



Nanocellulose chemical treatment reactions and their influence on the adsorption of aqueous transition metal ions-A Review

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ABSTRACT

This paper reports a detailed review of the chemistry and associated mechanisms of cellulose modification by chemical methods. Several chemical modification reactions are carried out on the surface of nanocellulose material to enhance their adsorption capacities for specific contaminants and take advantage of their biodegradability. Chemical modification of nanocellulose is an effective method of producing nanocellulose adsorbents with low hornification, improved dispersion in water, reduced swelling, and improved affinity for heavy metal ions. Standard modification processes reviewed include acetylation, esterification, and oxidation of the surface hydroxyl group. Modified nanocellulose materials are effective adsorbents for removing transition metal ions from water with over 80 mg/g adsorption capacities.

1. Introduction

Contamination of surface and groundwater by industrial revolutions is a serious environmental problem. Because of this, intensive research on the development of innovative materials or improvement of the conventional materials used in water remedies should be done[1]. Heavy metal ions are highly hazardous to human and aquatic life. The presence of pollutants in household water causes several health complications such as cancer, cholera, kidney disease, and high blood pressure. [2][3]. Several techniques are reported to be effective in removing pollutants from water, these include (but are not limited to) ion exchange, reverse osmosis, membrane filtration, and adsorption[4]. Adsorption is the uptake of adsorbate onto the surface of the adsorbent through weak or strong interactions [5]. It is a process that depends on the adsorption capacity of the adsorbent and the nature of the adsorbate. The limitation of the common adsorbents (such as carbon-based adsorbents and clays) in removing dissolved heavy metal ions is hydrophilicity [1] [9],

which causes competitive adsorption between the uptake of water molecules versus the contaminants onto the adsorbent. Nanocellulose that has been chemically treated is modified to suit the adsorption of specific adsorbates (type of metal ion) as it overcomes the hydrophilicity disadvantage. Nanocellulose is also reported to have high specific surface area-to-volume which is a good property of a better-performing adsorbent.[8]. However, nanocellulose materials easily agglomerate and harden, and this leads to low dispersion in water as a medium of adsorption, thus hindering the adsorption of contaminants [9]. To enhance the application of nanocellulose in water purification studies, surface chemical modification techniques are used to improve the dispersion, hornification, and agglomeration[10]. Surface modification of cellulose material is dependent on the reactivity of the alcohol(OH) functional groups present in the structure of cellulose. The modification process is a basic reaction between the primary and secondary alcohol(OH) functional groups of cellulose and the different substituent groups from the

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chemical reagents[11]. The substitution of these OH-functional groups is reported to greatly reduce flocculation in nonpolar solvents (caused by a high degree of hydroxyl groups) and water.[2]

1.1. Cellulose chemical structure

Cellulose is a poly carbohydrate made up of an anhydrous glucose unit (AGU) linked by the β -1,4 glycosidic bonds(Fig 1). Each 6-membered ring of cellulose contains three free alcohol(OH) functional groups, of which two are secondary alcohols and one is a primary alcohol. Fig 1 shows the chair conformers bearing the primary alcohol(OH) at carbon 6 while the secondary alcohols are at carbon 2 and 3. Several chemical reagents can specifically target these different alcohol(OH) functional groups. The cellulose structure is also characterized by the 1,4 glycosidic bonds, which link the 6-membered rings together into a biodegradable polymer[2]. The AGU can form internal hydrogen bonding at the OH that is in the equatorial position at carbon 3 (Fig 1). The internal hydrogen bonds that form between two linking 6-membered rings hinder the possibility of structure rotation between the glucopyranose rings around the glucosidic bonds, and this causes cellulose to have a rigid and stiff structure[2,12]. The removal of multivalent transition metal ions from aqueous solutions is usually difficult using native (unmodified) nanocellulose as an adsorbent due to competitive adsorption between the adsorbate and the water molecules which results from the high swelling property of cellulose material.

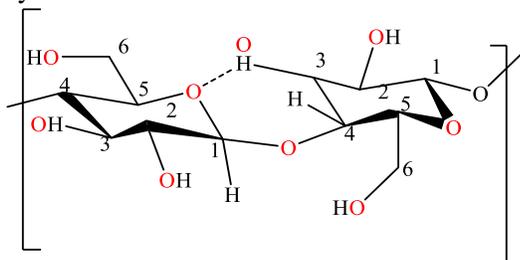


Fig 1: Chair conformation structure of cellulose

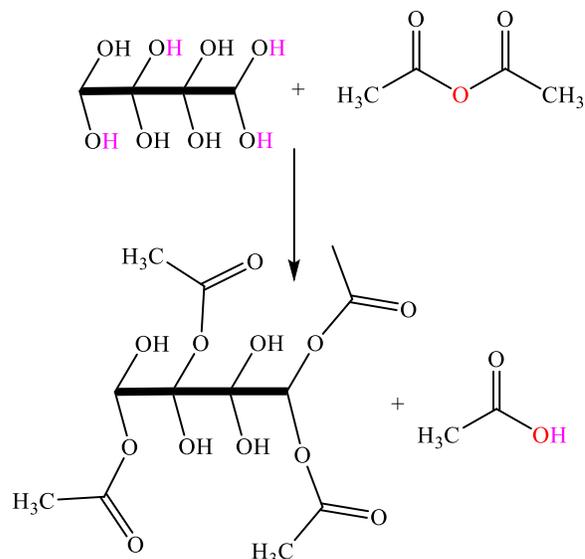
This paper focuses on the review of chemical modification methods that are used to produce nanocellulose material with excellent adsorption properties and their application as adsorbents for the removal of multi-valent transition metals from aqueous solutions.

2. Chemical treatment methods

2.1 Acetylation and Esterification

Acetylation is a reaction in which the hydrogen atom in the OH group is replaced with the acetyl

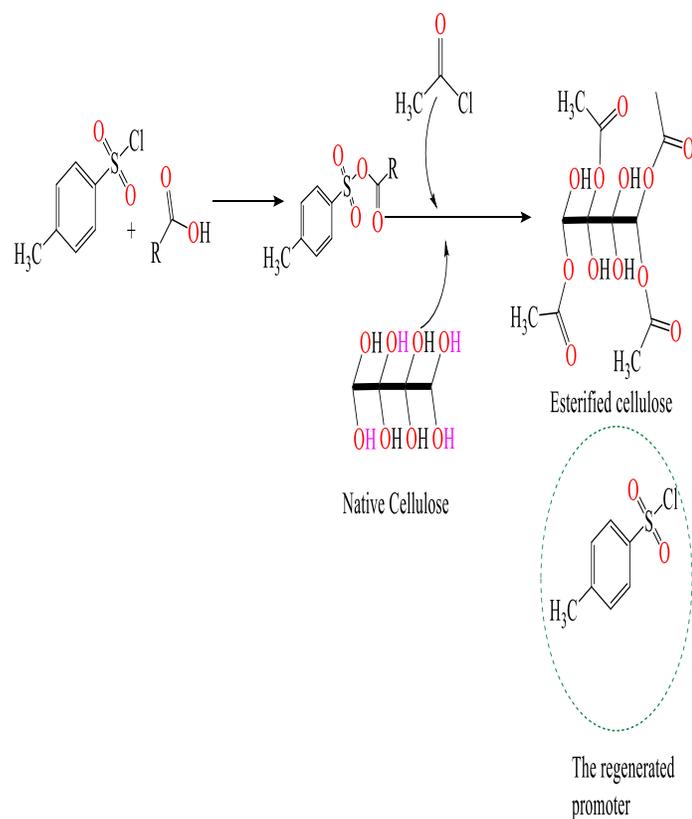
functionality($\text{CH}_3\text{C}=\text{O}$), while in esterification the hydrogen atom from the hydroxy functionality of the cellulose is replaced with the RCOO functionality. Both methods of treatment introduce a hydrophobic functionality on the surface of nanocellulose[13]. Acetylation is a reaction between an alcohol and a diketone to produce a nanocellulose surface with enhanced adsorption properties and enhanced hydrophobicity. The acetyl functionality offers possible further reactions with polymer solutions to produce polymeric nanocellulose materials such as poly acetonitrile cellulose(PANC/PAC) or polypyrrole nanocellulose(PPNC). [14]. Scheme 1 shows a typical cellulose acetylation reaction. In this reaction, nanocellulose is acetylated using acetic anhydride (see scheme 1) in an inert atmosphere, followed by a solvent exchange using organic solvents (such as dimethyl formamide (DMF) or toluene)[15,16], and then freeze-dried. Recent studies emphasize that the mode of drying acetylated nanocellulose material has a great effect on the surface and bulk reactivity of the hydroxyl moieties[17–19]. In Scheme 1, the hydroxy functionality is substituted by the acetyl functionality. This bulky acetyl functional group reduces the hydrogen bonding between the water molecules and the nanocellulose which in turn gives the desired hydrophobic nature.



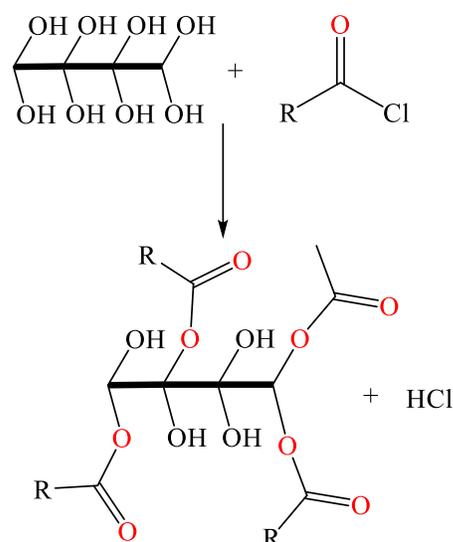
Scheme 1: Scheme showing acetylation reaction b[20]

Esterification of the nanocellulose is mostly effective when freeze-dried native cellulose is used as a starting material. The freeze-dried nanocellulose is reacted with an acidic reagent such as palmitoyl chloride(reactant)[21]. The acidifying medium is introduced onto the surface of the nanocellulose allowing

the hydrogens in the accessible hydroxyl groups to be replaced with the RCOO^- functionality (Scheme 2). The reaction conditions can be optimized to get the desired substitution products[22]. Esterification of nanocellulose is reported to use limited solvents in the solvent exchange steps[23,24]. As the hydrogens in the accessible alcohol functional groups are replaced by the RCOO^- functionality, a layer of an ester forms on the surface which acts like a skin-core structure that enhances the affinity for metal ions [25]. Other reagents that can be used for esterification reactions include among others, decanoyl chloride, sebacoyl chloride, and succinic anhydride [26]. Esterification, acylation, and acetylation of nanocellulose are promising routes to the production of cellulose nanocrystals CNCs[27]. Acetylation is also used in studies of cellulose treatment with solvent ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc)[27,28], which are reported to both degrade and to acetylate swollen (non-dissolved) cellulose, leading to CNCs directly from a wood substrate (Scheme 3). The *p*-toluene sulfonyl chloride is used to modify nanocellulose material in solvents such as pyridine. This reaction generates anhydrides which act as acetylation promoters [25].



Scheme 2: Esterification of cellulose with acetyl chloride[29].



Scheme 3: Acylation of cellulose[2]

Dicarboxylic acids are advantageous in the esterification reactions because esterification can occur on a single carboxyl group and impart charge on the nanocellulose crystal leading to stable dispersions in water and reducing agglomeration[30]. Hornification of acetylated nanocellulose can then be reduced by solvent-water exchange treatments using different solvents. [31]. Various carboxylic acids are also excellent sources of carboxylate moieties that can be introduced on the surface of nanocellulose, these include common acids such as acetic, hexanoic, and dodecanoic acid. The presence of the carboxylate moiety is reported to reduce the hornification (stiffening upon drying) of the nanocellulose network and hence improve the redispersion of dried cellulose in different solvents[32][27].

2.2 Oxidation of NC using different oxidizing agents

The oxidation of cellulose is a very important treatment method for producing nanocellulose with attractive adsorption capacities for application as adsorbents of water-soluble pollutants [33]. Cellulose oxidation produces polyglucopyranosic and cellulosic acids, which are rare to be found in nature [9], [38]. These are important additives in the synthesis of fine chemicals. Successful oxidation of cellulose gives water and carbon dioxide as side products and carbon dioxide can be further hydrogenated to give environmentally friendly products such as formic acid or methanol[7,9,34–36]. Cellulose can be oxidized on the primary and secondary hydroxy moieties or by the opening of the glucopyranose ring. During the oxidation reaction, the surface hydroxyl moieties are converted to ketones (secondary hydroxyl), aldehydes (primary hydroxyl), and carboxy

moieties(primary hydroxyl)[37]. Aldehydes can also be formed during the reaction because of the degradation of the cellulose polymer[38–41]. The following oxidizing agents are reported to give oxidized nanocellulose materials with improved adsorption properties.

2.2.1 Oxidation using Nitrogen oxides

The preparation of oxidized cellulose using gaseous nitrogen dioxide was first reported by Yackel and Kenyon in the 1940s. They reported successful oxidation of nanocellulose with up to 15% by weight of COOH content without affecting the original fibrous morphology. Gaseous NO₂ oxidation is highly selective to primary alcohols. The primary alcohols of the cellulose are proposed to be oxidized through the nitrite derivatives to oximes or hydroxamic acid intermediates[42], which are hydrolyzed to carboxylic acid groups by concentrated acids present in the reaction mixtures[43]. A proposed reaction scheme for the NO₂ oxidation of the primary alcohols of cellulose is as follows:

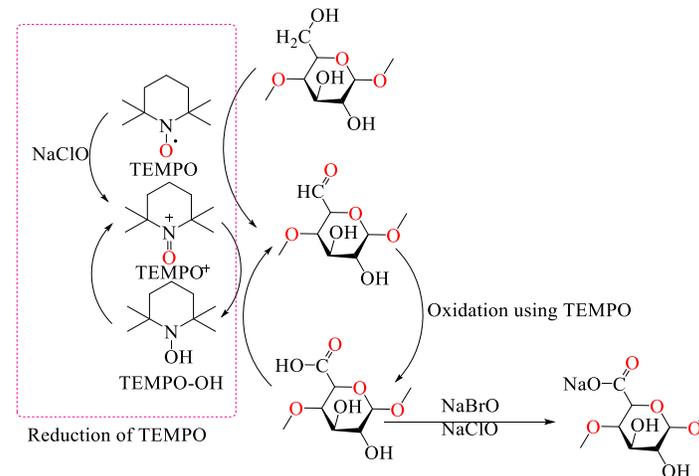


Several authors also report the use of 85% phosphoric acid coupled with sodium nitrite as oxidants, which improves the efficiency of cellulose oxidation[27,44,45]. The efficiency of the oxidation process using NaNO₂/H₃PO₄ as oxidizing agents also depends on the extent of polymerization of the starting material[46]. The carboxyl group content introduced in the nanocellulose has been reported to increase linearly with the molecular weight of the starting material. The catalytic amount of sodium nitrite is added to reduce the induction time[47]. The fibrillation and gel formation properties of the oxidized cellulose pulp can be further improved by the conversion of the carboxy groups into their sodium salt form[48]. The oxidized pulps were reported to have increased crystallinity with only traces of nitrogen present in the pulp, possibly as nitrate esters. The method is said to give yields comparable to those already used in industry(made using mineral acids as oxidizing agents)[29,49–51].

2.2.2 Oxidation using tetramethylpiperidine-1-oxyl reagent.

(2,2,6,6-tetramethyl piperidine-1-oxidany) [TEMPO] is a nitrox radical that is reported to be an active radical that is easily reduced when added to primary alcohols[52]. In addition, hypochlorite and sodium bromide can be used in stoichiometric amounts with TEMPO[53] to facilitate the fast kinetics of oxidizing the OH functionality, while the TEMPO gets reduced. The catalytic oxidation using TEMPO converts the primary hydroxyl

groups to aldehyde under aqueous and mild conditions[54]. TEMPO-mediated oxidation is used to prepare cellulose nanofibers hereinafter referred to as TOCN. It is also reported to be highly selective in oxidizing the primary alcohols of cellulose to aldehydes and subsequently to carboxyl groups without disrupting the fibrillar structure or crystallinity of untreated cellulose[55–57]. The mechanism of TEMPO oxidation is another subject that is under scrutiny in this area of study. Several authors have proposed the following steps as part of the mechanism. Firstly, TEMPO is oxidized to the nitrosonium ion (TEMPO⁺) using sodium chlorite (Scheme 4). TEMPO⁺ can be used for oxidation in stoichiometric amounts, however, it can also be oxidized and regenerated by an oxidant in situ, [58]. The nitrosonium ion then undergoes reduction to form a hydroxylamine (TEMPO-OH) species. In this proposed mechanism, the oxidation of TEMPO to TEMPO⁺ is the rate-limiting step in bromide-free systems for the oxidation of alcohols[55], however, some authors report that this step is much faster for the oxidation of primary alcohols[55] compared to secondary alcohols. The regioselectivity in the tempo oxidation and reduction reactions is attributed to the four methyl groups in TEMPO, which sterically block access to the secondary alcohols [57,58].



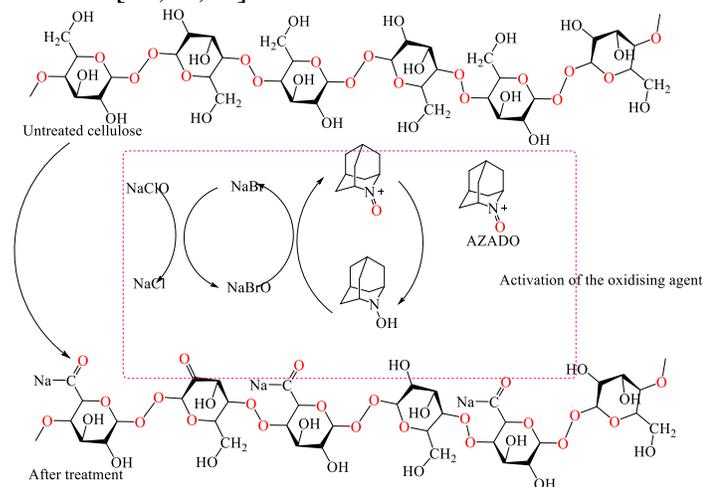
Scheme 4: Oxidation of nanocellulose using (2,2,6,6-tetramethylpiperidine-1-oxidany) [TEMPO] [2][59]

The quantified surface charges in 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-treated nanocellulose pulps are often higher compared to those found in both nanocrystals CNCs (<0.4mmol/g) and Nanofibrils' (0.04–0.07mmol/g) [59], [35]. The use of TEMPO to treat cellulose is used by several industrial companies such as Nippon Paper and UPM and they can produce large-scale commercial nanocellulose. The

kinetics of TEMPO oxidation are greatly influenced by the pH of the solution, showing a highly favored mechanism at $\text{pH} \geq 10$ [60]. However, at this pH, several researchers report that the oxidized cellulose is prone to degradation, leading to the elimination of the aldehyde groups[35,61].

2.2.3 Oxidation using 2-azaadamantane *n*-oxyl

Another oxidizing agent reported for the oxidation of cellulose is 2-Azaadamantane *N*-oxyl also known as methyl-AZADO[50]. This reagent oxidizes all the alcohols functional (Scheme 5) in aqueous systems, in the presence of a strong oxidizing agent (NaBr/NaOCl) [62]. This lack of selectivity during the oxidation of the hydroxy functional groups of cellulose is caused by the absence of sterically hindering groups on the oxidizing agent. The proposed mechanism steps are like the previously discussed (nitrosyl radical-mediated chemistry as TEMPO oxidation). AZADO-oxidised native cellulose samples are reported to have a lower amount of ketone groups compared to the TEMPO-oxidised samples (0.03 and 0.08-mmol/g, respectively)[2]. Also, the AZADO/ NaBr/NaOCl system gives shorter reaction times compared to the TEMPO/ NaBr/NaOCl system. The AZADO oxidizes cellulose to yield 2,3,6-tricarboxylate cellulose[23,33,63].

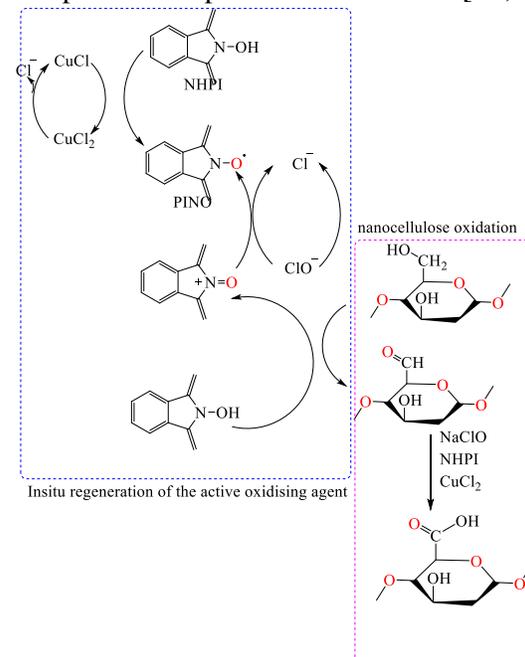


Scheme 5: AZADO-mediated oxidation[34]

2.2.4 Oxidation using *n*-hydroxyphthalimide

N-hydroxyphthalimide (NHPI) is another commonly reported oxidizing agent used in chemically modifying cellulose[55,64]. NHPI bears methylene($\text{CH}_2=\text{CH}_2$) groups which induces steric hindrance on accessible OH functionality on the cellulose surface and this leads to the selective oxidation of the primary OH groups only. It follows that is also a nitrosyl radical-mediated oxidation

mechanism, of which in this case, the phthalimide *N*-oxyl (PINO) is the radical that initiates the reaction[65](Scheme 6). The oxidation mechanism is also facilitated by NaBr and NaOCl as co-catalysts. However, for PINO, NaBr is replaced with CuCl_2 , which is reported to improve the conversions[13,24,66].

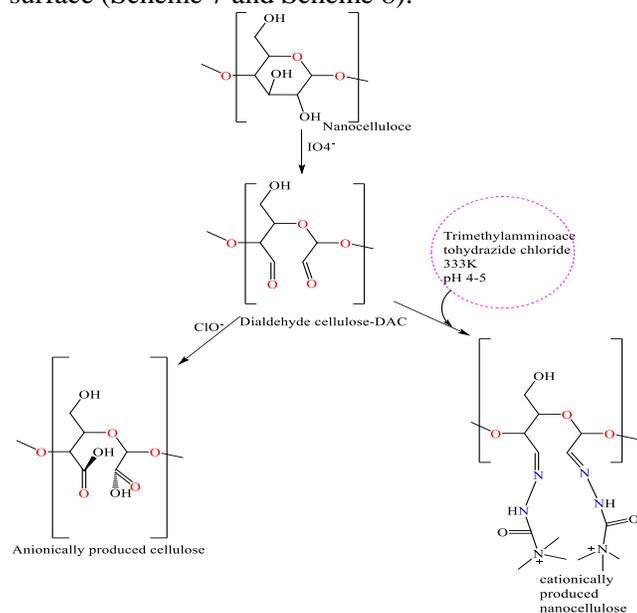


Scheme 6: Oxidation of cellulose in water at pH 10 using NHPI and NaClO as a co-catalyst [67][68]

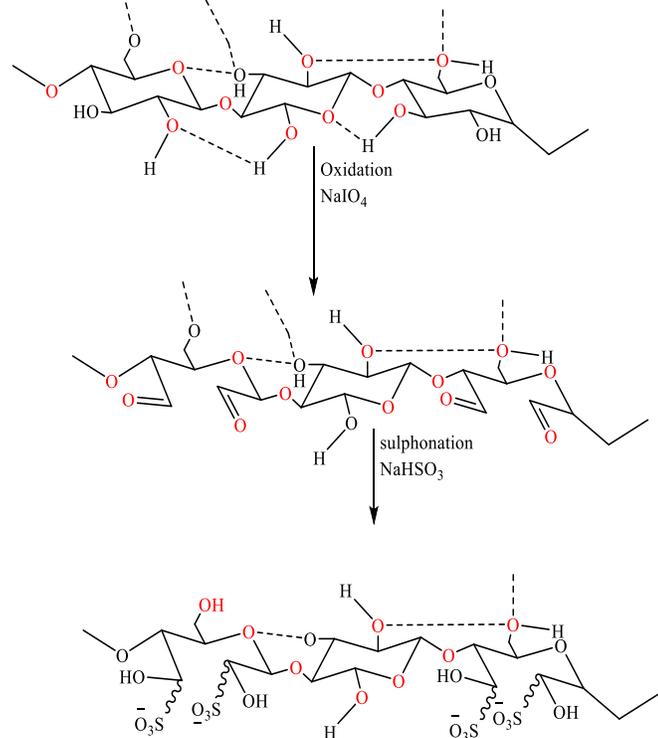
2.2.5 Oxidation using periodate (IO_4^-)

Oxidation using periodate ions offers selectivity based on the opening of the glucopyranose ring at carbon position C2 and C3 position resulting in 2,3-dialdehyde cellulose (DAC)(Scheme 7) [27,69], which is selective towards oxidizing the secondary alcohols in cellulose. Despite the ring opening, the degradation of the structure during treatment is not reported. periodate oxidation is popularly reported to be applied in the production of cellulose functionalized for the adsorption of metal toxins from aqueous systems[70]. The rate and the extent of periodate oxidation are dependent on the concentration of periodate and reaction temperature[37]. The periodate oxidizing agent, though it leads to the glucopyranose ring opening, is reported to not influence the cellulose degradation at low degrees of oxidation[28], however at higher degrees of oxidation, the cellulose polymer is reported to highly degrade, aggregate, and hornifies and becomes more compact[29]. To reduce this problem, NaBH_4 is coupled with the periodate to yield very flexible chains, which results from hemiacetal cross links[71]. The DAC is water insoluble in cold water, but soluble in hot water, however, the hot water causes minor

degradation to the cellulose in hot water[72]. The DAC can further be modified to yield desired nanomaterials using reagents that can react with the aldehyde groups to induce a negative or positive charge on the cellulose surface (Scheme 7 and Scheme 8).



Scheme 7: Reaction scheme for periodate oxidation with subsequent steric, anionic, and cationic treatments to produce stabilized nanocellulose samples [2].



Scheme 8 Schematic diagram showing oxidation and sulphonation of nanocellulose[2][71]

Water solubility and non-degradation of DAC can be used to advantage in the production of dialdehyde-modified nanocrystalline cellulose (DCNC)[66,73].

3. Application of chemically treated nanocellulose as adsorbents of aqueous transition metal ions

Transition metal ions are major contaminants in water which can be removed by adsorption. The process of adsorption is highly dependent upon the cellulose and the transition metal interactions, solvent, temperature, and pH of the solution[20]. The thermodynamics of adsorption are often studied by fitting the experimental data into different mathematical models such as the Langmuir isotherms, Temkin, and Freundlich isotherms however, for the behavior of cellulose as an adsorbent[59], the Langmuir adsorption isotherms is reported to be a better fitting model[55,74]. In the Langmuir adsorption model, the adsorption process is assumed to form a monolayer of the adsorbate on the adsorbent surface, also the surface of the adsorbent is assumed to be made up of homogeneous adsorption sites with similar adsorption energies[74], these assumptions are often not matching the actual process that is taking place, as the surface of the adsorbent can be inhomogeneous. The Langmuir isotherm mathematical assumptions are shown in Equation 1.

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad \text{Equation 1}$$

where C_e (mg/L) is the concentration at equilibrium of the metal ions (M^+) that is adsorbed per.

q_e (mg/g) is the quantity of the metal ions adsorbed on the surface of cellulose at equilibrium.

Q_{max} is the maximum amount of metal ions that can be removed from the aqueous solution.

K_L is the Langmuir adsorption constant constant.

Both Q_{max} and K_L are experimentally deduced in a plot of a linearised Equation 1.

The Freundlich isotherms is another type of thermodynamic model that is used to elucidate the thermodynamics of an adsorption process. The mathematical formula of the Freundlich isotherm is shown in Equation 2:

$$q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Equation 2}$$

where K_F and n are Freundlich constants which indicate the amount of metal ion that can be removed per gram of nanocellulose used and the intensity of the adsorption process. This model assumes a heterogeneous surface, multilayer formation and mass transfer effects are dominant in the adsorption process. These two models

are often used together, to explain the adsorption process taking place at the surface of the adsorbent[17,75].

The removal of transition metal ions from water is effectively achieved when the surface of nanocellulose is functionalized with negatively charged functionalities. The TOCNF are reported to have a greater affinity for metal ions such as divalent Lanthanum, lead, and copper due to the attraction between the nanocellulose and the metal ions[76,77]. The adsorption of Cu^{2+} on TEMPO-treated nanofibers is dependent on the acidity of the aqueous solution[2]. The adsorption of these transition metal ions increases linearly with the carboxyl content on the cellulose surface in the pH range of 3–7. The adsorption of Fe^{2+} , Fe^{3+} , Ag^+ , and Cu^{2+} from water using TEMPO-treated nanocellulose membranes has been studied using the zeta-potential, and from this study, the authors established that the negative charge on the surfaces of nanocellulose greatly increases the adsorption capacities of the adsorbent[72]. These findings were also supported by studying the thermodynamics of adsorbing of Cu(II) ions onto TOCNF[2], where it has been established that the Cu(II) ions are attached to the surface of TOCNF through the interaction with the carboxylate groups forming a Cu(II) monolayer[78], confirming the Langmuir model of adsorption. It has been demonstrated that the esterification of nanocellulose using succinic anhydride greatly improves the affinity of nanocrystals for the divalent cadmium and lead ions[2]. Both (SCNC) and Na-SCNC are reported to give high adsorption capacities for the adsorption of divalent cadmium and lead ions when compared to untreated nanocellulose. This adsorption process is also reported to be influenced by the pH [79]. Heavy metal ions such as silver, iron, and copper adsorbed onto phosphorylated cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) by Liugave adsorption capacities in the range (148-154)mg/g at optimum pH of 6[80]. Navarro[81] reported the high efficiency of polyethyleneimine-grafted cellulose for adsorbing mercury ions, giving 85% efficiency compared to untreated nanocellulose. Polyacrylonitrile (PAN) is reported not only to modify the surface of nanocellulose but also to cause the arrangement of the fibers to form nano mats. The adsorption capacities(Langmuir) of the PAN-modified nanofibers were observed to be in the order 150.6, 155.5, 116.5, and 60.6 mg/g for the metal ions Ag^+ , Cu^{2+} , Pb^{2+} , and Fe^{2+} respectively[2]. These spent nano mats were regenerated by treating the spent adsorbent with hydrochloric acid (HCl). To improve metal adsorption, polymers can be coupled in a 1:1 ratio, such as polyacrylonitrile/polypyrrole (PAN/PPy)as reported by several researchers[2,82,83]. Mercury, Hg^{2+} is removed

from aqueous solutions with cellulose acetate (CA) non-woven membrane treated with poly (methacrylic acid), leading to non-woven cellulose membranes with a skin-core layer of methacrylate, which is reported to also depend on the pH of the solution[84], as an increase in the pH of the solution increased amount of metal ion adsorbed[2,85]. Due to the improved affinity of the metal ions on the CNC surfaces at higher pH, higher adsorption capacities are reported for a wide range of metals like divalent Pb[86], Cu[85], Cr[78], and Zn[87] ions. Competitive adsorption between H^+ and M^+ , at lower pHs reduces the adsorption capacities of several adsorbents, oxidized however, the opposite was observed in several studies where lead, copper, chromium, and zinc were removed from water using nanocrystals and nanofibers [10].

4. Conclusion

In this literature review, the selected chemical modification processes that are not disruptive to nanocellulose, and the mechanism of modification producing nanocellulose material with tailored properties for heavy metal ions adsorption are discussed. The hydrophilic nature of untreated cellulose is a major drawback that limits its use for water purification, which has led to intensive research on chemical modifications to be employed. Oxidizing nanocellulose material is highly advantageous compared to other methods as it yields excellent adsorbents, and intermediates for further modification. In general, treating cellulose with chemical reagents improves the adsorption of metal ions by over 90%, with recyclability over several adsorption cycles without degradation. The stability of all chemically modified nanocellulose materials is one area under investigation and scarcely reported; hence it is important to study the longevity and shelf life of these materials with the possibility for industrial commercialization. In addition, there is a need to study other possible modifications that can be used to improve nanocellulose material specifically for application in removing biological contaminants from water., as well as investigating the possible toxicity of these chemically modified nanomaterials.

Acknowledgments

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