# *Chapter-1*

# Introduction

### 1.1 Overview

Over the past few years, there has been increased global attention towards sustainable practices, specifically focusing on discovering creative solutions to reduce environmental damage while promoting economic development. An area of significant concern is the management of agricultural biomass post-harvest, which has historically been disposed of by burning or burying it in landfills, releasing greenhouse gases and deteriorating soil quality. The depletion of finite resources and increasing ecosystem pressure necessitate the exploration of sustainable alternatives, such as agricultural biomass for value-added products. Nevertheless, there is a growing interest in investigating new methods to transform agricultural biomass into valuable products, reduce waste, and generate economic development. This thesis explores and extracts agricultural biomass, an underutilized resource, to convert it into products through sustainable technologies to unlock its potential for economic and environmental benefits. The conversion of agricultural waste into value-added products creates economic opportunities for rural communities, fostering local development and livelihood improvement. Through its multidisciplinary approach and focus on sustainability, this thesis aligns with the United Nations' Sustainable Development Goals, particularly those related to responsible consumption and production, climate action, and sustainable communities.

Considering the abovementioned prospects and challenges associated with agricultural biomasses, this thesis seeks to contribute to the emerging application by examining the conversion of different agricultural biomass into products that have increased value through a series of consecutive processes.

## 1.2 Introduction

Synthetic polymers have wreaked havoc on the environment since the 1990s due to their non-degradability, generating microplastic pollution and difficulty in its disposal. Fossil fuels have long been utilised as a source for energy generation and polymer production, which is one of the main factors contributing to greenhouse gas emissions. Plastic pollution is an alarming concern, and it has always been getting worse due to improper recycling, poor waste management and overutilization of petroleum-based resources [1]. Due to the growing environmental concern from the extensive utilization of petroleum-derived polymer, plastic waste generation, global climate change, and diminishing reserves of fossil fuels, there has been increased focus on advancing research in field of bio-based polymers. Given the gravity of the situation, there has been increased demand to shift from utilization of petroleum-based polymers to cost-effective, environmentally-friendly alternatives that are sustainable and renewable using emerging technologies and processes. Due to this transformation, researchers and industries have encountered significant challenges in developing commercially viable renewable bio-polymers [2]. The urgent need to replace conventional polymer production methods has drawn considerable focus to biopolymers, offering potential solutions for mitigating environmental challenges [3]. In this context, agricultural biomass and waste are viable options for producing various value-added products and minimizing adverse environmental impacts. Among different types of bio-based polymers, cellulose stands out as the most favourable choice for biopolymer production due to its inherent biodegradability, functionality, environmental-friendliness, non-toxicity, improved physiochemical and structural properties, affordability, and widespread availability [4]. Several other remarkable features of cellulose and its derivatives include adjustable aspect ratios, regulated morphology, outstanding structural (mechanical) characteristics, and hydroxyl functionality that can undergo chemical modifications tailored to specific applications.

Cellulose and its derivatives can be customized and modified to create diverse materials and structures, including microfibers, nanofibers, aerogel, gels, films and hydrogels [5]. The increasing demand for cellulose and cellulose-based materials (MFC, NFC, CNC, MCC) in recent years has led to the establishment of numerous cellulose manufacturing companies, including Borregarrd chemical company (Norway, 1992) [6], Daicel Corporation (Japan, 1919) [7], FiberLean technologies Ltd (UK, 2016) [8], J. Rettenmaier and shone (Germany, 1878) [9], Nippon paper industries Corporation Ltd (Japan, 1949) [10], Norske Skog ASA (Norway, 1962) [11], Sappi limited (South Africa, 1936) [12], and Stora Enso Oyj (Finland, 1996) [13]. Borregarrd is the first company to manufacture MFC at industrial scale with annual production capacity of 10 metric tonnes for 10% paste, 50 metric tonnes for 2% suspension, and 1 metric tonne for dry MFC for application in emulsion, paper and packaging, food, pharmaceutical ingredients and so on. Daicel Corporation mainly produces cellulose acetate to develop moulded products, fabrics, paints, membranes for wastewater remediation, and LED panels. Similarly, FiberLeans also produces MFCs for the production of packaging and building construction materials. J. Rettenmaier and Shone produce different forms of cellulose, including cellulose powder, granules, flours, and gels for applications in automobile industries, pharmaceutical industries, insulation, road construction, and paper and cardboard industries. Similarly, Nippon Paper

Industries Corporation, Norske Skog ASA, Sappi Limited, and Stora Enso Oyj are the major MFC producers for different applications such as paper, paper board, paper straws, kitchen products, etc. This versatility of cellulose and its derivatives unlocks a myriad of technological advancements and potential commercial opportunities in various sectors.

Cellulose is one of the most abundantly available biopolymers in which two *D*-glucose monomeric units are joined together by $\beta$ *-1,4* glycosidic linkage, and each alternate unit shows a turn of 180°. Currently, cellulose, cellulose nanocrystals (CNC), micro-fibrillated cellulose (MFCs), and nano-fibrillated cellulose (NFCs) have found widespread high-performance applications in high-performance applications, leading to the development of a diverse range of value-added products. These applications demonstrate the considerable potential of cellulose in various everyday uses, including (i) creating adsorbents and catalysts for wastewater remediation [14,15], (ii) manufacturing food packaging films [16], (iii) developing aerogels for thermal insulation [17], (iv) formulating bio-inks for 3D printing [18], (v) constructing scaffolds for bone and tissue engineering [19], (vi) serving as carriers for drug delivery [20], (vii) contributing to the production of smart textiles and fabrics [21], (viii) acting as reinforcement materials for construction, such as cement and concrete [22], (ix) forming proton exchange membranes for fuel cells [23], (x) participating in supercapacitor technology [23], (xi) being utilized in tableware [24], (xii) contributing to the creation of paper-based microfluidic devices [25], (xiii) enabling radiative cooling homes and buildings [26] and (xiv) flame retardant material [27] etc and other several high end application. Incorporating eco-friendly and renewable cellulose-based material in designing and producing various biodegradable and sustainable products presents an opportunity to tackle environmental pollution. While the discovery of cellulose dates back to the previous century (**Figure 1.1**), its significance in research for the advancement of new technologies has only begun to be thoroughly investigated in recent times. Anselmen Payen discovered cellulose in 1838 and reported it as a water-insoluble and hydrophilic biopolymer. One of the cellulose derivatives produced by acid hydrolysis, was described by Nickerson et al. in 1947 under the name "cellulose micelles and crystallites."[28] and *Ranby et al.* later changed the nomenclature to "crystallites" in 1949. First electron micrograph imaging of CNC was performed by *Mukherjee et al*. in 1953 revealing that NCs do not form micelles, rather it exist in a rod-shaped form [29]. In 1970, gel-like products were created through the homogenization of wood pulp in a high-temperature and pressure environment, and the term "Nanocellulose" (NCs) was coined for this development by Turbak et al. [30]. Subsequently, ITT Rayonier was awarded multiple patents in the early 1980s that outline the manufacturing process and uses of nanocellulosic products [31]. The research in the area of nanocellulose has undergone significant development in terms of fundamentals as well as applied research. In the year 1990, the liquid crystalline nature of NCs were first reported whereas its potential as a reinforcing agent was reported in 1995. Bacterial cellulose (BC) is the name given to NCs derived from bacteria in a bottom-up fashion. In the late 1800s, A.J. Brown extracted BC from the pellicles of the bacterium *Gluconacetobacter xylinus.* Bacterial strain such as *Pseudomonas, Acetobacter, and Gluconacetobacter* have been significantly reported for their bacterial cellulose production. However, the underlying mechanism and biosynthetic pathways were studied and discovered in the early 20$^{th}$ century [32]. The enzyme (BC synthase) responsible for its production was successfully purified and characterized in the 1990s [33]. BC is the purest cellulose form and is free from both lignin and hemicellulose, and has been explored in wound healing, tissue engineering, food industries, prosthetics, cosmetics, composites and drug delivery etc. The chemical modification of nanocellulosic and microcellulosic forms haven been explored in recent decades with phosphorylation of MCC by Suflet et al. [34], and phosphorylation of BC in 2006 by Wan et al [35]. In year 2012, CNC phosphorylation was first performed by Lemke et al.[36] ,whereas of CNF phosphorylation was done by Ghanadpour et al in 2015 [37]. In 2011, the International Nanocellulose Standards Coordination Committee (INSCC) was established by TAPPI to suggest global standards for nanomaterials derived from cellulose to establish a uniformity and to reduce the trade barrier and ambiguity. These standards aimed to eliminate trade barriers and promote consistency in research and development related to products based on nanocellulose. Implementing these standards makes classifying nanocellulose into specific types easier based on their inherent properties.

In this thesis, production of MFCs and its chemical modifications has been carried out using sustainable approaches, followed by strategic modifications to improve physiochemical, structural, and functional properties through scalable processing technologies. The physical, chemical, and structural attributes of nanocellulose or micro-fibrillated cellulose exhibit significant dependence on the initial biomass types, microbial source, cellulose polymorphs, and the pre-treatment methods applied during the extraction process.

MFCs are also referred to as cellulose microfibril or microfibrillar cellulose [38]. MFC is essentially formed by clusters of assembled cellulose microfibrils, exhibiting a diameter spanning from 20 to 60 nm and a length extending over several micrometres [39] containing both amorphous and crystalline components. Moreover, MFC possesses a notably high L/D ratio, contributing to an exceptionally low percolation threshold, establishing a rigid network, and improving the mechanical and structural properties. MFC can be produced from different sources such as Kraft pulp, wheat straws, wood pulp, hemp fibres, and sugar beet pulp through different physical treatments such as cryo-crushing [40], grinding [41], homogenization [42] and ball milling [43]. Importantly, the production of MFC involves the mechanical disintegration of cellulosic materials without undergoing hydrolysis [44]. In 1985, Turbak and colleagues pioneered patenting a novel method for manufacturing MFCs, which involved passing a suspension of wood fibres multiple times through a narrow gap of homogenizer under elevated pressure, forming a viscous gel [45]. This cost-effective method for the production of MFC demonstrated promising uses, including serving as a paper binder and viscosity modifier [46]. This patent marked the beginning of numerous noteworthy research endeavours aimed at refining the mechanical process and exploring the exceptional properties of MFCs for the desired application, resulting in further advancement in the cellulose field.

MFC is produced using various cellulosic sources, including agro-waste [47] and wood [48]. Among these sources, wood stands out as the predominant industrial source, making it the primary raw material for manufacturing MFC. However, the increasing demand for wood in other sectors, such as furniture, building and construction, shifted the focus on the utilization of agro-biomass for the extraction of MFC due to their abundant availability following sustainable process which requires lower energy consumption. Unlike wood, where cellulose fibres are found in the secondary wall of plant cells, cellulose microfibrils obtained from agricultural fibres are more straightforward to extract from the primary wall and require less energy [49]. In literature, cellulose has been extracted from different agricultural biomass such as rice straw [47], sugarcane bagasse [50], wheat straws [51], corn stover [52], pineapple leaves [53], cotton stalks [54], and citrus pomace [55]. These extracted MFCs have been widely utilised for applications such as paper making, packaging films, aerogels, composites, and filler materials. MFC can be produced from different sources such as Kraft pulp, wheat straws, wood pulp, hemp fibres, and sugar beet pulp through different physical treatments such as cryo-crushing [40], grinding [41], homogenization [42] and ball milling [43]. Chemical treatments such as acids [56], alkali [57], and enzymatic treatment (endoglucanase) [58] have been utilized for MFC production. Chemical modification routes such as Tempo-oxidation [1] and phosphorylation [1] have also been utilized to produce MFCs. MFCs have also been mixed with different polymers such as polyvinyl alcohol [59], starch [60], polylactic acid [61] and polypropylene for the production of composites for a wide array of applications. Processes such as solution casting, wet spinning, freeze drying, moulding and 3D printing (***Figure 1.2***) can generate different forms of MFCs, including films, aerogels, cups, plates, and complex structures for different applications, as depicted in ***Figure 1.3***.

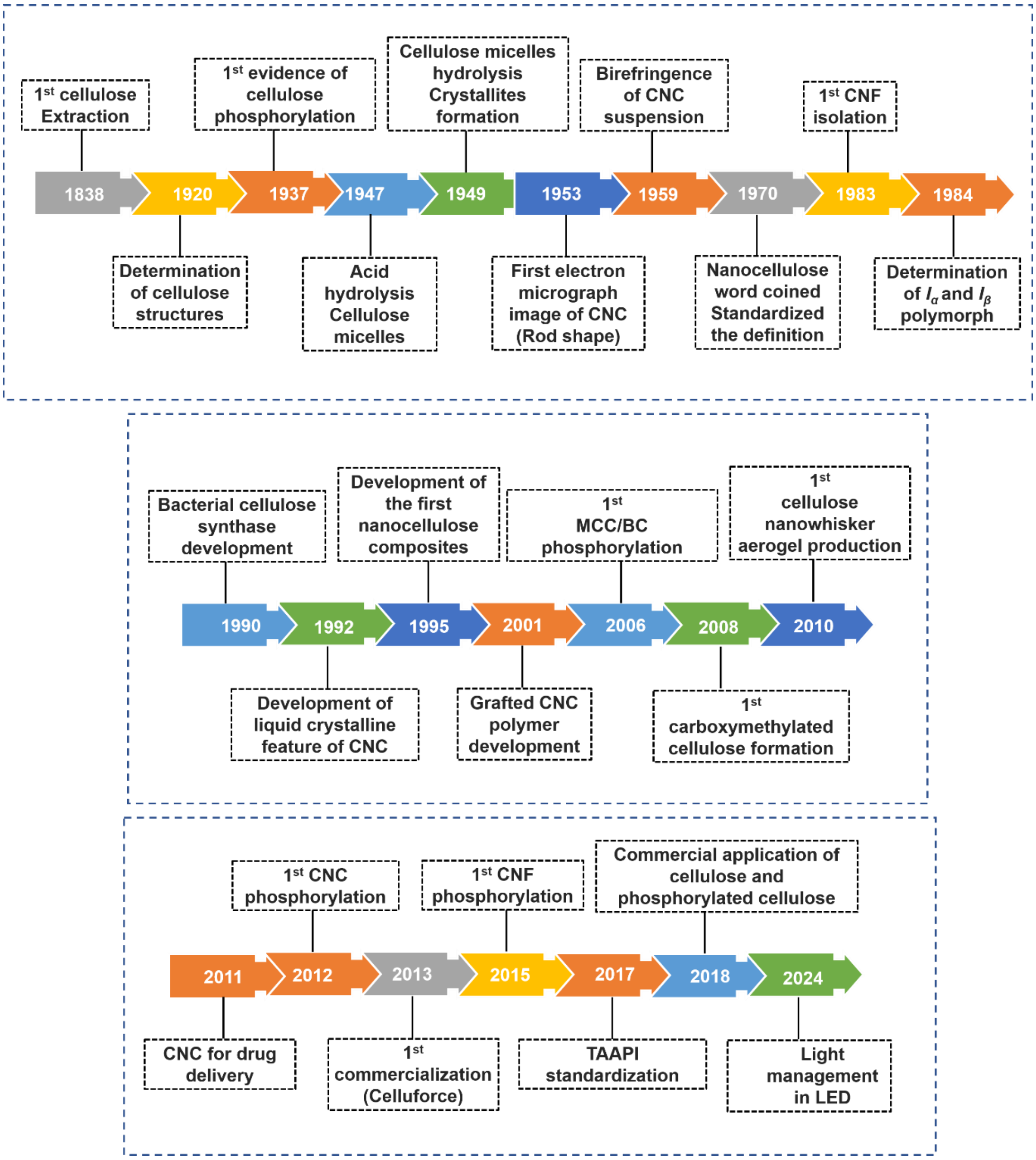


***Figure 1.1*** *Roadmap for the technological development in the field of cellulose and phosphorylated cellulose.*

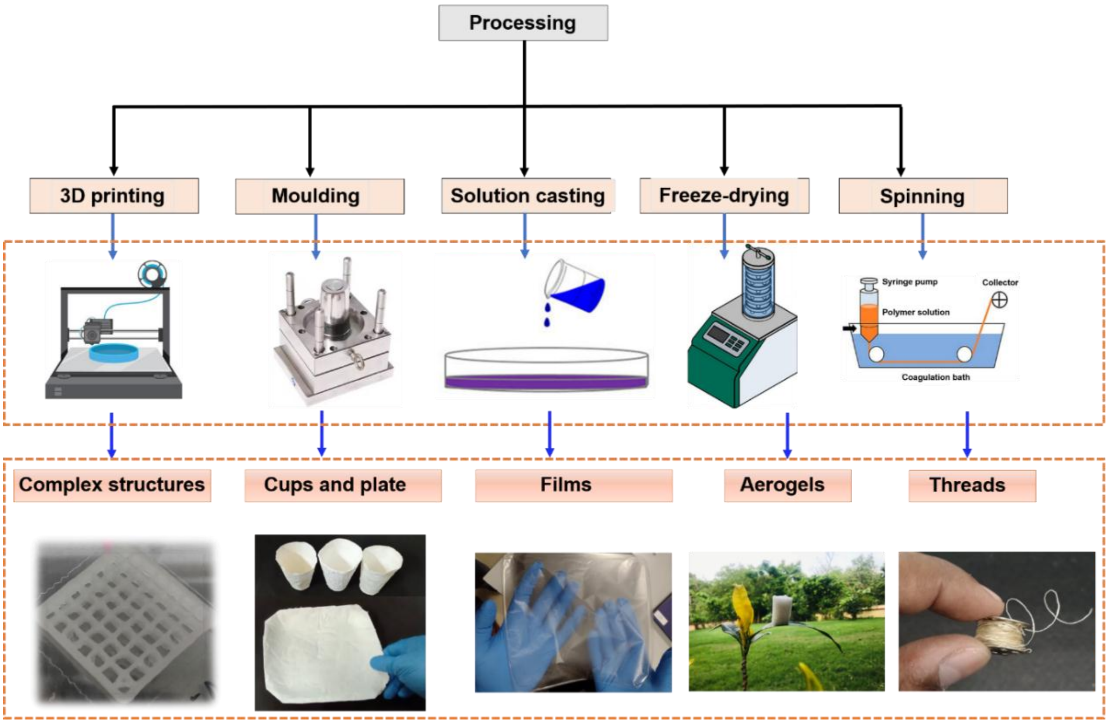


***Figure 1.2*** *Routes for the processing of cellulose for development of value-added products.*

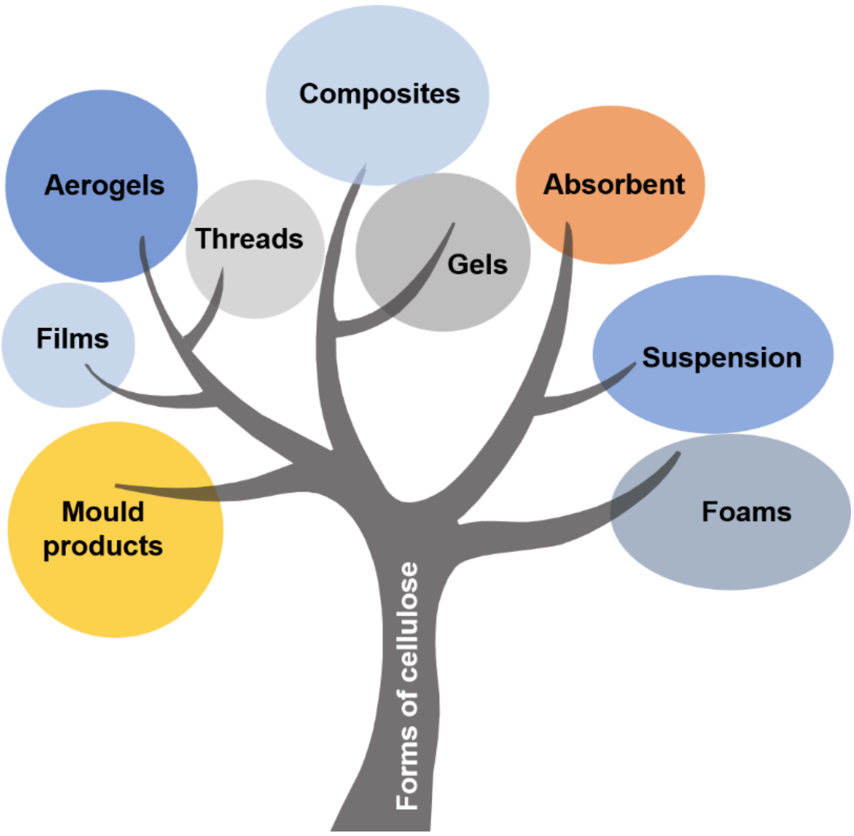


***Figure 1.3*** *Different forms of cellulose for targeted applications*

## 1.3 Traditional routes for MFC production

Out of variously utilized methods such as grinding, homogenisation, cryo-crushing, and micro-fluidization, dissolution, esterification, acid-hydrolysis, and oxidation. TEMPO-Oxidation is a widely utilised chemical process for chemical modification of cellulose to graft or add a negative charge. The methodologies for cellulose oxidation were first studied by Nooy et al.[62] The experiments were performed in very alkaline conditions with a pH range of 10-11, utilising NaBr as a catalyst and NaClO as primary oxidising agents at room temperature. In the TEMPO-Oxidation process, HCl is utilised to terminate the reaction and reduce their pH to a level of 7. The production of TEMPO-oxidised cellulose requires higher electricity demand, as reported by many researchers [63] [64] [65]. For example, Isogai et al. reported that the energy required to produce one ton of TEMPO-oxidised cellulose was 700 MJ/kg [63]. Syverdu et al. reported that producing one ton of TEMPO-oxidised cellulose required 10000 kWh under an applied pressure of 1000 bar [64]. In addition, Zhu et al. stated that the energy consumption for manufacturing oxidised cellulose was around 446 kilowatt-hours per metric tonne [65]. The manufacturing process of TEMPO-oxidized cellulose requires a significant amount of energy and involves very hazardous chemicals such as NaBr and HCl. Li et al., conducted LCA of TEMPO – oxidized nanocellulose and observed carbon foorprints than the carboxymethylation modification [66]. Arfelis et al., compared TEMPO oxidation of cellulose microfibers with the enzymatic modification and confirmed it to be a greener method than enzymatic modifications [67]. Consequently, this thesis reports a green and sustainable phosphorylation methods which is scalable with low environmental as evident from LCA studies. Only two chemicals, DAHP and urea, were utilised exclusively for the functionalization process, were readily accessible, cost-effective, and commonly employed in agriculture by farmers. The phosphorylation method or reaction is a simplistic approach, conducted at 150 °C for short durations of 15 minutes to 2 hours to funtionalized cellulose with tunable charge content. The life cycle assessment (LCA) of phosphorylated cellulose synthesis resulted in a comparatively reduced environmental effect compared to the TEMPO-oxidation method. Additionally, the phosphorylated cellulose manufacturing process is more environmentally sustainable due to its lower energy consumption and usage of eco-friendly chemicals.

### 1.4 Circular economy aspect of the thesis

This thesis presents a comprehensive method for using circular economy concepts by converting agricultural waste into valuable items for wastewater treatment and food packaging (***Figure 1.4***) as mentioned below.

**Resource Extraction from Agro-Waste:** Utilising agro-waste, the cellulose extraction process effectively repurposes, otherwise typically discarded as waste material. Utilising agro-waste as a resource, the thesis taps into a sustainable source of raw material, thereby reducing the strain on traditional resources.

**Closed-loop Production:** The process of extracting cellulose from agricultural waste initiates a closed-loop production cycle. Rather than being discarded, the waste material undergoes a transformation process to convert it into usable cellulose, which becomes the basis for further developments in material development.

**Transformation into Various Products:** Cellulose gels have versatile applications in producing various items, including films, cups, aerogels, and thermal insulation boxes, often employed for food packaging. By diversifying the product spectrum, the process maximises the value derived from cellulose and fulfils different market needs.

**Biodegradability and End-of-Life Management:** All manufactured materials presented in this thesis have been tested to be capable of being broken down by natural processes in soil, making them biodegradable. This feature guarantees that when the items reach the end of their lifespan, they can be returned to the environment without any harm, encouraging the replenishment of natural resources and completing the cycle in the circular economy.

To summarise, the thesis demonstrates the circular economy model by:

- Transforming waste products into valuable resources such as rice husk and sugarcane bagasse.
- Continuously upgrading and repurposing materials through various processes such as 3D-printing, moulding, solution casting, freeze-drying, and spinning.
- Diversifying end products to maximize utility such as films, foams, and composites in packaging, thermal box, and biocatalysts.
- Ensuring biodegradability to facilitate natural decomposition and minimize waste accumulation as well as LCA study has been carried out and processes are optimized to minimize the environmental impacts.

The thesis showcases a comprehensive strategy for implementing circular economy concepts. This is achieved by converting agricultural waste into valuable resources that can be used for treating wastewater and creating sustainable packaging. The research contributes to developing a more sustainable and regenerative economic model by focusing on resource efficiency, waste valorisation, farmer income and end-of-life issues

### 1.5 Alignment of thesis chapters with different UN-sustainable development goals

The Sustainable Development Goals (SDGs) were established by the United Nations in 2015 as part of the 2030 Agenda for Sustainable Development [68]. They serve as a worldwide plan for achieving a sustainable future. The 17 interconnected objectives strive to eradicate poverty, safeguard the environment, and promote universal prosperity.

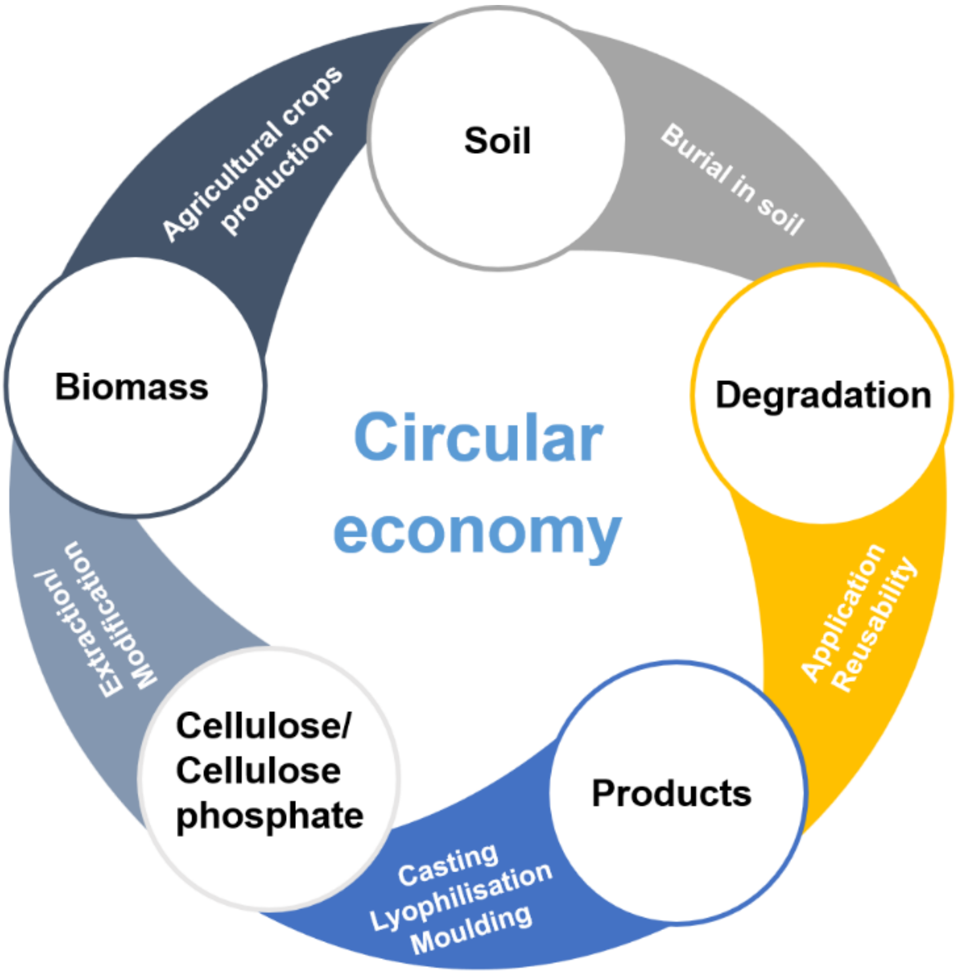


***Figure 1.4** Circular economy aspect of the thesis.*

The goals expand upon the Millennium Development Goals and tackle more extensive concerns such as climate change, inequality, and sustainable consumerism. The main themes encompass eliminating poverty, advancing health, guaranteeing high-quality education, achieving gender equality, nurturing sustainable cities, battling climate change, and preserving biodiversity. Attaining the Sustainable Development Goals necessitates the joint efforts and cooperation of governments, civil society, the commercial sector, and individuals globally. Hence, this thesis encompasses the execution of specific projects in each chapter to accomplish specific Sustainable Development Goals (SDGs) as elaborated in the subsequent section (***Figure 1.5***).

**Chapter 4** focuses on extracting cellulose from various agricultural biomass sources and modifying it *in situ* for scalable and continuous wastewater treatment applications. The prepared materiasl and composites demonatrate photodegradation of toxic dyes and pathogenic microbiota. This aligns with multiple SDGs, which encompass:

**SDG 6: Clean Water and Sanitation** - This chapter contributes significantly to SDG 6 by offering sustainable ways to improve water quality and sanitation by studying modified cellulose for wastewater treatment.

**SDG 12: Responsible Consumption and Production -** Using agricultural biomass to produce value-added goods rather than burning or disposing of it in landfills aligns with promoting sustainable consumption and production patterns, as outlined in SDG 12.

**SDG 14: Life Below Water -** The efficient removal of dyes from wastewater using modified cellulose contributes to SDG 14 by minimising water pollution and protecting marine ecosystems.

**SDG 3: Good Health and Well-Being -** By utilising modified gels, the remediation of pollutants from water sources plays a crucial role in achieving SDG 3. This approach helps in ensuring access to clean water and ultimately leads to improved health outcomes.

**Chapter 5** focuses on developing scalable phosphorylated gels from viscose cloth for 3D printing of grid-like structures for continuous, and cyclic methylene blue removal. In addition, the gels have been modified with $MoS_2$ to enhance their ability and reusability to adsorb and catalyse MB using sunlight. This chapter aligns with various Sustainable Development Goals (SDGs), such as:

**SDG 13: Climate Action -** Through the use of sustainable materials and environmentally-friendly practices for dye cleanup and chemical modification for cellulose, SDG 13 is advanced by minimising the impact of climate change and promoting eco-friendly activities.

**Chapter 6** and **Chapter 7** explore the application of rice straw and sugarcane bagasse waste in the production of food packaging films with heat sealable, and flame retardant propertiers as a potential replacement to PET film utilized commercially. Aerogel/thermal boxes with low thermal conductivity, biodegradability, and flame retardancy can serve as a potential replacement to non-degradable, heat-senstive polystyrene, and polyethylene boxes. This chapter is in accordance with the following SDGs:

**SDG 2: Zero Hunger -** The utilisation of rice straw waste and sugarcane bagasse in the production of biodegradable packaging contributes to achieving SDG 2 by mitigating food waste and promoting the use of environmentally friendly materials for packaging food and will improve farmer income.

**SDG 15: Life on Land -** Through the utilisation of agricultural waste for value-added products, this chapter makes a significant contribution to SDG 15 by advocating for sustainable land use practices and mitigating land degradation.

**SDG 12: Responsible Consumption and Production -** This chapter contributes to the target of fostering responsible consumption and production patterns outlined in SDG 12 by advocating for the utilisation of sustainable packaging materials obtained from agricultural waste. In general, the chapters of this thesis are in line with several (SDGs) as they tackle important environmental and social issues, encourage sustainable behaviours, and encourage innovative approaches to resource utilisation and waste management.

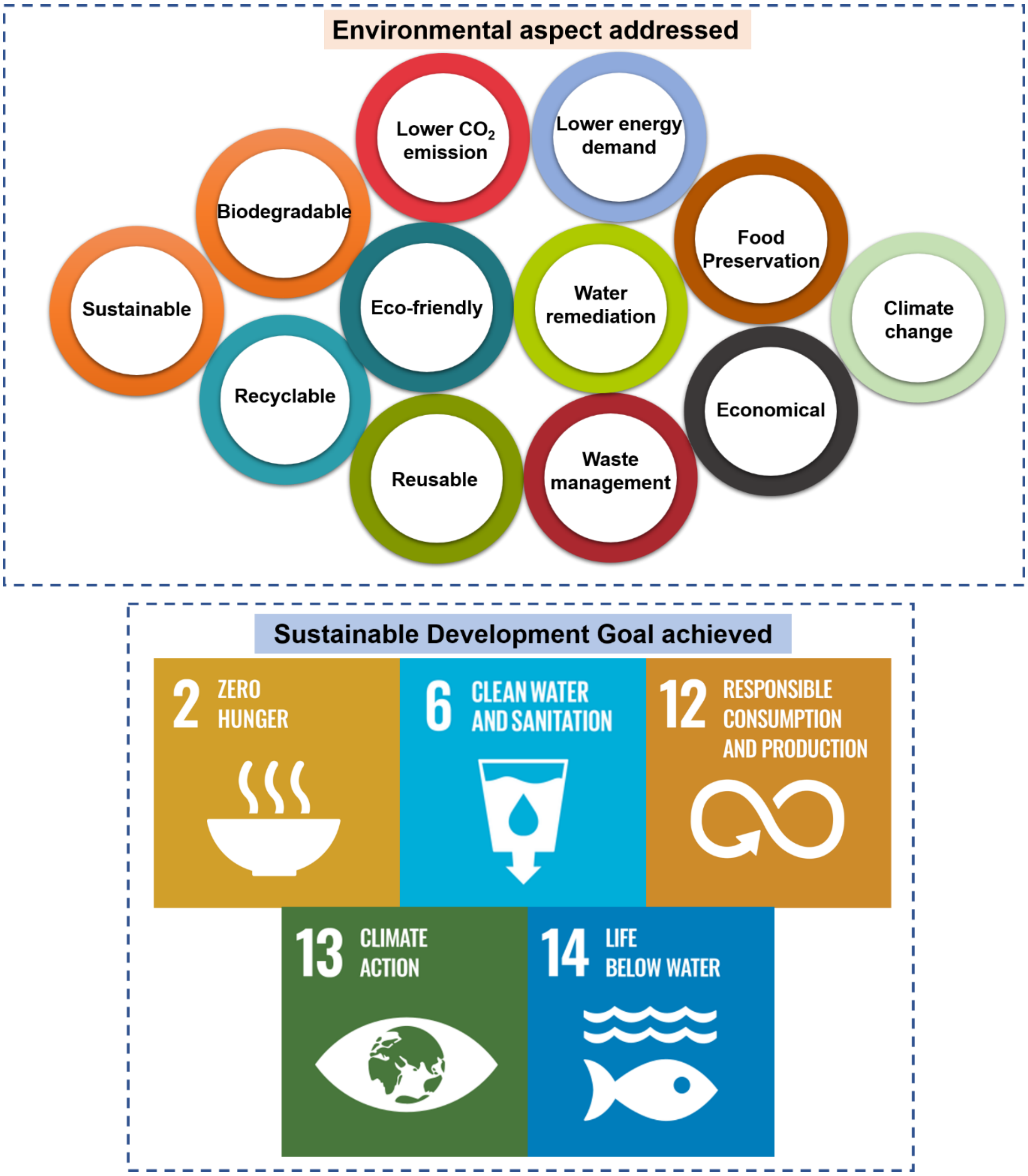


***Figure 1.5*** *Alignment of the thesis with different environmental aspects and SDGs.*

### 1.6 Scope and structure of thesis

In this thesis, various agricultural biomass such as rice straw, rice husk, and sugarcane bagasse have been utilized as sources of cellulosic precursors, utilising delignification and phosphorylation processing techniques. LC was conducted to compare the approach performed with the traditional processes to compare the environmental impacts. Traditionally, MFC is manufactured through various methods including acid hydrolysis [69], enzymatic hydrolysis [70], followed by distinct mechanical treatments such as blending [71], homogenisation [72], cryo-crushing [73], extrusion [74], and electrospinning [75]. The acid and base hydrolysis processes are time-consuming and utilize concentrated acid, which may sometimes lead to the degradation of the cellulose precursor itself and generates environmental toxicity. Enzymatic pre-treatment approaches involve selective hydrolysis processes that necessitate extensive optimisation for MFC production, reduced activity and poor recyclability of the enzymes. Most mechanical defibrillation methods documented in the literature are characterised by high energy consumption. For instance, the micro-fluidization process to produce 10 litres of cellulose (1-2 wt.%) demands 8.5 kW of power [76]. The TEMPO-oxidation techniques used for cellulose functionalization in the production of MFC involve the use of various chemical reagents, including NaClO, NaBr, and 2,2,6,6 tetramethyl-1-piperidinyloxy (TEMPO) under highly basic condition (pH of 10-11) [77]. Using multiple chemical reagents and the associated high costs render the entire process non-economical and less environmentally friendly. Furthermore, the production of MFC in an environmentally friendly manner involves using less energy-intensive mechanical processes and less harmful chemical reagents, including acids and bases. Achieving this goal with minimal reliance on mechanical defibrillation methods while ensuring higher yield and consistency, particularly using renewable agro-waste, becomes crucial due to variations in cellulosic sources. Furthermore, concentrated phosphoric acid (PA) is extensively utilized as an effective agent for the production of MFC, contributing to the production of both soluble and insoluble cellulose phosphate. This process yields cellulose phosphate with less than

10% phosphorus content and is responsible for the degradation of cellulose fibres. In the process of phosphorylation, phosphorus atoms can form covalent bonds with hydroxyl groups on the cellulose backbone, creating cellulose phosphate, cellulose phosphite, and cellulose phosphonic acid groups. In recent decades, attempts have been made to phosphorylate cellulose using molten urea and PA and an aqueous solution of urea and PA which has led to improved yields and the substitution of phosphate groups. Nevertheless, the acid-mediated approach for producing PC is undesirable due to the high processing costs and labour-intensive processes, which also result in polymer degradation [78].

In this thesis, simple, environmentally friendly, cost-effective, and energy-efficient methods have been developed to enhance the processability of cellulose obtained from agricultural waste via the phosphorylation process, utilizing easily, agro-based accessible di-ammonium hydrogen phosphate and urea. The developed process in this thesis enhances cellulose dispersibility, increases thermal stability, decreases flammability, improves gel yield, and enhances crosslinking capability and stability in water. Introducing anionic phosphate groups to MFC confers cation-exchange properties to cellulose phosphates, providing exceptional chelating characteristics to the polymer chains. This makes them advantageous for applications such as metal chelation, cation exchange, and adsorption in pollution treatment. Furthermore, the phosphorylation method produces gel that can be processed into complex shapes and structures, using additive manufacturing techniques such as 3D printing. The developed PC gels were processed with scalable technologies into aerogels, cups, and films, through freeze-drying, casting, and moulding techniques. The production of PC has been done with various sources; and the resulting environmental impacts or global warming potential during the production processes have been studied in detail and compared with commercially available TEMPO-oxidation. Production of transparent, flame retardant, heat sealable, and ultrasonic sealable packaging film has been performed in this thesis. The aerogels were also prepared which show flame-retardancy, thermal insulation, and mechanical stability that can be utilized as a suitable replacement to polystyrene boxes. The work also covers the development of solvothermal stable, water stable, and thermal insulating cups as a replacement to plastic, and *kulhad* cups used currently as well as developed fruit foams with their high thermal insulation, mechanical strength and flame retardancy can be utilized as a replacement to conventionally utilized polyethylene foams. Commercial and large-scale production of PC using an efficient, simple, and economical process is the need of the hour towards growing demand for applications in various sectors.

Therefore, this thesis focuses on utilising different agro-wastes to extract cellulose, their *in-situ* modification, and phosphorylation for high-performance applications. The cellulose extraction and phosphorylation of extracted cellulose have been performed using an industrially viable, scalable, and green approach. The strategic functionalization of cellulose resulted in the adsorption and degradation of dyes, the preparation of biodegradable films and aerogels for food packaging and the 3D printing of gels. The substantial findings from the conducted research are gathered in seven chapters (from chapter 2 to chapter 8). The structure of the thesis and the content of each chapter are briefly outlined in the next section ***Figure 1.6***.

Chapter 2 summarizes the literature related to cellulose and cellulose phosphate, and from this literature review and research gap, we have developed our research hypothesis.

Chapter 3 presents details of materials or chemicals utilized and a detailed description of the methodologies employed for extracting cellulose from various agricultural biomass sources. It also covers the phosphorylation of cellulose, *in-situ* modification of cellulose, and the analytical instruments utilized in conducting the research works.

Chapter 4 details the extraction of cellulose from sugarcane bagasse (SB) and rice husk (RH). The cellulose obtained from both SB and RH is utilised for its capacity to adsorb methylene blue and malachite green dyes. Furthermore, we subject the extracted cellulose (DSB/DRH) to modify with molybdenum salt, utilising a hydrothermal approach. The DSB- $MoS_2$ material exhibits adsorption capabilities for MB, while the DRH- $MoS_2$ material shows adsorption capabilities for MG. Furthermore, these materials demonstrate efficient photodegradation of MB and MG dyes in both batch and continuous modes. DRH-$MoS_2$ and DSB-$MoS_2$ demonstrate antibacterial properties against *Escherichia coli* and *Staphylococcus aureus*. The present study 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.

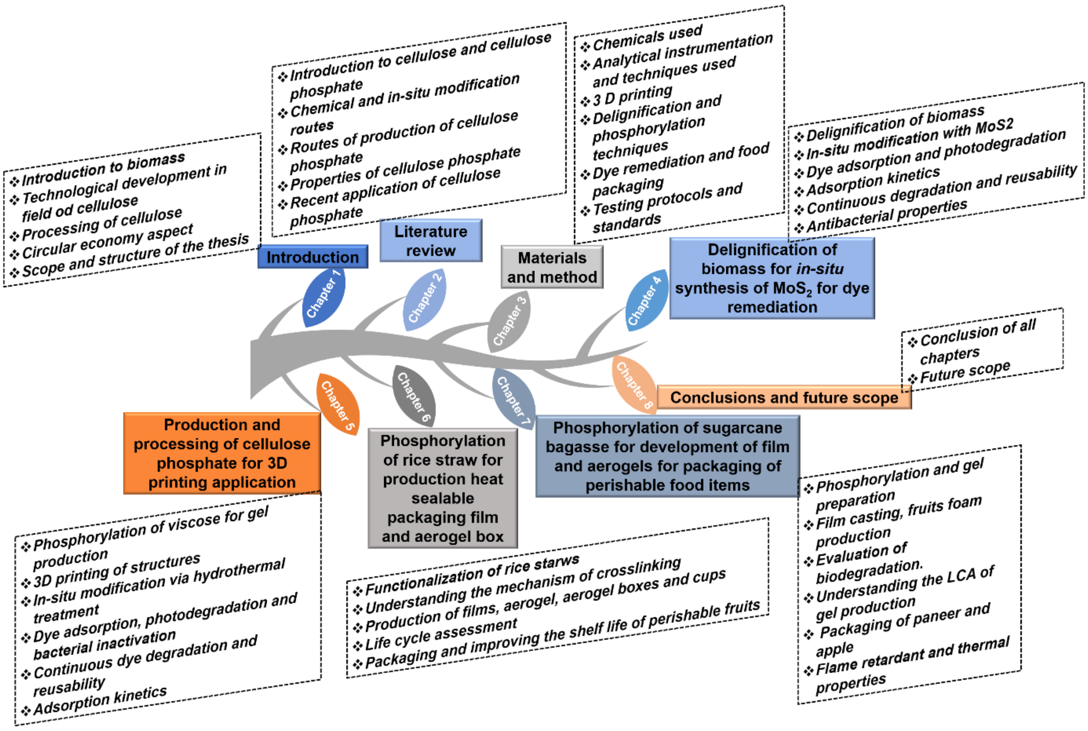


***Figure 1.6*** *Outline of the thesis with all the chapters and their contents.*

Chapter 5 presents a detailed description of using viscose cloth to produce gel *via* phosphorylation techniques followed by 3D printing of complex structures. The resulting phosphorylated gels were transparent and negatively charged with high consistency, charge content (CC), degree, and increased yield with high water absorption and swelling capacity. The life cycle assessment (LCA) shows that PC gel production via phosphorylation is more ecologically favourable than traditional TEMPO oxidation. The rheological studies of PC gels show shear-thinning behaviour with improved 3D printability followed by heat-induced crosslinking phosphate groups. The structures show improved MB remediation capabilities and more than seven times reusability. Moreover, an *in-situ* modification was carried out using $MoS_2$ to improve the adsorption capacity of PC and introduce photocatalytic and antibacterial properties. PCMo@0.5% exhibited an enhanced adsorption capacity and achieved a photodegradation efficiency for methylene blue. It also demonstrated potent antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. The PCMo@0.5% also showed simultaneous dye degradation and bacterial inactivation for high volume of wastewater representing its applicability in practical application in real wastewater. This work 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.

Chapter 6 detailed delignification and phosphorylation rice straw waste for developing food packaging films, cups, and thermal boxes. The phosphorylated films, boasting a high CC, demonstrate enhanced mechanical strength in dry and wet conditions and improved thermal stability and flame-retardant qualities, maintaining structural integrity post-burning. The chapter also thoroughly studied the mechanism of silica-phosphate cross-linkages during heating. Additionally, rice straw films are applied to store highly perishable fruits like apples, kiwi, and pears. Moreover, the development of biodegradable cups from rice straws is discussed, highlighting their favourable solvothermal stability, thermoregulatory capacity, and anti-fizzing properties. Furthermore, aerogels are also produced from rice straws and exhibit low thermal conductivity, excellent compressive strength, low density, and high porosity. Thermal boxes are also produced in this chapter and utilized for the storage of butter which can minimize the energy requirement during cold storage and transportation. The developed thermal boxes also show flame retardant and low thermal conductivity, which can replace PU or polystyrene foam, which are highly flammable and non-biodegradable. The LCA studies suggest that the production of thermal boxes generates relatively lower $CO_2$ emissions, confirming its sustainability over PU foam boxes. The proposed valorization of rice straws to packaging films, beverage cups, and thermal boxes with lower ecological impacts and commercial feasibility sustainable alternative with a native with the promising plastic-free world.

Chapter 7 provides a comprehensive overview of developing phosphorylated films, aerogels and fruit foams using sugarcane bagasse. The resulting films were transparent, mechanically strong, flame retardant, exhibited lower migration, and possessed thermal stability and biodegradability. These films, designed as food pockets, are effectively utilised for packaging paneer, improving the shelf life by upto 7 days. Furthermore, aerogels were transformed into fruit foam and modified with gallic acid, presenting a sustainable and biodegradable alternative for packaging apples compared to polyethylene foams. This proposed valorization of SB into films, fruit foams or aerogels presents a promising and eco-friendly alternative for food packaging, countering the environmental challenges posed by traditional plastic packaging.

Chapter 8 summarises the chapter's conclusion and highlights the important outcomes. Technical processes and products associated in each chapter. The effects of delignification time, temperature, and chlorite concentration on cellulose extraction from various agro-waste have been highlighted. The *in-situ* modification of DSB and DRH with improved adsorption properties, catalytic properties and antibacterial properties have been highlighted. The effects of different curing times on the phosphorylation of extracted cellulose from agro-waste have been comprehensively studied and compared with their native materials. The effects of curing time on CC, degree of substitution, further their effect on physiochemical, structural, mechanical, thermal, water absorption, swelling, migration of the products have been discussed in detail. The LCA of the production of phosphorylated cellulose and films from different agricultural sources and viscose has been extensively discussed and compared with the traditional TEMPO-oxidation method. Conclusions from the overall findings in the thesis, and recommendations are put forth for potential future research endeavours focusing on the creation of advanced functional materials based on chemical modification of cellulose with an emphasis on high-performance applications.


***Figure 1.7*** *Different products produced from modified cellulose in current thesis.*