REVIEW

Exploring of Cellulose Nanocrystals from Lignocellulosic Sources as a Powerful Adsorbent for Wastewater Remediation

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Abstract

The increasing global concern over the contamination of natural resources, especially freshwater, has intensified the need for effective water treatment methods. This article focuses on the utilization of Cellulose nanocrystals (CNCs), sourced from lignocellulosic materials, for addressing environmental challenges. CNCs a product of cellulose-rich sources has emerged as a versatile and eco-friendly solution. CNCs boast unique chemical and physical properties that render them highly suitable for water remediation. Their nanoscale size, excellent biocompatibility, and recyclability make them stand out. Moreover, CNCs possess a substantial surface area and can be modified with functional groups to enhance their adsorption capabilities. Consequently, CNCs exhibit remarkable efficiency in removing a wide array of pollutants from wastewater, including heavy metals, pesticides, dyes, pharmaceuticals, organic micropollutants, oils, and organic solvents. This review delves into the adsorption mechanisms, surface modifications, and factors influencing CNCs' adsorption capacities. It also highlights the impressive adsorption efficiencies of CNC-based adsorbents across diverse pollutant types. Employing CNCs in water remediation offers a promising, eco-friendly solution, as they can undergo treatment without producing toxic intermediates. As research and development in this field progress, CNC-based adsorbents are expected to become even more effective and find expanded applications in combating water pollution.

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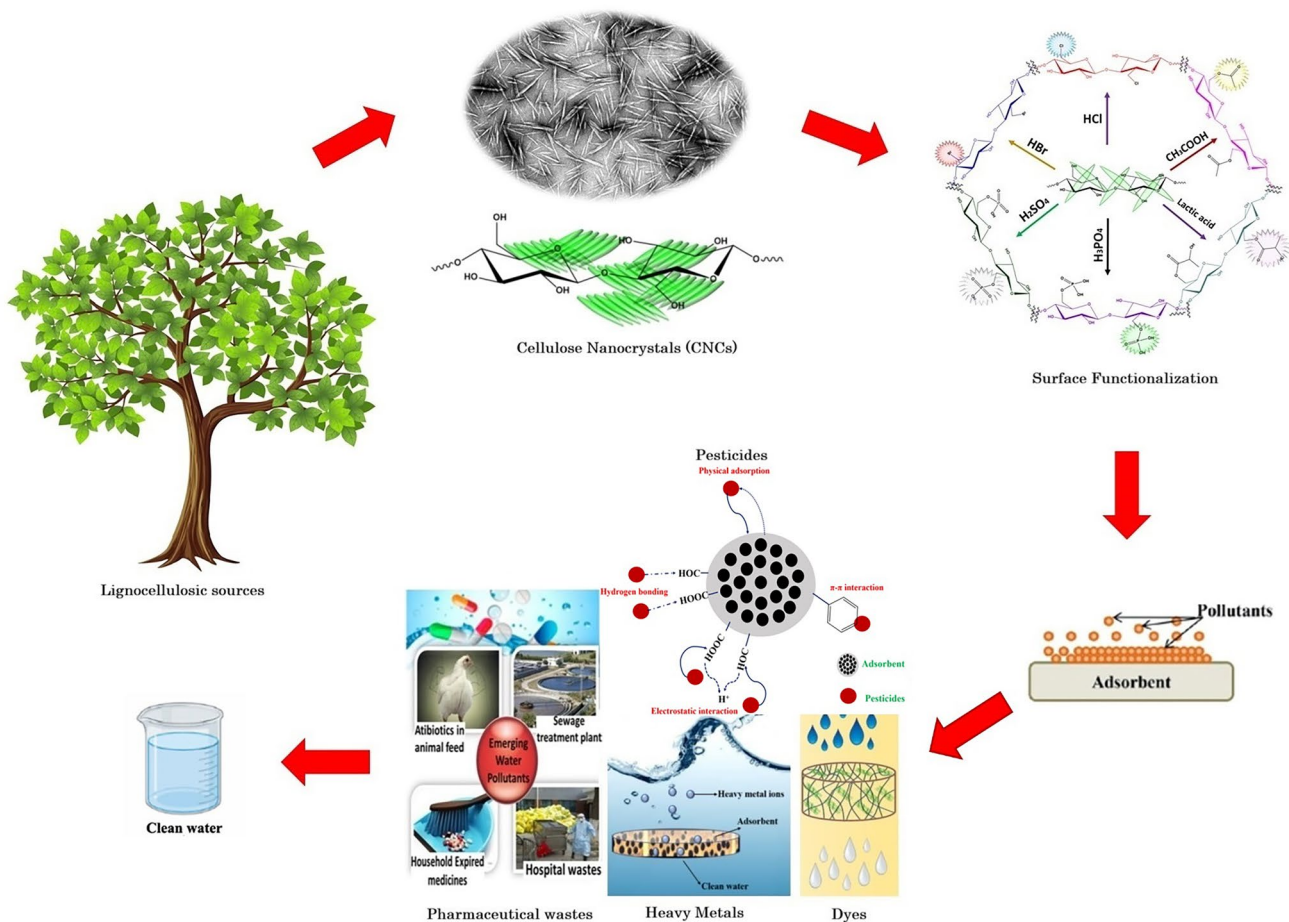
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Graphical Abstract

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Adsorbent

Pesticides
Physical adsorption

Hydrogen bonding

π-π interaction

Adsorbent

Pesticides

Electrostatic interaction

Emerging Water Pollutants

Atibiotics in animal feed

Sewage treatment plant

Household Expired medicines

Hospital wastes

Pharmaceutical wastes

Heavy metal ions

Adsorbent

Clean water

Heavy Metals

Dyes

Clean water

Keywords Cellulose nanocrystals · Adsorption · Separation · Pollutants · Water remediation

Introduction

Water, which covers about 71% of the earth's surface [1], with nearly 97% of the water being too salty for drinking or irrigation of crops. The remaining 3% of fresh water on earth is suitable for human consumption [1, 2], however, only around 0.4% of the Earth's water is accessible and available for distribution among the planet's 7 billion inhabitants [3]. As a result, limited accessibility of water meets the needs of billions of individuals, and as the global population grows, the situation is anticipated to deteriorate [4]. Fresh water, in reality, is a renewable resource, but the available fresh water has become highly contaminated [5] as a result of industrial, agricultural, and household activities [6]. An example of environmental pollution can be seen in the Klang Valley region of Malaysia, where the Sungai Gong River was recently contaminated. This pollution was attributed to various activities, including the discharge of wastewater

from factories in the vicinity. The discharge point from the final tank and the factory's machinery were observed to release blue-colored water. As a result, the pollution posed a significant risk, leading to the potential shutdown of four water treatment plants in Selangor [7]. This incident had far-reaching implications, including water supply interruptions, and affecting communities in the Klang Valley region.

Industrial wastewater treatment is necessary to mitigate the health risks associated with contaminated water [8–10]. A large portion of highly polluted wastewater, approximately 80 to 90%, remains untreated and unutilized out of the total wastewater generated by human activities [1]. Wastewater contains common contaminants such as oil and organic solvents, pesticides, dyes, heavy metal ions, and pharmaceutical pollutants pose significant risks to human health and the environment. These contaminants endanger natural aquatic habitats and species, leading to water contamination and negatively impacting biodiversity [6, 11]. Lack of

wastewater treatment leads to a significant global issue, as billions of people around the world do not have access to safe drinking water and proper sanitation facilities [1]. There is a growing global concern that the volume of sewage generated by industrial, agricultural, and human activities is increasing at a pace that surpasses the capabilities of current wastewater treatment technologies. This raises concerns about our ability to effectively treat and manage the escalating volume of sewage using existing technological solutions [12, 13]. Natural polymers such as cellulose, starch, chitosan, chitin, gelatin, and alginate, which are readily available, have shown great potential in wastewater treatment [14, 15]. Cellulose can be found in bacteria, algae, tunicates, woods, rice husks, bamboo, hemp, sisal, kenaf, flax, and oil palm biomass, is the most abundant natural material on the planet, with an annual production of 10^{11} to 10^{12} tonnes [16]. Extensive research has been conducted on modifying cellulose polymers through chemical and mechanical means to produce cellulose nanocrystals (CNCs), a valuable class of nanomaterials, which offer promising solutions for filtering impurities and adsorbing pollutants [6].

Given its nanoscale dimensions and fibrous structure, CNC has a large surface area per unit mass [17–19]. This large specific surface area offers numerous active sites in the form of hydroxyl groups, which are highly effective in adsorbing and interacting with contaminants present in wastewater [20]. The hydroxyl groups on CNCs could form hydrogen bonds with various contaminants, while the combination of their nanoscale size and large specific surface area allows for enhanced contact and adsorption capacity. Nevertheless, the surface charge, surface reactivity, and mechanical strength of CNCs can be tailored to suit specific wastewater treatment applications by controlling the crystal structure [21]. The crystal structure of CNCs can be modified during synthesis, resulting in different properties and functionalities [22], enabling even higher specific surface areas to be achieved. The functionalization of CNCs involves the attachment of various functional groups, such as carboxyl [23–25], amino [22], hydroxyl [26], sulphate [27], or phosphate [28] groups, onto the surface of the CNCs. These functional groups introduce new active sites that facilitate specific interactions with pollutants present in wastewater, thereby enhancing the adsorption properties of the CNCs. The selection of a particular functional group depends on the target pollutants and the desired adsorption mechanisms. This process can be achieved through surface modification techniques, including chemical reactions, physical adsorption, or grafting methods. Through grafting, functionalizing, and crosslinking, different levels of functional attachments can be achieved, leading to the fabrication of CNC-based grafts [29, 30], polymer nanocomposites [25, 27], nanofiber aerogels [31], membranes [32] and microspheres [33] to overcome its limitations to enhance its adsorption ability for

wastewater treatment. The increased specific surface area of CNCs significantly enhances their adsorption capacity, making them an effective material for water remediation [34]. The specific surface area of CNCs can vary depending on the production method and processing conditions, typically ranging from 10 to 250 m^2/g [35].

By incorporating nanoparticles such as metal nanoparticles or metal-organic frameworks, it becomes feasible to enhance the surface properties of the adsorbent to selectively remove specific pollutants. This approach enables the development of customized active sites with catalytic or adsorption properties that are specifically relevant to wastewater treatment, thereby further improving the adsorption capabilities. Besides, bimetallic supports provide synergistic effects, as the combination of different metals not only creates customized active sites but also enhances the overall stability of the adsorbent. This, in turn, can significantly improve the efficiency and selectivity of adsorption in wastewater treatment applications [36]. Overall, the shape and specific surface area, crystal structure, and bimetallic support of CNC play vital roles in optimizing their performance for wastewater treatment. Modifications to well-defined crystal structures improve CNC adsorption capacity or stability in harsh wastewater conditions [37], allowing for stronger interactions with pollutants. The functionalization techniques and the inherent properties of CNCs play a vital role in the formation of active sites on their surface. These active sites enable CNCs to efficiently adsorb and eliminate pollutants from wastewater, making them highly valuable materials for wastewater treatment applications. Gaining a comprehensive understanding of these factors and effectively manipulating them can lead to the advancement of more efficient and effective adsorbents for a wide range of pollutants found in wastewater.

Recently, there has been a significant focus on finding innovative and environmentally friendly materials for water purification that are cost-effective, require low energy input, and do not produce hazardous by-products [38]. Given its diverse attributes, natural abundance, biodegradability, and non-toxic nature, researchers have extensively studied cellulose polymer for chemical and mechanical modifications to produce cellulose nanocrystals (CNCs). The presence of numerous functional groups, the ability to tune their surface properties, their hydrophilicity, high tensile strength, and flexibility make CNCs a promising option for wastewater treatment [39]. In this regard, CNCs is a possible nanomaterial for wastewater treatment that offers promising options for pollutant and impurity elimination. The application of nanocellulose-based aerogels [39–41], membranes [42], adsorbents [43] for water remediation has been widely described in recent years. Thus, a thorough overview of the research conducted on materials based on nanocellulose specifically, CNCs is presented in this review. The

review encompasses the fundamental properties of CNCs-based materials and explores their innovative applications in wastewater treatment. Additionally, it delves into the adsorption capacities of CNCs-based materials and discusses their potential applications in removing various pollutants, including oil and organic solvents, pesticides, heavy metals, dyes, and pharmaceuticals, in wastewater treatment processes.

Isolation Approaches and Enchanting Properties of CNCs

CNCs Isolation Technique

As interest in sustainability and nanotechnology has grown, so is the use of CNCs in wastewater treatment applications. In-depth research has been done on the use of CNCs in a range of wastewater treatment procedures, such as absorption, adsorption, membrane filtration, flocculation, disinfection, and catalytic degradation [21]. CNCs are produced through a series of chemical procedures such as pulping, bleaching, and acid hydrolysis [44–48]. Common procedures including pre-treatment with physical, chemical or enzymatic hydrolysis methods, followed by acid hydrolysis of amorphous region and extraction of nanocellulose under regulated conditions for temperature, duration, and the ratio of acid to cellulosic fiber [17, 49–51]. CNCs are usually extracted using the sulphuric acid (H_2SO_4) [52, 53], nitric acid (HNO_3) [54], hydrochloric acid (HCl), phosphoric acid (H_3PO_4) [55], hydrobromic acid (HBr) and phosphotungstic acid ($H_3O_{40}PW_{12}$). Concentrated mineral acids, such as H_2SO_4, are frequently employed for hydrolysis during isolation to eliminate the amorphous area comprising lignin and non-cellulosic components [49]. The hydronium ions (H_3O^+) formed during the acid treatment can cleave apart the 1,4-glycosidic linkages within a single cellulose chain,

weakening the strong hydrogen bonding network between the cellulose chains [49]. Acid molecules infiltrate into the fibers, followed by the cleavage of glycosidic bonds. In addition to disordered or amorphous regions of cellulose, domains characterized by high crystallinity have a longer resistance to hydrolysis, thus making them easier to separate from the acidic solution. As demonstrated in Fig. 1, crystalline cellulosic nanoparticles are released from nanocrystalline and amorphous regions of cellulose fibers [56].

Each acid treatment adds different functional groups to the surface of the CNCs, which affect colloidal stability of the CNCs. CNCs derived from HCl have lower colloidal stability than CNCs derived from H_2SO_4, which have negatively charged sulphate ester groups (OSO_3^-) on their surface and hence exhibit electrostatic repulsion [58]. H_2SO_4 undergoes esterification with hydroxyl groups on the CNC surface during hydrolysis [26]. This allows anionic sulphate ester groups to be randomly grafted onto the surface [59]. When negatively charged sulphate ester groups are present during the dispersion of nanocrystals in water, a negative electrostatic layer that covers the nanocrystals forms. The exceptional stability of H_2SO_4 hydrolyzed CNCs is due to electrostatic repulsion between individual nanoparticles [56]. It has been demonstrated that hydrolysis with H_2SO_4 is the most effective method for preparing CNCs. H_2SO_4 hydrolysis with an acid concentration of 64 to 65 wt%, a temperature of 40 to 45 °C, and a reaction duration of 40 to 60 min were the most commonly used conditions [60]. The crystallinity of a CNC extracted by H_2SO_4 was 95.2% [61] and the yield was 83.03% [52]. After acid hydrolysis, post alkaline treatment is a typical approach for recovering the effect of H_2SO_4 by neutralizing the acid with a strong basic such as sodium hydroxide (NaOH) [44]. CNC can be neutralized by NaOH to increase thermal stability by increasing the degradation and melting temperatures [44, 62].

Figure 2 depicts the rod-like structure of CNCs [63], which can be made of a variety of lignocellulosic materials,

Fig. 1 Cellulose reacts with strong acid to obtain a cellulose nanocrystal (CNCs) [57]
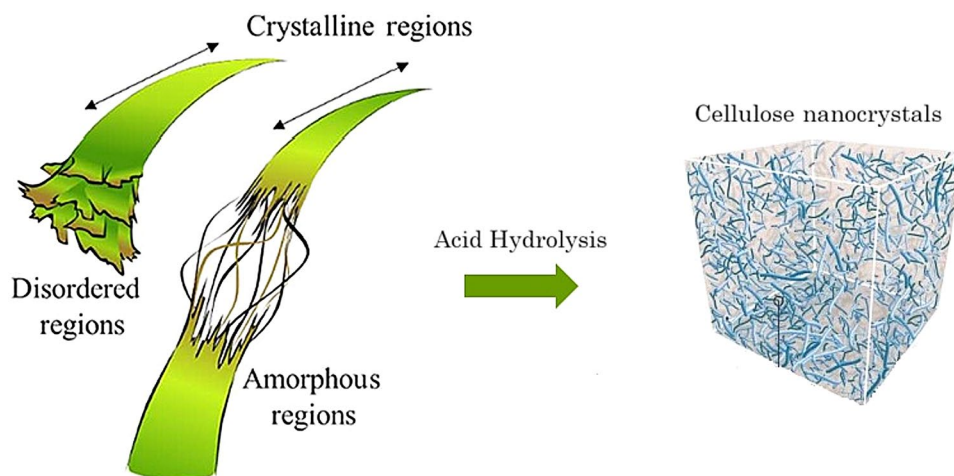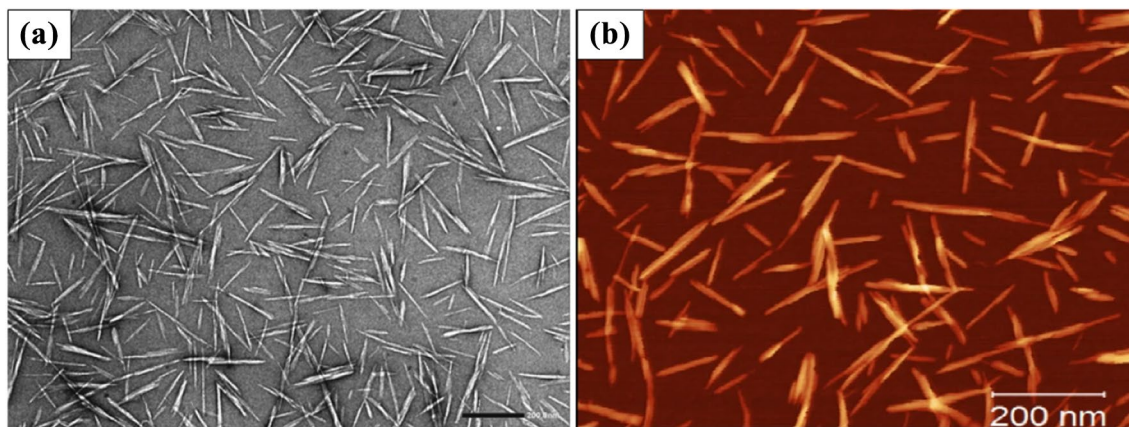
Fig. 2 Rod-like structure of cellulose nanocrystal (CNCs) using **a** Transmission electron microscopy (TEM) [71] and **b** Atomic force microscopes (AFM) [63]

including wood, cotton, ramie, wheat straw, and tunicate and has been used in many applications [35, 64–68]. CNCs produced by chemical treatments are extremely crystalline, with average lengths of less than 500 nm [49]. CNCs after sulphuric acid hydrolysis are crystalline rod or needle-shaped materials with lengths ranging from 100 to 200 nm and diameters ranging from 1 to 20 nm [69]. However, there is a major discrepancy in the size of the CNCs nanoparticle depending on the source of cellulose. For example, hardwood CNCs have lateral and length dimensions of 3 to 5 nm and 100 to 300 nm, respectively, whereas tunicate CNCs have 15 to 30 nm and 1000 to 1500 nm [35]. Additionally, utilizing ultrasound-assisted acid hydrolysis, cotton can be synthesized into rod-shaped CNCs with a crystallite size ranging from 10 to 50 nm diameter and 221 nm length, a crystallinity of 81.23%, and thermal properties that remain stable between 140 and 180 °C [70].

CNCs Remarkable Properties

Plant-based materials, including wood [72–74], sugarcane [75], and bamboo [76], have been the subject of research for water purification applications. Derived from renewable sources, CNCs contribute to sustainability by reducing reliance on non-renewable materials [77]. CNCs have attracted a lot of interest for application as a nano-adsorbent due to their unique properties [78, 79]. CNCs are particularly desirable due to their physical and chemical properties, including high mechanical strength, large specific surface area, rod-like morphology, liquid crystalline nature, biocompatibility, and hydrophilicity [80–82]. Furthermore, increased rheological characteristics, orientation and alignment, low coefficient of thermal expansion, chemical inertness, low density and dimensional stability, biodegradability, and renewability, are all appealing for wastewater treatment applications [20,

83, 84]. Their biodegradability and non-toxic nature ensure they pose no harm to the environment. CNCs' exceptionally large specific surface area, thanks to their tiny size and crystalline structure, makes them adept at adsorption a wide array of contaminants from wastewater, including heavy metals, dyes, and organic compounds, enhancing water quality [21]. They can be integrated into filtration membranes to improve particle removal efficiency and act as flocculants to facilitate the settling of impurities [85]. Some CNCs even possess antibacterial properties for water disinfection [86]. Their pH stability and customizability make CNCs versatile across various water treatment scenarios. Additionally, they can be cost-effective, reducing the need for additional treatments, and they contribute to lower sludge generation. Overall, CNCs are a promising and sustainable solution for addressing water quality and purification challenges [87].

Chemical Features

CNCs have several functional moieties, including aldehyde and hydroxyl groups, which allow for a wide range of changes to regulate their physical or chemical characteristics [88]. CNCs have both intermolecular and intramolecular hydrogen bonding due to the presence of hydroxyl groups. These hydroxyl groups on the surface give an accessible platform for chemical modification, which might be changing them to carboxylic acid, amine, aldehyde, or thiol groups [35]. These might then be utilized to make additional alterations, including grafting bigger macromolecules like polymers or proteins onto smaller molecules like biomarkers or metal nanoparticles. The hydroxyl groups can be chemically altered to increase the affinity of nanocellulose for anionic and non-ionic contaminants. The negatively charged of hydroxyl groups exhibit electrostatic attraction to cationic water contaminants including heavy metals and cationic

dyes [21]. Additionally, these hydroxyl groups provide purified CNCs with hydrophilic properties [89], which could increase their capacity to disperse in polymer matrices. Due to hydrogen bonding induced by the many hydroxyl groups on the CNCs' surface, they tend to clump together after drying and are challenging to dissolve due to surface functionalization of hydroxyl groups by radical grafting, esterification, etherification, oxidation, and silylation that would boost the nanocellulose's ability for adsorption [80]. Furthermore, the inclusion of aldehyde groups at the end of a CNCs allows for the selective alteration of reactive reducing ends in order to produce amphiphilic CNCs with unique properties [88]. Table 1 includes a list of examples showcasing the surface modification or functionalization of CNCs.

CNC-based adsorbents are less likely to become biofouling due to CNCs' exceptional water stability. Due to the high concentration of hydroxyl and carboxylate groups, materials utilized in cellulose-based wastewater treatment have negatively charged surfaces [21]. A stronger electrostatic

repulsive force is thus generated between the surface layer and the majority of model foulant. Due to their non-toxicity and biodegradability, CNCs are excellent adsorbents for wastewater treatment [103]. Additionally, the sulphate lipid group creates a negative electric layer on the surface of the CNCs, which is extremely dispersible in polar solvents like water. If the concentration is less than 2 wt%, CNCs have the ability to create stable, thixotropic distributed systems [104]. The CNCs particles form a three-dimensional network with a slightly crosslinked structure after solvent melting as a result of hydrogen bonding. After the external force is removed, the system's structure can be recovered [104].

The introduction of cellulose nanomaterials into membrane matrices can bring about significant alterations in membrane characteristics [105]. For instance, the incorporation of these highly biocompatible and eco-friendly nanocomposite materials can lead to enhancements in tensile strength, hydrophilicity, permeability, biofouling resistance, and selectivity. These improved attributes make such

Table 1 Surface modification or functionalization of cellulose nanocrystals (CNCs)

Surface modification	Properties	Functional group	Agent	References
Amination	Hydrophilic	Amino ($-NH_2$)	Ethylenediamine (EDA) Tris(2-aminoethyl)amine (TRIS) Poly(ethyleneimine) (PEI)	[22, 90]
Etherification	Hydrophobic	Ether ($-O-$); methyl, ethyl, or propyl groups	etherifying agents:- alkyl halides alkyl sulfonates	[91]
Esterification	Hydrophobic	Ester ($-COO-$); acetate or succinate groups	Esterifying agents:- Carboxylic acids Succinic anhydride Acid chlorides	[39, 92]
Silylation	Hydrophobic	organosilane ($-SiR_3$)	silylating agents: - N-(2-aminoethyl)-3aminopropylmethyldimethoxysilane (AEADMS) Trimethylchlorosilane (TMCS) Hexamethyldisilazane (HMDS)	[39, 93–95]
Sulfonation	Hydrophilic	Sulfonic acid ($-SO_3H$)	Sulfonating agents:- Sulphuric acid (H_2SO_4) Chlorosulfonic acid (SO_2ClOH)	[39, 51]
Oxidation	Hydrophilic	Aldehyde or carboxyl groups	Oxidizing agent:- Sodium periodate	[91, 96]
TEMPO oxidation	Hydrophilic	Aldehyde or carboxyl groups	Oxidizing agent:- Sodium hypochlorite	[97–99]
Carboxymethylation	Hydrophilic	Carboxyl groups ($-COOH$)	Carboxylation agents:- Monochloroacetic acid (MCA) Sodium chloroacetate (SCA)	[100–102]
Phosphorylation	Hydrophilic	Phosphate group ($-PO_3H_2$)	Phosphoric acid (H_3PO_4) Phosphorus oxychloride ($POCl_3$) Phosphorus pentoxide (P_2O_5) Phosphorus trichloride (PCl_3)	[39, 94]

membranes particularly well-suited for practical applications across such as pharmaceutical, biomedical, and environmental [106]. Moreover, surface modifications of cellulosic nanomaterials can be achieved by introducing both organic and inorganic groups. For example, the incorporation of titanium dioxide in the atomic layer of nanomaterials has been demonstrated, resulting in the creation of low-energy surfaces on fibers [107]. This modification imparts oleophilic and hydrophobic properties to nanocellulose-based materials, enabling them to absorb up to 80–90% vol/vol of oils and various organic solvents from water surfaces [58].

Physical Properties

Nano-adsorbent, CNCs have extremely small pores and a large specific surface area [108, 109]. Nearly minimal electrical conductivity exists in CNCs because of its large specific surface area, nanocellulose's ability for adsorption may be boosted by going from micro to nanoscale [110]. CNCs showed a high aspect ratio, reasonably high crystallinity, and hydrophilic surface characteristics. According to sources of nanocellulose and the method of treatment, CNCs have a high aspect ratio of 10 to 80. High aspect ratio properties encourage the formation of percolated CNCs networks bonded together by strong hydrogen bonds, increasing the mechanical strength of the adsorbent [108]. Furthermore, the high crystallinity of CNCs increases the adsorbent's

chemical resistance and decreases cellulose solubility even in highly polar solutions. This anticipated that CNCs' inherent hydrophilicity may lessen organic and biofouling. With a water surface tension of about 60 mJ/m^2, nanocellulose-based adsorbents can aid to enhance wetting properties and lessen biofouling during the wastewater treatment process [21].

CNCs have lower thermal stability than natural cellulose because of the presence of the sulphate group. However, it can be improved by converting the acid proton on the sulphate group to a cation [35]. In light of this, H_2SO_4 will react with the hydroxyl groups on the surface of cellulose to create sulphate half esters, which result in CNCs nanoparticles that are negatively charged and electrostatically stabilized [111]. Figure 3 illustrates the synthesis of sulphated CNCs via acid hydrolysis of cellulose.

In addition, when the concentration of nanocrystalline cellulose reaches a critical level, the suspension forms an ordered liquid crystal state [78]. It has been demonstrated that altering the surface charge, such as the amount of replacement of sulphate groups on their surfaces, may change how stable cellulose nanocrystal suspensions in water [78]. According to the study's findings, the surface charge had an impact on how viscous nanocellulose suspensions were, with CNCs with lower surface charges producing more viscous suspensions that went on to gel at lower concentrations [78]. It was found that after the
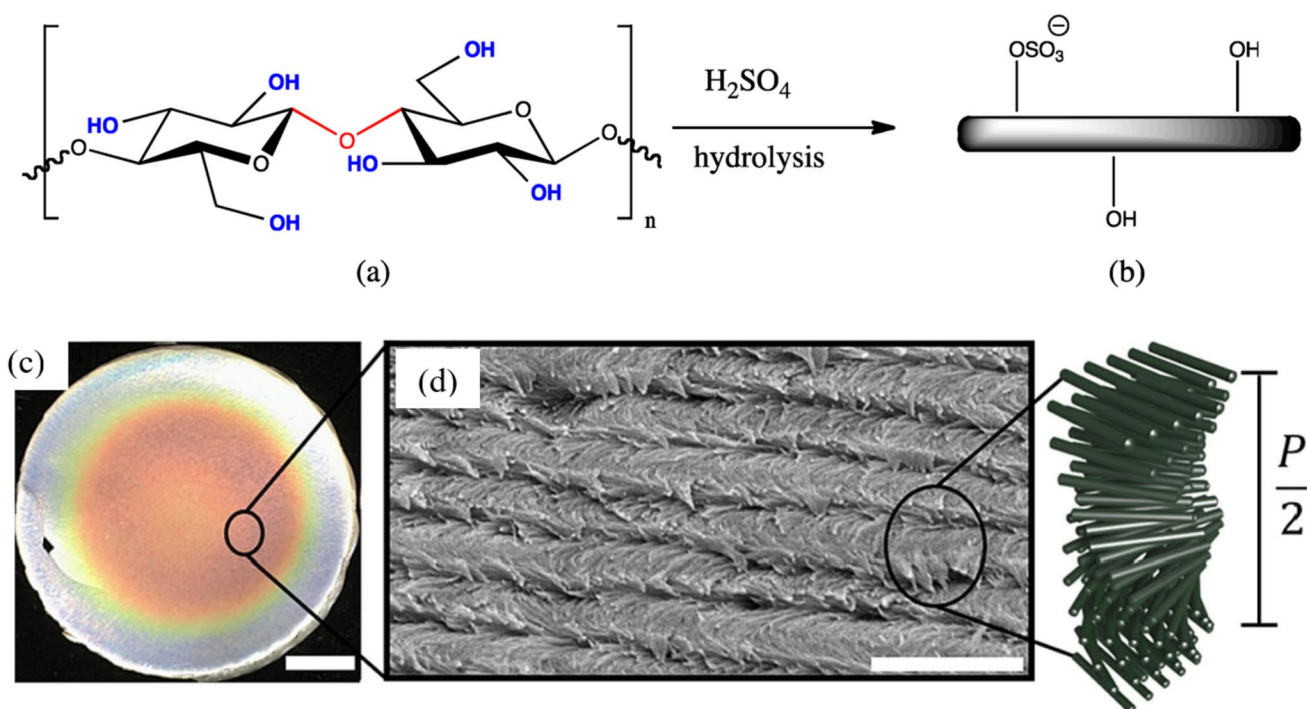
Fig. 3 Synthesis of sulphated cellulose nanocrystals (CNCs) from acid hydrolysis of cellulose (**a** structure of cellulose; **b** diagrammatic representation of rod-like sulphated CNCs) [112]; **c** Photograph and **d** scanning electron microscopy (SEM) image of CNCs film [113]

surface charge density of CNCs reaches a certain level, the effective volume of suspension significantly affected the spectrum of liquid crystalline phase growth.

CNCs are in the shape of rod-like self-align in water to form chiral nematic phases exhibiting liquid crystalline properties. Under certain conditions, their stiffness and dimension ratio make them ideal for showing liquid crystalline behavior. It is known that cellulose crystals have a spiral twist down their long axis that is responsible for creating a chiral nematic structure or a structure that can be differed by concentration with its structure stacked along the planes and aligned along a perpendicular axis [114]. Combined with the liquid crystallinity of nanocrystals, these crystals exhibited interesting optical properties. The type of acid used for hydrolysis can also affect the liquid crystalline characteristics. As a result of H_2SO_4 hydrolysis, negatively charged surface CNCs is more likely to disperse uniformly in water due to electrostatic repulsion [115]. Despite the strong interactions between nanocrystals, CNCs after sulfuric acid hydrolysis exhibits lyotropic behavior as a result of its easy dispersibility [116]. H_2SO_4 and H_3PO_4 derived CNCs usually have chiral nematic structures, while CNCs derived from HCl usually have birefringent glassy phases.

During the hydrolysis process, reaction time and temperature have a significant impact on CNCs yield and quality. Insufficient hydrolysis time may result in amorphous fractions remaining, resulting in a reduction in crystallinity and morphological changes in the particles. A longer duration of acid hydrolysis reduces the thermal stability and, consequently, the degree of crystallinity of nanocellulose [78]. In addition, the temperature of the reaction is the crucial part, as higher temperatures result in shorter CNCs [117]. Increased temperature and reaction time during hydrolysis eliminated amorphous components and even parts of the crystalline component, reducing CNCs crystallite sizes [118]. Moreover, any suspended particle, macromolecule, or material surface exhibits zeta potential, a physical property exhibited by all solid-liquid and liquid-liquid colloidal systems [119]. The formulation of protein solutions, suspensions, and emulsions may be improved as well as the ability to predict interactions with surfaces and produce films and coatings. Zeta potential measurements examine the strength of electrostatic attraction between adjacent, similarly charged particles in dispersion and give detailed information about how nanoparticles like CNCs disperse, aggregate, or flocculate in colloidal systems [50]. For pure CNCs, the zeta potential values are typically in the range of -20 to -50 mV, indicating that the particles are electrically stable, have a high degree of dispersion, and form aggregates [50].

Mechanical Behaviour

The range of Young's modulus for CNCs is from 110 to 220 GPa, and their tensile strength is 7.5 to 7.7 GPa [104]. The stiffness and cohesiveness of the adsorbent material were increased by the high mechanical rigidity of CNCs. Due to the high crystalline forms of CNCs, it arises in transparent and gas-impermeable forms with extremely high tensile strengths that are up to eight times that of steel [21]. Apart from that, it was found that CNCs derived from bacteria, tunicates, or Valonia are highly polydisperse in their molecular weights without any indication of a level-off degree of polymerization (LODP) [110, 120, 121]. The absence of a regular distribution of amorphous domains is likely to be the cause of this phenomenon. In addition, cellulase enzymes and mechanical shearing were used to isolate bacterial CNCs [122]. The nanocrystals produced using this approach have superior mechanical and thermal qualities than those produced by sulfuric acid hydrolysis. Highly crystalline domains of cellulose are more resistant to hydrolysis for a longer time than disordered or amorphous areas, making them simpler to separate from the acid media.

CNCs are a material with a lot of potential for high-performance membranes and filters that selectively remove contaminants from drinking and industrial waters. This is due to the combination of high strength, stiffness, and mechanical properties. CNCs with outstanding mechanical rigidity and strength are essential in high-pressure wastewater treatment applications. Table 2 provides a comprehensive inventory of the properties and distinguishing features of cellulose nanocrystals (CNCs) utilized in the capacity of adsorbents. Directing our focus towards Table 3, a comprehensive compilation of the distinctive attributes and adsorption capacity of adsorbents utilizing cellulose nanocrystals (CNCs) is meticulously presented, providing valuable insights into their functional capacities. Furthermore, Table 4 extensively elucidates the mechanical features of these CNCs-based adsorbents, intricately linked with their outstanding adsorption ability, providing an in-depth understanding of their multidimensional potential in adsorption applications.

CNCs as Adsorbents and Their Mechanisms

The most popular method for treating water with nanocellulose-based products is the adsorption procedure. Adsorption was thought to be a viable and inexpensive option for cleaning up polluted environments [132–134]. Furthermore, its universal nature allows for the effective removal of both soluble and insoluble pollutants, along with biological contaminants, with a high removal efficiency ranging from 90 to 99% [135]. This is because it can be deployed which prevents the production of several hazardous intermediates

Table 2 The properties and characteristics of CNCs as adsorbent

Properties	Performance	References
Structure	Rod-like particles	[49]
Length	100–500 nm	[49]
Diameter	2–20 nm	[123]
Aspect ratio	10–80	[124]
Density	Low	[35]
Thermal expansion	Low	[125]
Mechanical strength	Young's modulus less than 140 GPa	[104]
Tensile strength	High (7500 MPa)	[35]
Electrical conductivity	None	[106]
Optical properties	Left-handed cholesteric liquid crystal spontaneously assembled	[126]
Zeta potential values	-20 to -50 mV	[50]
Biological toxicity	Low toxicity	[103]
Water permeability	82.6%	[104]
Antifouling ability	77%	[104]
Crystallinity index	60–80%	[127]
Magnetic response	High	[49]
Specific surface area	Large (~ 250 m^2/g)	[35]
Pore size	10–15 nm	[128]
Surface chemistry	Hydrophilic	[89]
Reactivity	Chemically inert	[21]
Surface tension	60 mJ/m^2	[21]

that are produced while aqueous solution treatment of new organic pollutants is conducted. An adsorbent, a solution, and an adsorbate are all components of the adsorption system. An adsorbate is a substance (pollutant) that attaches to or adheres to a solid surface, whereas an adsorbent refers to the solid surface itself [135]. A solid material known as an adsorbent is used to draw impurities out of liquid or gas that might be harmful to the environment. Large surface area, readily accessible polar sites, and consistent activation capabilities are the qualities of a good adsorbent that are most crucial [136]. The most challenging part in regulating and replicating is the repeatability in the degree of activation, which is a measure of the adsorbing power and frequently relates to the level of removal of surface water [137].

The research community has given much attention to the application of nanotechnology in the purification of water. Materials having a structural unit size of less than 100 nm are referred to as nanomaterials or nanoparticles. These substances represent fundamental shifts and crossings between the characteristics of atoms, molecules, mass, and typical macroscopic materials [110, 138]. Matter particles will exhibit powerful small-size, quantum, and enormous surface effects as they reach the nanoscale scale [110]. Nanomaterials have an increased number of unsaturated bonds and a larger specific surface area because there are more surface atoms and a larger surface area available. Consequently, these surface atoms have tremendous adsorption capability and are extremely active, very unstable, and quick to interact

Table 3 The characteristics and adsorption efficiency of CNCs-based adsorbents

| CNC as adsorbents	Structure	Diameter (nm)	Length (nm)	Specific surface area (m²/g)	Crystallinity index (%)	Pollutants	Adsorption efficiency	References
CNCs	Rod-like shapes	6–10	200	138–226	72.3	Silver (Ag$^+$)	34.4 mg/g	[129]
CNCs	–	6–7	130	426	–	Methylene blue (MB)	101 mg/g	[89]
CNC$_{SL}$	–	5–10	–	131	–	Ag$^+$	56 mg/g	[28]
						Cu^{2+}	20 mg/g	
						Fe^{3+}	6.3 mg/g	
Phosphorylated nanocellulose (Phos-CNC$_{SL}$)	–	20	–	66	–	Ag$^+$	136 mg/g	
						Cu^{2+}	117 mg/g	
						Fe^{3+}	115 mg/g	
Amino-functionalized nanocrystalline cellulose (ANCC)	Whisker shapes	3.26	–	12.5	59.8	Acid red (GR)	555.6 mg/g	[22]
Carboxylated CNCs	Rod-like	15.9 ± 3.0	215.8 ± 23.2	165.6 ± 26.3	91.4	Dye	92.3%	[24]
Fe-Cu alloy coated CNCs (Fe-Cu@CNC)	Rod-like shapes	20	200–300	–	–	Lead (Pb^{2+})	85.8 mg/g	[130]

Table 4 The mechanical properties and adsorption capacity of CNCs-based adsorbents [131]

Cellulose nanocrystals-based adsorbents	Structure	Diameter (nm)	Specific surface area (m²/g)	Stress at break (MPa)	Modulus of elasticity (MPa)	Pollutants	Adsorption capacity (mg/g)
CNC_{SL} membrane	Rod-like shapes	5–10	26.3	13 ± 0.3	362 ± 0.3	Ag^+	0.82
						Cu^{2+}	28
						Fe^{3+}/Fe^{2+}	48
CNC_{BE} membrane			32.6	19 ± 0.8	647 ± 0.4	Ag^+	0.87
						Cu^{2+}	67
						Fe^{3+}/Fe^{2+}	102
Phosphorylated nanocellulose ($PCNC_{SL}$) membrane	Whisker shapes	20	18.8	16 ± 0.5	402 ± 0.9	Ag^+	0.81
						Cu^{2+}	358
						Fe^{3+}/Fe^{2+}	512

with other atoms. Additionally, nanoparticles feature active groups, such as hydroxyl groups, on their surfaces that have the ability to bind with heavy metals and organic molecules present in wastewater [35]. For instance, Mohamed et al. [102] discovered that CNCs derived from waste cotton cloths (WCCs) via sulphuric acid hydrolysis are excellent Cr(IV) adsorbents (Fig. 4). The CNCs derived from the WCCs had a rod-like structure with a porous surface, showing crystalline characteristics. These CNCs had an average length of 100.03 ± 1.15 nm and a width of 7.92 ± 0.53 nm. Furthermore, the CNCs obtained from WCCs had a pore width of 1.34 nm, an average pore volume of 0.005 cm³/g, and a significant specific surface area of 26.12 m²/g. The surface of the CNCs had uniform nano-size particles and carried a negative charge. In terms of their effectiveness, the highest

removal efficiency for Cr(VI) was 96.97% under specific conditions: adsorbent dosage of 1.5 g/L, temperature of 60 °C, and treatment time of 30 min with pH 2.

Conventional adsorbents such as activated carbons are costly, energy-intensive, and contribute to greenhouse gas emissions during their production. Making alternative, affordable adsorbents from agricultural and industrial waste, therefore, offers up a wide range of new opportunities. Utilizing sustainable nanomaterials, such as CNCs, with their effective adsorption properties, can reduce the reliance on activated carbons and minimize the carbon footprint [139]. Moreover, the functional surface of CNCs allows for the attachment of chemical moieties, enhancing the effectiveness of pollutant binding. The approach for improving the adsorptive capacity of CNCs that has received the most research is
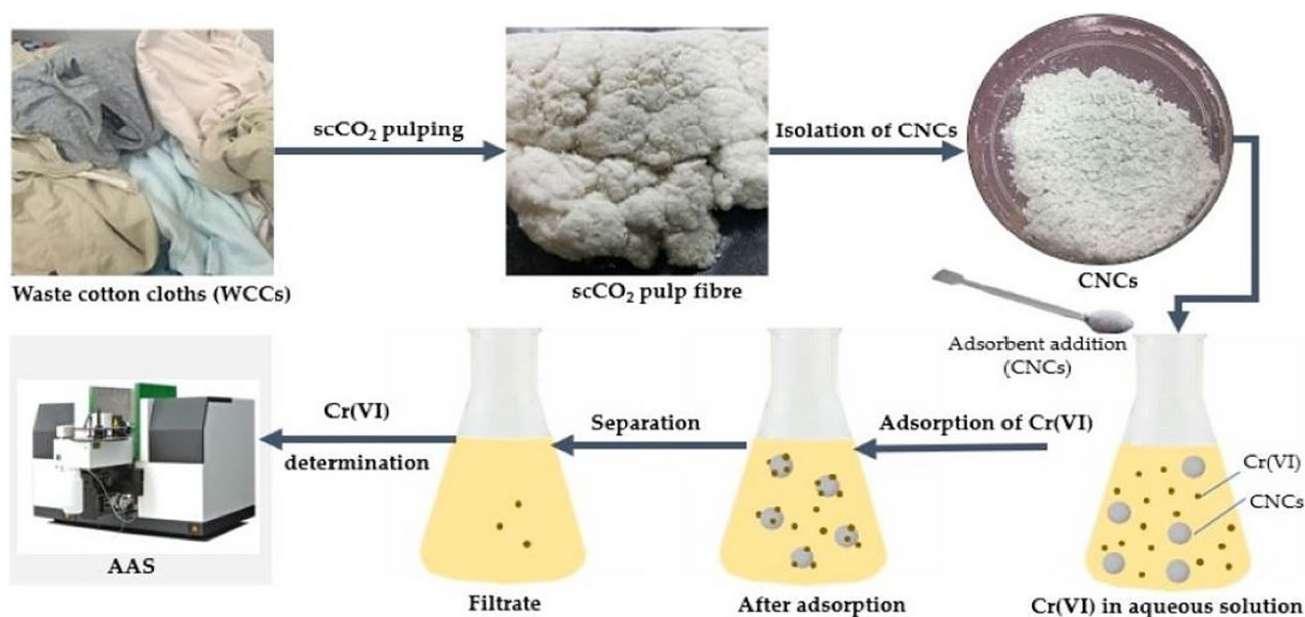
Fig. 4 CNCs have demonstrated remarkable effectiveness as adsorbents in the process of wastewater treatment [102]

carboxylation [106]. Due to several advantageous properties like a high surface area to volume ratio and porosity, abundant hydroxyl groups, biocompatibility, biodegradable, low cost, widespread availability, inherent environmental inertness, excellent chemical resistance, and favorable mechanical qualities, CNCs have garnered significant attention as a promising alternative for effective adsorbents in wastewater treatment [39]. These features contribute to CNCs' ability to achieve a high level of adsorption, making them highly suitable for this application.

The adsorption mechanism of CNCs involves the interaction between the CNCs surface and the adsorbate, which is the pollutant present in wastewater. The hydroxyl groups on the CNCs surface can form hydrogen bonds or engage in Van der Waals interactions with the pollutants, leading to their adsorption onto the CNCs [20, 140]. The adsorption mechanism can be described as a four-stage process. Initially, when a solution containing the contaminant encounters the CNCs adsorbent, the solute is transported to the adsorbent's boundary layer. The solute molecules are attracted to the surface of the adsorbent. In the second stage, diffusion and transfer processes occur. Concentration gradients force solute molecules from the adsorbent's boundary layer to its outer surface, allowing them to come into closer contact with the active sites on the outer surface. In the third stage, transfer takes place from the outer surface of the adsorbent to the active sites within the pores. Solute molecules move through the pore structure, searching for and binding to the active sites. Various interactions, such as Van der Waals forces, electrostatic interactions, and hydrogen bonding, facilitate this transfer process. Finally, in the fourth stage, the adsorbate is adsorbed by the solid phase. Adsorbate molecules establish chemical or physical connections with the CNCs adsorbent after firmly attaching to the active sites within the pores, completing the process of extracting the solute from the solution and immobilizing it on the adsorbent surface [141].

The adsorption mechanism for various pollutants were illustrated in Figs. 5, 6, 7 and 8. Adsorption of pharmaceutical pollutants, as shown in Fig. 5, involves a variety of mechanisms, including hydrogen bonding, π–π stacking interaction, electrostatic interaction, and hydrophobic effect [142, 143]. An amphiphilic cellulose aerogel (HCNC-TPB/TMC) was fabricated by grafting 1,3,5-Tris (4-aminophenyl) benzene (TPB) and trimesoyl chloride (TMC) onto aldehyde CNC through Schiff alkali and substitution reactions. The resulting HCNC-TPB/TMC possessed favorable morphology and comprised both hydrophilic amino and carboxyl groups and hydrophobic aromatic groups. The presence of carboxyl aromatic groups on TMC strengthened the hydrogen bonding and π–π stacking between HCNC-TPB/TMC and sodium diclofenac (DCF) [142]. The presence of polar molecules in the solvent often reduces the hydrogen bond between the adsorbent and the adsorbate in polar solvent systems such
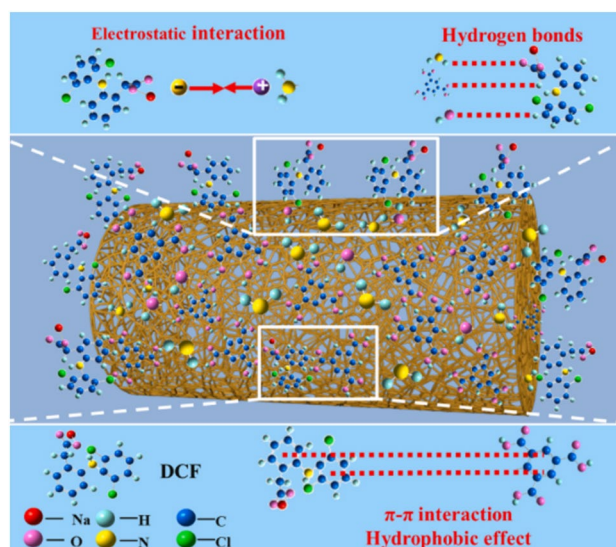

Fig. 5 Proposed synergetic adsorption mechanisms of amphiphilic cellulose aerogel (HCNC-TPB/TMC) for sodium diclofenac (DCF) [142]
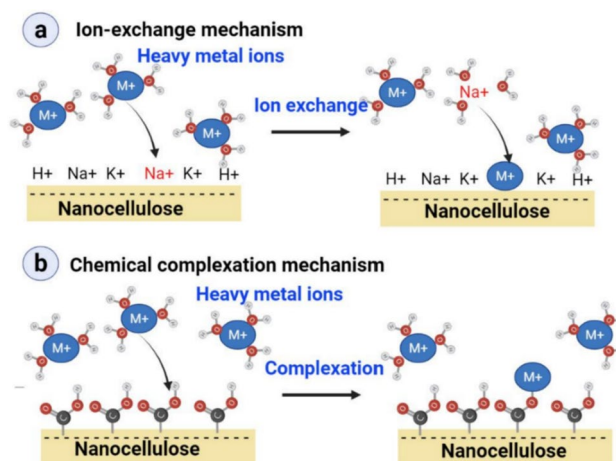

Fig. 6 Heavy metal removal mechanism from water system using nanocelluloses: **a** Ion exchange mechanism which involves the adsorption of hazardous metal ions (M^{n+}) takes the place of other ions (K^+, Na^+, H^+) already associated with the nanocellulose surface; **b** chemical complexation mechanism in which the carboxyl (–COO−) and hydroxyl (–OH) groups of the nanocelluloses have specific site interactions with particular hazardous metal ions [21]

as water. The π–π stacking interaction, on the other hand, occurs mostly between electron-rich and electron-poor molecules and is generally unaffected by polar molecules in the solvent [144]. Thus, the hydrophobic hexatomic benzene rings in the adsorbent can generate significant π–π stacking interaction with the benzene ring of DCF, thereby reducing steric hindrance and facilitating adsorption. Furthermore, the adsorbent comprises –COOH functional groups, whereas

--- hydrogen bonds --- π–π/p-π interactions --- ion exchange ⊕⊖ electrostatic interactions
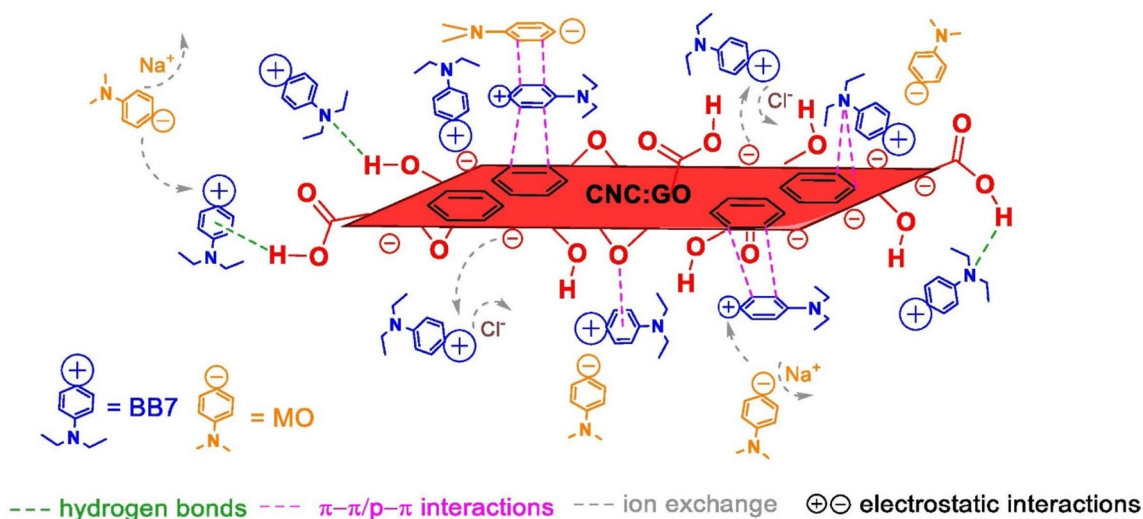
Fig. 7 Basic blue 7 (BB7) elimination adsorption method employing CNC:GO −70:30 nanocomposite via ion exchange (in grey), hydrogen bonds (in green), π-π/p-π (in purple), and electrostatic interactions (in black)

Fig. 8 Scheme to describe the MB adsorption behavior of HPAM/CNC nanocomposite hydrogels
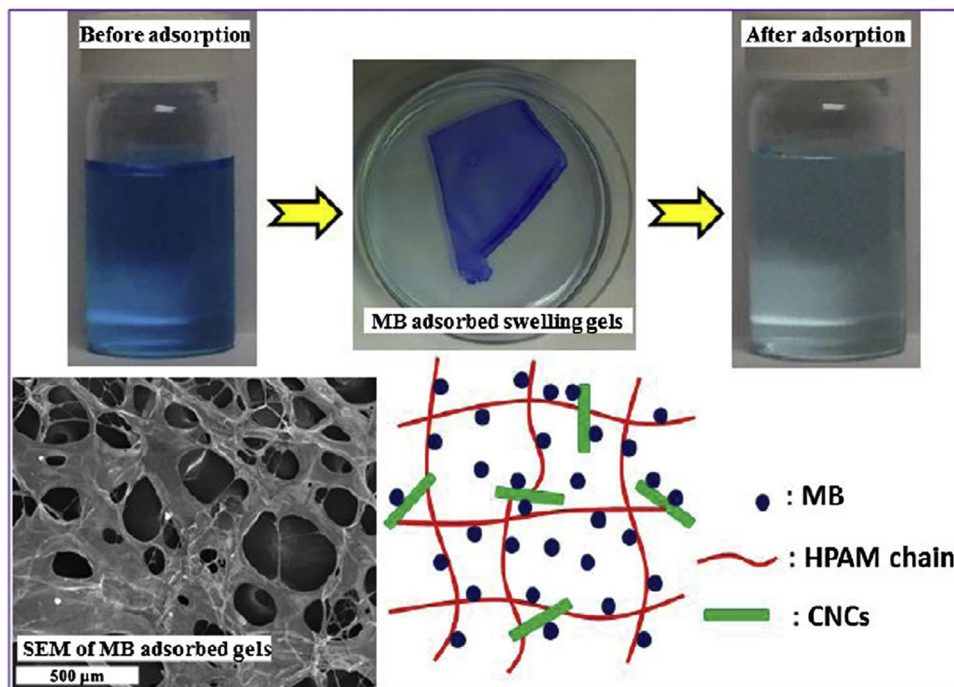
DCF has many hydrogen donors and receptors. Therefore, when steric hindrance is reduced, multiple hydrogen bonds can be formed to enhance the adsorption between DCF and the adsorbent [142]. The synergetic adsorption mechanisms of HCNC-TPB/TMC for DCF are depicted in Fig. 5.

In another study, researchers fabricated graphene-nano-crystalline cellulose (G-CNC) as an adsorbent for pharmaceuticals like aspirin (Asp) and acetaminophen (Acet) [143]. At lower pH levels, electrostatic ion interaction plays a role in the adsorption mechanism. Electrostatic interaction

refers to the attraction or repulsion between molecules with opposite charges [145]. In order to improve pharmaceuticals uptake, the interaction between the adsorbate and the adsorbent must be attractive. In this study, the adsorbent surface is mainly positively charged, while Asp is negatively charged, leading to increased electrostatic attraction and greater adsorption efficiency. The adsorption capacity of G-CNC is also attributed to hydrophobic interaction and π–π conjugation between the adsorbent and the adsorbate. This is due to the presence of aromatic rings on Acet and

the hydrophobic nature of G-CNC. For hydrophobic interaction, pharmaceuticals with low solubility tend to be adsorbed [146]. In the case of ciprofloxacin (CIP) uptake, the presence of a benzene ring in the CIP structure allows for π–π interactions with adsorbents. The electron-rich nature of the benzene ring leads to a stacking effect. CIP typically serves as the donor and the adsorbate as the acceptor in the acceptor-donor relationship of π–π interactions. These interactions are more prominent when the solution pH is close to neutral, where the adsorbate exists as a zwitterion [147].

Ion exchange and chemical-complexation are the major two mechanisms involved in heavy metal uptake when using nanocellulose-based adsorbents. Figure 6 illustrates the interaction between negatively-charged CNCs with carboxylate, amine, and sulphate groups and positively charged ions, polyelectrolytes, and nanoparticles in treated water, leading to the adsorption and removal of heavy metal ions [21]. In ion exchange mechanism, hazardous metal ions (Mn^+) displace other ions (K^+, Na^+, H^+) already present on the nanocellulose surface (Fig. 6a). On the other hand, chemical complexation mechanism involves specific interactions between the carboxyl (–COO−) and hydroxyl (-OH) groups of nanocelluloses and the targeted metal ions ($Mn+$) (Fig. 6b). The adsorption capacity of nanocelluloses is determined by their functionality, surface area, and stoichiometry rules. Consequently, enhancing surface area and functionalization is crucial to introduce more sites for complexing hazardous metal ions.

The adsorption mechanisms of CNC and graphene oxide (GO) nanocomposite for the removal of complex dyes basic blue 7 (BB7), reactive orange 122 (RO), and rhodamine B (RhB) in binary systems with non-complex dyes methyl orange (MO) and basic brown 4 (BB4) involve electrostatic interactions and ion exchange [148]. Figure 7 illustrates the potential adsorption mechanism of BB7 removal using the CNC:GO nanocomposite, which includes ion exchange, hydrogen bonds, π–π/p–π interactions, and electrostatic interactions.

CNC can be combined with zinc oxide (ZnO) nanoparticles to produce a nanocomposite for the removal of methylene blue (MB) dye [149]. The adsorption kinetics of MB onto the CNC/ZnO nanocomposite primarily involve diffusion-based mechanisms. This means that different adsorption sites on a homogeneous solid substrate collide randomly and diffuse through the pore size of the adsorbent during a rate-limiting step [150]. In another study, a hydrolyzed polyacrylamide/CNC (HPAM/CNC) nanocomposite hydrogel was developed for MB removal. The active sites of HPAM/CNC, including –CONH₂ and –COOH groups in HPAM chains, as well as –OH and sulphate groups on the surface of CNCs, played a crucial role in determining the adsorption mechanism of the dye. According to the intraparticle diffusion model, surface effects may be combined with chemical effects during the initial adsorption stage of HPAM/CNC nanocomposite hydrogels at low dye concentrations. However, during the eventual or equilibrium adsorption stage of the nanocomposite gels, the sorption sites (amount and chemical interaction with the dye) are primarily responsible for the adsorption behavior. The incorporation of CNCs into HPAM hydrogels (as shown in Fig. 8) not only facilitates the formation of a crosslinking network but also enhances the dye adsorption capacity, particularly for HPAM/CNC nanocomposite hydrogels with low swelling rates [151].

It is important to consider that the efficiency and effectiveness of the adsorption mechanism can be influenced by various factors. These factors include the surface area, functionality and pore size of the adsorbent, the solute concentration in the solution, the characteristics of both the solute and adsorbent, as well as the temperature and pH conditions. By understanding and optimizing these factors, it becomes possible to enhance the adsorption capacity and selectivity of the adsorbent material for specific applications. According to Samer [132], the equilibrium adsorption capacity of CNCs is affected by factors such as pollutant concentration, adsorbent dosage, pH, temperature, contact time, and particle size [141, 152–154]. Specifically, adsorption is inversely proportional to adsorbent particle size and pH, and directly correlated to adsorbate concentration, surface area, and temperature, depending on the composition and pore structure [132]. The removal capacity of pollutants increases with a higher dosage of adsorbent due to the availability of a larger surface area and more active adsorption sites [155]. For instance, the percentage of Cr(VI) removal showed an increase as the dosage of CNCs was increased from 0.5 g/L to 1.5 g/L. This increase in Cr(VI) removal with higher CNCs dosage can be attributed to the increased negative surface charge, which facilitates the adsorption of Cr(VI). The highest percentage of Cr(VI) removal achieved was 88.59% at a dosage of 1.5 g/L. Beyond this dosage, the percentage of Cr(VI) removal remained constant due to the saturation of the CNCs' surface with adsorbed Cr(VI) [156]. Additionally, the aggregation of particles caused by a higher amount of CNCs resulted in a decreased affinity for adsorbing Cr(VI) on the surface of CNCs [102].

The pH of the solution plays a crucial role in the adsorption process, particularly in the effective removal of pollutants such as metal ions. The pH of the solution impacts the interaction between hydrogen ions and functional groups such as hydroxyl (OH), carboxyl (COOH), amine (NH_2), and metal ions on the surface of the adsorbent [157, 158]. In the case of Cr(VI) metal ions, they exist in aqueous solution as chromate ($CrO4^{2-}$) and dichromate ($Cr_2O_7^{2-}$) [156, 158]. At low pH levels (pH 1 to pH 2), there is a high percentage of Cr(VI) removal because of the abundance of proton H^+. As a result, CrO_4^{2-} and $Cr_2O_7^{2-}$ become protonated and adsorbed onto the CNCs [156, 159]. However, as the pH increases

beyond 2, the percentage of Cr(VI) removal decreases due to a decrease in the concentration of proton H$^+$ in the aqueous solution, which is necessary for protonating Cr(VI) metal ions. Moreover, at higher pH levels, the percentage of Cr(VI) removal is low due to the abundance of OH$^-$. Consequently, electrostatic repulsion occurs during adsorption, leading to a decreased percentage of Cr(VI) removal [102]. A similar study conducted by Billah et al. [160] reported an increase in Cr(VI) adsorption between pH 1 and 3, with maximum adsorption occurring at pH 3, attributed to the electrostatic interactions between the adsorbent and the adsorbate. However, further increase in the solution pH from 4 to 7 resulted in decreased Cr(VI) adsorption [160].

The pH of the solution plays a crucial role in the removal of dyes, as it affects the electrostatic or molecular interaction between the adsorbent and the dye based on the charge distribution on the material [161]. In the study conducted by Jin et al. [22], the impact of pH on dye removal percentage was investigated within a pH range of 4.0 to 9.0. The results showed that at an acidic pH of 4.7, the dye removal percentage was 67.3% (qt = 134.7 mg/g), which was higher than the 52.2% (qt = 104.5 mg/g) observed at a neutral pH of 6.7. This suggests that under acidic conditions, the interaction between the protonated amine and the anionic site of the dye enhanced the adsorption onto the amino-functionalized nanocrystalline cellulose (ANCC). However, at a pH of 9.0, the dye removal percentage significantly dropped to only 31.3% (qt = 62.6 mg/g). In the alkaline region, the surface charge of ANCC became negative, resulting in limited chemical interaction with the anionic site of the dye due to electrostatic repulsion. It was also noted that anionic dye adsorption was favored at pH values below the isoelectric point of the adsorbent, where the surface became positively charged, while cationic dye adsorption was favored at pH values above the isoelectric point of the adsorbent.

The adsorption process requires a specific amount of time to reach equilibrium, which signifies the completion of adsorption [162]. The time required to achieve equilibrium varies depending on the adsorbent material and adsorbate [141]. In the case of Cr(VI) removal, the percentage of removal increased as the treatment time increased from 5 to 30 min. This can be attributed to the attainment of the necessary contact time between the surface of CNCs and Cr(VI) for adsorption to occur [102]. Initially, the adsorption process exhibited rapid uptake of Cr(VI). This initial rapid uptake can be attributed to external surface adsorption, as there were numerous unsaturated adsorption sites available. As the process progressed, a slower and more stable uptake of Cr(VI) was observed, indicating that adsorption was primarily governed by the transportation of Cr(VI) ions into the internal surface of the adsorbent (internal surface adsorption). The disparity in equilibrium time observed among different adsorbents

can be attributed to surface modifications, which enhance their ability to rapidly remove Cr(VI) ions [160]. However, after 30 min of treatment time, the percentage of Cr(VI) removal became insignificant due to the saturation of the CNCs' surface with adsorbed Cr(VI) [96].

The temperature of the contact also influences the adsorption process by affecting physicochemical reactions [163]. In a study conducted by Mohamed et al. [102], it was observed that the percentage of Cr(VI) removal increased as the temperature rose from 28 ± 1 to 60 °C. This can be attributed to the increase in kinetic energy, which facilitated the binding of Cr(VI) on the surface of the CNCs and consequently enhanced Cr(VI) adsorption. The highest percentage of Cr(VI) removal achieved was 96% at 60 °C. Additionally, an increase in temperature resulted in a decrease in the solution's viscosity, leading to a significant increase in the interaction between CNCs particles and Cr(VI), thereby enhancing Cr(VI) adsorption [160, 164]. However, beyond 60 °C, there was a decrease in Cr(VI) removal with increasing temperature. This was due to the degradation of the CNCs particles, which weakened the intermolecular forces between them and subsequently reduced the binding of Cr(VI) on the surface of the CNCs particles [96, 165]. According to the findings of Xu et al. [163], in endothermic reactions, raising the temperature would cause an increase in the reaction rate. On the other hand, in exothermic reactions, an increase in temperature would lead to a decrease in the reaction rate. Experiments conducted by Moradeeya et al. [166], Batmaz et al. [167], Qiao et al. [168], Pinto et al. [169], Anirudhan and Shainy [170], and others have reported various examples of exothermic reactions.

Indeed, the adsorption mechanisms of heavy metal ions by CNCs differ significantly from those of organic pollutants like organic dyes and oils due to the distinct chemical properties and interactions involved. Heavy metal ions are inorganic species with charged ions (cations) that can form electrostatic interactions with the negatively charged surface groups of CNCs, primarily hydroxyl (-OH) groups [171]. These interactions involve ion exchange and coordination, where heavy metal ions are attracted to and bond with the hydroxyl groups on the CNCs surface. In the case of heavy metal ions, surface complexation reactions play a significant role [21]. CNCs' surfaces provide numerous active sites for the complexation of heavy metal ions [172]. The interaction involves the formation of surface complexes, where heavy metal ions bond to multiple hydroxyl groups on the CNCs surface, effectively immobilizing them. The adsorption of heavy metal ions onto CNCs is often sensitive to the ionic strength and pH of the solution [173]. Changes in pH can influence the surface charge of both CNCs and heavy metal ions, affecting the electrostatic interactions. Additionally, the presence of competing ions in solution can impact the adsorption efficiency.

CNCs can exhibit selectivity in adsorbing heavy metal ions based on their charge and size [101]. For example, certain heavy metal ions may have a higher affinity for CNCs due to stronger coordination bonds. Unlike organic pollutants, heavy metal ions adsorbed onto CNCs may be more challenging to desorb, making the process of heavy metal removal potentially more irreversible. This property can be advantageous in applications where the goal is permanent removal and immobilization of heavy metals. In contrast, the adsorption of organic pollutants like organic dyes and oils onto CNCs typically involves physical interactions, such as van der Waals forces, hydrophobic interactions, and hydrogen bonding [174]. These pollutants do not typically form surface complexes or coordinate with CNCs in the same way as heavy metal ions. Consequently, the mechanisms and conditions for adsorbing heavy metal ions by CNCs indeed warrant a thorough and distinct discussion from those of organic pollutants.

CNCs Based Materials for Wastewater Treatment Applications

In comparison to commercial ion exchange sorbents, CNCs are inexpensive and abundant, making them an excellent adsorbent. Figure 9 presents cellulose nanomaterials adsorbent applications. In this section, the most possible applications of CNCs as an adsorbent in wastewater treatment will be discussed, including the removal of oil and organic solvents, pesticides, heavy metals, dyes, pharmaceuticals, organic micropollutants and other pollutants.

Oil and Organic Solvents Separation

Oil pollution is becoming a critical issue as industrial development accelerates. Industrial oil emissions continue to have a detrimental effect on the aquatic ecosystem and ecology, such as crude oil leaks, industry oil discharges, or residential cooking oil discharges. Pollution from oil spills in wastewater can persist for many years. Most of the oil pollution is caused by tanker oil spills, but there are also other additional sources that cumulatively contribute to oil
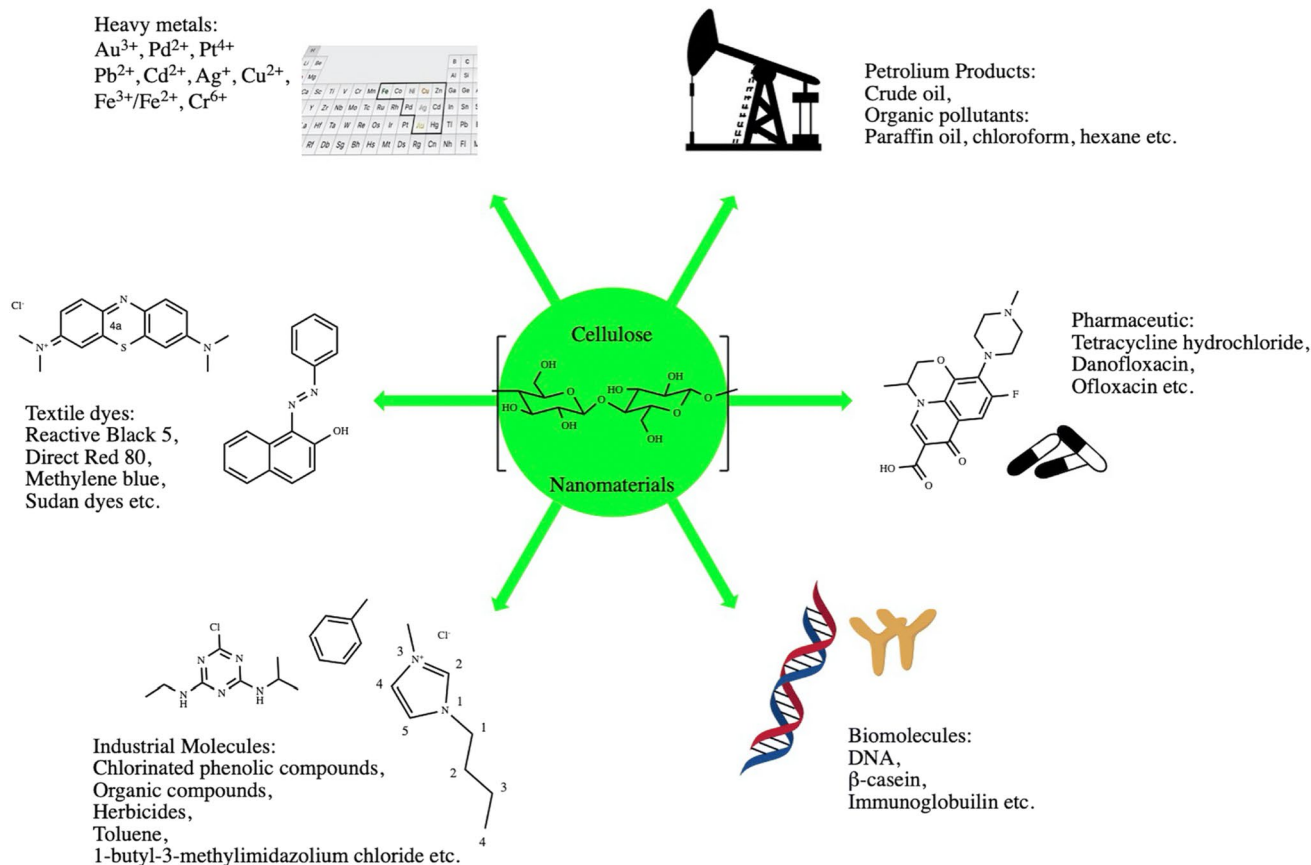

Fig. 9 Applications areas of cellulose nanomaterials as adsorbents [175]

pollution. According to the statistic from the International Tanker Owners Pollution Federation Limited (ITOPF), in 2021, about 10,000 tons of oil were lost to the environment as a result of a tanker spill [176]. The major problem with oil pollution is that it spreads quickly, especially with lighter oils. It also covers the surface of the water, harming the aquatic ecosystem and contaminating mankind's drinking water. Regarding this issue, filtration, in situ burning of floating oil, gravity separation, and adsorption are typically used to treat oily wastewater effluents. Adsorption is said to be the most trustworthy, economical, and ecologically beneficial approach since it effectively removes the contaminant from water without creating any extra intermediates [177].

CNCs' adsorption properties may be applied to oil-water separation methods, which are crucial for limiting chemical and oil leaks. The large number of hydroxyl groups on the surface and the nanoscale structure of CNCs made it possible to take advantage of a new property called "super wettability". This property makes CNCs-based materials repel oil very strongly underwater [178]. However, the hydroxyl group (OH) in cellulose's molecular structure is the main cause of their inability to disperse in many solvents and polymers, leading to nanofiber aggregation. Therefore, the readily available hydroxyl functional groups of CNCs enable a vast scope of designing part in order to improve the hydrophilicity/hydrophobicity, compatibility, and reactivity of the material in practical implementation [78, 179]. Good lipophilicity and hydrophobicity, large load capacity, rapid oil adsorption rate, inexpensive, and elevated buoyancy are all required characteristics for a remarkably effective oil adsorbent material [180].

In previous study, researchers have explored the use of CNCs in various membrane materials for oil/water separation. For example, Almeida et al. [181] deposited CNCs on cellulose acetate (CA) electrospun non-woven membranes, all-cellulose membranes [178], and filter paper [182] to enhance their separation properties. Almeida et al. [181] developed a CA electrospun non-woven membrane with stamped CNCs patterns, which effectively removed microdroplets of oil from water. Li et al. [178] employed a large-scale additive printing technique to deposit CNCs onto mixed-cellulose esters, resulting in all-cellulose

membranes with nanoporous architecture. These membranes exhibited superhydrophilicity and underwater superoleophobicity, enabling efficient separation of oil/water nanoemulsions with high water flux and ultrahigh efficiency of over 99%. They also demonstrated excellent stability and reusability for long-term separation, retaining their performance under various acidic, basic, and salty conditions. Huang et al. [182] created a functional adsorbent with 97% efficiency by either physically coating tunicate CNCs on the surface of filter paper via hydrogen bonding formation or chemically fixing CNCs on the filter paper surface through crosslinking of hydroxyl groups with epichlorohydrin (ECH). These approaches enhanced the separation properties of the filter paper, making it effective for oil/water separation applications.

In recent research, a CNCs/PVA aerogel treated with methyltrichlorosilane to become hydrophobic, enabling it to absorb oil up to 32.7 times its initial weight. The CNCs aerogel possesses key characteristics such as high porosity ($>97.7\%$), a 3D interconnected microstructure, ultralight density ranging from 22.5 to 36.1 mg/cm³, and the ability to float on water, which greatly facilitates its oil absorption capabilities [104, 183]. When CNCs are exposed to a single chemical, they tend to absorb a significant amount of water. To address this, elastic aerogels were developed by ice-templating CNCs water suspensions with polyethyleneimine (PEI) and epoxy crosslinking agents. These aerogels exhibited highly porous structures and enabled rapid solvent absorption, including capillary force absorption of water. To further enhance their performance, graphene sheets were chemically attached to the pore surface of the aerogel using a dip coating process. The resulting CNCs/graphene aerogel, with weight ratios ranging from 25 to 58 g/g, demonstrated selective absorption of organic solvents [184]. These findings highlight the importance of altering the hydrophilicity of CNCs when they are utilized as additives in absorbent materials to prevent oil chemical leakage. The modification of CNCs-based aerogels and the incorporation of graphene sheets offer promising solutions for efficient oil absorption and selective solvent absorption in various applications. Table 5 listed the CNCs-based adsorbents for the removal of oil and organic solvents.

Table 5 CNCs-based adsorbents for the removal of oil and organic solvents

CNCs-based adsorbents	Pollutants	Efficiency (%)	References
Non-woven membranes stamped with CNCs	Oil microdroplet/ water separation	80	[181]
Filter paper-coated tunicate CNCs	Oil/water separation	97	[182]
CNCs/PVA aerogel	Oil and organic solvents	n/a	[183]
CNCs/graphene aerogel		n/a	[184]
All-cellulose membranes deposited with CNCs	Oil/water separation	>99	[178]
Chitosan-CNCs multilayer on stainless steel mesh (SSM)	Oil/water separation	99.5	[185]

The effective pore size, thickness, and hydrophilicity of the membranes have additive effects on oil separation. When the membrane is submerged, water molecules readily pass through the membrane, however, oil droplets are repelled underwater, resulting in oil-water separation. Water, being denser than oil, forms a barrier-like film on the membrane's surface, preventing direct contact with the film's surface. The improved film's underwater oil-water separation process is considerably enhanced by the CNCs' abundant hydroxyl groups and their nanostructures, which provide it superhydrophilicity and superoleophobicity properties. As reported in Wang et al. [185], a separation efficiency of more than 99.5% for an oil-water mixture and other oil-in-water emulsions was achieved by depositing chitosan (CS)-cellulose nanocrystals (CNCs) multilayer on stainless steel mesh (SSM) through simple layer-by-layer (LBL) self-assembly method.

Pesticides Decomposition

Pesticide usage in agriculture contributes greatly to increasing crop yields and warding off harmful pests and exotic weeds [186]. The world's use of pesticides has significantly expanded because of the world's population's rapid growth and the resulting rise in food consumption. Currently, the most often used pesticides are the organophosphorus (OP) class of agrochemicals. The excessive use of pesticides has resulted in widespread pollution that is seen in every aspect of the environment. Since pesticide formulations frequently contain hazardous, comparatively stable, and less soluble active compounds, this pollution presents a multitude of health risks to the general people and ecological species that are not the intended targets. Water sources have become contaminated because of the growing use of pesticides and the delayed environmental breakdown of residual pesticides.

In a study conducted by Swasy et al. [90], an experiment was done to investigate different pesticides that are capable of being broken down by amine-functionalized CNCs and transformed into the relevant by-products with reduced molecular weights in both organic and aqueous environments. The structures of amine-modified CNCs are presented in Fig. 10a and the proposed degradation pathway of malathion and deltamethrin upon treatment with CNC-PEI. According to the experiment, CNCs that have undergone amine alteration might be used to successfully break down a few pesticides in aqueous conditions. It was found that poly(ethylenimine) cellulose nanocrystal (CNCs-PEI) with a loading of 50 mg exhibited degradation rates of 78% for permethrin, 95% for deltamethrin, and 100% for malathion at a concentration of 165 ppm. The exceptional performance of CNCs-PEI can be attributed to the presence of reactive sites on the surface of the CNCs. The use of amine derivatizing agents independently resulted in some degradation of

malathion. By grafting amine compounds into solid CNCs, several advantages are achieved, including the ability to utilize smaller amounts of the amine compounds, reusability, and the option to use it in solid or solution form. The pH level was found to play a crucial role in the degradation of malathion by CNCs-PEI. Increasing the pH accelerated the degradation rate by reducing the protonation level of the CNCs-PEI material. Conversely, lowering the pH increased the protonation level of the CNCs-PEI material, thereby slowing down the degradation rate. Furthermore, the reusability of CNCs-PEI was investigated. After two wash and reuse cycles, the CNCs-PEI material retained its ability to degrade malathion, demonstrating its potential for repeated use. In summary, the study highlights the effectiveness of CNCs-PEI in degrading pesticide compounds, with malathion being completely degraded. The presence of reactive sites on the CNCs surface, the influence of pH, and the reusability of CNCs-PEI contribute to its superior performance as a degradation agent for pesticides.

In a study conducted by Moradeeya et al. [166], CNCs was investigated for its ability to biosorb chlorpyrifos (CP), an insecticide. The results showed that 1.5 g/l of CNCs required 20 min to biosorb 5 mg/l of CP from an aqueous solution, achieving a remarkable removal effectiveness of 99.3%. It was observed that as the temperature increased from 288 to 308 K, the maximum adsorption capacities decreased from 12.325 to 7.247 mg/g, indicating that the biosorption of CP is an exothermic process. Desorption of CP from CNCs could be achieved by using two cycles of operation with a solution consisting of 80% methanol and 20% water. In another study by Yi et al. [187], magnetic partially carbonized cellulose nanocrystals (MPC-CNCs) were developed by treating microcrystalline cellulose (MCC) with sulfuric acid and loading it with magnetic Fe_3O_4 nanoparticles. MPC-CNCs demonstrated suitability as a material for magnetic solid phase extraction of triazine and triazole pesticides from water. Under optimal conditions, 100 mg of MPC-CNCs exhibited approximately 90% adsorption efficiency within 16.5 min. Furthermore, it could be reused up to nine times without significant loss of its adsorption ability.

Heavy Metal Elimination

Heavy metal refers to any naturally occurring element with an atomic weight or density five times greater than that of water, exhibiting high reactivity and even toxicity at minimal concentrations [58]. The presence of heavy metals in water has become increasingly widespread due to the expansion of industrial and human activities, including battery manufacturing, metal smelting, electroplating, textile production, mining, petrochemicals, and more. These heavy metals, such as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb),
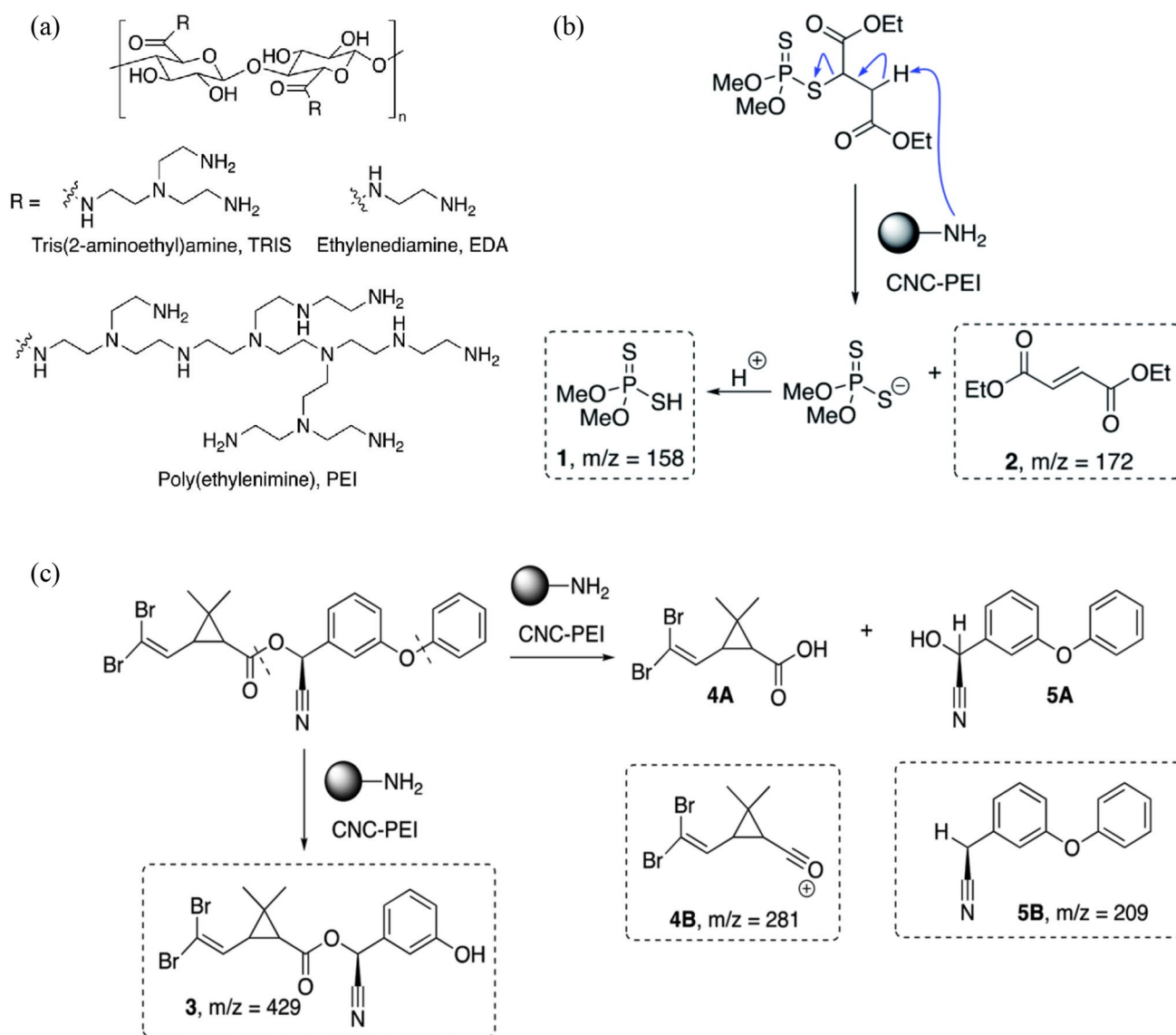
Fig. 10 **a** Amine-modified cellulose nanocrystal structures, **b** Proposed degradation pathway of malathion upon treatment with CNC-PEI, and **c** Proposed degradation pathway of deltamethrin upon treatment with CNC-PEI [90]

mercury (Hg), nickel (Ni), and thallium (Tl), are among the most perilous environmental pollutants [188, 189]. They are potentially hazardous in mixed or elemental forms [189] and are easily absorbed by living organisms because they are highly soluble in watery settings [190]. Numerous studies have detected heavy metals in the gills, livers, and muscle tissues of diverse fish species from polluted marine ecosystems [191]. Consequently, once heavy metals enter the food chain, they can accumulate within the human body [192]. Given the widespread industrial use of most heavy metals, residents and workers residing in proximity to such facilities may face exposure and associated health risks. Elevated concentrations of heavy metals beyond safe levels can have adverse consequences on human health, the environment,

and the ecosystem overall [193]. As a result, the minimal human health risk is related to permitted safe levels of heavy metals in dietary samples.

The most widely used heavy metals removal technology among the several provided options is the adsorption approach. Bio-adsorbents like CNCs have gained popularity as heavy metals adsorbents due to the current emphasis on sustainable materials [194]. In order to enhance their capacity for heavy metal adsorption, CNCs typically require treatment with suitable functional groups [195]. Park et al. [29] synthesized polyacrylamide hydrazine (PAH) grafted CNCs (CNCs-PAH) for the removal of heavy metal ions. The presence of densely packed amines on the surfaces of CNCs-PAH enables strong electrostatic, hydrogen bonding, and

chelation processes, allowing for the adsorption of Cr(VI) ions [29].

Nanoparticles capture heavy metal ions from water primarily through surface adsorption, driven by electrostatic interactions. Among various bionanomaterials, CNCs with negative surface charge and negatively charged functional groups have excellent adsorption properties for positively charged Ag^+ ions. Positive-negative interactions are the main mechanism for Ag^+ adsorption in CNCs. The adsorption behavior is influenced by pH levels, with decreasing pH leading to lower adsorption capacities due to competition between positively charged Ag^+ ions and H^+ ions for adsorption onto negatively charged functional groups like SO^{3-} and COO^-. Electrostatic interactions drive this competition. At a pH above 4.8, CNCs exhibit the highest adsorption capacity [129].

The effect of pH on the adsorption of Co(II) was investigated using cobalt (Co(II)) solutions of 100 and 200 mg/L, with pH values ranging from 3.0 to 8.0. The adsorption capacity increased from 45.5 to 98.8% for 100 mg/L and from 43.52 to 95.0% for 200 mg/L as the pH increased from 2.0 to 6.0. This increase in adsorption capacity can be attributed to the complexation of Co(II) with carboxyl groups. Various amounts of adsorbent ranging from 0.05 to 5.0 g/L were conducted to examine the impact of adsorbent dose on Co(II) adsorption on P(IA/MAA)-g-NC/NB. The adsorption capacity increased with higher adsorbent doses, and a minimum dosage of 2.0 g was sufficient for complete removal of Co(II) from a 1.0 L aqueous solution. Increasing the agitation speed from 100 to 200 rpm resulted in an increase in Co(II) removal from 79.34 to 99.6%. This improvement in adsorption efficiency can be attributed to the exposure of adsorption pores generated by the higher agitation rate. It is possible that adsorption is controlled by intra-particle pore diffusion or pore diffusion, and the adsorption of the metal occurs primarily at the surface of the adsorbent. The desorption capacity of P(IA/MAA)-g-NC/NB using 0.1 M Hydrochloric acid (HCl) was 99.6% even after six regeneration cycles, and only a slight decrease in adsorption capacity was observed, from 99.15 to 88.9% [25]. HCl has been identified as the most suitable reagent for the removal of Hg(II) ions from 2-mercaptobenzamide modified itaconic acid-grafted-magnetite CNCs (P(MB-IA)-g-MNCC), achieving a desorption percentage of 98.5%. Adsorption-desorption studies were conducted using 0.1 M HCl for five cycles, resulting in a decrease in the adsorption capacity of P(MB-IA)-g-MNCC from 96.0 to 86.0% over the course of the five cycles. It is evident that the spent adsorbent retains a high adsorption capacity even after multiple cycles, indicating its potential for repeated use [170].

The effect of pH on metal ion morphologies may influence how well adsorption works [104]. Raising the adsorbent's isoelectronic can fix this problem. The isoelectronic point of amino-functionalized nanocellulose (ACNC), for instance, ranges between 8 and 9. The free amine groups of ACNC are protonated in neutral and acidic environments, producing a positive zeta potential [104] and adsorbable to their highest capacity at pH 2, while Cu^{2+} and Pb^{2+} were adsorbable to their maximum capacities at pH 6 [196]. Additionally, the adsorbent's structure is crucial to the process of adsorption. An example of this is the Polydopamine (PD) modified CNCs (CNCs@PD) nano sorbent, which has a coating of PD on it and displays a high specific surface area, assisting in the adsorption of 205 mg/g Cr(VI) [104].

The Fe-Cu alloy coated CNCs (Fe-Cu@CNCs) possess carboxyl and hydroxyl functional groups that are electron-rich and tend to donate electrons to electropositive metals. These functional groups can form electrostatic attractions with Pb^{2+} ions. As the concentration of Pb^{2+} ions increase from 20 to 50 mg/L, the removal ratio of Pb^{2+} metal ions decrease from 93.98 to 65.56% for the Fe-Cu@CNCs composite. This decrease in removal ratio is attributed to the saturation of adsorption sites on the surface of Fe-Cu@CNCs composites at higher initial concentrations of Pb^{2+} ions. Furthermore, the Fe-Cu@CNCs composite demonstrates excellent reusability, as it retains 80.41% of its original adsorption capacity after six cycles [130].

In a study conducted by Singh et al. [197], the reinforcement of cellulose nanocrystals (CNCs) through succination and amination was investigated for the purpose of decontaminating Cr(III) and Cr(VI) from water. CNCs possesses unique properties such as an increased surface area-to-volume ratio, quantum size effects, and the ability to modify surface properties through molecular modifications, making it an ideal material for metal remediation. The study determined the optimal conditions for the removal of Cr(III) and Cr(VI) as follows: a biomass dosage of 2.0 g, a metal concentration of 25 mg/L, a contact time of 40 min, and a test solution volume of 200 mL. The pH values of 6.5 and 2.5 were found to be optimal for Cr(III) and Cr(VI), respectively. By mobilizing amine groups on the surface of CNCs, more than 98% of anionic chromate containing Cr(VI) in the concentration range of 12.5 mg/g was successfully removed. This study highlights the potential of reinforced CNCs for the decontamination of Cr(III) and Cr(VI) from water. The ability to modify the surface properties of CNCs through succination and amination provides an effective approach for metal remediation applications.

According to a study by Nasrollahzadeh et al. [58], adding succinic acid groups to CNCs significantly increased the binding effectiveness of Pb^{2+} and Cd^{2+} in water substantially. In particular, the conversion of carboxylic acid groups to sodiated carboxylates boosted their capacity to remove harmful metal ions from liquids. Besides, phosphate groups that serve as heavy metal ion binding sites were added to the surface of CNCs via the process of enzymatic

phosphorylation. Phosphorylated CNCs showed an improved ability for adsorption compared to pristine CNCs [35].

Furthermore, functionalized CNCs (electrosterically stabilized nanocrystalline cellulose (ENCC)), has a maximal Cu^{2+} absorption capacity of 185 mg/g at pH = 4 [198]. The absorption of Cd^{2+}, Pb^{2+}, and Ni^{2+} from aqueous solutions utilizing carboxylate CNCs at pH = 6.5 is often much greater than using unmodified CNFs generated by mechanical treatment (11 mg/g for Cd^{2+}, 10 mg/g for Pb^{2+}, and 11 mg/g for Ni^{2+}) [198]. The importance of surface functionalization is further shown through this study. Table 6 listed the examples of CNCs-based adsorbents for the removal of heavy metal ions from wastewater.

Dye Extraction

Dyes are chemicals that may attach to surfaces or textiles to produce brilliant and long-lasting colors [202]. As a result of all of these advancements, there are now over 100,000 commercially accessible dyes, with azo dyes accounting for over 70% of the total by weight, and over 1 million tons of dyes are produced each year, with textile dyes accounting for 50% [203]. Among the primary industries that contribute to dye pollution are paints, inks, plastics, paper, energy transfer cascades, displays, dye-sensitive solar cells, laser welding processes, light-emitting diodes, and food and/or cosmetic dyes generated predominantly from azo dyes are the key industries that contribute to dye pollution [58]. The effluent from textile dying operations is challenging to handle effectively because of the significant composition diversity and high color intensity. According to estimates, 2% of dyes generated are discharged directly into aqueous effluent, while the remaining 10% are lost throughout the coloring process [203]. Due to the harmful impact that waste dyes have on people, animals, and plants, dye effluents are the most common industrial colorants and pose a danger to aquatic habitats. Toxic dye effluents are dangerous, non-biodegradable, physiologically and chemically stable, and water-soluble organic pollutants that contribute to a wide range of human illnesses, including skin rashes, renal failure, liver disease, and nervous system damage.

Anionic moiety-modified CNCs can function as adsorbent materials or catalysts to remove various cationic dyes. Based on studies by He et al. [89], the adsorption properties of carboxylated nanocelluloses generated utilizing a single-step hydrolysis process were investigated. Ammonium persulfate is used to hydrolyze microcrystalline cellulose to produce carboxylated or COO-modified CNCs, which have carboxyl groups added to their surface during cellulose hydrolysis (APS). Adsorption studies for cationic dyes like methylene blue (MB) have demonstrated the possibility of carboxylate groups attaching to positively charged dyes. Adsorption of dye-contaminated wastewater is a common method, but achieving high removal capacity with cost-effective adsorbents is a challenge. Electrosterically stabilized nanocrystalline cellulose (ENCC), a form of hairy nanocellulose, shows potential for high adsorption capacity [204], as displayed in Fig. 11a. It effectively adsorbs methylene blue dye through an ion-exchange mechanism, influenced by other ions. Composite hydrogel beads of sodium alginate and ENCC (ALG–ENCC beads) maintain a high removal capacity (1250 mg/g), making them suitable for large-scale wastewater treatment. Figure 11b depicts the structure of cationic dyes bonded to the anionic sulphated or carboxylated CNCs. The adsorption capacity of MB onto CNCs, therefore, started to balance after 10 min at 22 °C (0.32 mmol/g) [58]. This discovery is the result of the modification of carboxylated CNCs surfaces, where more carboxyl groups may effectively function as a dye-binding site.

Moreover, CNCs surfaces include large amounts of hydroxyl groups and have high specific surface areas. Due to this, hydroxyl groups on the surface of CNC can be oxidized to carboxyl groups by H_2O_2 treatment and promoting the dye adsorption. The methylene blue (MB) clearance rate, for instance, increased from $90.85 \pm 2.34\%$ to $98.76 \pm 2.21\%$ [205]. CNCs that have been treated with polydopamine (PD) may completely adsorb MB [104]. This occurred because of MB's ability to be adsorbed by PD-CNC via electrostatic attraction, hydrogen bonding, and π-π stacking. The porosities of CNCs were altered in addition to surface functionalization to enhance their adsorption capabilities. Sodium alginate cross-linked ($CNCs-MnO_2$), for instance, created porous microspheres with 98.23% porosity and low densities. Methylene blue decolorization achieved 95.4% efficiency in approximately ten minutes [104]. Besides that, Song et al. [33] observed that cellulose nanocrystal (CNCs)/transition metal oxide hybrid porous microspheres have high adsorption performance and degradability in wastewater treatment. A CNCs/manganese dioxide/titanium dioxide microsphere is prepared using a bubble template and ionic crosslinking. The synergistic effect of the metal oxides achieves 97.0% degradation efficiency for methylene blue, easy recovery, and rapid regeneration. The material's maximum dye removal is 310.2 mg/g, surpassing other CNCs-based adsorbents, possibly due to concerted catalysis. Table 7 presents a comprehensive compilation of studies exploring the application of cellulose nanocrystals (CNCs) as adsorbents for the efficient removal of dyes from wastewater.

Pharmaceutical Waste Removal

Many urban and rural groundwater sources, while safe to drink, may include trace amounts of pharmaceutical substances such as birth control pills, antidepressants, pain relievers, shampoos, anti-epileptics, caffeine, and a variety of other pharmaceutical ingredients [207]. For the health
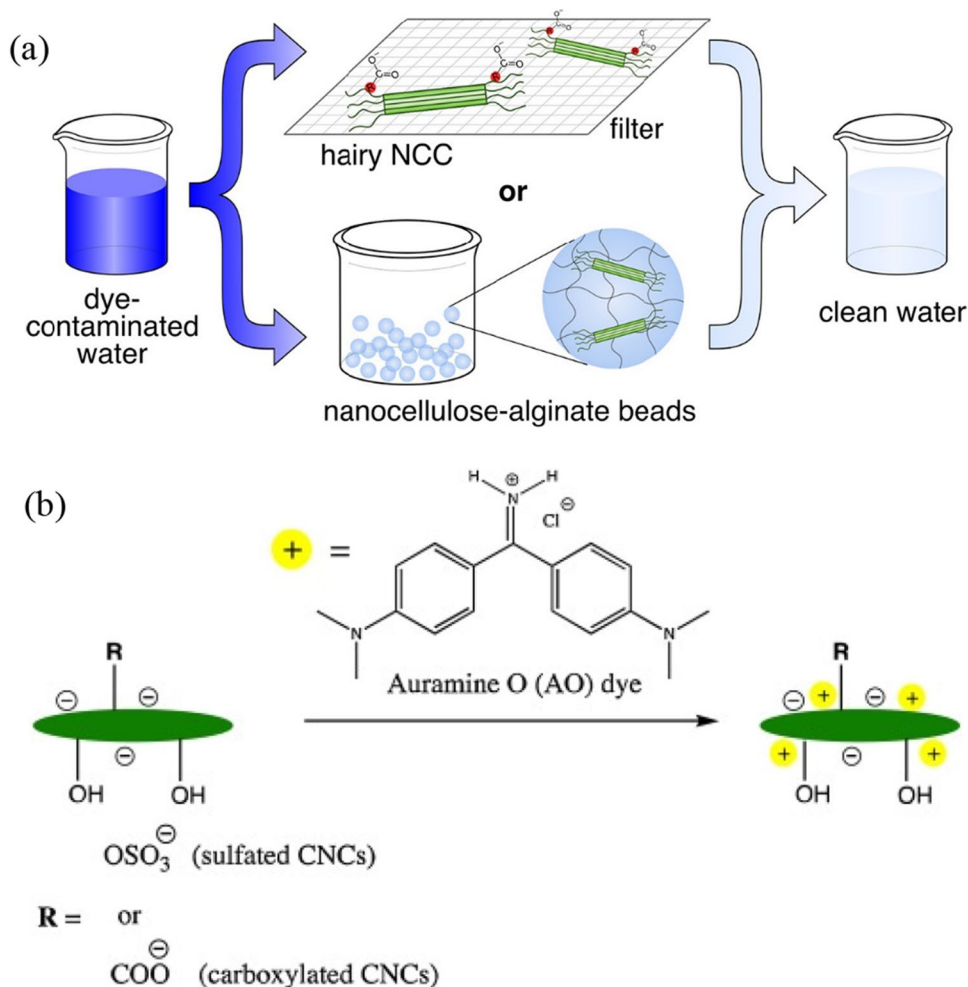
Table 6 CNCs-based adsorbents for heavy metal ions removal from wastewater

CNC Adsorbent	Heavy Metal	pH	Concentration of pollutants (mg/L)	Adsorbent dosage (g/L)	Adsorption Capability (mg/g)	Removal efficiency (%)	References
CNCs	Ag^+	6.39	107.8	2.0	34.35	64	[129]
Chitin nanocrystals (ChNC)		6.63	107.8	2.0	19.80	37	
Pristine CNCs (CNC_{SL})		3.5–4.5	62.5	2.0	56	–	[28]
Phosphorylated CNCs ($PCNC_{SL}$)			62.5	2.0	136	–	
Pristine CNC (CNC_{SL})		9.1	1.48	–	0.82	100	[131]
CNC_{BE}			1.48	–	0.87	100	
Phosphorylated CNCs ($PCNC_{SL}$)			1.48	–	0.81	100	
Pristine CNCs	Cd^{2+}	6.0	200	1.0	1.9	–	[199]
Carboxylated CNCs (SCNCs)			200	1.0	259.7	–	
Sodic nanoadsorbent (NaSC-NCs)			200	1.0	344.8	–	
Rice straw CNCs		6.0	25	0.5	9.7	90.7	[200]
Pristine CNCs	Cu^{2+}	3.5–4.5	62.5	2.0	20	13.8	[28]
Phosphorylated CNCs			62.5	2.0	117	99.4	
Pristine CNCs (CNC_{SL})		2.3	330.2	–	28	13	[131]
CNC_{BE}			330.2	–	67	36	
Phosphorylated CNCs ($PCNC_{SL}$)			330.2	–	358	86	
Carboxylated cellulose nanowhiskers (CNWs)		6.0	10–60	0.2–10.0	14.65	–	[23]
Fe-Cu alloy coated CNCs (Fe-Cu@CNCs)	Pb^{2+}	–	–	–	85.8	93.98	[130]
Pristine CNCs		5.5	300	1.0	27.9	–	[199]
Carboxylated CNCs (SCNCs)			300	1.0	367.6	–	
Sodic nanoadsorbent (NaSC-NCs)			300	1.0	465.1	–	
Rice straw CNCs		6.0	25	0.5	9.42	94.2	[200]
2-mercaptobenzamide modified itaconic acid-grafted-magnetite CNCs	Hg^{2+}	8.2	100	2.0	240	96	[170]
Poly (itaconic acid/methacrylic acid)-grafted-CNCs/nanobentonite composite	Co^{2+}	6.0	100	2.0	350.8	98.8	[25]
Pristine CNCs	Fe^{3+}	3.5–4.5	62.5	2.0	6.3	39.8	[28]
Phosphorylated CNCs			62.5	2.0	115	100	
Pristine CNCs (CNC_{SL})		2.3	550.5	–	48	14	[131]
CNC_{BE}			550.5	–	102	33	
Phosphorylated CNCs ($PCNC_{SL}$)			550.5	–	512	74	
CNCs	Cr^{3+}	6.5	25	2.0	–	62.4 ± 0.03	[197]
Succinated CNCs			25	2.0	–	94.84 ± 0.06	
CNCs	Cr^{4+}	2.5	25	2.0	–	5.72 ± 0.09	[197]
Aminated CNCs			25	2.0	–	98.88 ± 0.08	
Rice straw CNCs	Ni^{2+}	6.0	25	0.5	8.55	85.5	[200]
Diethylene triamine grafted dialdehyde CNCs (DETA-g-DA-NCC)	As^{3+}	7.5	25	0.5	10.56	92.84	[201]
	As^{5+}	2.5	25	0.5	12.06	97.86	[201]

of humans, pharmaceuticals are crucial. Nonetheless, they are becoming more and more recognized as a rising concern pollutant. The amount of pharmaceutical waste in the environment, landfills, or disposal sites is periodically increased by the release of pharmaceutical waste or by-products into open fields and nearby natural water bodies. As a

Table 7 CNCs-based adsorbents for efficient dyes removal from wastewater

CNCs Adsorbent	Dye	pH	Concentration of pollutants (mg/L)	Adsorbent dosage (g/L)	Adsorption capability (mg/g)	Removal efficiency (%)	References
Nanocrystalline cellulose (NCC)	Methylene blue	–	–	–	101.16	–	[89]
Carboxylated CNCs		7.0	500	18	–	92.8	[24]
			200	20	–	92.3	
CNCs/partially hydrolysed polyacrylamide (HPAM) nano-hydrogels		6.5	5	–	19	–	[206]
CNCs		9.0	500	12.17	118	–	[167]
Oxidised CNCs		9.0	500	12.17	769	–	
CNCs	Crystal violet	6.0	400	500	185.2	–	[168]
Maleic anhydride grafted CNCs			400	500	243.9	–	
Amino-functionalised CNCs (ANCC)	Acid red GR	4.7	100	0.5	134.7	67.3	[22]

result, pharmaceutical waste is the developing contaminant that is most frequently found in water [208].

The surface of nanocrystal cellulose (CNC) has been modified to effectively absorb medicines. One method is to build composites of CNCs modified with polyethylene glycol (PEG), which have demonstrated improved adsorption ability for several medicinal compounds in aqueous solutions. Acetaminophen, sulfamethoxazole, and N, N-diethyl-meta-toluamide (DEET) are examples [209]. The ability of cellulose-based nanocomposites to extract hydrophobic

pharmaceuticals from water has been established. The interaction between PEG-functionalized CNCs and the medicines is responsible for the increased adsorption capability. The composite is made by carboxylation the CNC surface with 2,2,6,6-tetramethyl-1-piperidinyloxy, then covalently attaching a 600 g/mol hydrophilic polyether diamine using the sodium salt of N-(3-dimethylaminopropyl)-N-ethyl-carbodiimide/N-hydroxysulfosuccinimide [209]. Another study synthesized dialdehyde cellulose nanocrystals (DCNCs) by oxidizing cellulose nanocrystals (CNCs) with sodium periodate to remove creatinine [210]. The adsorption capacity of DCNCs increased with increasing aldehyde content, as more aldehyde groups provided more adsorption sites. Furthermore, smaller DCNCs resulted in faster adsorption rates while having little effect on adsorption capacity. Under conditions such as an initial creatinine concentration of 100 mg/L, an 8-hour treatment time, and a pH of 7, the maximum adsorption of creatinine onto DCNCs (with an aldehyde content of 4.41 mmol/g) was determined to be 1.50 mg/g. These findings imply that DCNCs have the potential to be used as a creatinine adsorbent in the treatment of chronic renal failure [210]. Furthermore, polypyrrole/cellulose fibers (PPY/CF) for the removal of potassium diclofenac (PD) from aqueous solutions have been synthesized. The percentages of PD adsorption were found to be considerable over a wide pH range of 2.0–10.0. The PPY/CF composite, which contains amino functional groups and aromatic rings on polypyrrole as well as different CF ester, ether, and hydroxyl groups, contributes to the high adsorption capacity of PD through hydrogen bonds, dipole-dipole forces, and π-π interactions [211].

In a study by Chen et al. [212], an inorganic-organic adsorbent called β-Cyclodextrin-modified CNCs@Fe_3O_4@SiO_2 superparamagnetic nanorods was developed for the removal of procaine hydrochloride and imipramine hydrochloride. The adsorption capacities for procaine hydrochloride and imipramine hydrochloride were determined to be 13.0 ± 0.09 mg/g and 14.8 ± 0.16 mg/, respectively. In another study conducted by T.S. Anirudhan and Rejeena [213], a cellulose-based hydrogel known as poly(acrylic acid)-modified poly(glycidylmeth-acrylate)-grafted nanocellulose (PAPGNC) was synthesized through graft copolymerization. The maximum adsorption capacity of PAPGNC was found to be 140.65 mg/g at pH 6.5 and 30 °C, with equilibrium reached within 90 min. The adsorbent could be effectively regenerated using 0.1 M potassium thiocyanate (KSCN), with a retention of 87% in catalytic activity even after four cycles.

The adsorption of hemoglobin onto P(MAA-co-VSA)-g-MNCC was found to be influenced by the initial concentration and temperature. Higher initial concentrations (ranging from 25 to 100 mg/L) and temperatures (ranging from 10 to 40 °C) resulted in increased adsorption capacity. However, at temperatures exceeding 40 °C, the unfolding of hemoglobin molecules caused agglomeration, leading to a decrease in adsorption. This decrease was attributed to the interaction between the hydrophobic part of the adsorbent and the hydrophilic part of hemoglobin [27]. Other examples of CNC-based adsorbents for pharmaceutical pollutants removal were presented in Table 8.

Organic Micropollutants Degradation

Micropollutants and trace organic compounds, both synthetic and natural substances, pose potential risks to the environment and human health [214]. Factors such as uncontrolled urbanization, industrial growth, healthcare activities, agriculture, and transportation contribute to their presence in the environment [215]. Examples of these developing pollutants include pharmaceuticals, pesticides, personal care products, hormones, disinfectants, disinfection by-products, surfactants, and perfluorinated chemicals [215]. Despite their trace concentrations in water systems and wastewater treatment processes, there is still a substantial risk of these contaminants reaching our drinking water due to ineffective monitoring. These contaminants often exist as complex mixtures with potentially harmful synergistic effects [216]. Therefore, more knowledge is needed to understand their origins, consequences, and ecological impacts.

Table 8 CNCs-based adsorbents for pharmaceutical pollutants removal from wastewater

CNC Adsorbent	Pollutants	pH	Concentration of pollutants (mg/L)	Adsorbent dosage (g/L)	Adsorption Capability (mg/g)	References
Dialdehyde cellulose nanocrystals (DCNCs)	Creatinine	7.0	100	–	1.50	[210]
Poly(acrylic acid)-modified poly(glycidylmeth-acrylate)-grafted nanocellulose (PAPGNC)	Trypsin	6.5	500	2	140.65	[213]
Poly(methacrylic acid-co-vinyl sulfonic acid)-grafted-magnetite CNCs	Haemoglobin	6.5	100	2	248.19	[27]
β-Cyclodextrin-modified CNCs@Fe_3O_4@SiO_2 superparamagnetic nanorods	Procaine hydrochloride	–	–	–	13 ± 0.09	[212]
	Imipramine hydrochloride	–	–	–	14.8 ± 0.16	

Biopolymers, particularly CNCs, have shown significant potential in adsorbing heavy metal ions, dyes, and other micropollutants at low concentrations [217]. CNCs offer several advantages, including biocompatibility, biodegradability, non-toxicity, reactivity, film and fiber-forming capabilities, and high hydrophilicity. They exhibit excellent sorption and selectivity for trace pollutants. The adsorption process of CNCs is based on the dissociation of ions from the surface and subsequent electrostatic attraction to charged surface functional groups. When water with solutes comes into contact with the active layer of an adsorptive membrane, molecular sieving rejects solutes larger than the membrane's pore size [218]. Smaller solutes, however, can enter the active layer and behave as microspheres of adsorption material in the support layer. These solutes eventually form a compact internal spherical complex, allowing the adsorptive membrane to produce filtered water that meets required standards [217]. Adsorbent membranes are modified with reactive functional groups such as -NH$_2$ and -COOH to facilitate surface complexation, physical adsorption, electrostatic interactions, or ion exchange interactions with solutes [219].

Others

Natural organic matter (NOM), a different class of contaminants, causes concern when it is found in drinking water. A hydrophobic NOM called humic acid is produced when environmental biomass decomposes. Due to the composting actions of bacteria on deceased species and plant tissues, certain natural streams have a brownish-yellowish hue [220]. To eliminate humic acid from aqueous solutions, amino groups are one sort of functional group that may be added to nanocellulose [93]. Electrostatic interactions between the carboxyl and hydroxyl groups on humic acid and the amine functional group on nanocellulose created the adsorption process [194].

Furthermore, non-biodegradable nitrophenols are exceedingly dangerous, carcinogenic, and the cause of many human diseases. Therefore, it is crucial that they are removed throughout the water treatment process. They are used in a wide range of industries, including the production of synthetic polymers, dyes, explosives, resins, and medicines, which use anilines as key feedstocks and are on the list of regulated materials. Shi et al. [221] created CNCs-supported gold NPs with a fast swelling rate and superior catalytic prowess to catalyze the aqueous sodium borohydride (NaBH$_4$)-mediated reduction of pollutant, 4-nitrophenol (4-NP), with turnover frequency value and maximum rate values of 641 h^{-1} and 0.0147 s^{-1}, respectively [58]. This synthesis was carried out by electrospinning and thermally treating polyethylene glycol, CNCs, and H[AuCl4] for 60 min at 80 °C, where CNCs and polyethylene glycol serve as the support and reductant, respectively [58].

Outlook and Challenges

Although CNC-based adsorbents have a bright future in the removal of heavy metal ions and organic dyes from water, there are still several obstacles that are mostly related to their manufacturing processes that limit the use of CNC, such as their low adsorption capacity limits their potential as effective adsorbents. More study is necessary to investigate and enhance the application of CNCs-based adsorbents in different fields. Furthermore, the cost of producing CNC from raw materials is the biggest obstacle to commercialization. Large-scale CNC isolation can be an expensive, energy-, and time-intensive procedure, which may limit their utilization in large-scale wastewater treatment applications. Some studies advise using feedstocks other than woody cellulose, such as agricultural waste [222]. Some researchers recommend an enzymatic or chemical pre-treatment before the mechanical treatment [57]. Current research and developments in isolation techniques may aid in overcoming this limitation in the future. Besides, due to its potential to permanently combine when dried, another problem is the challenge of maintaining the nanoscale structure of CNC throughout handling and storage. For simpler transportation and long-term application, nanocellulose's surface modification, and dispersibility may be crucial factors.

Apart from that, for large-scale applications, the unknown toxicity of newly developed modified nanocellulose materials may be a barrier. Despite the fact that functionalized nanocelluloses and nanocomposites are safe to use, toxicological research on them is still insufficient for widespread adoption [194]. Therefore, before commercialization, understanding the potential long-term toxicity of nanocomposites on a batch and pilot size is essential. Another evident challenge is the homogeneity of the chemistry and properties of nanocellulose-based products during their manufacture. Variability from one batch to the next may be caused by feedstock, processing techniques, and other factors, which makes it more challenging to manage in large-scale usage [194]. Additionally, extensive study is needed to develop CNC-based adsorbents that aim to simultaneously remove different species from a multicomponent contaminated system, mimicking the properties of real wastewater.

The challenge of dispersing CNC in hydrophobic polymer matrices persists due to the inherent difficulty of removing individual nanocellulose particles from water systems [21]. This problem arises because, following the water treatment process, their great dispersion stability made it essential to add salt or alter the pH. However, it is possible to accomplish the surface grafting of CNCs with low molecular weight polymers to disperse them in

polymer blends for ecologically friendly wastewater treatment applications [21]. The main difficulties in the preparation process include high water and energy consumption and yield, as well as by-product toxicity, which is an obstacle to the usage of CNCs in wastewater treatment. For instance, the washing procedure often produces acid wastewater that is used to balance the pH of the nanocellulose solution.

Another area of interest is the post-treatment regeneration and reusability processes of CNC-based materials for long-term uses. Numerous investigations on nanocellulose adsorbents are lacking in terms of good biodegradation processes or numerous adsorption-desorption cycles. While they can be partially regenerated, repeated usage may result in a decline in adsorption capability over time. Current research is focused on developing effective regeneration methods and understanding the long-term stability of CNCs. Finally, research on the use of magnetic nanocellulose composites in the form of aerogel or hydrogel, which would make it simple to separate from sludge and prolong their lifespan, is conceivable. The field of CNC-based adsorbents for the removal of toxins from wastewater might encompass newly emerging contaminants. The outstanding simultaneous photo adsorption and photodegradation capabilities of the impregnation of photocatalytic nanomaterials with CNC-based materials should be further studied for water remediation applications [194].

Concluding Remarks

Efforts to synthesize effective and environmentally friendly wastewater treatment materials have piqued the interest of academia and industry. Clean water is one of the most important global concerns of the twenty-first century, and numerous solutions have been proposed. Nanocellulose stands out as one of the most effective and efficient sustainable materials available for wastewater treatment. There are various advantages to using nanocellulose materials such as cellulose nanocrystals, cellulose fibers, and bacterial cellulose. They are light, chemically inert, and can be customized with various surface chemistries. Furthermore, they have lower production costs than inorganic nanomaterials. Researchers have achieved considerable advances in nanocellulose synthesis and have effectively used these materials for wastewater treatment. For water treatment applications, nanocellulose-based membranes, filters, and adsorbents have been produced. Heavy metals, pesticides, organic dyes, pharmaceutical pollutants, organic micropollutants, oils, and organic solvents have been shown to be removed from water by these materials. CNCs are interesting due to their low cost and widespread availability. Since cellulose can be extracted from both land and sea sources, there is always

a supply to fulfill the rising demand for goods in various industrial sectors. The well-being of society exposed to such toxins will increase when waste and harmful contaminants are removed from wastewater utilizing renewable resources from the environment. They are essential for the design and development of effective bio-adsorbents that guarantee the most efficient elimination of hazardous pollutants because of their huge specific surface area.

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