

Cellulose nanocrystals: source, production and application as a coagulant for water purification

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ABSTRACT

The coagulation/flocculation technique is an old proven method that utilizes chemical coagulants for water purification but there are health and environmental challenges associated with the long-term application of such coagulants. Cellulose fibre is a renewable, eco-friendly polymer found in many materials. It has been widely researched due to its unique properties, especially when processed in the 'nano' form as cellulose nanocrystals (CNCs) but nanocelluloses require surface functionalization in order to improve their suitability for various applications. The aim of this review is to provide an in-depth discussion of the current progress in the synthesis of CNCs with recourse to their source, surface chemistry and extraction procedures. Various techniques used for the conversion of CNCs into coagulants were extensively reviewed while the current development on the potential application of CNCs as a coagulant for water remediation was presented. The results obtained from the potential application of modified CNC-based coagulants demonstrate their remarkable coagulation efficiency for the purification of contaminated water. Therefore, global research into the development of CNC-based coagulants at all levels is crucial in order to generate interest in natural coagulants as a potential replacement for chemical coagulants. Furthermore, potential areas for more research were proposed in this review.

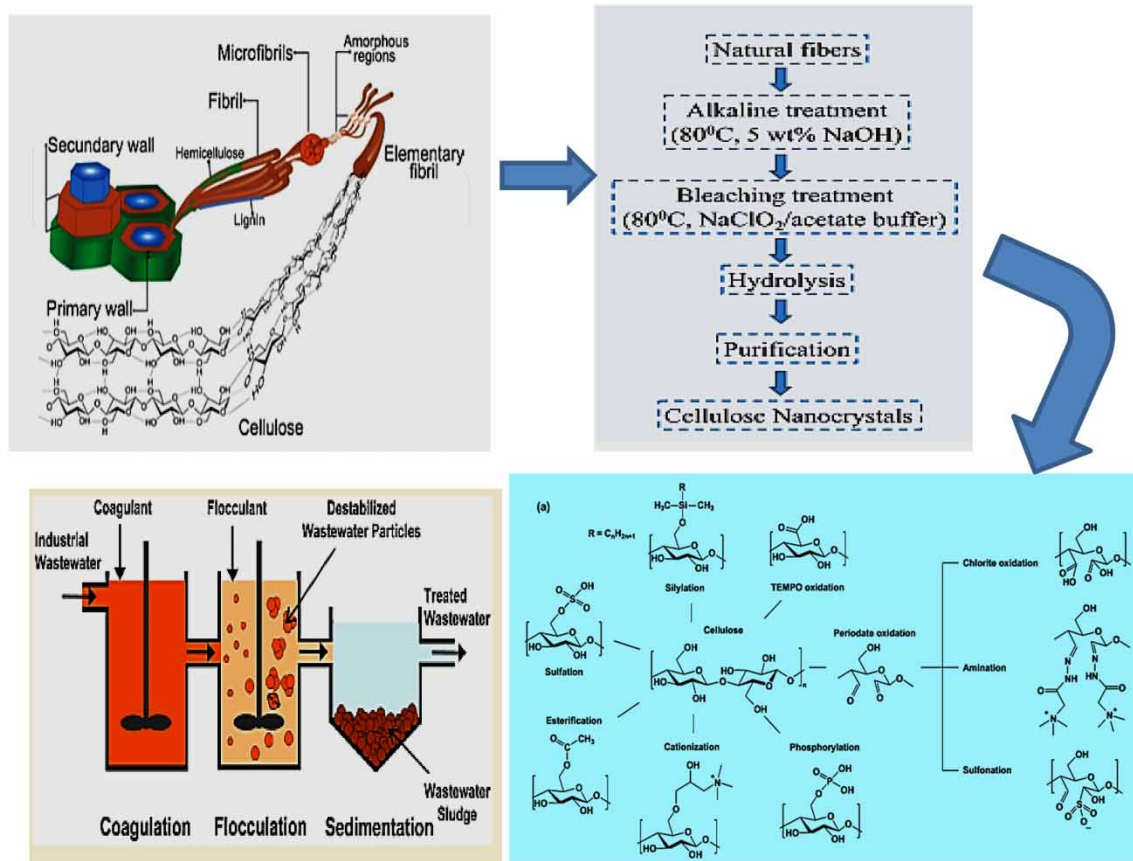
Key words: biopolymers, cellulose, cellulose nanocrystals, modification, natural coagulant, water treatment

HIGHLIGHTS

- Cellulose fibre obtained from plant biomass as a precursor for the production of cellulose nanocrystals (CNCs) was appraised.
- An assessment of recent techniques for the modification of CNCs was provided.
- Functional groups incorporated onto the CNCs surface improve their performance as coagulants for removal of specific contaminants.
- The production methods for CNCs coagulants involve the 'Green chemistry approach'.

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GRAPHICAL ABSTRACT

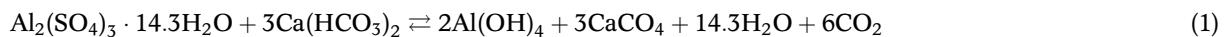


1. INTRODUCTION

Global environmental pollution has been greatly affected by the rapid population increase, economic expansion and other environmental issues, which is alarming in terms of its negative effects on water quality. Water pollution refers to the undesirable change in the physico-chemical characteristics of water which could be detrimental to humans and the ecosystems. Water pollution can adversely affect humans, the aquatic biota and the economic development of a nation (He 2015). Statistics provided by the United Nations International Children Emergency Fund (UNICEF) show that more than 1.5 million cases of death from water-related diseases have been recorded due to the consumption of contaminated or poorly treated water. According to reports, 90% of these occurrences involve children below 5 years of age (Noori *et al.* 2019). In order to ensure improved water quality and ensure compliance with stipulated regulatory agencies, the removal of impurities becomes crucial. Achieving good water quality can be accomplished by using the appropriate treatment technology (Oelofse *et al.* 2016). Several treatment technologies have been successfully employed for water purification. These include chemical precipitation, adsorption, electrocoagulation, advanced oxidation, ion exchange and other biological processes among others (Wiesmann *et al.* 2007; Omar *et al.* 2018; Othmani *et al.* 2022; Al-hashimi *et al.* 2023). Most of these treatment options are expensive to run, especially for small- and medium-sized industries and sometimes, may necessitate the use of significant quantities of chemicals for effective treatment. Additionally, effluent containing recalcitrant contaminants are known to corrode treatment reactors, which reduces the efficacy of the treatment facility (Ukiwe *et al.* 2014; Muruganandam *et al.* 2017).

The coagulation/flocculation (CF) technique is a renowned treatment method recognized for its effectiveness in treating various water matrixes. The CF technique is accepted globally due to its cost-effective and ecologically friendly process, simplicity of use and potential for automation for enhanced performance (Fard *et al.* 2016; Wei *et al.* 2018). Furthermore, due to its unique characteristics, the CF method can be used in conjunction with other treatment methods (Sahu & Chaudhari 2013; Ukiwe *et al.* 2014; Muruganandam *et al.* 2017). Although the terms 'coagulation and flocculation' are interchangeable, coagulation refers to the neutralization of negatively charged

colloidal particles (contaminants) in water by using coagulants with opposite charge. As a result, the finely distributed suspension becomes unstable and aggregates. Flocculation, on the other hand, is the gentle mixing or stirring of the aqueous medium to facilitate the growth of the agglomerated particles into larger flocs which settle under gravity and are removed by filtration (Teh *et al.* 2016; Dayarathne *et al.* 2021). Chemical coagulants that are utilized for the remediation of polluted water include the salts of aluminium e.g. aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$) and aluminium chloride (AlCl_3) and salts of iron e.g. ferric chloride (FeCl_3) and ferric sulphate (FeSO_4). These coagulants have demonstrated high efficiency in removing toxic substances, suspended/dissolved solids and other pollutants (Parmar *et al.* 2011; Omar *et al.* 2018). Aluminium sulphate (alum) is the most often used coagulant in water purification. It is effective for the removal of alkalinity as shown in Equation (1) (Parmar *et al.* 2011). The water's alkalinity and the alum combine to form an insoluble metal hydroxide floc that completely covers the colloidal particles. A decrease in the average number of molecular weight values occurred during the coagulation process, which proves that a significant portion of the high molecular weight natural organic matter (NOM) molecules were eliminated by the alum (Parmar *et al.* 2011).



In a recent study, Al-Hashimi *et al.* (2023) created an engineered adsorbent using quartz sand coated with calcium ferric oxides (QS/CFO) generated from wastepaper sludge ash (WPSA). The adsorbents were used to eliminate tetracycline (TC) from simulated wastewater. According to the results of the batch coagulation studies, the designed adsorbent could remove up to 90% of the TC (21.96 mg/g) in about 180 min. In a similar research, Jalal *et al.* (2021) studied the efficiency of aluminium-based coagulant by applying aluminium chloride alone and in combination with alum to eliminate the organic matter, turbidity and colour from textile wastewater. Coagulation experiments were conducted and the findings indicated a 98, 98 and 99% decrease in colour, chemical oxygen demand (COD) and turbidity, respectively, at pHs between 6.5 and 7.5.

Unfortunately, chemical coagulants have some adverse health and environmental implications. Researchers have reported the possibility of re-contaminating treated water and groundwater with residual aluminium that could be a threat human at elevated concentrations (Mathuram *et al.* 2018; Maćczak *et al.* 2020). A substantial amount of hazardous sludge and secondary pollutants are also produced by these synthetic chemical coagulants, which are non-biodegradable and may affect the ecosystem (Mathuram *et al.* 2018; Kurniawan *et al.* 2020; Maćczak *et al.* 2020; Zaman *et al.* 2020). The search for safer and eco-friendly coagulants has led to renewed interest in natural coagulants as an alternative to chemical coagulants. Natural coagulants of plant origin have been utilized traditionally for water purification for centuries before the advent of chemical coagulants. Their long-standing usage is due to their superior performance and simple operation (Teh *et al.* 2016). They are also known as biopolymers since they are from plant and animal-based materials such as agricultural wastes (fruit peels, husks, plant stems), fish bladders and shells of crabs and crustacean (Choy *et al.* 2015; Nandini & Sheba 2016). These natural coagulants are easily degradable, renewable, eco-friendly and produce a smaller volume of sludge (Kiew & Chong 2017). Plant-based biopolymers such as starch, cellulose and gelatine are much preferred and researched as possible alternatives to chemical coagulants due to their availability and natural abundance (Choy *et al.* 2015; Trache 2018). Cellulose is the most abundant, sustainable biopolymer in existence, with a unique composition that enhances its suitability for several industrial purposes (Vazquez *et al.* 2015). The application of cellulose for making greener and more substantial industrial products is attributed to its no-carbon footprint and unique properties that allow for chemical modification (Vazquez *et al.* 2015; Hamad 2017). Nanocelluloses, such as cellulose nanocrystals (CNCs), can be produced from cellulose. The CNCs are rod-shaped cellulose particles with at least one dimension equal to or less than 100 nm and have a highly crystalline structure (Alatawi *et al.* 2018). Investigations into the morphology of the CNCs have revealed their exceptional mechanical and elastic properties (high specific strength and modulus), large specific surface area, high aspect ratio, ultralow density, tunable porous structure, low environmental impact and reduced production cost (Mathew *et al.* 2014; Larissa *et al.* 2015; Thompson *et al.* 2019). Nanocelluloses have low coagulation performance when utilized in their natural form and require some surface modification to improve their coagulation capabilities. The introduction of cationic or anionic functionalities on the surface of nanocelluloses by modification techniques like oxidation, etherification, esterification and polymerization reaction, improve their compatibility and adsorption efficiency for the removal of specific pollutants from water (Rana *et al.* 2021).

Currently, there is limited and fragmented information in literature on the correlation between cellulose and CNCs and the progress made in improving their performance as natural coagulants. This article, therefore, provides an overview of cellulose, its composition and properties which makes it a high-performing natural biopolymer of interest, especially when utilized in the nanoform as CNCs. It discusses the synthesis of CNCs and the recent modification strategies employed for improving their performance as coagulants. Furthermore, this review presents areas for more global research in the development of CNC-based coagulants.

2. COAGULATION

2.1. Coagulation process

Coagulation is the process by which the elements that contribute to a suspension's stability are eliminated, and the suspension subsequently destabilizes to form agglomerates. The term 'flocculation' describes the gentle mixing or agitation of the destabilized water in order to promote the development of the coagulated particles into bigger, more dense flocs that separate from the water via a sedimentation or precipitation mechanism (Teh *et al.* 2016). A coagulant is an electrolyte that, when dissolved in water, produces ionic charges that are opposite to the stable colloidal particles (and other contaminants) in water. Wastewaters contain particles that are negatively charged at a pH between 5 and 9. For this reason, the particles are well-dispersed and resistant to agglomeration. Therefore, coagulants are needed to destabilize the particles and induce agglomeration (Teh *et al.* 2016). The addition of coagulants neutralizes the opposing charges on the colloidal particles while the neutralization effect produces a spongy jelly-like mass known as 'floc' (Sahu & Chaudhari 2013; Muruganandam *et al.* 2017). The chemical coagulants frequently utilized in water treatment include $\text{Al}_2(\text{SO}_4)_3$, aluminium sulphate hydrate [$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$], potash alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$], polyaluminium chloride [$\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$], ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) and ferric chloride (FeCl_3) (Parmar *et al.* 2011; Omar *et al.* 2018). These electrolytes are hydrolyzed in solution to form agglomerated hydroxides that adhere to the surface of particles present in water. Flocculants (ionic or non-ionic polymers) are sometimes introduced into the treatment stream usually after the addition of inorganic coagulants, in order to increase the rate of agglomeration of the coagulated particles. Subsequently, the agglomerated particles settle under gravity and are filtered out of the water (Maćczak *et al.* 2020).

The coagulation–flocculation approach with chemical coagulants has been proven by research to be successful. Further investigations, however, have shown that these inorganic coagulants may be left in treated water in trace amounts. The long-term build-up of aluminium in the blood and brain has been linked to severe encephalopathy, Alzheimer's disease, dementia and autism in recent studies (Muruganandam *et al.* 2017; Mathuram *et al.* 2018; Marey 2019; Gautam & Saini 2020). Controversies surrounding aluminium's neurotoxicity exist as several researchers have disputed its association with Alzheimer's disease. They affirm that only extremely low quantities of aluminium reach the brain because excess aluminium is expelled from the body rather than retained. Nevertheless, the application of chemical coagulants for water remediation must be done with caution due to these opposing views (Kurniawan *et al.* 2020). Another related health risk is the utilization of synthetic polymers for water treatment. Some synthetic polymeric coagulant derivatives have low biodegradability properties and cannot be completely degraded during water treatment. They generate carcinogenic and hazardous intermediate by-products which are highly toxic to life forms (Oladoja *et al.* 2017; Mathuram *et al.* 2018). Ecosystems can be adversely affected by inorganic and polymeric coagulants. Treated water containing high levels of residual aluminium or metal salts can seep into groundwater or re-contaminate water sources through surface runoff, thereby destroying the ecosystems. In modern water purification technology, polymeric coagulants derived from natural sources (plants and animals) are being researched as a potential substitute for chemical coagulants due to their low cost, biodegradability and eco-friendly properties. The performance of bio-coagulant for the removal of pollutants from wastewater has been confirmed by researchers and their efficacy and capability as possible alternatives to the generally used chemical coagulants have been proposed (Kurniawan *et al.* 2020). A schematic presentation of the coagulation process is depicted in Figure 1.

2.2. Mechanism of coagulation/flocculation

The basic coagulation mechanisms which occur during water treatment are (1) charged neutralization, (2) adsorption/polymer bridging, (3) sweep or precipitative flocculation and (4) double-layer compression. The coagulation mechanism may occur successively or in combination with other types. The type of mechanism

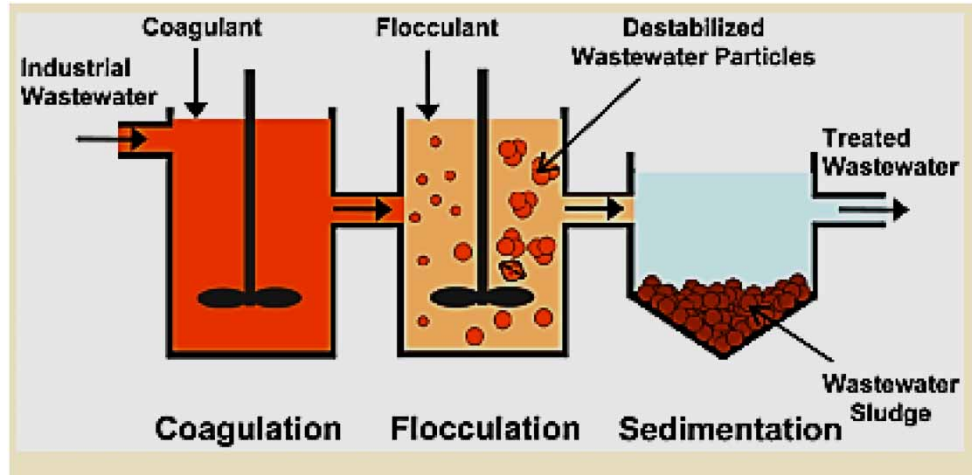


Figure 1 | Water purification via coagulation/flocculation process. Adapted with permission from Teh *et al.* (2016). Copyright (2016) American Chemical Society.

prevalent during a water treatment process is influenced by the type of coagulant used and the characteristics of the water matrix (Maćczak *et al.* 2020; Dayarathne *et al.* 2021).

2.2.1. Charge neutralization/adsorption mechanism

Charge neutralization mechanism involves the use of ionizable chemicals or polymeric materials (polyelectrolytes) to induce the coagulation of organic matter. It occurs when polyelectrolytes of highly charged density and oppositely charged to the colloidal particles, are adsorbed by the particles of lower charge density in a 'patch-wise' manner. This forms patches of positive and negative sites on the top layer of the particles. Due to the presence of sorbed polyelectrolyte patches, the colloidal particles have both negatively and positively charged areas that will be drawn to one another, creating a mechanism for flocculation. Thereafter, the added coagulants tend to neutralize the charged particles, lowering the electrostatic repulsion effect and promoting particle aggregation as shown in Figure 2 (Muruganandam *et al.* 2017; Mathuram *et al.* 2018). The neutralizing effect is detected by a decrease in zeta (ζ) potential (electrokinetic). The zeta potential is vital for the formation of intermolecular forces like van der Waals' attractive forces, which promote the aggregation and sedimentation of formed flocs. The adsorption process occurs when particles adhere to the cationic hydrolysis products (FeOH_2^+ and AlOH_3^+) formed during CF at a low pH (Dayarathne *et al.* 2021).

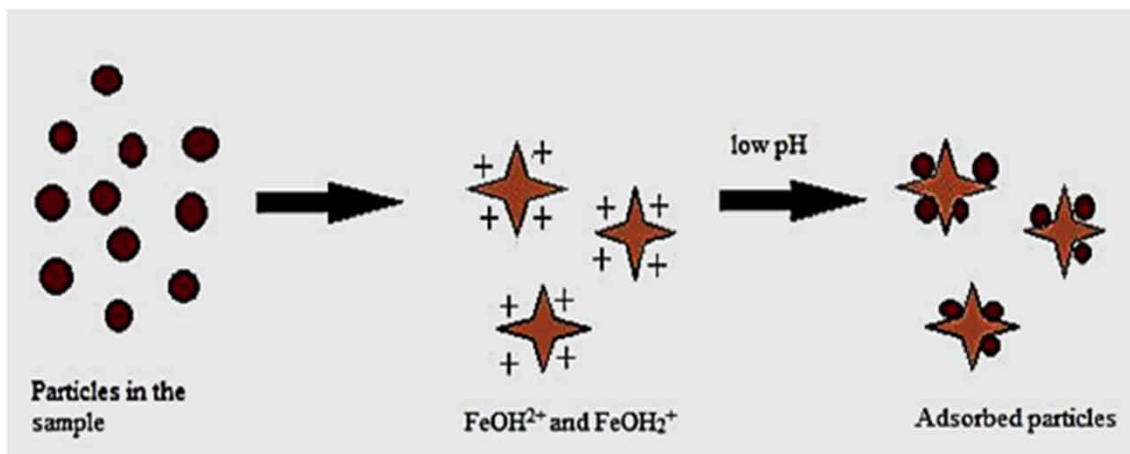


Figure 2 | Adsorption of negatively charged colloidal particles onto positively charged iron hydroxide precipitates (Charge neutralization/adsorption) (Mathuram *et al.* 2018).

2.2.2. Adsorption/interparticle bridging mechanism

Adsorptive and bridging coagulation mechanisms occur when a polymer chain that can adhere to multiple particles is formed by a coagulant. It involves the attraction of two long-chain polymers towards the colloidal particles, which eventually bind onto the surface. In some cases, polymer bridging precedes polymer adsorption (Amran *et al.* 2018). The mechanism occurs where polymers with high molecular weight (greater than 106 Da) have charges similar to the agglomerated particles. It also applies to non-ionic particles with a repulsive force greater than the electrostatic attractive forces. Polymer bridging requires a substantial amount of coagulant to ensure that particles overcome the colloidal repulsion (Kurniawan *et al.* 2020). The first step involves the uniform dispersal of the polyelectrolyte via diffusion into the solid-liquid interface of the solution. A functional group is initially adsorbed on the colloidal particles while the remaining polymer chain extends unattached into the solution. Several loops and tails which are the main basis for the bridging mechanism are thus formed and suspended in the solution. The loops and tails provide links for other particles to attach themselves, thereby aggregating into larger flocs (Alwi *et al.* 2013; Dayarathne *et al.* 2021). Brownian continuous motion causes the chain to become adsorbed at more points along its length until eventually there are no free ends in the solution phase (Maćczak *et al.* 2020). Figure 3 shows the formation of floc by the bridging coagulation mechanism. The adsorptive/polymer bridging mechanism is peculiar to natural coagulants (biopolymers) utilized for water purification.

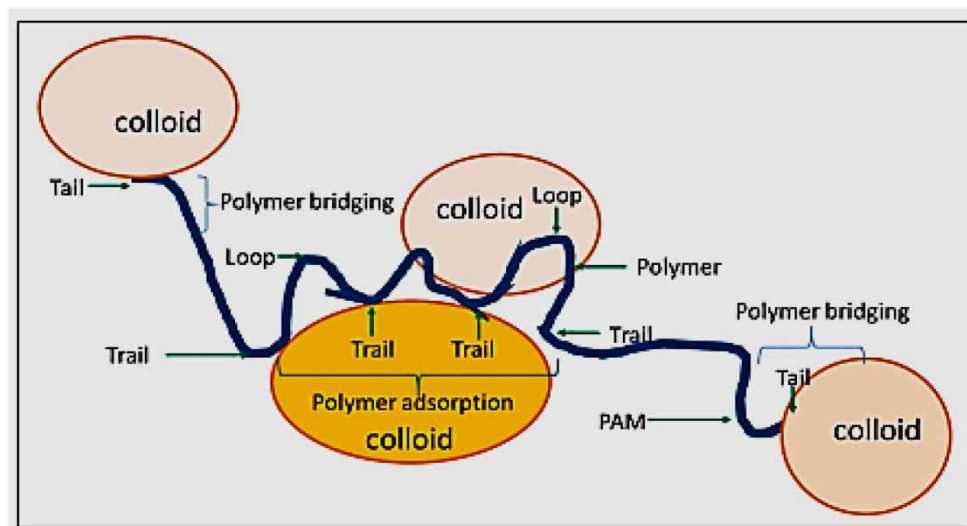


Figure 3 | Adsorption and bridging via loops and tails formation (Dayarathne *et al.* 2021).

2.2.3. Constriction of the electrical double layer

In the presence of liquid, a charged surface develops an electrical double layer (EDL). The surfaces in the context of coagulation and flocculation might be high molecular weight macromolecules or precipitates of metallic oxy-hydroxides. The constriction mechanism utilizes an excess coagulant with a highly charged density to alter the concentration of water and compress the electric double layer around the particle. The compression effect is removed when the repulsive forces within the particles are reduced. The DLVO theory, formulated by Derjaguin, Landau Verwey and Overbeek (Oyegbile *et al.* 2016), stipulates that the influence of attractive forces such as van der Waals becomes prevalent when the use of excess electrolytes decreases the double electrical layer. As the repelling force weakens, the molecular attraction between the particles is induced and the particles begin to aggregate into macro flocs. This process leads to the production of flocs. Agglomeration occurs when the critical coagulation concentration, which varies depending on the experimental conditions (mixing, time of measurement), is exceeded. The EDL plays a significant role in colloidal systems due to the extremely high relative surface area to volume ratio (Dayarathne *et al.* 2021).

2.2.4. Sweep mechanism

Sweep coagulation, also known as precipitate coagulation, occurs when colloidal particles get enmeshed in precipitates of metal hydroxides resulting in greater removal efficiency when compared with the neutralization

mechanism. Large aggregates (sweep flocs) are formed after the neutralization reaction occurs. Thereafter, the attractive force between these flocs and residual colloidal particles causes further agglomeration (as shown in Figure 4) which settles as sludge. This mechanism occurs frequently in wastewater with a low suspended solids content (10 mg/L) (Mathuram *et al.* 2018). In sweep coagulation, a high initial coagulant dosage is needed for efficient coagulation, which unfortunately results in a large volume of sludge being produced. Poly-electrolyte-based coagulants can only be used for double-layer compression, bridging/adsorptive mechanism or charge neutralization, but not for sweep coagulation (Amran *et al.* 2018; Maćczak *et al.* 2020).

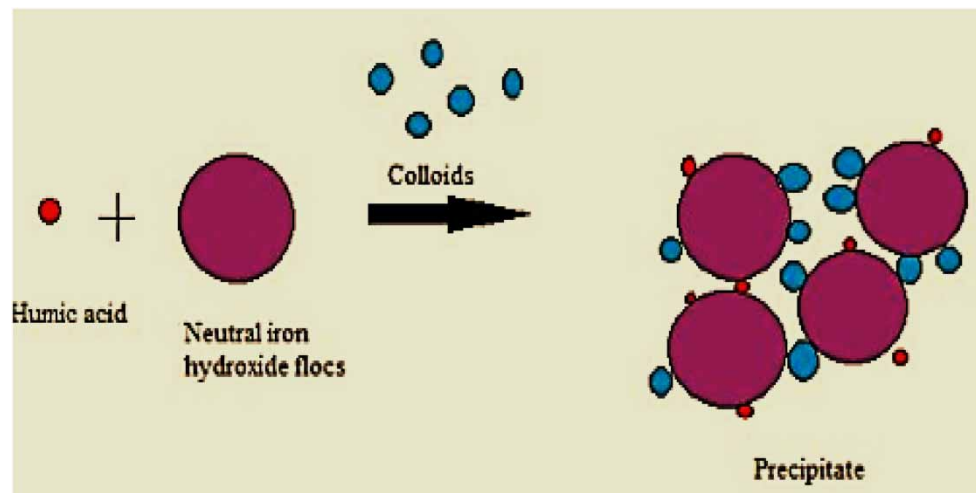


Figure 4 | Sweep coagulation (humic acid/colloids enmeshed into neutral iron hydroxide flocs) (Mathuram *et al.* 2018).

In conclusion, the CF process has been recognized as an essential method for treating water with a complex matrix and a range of contaminant concentrations. The chemical coagulants frequently utilized in water treatment include $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)$ and FeCl_3 . The coagulation mechanisms that occur during water treatment are primarily charged neutralization, adsorption/polymer bridging, sweep or precipitative flocculation and double-layer compression. The coagulation mechanism may occur successively or in combination. The type of mechanism prevalent during a water treatment process is influenced by the type of coagulant used and the characteristics of the water matrix. The use of chemical and synthetic polymeric coagulant has been discovered to be toxic to human health and the ecosystems. Therefore, in modern water purification technologies, polymeric coagulants from natural sources (e.g. plants) are being studied as a possible alternative to chemical coagulants because of their low cost, biodegradability and eco-friendliness.

3. CELLULOSE: A PRECURSOR FOR THE SYNTHESIS OF COAGULANTS

Cellulose, an insoluble polymer, was initially identified by Anselm Payen more than 150 years ago (Huber *et al.* 2012). Cellulose exists in the cell walls of vascular green plants, cotton plants, algae, bacteria and tunicates (Trache *et al.* 2017; Shak *et al.* 2018). It accounts for about 1.5×10^{12} tons of the total annual biomass generated by plants through photosynthesis. Cotton fibre is made up of about 90% cellulose, which is the highest in plants, while wood consists of 45–50% cellulose. Ramin and flax (also known as bast fibres) contain cellulosic materials within the range of 70–80% (Börjesson & Westman 2015; Abdullah *et al.* 2021).

3.1. Source of cellulose

Natural biomaterials such as plants, algae, bacteria, fungi and tunicates are the main sources of cellulose fibre. Before being processed into nanocelluloses and other derivatives, cellulose must first be removed from its source (Kargarzadeh *et al.* 2017). The size, properties and amount of energy utilized in the extraction and conversion of cellulose to nanocellulose are greatly influenced by the source of the cellulose biopolymer. Cellulose contained in plant fibres is one of the well-researched primary sources of nanocellulose with a variety of applications. The plant-derived cellulose fibres are preferred over other cellulose derived from other sources like

the tunicate and bacteria because they produce thinner nanofibres and are readily available in larger quantities (Chirayil *et al.* 2014). Tunicates, specifically members of the Subphylum Tunicata, are the only aquatic invertebrate species with the ability to synthesize cellulose microfibrils (CMF). Cellulose extracted from tunicates is made up of almost pure CI allomorph cellulose with high crystallinity. Its nano/microfibrils' distinctive features include a low density, an aspect ratio between 60 and 70%, a large surface area between 150 and 170 m²/g and reactive surfaces (Zhao *et al.* 2015). Bacteria-based cellulose (BC) may be secreted by certain types of bacteria as a by-product of their metabolic activities. *Gluconacetobacter xylinus* is the most researched cellulose-producing bacterial genus. This species produces CMF as an exo-polysaccharide, mostly consisting of water (99%) under special culturing conditions (Campano *et al.* 2016). Various species of algae such as grey, red and brown algae are sources of cellulose. Species such as *Valonia*, *Micrasterias denticulate*, *Micrasterias rotata*, *Coldophora* and *Boerogesenia* can synthesize CMF in their cell walls. Due to their superior capacity to absorb carbon dioxide compared with bacteria, algae can be used for environmental clean-up. This would help reduce the concentration of greenhouse gas in the environment (Hua *et al.* 2015; Shak *et al.* 2018).

3.2. Cellulose composition

3.2.1. Molecular composition of cellulose

The D-anhydrogluco-pyranose unit (AGU), also referred to as a glucose unit (i.e. cellulose) and having the molecular formula (C₆H₁₀O₅)_n, is connected by a 1,4-glycosidic bond, which holds together a linear isotactic homopolymer like cellulose. The 1,4-linked, d-glucose molecules are arranged as linear chains, with each CI glucose molecule linked to the next at the C4 position as shown in Figure 5 (Vazquez *et al.* 2015; Kang *et al.* 2016). The cellulose molecule consists of unlinked hemiacetal/aldehyde at the reducing end group (C1 position), the free hydroxyl group at the C4 locations (non-reducing group) and internal glucosidal ring at both non-reducing end groups (C1 and C4 locations). Three hydroxyl groups exist at the C6, C3 and C2 positions of each internal AGU. The hydroxyl groups at C6 also referred to as the primary alcohol are the most reactive while those at the other locations are the less reactive secondary alcohols (Börjesson & Westman 2015; Tavakolian *et al.* 2020). Hydroxyl groups determine the chemical character and reactivity of cellulose in the AGU. Their presence on the cellulose surface enables cellulose functionalization. Due to the extensive hydrogen bond network that the hydroxyl groups in cellulose create, it is not soluble in the majority of liquids, including water and organic solvents. It is necessary to break both the intra- and intermolecular hydrogen bonds in order to increase the solubility of cellulose in liquid media (Kang *et al.* 2016).

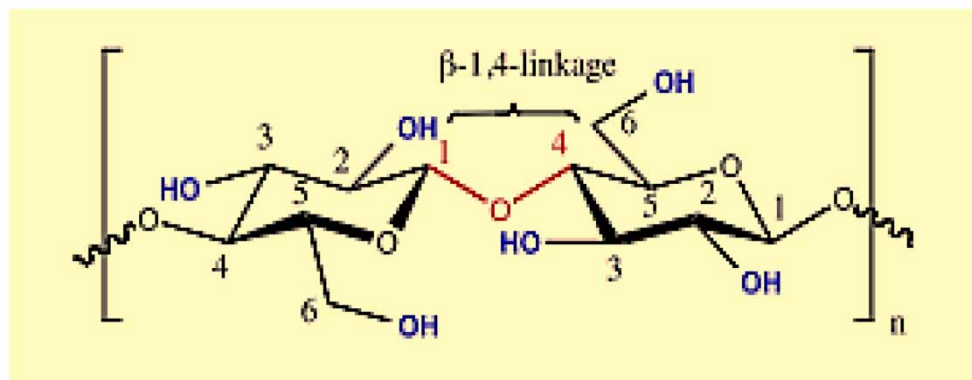


Figure 5 | The molecular structure of cellulose (Sunasee & Hemraz 2018).

3.2.2. Cellulose's supramolecular composition

Cellulose chains are prone to aggregation and the formation of strongly ordered structures and structural entities. This may be due to their extremely regular molecular structure, the stiffness of the molecular chain and the strong hydrogen bonds which facilitate molecular arrangement and aggregation (Lindman *et al.* 2017). Nishikawa and Ono, through the use of a highly defined X-ray diffraction pattern, discovered the supramolecular structure of fibrous cellulose in 1913. This discovery revealed the arrangements of individual cellulose molecules in a 'para-crystalline' form (Zugenmaier 2021). In the early 20th century, scientists asserted that cellulose was an oligomeric, perhaps ring-shaped glucan with up to 100 glucose units. These discoveries coupled with the proven

statements of Staudinger on the macromolecular structure, led to the development of the fringed fibrillar model of cellulose by scientists, which is now the widely accepted concept of the supramolecular structure. According to the supramolecular model, the cellulose chain is arranged in parallel alignment into crystallite fibres (Moon *et al.* 2011). Since the alignment of molecules in a cellulose fibre is not constant in the structure, it is presumed that areas of varying amount of disorientation or disorder also exists. The hydrogen linkage between the C6–OH and C3–OH is known to be the main factor responsible for the structure and uniform fibre alignment in cellulose. Similarly, the regular spatial occurrences and abundant hydroxyl groups regulate the stability of the interchain interactions (Kang *et al.* 2016; Zugenmaier 2021).

3.3. Structural (hierarchical) arrangement of cellulose

Cellulose occurs as a long chain of single molecules that could be spun into agglomerates of cellulose fibres in a hierarchical order during biosynthesis. The single cellulose chains merge or coalesce into elementary fibrils (protofibrils) of various orientations. The factors that govern its biosynthesis affect the various arrangements of elementary fibrils. Their diameters are usually below 20 nm, depending on the cellulose source (Jonoobi *et al.* 2015). The coalescence of the primary fibrils lowers the surface's free energy, resulting in the production of CMF with a diameter of around 3.5–50 nm and a length of 7 μ m. The microfibrils produced could further align into larger forms called macrofibrils that are about 60–300 nm wide, to form the familiar cellulose fibres as depicted in Figure 6. Intermolecular forces such as van der Waals forces and intra- and intermolecular hydrogen bonds, aid in the aggregation of the elementary fibrils. The microfibrils are composed of amorphous regions formed from disordered chains and crystallites formed from closely packed cellulose chains held closely by complex hydrogen bonds (Kang *et al.* 2016; Lindman *et al.* 2017).

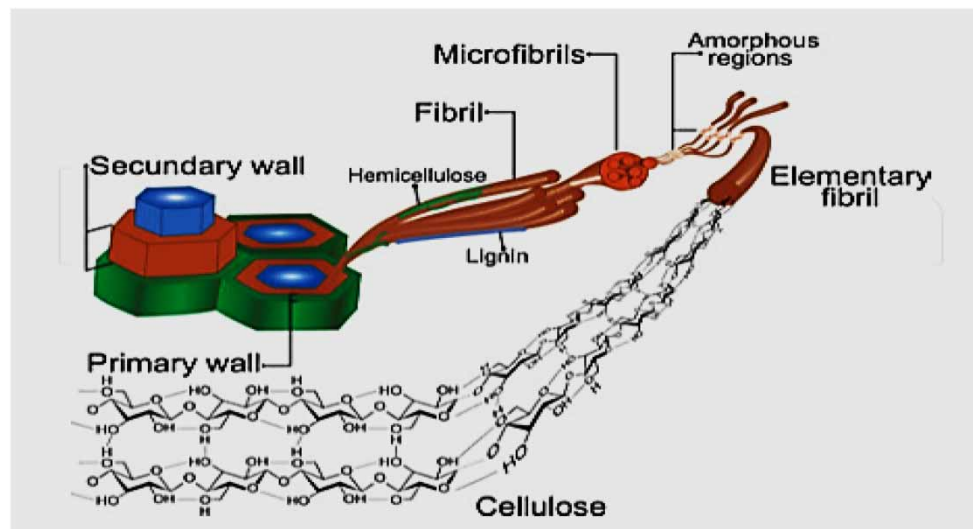


Figure 6 | Hierarchical form of cellulose isolated from plants (Rojas *et al.* 2015).

Cellulose has four main polymorphs based on its molecular orientations and intermolecular/intramolecular interactions. They are cellulose type I and its two crystalline allomorphs, cellulose type II, III and type IV cellulose (Trache *et al.* 2017). The properties of each type vary among the polymorphs and are influenced by the source from which the cellulose is obtained (Shak *et al.* 2018). Cellulose type I is a natural polymer and occurs as cellulose I α (triclinic structure) and cellulose I β (monoclinic structure). Both forms (I α and I β) are similar to each other but the packing pattern in the lattice differs, due to varying degrees of hydrogen bonding existing between the chains. Cellulose I α is often derived from microbial and algal species, while cellulose I β is found in the cell walls of higher plants (George & Sabapathi 2015; Joseph *et al.* 2020). Cellulose II, also known as regenerated cellulose, is a more soluble crystalline form, produced after recrystallization or mercerization of cellulose with sodium hydroxide solution. The main distinction between cellulose type I and type II is in the manner their atoms are packed: cellulose II has anti-parallel packing, while cellulose I have a parallel or aligned arrangement. The treatment of cellulose type I and II with ammonia yields cellulose III_I and III_{II}, respectively, while further treatment of cellulose type III yields the cellulose type IV (Gopakumar 2018; Wohler *et al.* 2022).

In summary, cellulose (C₆H₁₀O₅) is an essential biopolymer with distinctive characteristics like low toxicity, low density, high tensile strength and strong mechanical properties. It has been identified as the most abundant, sustainable biopolymer in existence, with a unique composition which makes it applicable for diverse industrial applications. Although cellulose can be found in plant cell walls and organisms like tunicates, bacteria and algae, plant-derived cellulose fibres are preferred over others because they are readily available and more abundant in nature. Cellulose consists of highly organized structures and structural entities in its cellulose chains. This is due to the regular molecular structure of cellulose, the rigid molecular chain and the strong hydrogen bonds that facilitate molecular arrangement and aggregation cellulose can exist in several polymorphs or allomorphs because of the various inter- and intramolecular arrangements. It can be categorized into four types of polymorph: cellulose I, II, III and IV. The physico-chemical parameters vary between these polymorphs.

4. PRODUCTION OF CNCs

4.1. Extraction of cellulose from plant biomass

The utilization of cellulose as flocculants is often limited due to its comparatively low chemical reactivity and insolubility in water. To address these deficiencies, cellulosic materials must be chemically engineered to improve their reactivity and compatibility for the elimination of contaminants from wastewater. An exponential rise in surface area, crystallinity, hydroxyl group and aspect ratio may be achieved by converting cellulose into CNC. Meanwhile, cellulose must first be separated from the biomass to facilitate reactions with chemical reagents and the removal of impurities before CNC production (Yoon *et al.* 2014; Shak *et al.* 2018). The common methods for the extraction of CNCs from cellulose are the mechanical technique, chemical hydrolytic process, biological hydrolytic technique or a combination of all the above methods (Yang *et al.* 2019). However, since cellulose is composed of glucose molecules, linked together by β -1-4-glucosidic bond, a process that involves the partial disintegration of the β -1-4-glucosidic molecular bond will be the best option for the isolation of CNC from cellulose. This is why the chemical technique using acid hydrolysis is often preferred as it facilitates the disintegration of the bonds (Shak *et al.* 2018). Chemical treatment is a well-known and widely used process that breaks the disordered and amorphous parts of the cellulose, releasing single and well-defined crystals in the process. In the first stage of the cellulose extraction process, alkali and acid-chlorite treatments are used to pre-treat the biomass precursor in order to remove hemicelluloses and lignin from the core cellulosic component (Phanthong *et al.* 2018; Sharma *et al.* 2019). Alkaline treatment has long been regarded as one of the most economical treatments for surface modification. During the cellulose extraction process, the biomass is hydrolyzed to enhance the removal of hemicelluloses and other impurities like wax, lignin, fats, pectin and protein using alkaline solutions. Thereafter, sodium chlorite acidified with glacial acetic acid or hydrogen peroxide/sodium hydroxide solution is used to remove the residual lignin from the cellulose. This step is also known as bleaching or delignification (Ravindran *et al.* 2019; Sharma *et al.* 2019). The delignification process improves the crystallization potential, enhances interfacial bonding and improves cellulose fibre compatibility for modification. As a result, the mechanical characteristic of the cellulose fibres is greatly enhanced (Lefatshe *et al.* 2017).

4.2. Conversion of cellulose to CNCs via acid hydrolysis

CNC is commonly produced by the chemical (acid) hydrolysis of nano and microfibrillated cellulose. During the hydrolysis, the acids release hydronium ions which easily react with the available oxygen on the glycosidic bonds of the amorphous regimes, thereby initiating the protonation of the oxygen element. This facilitates the hydrolytic cleavage of the glycosidic molecular bonds and results in the release of individual nanocrystals (Vazquez *et al.* 2015; Hamad 2017). The disordered or amorphous domains that occur as chain dislocations in some parts of the cellulose fibres are more susceptible to chemical reactions due to the weak hydrogen bonds and decreased steric hindrance. As a result, amorphous portions are more readily hydrolyzed by acids than the regularly aligned sections, which are more hydrolysis-resistant (Trache *et al.* 2017). Mineral acids, the most common of which is sulphuric acid, are the most used reagents for the extraction of CNCs (Hamad 2017; Sunasee & Hemraz 2018). During the production of CNCs, the cellulose is hydrolyzed using 55–64% H₂SO₄ for 45–60 min and thereafter, the reaction is stopped (after completion) by using 10-fold deionized water and NaOH solution for repeated rinsing of the CNC until a near-neutral pH solution is obtained. The sulphate functionality added to nanocellulose during an acidic reaction, which accelerates breakdown tendencies and results in cellulose with lower heat stability, is a significant drawback of H₂SO₄ hydrolysis. This affects the potential application of nanocellulose, particularly when used for strengthening nanocomposite materials. The use of mineral acids other than

H₂SO₄ for the hydrolysis of cellulose polymer has, therefore, been the subject of study in recent years. Hydrochloric acid (HCl), phosphoric acid, hydrobromic acid, organic solvent or a combination of both organic and inorganic acids have all been used to create CNCs with unique properties (Lizundia *et al.* 2016; Trache *et al.* 2017). Cellulose hydrolyzed by HCl has been successfully employed to produce CNCs. This was performed by using HCl to dissolve the amorphous material from the crystalline regions of cellulose, leaving behind crystals with essentially neutral surfaces and hydroxyl groups as the only functional group (Lizundia *et al.* 2016). The nanocrystals formed (HCl-CNC) possess strong hydrogen bond formation, low colloidal stability and a high propensity to aggregate. The colloidal stability of HCl-CNCs is influenced by their concentration in an aqueous medium; the higher their concentration, the more pronounced the aggregates produced. Nevertheless, CNCs formed by HCl hydrolysis have higher thermal stability than nanocrystals produced by H₂SO₄ hydrolysis (Xie *et al.* 2018a, 2018b). The presence or absence of a charge on CNC is influenced by the type of acid treatment used during the hydrolysis of the cellulose fibre. CNCs produced from HCl treatment have no surface charge (i.e. neutral) while H₂SO₄ will impact 0.5–2% anionic sulphate half-ester (–OSO₃[–]) groups onto the synthesized CNCs surface. The sulphated CNCs are electrostatically stable and possess high colloidal stability in water due to the repelling force between the negative charges (Lizundia *et al.* 2016; Trache *et al.* 2017).

A variety of experiments have focused on the replacement of liquid acids with solid acids in recent times. Liu *et al.* (2014) described a renewable process for the synthesis of CNCs from purified hardwood pulp via hydrolysis in distilled phosphotungstic acid crystals (H₃PW₁₂O₄₀). They obtained cylindrical-shaped CNCs with diameters between 15 and 40 nm and lengths greater than several hundred nanometres. Their findings revealed that the CNCs produced were more thermally stable in comparison to sparsely sulphated CNCs. Furthermore, the acid crystals utilized in the synthesis could be easily extracted with the aid of diethyl ether and re-used for subsequent hydrolysis. However, there are some limitations to this procedure, such as the high cost of the acid crystals, the prolonged hydrolysis time and the low yield it produces (Kargarzadeh *et al.* 2018). The operation time may be reduced from 30 h to 10 min when solid phosphotungstic acid is used in conjunction with the sonication process, with a 225 sonication capacity being the ideal setting. This results in CNCs with about 88% crystallinity and 85% yield (Bee *et al.* 2016). Another method for producing CNCs involves the hydrolysis of cellulose precursors with gaseous acid. This operation is performed using a variety of gaseous acids, including HCl, HNO₃ and trifluoroacetic acid (Kontturi *et al.* 2011). During the preparation, wet cellulose is hydrolyzed by a combination of high moisture and acidic gas that is absorbed by the cellulose fibres. As the acidic gas reacts with the moisture in the cellulosic material, a large amount of acid is generated locally. The cellulose amorphous domains and local interfibril interactions experience a high degree of hydrolysis because of this effect. For further defibrillation and the production of CNCs, mechanical treatment such as grinding or ultrasonication is required for this method (Kargarzadeh *et al.* 2018). A schematic representation of the extraction process of CNCs from cellulose is presented in Figure 7.

In conclusion, cellulose must first be purified to remove non-cellulosic components such as proteins, waxes, lignin and hemicellulose. The removal of these components results in the separation of individual cellulose fibres. Thus, the amorphous phase of cellulose is more susceptible to the cleavage of glycosidic bonds, and further hydrolysis with acids e.g. H₂SO₄ result in nanostructures with higher crystallinity like the CNCs, than the original fibre. In recent decades, more research into the use of chemical reagents and methods other than H₂SO₄ for hydrolysis of cellulose polymer has been conducted in order to produce CNCs with better surface characteristics. Chemical reagents such as HCl, hydrobromic acids, organic solvent and phosphotungstic acid crystals among others have been employed for the production of CNCs.

5. UNIQUE PROPERTIES OF CNCs

5.1. Crystallinity

The crystalline form of CNCs could be attributed to the parallel alignment of cellulose chains, facilitated by the strong inter-hydrogen linkage and van der Waals attractive force. The degree of crystallinity of CNC is the ratio of the mass of the crystalline regions to the overall mass of the CNCs. It is theoretically about 100% if the amorphous region is completely removed, but the presence of residual disordered region will affect its crystallinity (Tang 2016). The degree of CNCs crystallinity is influenced by the source and conditions for extraction, which is widely acknowledged to be within the range of 54 and 90% (Sinha *et al.* 2015). For example, rutabaga, flax and wood cellulose nanofibrils (CNFs) have a crystallinity of 64, 59 and 54%, respectively, while the crystallinity of CNCs isolated

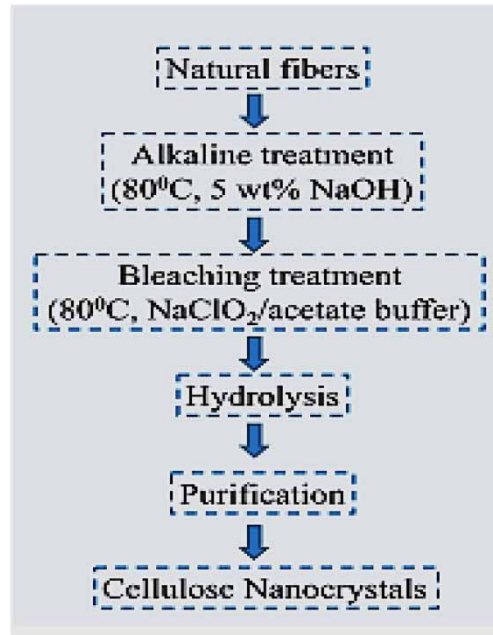


Figure 7 | Schematic representation of the preparation procedure for CNCs (Sunasee & Hemraz 2018).

from rice husk, cotton, sisal and commercial microcrystalline cellulose (MCC) were found to be 76, 94, 85.9 and 81.7%, respectively (Rojas *et al.* 2015). For some common fruits, their crystallinity content occurs in the order of pineapple > banana > jute and corresponds to the quantity of cellulose measured in these samples. In addition, CNCs extracted with H_2SO_4 normally have lower crystalline values than those made with HCl. The most popular technique for determining the crystalline index of CNC is Segal's method, which applies the following equation in calculating crystallinity from X-ray diffractometer (XRD) spectra (Thompson *et al.* 2019).

$$I_{Cr} = \left(\frac{I_{002} - I_{am}}{I_{002}} \right) \times 100 \quad (2)$$

where I_{Cr} is the crystallinity index, I_{002} represents both crystalline and amorphous regions taken at $2\theta = 22.6$ intensity and I_{am} is the amorphous region taken at $2\theta = 18$ intensity (Thompson *et al.* 2019). Segal's method makes crystallinity determination for cellulose and its derivatives fast and simple. However, since it is a relative calculation, there are certain concerns with this approach in terms of precision.

5.2. Surface area

The specific surface area of cellulose nanoparticles is usually high with values between 50 and 200 g/m^2 . The large specific surface area contains a lot of exposed hydroxyl group that improves their suitability for grafting or crosslinking with other compounds (Rojas *et al.* 2015; Lizundia *et al.* 2016). Furthermore, nanocellulose possesses a high adsorption potential due to its high specific surface area, which can be further improved by chemical modification. This means that it has a very high potential for use as an adsorption material in the research fields of water purification and other related fields (Shen *et al.* 2020).

5.3. Aspect ratio

Length (L) and diameter (D) are the physical dimensions which determine the aspect ratio (L/D) of CNCs. Thus, the aspect ratio of CNCs could be defined as the ratio of their length to diameter. The lengths of CNCs are within the range of 100 nm to μm and the widths could be less than 10 nm to around 50 nm (Thompson *et al.* 2019). The large range in the dimension of CNC may be attributed to several single fibres not being sufficiently separated during the production process. CNC has a significant aspect ratio due to the small width of the extracted nanofibres which ranges from a few nanometres to an average length of micrometres (Thompson *et al.* 2019; Yang *et al.* 2019). CNCs with a high aspect ratio facilitate the formation of percolated networks at low concentrations due to their needle-like structure, which largely enhances their flocculating properties. Furthermore, a higher aspect ratio

greatly increases the viscosity of CNC suspensions (Tang 2016). Several factors like the biopolymer from which cellulose is derived and their hydrolytic reaction conditions influence the aspect ratio of CNCs. Tunicates and BC have been reported to have larger dimensions than CNCs derived from wood or cotton. Nanocrystalline particles generated from hardwood had a diameter and length of 3–5 nm and 100–300 nm, respectively. Furthermore, CNCs with better crystallinity are produced with purer cellulose materials (Thompson *et al.* 2019).

5.4. Mechanical properties

Investigations into the morphology of CNCs have revealed their excellent mechanical and elastic properties. Their low weight and rigidity contribute to their application as a reinforcement material. At low filler loading, nanocellulose has proven to be a significant insulator, with a modulus of elasticity of up to 150 GPa and a low thermal expansion coefficient of 0.01 ppm/K. Nanocellulose has a tensile strength ranging from 7.5 to 7.7 GPa, which is higher than that of steel wire and general carbon fibre, even though its density (1.6 g/cm^3) is about one-fifth that of steel (Kargarzadeh *et al.* 2017; Thompson *et al.* 2019; Shen *et al.* 2020). XRD technique and atomic force microscopy (AFM) are indirect experimental measurements employed along with theoretical equations for the calculation of the elastic properties of CNCs. However, some difficulties encountered in quantifying the tensile modulus and resistance of CNCs are due to the limitations in calculating the mechanical properties of nanomaterials along multiple axes (George & Sabapathi 2015).

5.5. Rheological property

The rheological properties of CNCs suspension are influenced by analytical conditions (e.g. temperature, concentration of suspension, pH, shear rate, etc.) and other intrinsic factors such as gelation and liquid crystalline properties (Rojas *et al.* 2015). In diluted CNC suspensions, shear-thinning patterns appear, illustrating the impact of concentration, particularly at low concentrations. At significant levels, a peculiar pattern where the suspensions are lyotropic occurs. This could be attributed to the alignment of rod-shaped nanocrystals at a critical shear rate. After the shear rate reaches a critical level, the chirality of CNCs suspension disintegrates to a fundamental nematic structure, but if their aspect ratio is high, their viscosity may be enhanced (George & Sabapathi 2015; Tang 2016). The type of acid used to hydrolyze CNCs suspensions may also affect their rheological properties. Nanocrystals produced via H_2SO_4 hydrolytic reactions exhibit some shear-thinning effect that is unaffected by the length of time while nanocrystals produced by HCl treatment significantly exhibit higher shear-thinning. HCl-treated nanocrystals are anti-thixotropic at low concentrations and become thixotropic at high concentrations. CNCs suspension may become permanently agglomerated when dry, thereby affecting their size and peculiar properties. Horrification is the term used for irreversible agglomeration, which could be caused by the development of rigid hydrogen linkages. Agglomeration of CNCs can be avoided when a freeze-drying technique or supercritical drying is applied in the drying process (Baheti *et al.* 2013; Rojas *et al.* 2015).

5.6. Thermal properties

A crucial factor in the practical usage of CNCs is their thermal property. Understanding their thermal behaviour is, therefore, essential. Compared with hemicelluloses, nanocelluloses are more thermally stable and have a decomposition temperature of $350 \text{ }^\circ\text{C}$ (Rojas *et al.* 2015; Tang 2016). Furthermore, some factors which include the cellulose source can affect the thermal stability of nanocellulose. For example, the thermal stability of CNCs with neutral surface or lower sulphate moieties is higher than CNCs with a larger sulphate content (Xie *et al.* 2018a, 2018b). Furthermore, longer hydrolytic reaction periods may reduce the thermal stability of CNCs and subsequently lower the degree of crystallinity (Hamad 2017). The reduction of the amount of sulphate on sulphated CNCs and other physical or chemical modifications procedures may improve their thermal stability.

5.7. Surface chemistry of CNCs

The three hydroxyl groups which exist within the single glycosidic unit of the polymer chain of cellulose provide reactive sites for simple chemical modifications. The reactivity of CNC is considered to be felt less in the disordered cellulose region because most of the cellulose chains are hidden inside the crystalline planes. The hydroxyl groups in the 2nd and 3rd positions, bonded directly to alkyl groups on the anhydrous glucose units, experience a steric hindrance caused by the supramolecular structure of cellulose. The hydroxyl group in the sixth position, which is the primary alcohol, is attached to the single alkyl group on the glucose ring's side, and can thus react ten times faster than the other hydroxyl groups, especially in esterification reactions (Lizundia *et al.* 2016). Likewise, the OH-C2 group react twice as fast as the OH-C3 group in etherification reactions. Thus,

the overall reactivity of cellulose depends on the interfibrillar bonds, interfibrillar interstices and the capillary structure of the cellulosic material, as well as other reaction conditions such as solvent type or reactant utilized (Lizundia *et al.* 2016). In addition to the many OH groups, CNCs also contain additional types of functional groups that are associated with a specific modification method, set of reaction conditions or reagents utilized. Sulphate groups ($-\text{OSO}_3^-$), carboxyl groups ($-\text{COO}^-$) and acetyl groups ($-\text{COCH}_3$) are the most popular functional groups, while the amino groups ($-\text{NH}_2$), aldehyde groups ($-\text{CHO}$) and thiol groups ($-\text{SH}$) can be attached to CNCs via mild post-hydrolysis reactions (George & Sabapathi 2015; Tang 2016). The charge exhibited by CNCs is influenced by the type of functional groups on their surface. CNCs with sulphate or carboxylic functionality are negatively charged throughout a wide pH range (greater than pKa values), while CNCs with amino modifications are positively charged below the pKa values of the weak base. CNCs with quaternary ammonium functionality would also have a permanent positive charge (Rojas *et al.* 2015; Tang 2016).

5.8. Toxicity

Tests have been performed to determine the toxicity of CNCs concentrations and safety when consumed. Results obtained from these tests showed no obvious health associated with the use or ingestion of CNCs (Thompson *et al.* 2019). The co-toxicological tests performed with several marine species such as daphnia and rainbow trout showed that the toxicity and environmental risk levels of CNCs are very low. Furthermore, cytotoxicity (intracellular toxic effect) and the pro-inflammatory impact of CNCs are significantly lower than those for multi-walled carbon nanotubes (MWCNTs) and crocidolite asbestos fibres (CAFs). No known adverse health effects involving CNC-based products have been recorded, although the toxicity levels of these materials could be affected by production methodology, modifying agents and type of functionality imparted on the CNCs. Thus, safe/green chemicals should be considered during the synthesis of CNCs and toxicity evaluation must be regularly conducted (Rojas *et al.* 2015; Thompson *et al.* 2019).

In conclusion, the CNCs are more crystalline forms of nanocellulose due to the regular pattern of cellulose chain arrangement and strong inter-hydrogen linkage. CNCs have a large surface area with a high density of hydroxyl groups embedded in them. This provides more active sites for modification via the incorporation of diverse types of functional groups. CNCs possess a high aspect ratio, excellent mechanical properties, improved thermal stability, low toxicity levels and rheological properties that influence their forms in solution.

6. CONVERSION OF CNCs TO COAGULANT

6.1. Importance of CNC as a coagulant for water treatment

CNCs can be obtained from plant biomaterials; hence, it is inexpensive, sustainable and naturally abundant. This significantly reduces the expense of water treatment when applied as a coagulant (Amran *et al.* 2018). CNCs are a safer alternative to synthetic chemicals used in water treatment. Unlike residual chemical coagulants, their non-toxic and biodegradable qualities render their deposit in water harmless to humans. The sludge generated from CNCs treatment is biodegradable, less hazardous and does not change the pH of the water being used (Shaharom 2019). The chemical modification of CNC is necessary if CNC is to be utilized as a coagulant. The chemical modification of pristine CNC refers to the addition of a chemical functionality to its surface, which enhances the material's interactions with its surrounding media without adversely affecting the surface properties (Shak *et al.* 2018). The dispersion of CNCs in non-polar solvents and polymeric matrices is difficult due to the hydrogen bonding which causes the nanoparticles to rapidly aggregate. Functionalization, therefore, facilitates the tuning of surface energy properties for improved compatibility when utilized in such hydrophobic media (George & Sabapathi 2015). Thus, molecules with electrostatic charge can be imparted onto the surface of CNCs, resulting in improved dispersion in solvent. Functionalization of CNCs also improves their coagulative properties for the removal of specific pollutants from water. More reactive sites for grafting of functional groups are formed on their surface due to an increase in the available hydroxyl groups. In addition, functionalizing CNCs is appealing because it allows for the formulation of advanced nanomaterial with novel or enhanced properties (Wang *et al.* 2016). The quantity of charged molecules on the surface of CNCs (i.e. charge density) influences the dispersibility of the individual crystals in solution. It also determines the strength of the bond formed between the CNCs and the new functional groups (Wang *et al.* 2016). The challenge encountered in the chemical modification of CNCs is about preserving the CNCs' original morphology during the modification process (George & Sabapathi 2015). Therefore, the conditions for CNCs modification must be kept mild during the functionalization process to avoid the destruction of the cellulose nanocrystal's original morphology.

6.2. Recent strategies for the modification of CNCs

Surface covalent modifications of CNCs can be divided into two groups: (1) covalent modification which includes polymer grafting strategy and substituting the hydroxyl groups on CNCs surface with other functional molecules via esterification, silylation, etherification, carboxylation, etc., and (2) non-covalent modification.

6.2.1. Covalent modification: functionalizing (substituting) surface hydroxyl groups with small molecules

6.2.1.1. Esterification. Esterification is a popular method for modifying nanocellulose because it significantly replaces the OH groups on the pristine CNCs. A unique characteristic of this strategy is the mild reaction conditions required which enable the displacement of OH groups during CNC modification without destroying the crystallinity of the CNC (Rojas *et al.* 2015; Huang *et al.* 2019). The hydroxyl groups on the cellulose surface are transformed into esters during the esterification process. Sulphation and phosphorylation are two other common esterification reactions that are used to add electrostatic functionalities to CNC in order to obtain more stable aqueous suspensions (Rojas *et al.* 2015; Wang *et al.* 2018). Acyl chlorides or anhydrides can also be used to introduce ester groups onto the nanocellulose surface. However, acid chloride esterification of nanocelluloses may undergo significant bulk modification, which may adversely reduce their crystallinity while providing a high degree of substitution. Acetylation of nanocellulose is a well-researched method (among various post-modification reactions) employed to incorporate alkyl molecules onto CNCs. It involves the use of carboxylic acid derivatives (e.g. acetic anhydride) in the presence of a catalyst such as perchloric acid, sulphuric acid or pyridine for modification (Hokkanen *et al.* 2016; Wang *et al.* 2018). The reaction between the anhydrides and hydroxyl groups of CNCs produces an ester that imparts new properties on its surface (Thompson *et al.* 2019). Succinic anhydride is an effective reagent for functionalizing CNCs because it allows the inclusion of aliphatic chains and carboxylic end groups. Additional solvents are not required because the acetic anhydride when used in sufficient amounts allows effective dispersion and mixing of the CNCs. Leszczyńska *et al.* (2019) studied the esterification process of CNCs using succinic anhydride. They investigated the effect of reaction parameters which include temperature, time, thermal properties and reagent molar ratio on the morphology, across a broad range of values via the X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared microscopy (FTIR), scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD) curve and thermogravimetric analysis (TGA). According to Leszczynska and his colleagues, CNCs with high surface quality and thermal stability was produced. They reported that the degree of modification increased as the reaction time and molar ratio of succinic anhydride to nanocellulose hydroxyl groups (SA:OH) increased.

6.2.1.2. Oxidation. The oxidation method has been used to produce carboxylated nanocellulose. This method is often used because it easily oxidizes C6-OH into a carboxyl group. The different oxidative methods that are now available are quite effective in producing carboxylated CNCs with charged groups. These include ammonium persulphate (APS) oxidation, citric/hydrochloric acid hydrolysis, nitric/hydrochloric acid hydrolysis, periodate chlorite oxidation and two-step radical oxidation of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Takaichi & Isogai 2013; Batmaz *et al.* 2014; Yu *et al.* 2016a; Song *et al.* 2019). TEMPO-oxidation is a method that produces a high yield of carboxyl group. It consists of a combination of the TEMPO reagent, NaBr and NaClO for the modification process. The TEMPO-oxidation process is more often used because of its effectiveness and easy reaction mechanism. Batmaz *et al.* (2014) reported a two-step TEMPO-oxidation mechanism in conjunction with NaBr and NaOCl, which produced carboxylated CNCs with a higher carboxyl content of 2.1 mmol/g. They reported that the modified CNCs could remove cationic dyes with greater efficiency (769 mg dye/g CNC). Unfortunately, only the C6 position on the CNCs surface produces carboxylate groups by TEMPO radical oxidation, inhibiting further oxidation of the other OH groups (Song *et al.* 2019).

6.2.1.3. Etherification. Esterification is an effective functionalization process that typically employs an epoxy molecule (modification agent) in conjunction with organic liquid and a heating device for etherification. The reaction between the epoxy group and the OH group on CNC results in the formation of an ether molecular bond and more OH groups at the β -position. However, polymerization is also likely to occur on the nanocellulose surface if the OH group produced continues to react with the epoxy groups (Lizundia *et al.* 2016). The polymerization reaction is highly undesirable as it tends to significantly reduce the efficiency of this process. Although polymerization cannot be completely eliminated, it can be partly overcome by adjusting the reaction conditions (Huang *et al.* 2019).

6.2.1.4. Amidation. The amidation method involves a mild and efficient modification process that utilizes biomolecules containing amine groups to functionalize the surface of nanocellulose. The reaction occurs during the conjugation of two molecules, each consisting of an amine and a carboxyl group. However, since these functionalities are absent on nanocellulose surface, they must be incorporated onto the nanocellulose surface via appropriate modification methods (e.g. TEMPO-oxidation) before amidation modification (Huang *et al.* 2019; Rana *et al.* 2021). The amidation process could be performed in aqueous solutions or organic solvents such as dimethylformamide (DMF). During the process, *N*-hydroxysuccinimidyl (NHS) esters are formed, which activate the TEMPO-oxidized carboxylated nanocellulose in an aqueous reaction system. This activation increases the reaction between the carboxyl molecules of the nanocellulose and the generated amide groups. The second stage in the amidation process involves the combination of amide molecules and NHS-activated carboxylated nanocellulose, which are then conjugated to the nanocellulose surface through amide bonds (Huang *et al.* 2019). Le-Gars *et al.* (2020) investigated a two-step reaction path used in the grafting of 1-methyl-3-phenylpropylamine (1-M-3-PP) on CNCs. They first oxidized CNCs with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and then performed an amidation reaction in an aqueous medium under moderate conditions with *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide (ECD)/*N*-hydroxysuccinimide (NHS) as a catalytic agent. A modified CNCs was obtained after an amidation reaction with 1-M-3-PP (CNC-1-M-3-PP).

6.2.1.5. Silane coupling reaction. Silane coupling reagents have been poorly explored for CNCs surface functionalization. The coupling reagents that have been studied involve the reaction between the 'oxy' group and the hydroxyl groups on the surface of the CNC. Alcohol is a by-product of this reaction. Silane reagents normally have linear chains, which is beneficial when attempting to decrease CNC's hydrophilic properties. These binding agents have the benefit of enabling more modification of the grafted nanocellulose chain based on the type of coupling agent used (Thompson *et al.* 2019). Various techniques and reagents have been investigated for the functionalizing procedure. Kargarzadeh *et al.* (2015) performed silane modification of CNCs by using *N*-(aminoethyl)-amino propyltrimethoxy silane (APS). During the reaction, CNC was dispersed into a solution of ethanol, water and silane agent. The mixture was sonicated for a few minutes and then allowed to sediment for 2 h (after pH adjustment). This method is advantageous because it is a one-pot reaction that, except for sonication, requires no extra energy to efficiently spread the CNC in an ethanol/water solution.

6.2.1.6. Carbamation. Isocyanates are used in carbamate reaction to incorporate functional groups onto the surface of CNCs. The use of isocyanates for surface modification was investigated by Siqueira *et al.* (2010). They modified sisal-based CNCs using *n*-octadecyl isocyanate as a catalyst. The procedure for using isocyanates is similar to using a silane binding agent, where the hydroxyl group was the point of contact for the functionalization mechanism and reacts with the oxygen at the functional group's end. According to Siqueira and his colleagues, a urethane chain was formed and grafted onto the CNC's surface. Surface functionalization with isocyanate was investigated by Girouard *et al.* (2016). This was performed using isophorone di-isocyanate (IPDI). The CNC was dissolved in dimethyl sulphoxide (DMSO) and sonicated. The resulting solution was reacted with IPDI at 60 °C overnight in the presence of nitrogen and a catalyst. According to Girouard and colleagues, the modified CNC materials had better dispersion ability than pristine CNC, when immersed in a polyurethane matrix.

6.2.1.7. Cationic modification. Weak or highly charged ammonium-containing compounds, such as EPTMAC (2,3-epoxypropyl-trimethylammonium chloride), can be grafted onto the surfaces of CNCs because positive charges can be easily incorporated onto CNCs. Cationization of CNCs occurs by reacting OH groups of alkali pre-treated cellulose with the charged EPTMAC. Thus, well-dispersed aqueous CNCs suspensions are formed by the attachment of EPTMAC to the surface of CNCs by nucleophilic addition. The nanocrystal properties were preserved during modification while the grafting process caused a decrease in the overall surface charge density, with a reversal of the initial negative surface charge of CNCs to cations (Lizundia *et al.* 2016). However, due to the high viscosity of the solution, shear birefringence develops in the cationic-modified CNCs, preventing the formation of the chiral crystalline liquid phase. A cationic surfactant, hexadecyltrimethylammonium (HDTMA) bromide, was used by Kaboorani & Riedl (2015) to modify the surface of CNCs. The CNC was subjected to chemical and structural characterizations both before and after modification. Their research's findings demonstrated that new chemical groups (such as CH₂, CH₃ and quaternary ammonium groups) were

incorporated onto the surface of the CNC as a result of the chemical interaction between CNC and HDTMA. According to Kaboorani and Riedl, the HDTMA transformed the CNC surface without affecting its reinforcing properties because no changes to its crystallite structure or size had occurred.

A summary of the common surface modification strategies used to functionalize CNCs is presented in Figure 8.

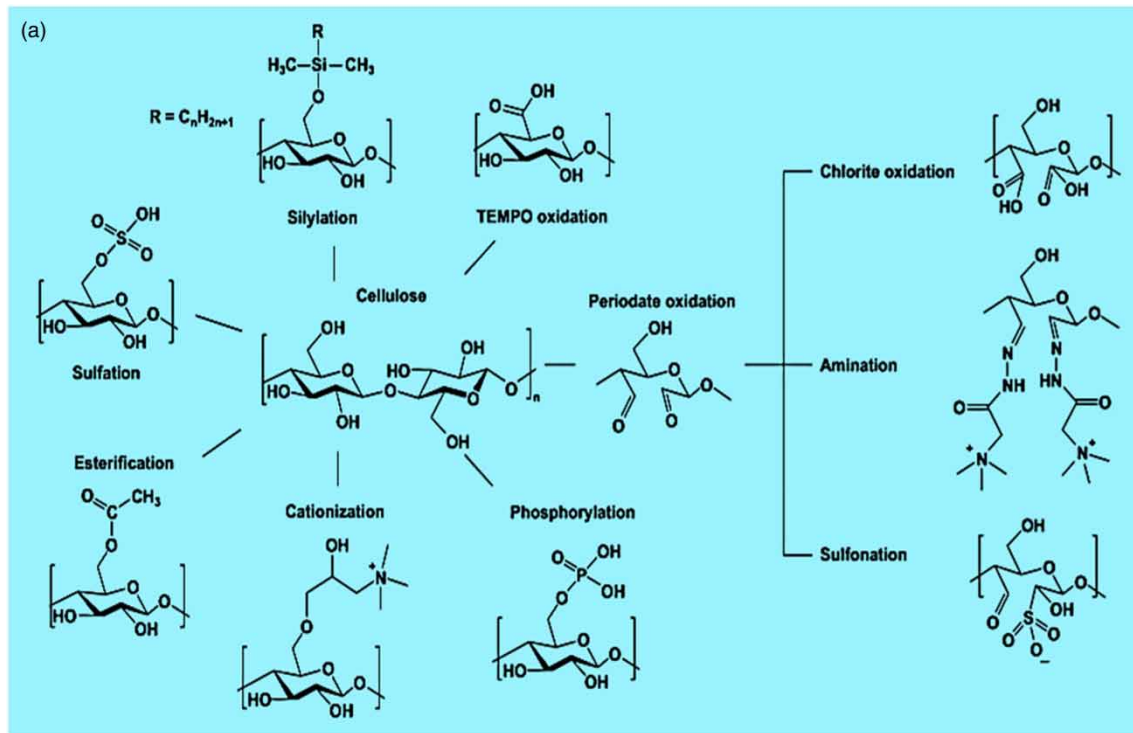


Figure 8 | Schematic representation of strategies for nanocellulose modification (Tavakolian *et al.* 2020).

6.2.1.8. Polymer grafting. Covalent polymer grafting on CNCs' surface has been accomplished via two popular methods: (1) the 'graft onto' method of surface functionalization with different coupling agents and (2) surface modification of polymers using the 'grafting from' technique which utilizes the ring-opening polymerization (ROP) mechanism, atom transfer radical polymerization (ATRP) and single-electron (SET-LP) for polymer surface functionalization (Habibi 2014; Thompson *et al.* 2019). The modification techniques earlier described (i.e. oxidation, esterification, amidation, acetylation, etc.) can also be incorporated in the polymers or oligomers grafting procedures for surface modification through the creation of new covalent bonds (Lizundia *et al.* 2016). The polymers to be grafted are typically lengthy chains with more hydroxyl groups compared with pristine CNCs' hydroxyl groups. The existence of these long chains and hydrogen bond linkage limits the reaction between the nanoparticles. The 'grafting onto' method involves using a binding agent to attach a target polymer to the hydroxyl group of the pre-synthesized cellulose polymer's surface. The 'polymer grafting from' approach focuses on the growth of polymer chains grafted *in-situ* onto a nanocellulose surface (Habibi 2014; Thompson *et al.* 2019). The hydroxyl groups, which serve as active sites, will bind the new chains as it increases on the surface. A few example of the mechanisms utilized in the 'grafting from' method include ring-opening polymerization (ROP) and radically induced polymerization approaches such as the atom transfer radical polymerization (ATRP) (Yu *et al.* 2016a, 2016b; Wang *et al.* 2018). ROP is a polymerization method that can polymerize lactides, lactones, siloxanes, cyclic carbonates, ethers and other cyclic monomers under controlled reaction (Lizundia *et al.* 2016). A catalyst such as Tin (II)-ethylhexanoate ($Sn(Oct)_2$) is widely utilized for the ring-open polymerization of monomers like caprolactone (CL), *p*-dioxanone and lactide (LA). Although ROP can be performed through a variety of procedures, the widely recognized mechanism for the activation of the process involves the transformation of $Sn(Oct)_2$ to Sn alkoxide. The alkoxide is the specific initiator formed when $Sn(Oct)_2$ react with alcoholic compound or protic compounds/impurities (i.e. the 'coordination-insertion' mechanism). The alcohol-to-monomer ratio can be altered to attain the desired molecular weight of the final polymer (Lizundia *et al.* 2016). The ATRP is a popular polymer grafting technique because it can undergo *in-situ* polymerization reaction. An example of the

ATRP is the grafting of methyl methacrylate monomer (MMA) and butyl acrylate monomer (BA) onto CNCs to produce strong CNC-based thermoplastic elastomers (CTPEs) (Yu *et al.* 2016a, 2016b). An initiator must be bound to the pristine CNCs surface in the form of 2-bromoisobutylryl bromide for ATRP reaction to occur. The *in-situ* polymerization takes place between the surface-bound bromide groups and the MMA and BA in solution. The synthesized CTPEs produced had enhanced mechanical properties and better compatibility with CNCs because CNC could disperse better in it. Deng *et al.* (2015) investigated a graft copolymerization that involved dispersing CNCs in a mixture of ceric ammonium nitrate (CAN)/nitric acid solution into which MMA has been dissolved. The solution was left to copolymerize at 45 °C for 3 h. Deng and colleagues reported that the synthesized MCC-g-PMMA had better thermal and reinforcing ability than pristine MCC; when applied as reinforcement fillers in natural rubbers (NRs). They attributed the enhanced surface properties of MCC-g-PMMA to the structure formed between grafted PMMA and NR. Espino-pérez *et al.* (2016) in a related study investigated the modification of nanocrystals polysaccharides with polylactide, using ozonolysis-promoted free radical polymerization. Ozonolysis is the process that refers to the disintegration of unsaturated bonds present in organic chains by ozone to generate new reaction sites. An additional reagent may be added for subsequent modification. According to their findings, the CNC's thermal stability increased after modification. They discovered that the compatibility with the polylactide was improved by grafting and formed nanocomposites with improved water vapour resistant properties. Espino-Pérez and his co-workers further reported that the increased effectiveness of the grafting process would facilitate the reduction of hydrophilic properties of the polysaccharides.

6.2.2. Non-covalent surface modification (via surfactants)

Non-covalent surface functionalization of CNCs is accomplished when oppositely charged polyelectrolytes, polymer coating or adsorption mechanisms of surfactants are utilized for the modification of CNCs. The intermolecular reaction which occurs between the modifying agents and the CNCs are the hydrogen bonding, electrostatic attraction and van der Waals attractive force (Zakeri *et al.* 2018). Mariano *et al.* (2017) prepared CNC-reinforced poly(lactic acid) (PLA) nanocomposites via non-covalent modification of CNCs with two different poly(L-lactide) (PLLA)-based surfactants: poly ethylene glycol block (PEG-b-PLLA) and an imidazolium group (Im-PLLA), in order to improve the filler/matrix compatibility. According to their report, the diverse adsorption processes on the CNC surface led to distinct rheological and mechanical characteristics while the application of the synthesized PEG-b-PLLA and Im-PLLA to CNC-reinforced PLA nanocomposites significantly improved the dispersion of the nanoparticles. The positive charged Im-PLLA's appears to generate ionic interactions between the CNCs and the ionic liquid block. Similarly, Zakeri *et al.* (2018) researched the non-covalent surface modification of CNCs using polyethyleneimine (PEI). They made a PEI solution with de-ionized water and dropped it into the CNC suspensions while mechanically stirring them. From the findings, they discovered an alteration in the apparent size of the CNC and its surface potential and described the degree of modification as a function of the volume of PEI. They also reported that adding PEI to the CNC suspension resulted in the formation of aggregates and phase separation of the CNC particles.

In summary, surface functionalization of CNC is necessary where CNC is to be utilized as a coagulant for water purification. CNCs modification improves their compatibility or suitability for the removal pollutants from water. Chemical modification of pristine CNC refers to the addition of a chemical functionality to its surface, which enhances the material's interactions with its surrounding media without adversely affecting the surface properties. The common modification strategies which involve the use of acids alkalis, and organic/inorganic compounds are oxidation, esterification, etherification, silane coupling reaction, carbamation, cationic modification, amidation and polymer grafting reactions among others.

7. POTENTIAL APPLICATION OF FUNCTIONALIZED CNCs AS A COAGULANT FOR WATER PURIFICATION

The scientific community has shown great interest in the potentials of nanomaterials for wastewater treatment in recent decades. Research opportunities into the usage of micro and nanocellulose biopolymers have been made possible by the global market for ecologically friendly and sustainable natural resources such as cellulose (Ganesan *et al.* 2018; Marey 2019). Cellulose nanomaterials have been proven to have the potential to improve the efficiency and cleaning up of polluted water at a reduced cost. CNCs, an important derivative of cellulose, are important nanomaterial that has acquired an advantage over native cellulose fibres due to their unique properties (Vazquez *et al.* 2015; Xie *et al.* 2018b). Novel cellulose-based products have been employed as photocatalysts,

adsorbents and flocculants in environmental remediation. However, the use of CNCs as coagulants for water purification is the main focus of this section.

Jiang *et al.* (2020) modified the surface of CNCs by grafting acryloyl oxy-ethyltrimethyl ammonium chloride (AETMAC) onto it with CAN as an initiator. The functionalized CNC (PAETMAC-g-CNC) was utilized as a coagulant for the removal of colour from dye solution (Reactive blue 19). PAETMAC-g-CNC was prepared by adding 10 mL of CAN and 50 mL of 20 g/L CNC suspension to a reactor being purged with nitrogen gas. Thereafter, a known amount of AETMAC was added to the mixture while the reaction proceeded in a nitrogen environment. According to Jiang and co-workers, the colour removal efficiency of the synthesized PAETMAC-g-CNC was over 80% at pH between 3 and 9 and a NaCl concentration of 60 g/L. They asserted that the high crystallinity and improved colloidal stability of the PAETMAC-g-CNCs and PAETMAC grafts greatly influenced the agglomeration of dye-containing flocs and accelerated their precipitation from the solution. It can be deduced from this study that PAETMAC-g-CNCs can decolourize RB-19 solutions within a short time, which is advantageous for industrial applications. Campano *et al.* (2019) in a related study investigated the flocculation performance of hairy cationic nanocrystalline cellulose (CNCC) in a kaolinite model suspension. CNCC is a new kind of cylindrical-shaped crystalline nanocellulose with functionalized amorphous chains on both ends. The CNCC was prepared in stages. First, dialdehyde-modified cellulose (DAMC) was produced by oxidizing 20 g of pulp with 19.6 g of NaIO₄ and 15.6 g of NaCl at room temperature for 24 h. Next, the DAMC was processed using a solution of 1 g of GT [(2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride, GT] and 2.4 g of NaCl per gram of DAMC for 24 h to produce cationic DAMC. In order to obtain the CNCC, the non-fibrillated fraction of the DAMC was removed after being sonicated and centrifuged at 5,000 rpm for 10 min. The result from this study showed that the CNCC is highly efficient in achieving clay particle aggregation, with immense flocculation efficacy over a broad range of 7.5–75 mg/g CNCC dosage.

Morantes *et al.* (2019) synthesized a novel water treatment flocculant via the cationic modification of CNCs with the quaternary compound 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC). Coagulation studies were performed to determine the ability of the synthesized coagulant to flocculate silica (SiO₂) suspension. During the preparation, NaOH solution was added to a CNC dispersion (2 wt%) to obtain a 2 M CNC concentration and thereafter, the solution was stirred at room temperature for 30 min. Next, various amounts of CHPTAC (6, 9 or 12) were added and the mixture was stirred at 25 °C for different periods (4, 8 or 24 h). The resultant cellulose nanocrystals-epoxypropyl trimethyl ammonium (CNC-EPTMAC) was thereafter washed and dried. According to Morantes and co-workers, the CNC-EPTMAC demonstrated a high flocculant performance for water treatment, by lowering turbidity by about 99.7%, at a concentration of only 2 ppm. Similarly, Song *et al.* (2019) in their research used an easy multibranch technique to functionalize CNC via sequential grafting of ascorbic and citric acid. They further investigated the coagulation/flocculation performance of the modified CNCs for the removal of turbidity from kaolin suspension. Briefly, CNC (3 g) was functionalized with 9 g of ascorbic acid by condensation polymerization with 6 M HCl as a catalyst, while being stirred mechanically (750 rpm) for 4 h at 80 °C. After that, the CNC-g-AA (3 g) was reacted with citric acid in a graft polymerization process with HCl (6 M) as a catalyst, under the same reacting conditions to produce CNC-g-AA-g-CA. Song and his colleagues reported that the synthesized CNC-g-AA-g-A could be used as excellent flocculants as a turbidity removal of 91.07% was recorded. In another study, Sheikhi *et al.* (2015) prepared electrosterically stabilized nanocrystalline cellulose (ENCC) by oxidizing wood pulp with periodate (NaIO₄) and chlorite (NaClO₂) reagents. Afterwards, the flocculation capabilities of the ENCC for the removal of copper ions from simulated water was investigated. During the process, 1 g of softwood pulp was initially oxidized by 1.33 g of NaIO₄ for 96 h in 66 mL of water in a beaker enclosed in aluminium foil. Then, 1 g of the periodate-oxidized pulp was oxidized overnight by a solution of 1.14 g of NaClO₂, 1.41 g of H₂O₂ and 2.93 g of NaCl at a pH of 5. Sheiki and colleagues observed that the ENCC could aggregate significant concentrations of copper ions and had a copper removal capacity of 185 mg/g. From this study, it can be deduced that ENCC is a viable option for the removal of heavy metals from wastewater. Furthermore, the highly charged dicarboxylated cellulose (DCC) polyanion chains that protrude from ENCC were believed to be responsible for the high removal efficiency.

The modified CNCs are materials of high potentials in water treatment technology. Their excellent flocculation performance could be attributed to the unique properties of the modified CNCs surface morphology, such as the increased carboxyl contents, the presence of new surface charges and functional groups, the high crystallinity and improved colloidal stability among others. The utilization of CNCs for the production of CNC-based coagulants eliminates the environmental issues associated with the use of inorganic and organic flocculants made from toxic

and non-biodegradable synthetic polymers. A summary of the application of CNCs-based flocculants for water treatment is presented in Table 1.

Table 1 | Performance of cellulose-based flocculants in wastewater treatment (Shak *et al.* 2018)

Flocculant	Pollutant matrix	An Analytical test	Max removal (%)
Anionic-sodium carboxymethyl cellulose	Natural surface water	Turbidity	95
Anionic dicarboxylic acid nanocellulose	Municipal wastewater	Turbidity COD	80 60
Crystalline nanocellulose grafted with cationic pyridinium functional groups	Freshwater microalgae	Microalgae Biomass	95
Nanofibrillated into cationic nanocellulose	Activated sludge	Turbidity COD	90 60
Cationic-dialdehyde cellulosic nanofibrills	Kaolin wastewater	Colloid aggregation	95
Anionic-sulphonated nanocellulose	Municipal wastewater	Turbidity COD	80 60
Hydroxypropyl methyl cellulose grafted with polyacrylamide	Mine wastewater	Turbidity	94
Cationic pyridinium CNCs	Microalgal biomass	Flocculation efficiency	100
Cationic-cellulose nanofibrills	Municipal activated sludge	Turbidity COD	90 20–70
Anionic carboxylated CNCs	Kaolin suspension	Turbidity	80.9
Rod-shaped CNCs	Flocculation and phase Separation of bacteria	Aggregation percentage	100
Poly(<i>N,N</i> -dimethyl acrylamide) and poly acrylamide-grafted cellulose	Kaolin suspension	Turbidity	69–91

8. CONCLUSION AND FUTURE PERSPECTIVE

This article summarizes the most recent developments in the extraction, modification and application of functionalized CNCs in wastewater treatment. The high demand for cleaner water supplies has prompted scientists to develop effective polymer flocculants made from CNCs. The CNC-based coagulants are safer for use than chemical coagulants due to their non-toxic and biodegradable characteristics. Surface functionalization of CNC may be required in order to improve their surface characteristics and performance as coagulants in water purification. Esterification, etherification, carbamation, amidation, silylation and grafting are some of the common strategies utilized for the surface modification of CNCs. Because cellulose can be extracted from plant biomass, it is possible to produce CNCs that are affordable, sustainable and easily accessible for a variety of industrial applications. Numerous massive manufacturing facilities to extract pure CNCs are in operation all around the world. Some of the facilities (and their daily production capacity) include: Holmen (Sweden): 100 kg/day; Celluforce (Canada): 1,000 kg/day; Alberta Innovates (20 kg/day); American Process (USA): 500 kg/day; US Forest Products Lab (10 kg/day); Indian Council for Agriculture Research (20 kg/day) and Blue Goose Biorefineries (20 kg/day). The synthesis of CNC-based coagulants from CNC is an area that is emerging and currently being explored in the scientific community. The results from the potential application of modified CNCs coagulants, as shown in this article, confirms their remarkable coagulation efficiency for the treatment of turbid and dye-contaminated water. Their extraordinary performance could be attributed to the functional moieties grafted to their surface during modification, along with the interplay of other coagulation mechanisms. Therefore, more research into the development of CNC-based coagulants should be encouraged globally. However, most of the investigations on the production and application of CNC-based coagulants are performed on a laboratory scale and upscaling could be very expensive. Therefore, there is a need for more research on the long-term viability and practicality of large-scale CNCs coagulant-based treatment systems.

AUTHORS' CONTRIBUTION

Both authors contributed to the study concept. The first author wrote the original draft of the manuscript while the second author reviewed and edited the manuscript.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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