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REVIEW PAPER

A critical review of cellulose-based nanomaterials for water purification in industrial processes

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Abstract At present, natural polymers have found applications in clothing, paper, medicine, fuel, etc. The advancement in science and technology has paved the way for nanotechnology, which combines the unique properties of these abundant polymers on a nanoscale to produce novel nanomaterials. Using mechanical or chemical treatment, cellulosic materials can be converted into cellulose nanofibers and nanocrystals which have excellent capabilities compared to microscale native cellulose fibers, especially in water purification applications. This review summarizes the most recent processing methods for nanocellulose and techniques employed for rational surface chemical modification. It also critically assesses the applications of cellulose-based nanomaterials with respect to their functionalization for removal of pollutants such as heavy metals, organic compounds and pharmaceutical residues from water.

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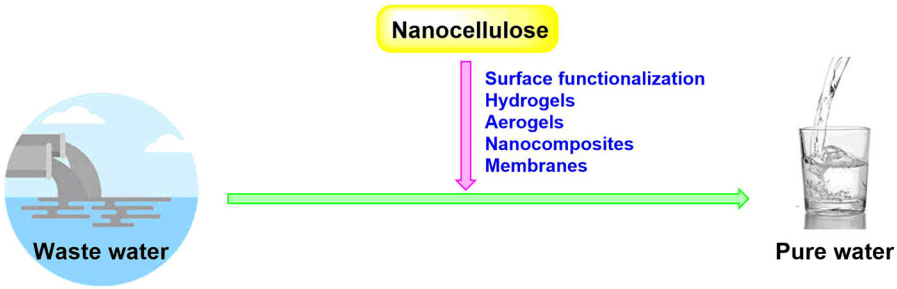
Graphical abstract



Keywords Nanocellulose · Water purification · Cellulose membrane · Heavy metal · Cellulose nanomaterials

Introduction

The growing demand for a clean environment has led to the fabrication of membranes and filters that are semi-permeable, allowing certain chemical species to pass through while retaining others. The selectivity and permeability of the membranes depend upon the microstructure and the chemistry of the material used. The emerging field of nanotechnology has shown tremendous developments in the use of nanomaterials derived from renewable natural resources for the removal of environmental pollutants. Among the natural materials, cellulose is one of the most abundant polysaccharides (Fig. 1). It is typically used for clothing, energy, and other commodities such as paper. Unlike the bulk form, nanocellulose exhibits properties such as high strength and large surface area, which make it a highly promising material for the fabrication of high-performance membranes and filters. Due to these properties, it is employed in many applications in removing contaminants and purifying industrial and drinking water systems. Moreover, the high mechanical strength and rigidity of nanocellulose render it useful in high-pressure water treatment applications (Tashiro and Kobayashi 1991; Šturcová et al. 2005). In recent literature, the standard surface area of cellulose pulp was increased from 4 m^2/g to over 500 m^2/g by conversion into cellulose nanopaper using preparation methods, such as mechanical mixing, treatment with enzymes, and electrospinning (Banavath et al. 2011; Sehaqui et al. 2011, 2014).

It is well known that various pollutants like heavy metals, organic compounds and pharmaceuticals in water ultimately end up in our bodies through the food chain. It is essential to develop cheap and effective filtration systems from readily available and cost-effective raw materials like cellulose to keep costs down in developing nations where clean water is becoming a growing pressure. Using mechanical or chemical treatment, cellulosic materials can be converted into cellulose nanofibers (CNFs), nanowhiskers (CNWs) and nanocrystals (CNCs) with an excellent capacity for water purification. These CNFs, CNWs and CNCs can be further fabricated into filter membranes through methods that will be described later in the review. Indeed, the expectations for these

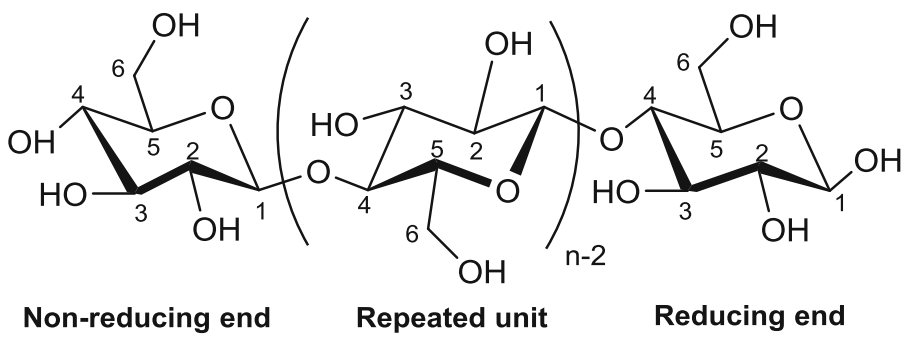


Fig. 1 The chemical structure of cellulose

materials are quite high and thus many reviews have been previously published in this area (Zhou et al. 2014; Carpenter et al. 2015; Jamshaid et al. 2017; Abou-Zeid et al. 2018b; Kargarzadeh et al. 2018).

In our review, we have mainly focused on the most recent research in the application of cellulose-based nanomaterials for water purification. We have focused on the most recent developments in the rational surface chemical functionalization of nanocellulose and the fabrication methods for nanocellulose-based membranes. We have also critically assessed the properties, applications and limitations of nanocellulose with respect to their functionalization for removal of pollutants such as heavy metals, organic compounds and pharmaceutical residues from water.

Nanocellulose: preparation, functionalization and processing

Preparation

Plant cellulose has crystallinities as high as 95% that contribute to the higher strength of the plant bodies (Mazeau and Heux 2003; Brinchi et al. 2013). However, it is difficult to isolate these natural cellulose fibrils from their sources due to hydrogen bonding and van der Waals forces. The function of the pretreatment process is to remove ash, wax, lignins, hemicellulose, and other non-cellulosic compounds to produce pure cellulose products. Mechanical processes including ultrasonication, high-pressure homogenization, grinding/crushing, and microfluidization are some of the physical techniques used to prepare CNFs from precursors such as wood pulp (Fig. 2). In the case of high-pressure homogenization, more energy is generally required and the product itself is mostly a micrometer-sized material (Pääkko et al. 2007). Further, the product consists of bundles of CNFs rather than individual fibrils. CNWs are produced by acid hydrolysis and are composed of short fibrils. However, the yield and the shorter fiber lengths are a concern in using this method for the preparation of nanocellulose (Goffin et al. 2011, 2012; Ma et al. 2012a). Additionally, bacterial nanocellulose (BNC) fibrils are interesting as they offer an opportunity to obtain the fibrils on the nanoscale naturally (Lee et al. 2014; Mohite and Patil 2014). The characteristics and sources of various types of nanocellulose are presented in Table 1.

The below paragraphs highlight some of the commonly used techniques employed to prepare nanocellulose. During the high-pressure homogenization (HPH), a cellulose slurry is pumped at an elevated

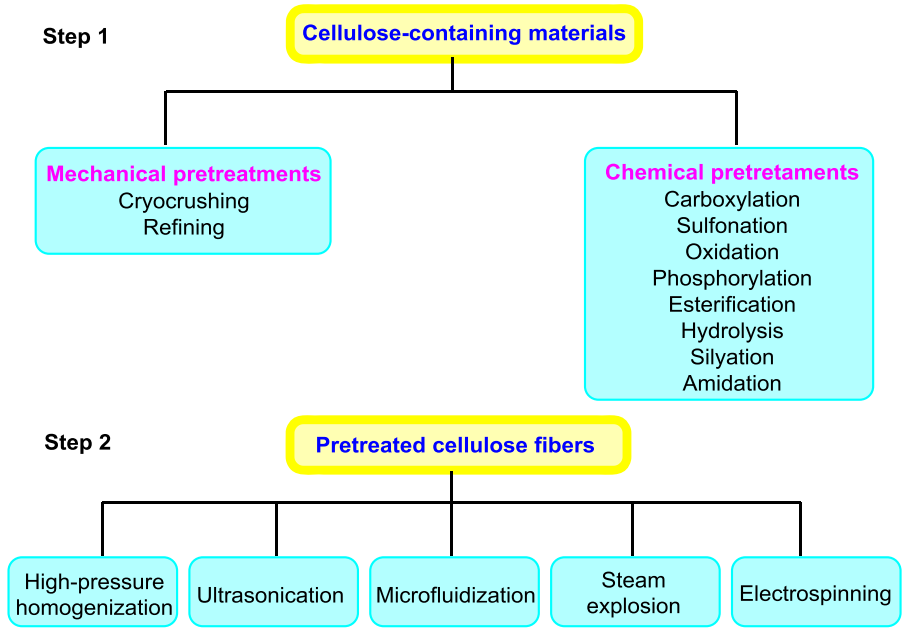


Fig. 2 Steps involved in the preparation of nanocellulose

Table 1 Types and sources of nanocellulose

Type	Origin	Average size
Cellulose nanocrystals (CNCs)	Wood, cotton, hemp, flax, straw, tunicin, Avicel	Width: 5–70 nm Length: 100 nm to several micrometers
Cellulose nanofibrils (CNFs)	Wood, cotton, hemp, flax, straw, tunicin, tubers, algae, bacteria	Width: 5–60 nm Length: several micrometers
Cellulose nanowhiskers (CNWs)	Wood, cotton, hemp, flax	Width: 2–60 nm Length: 100–500 nm
Bacterial nanocellulose (BNC)	Sugar, alcohol	Width: 5–70 nm Length: several micrometers

pressure through spring-loaded valves where they are subjected to shearing and impact forces. This results in a high degree of microfibrillation of the cellulose fibers depending upon the number of homogenization cycles as well as applied pressure. Electrospinning is one of the most popular techniques for preparation of nanofibrous materials from natural polymers. Since natural polymers such as cellulose are known for their insolubility in most of the common organic solvents, most of the reports on electrospun CNFs use a soluble precursor such as cellulose acetate (Frey 2008; Zhang et al. 2018). Meanwhile, there was very little research reporting the preparation of pure CNFs from the natural cellulose itself. In most cases, the strategy is to adopt the cellulose solution from a wet spinning technique. This involves high temperature, concentrated harmful salts such as lithium, application of higher voltages, and in some cases, the use of an oxidizing agent before spinning the fibers. However, Ohkawa et al. (2006, 2009) and Ohkawa (2015) reported preparation of pure CNFs and its chitosan composites from natural sources such as cotton, wood pulp, and bamboo cellulose using an acidic solvent. Using this robust strategy, the authors were able to produce cellulose and/or chitosan composite nanofibrous mats.

Very recently, Zhou et al. (2018) reported the acid-free preparation of CNCs by 2,2,6,6-tetramethylpiperidine1-oxyl (TEMPO) oxidation and subsequent ultrasonication in water from softwood bleached kraft pulp. Compared with typical CNCs acquired through acid hydrolysis, the TEMPO-CNCs prepared through the acid-free procedure displayed superior mass recovery ratios, higher number of surface anionic groups, and smaller and homogeneous dimensions.

Functionalization

It is essential to address the challenges associated with the application of nanocellulose to water purification, such as its agglomeration, difficulty in separation from effluent, and recyclability. There are a large number of ways in which the nanocellulose filtering membranes can be rationally designed depending upon the chemistry of the biosorbent and the complexity of the solution that needs to be purified. The functional groups or molecules can be grafted onto the nanocellulose's surface through techniques such as carboxylation, sulfonation, oxidation, phosphorylation, esterification, etherification and amidation (Fig. 3) (Isogai et al. 2011; Božič et al. 2014; Singh et al. 2014). It has also been demonstrated that carboxyl, sulfonate, and phosphonate groups, when present on nanocellulose can exhibit selective uptake of contaminants, such as metal ions, dyes and microbes for water purification (Wang et al. 2013; Liu et al. 2014, 2016; Suman et al. 2015; Zhu et al. 2015; Sehaqui et al. 2016; Thakur and Voicu 2016).

Among the different functionalizing methods, carboxylation of nanocellulose for the adsorption of cationic species has been the most widely studied (Hasani et al. 2008; Qiao et al. 2015). This method has the maximum adsorption efficiency for most metallic cations and cationic dyes. Also, esterification with a dicarboxylic acid or TEMPO-mediated oxidation can lead to more sorption of cationic species. The grafting of polymers that contain reactive moieties is an emerging technique used to produce cellulose with high adsorption for various species. Though these polymers normally result in relatively low adsorption rates for metallic cations, when the cellulose extracted from sawdust was grafted with carboxylic-containing

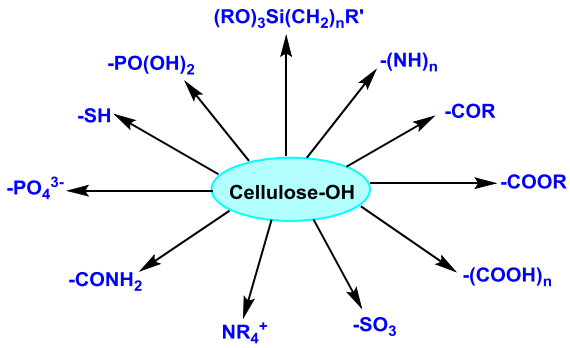


Fig. 3 The major surface chemical functionalizations of nanocellulose for application in water purification

polymers it led to higher adsorption capacities for cations (Geay et al. 2000). This created a scope for increased adsorption through a decrease in the size of systems. When the polymers containing amino groups were grafted to nanocellulose, they showed a significantly higher adsorption rate for a variety of dyes due to the interactions between dye and amino group (Jin et al. 2015a). However, the disadvantage of this method over direct functionalization is the difficulty to incorporate the polymers containing amino groups into filtration membranes as the nanocellulose properties and dispersibility are greatly modified.

Processing of nanocellulose-based water purification membranes

The application of nanocellulose membranes depends on the pore structure and the flow mode, i.e., static or cross-flow mode. The CNFs have a high surface area, and the performance of these membranes is mostly related to their potential of selectively adsorbing contaminants from water. The selective adsorption by CNCs is significantly correlated to the different surface functionalization groups as described earlier. CNCs have inherent hydrophobicity and when this property is used with a controlled surface chemistry, it can be used to eliminate bio-fouling and hydrofouling which are basic hurdles in membrane technology. In the design of nanocellulose-based membranes, the main challenge is to ensure sufficient access to functional sites, along with high flux and mechanical stability.

The nanocellulose membranes are frequently processed using the following methods: (a) impregnation of electrospun mats with functionalized nanocellulose; and (b) vacuum filtration and coating. Impregnation of the electrospun mats with modified nanocellulose involves the impregnation of nanocrystals of different aspect ratios on the mats (Akhlaghi et al. 2014). Hence, the possibility of processing charged microporous membranes which had both isotropic and anisotropic structures was demonstrated (Ma et al. 2012b). This technique produced mechanically strong composite nanofibrous membranes. The first step was to introduce the TEMPO-oxidized cellulose nanocrystals (TOCNCs) into an electrospun polyacrylonitrile (PAN) nanofibrous frame. Then, the resulting material was heated to 100 °C for 10 min to obtain cross-linking. A sturdy polyethylene terephthalate (PET) non-woven substrate was used to support the membrane and the pore diameter of the membrane was around 50 nm. The membranes produced by this TOCNC composite possess a high negative surface charge density and demonstrated 16 times higher adsorption uptake of positively charged crystal violet dye than that of the commercial nitrocellulose-based microfiltration (MF) membrane. A fully bio-based membrane was developed by Goetz et al. (2016) by following a similar technique. The process used cellulose acetate (CA) polymer-based electrospun mats in order to support chitin or cellulose nanocrystals and did not use the extra non-woven support. This resulted in a thin microfiltration membrane with a hydrophilic surface with pore diameter around 100 Å and porosity of 85.6%.

Vacuum filtration is one of the fastest and simplest, yet scalable, processes used to fabricate CNCs with layered structures. Vacuum filtration can be used to create fully bio-based membranes based on nanocellulose by incorporating hot pressing in a process called ‘Nano paper approach’ (Mautner et al. 2014, 2015). The resulting membrane has nanofibrils that are densely packed and form a network with pore dimensions similar to that of the CNCs’ diameter. This property helps to modulate the pore size, and by varying nanocellulose with different aspect ratios, the molecular weight of the membranes can be controlled. The Nano paper method has produced membranes that can adsorb metal ions, fluorides, nitrates, phosphates, sulfates, and organic compounds effectively (Mautner et al. 2016a). Table 2 gives a tabular representation with respect to the pore size of filtration membranes and what can be excluded.

Table 2 Relationship of pore size to standard excluded species

Membrane type	Pore size	Size excluded species
Reverse Osmosis	< 1 nm	Aqueous salts (0.3–1.2 nm)
Nanofiltration	1–10 nm	Pesticides and herbicides (0.7–1.2 nm)
Ultrafiltration	10–100 nm	Virii (10–100 nm)
Microfiltration	0.1–50 microns	Bacteria (200 nm–30 micron)

Metreveli et al. (2014) demonstrated that a large number of viruses with size > 50 nm can be removed by cladophora nanocellulose-based filter paper membranes. The process of vacuum filtration of a thin film of CNCs onto a supporting layer produced multilayered anisotropic membranes (Karim et al. 2016). Another process where cellulose nanofiber suspensions are vacuum filtered and then dip coating thin films into a dispersion of CNCs with sulfate or carboxyl surface groups. The membranes thus produced had a narrow pore size of 74 Å. By treating them with acetone, the pore size could be increased to 194 Å, and the flux to 250 Lm^{-2} h^{-1} bar. The uptake capacity of these membranes for Ag^{+}, Cu^{2+} and Fe^{3+} ions was high, showing that the high efficiency was due to both electrostatic interaction and size exclusion. The tight support layer resulting in a low flux of this membrane proved to be a drawback.

In order to overcome the issue of low permeability, cellulose microfibers and CNCs surface-functionalized with sulfate, carboxyl, and phosphoryl groups were fabricated in a gelatin matrix as a nanoporous upper layer (Mautner et al. 2016b). The pore sizes were in the range of 5.0–6.1 μm and this helped a very high permeability for water at pressures of < 1.5 bars. The mechanical strength of these membranes was excellent and being anisotropic negatively-charged, they could adsorb Ag(I) and Cu^{2+}/Fe^{2+}/Fe^{3+} ions from industry effluents. The adsorption capacity of these CNC membranes was highest for the phosphorylated ones, followed by carboxylated and sulfated CNCs. Zhu et al. (2017) prepared the CNC/poly(vinyl alcohol-co-ethylene (PVA-*co*-PE) composite functionalized with 1,2,3,4-butanetetracarboxylic acid (BTCA) to adsorb the heavy metal ions. The adsorption capacity enhanced after the CNC was coated onto the PVA-co-PE nanofibrous membrane because CNC possessed abundant hydroxyl groups to react with the carboxyl group. The maximum adsorption of Pb^{2+} reached 471.55 mg/g and 58.08% using 1000 ppm lead nitrate solution at 15 °C. The adsorption kinetics indicated that the adsorption involved surface adsorption and intra-particle diffusion.

Functionalized cellulose nanomaterials for sorption of heavy metals from water

Heavy metal ions and compounds can evolve from manufacturing processes which may potentially mix with water and naturally toxic pollutants. The heavy metal species are mostly non-biodegradable and can be only transformed into lesser toxic species and not fully broken down. The heavy metal ion-sorption materials should be designed with the consideration to identify the dominant species in the contaminant. The uptake capacity, partitioning coefficient and selectivity should be maximized by optimizing the chemistry of the absorbent material. The pH level of the solution plays an important role in choosing adsorbents. It was found that the best adsorption rate was near neutral pH and when the pH was acidic, the uptake rate was significantly lower. A large number of hydroxyl groups on the nanocellulose surface renders it inherent hydrophilicity, which hinders its applications in polymeric matrices. Nevertheless, the presence of numerous hydroxyl groups makes nanocellulose amenable to a range of surface modifications, extending its use to sophisticated applications.

Carboxylated nanocellulose

The pioneering work by Saito and Isogai (2005) in this field has led to the use of TEMPO-oxidized cellulose nanofibers (TOCNFs) in the removal of various elements like Pb^{2+}, La^{3+} and Ag^{1+} ions from water. This was done by the selective formation of C6 carboxylate groups from hydroxyl groups on the surface of CNFs using TEMPO. This reaction weakens the bonds between cellulose fibrils, consequently preventing the formation of strong interfibril linkages (Gamelas et al. 2015). In another study, the same

method was used to observe the adsorption rate of Cu^{2+} on the fibril surface by varying the pH and the carboxylate content (Sehaqui et al. 2014). This study revealed that the increase in the Cu^{2+} adsorption was directly proportional to the carboxylate content. It was noted that in addition to enhanced adsorption, effective desorption by acidic washing was possible in this technique and TOCNFs can be regenerated easily. It was demonstrated that TOCNFs adsorbed up to 167 mg/g of radioactive uranyl ions (UO_2^{2+}) from solutions at pH 6.5, which was 2–threefold superior to that attained with conventional adsorbents such as hydrogels, montmorillonite and silica (Ma et al. 2012c).

Carboxyl groups were created through selective oxidation of the C_2 and C_3 hydroxyl groups to aldehyde groups and then to 2,3-dicarboxyl groups in acidic media (Yang et al. 2013). It was reported that the CNC created and functionalized using this technique attained a maximum uptake of 185 mg/g for Cu^{2+} at pH 4 (Sheikhi et al. 2015). These observations led to the conclusion that the maximum uptake of cellulose fibrils created using mechanical treatment was much lower than the carboxylated CNCs (11 mg/g for Cd^{2+}, 10 mg/g for Pb^{2+}, 11 mg/g for Ni^{2+} at p^H 6.5) (Kardam et al. 2014). Even CNFs with surface aldehyde functional groups, prepared through a mild periodate oxidation process, were applied as adsorbents for Cu^{2+} and Pb^{2+} from aqueous solutions with a maximum adsorption capacity of 38.36 and 157.73 mg/g, respectively (Yao et al. 2016).

2,3,6-tricarboxy cellulose nanofibers (TPC-CNFs) were synthesized by TEMPO oxidation of cellulose pulp (selective at C-6) followed by periodate-chlorite oxidation (selective at C-2 and C-3) (Abou-Zeid et al. 2018a). Efficient adsorption of heavy metal ions including Cu^{2+}, Ca^{2+} and Pb^{2+} from aqueous solutions was achieved using these TPC-CNFs. Zheng et al. (2014) established that the carboxylated CNFs incorporating polyvinyl alcohol (PVA) hybrid aerogels, fabricated by freeze-drying the crosslinked carboxylated CNFs/PVA composites, have excellent metal ions adsorption potential. Carboxycellulose nanofibers with lower crystallinity, higher surface charge, and hydrophilicity were synthesized from an Australian spinifex grass through a nitro-oxidation process with nitric acid and sodium nitrite (Sharma et al. 2018). The resultant nitro-oxidized carbon nanofibers (NOCNF) at low concentration (0.20 wt%) were effective in removing Cd^{2+} ions (50–5000 ppm) from water within 5 min. At lower Cd^{2+} concentrations (< 500 ppm), the adsorption was mediated by interactions between carboxylate functionalities on the NOCNF surface and Cd^{2+}. At higher Cd^{2+} concentrations (> 1000 ppm), the main remediation pathway involved the formation of $Cd(OH)_2$ nanocrystals. The peak Cd^{2+} uptake capacity of NOCNF was approximately 2550 mg/g, radically superior to those of any adsorbents reported earlier. Additionally, the maximum removal capacity was 84%, when the Cd^{2+} concentration was 250 ppm.

In situ functionalization of the nanocellulose membranes subsequent to fabrication is an innovative concept, where direct functionalization of the membrane surface presents a higher concentration of the functional entities on the surface and increased accessibility for interaction with the pollutants. This approach provides a means to increase the membrane functionality without changing the bulk structure. Karim et al. (2017) demonstrated the fabrication of nanocellulose membranes with high water permeability and mechanical stability through in situ TEMPO surface functionalization for improved adsorption of Ag^{+}, Cu^{2+} and Fe^{2+}/Fe^{3+} ions from aqueous media.

Succinylated nanocellulose

Succinylation on the surface of nanocellulose results in efficient, stable and recyclable adsorbents. It was reported by Yu et al. (2013) that esterification of hydroxyl groups on CNC with succinic anhydride produced an elevated maximum adsorption of Pb^{2+} (458 mg/g) and Cd^{2+} (335 mg/g) at pH 5.5 and 6.5, respectively. It was also found that the rapid adsorption process of Pb^{2+} and Cd^{2+} could be well fitted by the pseudo-second-order kinetic model because the chemisorption was the rate-determining step. Srivastava et al. (2012) demonstrated the capacity of functionalized CNFs obtained by succinic anhydride-modified mercerization to adsorb Ni^{2+}, Cr^{3+}, Cd^{2+} and Pb^{2+} with greater efficiencies relative to unfunctionalized CNFs. Mercerization before succinylation of CNFs resulted in an increased surface area and accessibility to a greater number of hydroxyl groups for succinylation. The nanocellulose had a maximum metal ion adsorption ranging from 42.3 to 218 mg/g. A different succinic anhydride-modified CNC was employed for the adsorption of Cr^{3+} ions with an

adsorption capacity of 94.84% (Singh et al. 2014). The modified adsorbent displayed adsorptions of 1.338, 0.744, 1.900, 1.610 and 2.062 mmol/g for the removal of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}, respectively (Hokkanen et al. 2013). The study showed that the absorbent can be successfully regenerated by ultrasonic treatment.

Functionalization of nanocellulose through grafting/immobilization

Polymer grafting is achieved by the substitution of hydroxyl moieties on the surface. There are studies of cellulose grafted by polymers with chelating or ionic functionalities, but there are not many theories supporting the same on nanocellulose. The maximum uptake capacity of Hg^{2+} by amino-treated polymers on cellulose was 288 mg/g at pH 7 (Araki et al. 2001). The same amino-terminated polymers can be grafted onto carboxylated CNCs by means of carbodiimide-mediated amidation in water (Zoppe et al. 2010). Amide-bearing polymers grafted onto sulfated CNCs through a free radical mechanism showed a very high uptake of mercury of 710 mg/g at pH 6.2. This process by which different polymers bearing carboxylic acid groups can be grafted onto diverse CNCs has helped in the observation of uptake capacities for various cations. (Poly)acrylic acid can be grafted onto CNCs from bamboo and the resulting modified CNCs can be used to eliminate Cu^{+2} ions from aqueous solutions whose adsorption capacity was 3 × greater than that of unmodified bamboo CNFs (Zhang et al. 2014). It was described by Zhang et al. (2016) that TOCNFs functionalized with polyethyleneimine (PEI) through crosslinking with glutaraldehyde showed a superior uptake of Cu^{+2} at pH 5 relative to PEI-grafted cellulose. Poly(itaconic acid/methacrylic acid)-grafted nanocellulose/nanobentonite composites consisting of multiple carboxyl groups were successful in adsorbing Co^{2+} ions from nuclear industrial water (Anirudhan et al. 2016). The water-soluble carboxymethyl cellulose (CMC) has chelating carboxyl groups and can also be grafted onto CNCs. It was found by Chen et al. (2016) that the CNF-CMC aerogels displayed adsorption capacities for Ag^{+}, Cu^{2+}, $Pb^{2+}$and Hg^{2+} of 106, 74.8, 111.5 and 131.4 mg/g, respectively.

Embedding nanocellulose in a polymer matrix allows the former to interact directly with heavy metal ions and allow for separation from water. In a recent paper, polyurethane (PU) foam was utilized to efficiently immobilize carboxymethylated cellulose nanofibrils (CMCNFs) in a cost-effective manner (Hong et al. 2018). The composite foams exhibited greater mechanical strength, high adsorption efficiency and recyclability. The maximum adsorption capacities were determined to be 78.7, 98 and 216.1 mg/g for Cu^{2+}, Cd^{2+} and Pb^{2+}, respectively.

Organosilylated nanocellulose

CNFs treated with silanes displayed improved physicochemical properties. Silanes can be either directly combined with CNF and polymer or silanes in organic solvents can be added to CNFs followed by blending with the polymer (Shokoohi et al. 2008). The efficiency of silylated CNFs is generally superior to that of alkali-treated CNFs which is subsequently higher than untreated CNFs. Hokkanen et al. (2014) obtained a material by treating the microfibrillated cellulose with aminopropyl triethoxysilane (APTES), with maximum uptake capacities for Ni^{2+}, Cu^{2+}, and Cd^{2+} of 179, 163, and 388 mg/g, respectively. The adsorption rate was highest at pH 4.5 and decreased at other pH values for this amino-functionalized system.

Thiolated nanocellulose

Hg^{2+} ions are considered a major health concern due to their toxicity and bioaccumulation. Recently, the applicability of spherical nanocellulose (SNC) was evaluated as adsorbents for metal ions from water (Peng et al. 2014; Luo et al. 2015). Ram and Chauhan (2018) reported the synthesis of new thiolated-SNCs via acid hydrolysis and lipase-catalyzed esterification with 3-mercaptopropionic acid (3-MPA). They displayed rapid adsorption of about 98.6% Hg^{2+} ions within 20 min from a 100 ppm solution, whereas the SNCs did not display adsorption in those conditions. The thiolated-SNCs can be reused up to nine times with cumulative adsorption capacity of 404.95 mg/g. The maximum adsorption was 88% from tap water and 78% in the presence of other ions, indicating a selectivity for Hg^{2+} ions.

Phosphorylated nanocellulose

In an interesting study, the enzymatically-phosphorylated CNCs exhibited a high uptake capacity at pH 4 for Ag^{+}, Cu^{2+}, and Fe^{3+} of 136, 117, and 115 mg/g, respectively. On the other hand, the enzymatically-phosphorylated CNFs displayed 120, 114, and 73 mg/g, respectively (Liu et al. 2015). When the cellulose fibers were disintegrated into their nano-sized constituents and after their surface phosphorylation, there was a $\sim$ 6000 $\times$ increase of Cu^{2+} uptake capacity.

Acetylated nanocellulose

The thermal stability of acetylated CNFs was superior to that of non-acetylated CNFs due to the substitution of the hydroxide with stable acetyl groups and with the elimination of hemicellulose during acetylation (Ashori et al. 2014). These results were validated through X-ray diffraction analysis on acetylated and non-acetylated nanofilms. Moreover, acetylation of CNFs decreases the water sorption. Cunha et al. (2014) demonstrated a 25% decrease in water sorption of epoxy and acrylic resins filled with acetylated CNFs relative to untreated CNFs.

Cationic nanocellulose

Nanocellulose can be functionalized with positively charged groups in order to adsorb anionic metallic species like arsenates and chromates. A way to obtain positively charged CNCs is by treating sulfated CNCs with epoxypropyl trimethyl ammonium chloride (EPTMAC) (Hasani et al. 2008). Vanadium in the form of metavanadate (VO_3^{-}) can be adsorbed at a rate of 194 mg/g at pH 2 by biphosphonated nanocellulose synthesized by consecutive oxidation with sodium periodate and reaction with sodium alendronate (Sirviö et al. 2016). On the other hand, aminated CNCs were investigated for the uptake of Cr^{6+} and their performance was compared with that of CNCs. The former displayed 98.33% adsorption capacity while the capacity of the latter was just 5.98% (Singh et al. 2014).

Other recent methods

Very recently, Hassan et al. (2018) reported the synthesis of a novel Cu-terpyridine-modified oxidized CNF membrane to purify effluents from the paper industry. Li et al. (2018) reported an aerogel adsorbent based on CNFs and polyethyleneimine (PEI) via physical electrostatic interactions. The aerogels possessed good structural stability, high porosity and shape recovery in water. Furthermore, they were exceptional adsorbents for Cu^{2+} (175.44 mg/g) and Pb^{2+} (357.44 mg/g) due to the abundance of amine groups. In another method, xanthated-nanocellulose synthesized through the steam explosion of banana fibers, acid hydrolysis and xanthation demonstrated an adsorption of 154 mg/g of Cd^{2+} at pH 6 (Pillai et al. 2013). The CNCs produced by the amino functionalization, which involved the reaction of epichlorohydrin and diethylenetriamine, displayed a maximum adsorption of Cu^{2+} and Pb^{2+} at pH 4.5 of 63 and 87 mg/g, respectively (Shen et al. 2009). If the pH of this system was lowered, the uptake capacity reduces significantly owing to the protonation of amine moieties.

Cellulose nanomaterials for removal of organic pollutants from water

The evolution of various industries has resulted in contamination of water especially by dyes, oils, pesticides and pharmaceutical products. The uptake of dyes and other organic compounds by diverse functionalized nanocelluloses are detailed below.

Carboxylated nanocellulose

Organic dyes typically possess a very complex structure, whether it be anionic, cationic or non-ionic. These chemicals interact with cellulose and have been widely studied (Timofei et al. 2000). Carboxylated CNCs have been observed for various adsorption capabilities of cationic dyes. The carboxylated CNCs prepared by the TEMPO-oxidation method with high carboxylic acid content had a superior adsorption (769 mg/g at pH 9) of methylene blue in comparison with the sulfated CNCs (118 mg/g at pH 9) (Batmaz et al. 2014). The carboxylated CNCs can also be produced through esterification of surface hydroxyl groups with maleic anhydride (Qiao et al. 2015). This proved a higher uptake efficiency of a variety of cationic dyes like crystal violet, methylene blue, and malachite green. The maximum uptake of violet

crystal at pH 4 was 244 mg/g. When the carboxylated CNCs were prepared through a one-step oxidation process, the adsorption capacity for methylene blue was 101 mg/g at a neutral p^H (Leung et al. 2011). In a different process, microcrystalline cellulose was extracted using hydrochloric and citric acid to produce carboxylated CNCs (Yu et al. 2016). The adsorption capacity for methylene blue was directly correlated to the number of carboxyl groups. Similar to the uptake of cationic metallic species, the carboxyl groups displayed a pH dependency to maximize adsorption. As the pH decreased, the uptake capacity also decreased owing to the protonation of carboxylic groups.

Amino-functionalized nanocellulose

CNCs with cationic functionalities, such as amino-functionalized CNC, are normally used for removing anionic dyes. One of the methods of preparing cationic CNCs was by the consecutive sodium periodate oxidation and then reacting it with ethylenediamine (Jin et al. 2015a). The CNCs prepared in this method exhibited the peak uptake of 556 mg/g for acid red GR. The adsorption performance of these cationic CNCs was influenced by the pH-dependent dissociation of functional groups. Unlike the carboxylated CNCs, the amine groups produce a peak adsorption at low pH values and as the pH values increase, the uptake capacity decreases. When the cationic CNFs were produced through quaternization with glycidyltrimethyl ammonium chloride (EPTMAC), it was found that the uptake capacity for Congo red was 664 mg/g and acid green 25 was 683 mg/g within a few seconds (Pei et al. 2013). Similar to aerogels, crosslinked microgels with polyvinylamine can also be formed from CNCs which display high affinity to both types of dye. It was found to have a maximum adsorption uptake of 896, 1469 and 1250 mg/g for acid red GR, Congo red 4BS, and reactive light yellow K-4G, respectively (Jin et al. 2015b). Zhu et al. (2016) found that a similar functionalization mechanism can be used on dialdehyde-functionalized cellulose with hyper-branched polyethyleneimine. This type of CNC showed a higher adsorption uptake of 2100 mg/g for Congo red and 1860 mg/g for cationic basic yellow.

Cationic nanocellulose

There are different types of negatively-charged water contaminants like fluoride, nitrate, sulphate and phosphate. The cationic CNFs can be used to adsorb these negatively-charged anions as their uptake capacity increases with surface charge density. They possess a greater selectivity for multivalent ions (PO_4^{3-} and SO_4^{2-}) than for monovalent ions (F^- and NO_3^-). When the cellulose nanocrystals were reacted with EPTMAC and put through further mechanical mixing, the cationic CNFs had a higher and faster adsorption of humic acid, which is a commonly found organic pollutant (Sehaqui et al. 2015). This humic acid uptake capacity (310 mg/mg) is known to be the highest in literature. A lower pH value meant coiled conformation of humic acid, which resulted in faster adsorption kinetics. A low pH range allowed the CNFs to adsorb thicker layers of humic acid.

Nanocellulose-based composites

Partially hydrolyzed polyacrylamide/cellulose nanocrystal (HPAM/CNC) nanocomposites were investigated for the uptake of methylene blue (Zhou et al. 2014). The adsorption capacity of the nanocomposite increased with an increase in the HPAM anionic character, increasing CNC concentration to 20% and decreasing pH. A maximum capacity of 224.8 mg/g was detected for the nanocomposite composed of 20% CNC at pH 6.5 and the kinetics followed a second order model. Montmorillonite (MMT) was utilized for the uptake of dyes owing to its large surface area and cation exchange efficiency. Since MMT was ineffective for the uptake of anionic dyes, functionalization of MMT with carboxymethyl cellulose (CMC) was considered as a potential alternative. This approach improved the inherent limitations of CMC such as low adsorption performance and poor water solubility attributed to excess negative surface charge. The CMC/MMT nanocomposite displayed uptake capacity of 161.1 mg/g at 30 °C for Congo red dye, which could be further increased to 298.3 mg/g by raising the adsorption temperature to 50 °C (Zhao and Wang 2012). This was attributed to the increased mobility of dye ions and probable swelling in the internal structure of the nanocomposite. Furthermore, increasing the pH from 4 to 12 led to a decrease of adsorption capacity to 32.5 mg/g. This reduction in adsorption capacity of

congo red with the increase in pH was ascribed to the electrostatic repulsion between anionic dye ions and increased negatively charged sites in solution.

Other recent methods

Phenol adsorption from water was explored for a composite film composed of CNF and in situ fabricated hydroxyapatite particles through wet-chemical precipitation (Narwade et al. 2017). Acidic v augmented the adsorption, which followed a pseudo-second order kinetic model. Moreover, optimum reusability was attained with 86% adsorption capacity of the preliminary value after the third run. In another study, a blend of sulfated CNCs and chitosan were subject to freeze drying followed by compaction, thereby creating 200 micron microporous membranes (Karim et al. 2016). These membranes had the ability to immobilize positively-charged dye molecules. They had a pore diameter of 10–13 nm and a low water flux of 64 $Lm^2\ h^{-1}\ MPa^{-1}$. Another drawback was inferior mechanical stability because of the absence of H-bonding. It was shown that the uptake rates of methyl violet 2B, rhodamine 6G, and victoria blue 2B from aqueous solutions at pH 5 were 84%, 69% and 98%, respectively. CNFs prepared using an acidified-chlorite bleaching method followed by dissolution using a high-speed mixer were used as adsorbents for methylene blue cationic dye (Chan et al. 2015). The maximum adsorption capacity was 123 mg/g at 20 °C and pH 9 within 1 min. This adsorbent can be reused up to six runs of adsorption–desorption cycling.

Cellulose nanomaterials for removal of pharmaceuticals

Another growing concern in today's modern world is the contamination of water resources by pharmaceuticals, which pose a serious threat to aquatic organisms. It is well known that CNCs are used as drug carriers, but there are not many studies regarding their use in absorbing drugs from water. It was first confirmed by Jackson et al. (2011) that sulfated CNCs had the capacity to adsorb drugs like doxorubicin hydrochloride (DOX) and tetracycline hydrochloride (TC) from the water. It was found that the ions and the ionic drugs can also be adsorbed subsequent to grafting a hydrophobic surfactant onto the CNCs. This had a maximum adsorption capacity of approximately 0.1 mg/g for docetaxel and paclitaxel. Another way to hydrophobize the CNC surface is by reacting it with alkyl isocyanate (Espino-Pérez et al. 2013). It was found by Rathod et al. (2015) that a very commonly found antibiotic, TC, can be adsorbed from water by sulfated CNCs with a maximum uptake of around 7 mg/g at pH 5 following a pseudo-second order kinetic model as the chemisorption controls the adsorption rate.

Residues of procaine hydrochloride and imipramine hydrochloride were adsorbed from wastewater by means of recyclable β-cyclodextrin-modified CNC/Fe_3O_4/SiO_2 super paramagnetic nanorods (Chen et al. 2014). When a mixture of contaminated water and the composite was passed through a high gradient magnetic separator (1.0 T), the magnetic nanorods remained in the separator, while the organic compounds were collected. This indicated the effective adsorption characteristics of the CNC composite for pharmaceutical residues.

Anionic CNFs performed as excellent adsorbents for the ionizable drug, salbutamol (Selkälä et al. 2018). They were prepared from wood cellulose through nanofibrillation subsequent to the succinylation pretreatment in urea-LiCl eutectic solvent. The chemical functionalization of cellulose appreciably improved the adsorption of salbutamol and the maximum capacity was 196 mg/g. In addition, the adsorption performance was chiefly affected by the charge and colloidal stability of the nanofibril suspensions, as the adsorption was greatly enhanced at $pH > 7$ owing to the deprotonation of the carboxyl groups.

Although the amount of research done on the use of CNCs for the filtration of pharmaceutical molecules was limited, the focus of several research groups is shifting in this direction.

Conclusion

In this review, we have presented a comprehensive overview of the diverse surface functionalization methods of nanocellulose extracted from underutilized biomasses and correlated the surface characteristics to the adsorption capacities and kinetics. The nanocellulose systems can be considered as a promising means to fight the emerging global water pollution crisis, but challenges related to specificity, energy

consumption, cost-effective upscaling and surface modification routes need to be addressed for the commercial realization of this process. Even though functionalized nanocellulose often displays adsorption performance that is comparable or even superior to traditional adsorbents for the removal of heavy metals and organic pollutants, it is necessary to address and explore the selectivity in complex water systems and large-scale experiments. This might offer more insights into the efficiency and advantages of nanocellulose-based membranes in industrial applications in relation to other water purification techniques. In the future, the research in this field is anticipated to focus on hybrid membranes of nanocellulose with other nanomaterials to enhance morphology, structural stability, and adsorption performance. Furthermore, novel processing techniques such as in situ functionalization and 3D printing might facilitate the most favorable use of nanocellulose membranes for water remediation.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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