Nanocellulose Based Adsorbents for Heavy Metal Ions Removal

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Abstract

Heavy metal ion pollutions are of serious threat for our human health, and advanced technologies on removal of heavy metal ions in water or soil are in the focus of intensive research worldwide. Nanocellulose based adsorbents are emerging as an environmentally friendly appealing materials platform for heavy metal ions removal as nanocellulose has higher specific surface area, excellent mechanical properties and good biocompatibility. In this review, we briefly compare the differences of three kinds of nanocellulose and their preparation method. Then we cover the most recent work on nanocellulose based adsorbents for heavy metal ions removal, and present an in-depth discussion of the modification technologies for nanocellulose in assembling high performance heavy ions adsorbent process. By introducing functional groups, such as amino, carboxyl, phenolic hydroxyl, and thiol, the nanocellulose based adsorbents not only remove single heavy metal ions through ion exchange, chelation/complexation/coordination, electrostatic attraction, hydrophobic actions, binding affinity and redox reactions, but also can selectively adsorb multiple heavy ions in water. Finally, some challenges of nanocellulose based adsorbents for heavy metal ions are also prospected. We anticipate that the review supplies some guides for nanocellulose based adsorbents applied in heavy metal ions removal field.

1. Introduction

Nowadays, heavy metal ions has become the most serious problem in water environment due to their toxicity and incompatibility, which not only cause badly problems of environmental but also threaten health of human(Miretzky and Cirelli 2009). Excessive intake of heavy metal ions can cause body damage and even death, such as, Minamata(Petrova et al. 2020) disease in Japan caused by the excessive intake of organic mercury (Hg),some lungs or gastrointestinal tract disease caused by the accumulation of Cd$^{2+}$(Anetor 2012), and Alzheimer's and Parkinson's diseases(Du et al. 2018) caused by the excessive intake of Fe$^{3+}$and Al$^{3+}$.In addition, the rise of nuclear power plants will also cause many radioactive heavy metal pollution such as (Cs$^{137}$, Pu$^{239}$ and U$^{238}$)(Buesseler et al. 2012).It is challenging to attenuate or eliminate heavy metal ion pollutions.

There are many methods to solve heavy metal ions pollution problems in wastewater, mainly include chemical precipitation, ions exchange, ultrafiltration, flocculation, electrodialysis, adsorption and reverse osmosis, etc.(Fu and Wang 2011) Among these methods, adsorption is the most widely used one due to the high removal efficiencies, flexibility in the design and low cost(Shen et al. 2019). The adsorbents mainly include activated carbon, clay, biochar and polymers(Qin et al. 2019b). Recently, nanocellulose-based adsorbents become more and more popular as nanocellulose has higher specific surface area, excellent mechanical properties and good biocompatibility(Jordan et al. 2019).

In this review, we first summarize categories, characteristics and preparation methods of nanocellulose. Then, we present the most recent work on nanocellulose based adsorbents, and deeply highlight the roles of nanocellulose in nanocellulose based adsorbents. Finally, we conclude with perspectives on the remaining challenges and potential opportunities of nanocellulose based adsorbents.
2. Classifications Of Nanocellulose

Cellulose is photosynthesized from CO$_2$ and water, and accumulated as a major component in plants (Isogai 2020). It is a crystalline biopolymer possessing long chains of $\beta$-D-glucopyranose units joined by $\beta$-1,4 glycosidic linkage in which inter- and intramolecular hydrogen bonding restrict its main chain motion (Garba et al. 2020). It is evident that the adsorption properties of native cellulose can be increased by converting it to the nanostructure (Kardam et al. 2014). According to the work of Vadakkekara (Vadakkekara et al. 2019) et al. the maximum adsorption capacity (115 mg/g) of maleic acid-modified nanocellulose for Pb$^{2+}$ is higher than that of maleic acid-modified macro (20 mg/g) or micro cellulose (40 mg/g).

Nanocellulose (NC) is a cellulose material with at least one dimension in the nanometer size range separated from fiber raw materials through physical, chemical or biological treatment (Li et al. 2010). Depending on its cellulose source, processing conditions, size, function and preparation methods, it can be classified into three categories such as nanofibrillated celluloses (NFCs), bacterial nanocellulose (BNCs) and cellulose nanocrystals (CNCs). CNCs, also known as nanowhiskers, exhibit elongated crystalline rod-like shapes, and have high rigidity compared to NFCs since their amorphous regions are highly removed. Nanofibrillar cellulose, cellulose nanofibers, and cellulose nanofibrils are some of synonyms for NFCs (Li et al. 2017), and their cellulose chains are entangled and flexible with a large surface area. BNCs are fairly straight and continuous and have low polydispersity in terms of their dimensions. Scanning electron microscope (SEM) images of three types of nanocellulose are showed in Fig. 1a (NFCs (Wang et al. 2020a)), b (CNCs (Li et al. 2019b)) and c (BNCs (Zhu et al. 2011)).

To obtain different structures and properties of NFCs, some researchers usually use mechanical treatments, mainly including high-pressure homogenization, grinding, micro-jetting, freezing crushing, and high-intensity ultrasound (b et al. 2014), and combined with pretreatment technologies, such as, organic acid hydrolysis (Du et al. 2016), periodate oxidation (Larsson et al. 2014), TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) (Saito et al. 2007) oxidation, eutectic solution (Liu et al. 2019), ionic liquid (Ninomiya et al. 2018) etc. to prepared NFCs from cellulose raw materials. The preparing methods of CNCs mainly include acid hydrolysis and enzymatic (Tong et al. 2020) hydrolysis. Acid hydrolysis usually uses strong inorganic acids (Naduparambath et al. 2018; Yani et al. 2017) (such as sulfuric acid, hydrochloric acid, etc.) to hydrolyze the amorphous regions in the cellulose structure to separate cellulose crystals. In order to obtain the desired structures and properties of CNCs, some environmental friendly pretreatments also have been gradually applied in the preparing processes of CNCs, such as organic acid hydrolysis (Chen et al. 2016), solid acid hydrolysis (Liu et al. 2014b), eutectic solvent (Gan et al. 2020) etc. BNCs are produced by cultivating bacteria (*Gluconoacetobacter xylinus family*, Agrobacterium, Pseudomonas, Rhizobium, and Sarcina (El-Saied et al. 2004)) for a few days in an aqueous culture media containing glucose, phosphate, carbon, and nitrogen sources. To obtain the desired structures and properties of BNCs, we can realize by regulating the nutrient source, oxygen ratio, bacterial strain type, incubation time, and cultivation in a bioreactor (Tang et al. 2017).
To date, the three kinds of nanocelluloses are not only were used in conductive materials, oil-water separation, filter materials, food processing, sensor, capacitor, bio scaffold, and drug delivery fields, but also applied in the fields of heavy metal ions removal and become more and more popular.

3. Nanocellulose Based Adsorbents For Single Heavy Ion Removal

3.1 Nanocellulose based adsorbents for Cu\textsuperscript{2+} removal

Generally, natural nanocellulose is challenged by intrinsic hydrophilicity and inferior adsorption sites, which thus affect its performance in extraction of heavy metal ions (He et al. 2018). However, the high number of hydroxyl groups on the surface of cellulose fibers can provide a platform to modify it with different properties. Qin et al. (2019a) treated different amounts of wood fibers with monochloroacetic acid/sodium hydroxide and homogenization to obtain carboxymethylation CNF(CMCNFs) with different carboxyl content. CMCNFs showed diameters of 3.40 – 3.53 nm and lengths of 1210.6 – 383.3 nm. The carboxyl group content of CMCNF can reach up to 2.7mmol/g(CMCNF-2.7), and the maximum zeta potential value is -88.3mV. Since the carboxylate group of CMCNF can capture Cu\textsuperscript{2+} through electrostatic attraction, ion exchange and complexation actions, its maximum adsorption capacity for Cu\textsuperscript{2+} reaches 115.3mg/g at pH 5.

By controlling different degrees of Tempo oxidation, Liu et al. (2016) obtained two kinds of TOCNFs from Cellulose sludge with different carboxyl content (0.6, 1.5mmol/g). The adsorption mechanism and properties of Cu\textsuperscript{2+} were investigated. Cu\textsuperscript{2+} can be adsorbed on the surface by carboxyl groups, and then reduced to copper (0) or assembled copper oxide nanoparticles by micro precipitation. Copper adsorption increased with the enhancement of copper concentration up to 44.2 mg/g and 75 mg/g for TOCNF0.6 and TOCNF1.5.

Fan et al. (2019) obtained CNCs (CNCs-2h, 4h, 6h, 8h) with different carboxyl content through Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} oxidation of MCC for different durations (2,4,6,8 h). CNCs with a size of 92-140nm in length and 19-23nm in width. The results indicated that the CNCs-6h with the highest carboxyl content (2.2mmol/g) and the maximum zeta potential value is -41mV. Because the carboxylic acid groups in Carboxylated CNCs have a significant capability to bind Cu\textsuperscript{2+}, the maximum adsorption capacity is 51.1mg/g.

Tang et al. (2020a) firstly disperse CNF slurry with different concentrations in liquid nitrogen and rapidly freeze to form spherical beads and freeze-dry to obtain CNF cryogel beads. Then the carboxylated CNF/maleic anhydride cryogel beads (CNF-MA) was obtained by mixing and reacting the original CNF cryogel beads and maleic anhydride (MA) solution. Its carboxyl content reaches 2.78mmol/g and maximum adsorption capacity for Cu\textsuperscript{2+} reaches 82.17mg/g. Desorption experiments with EDTA-Na\textsubscript{2} showed that its adsorption capacity for Cu\textsuperscript{2+} decreased from 68mg/g to 45mg/g after 4 cycles.

Wang et al. (2018a) obtained 9-CNF, 7-CNF and 5-CNF with different carboxyl contents according to different ratios of hydrochloric acid/ citric acid (v/v = 9/1, 7/3, 5/5) waste ginger fiber. As a comparison,
S-CNF was obtained by traditional sulfuric acid hydrolysis. Hereafter, CNF suspension freeze-dried to obtain aerogels. 3D network structures of all aerogels were physically cross-linked by hydrogen bonding with mesopores to macropores (Fig. 2). Among them, 7-CNF had the largest aspect ratio (144) and the largest carboxyl content (1.18 ± 0.1 mmol/g) and largest negative zeta potential (-36 ± 3 mV). Compressive properties (99.5 kPa at 80% strain, 241.77 kPa at 90% strain) at a low density of 20.3 mg/cm$^3$. Its maximum adsorption capacity for Cu$^{2+}$ reached 45.053 mg/g due to the network capture effect, charge neutralization and chain bridging of high aspect ratio carboxylated CNF.

Lei et al. (2019) obtained NFCs suspension after grinding through Endoglucanase enzymolysis, adjusted the concentration of sodium periodate to 10 (DNFC-1), 40g/L (DNFC-2) to controlled the content of aldehyde group. DNFC-2 has the largest aldehyde content (1.95 mmol/g), biggest specific surface area (2.73 ± 0.08 m$^2$/g), and the surface charge density of (1.14 ± 0.07) × 10$^{-5}$ eq/g. The maximum adsorption capacity of DNFC-2 for Cu$^{2+}$ was 26 mg/g.

Ji et al. (2020) used a simple co-deposition coating process to cover tannic acid (TA) and different amounts of cardanol-derived siloxane (CDA) onto the CNF framework, and then freeze-dried to obtain a porous structure TA@CNF-CDA aerogel. Since TA contains many pyrogallol functional groups and has excellent chemical reactivity with thiol or amine terminal monomers (Wang et al. 2018d), so it can provide an active intermediate layer to improve adsorption efficiency for Cu$^{2+}$. The contact angle and Brunner–Emmet–Teller (BET) surface area of the aerogel are 121° and 75.66 m$^2$/g, respectively. Its maximum adsorption capacity for Cu$^{2+}$ reaches 45.6 mg/L due to the higher catechol groups on the surface of the aerogel.

Amino groups have a strong chelating ability to heavy metal ions, so increasing the amino group content can increase the adsorption capacity. Since polyethyleneimine (PEI) has plenty of primary, secondary and tertiary amines on the macromolecular chains, it was usually fabricated hydrogels or aerogels by crosslinking with an aldehyde or epoxy group for improving the adsorption capacity (Shao et al. 2017). Tang et al. (2020b) obtained a high amine group content (5.74 mmol/g) of cellulose nanofibril/PEI aerogel bead (CGP1.3) with the help of a cross-linking agent of 3-glycidyloxypropyl) trimethoxy silane (GPTMS) by quickly frozen with liquid nitrogen and freeze-dried methods. Its maximum Cu$^{2+}$ adsorption capacity reached 163.40 mg/g. Mo et al. (2019) used TO-CN and Trimethylolpropane-tris-(2-methyl-1-aziridine) propionate (TMPTAP) to react through a ring-opening reaction at room temperature, and post-crosslinked PEI to obtain a 3D multi-wall structure TO-CN/TMPTAP/PEI aerogel (TO-CTP) with pores. Since the aerogel had a large number of amino groups and oxygen-containing groups on the surface, its maximum adsorption capacity for Cu$^{2+}$ reached 485.44 mg/g. Moreover, after being treated with EDTA-2Na, the regenerated aerogels also retained high removal efficiency for Cu$^{2+}$ over four desorption-regeneration cycles.

Zhang et al. (2016) obtained TOCN by HCl hydrolysis and TEMPO oxidation, and then cross-linked with PEI under the action of glutaraldehyde (GA) cross-linking agent, then freeze-dried and grinded to get
TOCN-PEI adsorbent. Because of the linking between PEI and -COOH, the carboxyl content of TOCN-PEI decreased from 1.88 to 0.85 mmol/g, and its total amount of amino groups was 4.06 mmol/g. Its maximum capacities for Cu\(^{2+}\) reached 52.32 mg/g due to its abundant carboxyl and amino groups. After HCl cleaning, its adsorption capacity could still reach 33 mg/g.

Tang et al. (2020c) controlled different H\(_2\)O\(_2\) oxidation time (3h, 6h, 9h), and oxidized pomelo peel to obtain anionic/carboxyl nanocellulose (POCNF-3, 6, 9), the obtained POCNF-6 had the highest carboxyl group content (1.711 ± 0.173 mmol/g), highest aspect ratio (169) and largest negative zeta potential (30.5 ± 2.7). Hereafter, POCNF-6 crosslinked with PEI under the action of a glutaraldehyde crosslinking agent to obtain POCNF-PEI. Its maximum adsorption capacity for Cu\(^{2+}\) reached 74.2 mg/g. The Cu\(^{2+}\) adsorption capacity of POCNF-PEI remained to 66.2 mg/g after four adsorption-desorption cycles.

The composite of two or more polymers has become a new development trend of biomaterials in order to obtain certain excellent properties that a single polymer cannot achieve (Cui et al. 2015). Polydopamine (PDA), formed by self-polymerization of dopamine, is rich in catechol and amine groups, which facilitate covalent conjugation or other noncovalent interactions with organic and inorganic materials (Liu et al. 2011). Juntao et al. (2019) used a bio-inspires coating strategy to introduce PDA particles into the surface of CNFs, and then cross-linked PEI to form porous aerogel (PDA-CNF-PEI). Its maximum adsorption capacity for Cu\(^{2+}\) reached 103.5 mg/g, and its porosity and density were 98.5% and 25 mg/cm\(^3\), respectively. When it was regenerated for four cycles by using 0.1 M HCl treatment, its adsorption efficiency for Cu\(^{2+}\) still retained more than 91%.

Mautner et al. (2016) modified the cellulose nanofibrils from the fiber sludge with phosphoric acid to obtain phosphorylated cellulose nanofibrils, and then prepared nanopapers (CNF-P) through papermaking methods. Its maximum adsorption capacity for Cu\(^{2+}\) could reach 19.6 mg/g by the ion exchange capture action of phosphate groups in CNF-P (18.6 ± 2.3 mmol/kg). After a simple washing of phosphoric acid, the adsorption capacity of Cu\(^{2+}\) can still reach 19.4 mg/g.

### 3.2 Nanocellulose based adsorbents for Pb\(^{2+}\) removal

Francisco et al. (2020) obtained cellulose from raw agave leaves by benzyl alcohol extraction, sodium hydroxide alkali treatment and peracetic acid (PAA, H\(_2\)O\(_2\) + acetic acid + H\(_2\)SO\(_4\)), and then high-pressure treatment with a microfluidization process to obtain cellulose nanofibrils and nanosheet (CNF/CNS). The results showed that the CNF/CNS surface contained a lot of carboxyl groups. At low initial concentrations of Pb\(^{2+}\) (C\(_0\) < 100 ppm), the adsorption-mechanism is governed by electrostatic interactions between carboxylate groups and Pb\(^{2+}\); meanwhile, at (C\(_0\) = 1000 ppm) mono and bi-dentate complexes dominate the adsorption-mechanism. Finally, when 110 < C\(_0\) < 1000 ppm, both mechanisms co-exist. According to Langmuir model, the maximum adsorption capacity for Pb\(^{2+}\) was 43.55 mg/g.

Sharma et al. (2018b) used nitric acid/sodium nitrite to oxidize untreated jute fibers to obtain NOCNF slurry. Although its crystallinity was very low (35%), its carboxyl content and surface charge were very...
high (1.15mmol/g and −70mV). At a low NOCNF suspension concentration (0.23wt%), room temperature, pH = 7, the NOCNF could remove sharply Pb\(^{2+}\) ions of from 50 to 5000ppm in the initial steps, and finally its maximum adsorption capacity could reach 2270mg/g.

Graphene oxide (GO) was used to remove heavy metal ions due to its high specific surface area and large number of functional oxygen groups that could provide active sites for heavy metal ions (İlayda et al. 2016). Yu et al. (2020) used Fe\(^{3+}\) as crosslinking agent, carboxymethyl cellulose nanofibril as filler, and wet-spinning method to obtain GO/CMCNF composite fiber(CF). The fiber exhibited enhanced mechanical property up to 648MPa. Its maximum adsorption capacity for Pb\(^{2+}\) reached 99.0mg/g by electrostatic attraction, ion exchange and complexation of carboxyl groups and Pb\(^{2+}\).

Alginate could be also mixed with nanocellulose to remove heavy ions in water due to its non-toxic, biodegradable, low cost and rich carboxyl groups (Eldin et al. 2016). Hu et al. (2018) cross-linked carboxylated cellulose nanocrystal(CCN) and sodium alginate under the action of Ca\(^{2+}\) to obtain CCN-Alg hydrogel. It was easy to separate after adsorption, and had stronger mechanical strength and durability than pure sodium alginate beads. The proposed adsorption mechanisms could possibly include electrostatic attraction and complexation. Within two hours, 76% of Pb\(^{2+}\) could be removed, and adsorption equilibrium was quickly reached in three hours, and the highest adsorption capacity was 338.98mg/g.

Activated carbon (AC) is widely used in the removal of heavy metal ions due to its high specific surface area and fast adsorption speed (Lee et al. 2021). Sari et al. (2017) successfully extracted AC from recovered PACI-lignans containing black liquor sludge. In another work, Septevani et al. (2020) used sulfuric acid or phosphoric acid to hydrolyze oil palm empty fruit bunches to obtain nanocellulose (NCS, NCP). Then use the obtained AC to activate NCS/NCP. The SEM image showed that AC was dispersed in the NC matrix, forming a looser embedded network. Its adsorption mechanism was mainly the electrostatic attraction between adjacent hydroxyl groups and positively charged metal ions on the surface of the super-adsorbent, and its maximum adsorption capacity for Pb\(^{2+}\) reached 24.94mg/g.

In order to improve the hydrophobicity and flexibility of nanocellulose based adsorbents, Rani et al. (2019) used steam explosion method to extract CNCs from banana fiber, and grafted butyl acrylate (BA) onto CNCs to obtain CNCs-g-nBA membrane with the help of ceric ammonium nitrate initiator. Its adsorption capacity changed with the different pH values of the solution. At low pH, the concentration of protons in the solution was high, and the metal binding site became positively charged, repelling Pb\(^{2+}\) cations. As the pH raised, the negative charge density on the adsorbent increased due to the deprotonation of the metal binding site, and adsorption capacity enhanced, however, at pH > 6, the formation of aqueous metal hydroxide precipitation was the main mechanism for removal. At pH = 5, its maximum adsorption capacity with Pb\(^{2+}\) reached 159.53mg/g, and after 3 cycles of desorption with 0.1N HCl and 0.1M EDTA, its adsorption capacity could still maintain a high potential.
Polyvinyl alcohol (PVA) is an inexpensive polymer which possesses desirable properties such as water solubility, biocompatibility, and biodegradability. The application of magnetic adsorbents technology has become one of the promising ways to solve environmental problems (Feng et al. 2010). Zhou et al. (2013) used TEMPO to oxidize MCC to firstly obtain carboxylated cellulose nanofibrils (CCNFs) and then obtain CCNFs-filled magnetic chitosan hydrogel beads (m-CS/PVA/CCNFs) through an instantaneous gelation method. It had a 3D porous structure (Fig. 3(a)), m-CS/PVA/CCNFs hydrogel beads can be easily separated from water (Fig. 3(b)). Its removals for Pb\(^{2+}\) were mainly through amino chelation and carboxyl ion exchange. Its maximum adsorption capacity for Pb\(^{2+}\) could reach 171.0 mg/g. After four cycles with weak acid regeneration, its adsorption efficiency could still retain 90%.

Vadakkekara et al. (2020) obtained nanocellulose from jute fiber, and then modified it with sodium itaconate to obtain sodium itaconate grafted nanocellulose (SINC) adsorbent. The SEM image showed that the SINC surface was irregularity and smoothness. Its maximum adsorption capacity for Pb\(^{2+}\) was 85 mg/g at the pH value of 5.5.

### 3.3 Nanocellulose based adsorbents for Cr\(^{6+}\) removal

Cr is one of priority pollutants in water. Cr has two common oxidation states, Cr\(^{6+}\) is highly toxic, mutagenic and carcinogenic to the ecosystem, however, Cr\(^{3+}\) is a nontoxic substance (Wang et al. 2015).

For the removal of hexavalent chromium (Cr\(^{6+}\)) ions (Attia et al. 2010), most adsorbents have a higher efficiency when pH value was less than 3, but under neutral or alkaline conditions, the removal efficiency was relatively lower. Huang et al. (2020) oxidized sugarcane bagasse with sodium periodate and followed by cationization using Girard’s reagent T to obtain cationic dialdehyde cellulose (c-DAC). There were high density of quaternary ammonium groups and aldehyde groups on the surface of c-DAC. The electrostatic attraction between the positively charged quaternary ammonium salt group and the negatively charged dichromate was the main mechanism of adsorption, and there was a strong binding affinity between the adsorbent and Cr\(^{6+}\). When the adsorption reached saturation, the surface charge on c-DAC was neutralized to form c-DAC-chromium flocs, which could easily be removed by decantation or low-cost gravity-driven microfiltration. The maximum adsorption capacity for Cr\(^{6+}\) could reach 80.5 mg/g, and it had stable adsorption performance under a wide pH range (2–10).

Ferreira-Neto et al. (2020) prepared a self-supported hybrid aerogel film (BC/MoS\(_2\)) combining Bacterial nanocellulose-based organic macro/mesoporous scaffolds and MoS\(_2\) nanostructures (Fig. 4). Since MoS\(_2\) is a transition metal hydrogen disulfide, a layered structure composed of stacked two-dimensional nanosheets (Wang et al. 2018c), this film displays a large number of sulfide(S\(^{2-}\)) sites, which was easy to bind heavy metal ions by electrostatic or hydrophobic adsorptions. Its specific surface area and pore volume were 97-137 m\(^2\)/g and 0.28-0.36 cm\(^3\)/g, respectively. Cr\(^{6+}\) is removed through adsorptive-photocatalytic mechanism since MoS\(_2\) showed effective visible light photoactivity (Fig. 4(b)). Remove Cr\(^{6+}\) ion (88% removal within 120 min, K\(_{obs}\) = 0.0012 min\(^{-1}\)) in photos assisted in-flow.
Zhao et al. (2015) used bamboo pulp to perform ultrasonic and high shear homogenization to obtain CNFs ((Fig. 5 (a, b))). Then, the CNFs were modified with amino groups by Michael reaction, and finally the terminal ester groups were amidated with ethylenediamine (EDA). Repeated several times to obtain PAMAM-g-CNFs, and freeze-dried to obtain PAMAM-g-CNFs aerogel (Fig. 5 (c)). Poly(amidoamine) (PAMAM) (Han et al. 2012) contains a large number of amine groups and amide groups and is common dendrimers. The aerogel has a porosity of 99.39%, specific surface area is 82 m$^2$/g and a density of 0.01 g/cm$^3$. The aerogel removes Cr$^{6+}$ through ion exchange and redox reactions. First, the amino group is protonated under acidic conditions, and Cr$^{6+}$ is electrostatically attracted to the aerogel on the surface, part of Cr$^{6+}$ is reduced to Cr$^{3+}$ by the adjacent electron donor groups. The positively charged Cr$^{3+}$ is released in the water. Some Cr$^{3+}$ ions can still form stable complexes with the negatively charged groups of PAMAM-g-CNFs (Fig. 5(d)). These led to its maximum adsorption capacity of 377.36 mg/g for Cr$^{6+}$.

Ram et al. (2018) obtained spherical nanocellulose (SNC) through acid hydrolysis, then oxidized it with sodium periodate, and further processed it with 2-aminoethane-1-sulfonic acid to obtain Schiff base. Finally, a SNC-Chemosensor was obtained after adding mercaptopropionic acid (MPA) and a specific amount of lipase. Its adsorption mechanism mainly was the complexation of imine, sulfonate and thioester functional groups with Cr$^{6+}$, furthermore, the phenomenon of charge transfer from the ligand to the metal also led to the naked eye color sensing in the range of 30 ppb to 100 ppm of Cr$^{6+}$. Its maximum adsorption capacity for Cr$^{6+}$ was 130 mg/5 mg at pH = 7 and could be easily regenerated with 0.1 M NaOH since it contained imine, thioester and sulphonate groups.

Shahnaz et al. (2020a) hydrolysis cellulose with sulfuric acid to obtain spherical NC and coupled with polypyrrole (PPY) to obtain an adsorbent (NCPPY) for Cr$^{6+}$ removal in water. Since polypyrrole (Lei et al. 2012) is an organic polymer formed by polymerization of pyrrole ring (C$_4$H$_5$N), extensive studies on this polymer justifies its stability, low cost and eco-friendly nature. Compared with 197 m$^2$/g for NC, the specific surface area of NCPPY was significantly increased (488 m$^2$/g). The maximum adsorption capacity of NCPPY for Cr$^{6+}$ was 147.3 mg/g possibly due to the -OH and -NH$_2$ adsorption sites on its surface.

### 3.4 Nanocellulose based adsorbents for Hg$^{2+}$ removal

Silva et al. (2020). dissolved lysozyme protein extracted from egg white in a solution containing 20 mmol/L glutamic acid and 5% (V/V) DES (choline chloride/acetic acid) to obtain lysozyme nanofibrils (LNFs) (Silva et al. 2018), and then mixed with different proportions of CNFs to obtain dual-nanofibrillar films (CNFs/LNFs). Combined the advantages of CNFs with high specific surface area and LNFs with a large number of peptide R-groups on their surface, the films had a strong mechanical properties and binding capacity for Hg$^{2+}$. The removal efficiency is pH-dependent reaching a maximum of 99 % (50 µg/L) after 24 h at a pH value close to the isoelectric point of the protein.

It was reported that thiol groups had highly selective adsorption of Hg$^{2+}$ from wastewater (Yantasee et al. 2007). Geng et al. (2017) oxidized bamboo-derived cellulose with TEMPO to obtain TO-NFC, and then
subjected to facile freeze-drying in MPTs(3-mercaptopropyltrimethoxysilane) sols to obtain flexible aerogel(TO-NFC-Si-SH). The aerogel had a high SH content of 3.33mmol/g, and its porosity reached 99.1%, the BET specific surface area was 43.57m²/g, and the removal rate could reach more than 92% in the Hg²⁺ solution at range of 0.01-85mg/g. According to the hard – soft acid base (HSAB) (Wang et al. 2020b) theory, Hg²⁺ ions are classified as a Lewis soft acid, while thiol and carboxylate groups belong to Lewis soft and hard bases, respectively. Therefore, thiol groups on TO-NFC-Si-SH aerogel tended to be preferentially complexed with Hg²⁺ compared with carboxyl groups. Its maximum adsorption capacity for Hg²⁺ reached 718.5mg/g. Moreover, its adsorption capacity was nearly unchanged at a large pH range. After four adsorption/desorption experiments with 0.1M HCl/5wt% thiourea, its adsorption efficiency could still retain more than 90%.

Rong et al. (2018) used TEMPO to oxidize wood pulp to obtain CNF, and 3-mercaptopropyltrimethoxysilane (MPTMS) (MPTMS: CNF = 1/2) was added to the CNF suspension at room temperature to obtain CNF-1MPTMS and CNF-2MPTMA, then quickly frozen in liquid nitrogen and vacuum dried for 24 hours to obtain CNF-MPTMS sponge. There is a porous structure on the surface, the specific surface area and porosity of CNF, CNF-1MPTMS and CNF-2MPTMA are 12.99, 10.94, 8.84m²/g and 89, 93, 95% respectively (Fig. 6). The maximum adsorption capacity of CNF-2MPTMA for Hg²⁺ could reach 700mg/g. After using 0.1M aqueous disodium edetate dihydrate solution to remove Hg²⁺, the adsorption capacity of CNF-MPTMS sponges did not decrease significantly.

Chauhan (2018) obtained spherical nanocellulose (SNC) by the treating sequences with NaOH and mixed acid of sulfuric acid/hydrochloric acid and ultrasonication, and then enzymatically esterified SNC with 3-mercaptopropionic acid (3-MPA) to obtain its ester derivative (SNC-3-MPA). ¹³C-NMR (nuclear magnetic resonance) results showed that the thiol group was grafted onto C-6-0 of cellulose monomer rings. Since SNC has a higher specific surface area than cellulose and the presence of thiol groups had a high affinity for Hg²⁺, so the removal rate of Hg²⁺ at a concentration of 100 ppm could be as high as 98.6% within 20 minutes. It can be recycled with 0.1N HCl. The adsorbent can be regenerated and its reusability was studied up to nine cycles with cumulative adsorption capacity of 404.95 mg/g.

In order to use the two functional groups (thiol and amino groups) in its molecular structure, Li et al. (2019b) hydrolyzed the qualitative filter paper with sulfuric acid, followed by mechanical treatment to obtain CNC, oxidized the CNC with sodium periodate to obtain with different aldehyde group content dialdehyde cellulose nanocrystals (DAC₁₈₄,₂₂₅,₄₀₅). After modification of three DAC with cysteamine, Cys-CNC₁₈₄,₂₂₅,₄₀₅ were obtained. There was a strong binding interaction between thiol group and Hg²⁺ of Cys-CNCS. The maximum adsorption capacity of Cys-CNC₄₀₅ for Hg²⁺ is 849mg/g. In a 51mg/L Hg²⁺ solution, Cys-CNC₄₀₅ can remove 99% within ten minutes. 2M HCl and 0.5M thiourea as the eluent were used to regenerate Cys-CNCs. The removal percentage of Hg²⁺ for Cys-CNC₄₀₅ still remained 90% after four adsorption – desorption cycles.
3.5 Nanocellulose based adsorbents for radioactive heavy ions

At present, nuclear energy accounts for 14% of the total energy system and generates approximately 200 ~ 300 tons of nuclear waste every year. These radioactive nuclear wastes have harmful effects on animals and plants in the ecosystem, causing pollution to the environment (Park et al. 2020).

Ma et al. (2013) used TEMPO/NaBr/NaClO oxidation approach to prepare an aqueous suspension of 0.05wt% ultrafine cellulose nanofiber. The diameter of ultrafine cellulose nanofibers was found to be in the range of 5 to 10 nm, the average aspect ratio of the nanofiber estimated from the Transmission electron microscope (TEM) image was about 160, and the carboxyl group content (1.4 mmol/g). The maximum adsorption capacity for \( \text{UO}_2^{2+} \) could reach 167 mg/g due to the chelation between the carboxyl group and \( \text{UO}_2^{2+} \). After the \( \text{UO}_2^{2+} \) adsorption, the surface of cellulose nanofibers became covered with metal ionic crystals (Fig. 7). \( \text{UO}_2^{2+} \) could still be used as a “cross-linker” to convert aqueous CNF into gel.

Prussian blue (PB) (Wang et al. 2018b) is considered to be a promising material due to its excellent adsorption properties and high selectivity for Cs ions. However, the use of PB nanoparticles to remove Cs from a radioactive waste solution is limited by separation problems. Eun et al. (2020) freeze-dried Na-CMCNF solution to obtain CMCNF membrane, and then cross-linked it in Fe\(^{3+}\) solution, then reacted with 0.1 or 0.5M potassium hexacyanoferrate (HCF) for rapid synthesis of PB, PB nanoparticles were formed in situ and immobilized at the Fe\(^{3+}\) sites of a CMCNF membrane by reaction with HCF, and 0.1M-PB-CMCNF and 0.5M-PB-CMCNF were obtained. (Fig. 8) The PB nanoparticles, which exhibit an irregular morphology, are sparsely distributed on the surface of the 0.1M-PB-CMCNF sample, whereas PB particles densely cover the surface of the 0.5M-PB-CMCNF sample. The removal mechanism of Cs\(^{3+}\) due to ion exchange between Cs and K. The 0.5 M-PB-CMCNF membranes exhibited excellent Cs\(^{3+}\) uptakes of approximately 130 mg/g\(\text{PB−CMCNF}\).

Anirudhan et al. (2015) used ethylene glycol dimethacrylate (EGDMA) as the crosslinking agent, potassium peroxydisulfate (KPS) as the initiator, Modification of methacrylic acid (MAA) and itaconic acid (IA) in nanocellulose/nanobentonite (NC/NB) composite to obtain PIA/MAA-g-NC/NB (Fig. 9). U\(^{6+}\) is removed by ion exchange of carboxyl functional groups. The adsorbent dose is found to be 2.0 g/L for the removal of U\(^{6+}\) from 100 mg/L. The simulated nuclear industry wastewater was used to practical efficiency and effectiveness tested, and it was observed that 0.45 g/L adsorbent is sufficient for the complete removal of U\(^{6+}\). After 6 adsorption-desorption cycles with 0.1M HCl, a slight decrease in adsorption capacity was observed (from 94.22–89.60%).

Anirudhan et al. (2016) used same adsorbent for the removal of Co\(^{2+}\). An adsorbent dose of 2.0 g/L found to be sufficient for the complete removal of Co\(^{2+}\) from 100 mg/L at room temperature. After washing with 0.1M HCl solution, it can be carried out 6 adsorption cycles, and will not cause too much loss (from 99.15–88.9%), the adsorbent could be applied in nuclear industrial wastewater.
3.6 Adsorbents for other heavy ions

Liu et al. (2014a) compared the adsorption capacity of Ag⁺ on CNC hydrolyzed from cellulose sludge and CNF obtained from grinding. Zeta potential showed negatively charged surfaces for CNC and CNF. The capture of heavy metal ions is accomplished by electrostatic attraction. The presence of SO₃⁻ groups on the surface of CNC obtained by sulfuric acid hydrolysis has a greater impact on the adsorption of Ag⁺. The maximum adsorption capacities of CNC and CNF for Ag⁺ reached 34.4 mg/g at pH 6.39 and 15.45 mg/g at pH 5.45, respectively.

Sharma et al. (2018a) used nitric acid/sodium nitrite to oxidize untreated Australian spinifex grass to obtain NOCNF, which had low crystallinity of around 50%, high surface charge of -68 mV and high hydrophilicity (static contact angle 38°). The suspension (0.20 wt%) can remove Cd²⁺ in a large concentration range (50–5000 ppm) in a short time (≤ 5 min). When the Cd²⁺ concentration is 250 ppm, the removal rate can reach 84%. According to the Langmuir curve, the maximum adsorption capacity for Cd²⁺ can reach 2550 mg/g.

Arsenic is a metalloid that forms highly toxic compounds in many oxidation states including arsenate (As⁵⁺) and arsenate (As³⁺). (As³⁺) is reported to be more toxic than (As⁵⁺) and more difficult to remove from water (Bissen and Frimmel 2003). Zhang et al. (2019) used 1D negatively charged TEMPO-oxidized CNF and positively charged partly deacetylated chitin nanofiber to self-assemble into 3D biohybrid hydrogel (BHH) through electrostatic force at room temperature. Then freeze-drying to obtain biohybrid aerogel (BHA) (Fig. 10). The specific surface area of BHA is 54 m²/g, and the maximum adsorption capacity for As³⁺ is 217 mg/g.

Chai et al. (2020) used glutaraldehyde as a crosslinking agent to crosslink the NC and PEI oxidized by Tempo to obtain NC-PEI/GA nanoparticles. At pH 3, the adsorption equilibrium can be reached within 10 min, and the maximum adsorption capacity for As⁵⁺ is 255.19 mg/g. The adsorbent could be easily regenerated and reused via NaOH treatment, and the regeneration efficiency remained relatively steady even after eight cycles.

4. Nanocellulose Based Adsorbents For Multiple Heavy Ions Removal

4.1 Adsorbents for two heavy ions

Li et al. (2019a) used Tempo to oxidize Hardwood Kraft Pulp and added different amounts of NaClO solutions (150-310 g) in the oxidation process to obtain TOCNF with different carboxyl content. The obtained TOCNFs are with typical width of 5–8 nm and length of 1000–2000 nm, carboxylate contents were 0.70, 1.40 and 1.67 mmol/g (TOCNF 0.70/1.40/1.67), respectively. The adsorption process can reach adsorption equilibrium within 2 min. A combined interaction mechanism, including ion exchange,
coordination and accumulation, was proposed based on the study. The maximum adsorption capacity of TOCNF 1.40 on Cu$^{2+}$ and Zn$^{2+}$ was 102.9mg/g and 73.9 mg/g, respectively.

Because the nitrile groups on the surface of polyacrylonitrile (PAN) [108] can react with hydroxylamine in the aqueous solution at room temperature to form amidoxime groups, it has attracted widespread attention in the field of heavy metal ion removal. Yang et al.(2014) obtained oxidized CNFs through Tempo oxidation, were grafted with cysteine to get the thiol group, which were embedded in the electrospun PAN scaffold. The m-CNF membrane has a large surface-to-volume, the thiol group concentration is 0.9mmol/g, and the maximum adsorption capacity for Cr$^{6+}$ and Pb$^{2+}$ is 87.5mg/g and 137.7mg/g, respectively. The m-CNF membrane adsorbed by Cr$^{5+}$ and Pb$^{2+}$ is regenerated by HCl(2M) and EDTA (0.05M) solutions for 3 times. The m-CNF membrane still possessed 93% of the original Cr$^{6+}$ adsorption capacity and 95% of the original Pb$^{2+}$ adsorption capacity.

Since chitosan had strong ability to chelate heavy metal ions due to the amino and hydroxyl groups on its surface(Vakili et al. 2019), Rodrigues et al. (2019) based on chitosan-g-poly(acrylic acid) matrices filled with CNWs to obtain hydrogel composites (Chitosan-g-poly(acrylic acid)/CNWs). The adsorption performance of hydrogels on Pb$^{2+}$ and Cu$^{2+}$ was investigated by controlling the addition amount of CMWS. The highest adsorption of Pb$^{2+}$(818.4 mg/g) and Cu$^{2+}$(325.5 mg/g) is obtained within 30 min, at pH 4.0, using 20 mg of the hydrogel composite containing 10 w/w-% of CNWs. After washing with 0.1 mol/L HCl solution for five times, the results reveal that the reduction in the amount of metal adsorbed from the first to the last cycle was 10.7% for Pb$^{2+}$ and 18.2% for Cu$^{2+}$, respectively.

Usually, interpenetrating polymer networks(Ding et al. 2020) (IPNs) were composed of two or more different chemical networks that can enhance the mechanical strength of hydrogels. The excellent aspect ratio of NFCs was an ideal material for preparing IPN network hydrogels. Li et al. (2018b) used TEMPO-oxidized NFC and poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA) to crosslink through free radical polymerization to obtain NFC-PDMAEMAIPNs hydrogel(NPIH). According to the weight of the NFCs and DMAEMA different (0.1 :1, 0.2:1, 0.3:1, 0.4:1, 0.5:1, 0.6:1) the preparation of a series of hydrogel (NPIH-0.1, 0.2, 0.3, 0.4, 0.5, 0.6). These hydrogels possess uniform pore structure and high porosity (> 97%), high surface area (> 82m$^2$/g) and compressive strength (> 1.26kPa). The adsorption mechanism is chelation of amino group and ion exchange of carboxyl group. The adsorption capacity of NPIH-0.6 is the largest, the maximum adsorption capacity for Cu$^{2+}$ and Pb$^{2+}$ could reach 217.39 and 81.96mg/g, respectively.

Lignin is conjugated polymer with a high consistency of aromatic groups that can interact with cations, moreover, the oxygen-containing groups (the hydroxyl, methoxy, and phenolic groups) are potential interaction sites of lignin for water purification(Naseer et al. 2019). Sirvio et al.(2020) used DES (sulfamic acid and urea) to treat lignin-rich groundwood pulp and sawdust to obtain sulfation of sulfated wood nanofibers (SWNFs) and sulfated sawdust nanofibers (SSDNFs). As A comparison, lignin-free bleached cellulose fibers were treated with the same method to obtain sulfated cellulose nanofibers (SCNFs). The
adsorption capacity of three kinds of nanofibers on Cu$^{2+}$ and Pb$^{2+}$ was investigated. The maximum adsorption capacities of SCNFs for Cu$^{2+}$ and Pb$^{2+}$ were 2.2 and 1.1mmol/g, respectively. However, due to the presence of lignin, the adsorption capacity of SWNFs and SSDNFs was increased to a certain extent. The maximum adsorption capacity of SWNFs for Cu$^{2+}$ and Pb$^{2+}$ is 2.5 and 1.6mmol/g, and the maximum adsorption capacity of SSDNFs for the two are 2.2 and 1.4mmol/g, respectively.

Succinic anhydride is an active agent containing one anhydride group, which can react with the hydroxyl groups of cellulose. Yu et al.(2013) obtained CNCs by hydrolyzing cotton with sulfuric acid, subsequently, CNCs were modified with succinic anhydride, and the product SCNCs were then converted into the sodic form (NaSCNCs). The maximum adsorption capacities of NaSCNCs for Pb$^{2+}$ and Cd$^{2+}$ were 465.1 mg/g and 344.8 mg/g, which were higher than those of SCNCs 367.6 mg/g and 259.7 mg/g. NaSCNCs could be efficiently regenerated with a mild saturated NaCl solution with no loss of capacity after two recycles. The adsorption mechanism for SCNCs was a complexation process, while ion-exchange was the principal mechanism for the removal of heavy metal ions from NaSCNCs. Therefore, it was essential to convert the carboxyl groups into carboxylates for this adsorbent containing carboxyl groups.

Clay's high specific surface area, high cation exchange capacity and incredible physical and chemical stability can enhance adsorption(Uddin 2017). Hydroxyapatite(CHA) is an effective adsorbent material due to its capability for simultaneous removal of cationic and anionic contaminants from water(Fernando et al. 2015). Sanna et al. (2018) used NCC as a template, CHA particles and bentonite clay are dispersed in a cellulose matrix to obtain CHA-BENT-NCC particles. The maximum adsorption capacity for Ni$^{2+}$ and Cd$^{2+}$ were 22.96mmol/g, 9.71mmol/g. CHA-BENT-NCC can be regenerated by 0.1M HNO$_3$. After five cycles, the adsorption capacity of CHA-BENT-NCC was decreased from 97–74% for Cd$^{2+}$ and from 98–80% for Ni$^{2+}$.

Li et al.(2018a) obtained the NFC solution through TEMPO oxidation, and then achieved physically-crosslinked network NFC/PEI composite hydrogel(NPH13, NPH22, NPH31) through electrostatic combination with PEI solutions of different weight ratios (1:3, 2:2, 3:1). After freeze-drying, NPA13, NPA22, NPA31 aerogel were obtained. The maximum specific surface area of the aerogel is 42.5m$^2$/g, and it has good shape recover capacity (Fig. 10). The electrostatic attraction and cation exchange between carboxyl and amino groups on Cu$^{2+}$ and Pb$^{2+}$ are the reasons for the high adsorption capacity of aerogels. The maximum adsorption capacities of NPA22 for Cu$^{2+}$ and Pb$^{2+}$ are 175.44mg/g and 357.44mg/g, respectively. After three adsorption/desorption cycles, the adsorption capacity of NPAs still maintained more than 90%.

Yao et al.(2016) used TEMPO-mediated oxidized kraft eucalyptus pulps obtain CNFs hydrogel with carboxylate content (0.65mmol/g). Then Dialdehyde CNFs hydrogel (DACs) was obtained by oxidizing CNFs with NaIO$_4$. CNFs and DACs hydrogels were freeze-dried to obtain porous CNFs and DACs aerogels (Fig. 11). The specific surface area for CNFs and DACs aerogels was 185.1m$^2$/g and 134.4m$^2$/g. In the studied concentration range (0.6–1.0 mmol/L), a removal capacity of 0.75 mmol/g for Pb$^{2+}$ and 0.58
mmol/g for Cu$^{2+}$ was obtained. According to the pseudo-second–order, the theoretical maximum sorption capacity was 38.36 mg/g and 157.73 mg/g for Cu$^{2+}$ and Pb$^{2+}$, respectively.

Derami et al. (2019) incorporated of PDA particles into *Gluconacetobacter hansenii* broth under aerobic and static conditions. PDA particles were grown in situ on the BNC membrane (Fig. 12). The catecholamine group on the surface of PDA particles has a strong affinity to lead ions. Adsorption of PDA/BNC was tested in a mixed solution of Pb$^{2+}$, Cd$^{2+}$. The PDA/BNC membrane removed 5.3 g of Pb$^{2+}$ from water per square meter of the membrane area. The lowest performance was observed for Cd$^{2+}$ with 2.1 g of ions removed per square meter of the membrane area. After regeneration with 0.1M sodium citrate solution, the regenerated membranes exhibited excellent contaminant removal efficiency even after 10 cycles of filtration (about 90% of the initial performance retained).

4.2 Adsorbents for three heavy ions

Liu et al.(2015) prepared CNC$_{SL}$ and CNF$_{SL}$ from Cellulose Sludge respectively. Hexokinase enzymes as biocatalysts, grafting the phosphate group of adenosine-5’-triphosphate (ATP) on CNF$_{SL}$/CNC$_{SL}$, to obtain phos-CNC$_{SL}$ and phos-CNF$_{SL}$ adsorbent. As a contrast, nanocrystals (CNC$_{BE}$) prepared by bioethanol were also used to investigate the adsorption capacity of Ag$^+$, Cu$^{2+}$ and Fe$^{3+}$. The results showed that the maximum adsorption capacities of Phos-CNF$_{SL}$ for Ag$^+$, Cu$^{2+}$ and Fe$^{3+}$ were 120,114,73, which were all lower than the 136,117,115 of Phos-CNC$_{SL}$. It can remove more than 99% of Cu$^{2+}$ and Fe$^{3+}$ in the wastewater in the mirror making industry.

It was evident that tannins had a high chelating affinity for heavy metal ions due to its large number of adjacent phenolic hydroxyls content(Bacelo et al. 2016). Xu et al. (2017) used sulfuric acid to hydrolyze bleached kraft pulp to obtain NCC, and then oxidized NCC with sodium periodate to obtain dialdehyde nanocellulose (DANC), and then generated TNCC by reacting the aldehyde group on the DANC with the reactive hydrogen on the tannin molecule. DANC can be used as matrix and crosslinker. The adsorption mechanism is the strong complexing ability of phenolic hydroxyl groups on metal ions, on the other hand, ionization can enhance the electrostatic attraction ability of metal cations and anions TNCC. Calculated according to Sips model, the maximum adsorption capacities of TNCC for Cu$^{2+}$, Pb$^{2+}$, and Cr$^{6+}$ are 51.846, 53.371 and 104.592mg/g, respectively. The results showed that the maximum adsorption capacities of TNCC for Cu$^{2+}$, Pb$^{2+}$, and Cr$^{6+}$ are 49.140, 49.530 and 103.259mg/g. After 5 times of adsorption-desorption using 0.1M HNO$_3$ solution, the adsorption capacity of TNCC for Cu$^{2+}$ and Pb$^{2+}$ could still reach 43.12 and 45.69mg/g. However, the adsorption capacity(1.06mg/g) for Cr$^{6+}$ decreased greatly even after the first regeneration. The poor adsorption performance of TNCC after regeneration may be attributed to its redox adsorption for Cr$^{6+}$.

Feng et al. (2018) used electronspinning technique to prepare PAN/CA (cellulose acetate) composite nanofibrous membranes, and then amidoxime ployacrylonitrile/regenerate cellulose (AOPAN/RC) composite nanofibrous membranes were prepared by combining hydrolysis and amidoximation
CA can be dissolved in a variety of solvents, so it can become nanofibers through electrospun. The adsorption mechanism of the membrane is coordination/chelation between metal ions and amidoxime/hydroxyl groups. The maximum adsorption capacity of AOPAN/RC for Fe$^{3+}$, Cu$^{2+}$ and Cd$^{2+}$ are 7.47, 4.26, 1.13 mmol/g, respectively. After 5 adsorption/desorption experiments, its adsorption rate could still retain more than 80%.

Shahnaz et al. (2020b) hydrolyzed cellulose with sulfuric acid and oxidized sodium periodate to obtain dialdehyde-based nanocellulose (DANC). Bentonite was converted into NB under ultrasound. Chitosan was modified with chloroacetic acid to obtain carboxymethyl chitosan. CMC, DANC and NB are mixed to obtain hydrogel slurry, which is freeze-dried to obtain the nanobentonite incorporated dialdehyde nanocellulose-carboxymethyl chitosan aerogel (NBNC). The response surface methodology (RSM) method was used to analyze the optimal reaction conditions of NBNC to heavy metal ions. The adsorption capacity for Cr$^{6+}$, Co$^{3+}$ and Cu$^{2+}$ are 2749.68, 916.65, and 1937.49 mg/g, respectively.

Polyurethane (PU) (Kalaivani et al. 2016) has the advantages of high mechanical strength and stability, and high specific surface area under different environmental conditions, and can be applied to the adsorption of heavy metal ions. Hong et al. (2018) filled different concentrations of CMCNFs (2,3,4 wt%) in PU foam as filler to obtain PU/CMCNF (neat-PU, PU/CMCNF-2,3,4) foams. SEM images show that the surface of the composite foam material is rough and porous (Fig. 14). The maximum adsorption capacities of CMCNF embedded in PU foam were found to be 78.7 mg/g and 216.1 mg/g for Cu$^{2+}$ and Pb$^{2+}$ removal, respectively, in PU/CMCNF-2, while PU/CMCNF-3 exhibited maximum removal capacity for Cd$^{2+}$ (98 mg/g).

Magnetic separation technology is widely used in separation and purification. Super magnetic ion materials include Ni, Co, Fe, Fe$_2$O$_3$, Fe$_3$O$_4$, Fe-Co, and Ni-Fe (Zhu et al. 2011). Among them, Fe$_3$O$_4$ nanion is stable and widely used in culture mediums due to its low toxicity. Zhu et al. (2011) synthesized BC from Xylobacteria by agitated fermentation method, and biosynthesized spherical Fe$_3$O$_4$/BC nanocomposite by pH-controlled embedding method. The maximum adsorption capacities of Fe$_3$O$_4$/BC spheres for Pb$^{2+}$, Mn$^{2+}$ and Cr$^{3+}$ are 65, 33 and 25mg/g, respectively. Since the superparamagnetic spherical Fe$_3$O$_4$/BC nanocomposites are recycled using magnetic field separation, it can be utilized repeatedly. After recycling with 0.1 mol/L sodium citrate, the adsorption capacity of Fe$_3$O$_4$/BC spheres for the three ions decreased slightly.

Hosseini et al. (2020) prepared CNFs from date palm tree waste, cellulose nanobrills cryogels modified with 10% GO and 10% Fe$_3$O$_4$ nanoparticle as filler (CNFs/GO/Fe$_3$O$_4$) were prepared by facile freeze-drying methodology. CNF can enhance the mechanical strength and adsorption capacity of the adsorbent. The CNFs/GO/Fe$_3$O$_4$ cryogels has a low density of 0.0139g/cm$^3$ and an ultra-porosity of 99.46%, appropriate specific surface area ($S_{BET}=55m^2/g$), the maximum adsorption capacity of the CNFs/GO/Fe$_3$O$_4$ cryogels for Pb$^{2+}$, Hg$^{2+}$, Cr$^{5+}$ at 298±1 K are 126.58, 36.7 and 73.52mg/g, respectively.
Anirudhan et al. (2015b) used EGDMA as a crosslinking agent and K$_2$S$_2$O$_8$ as a free radical initiator, and it was grafted onto magnetite nanocellulose by itaconic acid, and then further modified by 2-mercaptobenzamide to obtain a new type of thiol and carboxyl functionalized magnetite nanocellulose composite particle (P(MB-IA)-g-MNCC) to remove Hg$^{2+}$ in chlor-alkali industrial wastewater. Hg$^{2+}$ is removed by the ion exchange of carboxyl groups and the complexation of thiol groups, and its maximum adsorption capacity is 240.0mg/g. They used the same adsorbent to remove Cd$^{2+}$ (Anirudhan and Shainy 2015a) and Co$^{2+}$ (Anirudhan et al. 2019), its maximum adsorption capacity is 262.27mg/g and 349.62mg/g, respectively.

### 4.3 Adsorbents for four heavy ions

Zheng et al. (2014) used eucalyptus kraft pulp for TEMPO oxidation to obtain CNFs, and then used glutaraldehyde as a cross-linking agent, cross-linked PVA and CNFs and then freeze-dried to obtain PVA/CNF aerogels, and then used methyltrichlorosilane to pass thermal chemical vapor After the deposition process, the silane-coated PVA/CNF aerogel is obtained, which has super-hydrophobic and superoleophilic capabilities (Fig. 15). The porosity of all aerogels is over than 98%. The carboxyl groups in the porous material have electrostatic attraction and chelation for heavy metal ions. The maximum adsorption capacity of PVA/CNF aerogel for Hg$^{2+}$, Pb$^{2+}$, Cu$^{2+}$ and Ag$^+$ is 157.5, 22, 110.6 and 24.5mg/g, respectively. The silane-coated PVA/CNF aerogel can be used to clean up oil/chemical spills/leaks contamination.

Carbon dots (CDs) have caused extensive research due to their chemical stability, excellent biocompatibility, non-toxicity and colorful photoluminescence (Zhou et al. 2018). Guo et al. (2019) obtained Carboxymethylated Cellulose Nanofibrils (CM-CMFs) after carboxymethylated Eucalyptus Kraft Pulp by sodium hydroxide/chloroacetic acid treatment and homogenization. The CM-CNFs were further modified with CDs based on a typical condensation reaction. A series of fluorescent nano cellulosic hydrogels (FNH-1, 2, 3, 4, 5, 6) were prepared through radical polymerization of CM-CNF-CDs, AA, AM and MBA (0.01, 0.02, 0.1, 0.55, 1.00, 1.45wt%) by using PPS as the initiator. High content of amino, hydroxyl, and carboxyl groups can provide adsorption sites, and the 3D network structure of the hydrogel promotes the adsorption of metal ions from the outside to the inside. The maximum adsorption capacity of the FNH-5 for Fe$^{3+}$, Ba$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ ions was tested, and they were 769 mg/g, 212 mg/g, 2056 mg/g, 1246 mg/g, respectively.

Hokkanen et al. (2013) used succinic anhydride to modify mercerized nanocellulose through succinylation reaction, and obtained a carboxyl-containing adsorbent. The SEM image showed that after the modification, the crystallinity increased significantly. Fourier Transform Infrared (FTIR) results show that there are carboxyl groups on the surface of the adsorbent. Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ can be effectively removed by ion exchange. The adsorption capacities of Mercerized Nanocellulose were 1.338, 0.744, 1.900, 1.610, 2.062mmol/g, respectively. Recycling of adsorbent can be realized by nitric acid and ultrasonic treatment with regeneration efficiencies ranging from 96–100%.

**Conclusions And Perspectives**
As an emerging materials platform for heavy metal ions removal, nanocellulose based adsorbents exhibit many advantages, but challenges are to be properly resolved in the future (Fig. 16). For instance, given strong negative ion groups, nanocellulose based adsorbents have a high electrostatic attraction ability, offering desired adsorbing sites for heavy metal ions. However, hydrophilic negative ion groups will decrease the hydrophobic ability and stability of the adsorbents in water. Possible solutions are, but not limited to, modifying the nanocellulose or integrating assemble processes to enhance the crosslinking behaviors among nanocellulose and the other furnishes.

Surface modifications of nanocellulose, such as, oxidation, phosphorylation and amination, could promote the adsorbing sites of nanocellulose based adsorbents, but likely result in the rapid decrease of their desorption ability. To increase the recycling times of adsorbents, more acid washing is required, which will also cause harm to the environment. To obtain the high desorption capacities, we can firstly try to find some groups which have different binding affinity for heavy metal ions, then assemble these groups into the multilayer 2D/3D nanocellulose based adsorbent aerogels or composites, finally prepare the high adsorption/desorption ability adsorbents.

To meet the requirements of recycling, selective adsorptions or desorption for different heavy metal ions, precisely controlled assembles of nanocellulose based adsorbents with tailorable hydrophilicities and mechanical properties are desired for the industrial applications. For example, to optimize the assembling process, crosslinking agent and functional additive kinds in adsorbent networks have to be properly selected to modulate the suitable porous structures and adsorption capacities. In addition, computational modeling and advanced in situ characterizations would be beneficial, which, in turn, will further guide researchers to the rational design of cellulose-based adsorbents for heavy metal ions removal.

**Abbreviations**
<table>
<thead>
<tr>
<th>NC</th>
<th>Nanocellulose</th>
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<tr>
<td>NFCs</td>
<td>Nanofibrillated cellulose</td>
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<td>BNCs</td>
<td>Bacteria nanocellulose</td>
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<tr>
<td>CNCs</td>
<td>Cellulose nanocrystals</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>TEMPO</td>
<td>2,2,6,6-Tetramethyl-1-piperidinyloxy</td>
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<td>CMCNFs</td>
<td>Carboxymethylation CNFs</td>
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<tr>
<td>MA</td>
<td>Maleic anhydride</td>
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<tr>
<td>TA</td>
<td>Tannic acid</td>
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<td>CDA</td>
<td>Cardanol-derived siloxane</td>
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<td>BET</td>
<td>Brunner – Emmet – Teller</td>
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<td>PEI</td>
<td>Polyethyleneimine</td>
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<td>GPTMS</td>
<td>3-glycidyloxypropyl trimethoxy silane</td>
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<td>TMPTAP</td>
<td>Trimethylolpropane-tris-(2-methy-1-aziridine) propionate</td>
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<td>TO-CTP</td>
<td>TO-CNF/TMPTAP/PEI</td>
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<td>GA</td>
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<td>Polydopamine</td>
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<td>Peracetic acid</td>
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<td>Cellulose nanosheet</td>
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<td>Graphene oxide</td>
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<td>CF</td>
<td>Composite fiber</td>
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<td>Polyvinyl alcohol</td>
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<td>m-CS</td>
<td>Magnetic chitosan</td>
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<tr>
<td>SINC</td>
<td>Sodium itaconate grafted nanocellulose</td>
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<td>c-DAC</td>
<td>Cationic dialdehyde cellulose</td>
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<tr>
<td>EDA</td>
<td>Ethylenediamine</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<td>NC</td>
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<td>Mercaptopropionic acid</td>
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<td>PPY</td>
<td>Polypyrrole</td>
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<td>LNFs</td>
<td>Lysozyme nanofibrils</td>
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<tr>
<td>HSAB</td>
<td>Hard-soft acid base</td>
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<td>MPTMS</td>
<td>3-mercaptopropyltrimethoxysilane</td>
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<td>SNC</td>
<td>Spherical nanocellulose</td>
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<tr>
<td>3-MPA</td>
<td>3-mercaptopropionic acid</td>
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<td>$^{13}$C-NMR</td>
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<td>Cys</td>
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<td>PB</td>
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<td>HCF</td>
<td>Hexacyanoferrate</td>
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<td>Potassium peroxydisulfate</td>
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<td>Biohybrid hydrogel</td>
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<td>Interpenetrating polymers networks</td>
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<td>Poly(2-(dimethylamino) ethyl methacrylate)</td>
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<td>Fluorescent nanocellulosic hydrogels</td>
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<td>FTIR</td>
<td>Fourier Transform Infrared</td>
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**Declarations**

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**Ethical approval:** This article does not contain any studies with human participants or animals performed by any of the authors.

**References**


86. Sharma PR, Chattopadhyay A, Sharma SK, Geng LH, Hsiao BS (2018a) Nanocellulose from Spinifex as an Effective Adsorbent to Remove Cadmium(II) from Water Acs. Sustainable Chemistry Engineering 6:3279–3290. doi:10.1021/acssuschemeng.7b03473


Figures

Figure 1

(a) SEM images of NFCs (Wang et al. 2020a). (b) CNCs (Li et al. 2019b). (c) BNCs (Zhu et al. 2011)

Figure 2

(a1, a2) FE-SEM images of aerogels pore structure and high magnification for S-CNF, (b1, b2) 9-CNF, (c1, c2) 7-CNF, (d1, d2) 5-CNF (Wang et al. 2018a)
Figure 3

(a) SEM image of m-cs/PVA/CCNFs hydrogel. (b) photographs of m-cs/PVA/CCNFs hydrogel in Pb2+ solution before and after magnetic separation by an external magnetic field.

Figure 4

Removing mechanism of heavy metal ions in BC/MoS2 hybrid aerogel (Ferreira-Neto et al. 2020)
Figure 5

(a) 0.1wt% dispersions of original cellulose fibers. (b) CNFs after being left to stand for 3 days. (c) The preparation method of PAMAM-g-CNFs. (d) The mechanism of PAMAM-g-CNFs to remove Cr6+ in water (Zhao et al. 2015)

Figure 6

(a) SEM images of CNF, (b) CNF–1MPTMS, (c) CNF–2MPTMS sponges (Rong et al. 2018)
Figure 7

(A) TEM image of the corresponding electron diffraction pattern of cellulose nanofibers; (B) high resolution TEM image of a cellulose nanofiber before the adsorption of UO22+; (C) high resolution TEM image of a cellulose nanofiber after the adsorption of UO22+; (D) After adsorption of UO22+, cellulose nanofiber Liq. was transformed into Gel (Ma et al. 2013)
Figure 8

SEM images of PB-CMCNF membranes (Eun et al. 2020)
Figure 9

Synthesis of P(IA/MAA)-g-NC/NB (Anirudhan et al. 2015)
Figure 10

Schematic of the self-assembly process for the production of BHH and BHA. (a-b) TEMPO- and mechanical-exfoliation to produce TOCNF; (c-d) NaOH- and mechanical-exfoliation to produce PDChNF; (e) electrostatic force induced self-assembly gelation of nanofibers with ionic interactions between TOCNF and PDChNF; (f) digital images illustrate the ultra-light BHA was captured by a marker pen due to static electricity; (g) scanning electron microscopy (SEM) image of BHA exhibits a highly porous structure (Zhang et al. 2019).

Figure 11
Shape recovery of NPA22 by absorbing water (Li et al. 2018a)

Figure 12
(a) SEM images of as-prepared CNFs. (b) DACs (Yao et al. 2016).

Figure 13
(a) Photographs of PDA/BNC membrane during different fabrication steps. (b) Schematic representation of the fabrication process of PDA/BNC membrane (Derami et al. 2019).
Figure 14

Schematic illustration showing the preparation and evaluation of electrospun AOPAN/RC blend nanofiber membrane for adsorption/removal of heavy metal ions from water (Feng et al. 2018).

Figure 15

(a) Surface SEM images of neat PU foam (b) PU/CMCNF composite foams of 2 wt%. (c) 3 wt%. (d) 4 wt% CMCNF. (Hong et al. 2018).
Figure 16

Water contact angle measurements of the PVA/CNF aerogels: (a) uncoated aerogel and (b) silane-coated aerogel. Optical images of (c) water droplets and (d) gasoline droplets squirted on a piece of silane-coated PVA/CNF aerogel (Zheng et al. 2014)
By regulating key elements including monomers/polymers with different functional groups, cross-linking types, desorption methods endorse nanocellulose based adsorbents with many advanced properties to excel in heavy ions removal applications.

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