Chapter-8

Conclusion and future scope

8.1 Conclusion

India's economy is mainly centred on agriculture, which includes crops such as paddy, sugarcane bagasse, wheat, corn, barley, and lentils. The cultivation of various crops has led to the generation and accumulation of agricultural biomass post harvesting. The absence of appropriate technology and approaches to repurpose agricultural biomasses has resulted in their accumulations and disposal techniques have known to cause significant environmental damage. Due to the inability to convert agro-biomass into valuable products, reliance on unconventional disposal methods such as stubble burning and landfilling in mass have been a major environmental concern. Hence, the primary goal of this thesis is to utilise agricultural waste to develop value-added products using sustainable technologies and mitigate the associated environmental impacts. The major innovation and diverse application of cellulose and functionalised cellulose with an aim to convert "waste-to-value" presented in this thesis includes (i) strategic delignification of cellulose from diverse agricultural wastes such as rice husk, rice straw, and sugarcane bagasse, (ii) *in-situ* modification of RH and SB biomass using MoS_2 for adsorption, and photodegradation of dyes such as MB and MG and inactivation of bacteria present in wastewater, (iii) phosphorylation of commercial viscose fabrics for gel production followed by 3D printing to produce complex structures for dye remediation, (iv) i*n-situ* growth of MoS_2 on 3D printed PC structures for MB adsorption, photodegradation and microbial decontamination, (v) phosphorylation of cellulose extracted from agro-biomass under different conditions using DAHP and urea, (vi) processing of PC for food packaging application in form of films, cups, aerogel, thermal boxes and fruit foam nets. This thesis has addressed the challenges of stubble burning and transforming waste to value-added products of commercial significance such as adsorbent, catalyst, gels, films, cups, aerogel, and food packaging boxes. The key findings of the thesis include the development of cellulose phosphate gels from different agro-waste, develop novel processing technique to produce complex structures by 3D printing and solution processing to form films for food packaging, aerogels and thermal boxes processed through freeze drying, moulding and casting to produce tableware. The detailed conclusion of individual chapters present in the thesis are summarised below.

Chapter 1 provides a comprehensive introduction of the thesis, delving into cellulose's historical background and advancements, establishing its importance on various Sustainable Development Goals (SDGs), and highlighting its significance within the circular economy framework. The discussion emphasised the utilisation of biomass to produce products and technologies which are both sustainable to environment as well as bring economic benefits, highlighting the importance of sustainable resource management. Furthermore, considering the potential efficacy and ecological consequences, selection to employ phosphorylation technique for processing of agro-biomass instead of traditionally used TEMPO-oxidation was evaluated, as environmentally sustainable methodologies have been discussed. The chapter briefly introduces the numerous products and processes developed in this thesis, preparing the way for the in-depth investigation in subsequent sections. Chapter 1 establishes the groundwork for exploring innovative solutions and sustainable technologies developed in area of cellulose, contributing to the circular economy, improving environmental sustainability and effective resource utilisation.

Chapter 2 is the literature review extensively explores and discusses on cellulose and its polymorph, providing detailed insights into the diverse sources, extraction techniques and their application. The chapter conducted a comprehensive analysis of the chemical modification processes used to modify cellulose, providing substantial insight into its applications. Detailed investigations were conducted to examine the phosphorylation of cellulose using different substrates and chemicals, highlighting the wide-ranging effects of this process on the characteristics of cellulose. The chapter extensively examines phosphorylation's influence on cellulose's characteristics and its diverse applications across several sectors. The chapter latter on comprehensively analyse the life cycle aspects of phosphorylated cellulose and TEMPO-oxidised cellulose production, specifically emphasising sustainability and environmental implications at each stage of the production process.

Chapter 3 provides a detailed discussion of materials and methods utilized throughout the experimental work conducted in the thesis. The techniques for isolating cellulose from agricultural biomass involve utilizing delignification, phosphorylation and *in situ* nanoparticle growth on different biomasses such as rice straw, rice husk, and sugarcane. This chapter analyses the phosphorylation process of cellulose obtained from biomass and commercial cellulose such as viscose. The study investigates the effects of optimization parameters such as curing time and temperature on the properties of phosphorylated cellulose. This chapter highlights many analytical techniques for the characterization of developed gels, aerogels, films, and catalysts using EM, FESEM, EDS, elemental mapping, XRD, TGA, FTIR, UV-spectroscopy, UV-DRS, texture analyzer, and XPS. A comprehensive discussion was conducted regarding dye remediation, photodegradation, microbial inactivation, and food packaging. A comprehensive analysis of the techniques used for adsorption, photodegradation, and the corresponding kinetics isotherms and reusability has been provided. The production procedures for films, aerogels, and thermal boxes have also been discussed. In the food packaging application, analysis of migration, change in pH, peroxide values, microbial growth and melting behaviour of butter have been discussed. For aerogel, the methodologies of thermal conductivity, flame retardancy, mechanical properties, and swelling properties have been discussed extensively. Life Cycle Assessment (LCA) techniques have been thoroughly examined for the production of phosphorylated cellulose from a different source, and their comparison with the traditional TEMPO-oxidation methods has been thoroughly performed. In summary, Chapter 3 serves as a comprehensive guide to the methodologies employed throughout the experimental phase of this thesis, laying the groundwork for the subsequent analysis and discussion of results in subsequent chapters.

Chapter 4 explored the utilisation of delignified agricultural biomasses, specifically rice husk (RH) and sugarcane bagasse (SB), as efficient carriers for in situ growth of MoS_2 nanoflowers and their subsequent utilization as pollutant remediation and microbial decontaminations. SB and RH, a major by-product of agro- industries are produced in large volumes, poses a significant disposal challenge. However, with the global shift towards a greener, more sustainable circular economy, SB and RH is widely recognized as a valuable resource for producing value-added products. In this study, a novel approach for volarization of SB and RH via delignification cum *in situ* growth of MoS_2 was performed to produce a catalyst for continuous remediation of pollutant dyes and decontamination of microbes present in the wastewater. The DRH-MoS_2 and DSB-MoS_2 composites exhibited remarkable characteristics, including outstanding adsorption capacities, elevated photodegradation efficiency, and potent antibacterial activity. DSB-MoS_2 and DRH-MoS_2 show a crystal structure with a hexagonal (*2H*-phase) phase and multi-layered nanosheet structures. The MoS_2 nanosheets were observed to undergo self-assembly to form nanoflower-like structures on the surface of the vertically aligned, rough, and porous surface of DSB and DRH. Industrial wastewater is challenging to remediate due to the presence of a combination of pollutants and microbial contaminants. While commercial technologies capable of simultaneously addressing both pollutants and microbes exist, they are prohibitively expensive. As a cost-effective alternative, the DSB-MoS_2 and DRH-MoS_2 catalyst developed in this study was applied for microbial decontamination and the remediation of pollutants like MB. The resulting MoS_2 nanosheets demonstrates *2H*-MoS_2 phase structure with outstanding catalytic performance, possessing a band gap measuring 1.37 eV, and exhibits an impressive scavenging activity of 74.2%. These catalysts exhibited exceptional performance in degrading methylene blue (MB) and malachite green (MG) dyes under light conditions. DSB-MoS_2 exhibited a significant enhancement in its ability to degrade MB, with a capacity of 158 mg/g, during light exposure compared to 114.3 mg/g under dark. However, DRH-MoS_2 exhibited an impressive adsorption capability of 550 mg/g, particularly when exposed to light. In addition, both catalysts demonstrated strong reusability, maintaining more than 80% of their degrading capability after three cycles. Moreover, both catalysts demonstrated strong antibacterial activities against prevalent pathogens such as *S. aureus* and *E. coli*, emphasising their future possibilities in water treatment applications. Overall, these findings highlight the potential of DSB-MoS_2 and DRH-MoS_2 as a versatile solution for pollutant dye adsorption, photodegradation and pathogen removal in wastewater, showcasing a sustainable and scalable valorization approach for abundant rice-biomass waste. From a circular economy perspective, using agricultural biomasses as carriers for catalyst synthesis is a sustainable technique that adds value to agricultural waste and reduces the environmental impact of dumping it. This is in line with the Sustainable Development Goals (SDGs), namely Goal 6 (Clean Water and Sanitation) and Goal 12 (Responsible Consumption and Production), as they tackle water pollution problems and encourage the sustainable use of resources. The findings presented in this chapter highlight the possibilities of delignified agricultural biomasses as efficient carriers for synthesising MoS_2-based catalysts with versatile properties. This contributes to both environmental sustainability and the progress of water treatment technologies.

Chapter 5 explores the processing of phosphorylated gels developed from commercial viscose through additive manufacturing techniques such as 3D printing, followed by strategic functionalization for applications in pollutant or dye remediation. The phosphorylated gels produced using agro-based chemicals through sustainable approach were cost-effective as well as scalable with lowered environmental impacts. The developed gels were transparent, viscous with maximum DS of 0.184 and CC of 1133.33 mmol/kg and high yield of 87 %. Interestingly, the phosphorylated gels exhibited remarkable shear-thinning capability, making them well-suited for 3D printing applications. Furthermore, incorporating molybdate salts in these gels facilitated the *in-situ* growth and generation of MoS_2 alongwith improved 3D printability, the mechanism of which were studied in details. The phosphate groups in 3D structures were easily cross-linked through heat-induced treatments, making it mechanically stable and flexible under both dry and wet conditions with excellent stability in both acidic and basic environment. The 3D-printed structures exhibit remarkable structural stability, water absorption, and swelling capability, making them suitable for pollutant remediation under both batch and continuous modes. Their efficacy in removing methylene blue (MB) is notably remarkable, with a maximum removal efficiency of 99 % for concentrations ranging from 10 to 200 mg/L. with remarkable reusability for more than seven cycles. Furthermore, the LCA demonstrated that manufacturing phosphorylated gels *via* phosphorylation is ecologically sustainable than traditional methods (TEMPO-oxidation), reducing CO_2 emissions and carbon footprint. The 3D printed PC structures show high adsorption capacity of 94.8–99 % for MB dye concentration range of~300–500 mg/L. Furthermore, adsorption kinetics and isotherm studies show that pseudo-second-order and Langmuir isotherm fitted well with experimental data. Reusability of PC structures shows that adsorption over seven-cycles led to 99 % removal of MB dye, however, desorption range between 70 and 93 % over seven cycles. Furthermore, the incorporation of MoS_2 into the phosphorylated gels resulted in the development of multifunctional structures capable of simultaneously degrading dyes and decontaminating microbes. The PC-MoS_2 composite was found to display maximum adsorption and photodegradation of MB dyes, with adsorption capacity of ~464.16 mg/g in three hours. The photodegradation of MB also showed excellent results with maximum photodegradation of ~99.4, 99.1, and 99.1% for concentration range of 100-300 mg/L within 40 minutes. The effect of dye concentration, pH, and temperature on photodegradation were studied in details and kinetic studies also reveal best fit with pseudo-second-order (PSO) kinetics model. Langmuir isotherms better described adsorption isotherms, indicating that the adsorption phenomenon occurred on monolayer. The PCMo@0.5% was found to be efficiently recycled for photodegradation of MB upto 5 cycles with ~94.7% efficiency. Further, PC-MoS_2 composites have demonstrated remarkable efficiency in degrading high concentrations of MB dye through photodegradation. In addition, they have shown potent antibacterial effects against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*). Utilising commercial viscose clothes as a raw material for producing phosphorylated gel is an environmentally sustainable technique that prioritises waste resources and reduces ecological harm. This initiative contributes to various SDGs, including promoting clean water and sanitation, developing innovation and infrastructure, and encouraging responsible consumption and production. The initiative tackles concerns such as water contamination, advocates for environmentally friendly industrial methods, and fosters the optimal use of resources. The results discussed in this chapter highlight the potential of phosphorylated gels and their MoS_2-composite derivatives as novel materials for treating wastewater. They provide an acceptable solution to environmental concerns and contribute to sustainability and circular economy.

Chapter 6 introduces a novel, eco-friendly method for valorization of rice straw waste to create diverse products with substantial commercial interests. The phosphorylated cellulose gels have been developed from rice straw waste through delignification and phosphorylation approach using low-cost agro-chemicals through a scalable and environmentally sustainable technology. The phosphorylated cellulose gels produced show high CC ~1850-2366 $mmol kg^{-1}$ which varies with curing time ~45-90 minutes and significantly affects the physio-chemical, structural, mechanical and thermal properties of processed films, aerogels and beverage cups. The mechanistic investigations shows formation of covalent linkage of phosphate groups with cellulose backbone alongwith with crosslinking with silica inherently present in rice husks to form silicon phosphate groups. The presence of such cross-linkages leads to improved mechanical strength under both wet and dry conditions for both films and aerogels developed. Interestingly, the processed RSF films shows heat sealing characteristics due to presence of silicon phosphate groups which undergoes cross-linking on local heating. The processed beverage cups shows high solvothermal stability in hot water (maintained at 100 °C) for upto 10 hours making it suitable for consumption of both hot and cold beverages. The phosphate functionalized films shows flame-retardancy with high char formation and maintains the structural integrity post-flame testing. The migration properties of films when in contact with food simulants ethanol (10%) and isooctane were well below the permissible limit (60 mg/kg). RSF-60 films were utilized for packaging of easily perishable food items such as apple, kiwi and pear, which shows reduction in oxidation (browning) as well as weight loss suggesting the developed packaging have potential oxygen and water vapor barrier properties. The aerogels exhibit exceptional water absorption capability, resilience in watery environments, and higher compressive strength. The aerogel-based packaging, namely RSA-60, demonstrates efficacy in maintaining the structural integrity of heat-sensitive food items such as butter while providing the added advantage of flame retardancy. Moreover, LCA findings validate that rice aerogel-based packaging is environmentally superior to traditional materials such as polyurethane foam and PET boxes. This superiority is principally attributed to its lower energy consumption and reduced CO_2 emissions. This highlights the capacity of these environmentally friendly solutions to decrease carbon emissions from waste incineration and food packaging materials. It provides a scalable and effective method for waste utilisation while lowering the need for refrigeration equipment and supply chains. In contrast to PET boxes, the LCA results for the rice aerogel box used for butter packaging indicate environmental friendliness primarily due to lower energy consumption and also resulted in lower CO_2 emission. The LCA of the transportation of butter in cold storage systems resulted in almost comparable CO_2 emission, which signifies the advantage of using rice aerogel for butter storage over PET boxes. This study showcases the technical feasibility and commercial viability of converting rice straw waste into valuable products. Additionally, it emphasizes the environmental advantages and potential societal effects of implementing sustainable practices in waste management and packaging industries. The study presents an eco-friendly method for utilizing rice straw waste to create products, aligning with Sustainable Development Goals (SDGs) and circular economy principles. The study contributes to SDG 12 (Responsible Consumption and Production) and SDG 9 (Industry, Innovation, and Infrastructure) by producing aerogels and packaging films. The lightweight, highly porous aerogels offer alternatives to conventional plastic packaging, reducing marine and terrestrial pollution. The flame-retardant properties of these films support SDG 11 (Sustainable Cities and Communities). This circular approach supports SDG 13 (Climate Action) by mitigating carbon emissions and reducing the carbon footprint of packaging materials.

Chapter 7 has shown the potential of transforming SB waste into valuable products such as phosphorylated gels, films, and aerogels using eco-friendly and sustainable methods. SB was converted into a phosphorylated cellulose gel using established techniques such as delignification and phosphorylation. The process resulted in a high yield of 85% phosphorylated cellulose in its dry form and produced a gel with desirable properties, such as tuneable optical transparency and charge content within range of 500-1130 mmol/kg. In addition, the gels can be transformed into films that exhibit remarkable mechanical strength, water resistance, thermal stability, and flame retardancy. These attributes render them well-suited for utilisation in food packaging. By employing these films in the packaging of paneer, its shelf life was significantly extended by upto 14 days. In addition, films were effective in minimising the possibility of microbial contamination and maintaining stable pH and peroxide levels with minimum alterations. The developed films shows improved biodegradability with degradation within 56 days under natural soil conditions. Moreover, the life cycle evaluation of the SCBF film's production demonstrated a decrease in carbon dioxide emissions, highlighting the improved environmental sustainability of the developed process. In addition, the aerogel produced from SB waste demonstrated highly favourable attributes, including high porosity, low density, low thermal conductivity, exceptional thermal stability, and flame-retardant properties. The processing of developed aerogel into foam nets for packaging of perishable fruits exhibited similar effectiveness in improving the self-life as well as maintaining the structural stability of fruits providing it to be a sustainable alternatives to polyurethane/polyethylene based foams. Additionally, the incorporation of gallic acid imparted antibacterial and antioxidant properties to the packaging material, rendering it effective against *E. coli* and *S. aureus*, and exhibiting an 88% DPPH free radical scavenging ability. The study's results align with the Sustainable Development Goals (SDGs), particularly Goal 12 (Responsible Consumption and Production). This research intends to convert SB waste into valuable products by implementing eco-friendly and sustainable processes with an objective to encourage responsible consumption and production behaviours. This study addresses the issue of waste reduction and resource efficiency by developing phosphorylated gels, films, and aerogels using SB waste as a starting material. Furthermore, the study illustrates the potential utilisation of these goods in food packaging to effectively prolong the freshness of perishable food items like paneer and fruits, contributing to the achievement of Goal 2 (Zero Hunger). Prolonging the longevity of food products is essential in reducing food waste and advancing food security. The study demonstrates the ideas of waste utilisation and resource efficiency. This research demonstrates a shift from the traditional linear model of 'take-make-dispose' to a circular approach that prioritises the reuse, recycling, or repurposing of materials by converting SB waste into valuable goods. This strategy effectively mitigates the demand for fresh resources and minimises the adverse environmental impact of waste disposal.

8.2 Future scope

Phosphorylated cellulose derived from agricultural biomass presents a favourable prospect for companies seeking eco-friendly, high-performance packaging applications and waste management products. The study demonstrates that phosphorylation can improve the physiochemical, structural and functional characteristics of cellulose. PC encompass higher charge densities, improved capacity to remove metal ions, increased thermal stability, and improved resistance to catching fire. These technological breakthroughs opens up new avenues for diverse applications of cellulose phosphate in multiple areas, such as electronics, fire prevention, thermal insulation, and textiles.

Moreover, the processing of phosphorylated cellulose through additive manufacturing exhibits significant promise in the bone and tissue engineering domain, introducing novel prospects for its implementation. This novel methodology offers tailored solutions for regenerative medicine, creating new opportunities for study and advancement. However, there are still challenges to address, such as the problem of low cellulose production and the intricacies associated with its processing and storage which needs to be addressed.

For electronic devices, precise temperature control is crucial. Phosphorylated nanocomposites with interesting thermal stability and insulation properties can revolutionise heat dissipation, increasing durability and enhance device performance. Furthermore, examining phosphorylated nanocomposites in the field of designing battery packages presents the possibility of developing energy solutions that are both eco-friendly and safer.

Cellulose phosphate exhibits fire-retardant characteristics, making it a potential candidate for incorporation into smart textiles and fabrics. This could enhance the safety of firefighters and workers exposed to dangerous environments. Moreover, a thorough understanding of the correlation between the structure and activity of phosphorylated cellulose and its mode of action is crucial for improving its efficacy in various applications. Further investigation is required to comprehend phosphorylated cellulose derivatives' extended consequences and biological behaviour. This would create possibilities for their utilisation in eco-friendly advanced engineering applications across diverse sectors, such as food packaging, electronics, medicines, and separation processes.

There is increasing interest in phosphorylated cellulose in the future, as evidenced by the large-scale production initiatives recently started by the companies such as Oji Holding Corporation and Betulium [466]. With its lower toxicity and improved efficiency, the pre-treatment process presents clear advantages over conventional methods, making it a promising option for industrial use.