thermal insulation, low thermal conductivity) and can acts as potential replacement of non-biodegradable and

highly flammable polyethylene and polyurethane, and polystyrene. In Chapter 7, we explore the potential of sugarcane bagasse and demonstrate the production of phosphorylated films, aerogels, and fruit foams that offer a wide range of functionalities. These materials possess transparency, mechanical strength, flame retardancy, thermal stability, and biodegradability, making them highly suitable for a wide range of packaging applications. The foams prepared with sugarcane bagasse biomass can become a suitable mechanically stable alternative for damage protection in perishable fruit products, as a potential replacement for non-biodegradable polystyrene foams used currently. It is worth mentioning that the use of these materials for packaging paneer and apples highlights their ability to prolong shelf life and provide environmentally friendly alternatives to traditional packaging materials. Together, this thesis highlights the importance of utilising agricultural biomass and waste to create sustainable materials that can be used in a wide range of applications. This not only helps address pressing environmental issues and UN SDGs, but also promotes innovation and progress in different industries. This thesis aims to make a valuable contribution towards a scalable, facile, low-cost, utilization of abundantly available waste biomass for making high value products with lower carbon footprints which can be utilized in the direction of the global efforts in achieving a sustainable and resilient future.