Chapter-2

Literature Review

2.1 Introduction

Cellulose is one of the most abundant and renewable polymer resources available, and it has been widely recognised in the forms of fibres and derivatives for approximately 150 years as essential components in a wide range of everyday products [79]. Cellulose is widely present in several organisms, such as bacteria, plants, tunicates (marine animals), algae, and fungi, and has an estimated yearly production of 7.5×10^{10} tonnes [80]. Cellulose is a strong and durable material with a fibrous structure that plays a vital role in maintaining the integrity of plant cell walls. Anselme Payen was the first to discover cellulose and report it as a water-insoluble and hydrophilic biopolymer. Cellulose remains popular among the materials community because of its remarkable physiochemical properties and its inherent biodegradability, renewability, and abundance. It has been extensively researched as reinforcing agents in nanocomposites because of their tuneable aspect ratio, widespread availability, sustainability, affordability and lightweight nature with tuneable shape and dimensions [79].

Cellulose is a linear biopolymer comprised of *D*-glucose monomeric units linked together by β-1,4 glycosidic bonds, and every other unit exhibits a 180° turn. The number of monomeric units is highly dependent on the source from which cellulose has been extracted, and degree of polymerization may range from 500 to 20000 units [79]. The structure of cellulosic chains is composed of reducing and non-reducing ends. The bond formation in cellulose is influenced by the non-reducing end of the glucose

units, specifically at the *C1* position (anomeric carbon), resulting in the formation of *β*-1,4 glycosidic linkage. At the same time, the aldehyde group is located at the reducing end of cellulose [81]. The *β-D*-glucopyranose rings typically adopt a $^{4}C_{1}$ chair conformation, in which the -OH groups are positioned in the equatorial plane of the ring and the hydrogen atoms in the axial direction. The structural integrity of the cellulosic network is maintained *via* an intramolecular hydrogen bonding network that stretches from the *O(3')-H* hydroxyl group to the *O(5)* ring oxygen of the adjacent unit through the glycosidic linkage and from the *O(2)-H* hydroxyl group to the *O(6')* hydroxyl group of the next residue [79]. The hydrogen bonds between and among the neighbouring cellulose chains significantly impact the physiochemical properties such as reactivity, hydrophilicity, and crystallinity [82].

There are six distinct polymorphs of cellulose: cellulose *I, II,* III_I, III_{II}, IV_I, and IV_{II} (***Table 2.1***). Plants and bacteria naturally contain Cellulose *I*, but the other kinds are synthesised through chemical processes. The cellulose *I* polymorph can be divided into two different allomorphic forms known as I_α and I_β, yet the distribution of these forms varies across plant species. The I_β allomorph of cellulose is the most common and abundantly present in lignocellulosic biomass derived from plants. Cellulose I_β belongs to the monoclinic $P2_1$ (space group) unit cell and has two cellulose chains per cell. The cellulose I_α, on the other hand, is a member of the triclinic P_1 (space group) unit cell and has one chain per unit cell [83]. Generally, cellulose *II* is produced by a mild NaOH treatment process from cellulose *I*, which leads to the generation of the $P2_1$ subspace group with monoclinic crystal structures [84]. Each unit cell has two antiparallel cellulose chains, which are more stable than the parallel chain present in cellulose *I*. Cellulose III_I and III_{II} are synthesised from cellulose *I* and *II* using liquid

ammonia as a chemical reagent at -80 °C. Cellulose III_I has a monoclinic crystal structure with one parallel cellulose chain per unit cell, similar to cellulose *I* but in a different conformation. However, the crystal structure of cellulose III_{II} is still unidentified or unexplained [83].

Table 2.1 *Representing the crystal structure, dimensions, and angle of different polymorphs of cellulose.*

Unit cell	***a (Å)***	***b (Å)***	***c (Å)***	***α (°)***	***β (°)***	***γ (°)***
Cellulose I_β	7.78	8.20	10.38	90	90	95.5
Cellulose I_α	6.72	5.96	10.40	118.8	114.8	80.38
Cellulose *II*	0.81	9.03	10.31	90	90	117.1
Cellulose III_I	4.45	7.85	10.31	90	90	105.1
Cellulose III_{II}	4.45	7.64	10.36	90	90	106.96
Cellulose IV_I	8.03	8.13	10.34	-	-	-
Cellulose IV_{II}	7.99	8.1	10.34	-	-	-

Both cellulose III_1 and III_{II} regain their original structure when exposed to boiling water. Furthermore, cellulose IV_I and cellulose IV_{II} were prepared from Cellulose III_I and III_{II}, respectively. A thermochemical treatment method was used in the synthesis process of cellulose *IV* with the aid of hot glycerol at 260 °C [79]. Gardiner et al., 1985 proposed that cellulose IV_1 had an orthorhombic crystal structure, with two cellulosic chains forming each unit cell. The cellulose IV_{II} structures were reported to have a similar size to cellulose IV_I but had different conformations [85]. The cell wall of a plant contains fibrils of cellulose chains with a diameter in the nanometre (nm) range. These fibres bundle together to form microfibrils, and their dimensions increase from nm to micrometres (µm) [86]. On comparison of mechanical properties of different polymorph, cellulose *I* show a maximum elastic modulus than other polymorphs. Cellulose *I* have a maximum tensile modulus of 137 GPa while cellulose

II, cellulose *III*, and cellulose *IV* have a maximum tensile modulus of 88 GPa, 87 GPa, and 75 GPa, respectively, mainly due to the considerable inter and intramolecular hydrogen bonding variation. Each polymorph's *f*-value (force required to stretch the molecules by one degree) also differs. For example, cellulose *I* require 4.4 dynes of force, while others need a force of 2.87 dynes, 2.95 dynes, and 2.45 dynes for cellulose *II*, cellulose *III*, and cellulose *IV*, respectively [87]. Based on the properties mentioned above of different polymorphs of cellulose, it can be used in bioethanol production [88], pharmaceutical industries [89], paper and pulp industries [90], hydrocarbon and water separation [91].

2.2 Sources of cellulose

Cellulose can be classified into many categories based on its source of origin, such as (i) wood cellulose, (ii) plant cellulose, (iii) algal cellulose, (iv) BC, and (v) animal cellulose (specifically from tunicates). Wood cellulose and plant cellulose are the most widely used types of cellulose in the long history of cellulose utilisation. This is mostly owing to their abundant availability and affordability, in contrast to BC, tunicate cellulose, and algae cellulose [80]. Depending upon the sources of cellulose, crystallinity, percentage of cellulose, the size and properties of the crystal vary [2]. In the section below, various sources of cellulose have been briefly discussed.

2.2.1 Wood sources

Wood has a hierarchical structure with pores in the cell wall ranging from the nanoscale to microscale in the woody stem. Biopolymeric components such as cellulose, hemicelluloses, and lignin present in the plant cell wall provide rigidity to the wood which integrate to form a fibril-based composite material. The properties of wood

are influenced by the orderly arrangement of cellulose fibrils within the matrix of lignin and hemicellulose [92]. Wood contains both crystalline and non-crystalline cellulose microfibril bundles. These bundles comprise elementary fibrils with a diameter of about 3 nm. Wood is composed of various cell types at cellular and tissue levels in different proportions depending on the tree species. For example, more than 90% of the wood portion is tracheid in softwood. These tracheid characteristics, such as cell diameter and cell wall thickness, vary depending on their specific functions [92]. Tracheid with larger diameters and thinner cell walls are known as "earlywood," whereas tracheid with smaller diameters and thicker cell walls provide mechanical strength and are known as "latewood." Hardwoods evolved at a later stage of evolution with specialized cell types to perform specific functions. Hardwoods use vessels for efficient water transport and fibers for increased mechanical strength. This evolution has given hardwoods a competitive advantage over softwoods in various climate zones. The open interiors, or lumina, of tracheid, vessels, and fibres form the hierarchical porous structure of wood. The diameters of these lumina range from a few μm to about half a millimetre. Furthermore, the structure is defined by μm-sized pits extending through the cell walls and nanometre-sized pores located between the cellulose fibrils within the cell walls. The lumina of vessels, tracheid, and fibers in plants are primarily oriented lengthwise at the microscopic level. Furthermore, on the nanoscale, cellulose nanofibrils within cell walls are aligned parallel to the cell axis but at different angles (usually ranging from 0 to 60°) depending on the tissue type and layer. Additionally, when the polymer matrix is partially or completely removed, the gaps between the cellulose nanofibrils form nanopores with a similar alignment to those of the cellulose nanofibrils. Cellulose chains are organised in a linear arrangement at the microscopic level. This unique

hierarchical structure, distinguished by different scales of pores, provides advantageous routes for the simultaneous movement of ions, molecules, gases, solid particles, and liquids, facilitating efficient transport. Cellulose can be derived from several sources, including softwood such as pine (38.7%), cedar (39.3%), and spruce (48%), as well as hardwood such as oaks (43.2%) and beech (36.3%) [53,93,94].

2.2.2 Plant sources

Plants are the primary cellulose source, including sugarcane, banana, potato, rice, hemp, flax, corn, and so on [95,96]. Cellulose content varies across biomass sources, with bamboo containing 40-55 %, barley straw 31-45 %, switch grass 45 %, hemp 70-75 %, peanut 49 %, jute 60-65 %, and sugarcane bagasse 40-50 %. Cotton is considered as a pure form of cellulose (90%) than wood since it includes very little or a negligible fraction of non-cellulosic components [81]. The cellulose present in wood and plants exhibit an intricate structure characterized by numerous hierarchical levels. They are linked to other polymers, such as hemicellulose and lignin. Although cellulose in wood and plants shares the same chemical composition, it displays a unique microstructural arrangement. Wood and plant cells contain cellulose chains organized into densely packed layers called nanofibrils that are bound together by a matrix made up of hemicellulose and lignin. Nevertheless, cotton fibre, despite being classified as a form of plant cell, does not contain substantial quantities of lignin or hemicellulose.

2.2.3 Bacterial sources

BC is a biomaterial with outstanding characteristics, such as high cellulose purity, mechanical strength, crystallinity, biodegradability and FDA approved [97]. BCs are also called as microbial cellulose and bacterial NC which has increased interest

in its possible use in the food industry and biomedical applications. BCs have traditionally been utilized as a raw component in Asian cuisine preparations. For example, Kombucha tea is a fermented beverage in northern China. During the fermentation of Kombucha tea, BC supports the growth of acetic acid bacteria and yeast. Nata de Coco is a Philippian beverage where BC is fermented in coconut water [98]. Brown, in 1886, reported the production of BC from *Acetobacter xylinum* using glucose as a carbon source under aerobic conditions [99]. Unlike cellulose generated from plants or other sources, BC does not produce lignin, hemicellulose, or pectin; thus, additional purification and extraction techniques are not required, making the entire production process economical, simple, and eco-friendly [33]. BCs have a high degree of polymerization (typically 7000 to 16000) and a high degree of crystallinity (80% to 90%). The diameter of the nanofibers obtained from BCs ranges from 20 to 100 nm. Furthermore, BC-derived cellulose nanocrystals have lengths ranging from 100 to 1000 nm and widths ranging from 10 to 50 nm. On the other hand, plant CNFs have fibre lengths exceeding 1000 nm and diameters ranging from 3 to 100 nm. Many studies have been performed on the production of BC using aerobic bacteria such as *Komagataeibacter sucrofermentas* [100], *Achromobacter strain ES 001* [101], *Rhizobium* [101], *Pseudomonas aeruginosa* [102], *Agrobacterium tumefaciens* [103], *Acetobacter xylinum* [104], *Komagataeibacter xylinus* [105], and *Komagataeibacter nataicola* [106]. *Komagataeibacter sp.* is a widely utilized and studied bacterial strain for BC production, as it can utilize a range of carbon and nitrogen sources under aerobic fermentation conditions. Under optimum fermentation conditions, BC is synthesized as the porous cytoplasmic membrane matrix's primary product in nanofibrils. These nanofibrils then aggregate to create ribbon-like structures with diameters ranging from

70 to 150 nm. Produced BC forms a thick gel that has more than 95% water content. Bacteria at the air-water interface first create pellicles during the static aerobic culture of BCs. Furthermore, the pellicle evolved into thin films and thickens with time. Under the agitated fermentation condition, BC formed as spheres or pallets of variable shapes, sizes, and masses with poor crystallinity and mechanical properties [107]. Toxicological studies show BC intake has no teratogenic, embryotoxic, or reproductive adverse effects [108]. Due to the above-mentioned properties, BC are largely utilized in the biomedical field for wound dressing, bone tissue engineering, and scaffolds [97]. Some other important applications of BCs are in the pharmaceutical, food, cosmetics, fuel cell, sensor, facial mask, contact lens, and stereo headphones [97,104,106,109].

2.2.4 Tunicate sources

Cellulose can also be obtained from animal sources, particularly from marine invertebrates. The most reliable and abundant supply of tunicates can be found in Prince Edward Island, Canada. Tunic tissues, found in marine invertebrates known as tunicates i.e., *Ciona intestinalis* [110], and *Styela clava* [111], acts as skeleton structure and are useful as internal organs [111]. Tunicates produce cellulose from outer tissues from which pure cellulose (*tunicin*) can be extracted. Fibrils in the tunicates attached parallel to the epidermis in multi-layered fashion and its length ranges between 100 nm to few μm and width ranges between 5 to 30 nm. Tunicates commonly composed of 60% cellulose and 30% nitrogenous compounds. Tunicin produced after the treatments from tunicates resembles $C_{I\beta}$ allomorph which has high crystallinity. Cellulose extracted from tunicin has a high aspect ratio (90 ± 57) [111] as well as a specific surface area of 150–170 $m^2 g^{-1}$ [112]. However, plant cellulose is typically found in the form of long, linear chains that assemble into microfibrils. These microfibrils further

bundle together to form macroscopic structures like fibers, giving plants their structural integrity. Plant cellulose fibres are larger in size, with microfibrils and nanofibrils ranging in diameter from 3 to 10 nm, and length greater than 1000 nm. Degree of polymerization of plant cellulose and animal cellulose ranges between 10000-20000 and 700-3500, respectively [80]. Plant cellulose is well-known for its exceptional mechanical properties. Plant cellulose microfibrils have a hierarchical arrangement which adds to their exceptionally high tensile strength and stiffness, allowing them to maintain structural integrity and stability. Tunicate cellulose, despite being composed of nanofibrils, exhibits significant strength, especially in relation to its dimensions. Tunicate cellulose nanofibrils have impressive mechanical properties regardless of their small dimensions. The elastic modulus of plant fibres (cellulose) ranges from 5-130 GPa, with tensile strength of 300-1050 MPa and elongation of up to 8%. However, the elastic modulus of tunic cellulose ranges from 60-220 MPa and tensile strength of 7500-7700 MPa [80].

2.2.5 Algal sources

Algal sources such as *Ulva lactuca* [113],(27) *Valonia ventricose* [114], *Eremosphaera viridis* [115], *Gelidium elegans* [116], and *Micrasterias denticulate* [117] have the potential to produce cellulose and NC. Usually, chemical, and mechanical processes are used to extract cellulose and NC from algae by breaking down the cell wall with an aspect ratio of more than 40, and its types vary with algal sources. The cellulose derived from algae is not completely pure because it contains protein molecules, lignin, and hemicellulose. Algal cellulose displayed various morphologies, such as fibrillar, net-like, and gel-like whereas plant cellulose fibres exhibit a greater degree of organisation and crystallinity. In general, plant cellulose has a greater degree

of polymerization, ranging from 1000 to 15000, compared to algae, which typically ranges from 2500 to 4300. Both algal and plant cellulose have comparable dimensions, with a length greater than 1000 nm and a width ranging from 5 to 30 nm [80].

2.3 Types of cellulose

Extraction of cellulose from primary sources involve a range of chemical and mechanical techniques. The Technical Association of the Pulp and Paper Industry (TAPPI) has established a standard (WI 3021) for defining cellulose and cellulose nanomaterials based on size. Cellulose can be further categorised into groups such as microfibrillated cellulose (MFC), nanofibrillated cellulose (CNF), cellulose nanocrystals (CNC), and BC, depending on its shape, size, and morphology. Chemical processes utilise acids, alkali, oxidising agents, enzymes, and ionic liquids, while mechanical processes involve grinding, homogenisation, cryo-crushing, ultrasonication, and micro-fluidisation [2,118].

2.3.1 Microfibrilliated cellulose

MFCs are commonly characterised by their elongated, flexible, and intricately shaped structure. It is achieved through a mechanical process that entails a rapid breakdown of cellulose pulp through shear and tear forces. Methods commonly utilised to produce MFCs are grinding, homogenisation, cryo-crushing, and micro-fluidization [118]. Turbak et al. and Herrick et al. attempted to physically break down softwood sulphite pulp under high pressure to produce MFCs in 1983 [8]. The method, however, created microfibrils but could not remove them from plant cell walls [119]. Taniguchi et al. attempted to produce MFCs in 1996 using a super grinder to disintegrate fibres as small as 100 nm. Still, this study could not determine the aspect ratio and size

distribution of the produced product. Generally, MFCs have a width of 10-100 nm and a length of 0.5-50 µm [39]. Recently, Kumar et al. isolated MFC from pine leaves and incorporated halloysite nanotubes to develop ethylene-scavenging paper. The composite paper showed a maximum contact angle of 64° and a water vapour permeability of 5.5 × 10−3 g/cm^2/day. Additionally, it demonstrated an ethylene scavenging efficiency of approximately 80% showing its potential application in active packaging [120]. Guan et al. created a piezoelectric nanogenerator using MFC, polyvinyl alcohol, and lead zirconate titanate, achieving 16.5 V in open-voltage and 0.86 µA in short-output current, with a sensitivity of 0.3168 V·kPa^{-1}. The nanogenerator detects facial and chest pressure waveform and generates a quick response in 54 ms [121]. Shen et al. in their recent study, developed MFC-based laminate composites with sodium borate via hot press technique which have shelf-cleaning properties with maximum contact angles of 152° with 6498 MPa elastic modulus [122]. Recent research demonstrates the range of uses of MFC-based materials and their adaptability in improving functionality across industries, from ethylene-scavenging paper for active packaging to piezoelectric nanogenerators that detect pressure waveforms and laminate composites with shelf cleaning properties.

2.3.2 Nanofibrilliated cellulose

Agricultural feedstock are the primary sources for cellulose production, and mechanical treatments are usually applied for the extraction processes. Grinding, cryo-crushing, homogenization, ultrasonication, ball milling, micro-fluidization, and steam explosion are well-known mechanical processes for CNF extraction (***Figure 2.1***). All mechanical processes are known for their high shear and tear forces, which aid in the breakdown of cellulosic fibres and their transformation into nano-fibrillated form.

CNFs are materials composed of nanoscale cellulose fibrils with a remarkably high aspect ratio. Typically, these fibrils have diameters ranging from 5 to 100 nm and lengths that extend over several μm [123]. These materials have crystalline and amorphous regions, resulting in remarkable flexibility. CNF can be produced through mechanical processes, regardless of any prior treatment they may have undergone. Enzymatic treatment, TEMPO oxidation, and mechanical defibrillation are widely employed methods for isolating CNF. Following the delamination process, a gelatinous dispersion of CNFs is formed in water. This dispersion exhibits a spaghetti-like structure, with a width between 20 and 50 nm and a length extending to several microns [124].

2.3.3 Cellulose nanocrystals

The first CNC was produced in 1949 by Rånby et al. *via* acid hydrolysis of cellulose fibres. Amorphous portions of cellulose are highly accessible to acid hydrolysis; however, crystalline portions are less prone to acid hydrolysis. Hydrolysis of the amorphous region could be achieved either by HCl or H_2SO_4. However, the suspension produced by HCl hydrolysis is not stable due to the unavailability of surface charges, whereas, in the case of H_2SO_4, the cellulosic surface gains negative charges due to the presence of ester sulfate groups [125]. Sulphuric acid is commonly used to hydrolyze the amorphous portion of the cellulose, and the remaining residue will be in crystal forms. Dong et al. also reported that CNC's length and surface charge depend on the hydrolysis extent. The higher the time of hydrolysis, the smaller the CNC size, and the higher the charge on the cellulose surface [126]. These methods help produce crystal like cellulose with sulphate groups intact on their surface. CNC has a spherical, rod or needle-like morphology with diameter ranging between 3-20 nm, length 100-

500 nm, and L/D ratio greater than 5. The nanowhisker's morphology, shape, and size depend on the source of cellulose and the preparation method.

2.3.4 Microcrystalline cellulose

MCC, obtained by subjecting α-cellulose to hydrolysis with hydrochloric acid, experiences partial depolymerization [127]. This process breaks down cellulose's amorphous (disordered) parts, forming smaller, more ordered particles like MCC that can be easily broken down by hydrolysis. MCC is highly compatible with active pharmaceutical ingredients due to its physiological inertness, ease of handling, biodegradable properties and reliable availability [80]. MCC typically consists of spherical or rod-shaped particle sizes ranging from 10 to 200 µm. MCC can obtained from diverse sources, including softwood, hardwood, and cotton [128]. It provides numerous benefits, including biodegradable properties, low aspect ratio, and high mechanical properties. Moreover, it possesses low density, impressive elastic modulus, thermal resistance and is exceptionally suitable for use as a filler in bio-composites [129]. Furthermore, MCC's substantial surface area and internal porosity enhance its capacity to maintain structural integrity in wet conditions.

2.4 Strategies of cellulose modification

Cellulose can be modified in two ways: (i) physical modification using non-covalent bonding and (ii) chemical modification using covalent bonding.

2.4.1 Physical modification of cellulose

Physical modification of cellulose can be achieved through non-covalent interaction of surfactant (cationic, anionic, or nonionic surfactants) macromolecules and block copolymers.

2.4.1.1 Adsorption

Cellulose surface modification can be accomplished *via* simple physical adsorption in which compounds such as surfactants, nanoparticles, and polymers adhere to the surface of cellulose through interactions such as hydrogen bonding, electrostatic attraction, weak van der Waals forces, and hydrophilic affinity. Several surfactants have been adsorbed onto the surface of cellulose such as cetyltrimethylammonium ammonium bromide, amphiphilic block copolymer (Pluronics) [130], dodecyl trimethylammonium bromide [131], and alkyl naphthalene condensate sulfonate [132]. The interaction of surfactant hydrophobic ends with cellulose hydrophilic ends results in the entrapment or absorption of hydrophilic residues into the cellulose matrix. As a result, the dispersion of cellulose increased, improving the mechanical properties of the generated composites. These surface phenomena reduce surface energy, promoting cellulose dispersion in the matrix and increasing interfacial contact. The performance of the modified cellulose will depend on the concentration and types of surfactants. However, excess amounts may hamper cellulose's physical integration and mechanical properties due to the plasticizing effect. For example, Mariano et al. utilized eucalyptus pulp to produce CNF foam using cationic surfactants such as dodecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, and tetradecyltrimethylammonium bromide. Mixing surfactants decreases zeta potential (35 to -8 mV) and enables hydrophobic interactions with surfactants on the surface of CNFs [133]. The surface modification of cellulose through physical adsorption offers a versatile approach for enhancing its dispersion and mechanical properties in composite materials, although careful consideration of surfactant concentration and type is necessary to avoid potential negative effects on integration and performance.

2.4.1.2 Absorption

Absorption is another approach of physical modification where small macromolecules get absorbed onto the cellulose surface. Due to numerous free hydroxyl groups in the cellulose structure, modifiers such as polyethene glycol and polyethylene oxide strongly bind to those -OH groups, and the binding affinity of the macromolecules to cellulose will depend on the molecular weight. For example, Lin et al. created a composite paper utilizing PEO and cellulose (amidated form) to improve nanogenerators' triboelectric characteristics and charge density. The presence of amino groups in the cellulose paper resulted in significant improvements in voltage, current, and power density upto 222.1 V, 4.3 μA, and 217.3 mW/m^2, respectively [134]. Cellulosic forms including MFC, CNC and CNF due to its high surface area with abundant hydroxyl group thus serve as interesting avenues for its modification *via* absorption.

2.4.1.3 *Ex-situ* and *in-situ* modification of cellulose

The fundamental requirement of cellulose modifications is to tune its physical and chemical properties based on the desired application Modification of cellulose can be further divided into two categories, (i) *in-sit*u and (ii) *ex-situ* cellulose modifications. [100].

In-situ modifications involve incorporating polymeric materials, additives, or chemical compounds into a culture medium of BC or adding nanoparticles onto the other forms of cellulose [135]. In the case of BC, these additives are directly incorporated into the fermentation medium to enhance the morphological, chemical, functional, mechanical, and physical properties of the produced NCs. Many studies

have been reported for the *in-situ* modification of cellulose using carboxymethyl cellulose [136], xanthan gum [60], polyaniline [138], ionic conducting polymer [139], PEG [140], β-cyclodextrin [141], hydroxypropyl methylcellulose [142], paraffin microspheres [143], deacetylated chitin nanocrystals [144], pectin, xyloglucan [60], and aloe vera [145]. For example, Wang we al., in their study, produced BC *via in-situ* modification using hyaluronic acid and silk sericin. The resulting BC composites had outstanding mechanical and swelling properties, were extremely porous, and had a crystallinity of 88.4 % [146]. Beekmann et al. utilized PEG as a modifier, supplemented in BC growth medium, which improved the thickness of BC from 3.5 to 5.5 mm, resulting in 41% transparency and enhanced biocompatibility [147]. Cellulose microfibers can be modified *in-situ* modification by incorporating different nanoparticles directly onto their surface or within their structure.

Different nanoparticles such as silver oxide, graphene oxide, molybdenum disulphide (MoS_2), titanium dioxide, and zinc oxide have been widely studied with cellulose for different applications. The crystal structures of MoS_2 nanomaterials can be classified into three unique phases: *1T*, *2H*, and *3R*. The physicochemical features of MoS_2 nanoparticles are diverse, encompassing excellent catalytic, photoluminescent, optical, and sensing capabilities. Their unique 2D structure and phase transition give rise to these features. The characteristics of MoS_2 nanomaterials are often affected by their number of layers. The diversity in layers can influence their possible applications and their interactions with toxins. Due to active catalytic sites, large surface area, photocatalytic, semiconductor, electronic, and optical properties, MoS_2 has gathered huge attention in the last decade [148]. The synthesis of MoS_2 can be achieved by a range of procedures, such as the hydrothermal method employing molybdenum salts

and thiourea, ball milling and sonication techniques from bulk MoS_2, and the dry ball milling process [149]. Hydrothermal-based approaches are widely used for the *in-situ* production of MoS_2 on cellulosic materials. Numerous investigations have been conducted employing hydrothermal methodologies to facilitate the *in-situ* growth of MoS_2 onto porous cellulose structures and improve wastewater remediation. In their study, Gopalakrishnan et al. employed a hydrothermal method to fabricate a hybrid material comprising MoS_2 nanosheets deposited over cellulose filter paper infused with graphene. A unique adsorbent was designed to remove MB from solutions, producing an adsorption capacity of 485.4 mg/g of MB [150]. In their study, Zhao et al. successfully synthesized nanosized MoS_2 using nanofibrous cellulose microspheres for removal capabilities for heavy metals, with approximately 80% of Pb^{+2}, and for organic dyes, a removal capacity of approximately 327.6 mg/g for Congo red. In addition, extensive research has been conducted on the antibacterial properties of MoS_2, leading to its effective use in decontaminating wastewater from harmful microbes [151]. Shen et al. created a composite BC, MoS_2, and chitosan composite material with a 99.9% reduction in *E. coli* and *S. aureus* when exposed to visible light due to photoinactivation properties [152]. The exceptional properties of MoS_2 nanomaterials, derived from their distinct 2D structure and phase transitions, offer great potential for various applications, including catalysis, sensing, and environmental remediation. MoS_2 and cellulose substrates as composites provide effective wastewater treatment solutions, demonstrating remarkable adsorption and photodegradation abilities. In addition, the remarkable antibacterial properties exhibited by composites containing MoS_2 highlight their promising application in addressing microbial contamination in water systems.

The most frequent and simple *ex-situ* physical modification technique is absorption, in which the modifier is trapped in the porous matrix of BC or plant cellulose. The presence of free hydroxyl groups in the cellulose structure allows for hydrogen bonding to favour the modification between cellulose and the absorbed compounds. Common polymers used such as BC modifiers include chitosan, hydroxyapatite, polyvinyl alcohol, poly (3-hydroxybutyrate), starch, benzalkonium chloride, soy protein, silver sulfadiazine, gelatine, PEG, polyaniline, and nanoparticles. There are many reported benefits of *ex-situ* modification of BC with plasticizer, such as improved mechanical properties, permeability, water retention, capacity transparency, antimicrobial, antioxidant, thermal properties, and biocompatibility [109]. In their study, Santos et al. explored two different methods to modify the surface of BC using [4-butyltrimethylammonium]-xylan chloride polyelectrolyte. Polyelectrolytes were introduced into the culture media of BC for the first modification, while polyelectrolytes were added to purified BC for the second modification. The composites exhibited reduced crystallinity and shine while showing increased roughness, high porosity, and burst indexes due to their closed surface, preventing airflow [153]. Both *in-situ* and *ex-situ* modifications offer diverse avenues for enhancing the properties of cellulose-based materials, catering to specific application requirements. *In-situ* modifications provide direct control over cellulose properties through the incorporation of various additives during synthesis, leading to improved mechanical, chemical, and functional characteristics. On the other hand, *ex-situ* modifications offer simplicity and versatility, allowing for post-synthesis alterations through absorption of modifiers into the cellulose matrix.

2.5 Chemical modification

Cellulose has abundant free hydroxyl groups in its structure, and one free hydroxyl group is present at position *C6* and is designated as a primary hydroxyl group. In contrast, hydroxy groups at positions *C2* and *C3* are secondary hydroxyl groups [154]. Hydroxyl groups present at position *C6* and position *C2* of adjacent cellulose units are hydrogen bond donors to the water molecules. In contrast, hydroxyl groups at position *C3* are hydrogen bond acceptors from water molecules but donors to the oxygen positioned at *C5*. Chemical modification of cellulose can be achieved through polymer grafting or functionalization of free hydroxyl groups available *via* covalent bonding. Different routes for chemical modification of cellulose induce negative or positive charges, which are as follows: carboxylation or oxidation, phosphorylation, sulfonation, carboxymethylation, and amidation which have been discussed in detail. Cellulose and its derivatives are widely recognised for their hydrophilic properties, making them particularly prone to moisture absorption. Polymer grafting is another chemical functionalization technique in which hydrophobic compounds are covalently grafted onto cellulose's surface, improving the hydrophobic properties and silanization is the most common technique. Surface modification techniques, such as polymer grafting, can greatly enhance the native properties of materials. This includes improvements in swelling, mechanical strength, hydrophobicity, adsorption, antibacterial properties, and biocompatibility. These enhancements can greatly enhance the overall customer experience across a wide range of applications. It is possible to graft cellulose, particularly on the primary and secondary hydroxyl groups of *D*-glucose. There are two main categories for grafting of cellulose: grafting-*from* and grafting-*to*. When polymerization initiates from the cellulosic surface, the resulting grafting process is

referred to as grafting-*from* [79]. Using the grafting from strategy involves growing a polymer chain through surface-initiated polymerization. This can be done either from a substrate that has a functional group capable of starting a polymerization reaction, or from a substrate that can immobilise the active initiator on its surface. Using the *grafting-to* method, a previously grafted substrate can be attached to cellulose or its derivatives, or a previously formed polymer may be attached to a new cellulose surface [155]. Using the *grafting-to* method is advantageous as it allows for utilising numerous reactive free hydroxyl sites on MFC and end-functionalized polymer. One advantage of *grafting-to* is the opportunity to analyse the grafted polymers before their attachment to MFCs, enabling precise control over the length of the polymer graft. Another factor that can restrict grafting is steric hindrance, which occurs when long-chain polymers become entangled or when diffusion of polymer chain ends to the MFC surface is hindered [156].

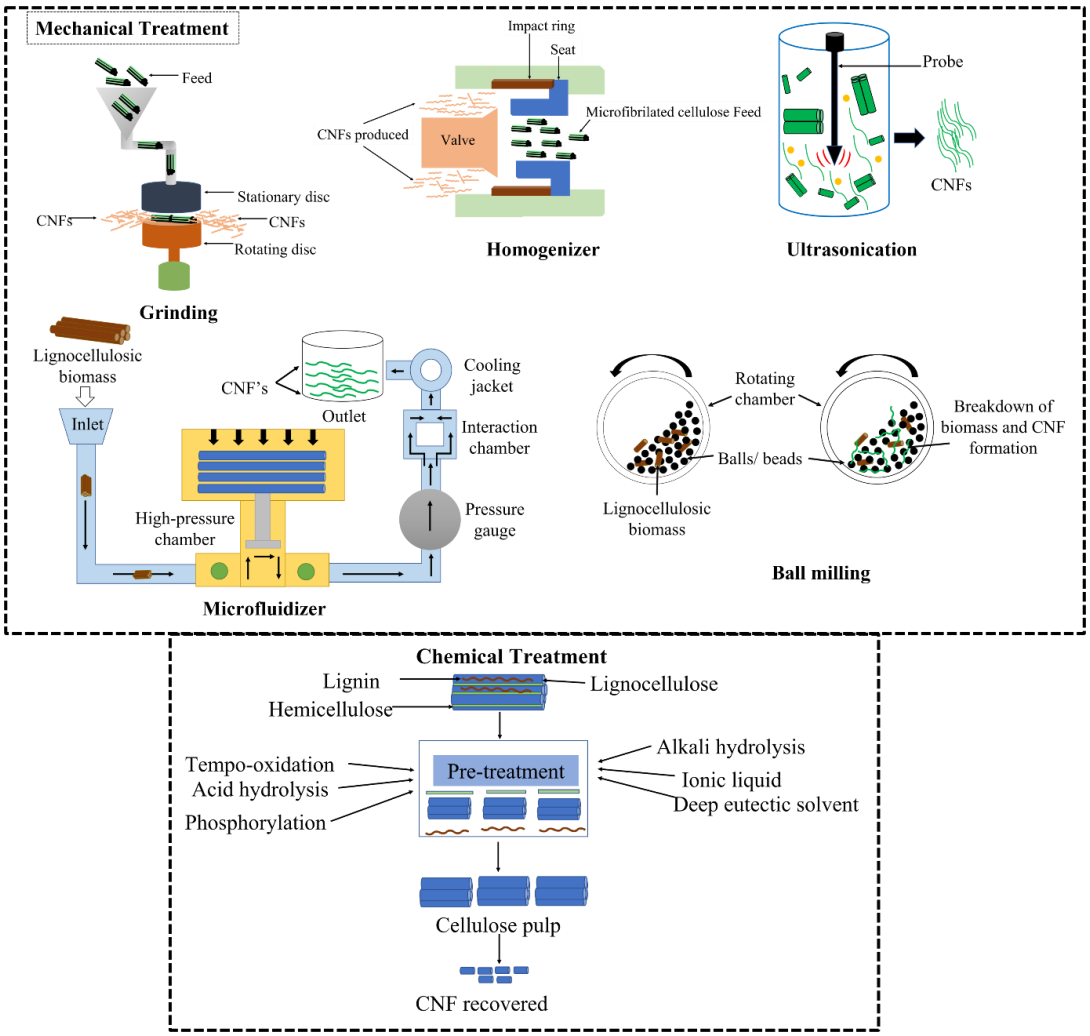

Figure 2.1 *Routes for the production of nanocellulose from different physiochemical and mechanical routes.*

2.5.1 Oxidation

Oxidation is the most common type of chemical modification, including replacing the free hydroxyl group at *C6* of *β*-1,4-anhydrous-*D*-glucopyranose into carboxylic groups. Oxidised NC or CMFs are used in tablet formulation, cosmetics, paper production, filler, or reinforcing material for composite developments. The chemical hydrolysis of cellulose and its derivatives, mediated by 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), is the most popular and widely used chemical approach for surface modification. Oxidation of NC or MFCs occurs in the aqueous

phase utilizing TEMPO, NaClO, NaBr, and HCl. In the first stage, NC/MFC is mixed into an aqueous TEMPO-NaBr solution, and then NaClO is added to initiate the reaction at pH 10. The free hydroxyl group at *C6* converted to the carboxylic group during the reaction (***Figure 2.2***). The amount of NaClO utilised during oxidation influences the number of carboxylic groups generated in the cellulose structure. The degree of polymerisation of cellulose decreases as the amount of NaClO increases [157]. The surface of NCs/MFCs retains a negative charge after oxidation, increasing electrostatic repulsion and swelling. Barbash et al. employed organosolv reed pulp to generate NC using TEMPO. Oxidation was performed at pH 10 in the presence of NaClO, NaBr, and TEMPO. Tensile strength (70 MPa), CC (1.18 mmol/g), and density (1.51 g/cm^3) of the generated NC increase with increasing TEMPO concentration and degree of oxidation, although crystallinity falls dramatically (78.8 to 64.9 %) [158]. Zhou et al. used two cellulose sources to create oxidised CNC (kraft pulp and MCC). The catalysts TEMPO, NaBr, and NaClO were used in the reactions, which were performed at room temperature with constant stirring and pH 10 before being caveated by ultrasound. CNC made from kraft pulp (width 3.6 nm) has a higher yield and CC (1.5- 1.74 mmol/g) than MCC [159]. In their study, Bakkari et al. used TEMPO oxidation to produce CNF from hardwood pulp. The CNFs produced had a density of 1.27 mmol/g and a width of 10-20 nm [160]. Another chemical agent used for the oxidation of NC is ammonium persulfate. It is an economical, eco-friendly, water-soluble oxidising agent widely used for surface modification of NC. Persulfate is highly sensitive to heat and high. Therefore, it is converted into $SO_4^{\bullet-}$ radical, and these radicals take part in polymerisation with another radical present. It is a single-step oxidation process of cellulose or other materials. Filipova et al. utilised kraft pulp in

their work to produce CNF *via* ammonium persulfate oxidation. The reaction proceeds with the addition of mechanically treated ammonium persulfate HCl at 60 °C for 4 hours. Lastly, the reaction was terminated by adding cooling water washed with distilled water, producing CNFs of 20-300 nm diameter [161]. The chemical modification of cellulose through oxidation, particularly utilizing TEMPO, NaClO, NaBr, or ammonium persulfate, offers a versatile means of enhancing its properties for various applications. Advantages of these methods include their effectiveness in generating carboxylic groups, controlling polymerization, and producing materials with tailored characteristics such as increased tensile strength and controlled crystallinity, thus expanding the potential utility of cellulose-derived materials in fields ranging from biomedicine to advanced materials science.

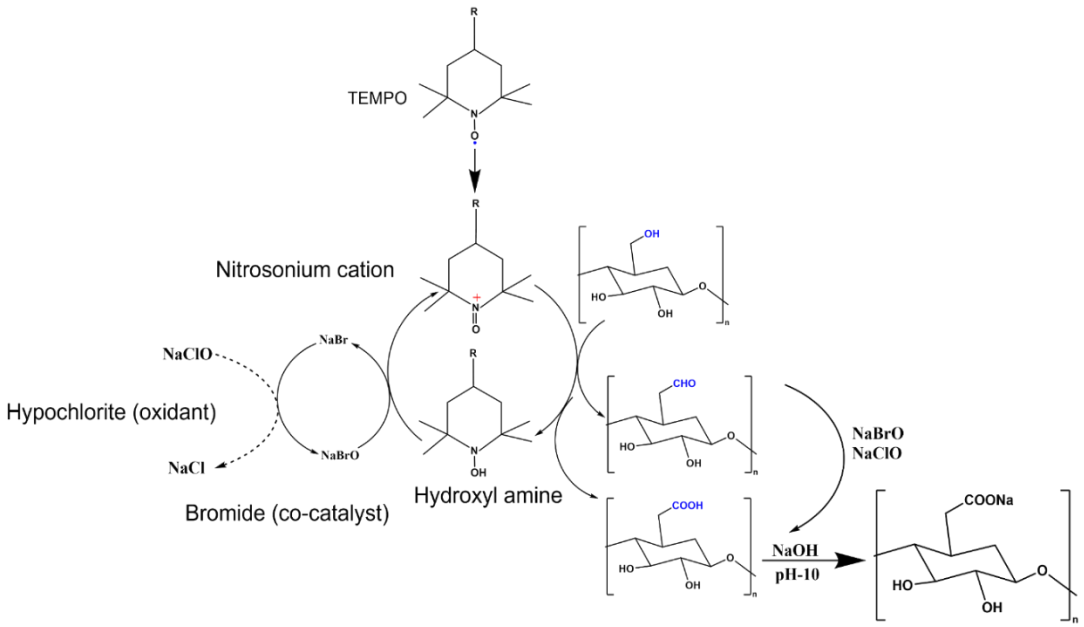

Figure 2.2 *Mechanism of TEMPO-oxidation for production of nanocellulose.*

2.5.2 Sulfonation

Sulfonation is a simple and single-step chemical modification technique in which the free hydroxyl group present at *C6* of *β*-1,4-anhydro-*D*-glucopyranose is replaced by negative sulphate half-ester groups shown in ***Figure 2.3***. This modification is primarily accomplished by hydrolysing NCs/CMFs with Sulphuric acid. The dispersibility of cellulose and its derivatives are enhanced by adding negatively charged sulphate half-ester ions because these ions prevent the formation of intramolecular hydrogen bonding [162]. This modification also aids in forming a stable colloidal suspension by preventing the formation of agglomerates [163]. Sulphuric acid, chloro-sulfonic acid [164], sodium vinyl sulfonate, and sulfamic acid [165] are commonly used chemical reagents for sulfonation of NCs/MFCs. Sulfonation using Sulphuric acid is a widely used and more economical route for developing sulfonated cellulose. This method was first used in 1993 by Wagenknecht et al. [166]. Sulfonated NCs have recently been used to produce highly charged CNFs [167], electrolyte membranes for fuel cells [168], and electronic skin [169], as well as heavy metal adsorption (Cu^{+2} or Cr^{+4}). Poor thermal stability is one of the main problems with sulfonation, which prevents it from being used to produce nanocomposite materials [170]. Sirviö et al. used sulfonation to create highly charged CNFs in their study using urea and sulphamic acid with the addition of cellulose and mixed at an initial temperature of 80 °C followed by curing at 150 °C for 30 minutes. The NCs produced had a width of 4 nm and sulphate charge content of 3 mmol/g [167].

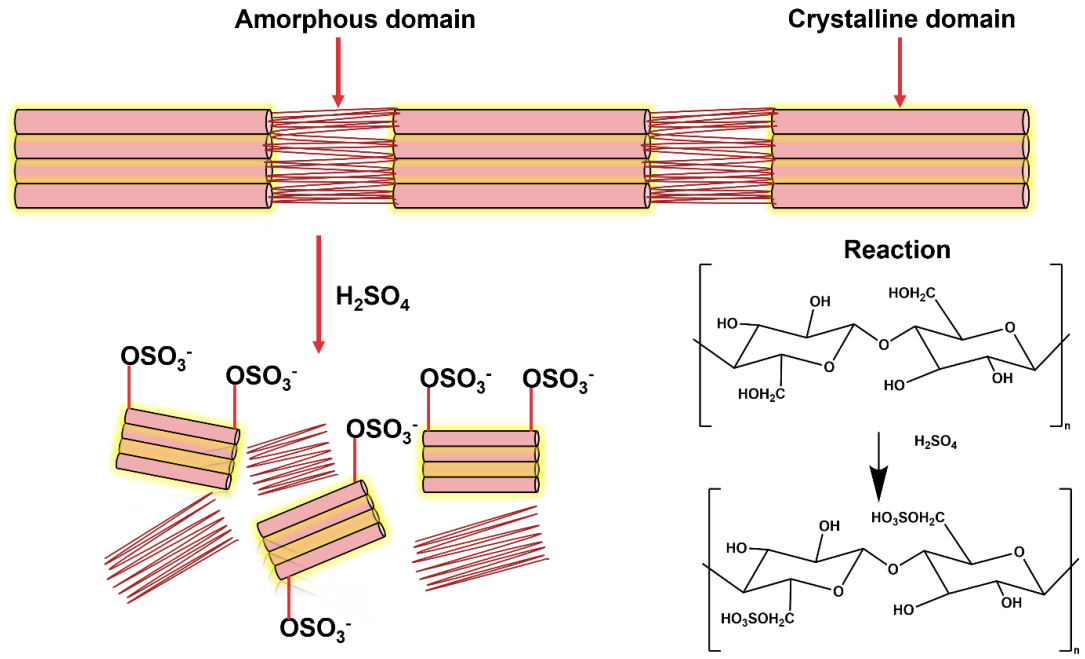

Figure 2.3 *Mechanism of cellulose hydrolysis with sulphuric acid for the sulfonation of cellulose.*

2.5.3 Carboxymethylation

Carboxymethylation is one of the oldest surface modification techniques developed in the early 20th century by Wagberg et al. for synthesising CNFs. The synthesis process included a series of different processes, such as chemical treatment (monochloroacetic acid, sodium hydroxide) and mechanical treatment [171]. It is a straightforward charge modification technique in which the free hydroxyl group present at *C6* of *β*-1,4-anhydro-*D*-glucopyranose is replaced by carboxymethyl groups, resulting in decreased crystallinity region (***Figure 2.4***). Sometimes, hornification also takes place, which reduces efficiency of carboxymethylation due to formation of irreversible hydrogen bonding [172]. Carboxymethylation was also found to change its structure from cellulose I to cellulose II. During preparation, fibres were the first ion exchanged in organic solvent and then immersed in monochloroacetic acid and NaOH (catalyst) aqueous solution for half an hour [173]. This modification may take place at

both primary and secondary hydroxyl groups of NCs [174]. A chemical reagent used to produce carboxymethylated NCs is monochloroacetic acid and acetic acid in the presence of HCl [175]. Several solvents have also been used for the carboxymethylation of NCs, such as propanol, ethanol, methanol, and NaOH. Introducing carboxymethyl groups onto the NC surface enhances its dispersion ability in organic solvent, further improving swelling and water uptake properties. Chen et al. created carboxymethylated CNFs using cotton fabric by first soaking the textile in NaOH, followed by 3 hours of reaction time monochloroacetic acid. After the reaction, the textiles were cleaned three times with water and dialysed to remove impurities. The process shows a high yield of 98 % carboxymethylated CNFs with aspect ratios ranging from 32 to 340 and a maximum DS ranging from 0.13 to 0.70 [176]. Wei et al. used cotton pulp and wood to create CNFs with a tree-like structure using monochloroacetic acid to produce carboxymethylated CMFs with high DS of 0.35 and fibre diameter of 35 nm.

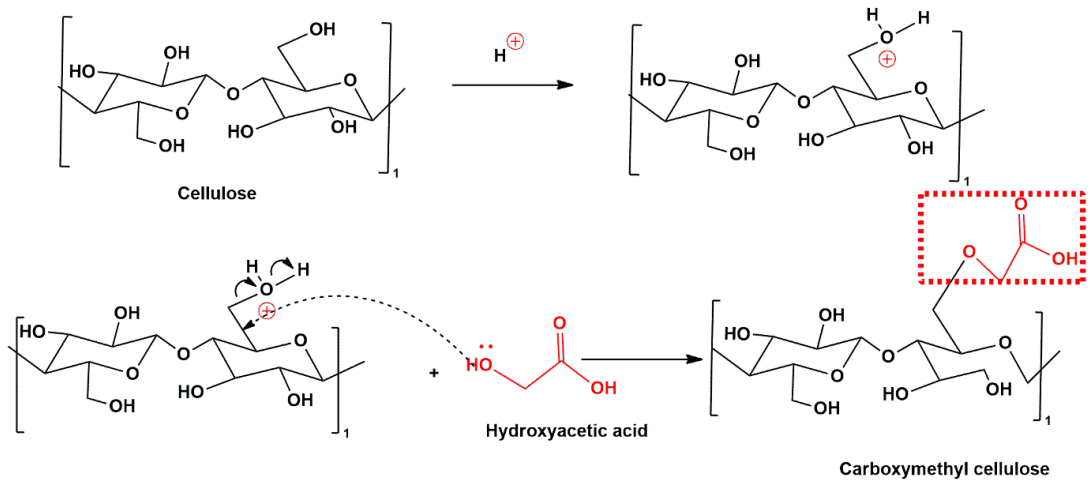

Figure 2.4 *Routes for the production of carboxymethylated cellulose*

In conclusion, carboxymethylation stands as an established technique for surface modification of cellulose, offering a straightforward method to introduce

carboxymethyl groups onto cellulose fibers, thereby altering their properties. Advantages of this technique include enhanced dispersion ability in organic solvents, improved swelling, and water uptake properties. However, challenges such as hornification and structural changes from cellulose I to cellulose II may affect efficiency. Application-wise, carboxymethylated cellulose finds utility in various fields including textiles, papermaking, and biomedical applications due to its enhanced properties and compatibility with organic solvents. Further research and development are warranted to address challenges and expand the scope of applications for carboxymethylated cellulose materials.

2.5.4 Amidation

Amidation is another surface modification process which have been widely studied recently to carry out the coupling reactions. It is a two-step process that includes TEMPO-oxidation followed by amidation of -*COOH* groups. In the TEMPO-oxidation free hydroxyl groups of the NCs positioned at *C6* of *D*-glucose get modified by carboxylic groups then amidation is carried performed on -COOH groups. Numerous coupling agents have been used to amidate cellulose, including N-(3-dimethylamino propyl)-N′-ethyl carbodiimide (EDC), N-hydroxysuccinimide (NHS) [177], undecyl- and dodecylamine, and undecylamine and dodecylamine [178]. Carbamide groups are the most commonly used chemical agents for amidating cellulose. Carbodiimide-containing compounds react with the carboxylic functional groups of other compounds to form an aminoacyl ester intermediate, which improves the coupling efficiency between carbodiimide with the -*COOH* and -NH_2 functional groups. However, the process is very slow, temperature- and pH-dependent. Gomez et al. recently reported using a "one pot" approach for amidation in their study. TEMPO-oxidized CNFs were

continuously mixed with dodecylamine, octadecylamine, DMF and *O*-(*1H*-Benzotriazol-1-yl)-*N,N,N′,N′*-tetramethyluronium tetrafluoroborate solutions for 2 hours at room temperature [179]. Recently, Gars et al. performed amidation on TEMPO-oxidised CNC with EDC-NHS, resulting in 0.05 DS [177]. Jaimes et al. synthesised amidated CNC by treating them with dodecyl- and octadecylamine, resulting in a DS of 0.21. The synthesized amidated CNC was utilized as a demulsifying agent, which efficiently break down a 55% water-heavy crude oil emulsion with a 74% water recovery [180]. Yamato et al utilized 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride to amidate polyalkylene glycol modified TEMPO-oxidised CNC resulting in 40-60 substitution of carboxyl groups which further increased to ~ 80 on addition of promoter 4-methylmorpholine [181].Cellulose amidation has been applied for oil-water separation, composite and film preparation in the recent years.

2.5.5 Silanization

Silainization is widely studied and simple surface modification techniques make cellulose surface hydrophobic. Silanization reduces the polarity of the cellulose surface and increases thermal stability. A large number of salinizing agents have been studied for hydrophobic modification of cellulose including silane, tetraethyl ortho silicate [182], 3-aminopropyltriethoxysilane [183] hexadecyltrimethoxysilane [184], glycidyl methacrylate grafting [185], [N-(*β*-aminoethyl)-*γ*-aminopropyltrimethoxysilane and bis-(3-triethoxysilylpropyl) tetrasulfide [186]. Methods that have been extensively studied for salinization are (i) dipping, (ii) sol-gel, (iii) chemical vapour deposit [182,187], (iv) plasma treatment, and (v) atomic layer deposition Polysiloxane-containing compounds are commonly used salinizing agents primarily consisting of

three functional groups: sulfhydryl, double bond, and fluorine. The fluorine functional group of siloxane plays a crucial role in reducing the surface energy of cellulose. Ahuja et al. created superhydrophobic foam from jute bags in their study. CNFs were extracted from the used jute bag first, then cellulose suspension was prepared using the freeze-drying method. Furthermore, the salinization technique modified the surface of the foam (dip coating). Hexadecyl trimethoxy silane and tetraethyl-orthosilicate were used as the salinization agent which led to formation hydrophobic foam 151° contact angle. Furthermore, foam was used to separate motor oil and diesel with a maximum efficiency of 98 % and 97 %, respectively. In their study, Akhlamadi et al. created an environmentally friendly, super hydrophobic aerogel from used tissue paper. To make CNC, tissue paper waste was first treated with NaOH, then mechanically mixed, bleached with $NaClO_2$, and hydrolyzed with acid (Sulphuric acid), followed by hydrophobic aerogel production using siloxane. Developed superhydrophobic aerogels were then utilized for the separation of oil and organic solvent with a maximum sorption rate of 69−168 g/g with ~90% reusability and with ~90% of shape recovery (compressive strength) [182]. CNC is used in developing superhydrophobic aerogel due to its high surface area, low density, high porosity, and good mechanical strength due to their structural reinforcement [182]. The versatility and effectiveness of silanization in modifying cellulose for superhydrophobic applications highlight its potential for addressing environmental challenges and advancing sustainable technologies across diverse industries. Continued research and development in this field are essential for optimizing performance, scalability, and expanding the range of applications for cellulose-based superhydrophobic materials.

2.5.6 Phosphorylation

Introducing phosphate moieties to the cellulose structure is a vital approach for developing a wide array of phosphate derivatives from cellulose. A reaction with hydroxyl groups allows phosphorus atoms to be covalently attached to the cellulose backbone, forming cellulose phosphate, cellulose phosphite, and cellulose phosphonic acid groups. The most frequently used phosphorylating agents are phosphoric acid [188], phosphorous acid [189], DAHP [190], ADP 169], phosphorus trichloride [191], phosphoryl chloride, tetra phosphorous decaoxide, phosphorus oxychloride, and di-propyl-hydrogen phosphate urea [192]. Phosphorylation of cellulose using DAHP and urea prevents cellulose degradation and improves the dissolution and swelling property, easing the penetration of the phosphorylating agent. According to Patoary et al., as curing time increases, the degree of phosphate ion substitution decreases gradually due to substrate degradation and hydrolysis of the pre-existing phosphate-ester bond. At temperatures above 150-160 °C, urea evaporates, reducing the amount available for swelling. As a result, the fibres start to dry out and degrade [193]. Phosphorylation improves some of the inherent properties of the NCs: swelling properties, flame retardancy, hydrophobicity, water retention capacity, mechanical properties, water dispersibility, and antioxidant and antibacterial properties. Phosphorylated cellulose can be used to produce materials such as aerogel, hydrogel, film, composites, and materials for additive manufacturing. Cellulose phosphate has been widely studied for different applications such as wastewater treatment, drug delivery, supercapacitor [23], lithium recovery [194], CO_2 separation [195], anti-corrosion inhibitor [196], tissue engineering[19] and flame retardancy [197].

2.6 Different routes for the production of phosphorylated cellulose

Phosphorylation of cellulose has been performed with different reagents, including acids, salts, ionic liquids, deep eutectic solvents, and enzymes in the recent years. The physiochemical properties of phosphorylated cellulose although having the same chemical modification, vary significantly depending on the phosphorylation strategy and cellulose source as discussed in the section below and ***Table 2.2***.

2.6.1 Acid derivative

Concentrated phosphoric acid **(*Figure 2.5*(b))** is extensively utilised as an effective agent for phosphorylation, contributing to the production of both soluble and insoluble cellulose phosphate. However, this process yields less than 10 % phosphorus content of cellulose phosphate. In 1949, Reid and colleagues developed phosphorylation techniques using phosphorus oxychloride to introduce phosphate groups to cotton fabrics, enhancing their flame-retardant characteristics. However, this process degraded the cellulose backbone, resulting in a reduction of the mechanical properties of the fabrics by almost 50 % [198]. In 1956, Touey et al. outlined a methodology for producing water-soluble and viscous cellulose phosphate with charge content of 2-13% by utilizing P_2O_5, phosphoric acid and liquid alcohol at 20-30 °C [199]. Inagaki et al. 1976 utilised PA and molten urea for phosphorylation of cellulose at 150 °C for 2 hours, resulting in the maximum degree of esterification of 1.5 with residual char generation of ~45-50% [200]. In 2001, Granja and colleagues developed phosphorylation methods using phosphorus pentoxide, phosphoric acid, *N, N*-dimethylformamide, and hexanol to produce a phosphorylated cellulose gel with a maximum DS of 2.5 and water sorption capacity of ~ 7000% [201]. In 2006, Suflet et al. produced monobasic phosphorylated MCC using urea solution, phosphoric acid and sodium hydroxide with a maximum DS of 1.0 with enhanced thermal stability upto 200

°C which can be utilized as a precursor for growing hydroxyapatite [34]. Another study by Wanrosli et al. utilised phosphorous pentoxide, phosphonic acid, triethyl phosphate, and hexanol as phosphorylating agents to generate phosphorylated cellulose gel from empty bunch tree fruits. The resulting cellulose showed a maximum of 75% yield, DS of 1.03 and swelling capacity of ~600% after 72 hours of reaction at 30 °C [202]. Concurrently, Vasiljevic et al. on phosphorylating cotton fabrics using 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide–vinyltrimethoxysilane resulted in the production of flame-retardant fabrics with maximum phosphate concentration of 3.6% and char residues of ~26% [203]. In 2014, Nehra et al., for the first time, utilised phosphoric acid, 2-hydroxy ethyl methacrylate ester, in the presence of azobisisobutyronitrile for the phosphorylation of cotton fabrics. The resulting fabrics yield a residual char length of 1 cm (total fabric length-16.5 cm), whereas the control completely transformed into ash within 46 seconds.[204]. Luneva et al. (2014) utilised ammonium polyphosphate and phosphoric acid in the presence of urea (160 °C for 60 min) to produce phosphorylated cotton fabrics with a phosphate content of 6.8 wt.%, which resulted in the formation of ~40% char residue [78]. In 2015, Kakol et al. utilised phosphoric with water (heterogenous solution) and molten urea (homogenous solution) to create dibasic and monobasic substituted cellulose phosphate from nano-fibrillated cellulose and nanocrystalline cellulose. Phosphorylation caused the formation of dibasic phosphate and monobasic tautomeric phosphite groups at the *C6* and *C3* positions of the cellulose backbone, resulting in a CC of 1173 mmol/kg for CNF and 1026 mmol/kg for NCC [205]. In their study, Zheng et al. (2016) utilised phosphoric acid and ethylenediamine to develop flame-retardant cotton fabrics. These fabrics exhibited a limiting oxygen index value of 35.4% and did not undergo continuous burning, with the shortest char length of 30 mm, whereas the control samples were

entirely burned. [206]. In 2016, Costes et al. conducted a study on the phosphorylation of MCC utilising PA, molten urea, and aluminium phytate, resulting in grafting 16.5 wt.% of phosphorous. The developed P-MCC was mixed with polylactic acid, decreasing the ignition time from 86 seconds to 55 seconds [207]. Eldin et al. employed phosphoric acid to prepare phosphorylated cellulose acetate membranes for methanol fuel cells, resulting in methanol permeability of 1.14 $\times 10^{-9}$ cm^2/s, ion exchange capacity of 1.19 meq/g and water absorption of ~55% [208]. Similarly, Srivastava et al. developed phosphorylated cellulose acetate to remediate Ni^{+2} with a maximum adsorption capacity of 64.1 mg/g at pH 6 after 12 hours of contact time [209]. In their study, Mautner et al. also used phosphoric acid to produce phosphorylated CNF paper, resulting in a maximum CC of 2.3 mmol/kg, zeta-potential of -60 mV and 20 mg/g of copper adsorption capacity [210]. Later, in 2017, Luo et al. utilized a similar process for phosphorylating cotton linter to develop phosphorylated cellulose microspheres with a maximum phosphate content of 1.82 wt%. The resulting microspheres showed a maximum adsorption capacity of 108.5 mg/g for Pb^{+2} at 25 °C and pH 5 [211]. Similarly, Allafchian et al. (2018) also performed phosphorylation on cellulose filter paper to develop a phosphorylated thin film extractor to detect Ni^{+2}. The developed paper was utilized as a colourimetric sensor and showed the standard detection limit of 18µg/L with maximum recoveries of 87% Ni^{+2} from river water. Sharma et al. in 2019 developed phosphorylated cellulose II utilizing phosphoric acid and ethanol, with a grafting of 3.8 wt.% of phosphate ions, zeta potential of -8.4 mV, surface area of 10.7 m^2/g and thermal stability upto 352 °C. The resulting phosphorylated cellulose was modified with ZnO nanoflower, showing 4421 mg/g adsorption capacity for arsenic at pH 7 [212]. Similarly, in 2020, Barbosa et al. also used a phosphoric acid-mediated process to develop phosphorylated cellulose nanostructures with phosphate content of

0.17 wt.% and zeta potential of -17.2 mV. The developed nanostructures were utilized to remove Cr (III) and Cr (IV) with a maximum removal efficiency of 88% and 93%, respectively [213]. Ablouh et al. (2020) also developed phosphorylated cellulose fibres by treating them with phosphoric acid at 120 °C for 12 hours. The developed fibres showed a maximum CC of 6000 mmol/kg, DS of 2.68 and char generation of ~49% at 700 °C. The abovementioned procedures for phosphorylation processes were time-consuming, expensive, involved complex reagent preparation, and contains harsh chemicals, making the process non-scalable. In conclusion, significant research on phosphorylation methods using phosphoric acid and its derivatives has produced phosphorylated cellulose materials with diverse properties and applications. These materials are useful in textiles and environmental cleanup due to their flame retardancy, adsorption capacity, and thermal stability. Despite their value, phosphorylation procedures require extensive reagent preparation, toxic chemicals, and time, making them less scalable and cost-effective. These methods have many benefits, but further study is needed to streamline and optimise them for practical use.

2.6.2 Phosphate salt

Cellulose has been phosphorylated using different salts derivatives, including DAHP [214], ADP ($NH_4H_2PO_4$) [215], sodium dihydrogen phosphate (NaH_2PO_4) [216], and di-sodium hydrogen phosphate (Na_2HPO_4) [217]. The properties of phosphorylated cellulose majorly depend on the cellulose source, which eventually dictates the resultant applications. In 2015, Ghanadpour et al. introduced a novel approach for phosphorylating sulphite wood pulps using DAHP in the presence of urea. In the reaction, the samples underwent drying at 70 °C, followed by curing at 150 °C, and mechanical defibrillation to produce nanofibers with a diameter of 3 nm, CC of 1800 μeq/g and DS of 0.41. During the reaction, an excess amount of urea was taken,

preventing the fibril's decomposition from PA release during the curing processes [37]. Niazi et al. followed similar methodology to phosphorylate sulphite wood pulp with a 50 minutes curing, resulting in the production of CNFs with a maximum CC of 2.32 mmol/g. The phosphorylated CNF, when composited with poly(vinyl alcohol), results in improved swelling, mechanical and thermal properties and has been applied for CO_2 separation [218]. Kumari et al. conducted a phosphorylation process on viscose fabrics utilising DAHP and urea for 2 min and 150 °C, yielding fabrics with a phosphate content of 4.09 wt. %. The study also compared plasma-based and salt-based phosphorylation and observed higher functionalization in the latter [190]. Noguchi et al. performed phosphorylation of softwood pulp using ADP and urea, producing CNFs with uniform widths of 3 to 4 nm and CC of 1.23 mmol/g. The generated phosphorylated CNF were highly transparent with ~100% transmittance. The authors noticed that excessive phosphorylation affects the viscosity, transparency, and gravimetric yield of the produced CNF [219]. In 2018, Ghanadpour et al. utilized a similar strategy to phosphorylate softwood pulp at 150 °C for 50 minutes and obtained CNF film with DS of 0.2 [220]. Ghanadpour et al. conducted another study of phosphorylation of softwood pulp with ADP and urea at 150 °C for 10 minutes, resulting in the formation of CNFs with CC of 1050 μeq/g, which was utilized for the fabrication of flame-resistant composite foams [221]. In 2019, Rol et al. used ADP and urea to phosphorylate bleached eucalyptus Kraft pulp at 150°C for 60 minutes. The technique produced CNFs with a maximum CC of 2.0 ± 0.2 mmol/g, which was utilized for making nanopapers with high mechanical strength (14 GPa) and transparency [154]. Patoary et al. also utilised ADP and urea to phosphorylate jute at 165 °C for 10-20 minutes, yielding a CNF with DS ~ 0.00042, and enhancement in the residual char and thermal stability. The authors also observed that presence of urea, reaction time, and

temperature affect the phosphorylation efficiency [193]. Harada et al., had explored the phosphorylation of cellulose acetate using sodium dihydrogen phosphate at 140-145 °C for 20 minutes, resulting in the formation of phosphorylated microfibers with a maximum DS ranging from 0.31 to 0.69. The study produced water-swellable hydrogel beads with the specific surface area of 36.5 m^2/g for the germination of plant seeds [222]. Recepoğlu and Yüksel phosphorylated hazelnut shell in the presence of PA, DAHP and urea at 150 °C for 120 minutes resulted in the formation of CMFs with a maximum phosphate content of 5.67 wt.%. The fabricated bio sorbent was utilized for the lithium recovery from aqueous solutions with 6.03 mg/g sorption capacity [194]. Moreover, from 2021 to 2024, researchers investigated the phosphorylation process using DAHP, ADP, sodium dihydrogen phosphate, di-sodium hydrogen phosphate and urea on diverse substrates, leading to the creation of cellulose phosphate with different CC/DS, as depicted in ***Table 2.3*** and ***Table 2.4.*** Modification of cellulose via phosphorylation depends majorly on source; for instance, DAHP and urea phosphorylation with CC of 1800 μeq/g or 2.32 mmol/g (sulphite pulp), phosphate content of 4.09 wt. %. (viscose) were generated with varied cellulose sources whereas ADP and urea phosphorylation results in CC of 1.23 mmol/g or 1050 μeq/g (softwood pulp), CC of 2.0 ± 0.2 mmol/g (bleached eucalyptus Kraft pulp), and DS of 0.00042 (jute). Phosphorylation with sodium dihydrogen phosphate results in DS ranging from 0.31 to 0.69 (cellulose acetate) whereas PA, DAHP and urea-based phosphorylation results in a phosphate content of 5.67 wt.%. (hazelnut shell). The variation in CC determines the applicability of phosphorylated cellulose, which requires the selection of appropriate phosphorylating strategies and source. Cellulose modification *via* salt derivatives is a facile, scalable, and low-cost approach which generates the highest CC, compared to the other strategies available.

Table 2.2 *Presents information on the treatment of phosphate acid derivatives used to produce phosphorylated cellulose, including details on treatment conditions, CC, and the resulting form of different cellulose derivatives.*

Cellulose Source	Treatment	Time & Temperature	Charge Content	Cellulose Form	Ref.
Cellulose ashless filter paper (CAFP)	PA	1.2-2hr, 100 to 120 °C	8.2 and 44.5 mmol kg^{-1}	CNC	[188]
Cellulose (Schieicher and Schull)	Phosphorous trichloride and phosphorous pentaoxide	12hr, 115 °C	-	CMF	[191]
Kraft pulp (Hardwood)	PA	5hr, 70 °C	-	CNC	[223]
Cotton linter and Eucalyptus hardwood	PA (99 %), phosphorus pentoxide (98.5 %), and triethyl phosphate	72 hr, 50 °C	3.34-4.91 wt. %	CNF	[224]
Giant Reed tree	PA	2 hr, 60 °C	254-3133 $mmolkg^{-1}$	CMF/CNC	[15]
Softwood Kraft	PA and urea	2hr, 120 °C	6608 mmol kg^{-1}	CMF	[225]
Hardwood pulp	PA and urea	8-16 hr, 160 °C	29 wt. %	CNF	[226]
Mercerised cotton	PA	1-5 hrs, 145-150 °C	0.950 mmol g^{-1}	CMF	[227]
BC	PA, DMF and urea	2 min, 540 W	-	CNF	[228]
Pinus radiata and *Eucalyptus globulus*	PA and urea	8-16hr, 165 °C	2.2-2.4 $mmolg^{-1}$	CNF	[229]
Flax fiber	PA and urea	3.5hr, 150 °C	-	CMF	[230]
Softwood bleached Kraft pulp	PA and urea	8-16hr, Microwave oven	1.1−1.8 mmol/g	CNF	[231]
Peeper plant residue	PA and urea	2hr, 100 °C	-	CNC	[232]
Filter paper	PA and urea	30 min, 150 °C	800 mmol/kg	CNC	[233]
Oil palm	Phosphorus pentoxide, triethyl phosphate, PA and urea	-	-	MCC	[189]

Table 2.3 *Presents information on the phosphate salt treatment used to produce phosphorylated CMF using cellulose from different sources, including details on treatment conditions, CC, and the resulting different form of cellulose derivatives.*

Cellulose Source	Treatment	Time & Temperature	Charge	Form of produced PC	Ref.
Woven viscose fabrics	Urea (1 mol) and DAHP (1 mol)	2 min and 150 °C	4.09 wt. %	Fabrics	[190]
	Plasma method (He gas)	2 min and 5.8 W	2.88 wt. %		
Woven viscose fabrics	Urea (1 mol) and DAHP (1 mol)	2 min and 150 °C	-	Fabrics	[234]
Alfa fibres	Urea (12 g) and DAHP (5.1 g)	1 hr and 150 °C	4844 mmol/Kg	-	[235]
Hazelnut shell	Urea (1 mol), PA (0.15 mol), and DAHP (0.2 mol),	2hr and 150 °C	5.67 wt. %	Powder	[194]
Softwood pulp (never dried)	Urea (4 mol) and DAHP (1 mol)	60 min and 150 °C	1540 μmol/g	Paper	[27]
Softwood Kraft fibre	Urea (4.9 g) and DAHP (1.2 g)	60 min and 150 °C	10,000 g/kg	Sheet	[236]
Esparto grass	Urea (12 g) and DAHP (5.1 g)	60 min and 150 °C	3.3 mmol/g	Paper	[237]
Cotton fabric	DAHP (2.5 mol), and urea (15 mol),	10 min and 135 °C	5.79 wt. %	Fibre	[238]
Softwood Kraft pulp	Urea (18.5 g) and DAHP (5-12.2g)	0-40 min and 150°C	1.9 and 2.7 mmol/g	Gel	[192]
Bamboo	Urea (2M) and DAHP (0.34M)	0.5-4 hr and 150 °C	0.6 – 1 mmol/g	Straw	[24]
Viscose fabrics	Urea: DAHP (1:2)	30 min and 150 °C	-	Fabric	[239]
Hemp stalk	Urea (1g) and DAHP (1g)	60 min and 150 °C	1.8-8.92 wt. %	Paper	[16]
Cellulose acetate	Urea (2 mol) and $(Na)H_2PO_4$ (1 mol)	20 min and 145 °C	0.31-0.69 (DS)	Hydrogel	[222]
Cellulose acetate	Na_2HPO_4 (11.1g), NaH_2PO_4 (24.9 g), and urea (18.7 g)	140 °C	-	Monolith material	[240]
Kapok fibre	$NH_4H_2PO_4$ (1-8 g) and urea (2-10 g)	20-100 min and 110-160 °C	127.7 mg/g	Paper	[215]
Bleached pulp fibre	$NH_4H_2PO_4$ (2.25 g) and urea (6g)	18 min and 165 °C	-	Film	[241]

Table 2.4 *Presents information on the phosphate salt treatment used to produce phosphorylated CNFs/CNCs using cellulose from different sources, including details on treatment conditions, CC, and the resulting form of different cellulose derivatives.*

Cellulose Source	Treatment	Time & Temperature	Charge	Cellulose form	Form of produced PC	Ref.
Softwood dissolving pulp	Urea (4 mol) and DAHP (1 mol)	30-90 min and 150 °C	1.84 μeq/g	CNF	Paper	[242]
Softwood dissolving pulp	Urea (4 mol) and DAHP (1 mol)	50 min and 150 °C	-	CNF	Membrane	[218]
Softwood dissolving pulp	Urea (4 mol) and DAHP (1 mol)	30-90 min and 150 °C	1.84 μeq/g	CNF	Gel	[243]
Wood cellulose	Urea (12g) and DAHP (5.1g)	60 min and 150 °C	2.64	MCC/CMF	Powder	[244]
Bagasse	Urea (2 mol) and DAHP (1mol)	15-60 min and 150 °C	2.56 mmol/g	CNF	Gel	[245]
Bamboo pulp sheets	Urea and DAHP	30 min and 150 °C	-	CNF	Composite	[246]
Eucalyptus sp.	Urea (4.9 g) and DAHP (1.2 g)	20 min and 150 °C	-	CNF	Film	[247]
Wood derived CNF	Urea: DAHP (1:2)	3 hr and 150 °C	-	CNF	Scaffold	[248]
Alfa fibres	Urea (12 g) and DAHP (5.1 g)	0.5 hr and 150 °C	3.7 mmol/Kg	CNF	Aerogel	[249]
Cellulose pulp	Urea (12 g) and DAHP (5.1 g)	0.5 hr and 160 °C	-	CNF	Membrane	[250]
Sulphite pulp	Urea (50 g) and DAHP (18 g)	10 min and 165 °C	-	CNF	Film	[251]
Softwood kraft pulp	Urea: DAHP (1.5:10)	150 °C	-	CNF	LED film	[252]

Soft pulp sheet	Urea (12 g) and NH_4H_2PO4 (4.5 g)	200 seconds and 165 °C	1.23 mmol/g	CNF	gel	[219]
Softwood pulp (never dried)	Urea: NH_4H_2PO4 (2:8)	150 °C	0.2 (DS)	CNF	Film	[220]
Softwood dissolving pulp	Urea: NH_4H_2PO4 (1.8:7.2)	10 min and 150 °C	1050 μeq/g	CNF	Aerogel	[221]
Bleached eucalyptus	Urea: NH_4H_2PO4 (1.2:4.9)	60 min and 150 °C	2.0 ± 0.2 mmol/g	CNF	Nanopaper	[154]
Softwood Kraft fibers	Urea (12 g) and NH_4H_2PO4 (4.5g)	10hr and 165 °C	0.30 wt. %	CNF	Powder	[253]
Softwood pulp sheets	Urea (12 g) and NH_4H_2PO4 (4.5g)	10hr and 165 °C	1.08-1.53 mmol/g	CNF	Suspension	[254]
Jute	Urea (12 g) and NH_4H_2PO4 (4.5 g)	10-20 min and 165 °C	0.00042 (DS)	CNF	Suspension	[193]
Eucalyptus	$NH_4H_2PO_4$: urea (1.2:4.9)	60 min and 165 °C	0.06-2.37 mmol/g	CNF	-	[255]

2.6.3 Phosphorylation using deep eutectic solvent and ionic liquids

With considerable advances in cellulose phosphorylation, researchers have tried other solvents, such as deep eutectic solvents (DEs) and ionic liquids (ILs) for phosphorylated cellulose production (***Table 2.5***). Various ILs such as 1,3-dimethyl imidazolium methyl phosphite ***Figure 2.6*****(c)** [256], 1,3-dimethyl imidazolium methyl phosphonate [257], 1-ethyl-3-methylimidazolium methyl phosphonate [258], 3,5-lutidinium methyl phosphate [259], and 1-ethyl-3-methylimidazolium diethyl phosphate [260]. For example, phosphorylation of MCC was carried out with the combination of ionic liquids 1-allyl-3-methylimidazolium methyl phosphonate and Na_2PHO_3 at 80 °C for 48 hours by Xu et al. This resulting MCC showed a decrease in the degree of polymerization from 304 to 218 compared to the control, with a transformation in the polymorph from cellulose I to cellulose II, a decrease in crystallinity (66% to 22%), and an enhancement in thermal stability [261]. Recently, Hopson et al. utilised 1-ethyl-3-methylimidazolium diethyl phosphate (ILs) to produce cellulose-rich ionogels from *Pinus radita*. The lignin was incorporated into the resulting ionogels and showed a viscosity of ~ 10^3 Pa, leading to improved thermal stability, flame retardancy, adsorption, and bioactivity [258]. In their study, Zhang et al. utilised 1,3-dimethyl imidazolium methyl phosphite to phosphorylate Lyocell fibre, showing phosphate content of ~1 wt.%, which minimised the peak heat release by ~51% compared to the control [256]. Zahibi et al. developed a new combination of chemical solvents, including a phosphate-based solvent, chloride, and sodium diphenyl phosphate to phosphorylate cellulose from a nutshell powder at 80°C for 18 hours. The resulting powder was used as filler material to improve the flame resistance capabilities of wood with limit oxygen index of 24.2%, peak heat release rate reduction by 74%

and char generation of 16.8%, making it suitable for flame-retardant filler materials [262]. In conclusion, exploring alternative phosphorylating solvents, such as DEs and ILs, has significantly advanced the field of cellulose phosphorylation, offering novel and greener pathways for producing phosphorylated cellulose with tailored properties and enhanced functionalities. However, the above studies showed that the phosphorylation resulted in a lower degree of substitution or CC and are costlier than other routes (acids and salts). Therefore, the production of economical ILs and DEs with improved phosphorylating efficiency is the need of hour.

2.6.4 Enzymatic treatment

Enzymatic treatment for producing phosphorylated cellulose is a greener route for phosphorylation than acid and salt-mediated routes ***Figure 2.6*****(d**). For example, Tzanov et al. in 2002, reported the phosphorylation of cotton cellulose for the first-time using hexokinase (enzyme extracted from baker yeast) and adenosine-5′-triphosphate (as phosphoryl donor). The reaction was performed at 30 °C for 6 hours using 40 U/mL of hexokinase, resulting in the phosphorylation of 0.03% of glucose [263]. Bozic et al. developed enzyme-based phosphorylation to produce cellulose phosphate from cellulose sludge, resulting in cellulose nanofibrils with a degree of substitution of 0.43. The reaction was conducted under conditions featuring adenosine triphosphate and magnesium ions at a temperature of 30 °C and a pH of around seven over 24 hours (as shown in ***Table 2.5***) [264]. The enzymatic routes offer easy recyclability and improved color ability and do not degrade the cellulosic fabric; however, they result in a lower degree of substitution, CC and efficiency.

Table 2.5 *Detailed the production of phosphorylated cellulose from ILs, DEs, and enzymes from different cellulose sources under different treatment conditions and their properties.*

Cellulose source	Treatment	Time & Temperature	Charge	Cellulose form	Application	Ref.
Lyocell fiber	1,3-dimethyl imidazolium methyl phosphite	-	<1 wt. %	CMF	Flame retardant fabric	[256]
Cotton fiber	1,3 dimethyl imidazolium methyl phosphonate and 1-ethyl-3-methylimidazolium methyl phosphonate	5hr and 100 °C	-	CMF	Flame retardant fabrics	[257]
MCC	1,3-dimethyl imidazolium methyl phosphite	2 hr and 140 °C	-	CNF	Iongel for supercapacitor	[23]
Macadamia nutshell powder	Glycidyltrimethylammonium Chloride and Sodium diphenyl phosphate	6 hr and 65 °C	-	CMF	Filler material	[262]
Avicell	3, 5-lutidinium methyl phosphate	6 hr and 120 °C	16.52 %	CNF	-	[259]
Pinus radiata wood	1-Ethyl-3-methylimidazolium diethyl phosphate	24 hr and 120 °C	-	CNF	-	[258]
Cellulose sludge	Hexokinae, adenosine triphosphate and magnesium ions	24 hr and 30 °C	0.00033-0.43	CNF	-	[264]
MCC	1-allyl-3-methylimidazolium methyl phosphonate and Na_2PHO_3	120 min, 80 °C	-	MCC	-	[261]

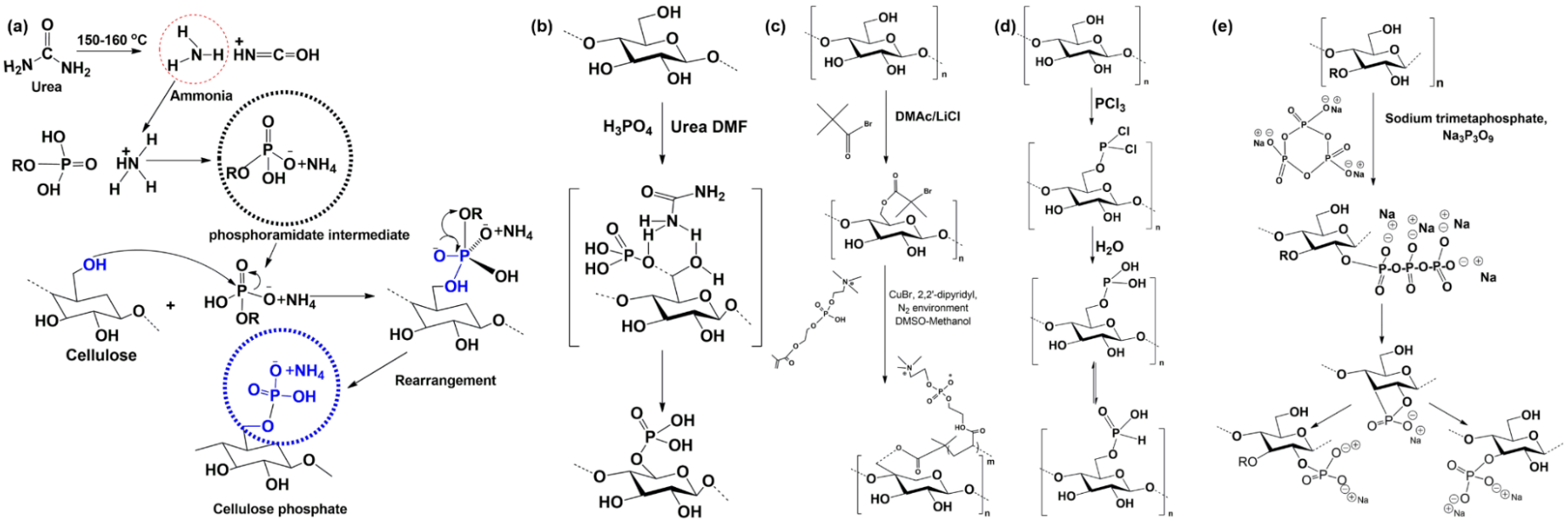

Figure 2.5 *Different routes for the phosphorylation of cellulose (a) DAHP and urea, (b)* PA*, urea and DMF, (c) 2-methacryloyloxyethyl phosphorylcholine, (d) phosphorous chloride, and (e) sodium trimetaphosphate.*

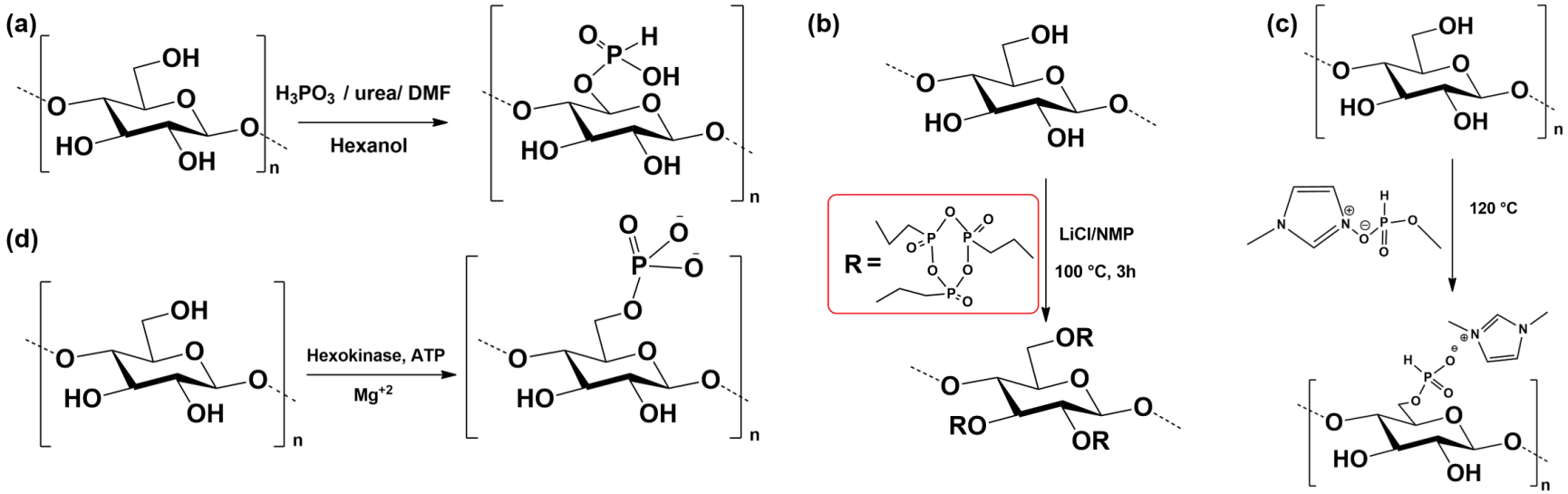

Figure 2.6*.Routes for the phosphorylation of cellulose (a) Phosphorous acid/urea/DMF in the presence of hexanol (b) LiCl/NMP/ n-propyl phosphonic acid anhydride, (c) 1,3dimethylimidazolium methyl phosphite, and (d) hexokinase.*

2.7 Applications of phosphorylated cellulose

Phosphorylation as a chemical modification method has recently attracted much interest from researchers and industrialists because of its interesting properties, including tuneable CC, high water absorption capacity, mechanical properties, adsorption capacity, thermal stability, low thermal conductivity, shear thinning properties and flame retardancy [265]. It can be processed into various forms, including films [252], powders [253], hydrogels, aerogels 130], and gels [245], resulting in applications in different sectors (shown in ***Figure 2.7***). Phosphorylated cellulose has been extensively utilized for different applications such as wastewater treatment [244], the development of flame retardant material [197], bone and tissue engineering [19], fuel cell technology [208], and packaging materials [266] have been discussed in the subsequent sections and tables (***Table 2.6*** - ***Table 2.8***).

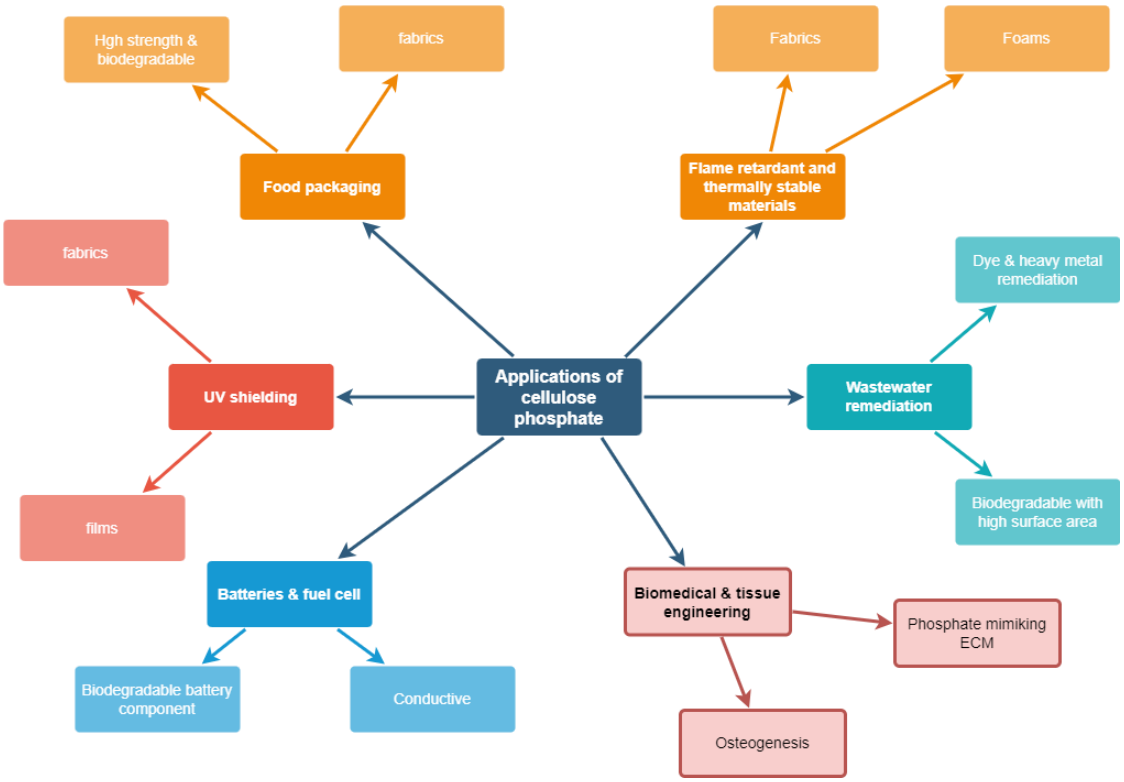

Figure 2.7 *Application of phosphorylated cellulose in different sectors and their properties.*

2.7.1 Flame retardancy

Cellulosic materials have been widely utilized in textile and packaging film due to their abundant availability. Nevertheless, their inherent high flammability poses limitations on their use. Therefore, integrating flame retardant properties into cellulosic materials would improve their practicality and safety in their application (***Table 2.6***). Flame-retardant properties of materials can be improved by coating a protective layer and incorporating a reinforcing agent. Various flame retardant composites have been developed from various synthetic polymers such as polyvinyl alcohol [267], polyurethane [268], polypropylene utilizing different

inorganic chemical and materials such as montmorillonite [269], MoS_2 [270], silica, melamine polyphosphate [271], ethylenediamine, triethyl phosphate [267], ammonium polyphosphate [267], and graphene [272]. However, the utilisation of these materials is limited due to their expensive and non-degradable nature. For several decades, halogen-containing compounds have been the primary choice for enhancing flame retardant properties of materials, yet they produce harmful gases when burned, posing health and environmental risks. Halogen-based flame retardants have been banned because they tend to release toxic gases that accumulate in animals and plants, posing significant ecological and health hazards [273]. Phosphorous-based compounds such as phosphoryl polyethyleneimine amide [1], 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide [1], 1, 4-phthalaldehyde, diethyl phosphite [1] have also been used to develop flame retardant materials. For instance, Sandoflame 5060, a potent and enduring flame retardant formulated with phosphorus, was developed by the Swiss company Sandoz. It is extensively used in developing fire-resistant viscose fibres. However, its commercialization was hindered due to its high cost and potential health risks, curtailing its widespread application [273]. In the production of flame-retardant fabrics, another challenge arises from the inadequate dispersibility of inorganic flame retardants in spinning solutions. Moreover, high concentrations of these additives can sometimes compromise the mechanical strength of the resulting materials [274]. Therefore, considering the above-mentioned issues related to halogen and phosphorous-based flame-retardant materials, the phosphorylation of cellulosic material with inorganic salts, acids, enzymes and ILs can serve as economical, sustainable, and less toxic routes for developing flame-retardant materials. Zhang et al. studied nanofibrilated paper using P_2O_5 and methanesulfonic acid for phosphorylation.

The resulting paper had a limiting oxygen index (LOI) of 30 % and a low heat release rate of 62.8 % compared to untreated cellulose [275]. Khakalo et al. performed phosphorylation of MFC using DAHP and urea, resulting in 11% weight loss when directly exposed to a butanol flame for 3 seconds [27]. In addition, the phosphorylated MFC exhibited a lower onset temperature (285.2 °C for MFC and 210 °C for P-MFC) and a lower maximum degradation temperature (346 °C for MFC and 280 °C for P-MFC) compared to the MFC. Zhang et al. reported that phosphorylated cellulose and its composite with lignin (BHL-PCNF), derived from bamboo, exhibited notable flame-retardant properties and structural integrity when exposed to direct alcohol flame for 25 seconds. The BHL-PCNF film exhibits a notable decrease in the peak and total heat release rates, with reductions of 87.3 % and 86.6 %, respectively, compared to the control [276]. Moreover, Zhang et al. found that phosphorylating lyocell fibres led to a 118% increase in char production at 700°C. Additionally, it significantly reduced overall and peak heat release rates by 87.6% and 82.4%, respectively, compared to untreated lyocell fibres [273]. Niu et al. examined the phosphorylation of MCC which led to the formation of char ranging from 8.9 % to 14 % and LOI from 42 % to 54 % [17]. Ding et al. created composite foam using CNF, phytic acid, and guanazole, exhibiting remarkable thermal stability and excellent thermal insulation (29.27 kW/m^2) characteristics. The composite foams exhibited a significant reduction of 49.4 % in the peak heat release rate compared to conventional CNF [197]. Phosphorylated nanocellulose has the potential to serve as a substitute for foam or fibreglass in exterior wall insulation, resulting in less heat loss and increased energy conservation.

Due to its fire-resistant properties and eco-friendly nature, this material is well-suited for application in vehicle interiors due to its reduced weight, enhanced fuel economy, and reduced environmental impact. In chapters 6 and 7 of the present thesis, flame retardant films, aerogels, and thermal boxes have been developed from phosphorylated rice straws and sugarcane bagasse for potential application in food packaging. This was achieved using an economical and environmentally friendly process involving the presence of DAHP and urea.

2.7.2 Wastewater remediation

The extensive industrialisation and population growth have significantly impacted water sources due to the improper release of pollutants such as dyes and heavy metals into water bodies. Various adsorbents, catalysts, biochar, metallic organic frameworks, covalent organic frameworks, and filtration methods have been developed for wastewater remediation *via* different processes such as adsorption, precipitation, coagulation, and photodegradation [277]. However, the aforementioned adsorbents are expensive and challenging to regenerate, which hinders their cost-effective utilisation [15]. Hence, cellulose, and phosphorylated cellulose are superior alternatives due to their sustainable, cost-effective, and abundant characteristics. Due to its abundance of free hydroxyl groups, larger surface area, and economical nature, cellulose has been widely studied for the adsorption of inorganic and organic pollutants. Phosphorylated cellulose is a negatively charged form of cellulose having tuneable CC, excellent water absorption capacity and adsorption properties; therefore, it is widely studied for the adsorption of dyes [278], antibiotics [20] and heavy metals [212] (***Table 2.7***).

For example, Luo et al. developed a phosphorylated cotton linter pulp using PA and urea, which successfully removed Pb (II) with a maximum adsorption capacity of 108.5 mg/g [211]. Allafchian et al. developed a phosphorylated cellulose sensor from cellulose acetate, which helped to detect Ni^{+2} with a lower detection limit of 18 µg/L [279]. Sharma et al. successfully synthesised phosphorylated cellulose and grew ZnO nanoparticles, which exhibited an outstanding adsorption capacity of 4421 mg/g for As (V) [212]. Yang et al. developed a phosphorylated microsphere from cotton linter pulp, exhibiting a remarkable adsorption capacity of 139.3 mg/g for ciprofloxacin [20]. The cellulose derived from Luffa rattan underwent phosphorylation to generate an adsorbent capable of absorbing U (VI) at a concentration of 197 mg/g [280]. In their recent study, Boukind et al. used phosphorylated cellulose extracted from Giant Reed, utilising agro-grade chemicals such as DAHP and urea showed a maximum CC of 7000 mmol/g and adsorption of 1200 mg/g [235]. Phosphorylated cellulose has demonstrated its promise as an adsorbent in several studies to remove positively charged heavy metals and dyes. However, most of these studies used batch-type adsorption techniques. Therefore, continuous remediation of pollutants from wastewater is need of hour. In chapters 4 and 5 of the current thesis, remediation of MB and MG has been performed with delignified RH, SB, and 3D printed PC structure in both continuous and batch mode. Furthermore, *in-situ* modification of the above-mentioned material with MoS_2 resulted in photodegradation and adsorption in both continuous and batch modes with bacterial inactivation.

Table 2.6 *Utilization of cellulose for development of flame-retardant material via phosphorylation reaction under different treatment conditions and their properties.*

Cellulose source	Treatment chemicals and condition	Charge	Cellulose form	Ref.
Flake fabrics	Vinyl phosphonic acid and DMF, 2hr, 100 °C	0.26-1.38 wt. %	CMF	[281]
Cotton fabrics	Phosphorous acid, 20 min, 120 °C	-	CMF	[282]
CNC	P_2O_5	3300 mmol g^{-1}	RCNC	[283]
MCC	PA, and P_2O_5, 48-72 hr, 30 °C	14.48 wt. %	MCC	[17]
Cellulose	Phosphite and urea, 5hr, 150 °C	-	CNF	[284]
Cellulose	PA and MU, 6hr, 150 °C	-	CMF	[285]
Cotton fabric	Phytic acid and urea 5-20 min, 155-185 °C	-	CMF	[286]
MCC	Phytic acid, 72 hrs., 70 °C	-	CMF	[287]
Cotton fabric	Phytic acid, 0.5 hrs., 130 °C	5.57 wt. %	CMF	[288]
Cotton fabric	PA and MU, 3 hrs., 110-175 °C	-	CMF	[289]
Cotton fabric	PA and urea, 2hr, 80 °C	3.52 wt. %	CMF	[290]
Lyocell fibers	PA and urea, 1hr, 140 °C	4.43 wt. %	CMF	[273]
Flax fiber	PA and urea, 3.5hr, 150 °C	-	CMF	[230]
Loblolly pine	Ammonium phytate, urea, 5hr, 100 °C	5.9 wt. %	CMF	[291]
Cotton fabric	PA and urea, 5 min, 170 °C	9.87 wt. %	CMF	
Softwood pulp	Phosphorus pentoxide, PA and urea ,7hr, 70 °C	4.8 wt. %	CMF	[292]
Kraft pulp fibres	Poly-PA, phosphorus pentoxide, and N, N-dimethylacetamide, 3 hr, 150 °C	4.8 wt. %	CMF	[292]
Cotton fabric	PA and urea, 1.5 hr, 145-150 °C	0.80 mmol/g	CMF	[293]
Filter paper	PA and urea 30 min, 150 °C	800 mmol/kg	CNC	[233]
Kapok fibre	Methyl phosphonic acid, dicyandiamide and urea 2-10 min, 160-200 °C	28-54 mg/g	CNF	[294]

Table 2.7 *Phosphorylation of cellulose from different sources under different reaction conditions utilizing PA for wastewater remediation application.*

Cellulose source/forms	Treatment	Time & Temperature	Charge	Application	Ref.
Cotton linter pulp/CMF	PA, urea, and DMF	8 hr, 350 °C		Pb^{+2} removal (108.5 mg g^{-1})	[211]
CAFP/CMF	PA and urea,	0.5 hr, 60 °C	-	Sensor for Ni^{+2} detection	[279]
Jute cellulose/MFC	PA & ethanol	0.5 hr, 70 °C	3.84 wt. %	Arsenic (V) removal (4,421 mg/g)	[212]
MCC and CNC	PA, and Tetrahydrofuran (THF)	-	-	Congo red and Malachite green removal	[295]
Saw dust/CMF	Phosphorous oxychloride and THF	12 hr, 70 °C	-	Lead (II), Cadmium (II) and chromium (III) removal	[296]
Cotton (Medical grade)/CNC	PA and urea	0.5 hr, 150 °C	-	La (III) (46 mg g^{-1}) removal	[297]
Eucalyptus residues/CNF	PA and urea	0.5 hr, 100 °C	-	Cr (VI) (71 % removal)	[213]
Birch pulp cellulose/CNF	-	-	0.66 $mmolg^{-1}$	U(VI) (1550 mg g^{-1})	[298]
Cotton wool and MCC/CNC	Phosphoryl chloride, THF, and hexachlorotricyclophosphazene	24 hr, 30 °C	-	Film, Haemoglobin adsorption upto 40 %	[299]

Cotton linter pulp/CMF	PA, urea and DMF	8 hr, 135 °C	-	Ciprofloxacin adsorption (139.36 mg g^{-1})	[20]
Orange peel/CMF	PA and urea	12 hr, 120 °C	4.75 wt. %	Powder, U (VI) removal (552.6 mg g^{-1})	[300]
Cotton fabrics/CMF	PA and urea	1.5 hr, 145-150 °C	0.20-2.00 mol L^{-1}	Fabric for 99 % Pu^{4+} removal	[301]
Luffa rattan/CMF	PA	24 hr	2.07 wt. %	U(VI) adsorption (197 mg g^{-1})	[280]
MCC/CNF	PA, DAHP and urea	2 hr, 150 °C	9.44 wt. %	Li recovery, 25-33 mg g^{-1}	[302]
Cellulose/CMF	PA and urea	>1hr, 150 °C	-	U(VI) removal (525-1006 mg g^{-1})	[303]
Moringa olifera/CMF	Ortho PA	30 min, 100 °C	-	Rhodamine B removal (91 % efficiency)	[304]

2.7.3 Biomedical and tissue engineering

The exceptional properties of phosphate-containing polymers in modulating bone cell development and calcification have garnered significant interest among researchers. In light of the increasing recognition of environmental concerns, there is a strong justification for exploring the application of environmentally friendly biomaterials in creating novel cell culture scaffolds for bone tissue engineering. For example, in their study, Liu et al. developed a scaffold using wood CNFs *via* a phosphorylation process using DAHP and urea. Through phosphorylation, CNFs experienced a significant boost in their zeta-potential values. This, in turn, led to the formation of scaffolds that exhibited remarkable uniformity and stability. Phosphate concentration was crucial in mouse osteoblast (MC3T3-E1) cell growth in cell culture. The osteoblast cells showed excellent adhesion and rapid proliferation on P-CNF0.78 and P-CNF1.05, with phosphate concentrations of 0.78 and 1.05 mmol/g, respectively. On the other hand, the cells grown on the initial CNF substrate formed clumps due to insufficient cell adhesion and showed limited cell growth. In addition, the P-CNF substrates with the optimal phosphate content provided a conducive environment for cells and successfully promoted osteogenic differentiation and calcification, even without a differentiation inducer. Bio-based P-CNFs are expected to mimic the properties of bone components and provide a means of regulating the growth and specialisation of osteoblasts in bone tissue engineering [248]. In their investigation, Zha et al. created a sponge from sodium alginate and cellulose, followed by phosphorylation *via* an esterification route to grow apatite crystals. The phosphorylated sponge exhibited a spherical development of appetite crystal, measuring 0.9 μm in size, which subsequently aggregated into rod-shaped crystals measuring micrometres in size. The findings indicate that phosphorylated cellulose/alginate composite surfaces can initiate

calcium phosphate production and facilitate the mineralisation process, leading to the development of hydroxyapatite for bone and tissue engineering purposes [19]. The study conducted by Wang et al. focused on the use of CNCs that were grafted with poly(ethyl ethylene phosphate) (PEEP) for loading and delivering the anticancer medication doxorubicin (DOX) to cancer cells. The study revealed that PEEP-g-CNCs exhibited biocompatibility with both L929 and HeLa cells. Additionally, it was observed that PEEP-*g*-CNCs loaded with DOX displayed a favourable anticancer effect, specifically against HeLa cells. Furthermore, PEEP-*g*-CNCs loaded with DOX exhibited a higher rate of DOX release at a pH of 5.0 compared to a pH of 7.4 [305]. Furthermore, phosphorylated-CNF resulted in an augmented biomimetic growth of hydroxyapatite crystals, highlighting this material's considerable potential for many biological applications. Schimper et al. investigated the hemocompatibility and inflammatory response of cellulose II aerogels derived from phosphorylated cotton linters and hardwood pre-hydrolysis Kraft pulp. The activation of plasmatic coagulation and subsequent initiation of a moderate inflammatory response is observed on the cellulose surfaces. Phosphorylation decreases the process of plasma coagulation and the activation of leukocytes. The activation of blood platelets for degranulation, which is advantageous for osteo-conduction and osseointegration, occurs due to partial calcification. Calcification inhibits the inflammatory response and the activation of leukocytes. The findings indicate the possibility of utilising alternative cellulose phosphate-based cell scaffolding materials in various applications [306].

2.7.4 Batteries and fuel cell

Various fillers have undergone thorough investigation and have been found to augment the electrochemical performance and ionic conductivity in lithium-ion battery applications. This is due to their capacity to function as an electric charge. Carbon

nanotubes, metal oxides, Al_2O_3 and 2, bisphenol A, ethoxylate diacrylate, metal-organic frameworks, and cellulose are among the most frequently used filler materials for lithium-ion batteries. Moreover, considerable emphasis has been put on the flammability of lithium batteries, particularly concerning the integration of flame-retardant fillers within the cell constituents [251]. Using polyethene oxide at temperatures above its melting point to achieve realistic conductivities in lithium batteries raises essential safety considerations. Therefore, phosphorylated cellulose has been utilised as a solid filler in lithium-ion batteries to incorporate eco-friendly and sustainable flame-retardant properties that improve the durability of solid electrolytes made from polyethene oxide. In the realm of composite solid polymer electrolytes (SPE), phosphorylated cellulose nanofiber (CNF-P) has emerged as a highly promising organic filler exhibiting an improved flame-retardancy characteristic. For example, Solid polymer electrolytes were synthesised by Aziam et al. using a composite material consisting of CNF-P and poly(ethylene oxide) in conjunction with lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI). At a temperature of 70 °C, the composite polymer electrolytes exhibited exceptional conductivity values exceeding 10^{-4} S/cm. Furthermore, they provide a broad electrochemical stability range exceeding 5 V compared to Li/Li^+ and show good cycling performance [251].

Phosphorylated CNF was also designed to produce a selective barrier that effectively filters ions, impeding the mobility of polysulfides and ultimately improving the efficiency of batteries. The phosphorylated CNF exhibited considerable electronegativity, impeding the penetration of polysulfide anions into the separator. Furthermore, the polar characteristics of phosphorylated CNF and the inherent ease of Li^+ dissociation can significantly improve the wettability of the electrolyte and facilitate the transfer of Li^+ ions. Consequently, rational ion management leads to enhanced

reversibility in the electrochemistry of sulphur and lithium. For example, Li et al. in their study, developed a separator for lithium-sulphur batteries which exhibit a low fading rate of merely 0.013% per cycle throughout 1000 cycles at 1 C. These batteries demonstrate a notable areal capacity of 5.37 mA-h-cm^2 while having a high sulphur loading of 5.0 mg-cm^2 and a restricted electrolyte of 6.0 mLg^{-1}. This study introduces a straightforward and efficient approach to mitigate the shuttle effect and enhance the durability of lithium-sulfur batteries [250]. Radiman and Rifathin used the microwave phosphorylation approach to fabricate a fuel cell membrane using cellulose derived from the *Acetobacter xylinum* bacterial strain. The developed membrane exhibited a proton conductivity and methanol permeability of 1.2×10^{-2} S/cm and 2.3×10^{-6} cm^2/s, respectively. This work presents a novel approach for advancing cost-effective and environmentally friendly polylectrolytic membranes for fuel cells [307].

2.7.5 Food packaging application

Food safety and health are becoming more and more significant to consumers, and concerns about food standards and preservation composition have drawn much attention. Degradation of food quality is one of the most serious issues, which is primarily caused by oxidation and microbial metabolism, which can be influenced by physical factors such as temperature, pH, moisture, physical damage, odour, heat shock, UV-radiation, and microbial attacks [308]. Packaging is a food preservation and storage method that maintains the food's quality, improves shelf life, and prevents toxins and biological degradation [308,309]. It is also essential for the transportation of foods such as fruits, vegetables, and meats, which protects it from perishing and abrasion, light, and shock. Different types of food necessitate distinct preservation, storage, and transportation conditions. For example, the preservation of perishable food items such as vegetables and fruits require reduced respiration and transpiration rates, which can

be accomplished by controlling the physical factors such as moisture, pH, temperature, gas level (oxygen, carbon dioxide, ethylene), etc. Petroleum-based synthetic plastics are widely utilized for food packaging applications. However, using plastic as a packaging material raises serious concerns about its degradability and recycling ability. The utilization of massive amounts of plastic leads to its accumulation in the environment and the degradation of soil quality. Therefore, alternative materials capable of replacing synthetic plastics as a packaging material are required. Cellulose and cellulose-derived polymers or their composites are potential candidates to meet the requirements mentioned earlier and the development of bio-bags/compostable bags. For example, You et al. created a CMC-based composite for fish packaging by combining blackcurrant anthocyanins and konjac glucomannan (tilapia). The developed film had good tensile and elongation properties, with 38.4 MPa and 3.67% values, respectively. The films also had excellent water permeability of 2.53 g.mm/m^2 day kPa, UV blocking abilities, and the ability to extend fish shelf life by up to 5 days [310].

Zhang et al. created a cellulose acetate-based film for beef packaging by coating it with cinnamaldehyde, and the developed film had an excellent tensile strength of 88.2 MPa and antioxidant properties. The developed film's water vapour permeability and oxygen transfer rate were 1.2 to 1.9 × 10^{-12} g m/m^2sPa and 2.6 to 3 cm^3/m^2. d.0.1 MPa, respectively, and extended the shelf-life of beef by 4-5 days [311]. Wen et al. developed TEMPO-oxidised BC-based film and composites incorporating anthocyanin and thymol for shrimp packaging. The film was tested for water vapour permeability, in which TEMPO-oxidised BC film (6.10 × 10^{-11} g·m·s^{-1}1 Pa^{-1}) exhibited superior barrier properties than the composite (5.20 × 10^{-11} g·m^{-1}·s^{-1} Pa^{-1}). The shelf life of the shrimps was also extended up to 48 h using TEMPO-oxidised BC/anthocyanin/thymol film [312]. Karkhanis et al. synthesized CNC composite film with poly (lactic acid) to

package saltine crackers. When the shelf life of the cracker was tested using both poly (lactic acid) film and CNC/ poly (lactic acid) film, the CNC/poly (lactic acid) film outperformed (86 h) the poly (lactic acid) film (63.4 h). The water vapour permeability of the CNC/poly (lactic acid) and poly (lactic acid) films were 341 and 200 × 10^{-16} kg/m^2/s-Pa, respectively [313]. Francisco et al. developed hydroxyethyl cellulose-based composite film by mixing acetylated cassava starch. The film (100% hydroxyethyl cellulose or 75% hydroxyethyl cellulose + 25% cassava starch) was used to coat guava, which increased the shelf life of the fruit by 13 days. The water vapour transmission rate increased by increasing hydroxyethyl cellulose concentration, ranging between 12.84 to 18.94 g h^{-1} m^{-2} [314]. However, none of the cellulosic forms in the above studies showed inherent heat-sealing properties.

Therefore, due to its tuneable CC and crosslinking ability, phosphorylated cellulose can serve as a better option for developing food packaging material soon. For example, Semlali et al. conducted a study that produced phosphorylated cellulose and utilised a thermo-compression technique to develop the paper. The paper was coated with a layer of poly [ethylene-co-(vinyl acetate)] measuring 40 µm thick, highly dense, with a crystallinity of 91 % and a low water vapour permeability of 20 %. However, in this study, the developed cellulose paper can potentially be used in food packaging applications without inherent heat-sealing properties [16]. In a recent study, Maliha et al. adopted spraying techniques to fabricate food packaging film using CNF-Bismuth (III) phosphinate composites. The composite films that were generated exhibited remarkable antibacterial properties against *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*, as well as antifungal characteristics against *Candida glabrata* and *Candida albicans*. The water vapour permeability of CNF-Bismuth (III) phosphinate composites was found to be within the range of 10^{-11} kg/m^2/s-Pa,

comparable to that of plastic packaging [266]. These studies offer exciting findings regarding the potential uses of phosphorylated cellulose in food packaging sectors without heat sealability. In chapter 6 of the thesis, RS straws have been phosphorylated to develop food packaging. Cellulose and its composite-based aerogels or foams have also been used for the packaging of food items due to its low thermal conductivity, high specific area, larger pores volume, biodegradable nature, low density and excellent compressive reversibility [315–318]. Similarly, phosphorylated cellulose aerogels and foam also showed above mentioned properties with additional inherent flame-retardant properties which is utilized as packaging materials to preserve perishable food items and prevent them from mechanical damage and fire during storage and transportation. For example, Zhang et al. developed cellulose-based foam from TEMPO-oxidise CNFs and thyme essential oil *via* a freeze-drying method to preserve beef. The developed aerogel has a density of 15 mg/cm^3 and a specific surface area of 23.2 m^2/g with excellent release of essential thyme oil. The foam, including 0.6% oil, exhibited a thiobarbituric acid value of 0.2-0.3 mg/g, a total volatile basic nitrogen content of less than 10 mg/100 g, a pH value of 5.5, and a total viable count of ~ 3 log CFU/g. These results suggest that the beef remained fresh for 5 days [319]. Similarly, Wu et al. developed composite foam from pectin, CNF, and thymol solution via freeze-drying techniques to preserve edible mushrooms. The foam had a maximum compressive stress of 45 kPa at 10% strain, 60% moisture absorption under 100% relative humidity, and sustained thymol oil release. The aerogels demonstrated antibacterial properties against *E. coli* and *S. aureus*, 30 U/mg antioxidant capacity, and 20% mushroom weight loss with ~500 g/kg phenolic compound over 5 days of storage, potentially increasing shelf-life by 5 days compared to control [320]. Zhang et al. developed a sponge from cellulose and silver nanoparticles *via* a freeze-drying method to preserve the

strawberries from mechanical damage during transportation. The sponge created had exceptional cyclic deformation characteristics, maintaining only a 16.8% deformation after 1000 cycles, preventing damage to strawberries during the supply chain. The developed sponge also showed antimicrobial properties against *E. coli*, *S. aureus* and *Rhizopus stolonifera,* thus extending its shelf-life up to 12 days [318]. Mirmoeini et al. also created a composite aerogel using CNFs, starch, and *Thymus diagenesis* oil through freeze-drying techniques to maintain the quality of the cheese. After 21 days of storage, the aerogel made with a 50x *Thymus diagenesis* oil demonstrated a 3-log reduction in psychrophile counts and a 1-log reduction in yeast and mould counts, indicating its potential application in food packaging [316]. Kurd et al. freeze-dried cellulose and PVA aerogel for meat packaging. The aerogel has 98% porosity, 16.39 kg/m^3 density, 0.033 W/m. K thermal conductivity, and 85% compressive recoverability at 50% strain. The aerogel's pH maintained between 5.71 and 5.75 after 12 hours of storage. The total volatile basic nitrogen ranged from 12.15 to 12.85 mg N/100 g and did not fluctuate with slight increase in viable culture form (2.11 to 2.89 log CFU/g). These findings indicate that the aerogel has promising potential in the cold supply chain [315]. In chapters 6 and 7 of the thesis, flame retardant and low thermal conductivity RS aerogel box and PSBC foam were designed to preserve butter and apples. The RS thermal box developed which prevented melting of butter for up to 5 hours at 30°C, suggesting its use in packaging. PSCB foams for apple packaging reduced mechanical impacts by 50%, suggesting their use in fruit transportation packaging. The foam and aerogel box's flame-retardant properties can replace non-biodegradable, highly flammable polyurethane foam.

Table 2.8 *Phosphorylation of cellulose using various cellulose sources following different processes with their detailed reaction conditions and potential applications.*

Cellulose source	Treatment	Time & Temperature	Charge	Cellulose form	Application	Ref.
BC	DMF, PA and urea	1 hr, 130 °C	-	CNF	Conductive membrane 182.9mWcm^{-2}	[321]
Cellulose (Hi-media)	PA	0.5hr, 25-30 °C	-	CNC	Drug release	[322]
Cellulose	PA, urea and DMF	1hr, 136 °C	2.08 wt. %	CMF	Sponge for bone tissue engineering	[19]
MCC/CNC	Phosphoryl chloride, hexachlorotricyclophosphazene, and THF	-	-	MCC/CNC	Film for wound healing	[323]
Cotton fiber	PA and urea	1hr, 150 °C	12.76 wt. %	CMF	Phosphopeptide enrichment	[324]
Cotton linter	Phosphorus pentoxide, triethyl phosphate, PA and urea	72hr, 50 °C	-	CNF	Aerogel for bone tissue engineering	[306]
BC	PA and urea	-	-	CMF	Fuel cell (Methanol permeability 2.3 × 10^{-6} cm^2/s)	[307]
Cellulose acetate	Na_2HPO_4 (11.1g), NaH_2PO_4 (24.9 g), and urea (18.7 g)	140 °C	-	CMF	Enrichment of phosphopeptides and glycopeptides (Monolith material)	[240]

Hemp stalk	Urea (1g) and DAHP (1g)	60 min and 150 °C	1.8-8.9 wt. %	CMF	Packaging material	[16]
Sulphite pulp	Urea (50 g) and DAHP (18 g)	10 min and 165 °C	-	CNF	Filler for Lithium-ion battery	[251]
Wood derived CNF	Urea: DAHP (1:2)	3 hr and 150 °C	-	CNF	Bone tissue engineering (scaffold)	[248]
Cellulose pulp	Urea (12 g) and DAHP (5.1 g)	0.5 hr and 160 °C	-	CNF	Ion sieve for Li-ion battery (Membrane)	[250]

2.8 Life cycle assessment of functionalized cellulose production

Life cycle assessment (LCA) is a globally recognised and standardised approach used to quantitatively evaluate the overall environmental impacts associated with various products, services, and processes. Environmental impacts generated from production process can be evaluated for different impact categories including climate change exogenic and endogenic, terrestrial acidification, photochemical ozone formation, human health cancerous and non-cancerous, freshwater consumption, marine ecotoxicity, stratospheric ozone depletion, fossils depletion and freshwater eutrophication. Recently, LCA has been extensively employed to assess the environmental impacts generated during production of CMFS, CNFs and CNCs. Gao et al. examined three distinct routes for synthesising 1g of phosphorylated CNC in their investigation. Route 1 involves the pre-phosphorylation of paper pulp by utilising DAHP and urea. Route 2 entails the *in-situ* hydrolysis of paper pulp using PA. In route 3, the initial hydrolysis of paper pulp is conducted using sulfuric acid, followed by post-phosphorylation using DAHP and urea. Six different impact categories such as ecotoxicity, global warming potential, water use, eutrophication potential, primary energy demand and acidification potential were considered during the study. The results showed that route 1 showed comparatively lower impacts among all the studied impacts than route 2 and route 3. In global warming and resource use categories, route 1 showed 20% lower impacts than route 2 and route 3. For impact categories water use, acidification, and ecosystem damage, route 1 cuts down 70% impacts than route 2 and route 3 [325]. The findings from LCA highlight the eco-efficiency of production process, indicating its great potential for widespread adoption in industrial settings.

This underscores the importance of incorporating sustainability considerations into material production processes to mitigate environmental impacts while also optimizing economic viability. Route 1 substantially reduced ecological impacts by more than 40% compared to Route 3. Several impact categories, including water consumption, acidification, and ecological damage, experienced a reduction above 85%. These findings indicate that Route 1 is a more environmentally friendly option for producing P-CNC [325].