CELLULOSE CHEMISTRY AND TECHNOLOGY

FUNCTIONAL CELLULOSE-BASED GELS USED IN WASTEWATER REMEDIATION, WITH A FOCUS ON HEAVY METALS AND DYE REMOVAL: A CRITICAL REVIEW

NDUDUZO L. KHUMALO,[*] SAMSON MOHOMANE,[*] ALBERTUS K BASSON[*]
and TSHWAFO E. MOTAUNG[**]

[*]*Department of Chemistry, University of Zululand, KwaDlangezwa Campus,*
Kwa-Zulu Natal Province, South Africa
[**]*Department of Chemistry and Chemical Technology, Sefako Makgatho Health Sciences University, South Africa*
✉ *Corresponding author: T. E. Motaung, Motaungte@live.com*

Received February 26, 2024

Water pollution remains a critical global challenge, exacerbated by increasing pressure on freshwater resources and the lack of access to clean drinking water for millions of people. This review investigates the potential of nanocellulose-based materials in water purification, with a specific focus on their application as an adsorbent, photocatalyst, and catalyst/support for adsorbents. To overcome the limitations of conventional treatment methods, various strategies for fabricating cellulose-based aerogels are examined. The review outlines the processes involved in biomass-derived cellulose extraction, nanocellulose preparation, and the development of hybrid aerogels.

A major source of water contamination is the presence of heavy metals and synthetic dye pollutants. This comprehensive review highlights the use of cellulose-based gel materials for the effective removal of heavy metals and dyes from wastewater. In addition, it explores the underlying mechanisms involved in mitigating the toxicity of these pollutants using cellulose-based aerogels, ion-exchange systems, flocculants, and other biosorbents incorporating nanocellulose.

Keywords: cellulose, adsorption, aerogel, biomass, hydrogel, water treatment

INTRODUCTION

One of the contemporary challenges the humanity is facing is the problem of water pollution. Clean and drinkable water stands as a fundamental requirement for the sustenance and progress of mankind. According to a recent publication from the World Health Organization (WHO), it was projected that by the year 2025, fifty percent of the global population would encounter situations of heightened demand for water due to stress on water resources.[1] According to WHO, there is an estimated 785 million people worldwide, who do not have access to potable water services.[1] Another concern is the continually decreasing clean potable water over time because of pollution. Even rainwater is regarded as acidic because of continuous pollution with toxic gases, such as nitrogen oxide and sulphur oxides. The possibility of using seawater is not feasible either, given that it is likewise tainted with various contaminants like organic compounds (for example, pharmaceuticals, antibiotics, and dyes), as well as heavy metals. Some of these organic pollutants and heavy metals are carcinogenic, mutagenic and teratogenic substances, which accumulate in the environment. Furthermore, unlike organic pollutants, pollutants containing heavy metals do not biodegrade in the environment. Therefore, it is necessary to obtain adsorbents that have a maximum adsorption capacity, and thus, remove a large amount of organic pollutants and heavy metal ions.[2]

Some alternative approaches, such as chemical precipitation, the ferric method, reverse osmosis, electrochemical techniques, ion exchange, adsorption, are commonly employed for treating water contaminated with heavy metals.[2-4] Both electrochemical and ion-exchange methods possess high selectivity and sensitivity. However, these methods are expensive and time-consuming. The benefits of the adsorption technique consist of

Cellulose Chem. Technol., ***59*** *(5-6), 665-682 (2025)*

the rapid adsorption rate, substantial adsorption capacity and straightforward operational procedures. Generally, the adsorption process is considered the most economical way to remove organic pollutants and heavy metals from wastewater, even though the preparation of the adsorption materials can sometimes be expensive and complex.[5-7] An additional advantage of this method is the recyclability of the adsorbent through appropriate desorption and regeneration processes offered by the adsorption.

Recently, a variety of adsorbents have been investigated for the removal of heavy metals and dyes from water.[11] Activated carbon, renowned for its high surface area and porosity, efficiently captures a broad spectrum of contaminants.[8-10,12] Zeolites, crystalline aluminosilicates with porous structures, selectively adsorb heavy metals based on their ionic radius.[13] Clay minerals like bentonite, featuring ion exchange capabilities, replace ions on surfaces, aiding in heavy metal adsorption.[14] Nano-sized materials, like graphene oxide and iron nanoparticles, possess high surface areas and reactivity, enabling effective adsorption of contaminants. Biosorbents prepared from natural materials, such as algae and agricultural by-products, leverage functional groups and surface properties to adsorb contaminants. Aerogels, characterized by high water retention capacity, exhibit selective adsorption of heavy metals and dyes.[15] Each adsorbent type offers distinct advantages in water treatment based on their specific properties and mechanisms of action.[16]

In this context, cellulose-based materials have garnered attention as highly effective adsorbents for eliminating heavy metals and dyes from water, owing to the abundance, cost-effectiveness and biodegradability.[12] Additionally, cellulose-based aerogels, often synthesized from cellulose derivatives or by mixing them with other polymers (composite aerogels), exhibit promising adsorption capabilities due to their porous structure.[17] The adsorption mechanism can be influenced by the porosity of the material, its specific surface area, the introduction of specific binding sites, and the possibility of establishing chemical interactions through functional groups, such as hydroxyl groups -OH.[18] An example in this sense is the derivatization of cellulose, such as cellulose acetate, which contributes to improving the adsorption capacity by introducing additional functional groups, such as acetate groups (-$OCOCH_3$). Although cellulose-based materials offer significant advantages, such as renewability, cost-effectiveness, and the ability to have designed properties, challenges remain in regenerating saturated adsorbents-based on cellulose, without compromising their efficiency and selectivity for specific contaminants.[19] Ongoing research aims to optimize cellulose-based materials as sustainable and efficient adsorbents in wastewater treatments and industrial water purification processes.

Common cellulose-based adsorbents often include nanocellulose (NCs), such as cellulose nanocrystals (CNC) and cellulose nanofibers (CNF), both possessing high surface areas, making them suitable for adsorbing contaminants. NCs can be utilized to develop thin films, sheets, and membranes for reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and other processes (Fig. 1). Also, CNC can be used to create three-dimensional (3D) materials (foams, aerogels, beads, and bio-ink for 3D printing (Fig. 1).

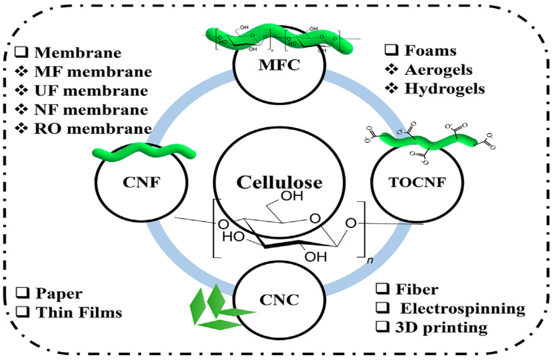

Figure 1: Nano- and microcellulose based materials (cellulose nanofiber (CNF), cellulose nanocrystals (CNC), TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) cellulose nanofiber (TOCNF) and microfibre cellulose (MFC)) used for the treatment of wastewater or other applications[34]

For the elimination of organic pollutants like oils and cyclohexenes, cellulose can be treated with hydrophobic or oleophilic moieties,[20-22] or used in combination with dendrimers,[23] chitosan[24,25] and other biopolymers,[26-28] and nanomaterials, like carbon nanotubes,[29] metal-organic frameworks (MOFs), zeolites,[30] and others.[31-33] The mechanical properties of cellulose are enhanced by chemical and physical modification, which also improves the efficacy of cellulose-based materials in the treatment of water.

POTENTIAL APPLICABILITY OF CELLULOSE IN WASTEWATER PURIFICATION

The application of cellulose in wastewater purification can be realized through a number of different approaches. In this section, only three most recent advances in this area will be overviewed, namely: (i) as an active agent, *i.e.*, as an adsorbent, (ii) as a photocatalyst by reducing the energy band gap, (iii) as a support for adsorbents.

There are several methods to introduce negative charges on the surface of cellulose, such as acid hydrolysis (sulphuric acid), when negatively charged sulfate ester groups ($-OSO_3^-$) are introduced, or by oxidation with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), when negatively charged carboxylic acid groups ($-COO^-$) are introduced.[35-37] Negatively charged cellulose molecules operate as the active ingredient for the absorption of cationic pollutants (*e.g.*, metal ions). As an example, cationic modified cellulose-based materials have been used as an adsorbent for insecticides, dyes, and anionic pollutants such As(V), As(III), and Cr(VI).[40,41] To boost the selectivity for particular elements, the surfaces of cellulose fibres have been functionalized either with amine ($-NH_2$) or thiol (-SH) groups, or with phosphoryl ($-PO_3^{2-}$), or sulfate ($-SO_4^{2-}$) ions.[38,39]

The improvement of photocatalyst performance is another approach to using cellulose in wastewater treatment. After the catalyst has been exposed to radiation, electron-hole recombination is impeded because electrons are instead absorbed by graphitic structures (such as cellulose char).[42] This electron capture results in holes being produced in the conduction band (CB), which increases the likelihood of superoxide radicals ($O_2^{-\bullet}$) being created when oxygen in solution interacts with electrons in biochar, as opposed to the creation of $HO^\bullet$ radicals. Therefore, cellulose acts in enhancing catalytic performance as a sustainable and renewable source of graphitic material.

The physical characteristics of cellulose, in particular, its porosity, are utilized when using it as a support for adsorbents.[43,44] Internal pores and adsorbents can act as nucleation and deposition sites between fibres, which can increase performance and lifespan by lowering attrition and loss. For instance, iron oxides are effective adsorbents for arsenic, whose groundwater poisoning has a major impact on the health of more than 40 million people globally.[45] The utilization of iron oxides for this purpose is complicated by the recovery from treated water. Recent research has demonstrated that cellulose–iron oxide composites can overcome this difficulty, improving the adsorbent's performance and longevity.[46] To enable the reuse and recycling of catalysts, a similar justification has been used in the design of catalysts for advanced oxidative processes.[47] In addition, it has been proposed that cellulose improves catalyst performance by offering settling sites for radicals and pollutants, increasing their interaction and the latter's subsequent degradation,[48] as well as by preventing catalyst aggregation, increasing access to active sites on the catalyst surface.[49]

Wastewater treatment technologies

There are rising worries that, by 2050, at least 2 million people will be at risk of having less access to fresh water. This is because access to clean water and sanitation is still a major worry for people all over the world. About 25% of people are likely to live in a country facing shortages of potable water.[34]

Water pollution can be treated using a variety of techniques, including physical, chemical, and biological ones (Fig. 2). Filtration, floating, sedimentation, degradation through light (photocatalysis), or heat (pyrolysis), and adsorption are all examples of physical methods. Chemical techniques make use of complexation, precipitation (by chemical or electrochemical means), and degradation (oxidation, reduction). Finally, the biological approach uses flocculation and degradation to remove pollutants. The treatment method is chosen based on several factors, including the type of pollutant, its concentration, possible interference *etc.* For instance, a treatment approach that works well to remove heavy metals would not work as well to remove dyes, and *vice versa*. Also, the effectiveness of the removal technique is determined by the pollutant concentration. Thus, generally, the removal effectiveness of the adsorption treatment declines as the pollutant's concentration rises. The adsorption efficiency is therefore improved by diluting the wastewater.[34]

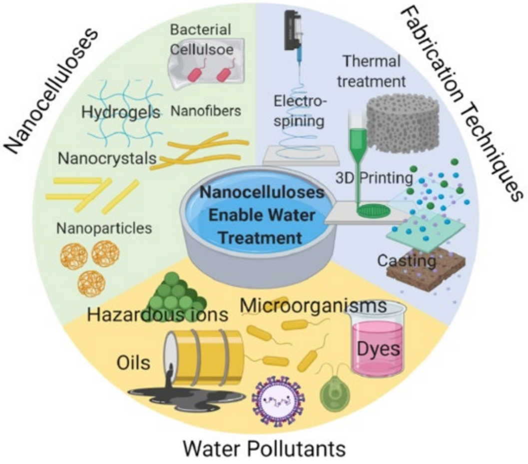

Figure 2: Use of cellulose-based materials for wastewater treatment[34]

Adsorbents can be hydrophilic, hydrophobic, or nonpolar, depending on their elemental composition and the nature of their functional groups. Traditional adsorbents, such as silica gel, activated carbon, and zeolites, have been widely used for applications, including gas purification, water filtration, and catalysis. Recently, cellulose nanomaterials (CNMs) have emerged as sustainable and abundant alternatives with properties that make them highly suitable for adsorption processes. These include a high aspect ratio, large surface area, excellent colloidal stability, mechanical strength, and the potential for surface functionalization. CNMs also offer ease of regeneration and the capacity to adsorb a wide range of contaminants. Advances in the modification of CNMs and the development of their composite forms have significantly enhanced their adsorption performance for water pollutants, such as heavy metal ions, dyes, and various organic compounds.

The adsorption technique is frequently used to remove different types of contaminants from water. Adsorption is a surface phenomenon that occurs when contaminants, or adsorbate molecules, deposit on the surface of an adsorbent (solid surface). Depending on the type of attraction forces between an adsorbate and an adsorbent, the process can be either physisorption (van der Waals adsorption) or chemisorption (activated adsorption via chemical bonding, electrostatic attraction, or π-π interaction, for example).[105] Much of the time, pollutants are drawn to the surface of adsorbents by imbalanced forces of attraction. Chemisorption requires activation energy and only ever creates monolayers, but physical sorption is faster and can form several molecular layers. Both processes are exothermic. The adsorbents used in water treatment to remove pollutants can be organic, mineral, or biological materials.[106]

Metal ions and anionic species are primarily removed through chemical treatment processes. In this process, a chemical reagent is introduced, where it reacts with the impurities to precipitate solid material. Therefore, the contaminants are eliminated by decantation and filtration utilizing membrane- or cellulose-based filter paper. Studies on precipitating agents combined with cellulose for the co-precipitation of metal ions, such Cd^{2+} and Cu^{2+} ions, respectively, were reported by Qin *et al.* and Zhu *et al.*[50,51] The precipitate is mostly filtered using Whatman cellulose filter paper.

PREPARATION METHODS

Synthesis of nanocellulose

Due to its accessibility, good mechanical properties, renewability attributes, low density, biodegradability, and high reinforcing capabilities, nanocellulose (NC) has recently attracted a lot of research interest,[12,13] especially for biomedical applications, as well as in cosmetics and food packaging.[14-16,52,53]

Nanocelluloses can be classified in: cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). Different techniques, like physical, chemical, biological, or a combination of these can be used to prepare these nanoscale materials.[54] Some preparation techniques are illustrated in

Figure 3. CNCs are most frequently prepared using sulfuric acid-mediated hydrolysis, in which the surface hydroxyl groups are simultaneously esterified to produce sulfate ester groups and the hydrolysis of the glycosidic bonds facilitates the removal of the amorphous cellulose segments.[55] The sulphuric acid method has a few disadvantages, though, which limit its use.[14-16,56-59]

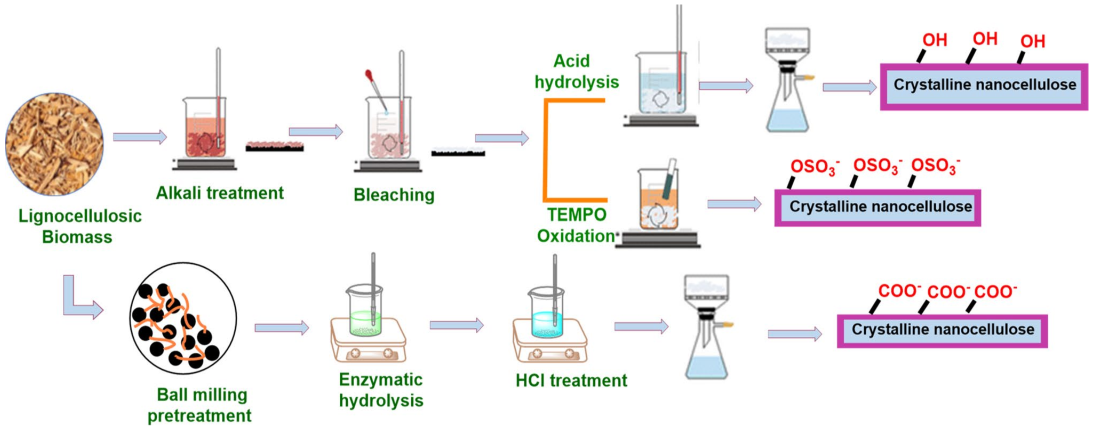

Figure 3: Preparation and surface modification techniques of nanocellulose

These downsides include equipment corrosion, the poor heat stability of CNCs, and high salt disposal costs. Other acids, such as hydrochloric acid, acetic acid, maleic acid, nitric acid, phosphoric acid, and hydrobromic acid have also been mentioned in the literature.[60-63] However, these acids promote aggregation in most polymers and liquids because of the many surface hydroxyl groups and the resultant intra- and intermolecular hydrogen bonding interactions.

Cellulose nanofibers (CNFs) are primarily produced through mechanical processes, with high-pressure homogenization being the most commonly used method. However, this technique often leads to clogging due to the direct feeding of untreated biomass into the homogenizer. To overcome this challenge, TEMPO-mediated oxidation can be employed to produce TEMPO-oxidized cellulose nanofibers (TOCNFs) in a mild aqueous environment. This chemical pre-treatment disrupts the hydrogen bonding network within the cellulose fibers, softening the rigid regions and thereby reducing the risk of clogging. TOCNFs typically have diameters of 3-4 nm and lengths of several microns.[64,65] According to the oxidation conditions, such as TEMPO/NaBr/NaClO at room temperature (RT) at pH 10 or TEMPO/NaClO/$NaClO_2$ at 60 °C, at pH 6.8, fibrils are produced with an average carboxylate content of 1.0–1.8 mmol/g. The steric barrier of the methyl groups of TEMPO molecules causes the oxidation process to be selective at the site of the C6-hydroxyl groups. Large negative zeta potential (75 mV), high aspect ratio (>100), and high crystallinity (65–95%, Table 1) are all characteristics of TOCNF.

Table 1
Comparison of different types of nanocelluloses

Parameter	CNFs	CNCs	TOCNFs
Preparation method	High pressure homogenization	Strong acid hydrolysis	1) TEMPO/NaBr/NaClO oxidation 2) Mild disintegration
Diameter	10-2000 nm	5-70 nm	3-10 nm
Size distribution	Polydisperse	Polydisperse	Polydisperse
Optical properties	Iridescent	Transparent	Transparent
Functional groups	O-H	OH OSO_3^{-} * OPO_3^{-} *	OH CHO COO^-
Cost	Low	Moderate	High

* differs as a function of the acid used during acid hydrolysis

It is important to note that CNCs with the highest carboxyl content, 2.2 mmol/g, and a zeta potential of 41 mV were produced by environmentally friendly oxidation of microcrystalline celluloses (MCCs) employing an oxidant of Fe^{2+} and H_2O_2.[66] The high abundance, high specific surface area, high surface-to-volume ratio, superior mechanical properties in aqueous medium, surface functional groups, and surface charge density are some of the properties of NCs, which recommend their use in wastewater treatment.

Preparation of cellulose-based aerogels

Cellulose is one of the most abundant renewable biopolymers on earth and it exists in all plant cells and algae, or can be synthesized by bacteria or tunicate. Cellulose based materials have gained a huge momentum in the past decade as new materials and the results are promising. Due to their high aspect ratio,[67] colloidal stability in aqueous media,[68] liquid crystalline properties,[69] and biocompatibility,[70] they have been used in a wide range of applications, including but not limited to electronics,[71,72] biomedical,[73] and lab-on-chip technologies.[74] The technological developments related to extraction of cellulose have been covered in full in several excellent review publications over the years.[13,75-80]

Aerogels were first discovered in the 1930s[17] through inorganic materials. This meant that the inorganic aerogels lacked key properties, such as mechanical flexibility, which limited their overall application, as opposed to their organic counterparts. Hence, the organic aerogels were discovered due to the sustainability of their precursor, mechanical flexibility and the ability to functionalise their surface to improve its overall properties.[18] Thus far, biopolymer-based aerogels have been synthesized from organic precursors, such as cellulose, chitosan, alginate, starch and pectin.[19] This review will focus on the cellulose-based aerogels.

There are two steps involved in the creation of aerogels. The initial process is the creation of the hydrogel, which is followed by the solvent being drained away through either supercritical, freeze, or oven drying methods. Maintaining the porosity cellular structure while the aerogel is drying is the most difficult and important stage in the production process. To reduce shrinkage caused by the capillary pressure the evaporating solvent applies, water must be replaced with a solvent with low interfacial tension, such as tertiary butanol.[81]

Cellulose-based aerogels can be derived from various sources of cellulose, such as cotton, wood pulp, or bacterial cellulose. For cross-linking, compounds like epichlorohydrin can be employed to create a stable gel structure. The process involves a dissolution step, by breaking down the cellulose structure until to the level of macromolecular chains, in the presence of different solvents, in order to achieve a uniform suspension. Subsequently, the cross-linking agent is added, allowing gelation to occur, followed by aging to solidify the gel. Drying methods involve either freeze-drying, which sublimes the frozen solvent under vacuum conditions, or supercritical drying, where a supercritical fluid like CO_2 replaces the solvent.

Aerogels are created using a two-step technique, as was already described. To increase functionality and mechanical stability, some aerogels also need a third phase known as post processing (annealing, surface modification, mechanical or thermal crosslinking). Aerogels made of cellulose have a limited range of applications due to their poor thermal stability, brittle structure, and intrinsic flammability.[82] Due to the greater functionality and tunability brought about by combining the intrinsic features of the organic/inorganic and cellulose components, the recent development of the cellulose-based hybrid aerogels has greatly broadened the range of applications for these materials.

Gel formation

To create hybrid aerogels, functional elements like metal organic framework (MOFs), silica, graphene, graphene oxide (GO), chitosan, and other synthetic or natural polymers have been combined with cellulose. Understanding how many components can be integrated during the fabrication process is critical when determining the performance and stability of the hybrid material. Generally, there are two methods for creating cellulose-based hybrid aerogels: chemical crosslinking and physical crosslinking. In contrast, the functional components are created during chemical integration when the cellulose precursor is present, which strengthens the interaction by creating a chemical bond between the cellulose component and the functional material.[83,84]

Physical crosslinking

Cellulose alone or cellulose with various organic or inorganic materials is mixed with different solvents, in order to create a gel. The common solvents include water, organic-based solvents like ethanol, acetone, methanol, tertiary butanol, and N,N-dimethyl formamide, as well as mixed solvents like water-toluene and water-ethanol. In this type of crosslinking, the structure of the hybrid aerogel is controlled by physical entanglement between the cellulose chains and the other components, or by different interactions, like hydrogen bonding, van der Waals interactions and electrostatic interactions.[82] However, weak interactions between precursors, which lead to reduced mechanical stability of hybrid aerogels, are a major disadvantage of this type of crosslinking.[82] Furthermore, the non-homogeneous mixing between components is possible, which would give to the final aerogel a non-uniform structure.[85-87]

Chemical crosslinking

Chemical crosslinking requires the use of crosslinking agents, such as epichlorohydrin, carboxylic acids, aldehyde-based agents, *etc.*[88,89] Chemical crosslinking of macromolecular chains is achieved through different types of reactions: ring-opening reactions (crosslinking reaction occurs between the epoxy group of the cross-linker and the hydroxyl group of cellulose) or by free radical polymerization, by a Schiff base, *etc*. Unlike the physical crosslinking strategy, the fundamental benefit of the chemical crosslinking approach is the creation of much stronger and irreversible covalent bonds between the components of the aerogel.

Aerogel fabrication

The most important phase in the entire aerogel fabrication process is the solvent removal, while keeping the aerogel's porous structure. A distorted aerogel or, to a lesser extent, the collapse of the aerogel can be caused by improper solvent removal.[90] It is important to note that the solvent removal approach affects both the structure and the physicochemical properties of the cellulose-based hybrids. There are three primary solvent removal processes used for fabricating aerogels, as depicted in the phase diagram in Figure 4 (*i.e.*, oven drying, freeze drying, and supercritical drying). The simplest way of solvent removal is accomplished either by increasing temperature at ambient pressure (ambient drying, Fig. 4 path b) or by decreasing pressure at a constant temperature (vacuum drying, Fig. 4 path a).[19] When mesoporous structure and low density are not desired characteristics from the resulting aerogels, path a is appropriate.

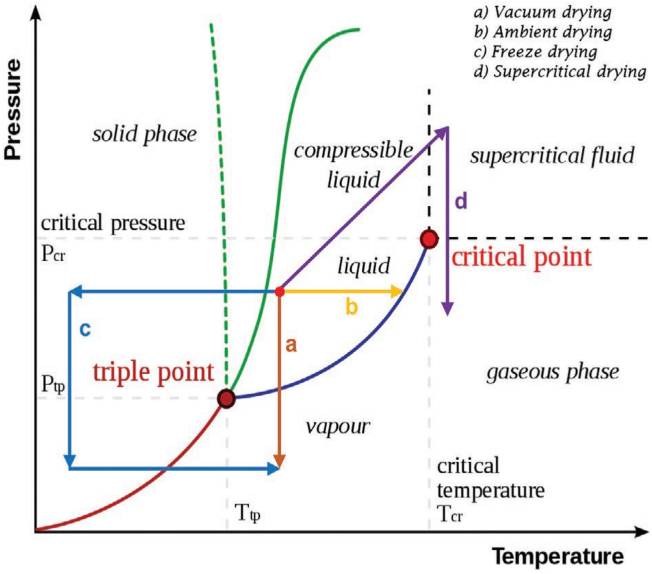

Figure 4: Temperature-pressure paths in various solvent removal techniques during the manufacture of aerogels[19]

The most popular technique for creating cellulose-based hybrid aerogels is freeze drying, which can be done without solvent exchange (using direct freezing) or by using organic solvent exchange. In the first method, the aerogel is frozen to a temperature below the freezing point of the liquid medium (water), after which the liquid is removed by sublimation. In the second lyophilization method, the solvent in the hydrogels is initially replaced with tertiary butanol, followed by freezing and sublimation. By reducing capillary forces and the subsequent growth of the liquid-gas interface, this method preserves the mesoporous structure of the final aerogel. The first stage in this procedure is the freezing process, dry ice or liquid nitrogen is used to drop the temperature beneath the triple point of the solvent.[91] For the creation of cellulose-based hybrid aerogels, tertiary butanol and water are frequently employed solvents because they quickly approach triple points of 20 ºC, 39.37 millibar, and 0 ºC, 6.11 millibar, respectively. However, cellulose-based hybrid aerogels are also prepared using other solvents, such as ethanol, acetone, and methanol.[92]

The third technique, known as supercritical drying, has been utilized to remove solvents without creating liquid-gas interfaces or the capillary forces that occur from them. The solvent is moved to the supercritical zone, while performing the supercritical drying by simultaneously increasing temperature and pressure, followed by a decrease in pressure (Fig. 4 path d). Due to the high critical pressure and temperature of common solvents (*i.e.*, 374 ºC and 221 bar for water, which can degrade the cellulose structure[92]), the solvent is frequently replaced by supercritical fluids, as a rule, carbon dioxide (CO_2). This is due to its (a) easily reachable supercritical point at 31.3 ºC and 73.9 bar, (b) safe nature in preventing thermal degradation of the cellulose structure, and (c) low cost. Although supercritical drying has historically been thought of as a classic method for creating cellulose-based hybrid aerogels, its use is constrained by how difficult and expensive it is.[19,88,93]

Aerogel post-processing

Manufactured cellulose-based hybrid aerogels sometimes have insufficient functionality in their unprocessed state, which must typically be improved by various post-processing procedures. The functionality of these aerogels is increased through the application of surface modification, annealing, and thermal or chemical crosslinking.[91,94,95] The hybrid aerogel's mechanical flexibility and robustness can also be enhanced by post-processing techniques. For instance, Pirzada *et al*. enhanced the chemical connection between cellulose diacetate (CDA) and silica via thermal treatment, which increased the mechanical flexibility of CDA-silica hybrid aerogel.[91] A cellulose nanofiber–metal organic framework (CNF-MOF) hybrid aerogel was given new functionality by Fei *et al*. by being annealed at various temperatures between 700 and 900 °C. Their aerogels developed into powerful electromagnetic radiation adsorptive materials, making them useful for EMI shielding.[96]

APPLICATIONS IN WASTEWATER TREATMENT

Removal of heavy metals

Most of the ground and surface water contamination with metal ions, such as mercury (Hg), arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), and others, which are toxic or carcinogenic and non-biodegradable in nature, is caused by natural weathering and anthropogenic processes (agricultural, industrial, wastewater, mining, and metallurgical). For the treatment of polluted waters, methods like adsorption, membrane, ion exchange, and coagulation/flocculation are frequently used to remove metal ions and other impurities (Fig. 5). From the literature, it is evident that CNMs have been widely studied for their potential to remove different metal ions from wastewater.[97] Most sorption investigations are typically conducted using mixed metal ion salt solutions and lower concentration single salt solutions. The density of functional groups, the ionization potential of the functional groups present on CNFs and CNCs, and the status of metal ions in solution, all of which are pH-dependent, determine the absorption capacity. Since most metal ions are cationic (have a positive charge) in nature, their electronegativity is crucial for adsorption via complexation and ion exchange mechanisms. The adsorption of metal ions is decreased at low pH due to protonation of anionic groups (carboxylic, phosphate and sulphate) present on the nanocelluloses, whereas the adsorption process is favoured at higher pH levels. In order to extract metal ions, it is crucial to optimize the pH of the metal ion solution.[98]

The predominant adsorption process for nanocellulose containing amino functional groups is complexation (chelating action), in which amino groups function as ligands. Increasing pH can reduce protonation of amino-modified cellulose and increase the adsorption capacity through complexation. Due to the protonation of amine groups at acidic pH, ion exchange mechanisms play a significant role in the adsorption of metal ions,[99] while quaternary amine-functionalized CNCs can successfully bind negatively charged arsenic species.[100] By washing with ethylenediamine tetra-acetic acid (EDTA) or a diluted solution of nitric acid, hydrochloric acid, or sulfuric acid, nanocelluloses (CNFs and CNCs), as well as metal ions, can be regenerated. Additionally, there is a relation between the ability of nanocellulose to remove metal ions and its ability to regenerate. It has been observed that as metal ion affinity for nanocellulose increases, so does its ability to regenerate.[101]

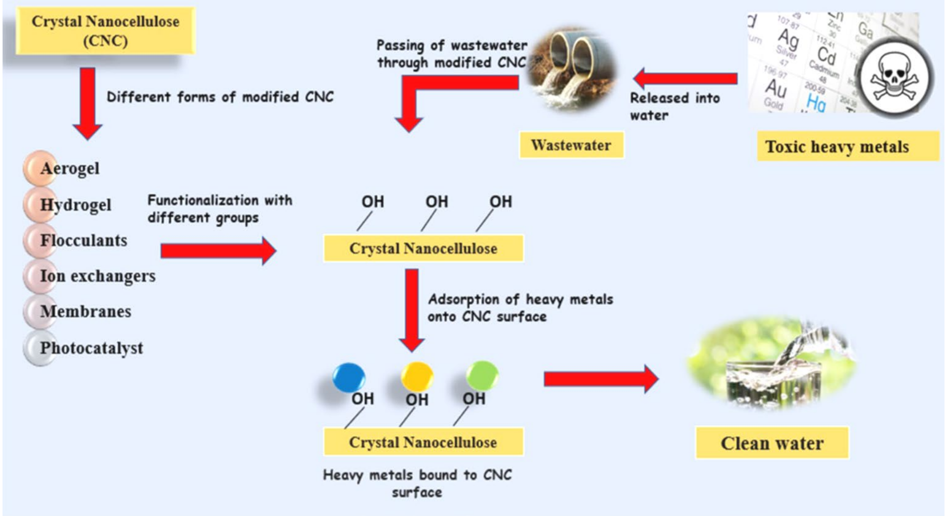

Figure 5: Removal of toxic heavy metals using functionalised cellulose-based adsorbents[97]

Extraction of dyes from contaminated water

The main consumers of dyes are the pharmaceutical, textile, pulp and paper, and leather tanning industries. Industrial effluents from these industries are the main sources of organic dyes, which significantly pollute natural water bodies. Also, the by-products of dye degradation are inherently carcinogenic. Electrochemical coagulation, reverse osmosis, nanofiltration, and adsorption techniques are therefore being used for the treatment of wastewater containing dyes in order to prevent harmful effects on human health.[102]

Adsorption is a more efficient and cost-effective approach for removing colour from wastewater. It is possible to conduct an adsorption study in a static or dynamic manner. In the static mode, cellulose materials are distributed in a diluted dye solution and the solution is examined at various time intervals until equilibrium is attained. Here, the initial equilibrium concentration of the dye solution determines the adsorption capacity. To determine the maximal theoretical dye adsorption capacity, experimental data are then fitted using the Freundlich or Langmuir isotherm models. In the dynamic mode of operation, a dye solution is continuously pumped through a nanocellulose-packed column.[103] Various time intervals are used to determine the dye concentration in the eluent. Here, the flow rate, the initial dye solution concentration, and the physical properties of the adsorbent, namely, surface area, aspect ratio, and morphology all affect adsorption capacity.

The interaction between a dye and a nanocellulose molecule depends on the functional groups on the nanocellulose and the dye molecules.[104] Dyes can be cationic, anionic, or non-ionic in nature. Typically, cationic functionalized nanocellulose is used to remove anionic dyes, such as acid red GR, Congo red 4BS, and reactive yellow K-4G; while sulfonated, carboxylated or anionic functionalized nanocellulose is used to adsorb cationic dyes like basic fuchsin, methylene blue, malachite green, and crystal violet.[105] Due to the dissociation of ionic or functional groups on the adsorbate and adsorbent molecules, the strength of electrostatic attraction and ion exchange capacity is pH dependent.[106] By using an appropriate eluent, such as ethanol or a diluted acid solution, to desorb the colours from the CNMs, cellulose nanomaterials can be regenerated.

Adsorption mechanism of heavy metal ion removal

Heavy metal ion adsorption is widely reported in the literature to occur through complexation interactions between the metal centres and specific anionic surface functional groups on the adsorbent, typically forming either monodentate or bidentate complexes.[107] Furthermore, electrostatic interactions can also result in the adsorption of heavy metals.[108] A gelation agent, such as $CuSO_4$ and $CaCl_2$, can crosslink the easily changeable hydroxyl functional groups on the surface of nanocellulose to generate hydrogel beads. Crosslinking is also encouraged by surface alteration through carboxylation due to COO^- groups. As a result, the high density of negative charges and abundance of hydroxyl and carboxyl groups on the surface of nanocellulose are advantageous for the adsorption of heavy metal ions.[109] A possible process for the adsorption of heavy metals onto carboxylated cellulose nanocrystal-alginate hydrogel beads is shown in Figure 6.

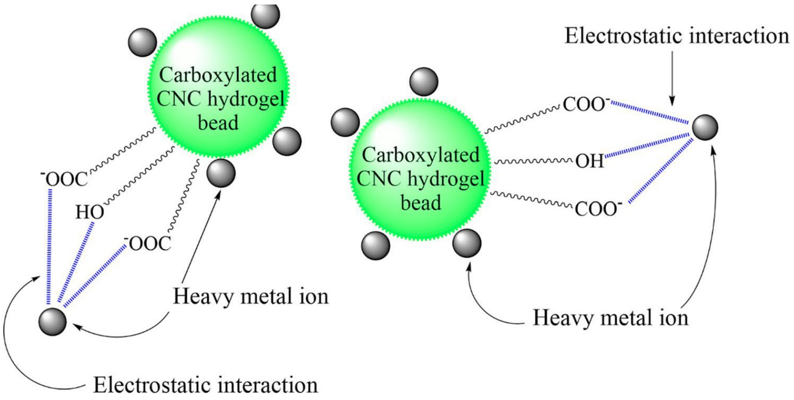

Figure 6: A plausible mechanism for the adsorption of heavy metals onto carboxylated cellulose nanocrystal (CNC)-alginate hydrogel beads[109]

According to a study by Abou-Zeid *et al.*, alginate-based nanocellulose hydrogel beads with a greater carboxylate content and more granular structure are more effective at removing divalent cations.[110] Due to having cations, Cu^{2+}, Pb^{2+}, Mg^{2+}, and Fe^{2+} adhere to alginate-nanocellulose hydrogel beads. Three types of nanocellulose were combined with alginate to create bio-polymeric beads, including tricarboxylic acid-cellulose nanofibers, 2,2,6,6-tetramethylpiperidine-1-oxyl-oxidized-cellulose nanofibers, and cellulose nanocrystals (microcapsules). Excellent cation removal efficiency was recorded for 2 g of alginate-tricarboxylic acid-cellulose nanofiber beads at pH 6-7, with 2 mmol g^{-1} carboxylate content, namely, up to 92% for Cu^{2+} and 95% for Pb^{2+}.[110,111]

Bagasse pulp was used to make cellulose nanocrystals, 2,2,6,6-tetramethylpiperidine-1-oxyl-oxidized cellulose nanofibrils, and tricarboxylic cellulose nanofibrils, among other nanocelluloses.[112] Using modified carrageenan gel beads and nanocellulosic materials, the cations were removed with a high removal efficiency. In comparison with other modified nanocellulose-based beads, the study found that 1 g of carrageenan-tricarboxylic cellulose nanofibril hydrogel beads soaked for 2 hours achieved the highest levels of detoxification efficiency, up to 83 and 91% for Pb^{2+} and Cu^{2+}, respectively. This may be due to the higher carboxylate content (2 mmol g^{-1}) on the tricarboxylic cellulose nanofibril surface than other nanocellulose forms. Images taken using scanning electron microscopy showed that carrageenan beads treated with tricarboxylic cellulose nanofibrils had rougher surfaces and more noticeable irregularities in their spheres, which may play a key role in their increased capacity for detoxification.[112] The research study concluded that, in contrast to other surface functional groups, carboxylic groups lead to enhanced binding capability toward heavy metal ions.

Both aerogel and hydrogel beads made of nanocellulose can be used to successfully remove chemical pollutants from wastewater. To efficiently detoxify Cu^{2+} and Pb^{2+} ions in aqueous solutions, Li *et al.* created novel mesoporous 2,2,6,6-tetramethylpiperidine-1-oxyloxidized nanocellulose/alginate/carboxymethyl chitosan aerogel beads by crosslinking them in $CaCl_2$ solution.[113] The maximum adsorption capacities were achieved at 30 °C and pH 5, while shaking the suspensions for 24 hours. Because Pb^{2+} ions have a larger ionic radius than Cu^{2+} ions, they may have a stronger affinity for the anionic binding sites of nanocellulose and carboxymethyl chitosan, leading to increased adsorption capacity and removal adsorption efficiency. According to the study, nanocellulose had a 1.74 mmol g^{-1} carboxyl content, indicating that a significant amount of the hydroxyl groups in nanocellulose were oxidized by

2,2,6,6-tetramethylpiperidine-1-oxyl to form –COOH.[109] The carboxyl (-COOH) and hydroxyl (-OH) strong binding sites of 2,2,6,6-tetramethylpiperidine1-oxyl-oxidized nanocelluloses, as well as the hydroxyl (-OH) groups of carboxymethyl chitosan, and amine (-NH_2), were found to be involved in the adsorption of the heavy metal ions, according to X-ray photoelectron spectroscopy analysis.[113] The effects of optimal nanocellulose loading, pH, and background/co-existing/interfering ions on the rate of heavy metal ions adsorption were examined. Aerogel beads were shown to have the maximum adsorption capacity at 0.7 g of nanocellulose loading. Because nanocellulose and alginate are more electrostatically attracted to one another, higher nanocellulose loading significantly lowered the adsorption capacity. Due to the availability of deprotonated hydroxyl, carboxyl, and amine ions (free form) on the aerogel bead surface, the adsorption rate increased with increasing pH from 2.0 to 5.0. Investigating how interfering ions (Ca^{2+}, Na^+, and Mg^{2+}) affected the elimination of Cu^{2+} revealed that Ca^{2+} had a significant impact, but Na^+ had the least interfering effect.[113] Ion adsorption is higher with a smaller hydrated radius because pore penetration is simpler. A comparable chemical adsorption mechanism was put forth by Zhao *et al.* A shift in the binding energies of C=O and C-O, which correspond to the -COOH and -OH groups, was discovered by X-ray photoelectron spectroscopy study.[114] The participation of these functional groups raises the possibility that electrostatic attraction and complexation may play a significant role in the heavy metal ion adsorption mechanism onto the aerogel beads, which is supported by the results of Fourier transform infrared analysis. C=O, COOH, and O-H stretching vibration peaks were confirmed by Fourier transform infrared analysis at 1635, 1406, and 438 cm^{-1}, respectively.[114] The influence of the solution pH in the range of 2–6 was investigated by the authors since the adsorption mechanism was primarily controlled by electrostatic attraction and complexation. The hydrogel beads were discovered to be negatively charged across the whole pH range, supporting the adsorption mechanism of Pb^{2+}. The adsorption capacity was shown to be positively associated with temperature, according to the effect of solution temperature on the adsorption process.[114]

Ren *et al.* noted that the interaction (chelation) between unoccupied orbitals in Pb^{2+} and the lone pair electrons on oxygen, namely the -OH and -COO groups (Fig. 6), led to the adsorption kinetics of Pb^{2+} uptake by sodium alginate-carboxymethyl cellulose hydrogel beads primarily via chemical adsorption mechanism.[115] A plausible mechanism for the adsorption of heavy metals onto carboxylated cellulose nanocrystal (CNC)-alginate hydrogel beads has been proposed. The carboxylated cellulose nanocrystal-alginate hydrogel beads can form electrostatic attraction forces with the heavy metal cations due to the hydroxide (OH^-) and carboxylate (COO^-) groups that are present on their surface. The effective adsorption of heavy metal ions onto the gel beads made of alginate and carboxymethyl cellulose is made possible by these electrostatic interactions.[115]

Due to the high surface area and porosity obtained through functionalization using carboxymethyl cellulose crosslinking, providing more adsorption sites for Pb^{2+} and adsorption through electrostatic interactions, adsorption isotherm modelling and structural characterization analyses validated that the adsorption mechanism could also rely on physical adsorption. Positively charged Pb^{2+} cations adhered to the negatively charged alginate-carboxymethyl cellulose gel bead surface through electrostatic adsorption. The scientists looked at the impact of solution pH (pH 2-6) on Pb^{2+} removal because it has a significant impact on the ionization of functional groups on the adsorbent, surface charge at adsorption sites, and solubility of heavy metal ions. The maximum lead ion uptake was observed in solutions with pH values of 5, where there was abundant free COO^- groups that facilitated chemical adsorption.[115]

According to the hypothesis of Xu *et al.*, Pb^{2+} adsorption by carboxylated cellulose nanocrystal-carboxylated chitosan aerogel beads could progress through chemisorption involving amino (NH_2) and hydroxyl (OH^-) groups on the hydrogel beads, as well as electrostatic attraction between the carboxyl (COO^-) groups and Pb^{2+}.[128,129] The pseudo-second-order model more accurately captured the kinetics of adsorption, and the adsorption behaviour was compatible with the Langmuir isotherm, indicating monolayer adsorption. Due to the abundance of functional groups, the initial rate of adsorption was quick, and at equilibrium, the removal of Pb^{2+} reached up to 96.73%.[129]

Li *et al.* investigated the adsorption mechanism of Hg^{2+} and Cu^{2+} by modified porous microcrystalline cellulose beads.[133] According to their X-ray spectroscopy study, the functionalized bead surface's -NH_2 and -NH moieties interacted with heavy metal ions through coordination bonds (chelation). At the same time, heavy metal ions received electron donations from lone pairs of electrons on oxygen atoms in the C=O and C-O groups through the development of electrostatic interactions.[109] Similar results on the adsorption method for the Cu^{2+} uptake by mesoporous nanocellulose-alginate-carboxymethyl chitosan aerogel beads were published in another study.[113]

The application of the preliminary chemical crosslinking approach during the synthesis of cellulose-based beads was shown to significantly enhance porosity, specific surface area, and mechanical strength in a study by Qiao *et al.*[134,135] For batch adsorption tests of Cu^{2+} removal, the researchers used super porous microcrystalline cellulose beads modified with glutamic acid. Then, they investigated the adsorption mechanism using the Freundlich and Langmuir isotherm models. Glutamic acid was chosen as the functional ligand due to its plentiful N and O donor atoms and straightforward chemical structure, in addition to being non-toxic. According to the Langmuir isotherm, the corresponding isotherm adsorption parameters were better defined, suggesting monolayer adsorption on the porous surface.

Table 2

Cellulosed-based hydrogel/aerogel beads for adsorptive removal of heavy metals and dyes in contaminated water

Adsorbent	Pollutant	Q$_{max}$ (mg g^{-1})	Adsorption mechanism	Recyclability	Ref.
Cellulose-based hydrogels					
Carboxymethyl cellulose-alginate/ graphene oxide hydrogel beads	MB	78.5	Electrostatic interaction, π-π staking and hydrogen bonding	4	116
Bleached almond shell derived cellulose hydrogel beads	Cu^{2+}	128.24	Valence forces through sharing or exchange of electrons	2	117
STMP-modified porous cellulose hydrogel beads	Pb^{2+}	150.6	Chelation	2	118
Hollow PEI grafted CMC beads	Cr^{6+} Phosphate	568.62 136.38	Electrostatic attraction with reduction effect	622	119
β-Cyclodextrin grafted cellulose beads	Bisphenol A	30.77	Formation of inclusion complexes via host-guest interactions	4	120
Modified activated carbon embedded magnetic cellulose-based beads	Cu^{2+} Pb^{2+} Zn^{2+}	47.64 37.99 22.30	Electrostatic attraction	5	121
Diethyl diallyl ammonium chloride grafted chitosan/genipin/cellulose hydrogel beads	Reactive red 195 MO	1333.5 190.48	Chemisorption involving sharing or exchange of electrons	55	122,123
Glutaric anhydride-grafted porous ferromagnetic microcrystal cellulose Fe$_3$O$_4$ beads	MB Rhodamine B	1186.8 151.8	Outer-sphere surface complexation at low pH and inner-sphere surface complexation at high pH	55	124
PEI-grafted porous cellulose beads	MB Rose Bengal	1550.6 467.95	Electrostatic and hydrogen bonding electrostatic interaction	88	125
CNM-based hydrogels					
CNC-alginate hydrogel beads	MB	256.41	Physisorption	5	126
Carboxylated CNC micro-beads	MB	130	-	-	127
Sodium trimetaphosphate (STMP) modified CNF hydrogel beads	Cu^{2+}	147.9	Surface complexation and ion exchange	2	116
Caboxylated CNC-carboxylated chitosan hydrogel beads	Pb^{2+}	334.92	Chemical and electrostatic adsorption	4	128, 129
CNM-based aerogels					
Polyethyleneimine (PEI) grafted CNF aerogel beads	Cu^{2+}	126.1	Chemisorption through chelation	5	130
(ZIF-8)-(TEMPO-CNF)	Rhodamine B	83.3	-	-	84
(ZIF-8)-CNF	Cr^{6+}	35.6	-	-	131
(ZIF-67)-Chitosan-BC	Cu^{2+} Cr^{6+}	200.6 152.1	- -	- -	132
(UiO-66)-CNC	Cr^{6+}	6.1	-	-	83
(MIL-100(Fe))-CNC	Rhodamine B	2.32	-	-	83
(ZIF-8)-CNC	Rhodamine B	39.06	-	-	83

The initial chemical crosslinking reaction produced super porous, microcrystalline cellulose beads with a large surface area, and as a result, the Cu^{2+} adsorption capacity increased to 98.86 mg g^{-}

^{1}.[135] Table 2 summarizes a comparison of cellulose-based beads for the adsorptive removal of various contaminants in aqueous solutions from current research.

Adsorption mechanism of dyes ion removal

In addition to ion-exchange, electrostatic interactions, and hydrogen bonding, complexation, van der Waals forces, and π-π interactions can also drive adsorption in the direction of dye removal[136] (Fig. 7). A group of researchers investigated the methylene blue's capacity to bind to cellulose nanocrystal-alginate hydrogel beads in aqueous solutions.[126] They revealed through thermodynamic research that the uptake of methylene blue by aerogels beads was solely a physisorption process. Based on the study by Ding *et al.*, porous aerogels beads with polyethyleneimine grafted onto them were more effective and capable of adsorbing more methyl blue than rose Bengal.[125] They emphasized that the availability of N-containing groups and three sulfonic acid groups in methylene blue, as opposed to one carboxyl group and multiple halogens (I and Cl) in rose Bengal, was the reason for the better adsorption performance. They concluded that electrostatic attraction was the dominant adsorption mechanism for rose Bengal dye. Due to the electron-rich functional groups, hydrogen bonds and van der Waals forces were the main adsorption processes in the removal of methylene blue.[125] Since both dyes have conjugated rings, π-π interactions might possibly take place to some extent. Also, they looked at the zeta potential of porous cellulose beads with polyethyleneimine grafts and how the pH of the solution affected the chemical structure of the dyes. For rose Bengal, a pH range of 2–10 was chosen, whereas pH 3–10 was tested for methyl blue. According to the findings, solution pH had no discernible impact on the uptake of the methyl blue dye. Rose Bengal anionic dye's adsorption capacity gradually decreased from pH 2 to 10, with a sharp loss in adsorption capacity seen at pH 2-4. The protonation of amine groups in cellulose beads produced a positively charged surface, increasing the adsorption capacity at low pH.[109] The presence of OH ions, which would compete with anionic rose Bengal to be adsorbed onto the bead surface, correlated to the reduced adsorption capacity at high pH. Hence, electrostatic attraction controlled the adsorption behaviour of rose Bengal, according to the results of pH analyses.[125]

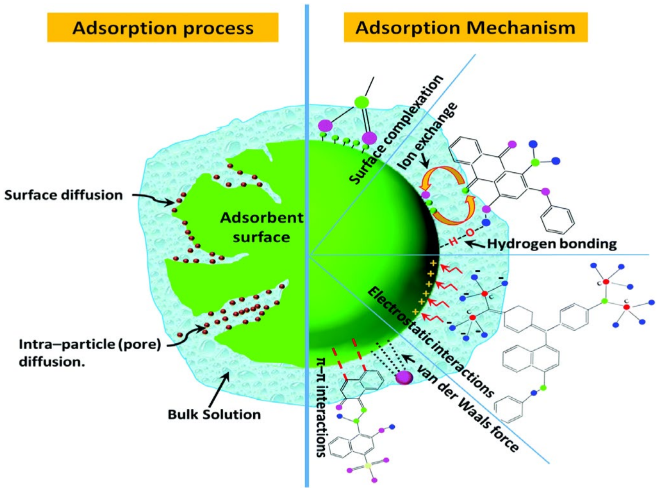

Figure 7: Adsorption processes and mechanisms for dye removal from contaminated water[137]

Li *et al.* hypothesized that inner-sphere surface complexation at high pH and outer-sphere surface complexation at low pH governed the adsorption mechanisms for methylene blue dye and rhodamine B dye uptake by glutaric anhydride-grafted porous ferromagnetic microcrystalline cellulose/Fe_3O_4 aerogels beads.[124] The effects of pH on methylene blue dye and rhodamine B dye uptake were observed by the researchers, and this was attributed to the variable surface charge characteristics of the adsorbents affected by the varied pH values of methylene blue dye and rhodamine B solutions. Due to the deprotonation of carboxyl groups in the porous ferromagnetic microcrystalline cellulose/Fe_3O_4 beads with increasing pH, the adsorption capacity of microcrystalline cellulose/Fe_3O_4 beads increased with increasing pH from 1 to 9 in the case of methylene blue adsorption. Deprotonation thus led to strong electrostatic attraction, which is what produced the high methylene blue adsorption capacity. On the other hand, because the porous ferromagnetic microcrystalline cellulose/Fe_3O_4 beads' carboxylic group content would be lower at pH values above 9, their adsorption ability was decreased. The dye adsorption process using rhodamine B showed a similar pattern.[124]

Liu *et al*. investigated the adsorption behaviour of dimethyl diallyl ammonium chloride-grafted chitosan/genipin/cellulose aerogel beads and established the adsorption mechanism of methyl orange and reactive red 195.[122,123] Due to the high density of available adsorption sites and the high concentration of dyes, methyl orange and reactive red 195 showed quick initial adsorption on the produced cellulose-based hydrogel beads. The adsorption rate, however, steadily dropped after the abrupt increase in adsorption capacity until a steady-state adsorption equilibrium was attained. Methyl orange and reactive red 195 anionic dyes were able to bind to hydrogel beads through strong hydrogen bonds and electrostatic attraction. At a temperature of 30 °C, they investigated the impact of pH on the reactive red 195 dye adsorption. The adsorption capability toward reactive red 195 gradually decreased as pH was raised.[122] Chitosan's amino groups protonate to NH_3^+ (a positively charged adsorbent) under acidic conditions, which makes reactive red 195 binding easier. It was noted that at high pH, the medium would include more hydroxide ions, where the OH ions would compete with the anionic dyes for adsorption, resulting in decreased adsorption capacity. The quaternary ammonium protonated amino groups, and sulfonate (SO_3^-) groups of anionic dyes interacted in the hydrogel beads.[123]

The scientists found that the adsorption capacity of reactive red 195 (1333.52 mg g^{-1}) was significantly larger than the value obtained for methyl orange (190.48 mg g^{-1}).[123] The apparent discrepancy might be explained by the fact that reactive red 195 contains a high concentration of sulfonate groups, but methyl orange only contains one SO_3^- group. González-López *et al.* hypothesized that electrostatic interactions between the sulfonate and amine groups in Congo red and the OH groups in cellulose, as well as secondary interactions between the π orbitals of aromatic rings, were responsible for the adsorption of Congo red onto the cellulose-based graphene nanoplatelets aerogel beads.[109]

CONCLUSION

To solve the issues of polluted wastewaters and freshwater contamination, the use of organically produced raw materials to create efficient and affordable adsorbents has attracted considerable attention. The treatment of wastewater for the removal of heavy metal ions, dyes, and other organic pollutants has been proven efficient through the use of cellulose-based aerogels, which include a three-dimensional polymeric network of hydrophilic groups. Functionalized cellulose-based gel materials have shown great promise for the removal of a variety of chemical species from water bodies due to their beneficial qualities, including high abundance, low biological toxicity, recyclability and reusability, low cost, biodegradability and high adsorption capacity. Their three-dimensional polymeric network, rich in hydrophilic groups, contributes to their high adsorption capacity and allows for interactions with various chemical species. The use of natural polymers to prepare such materials makes them environmentally friendly alternatives to those based on conventional synthetic polymers. The surface functionalization of cellulose-based gels can significantly improve their adsorption properties, although this comes at a higher production cost. Despite this, their potential for regeneration and reusability provides a sustainable edge. Still, further studies are required to optimize the regeneration processes, without compromising their structural integrity or adsorption performance.

Cellulose-based aerogels, specifically, offer a unique set of advantages, including ultralight weight, high porosity, superior mechanical strength, and thermal stability. Their structure facilitates fast and efficient diffusion of pollutants due to a large specific surface area and interconnected pore networks. Functionalizing aerogels with other biopolymers, such as chitosan or with magnetic nanoparticles (*e.g.*, Fe_3O_4 or γ-Fe_2O_3), further enhances their adsorption capabilities and allows for easy magnetic recovery – an essential feature for real-world industrial applications. Aerogels have demonstrated stable performance over multiple adsorption-desorption cycles, making them ideal for scale-up and integration into continuous treatment systems.

REFERENCES

[1] H. N. Abdelhamid and A. P. Mathew, *Front. Chem. Eng.*, **3**, 790314 (2021), https://doi.org/10.3389/fceng.2021.790314

[2] D. Zheng, Y. Zhang, Y. Guo and J. Yue, *Polymers*, **7**, 11 (2019), http://doi.org/10.3390/polym11071130

[3] Z. Chen, B. Tang, Y. Niu and H. X. Chen, *Fuels*, **4**, 286 (2021), http://doi.org/10.1016/j.fuel.2020.119287

[4] M. Mariana, K. Abdul, E. M. Mistar and E. Yahya, *J. Water Process. Eng.*, **43**, 102221 (2021), http://doi.org/10.1016/j.jwpe.2021.102221

[5] Y. J. Shih, S. K. Chien, S. R. Jhang and Y. C. Lin, *J. Taiwan Inst. Chem. Eng.*, **100**, 151 (2019), http://doi.org/10.1016/j.jtice.2019.04.017

[6] H. Cheng, C. Chen, S. Wu and Z. Mirza, *J. Clean. Prod.*, **144**, 559 (2017), http://doi.org/10.1016/j.jclepro.2016.12.053

[7] M. Hema and S. Arivoli, *Int. J. Phys. Sci.*, **2**, 10 (2007)

[8] X. Li, Z. Wang, H. Liang, J. Ning, G. Li *et al.*, *Environ. Technol.*, **40**, 112 (2019), https://doi.org/10.1080/09593330.2017.1380712

[9] Y. J. Liu, S. Liu, Z. W. Li, M. J. Ma and B. Mang, *RSC Adv.*, **8**, 7892 (2018), https://doi.org/10.1039/c8ra00012c

[10] S. Liu, *Sci. Adv. Mater.*, **11**, 33 (2019), https://doi.org/10.1016/j.arabjc.2021.103301

[11] J. L. Weidman, R. A. Mulvenna, B. Boudoiris and W. A. Phillip, *ACS Appl. Mater. Int.*, **9**, 19152 (2017), http://doi.org/10.1021/acsami.7b04603

[12] Arserim-Uçar, F. Korel, L. Liu and K. L. Yam, *Food Chem.*, **336**, 127597 (2021), https://doi.org/10.1016/j.foodchem.2020.127597

[13] Y. Haibo, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, **110**, 3479 (2010), http://doi.org/10.1021/cr900339w

[14] H. Ji, Z. Xhiang, H. Qai and T. Han, *Green Chem.*, **21**, 1956 (2019), http://doi.org/10.1039/C8GC03493A

[15] N. Pandi, S. H. Sonawane and K. A. Kishore, *Ultrason. Sonochem.*, **70**, 105353 (2021), https://doi.org/10.1016/j.ultsonch.2020.105353

[16] L. Chazeau, Y. Cavaille, G. Canova, R. Dendievel and B. Boutherin, *J. Appl. Polym. Sci.*, **71**, 1797 (1999), https://doi.org/10.1002/(SICI)1097-4628(19990314)71:11%3C1797::AID-APP9%3E3.0.CO;2-E

[17] S. S. Kistler, *J. Phys. Chem.*, **36**, 52 (2002), https://doi.org/10.1021/j150331a003

[18] M. A. Aegerter, N. Leventis and M. M. Koebel, in "Aerogels Handbook", edited by M. A. Aegerter, N. Leventis and M. M. Koebel, Springer, New York, 2011, p. 891, http://doi.org/10.1007/978-1-4419-7589-8_42

[19] S. Zhao, W. Malfait, N. G. Alburquerque and M. Koebel, *Angew. Chem. Int. Ed.*, **57**, 7580 (2018), http://doi.org/10.1002/anie.201709014

[20] X. Zhang, J. Zhao, L. Chen, C. Lu, Y. Wang *et al.*, *RSC Adv.*, **4**, 98 (2014), https://doi.org/10.1039/C4RA08307E

[21] Z. Zhang, G. Sebe, D. Rentsch and T. Zimmermann, *Chem. Mater.*, **26**, 2659 (2014), http://doi.org/10.1021/cm5004164

[22] X. Wang, Z. Wang, R. Yang and T. M. Yeh, *Polymers*, **55**, 1358 (2014), http://doi.org/10.1016/j.polymer.2013.12.007

[23] J. Zhao, X. Zhang, X. He, M. Xia, W. Zhang *et al.*, *J. Mater. Chem. A*, **3**, 14703 (2015), https://doi.org/10.1039/C5TA03089G

[24] H. P. S. Abdul, C. K. Saurah, A. S. Adnan and M. R. N. Fazita, *Carbohyd. Polym.*, **150**, 216 (2016), http://doi.org/10.1016/j.carbpol.2016.05.028

[25] S. Olivera, K. Venkatesh and V. K. Guna, *Carbohyd. Polym.*, **153**, 600 (2016), http://doi.org/10.1016/j.carbpol.2016.08.017

[26] R. Kumar, R. K. Sharma and A. P. Singh, *J. Mol. Liq.*, **232**, 62 (2017), http://doi.org/10.1016/j.molliq.2017.02.050

[27] D. K. Patel, S. D. Dutta and K.-T. Lim, *RSC Adv.*, **9**, 33 (2019), http://doi.org/10.1039/C9RA03261D

[28] A. Aguilar-Sanchez, B. Jalvo, A. Mauter, V. Rissanen, K. S. Konttuni *et al.*, *RSC Adv.*, **11**, 6859 (2021), https://doi.org/10.1039/d0ra10220b

[29] Y. D. Dong, H. Zheng, G. Zhong and G. Yao, *Chem. Eng. J.*, **405**, 126980 (2021), http://doi.org/10.1016/j.cej.2020.126980

[30] K. Baghdad and A. M. Hasnaoui, *J. Environ. Chem. Eng.*, **8**, 104047 (2020), http://doi.org/10.1016/j.jece.2020.104047

[31] H. N. Abdelhamid and A. P. Mathew, *Carbohyd. Polym.*, **274**, 118657 (2021), http://doi.org/10.1016/j.carbpol.2021.118657

[32] H. N. Abdelhamid, *Curr. Med. Chem.*, **28**, 7023 (2021), http://doi.org/10.2174/0929867328666210608143703

[33] H. N. Abdelhamid and A. P. Mathew, *Chem. Eng. J.*, **426**, 131733 (2021), http://doi.org/10.1016/j.cej.2021.131733

[34] H. N. Abdelhamid and A. P. Mathew, *Front. Chem. Eng.*, **74** (2021), http://doi.org/10.3389/fceng.2021.790314

[35] D. Georgouvelas, H. N. Abdelhamid, J. Li and U. Edlund, *Carbohyd. Polym.*, **264**, 118044 (2021), http://doi.org/10.1016/j.carbpol.2021.118044

[36] R. E. Abou-Zeid, S. Dacrory, K. Ali and S. Kamel, *Int. J. Biol. Macromol.*, **119**, 207 (2018), http://doi.org/10.1016/j.ijbiomac.2018.07.127

[37] B. Ram and G. S. Chauhan, *Chem. Eng. J.*, **331**, 587 (2018), http://doi.org/10.1016/j.cej.2017.08.128

[38] S. Hokkanen, E. Repo and M. Sillanpää, *Chem. Eng. J.*, **223**, 40 (2013), http://doi.org/10.1016/j.cej.2013.02.054

[39] S. Hokkanen, H. Liimatainen, E. Repo and T. Suopajarvi, *Cellulose*, **21**, 1471 (2014), http://doi.org/10.1007/s10570-014-0240-4

[40] G. G. Chan, C. M. Koch and L. H. Connors, *J. Prot. Res.*, **16**, 1659 (2017), https://doi.org/10.1021/acs.jproteome.6b00998

[41] A. Etale, D. Nhlale, A. Mosai and J. T. Mhlongo, *AAS Open Res.*, **4** (2021), http://doi.org/10.12688/aasopenres.13182.1

[42] A. Geng, L. Meng, J. Hen and Q. Zhong, *Cellulose*, **25**, 4133 (2018), https://link.springer.com/article/10.1007/s10570-018-1851-y

[43] H. Fu, S. Ma, P. Zheng and S. Xu, *Chem. Eng. J.*, **360**, 157 (2019), https://link.springer.com/article/10.1007/s10570-019-02344-w

[44] M. El-Achaby and M. R. Ramson, *Cellulose*, **26**, 3873 (2019), https://link.springer.com/article/10.1007/s10570-019-02344-w

[45] C. Sudhakar, A. A. Kumar, R. G. Bhuin, S. S. Gupta, G. Natarajan *et al.*, *ACS Sustain. Chem. Eng.*, **6**, 9990 (2018), https://doi.org/10.1021/acssuschemeng.8b01217

[46] S. Mukherjee, A. A. Kumar, C. Sudhakar, R. Kumar, T. Ahuja *et al.*, *ACS Sustain. Chem. Eng.*, **7**, 3222 (2018), http://doi.org/10.1021/acssuschemeng.8b05157

[47] M. Du, Y. Du, Y. Feng and Z. Li, *Cellulose*, **26**, 5543 (2019), https://link.springer.com/article/10.1007/s10570-019-02474-1

[48] L. Gan, Q. Zhong, A. Geng, L. Wang, C. Song *et al.*, *Sci. Total Environ.*, **694**, 133705 (2019), https://doi.org/10.1016/j.scitotenv.2019.133705

[49] L. Chen, S. Yang, X. Zau and Y. Haung, *Chem. Eng. J.*, **354**, 856 (2018), http://doi.org/10.1016/j.cej.2018.08.098

[50] F. Qin, Z. Fang, J. Zhou and C. Sun, *BioMacromolecules*, **20**, 4466 (2019), http://doi.org/10.1021/acs.biomac.9b01198

[51] C. S. Zhu, C. Monti and A. P. Mathew, *Carbohyd. Polym.*, **229**, 115510 (2020), http://doi.org/10.1016/j.carbpol.2019.115510

[52] X. Yang, F. Han, C. Xu and S. Juang, *Ind. Crop. Prod.*, **109**, 241 (2017), http://doi.org/10.1016/j.indcrop.2017.08.032

[53] M. Pan, X. Zhou and M. Chen, *BioResources*, **8**, 933 (2013), http://doi.org/10.15376/biores.8.1.933-943

[54] H. Xie, H. Du, X. Yang and S. Chuanling, *Int. J. Polym. Sci.*, **2018**, 1 (2018), http://doi.org/10.1155/2018/7923068

[55] P. Lu and Y.-L. Hsieh, *Carbohyd. Polym.*, **82**, 329 (2010), http://doi.org/10.1016/j.carbpol.2010.04.073

[56] A. Dufresne, M. B. Kellerhals and B. Witholt, *Macromolecules*, **32**, 7396 (1999), https://doi.org/10.1021/MA990564R

[57] J.-J. Luo and I. M. Daniel, *Compos. Sci. Technol.*, **63**, 1607 (2003), http://doi.org/10.1016/S0266-3538(03)00060-5

[58] P. Terech, L. Chazeau and J. Cavaille, *Macromolecules*, **32**, 1872 (1999), https://doi.org/10.1021/MA9810621

[59] M. Alexandre and P. Dubois, *Mater. Sci. Eng.*, **28**, 1 (2000), http://doi.org/10.1016/S0927-796X(00)00012-7

[60] M. M. González, C. Blanco-Tirado and M. Y. Combariza, *Fuel*, **264**, 116830 (2020), http://doi.org/10.1016/j.fuel.2019.116830

[61] S. Ghafary, S. Ranjbar, B. Larijani, M. Amini, M. Biglar *et al.*, *Int. J. Biol. Macromol.*, **135**, 978 (2019), https://doi.org/10.1016/j.ijbiomac.2019.05.201

[62] S. B. Abd Hamid, A. T. Zain, R. Das and G. Centi, *Carbohyd. Polym.*, **138**, 349 (2016), http://doi.org/10.1016/j.carbpol.2015.10.023

[63] A. G. Souza, F. Kano, J. Bovet and D. S. Rosa, *Mater. Res.*, **20**, 209 (2017), http://doi.org/10.1590/1980-5373-mr-2016-0863

[64] T. Saito and A. Isogai, *Biomacromolecules*, **5**, 1983 (2004), http://doi.org/10.1021/bm0497769

[65] A. Isogai, T. Saito and H. Fukuzumi, *Nanoscale*, **3**, 71 (2011), http://doi.org/10.1039/c0nr00583e

[66] X.-M. Fan, H. Yu, D. C. Wang and Z. H. Mao, *ACS Sustain. Chem. Eng.*, **7**, 18067 (2019), http://doi.org/10.1021/acssuschemeng.9b05081

[67] Q. Wu, Y. Meng, S. Wang and Y. Li, *J. Appl. Polym. Sci.*, **131**, 15 (2014), http://doi.org/10.1002/app.40525

[68] D. S. Viet, B. Candanedo and D. G. Gray, *Cellulose*, **14**, 109 (2007), http://doi.org/10.1007/s10570-006-9093-9

[69] J. F. Revol, H. Bradford, J. Giasson, R. H. Marchsault and D. G. Gray, *Int. J. Biol. Macromol.*, **14**, 170 (1992), https://doi.org/10.1016/S0141-8130(05)80008-X

[70] M. Roman, *Ind. Biotechnol.*, **11**, 25 (2015), http://doi.org/10.1089/ind.2014.0024

[71] V. Favier, H. Chanzy and J. Cavaille, *Macromolecules*, **28**, 6365 (1995), https://doi.org/10.1021/ma00122a053

[72] S. Y. Liew, W. Thielemans and D. A. Walsh, *J. Phys. Chem. C.*, **114**, 17926 (2010), http://doi.org/10.1021/jp103698p

[73] J. K. Jackson, K. Letchford and B. Z. Wasserman, *Int. J. Nanomed.*, **6**, 321 (2011), http://doi.org/10.2147/IJN.S16749

[74] B. Frka-Petesic, G. Guideti, G. Katima and S. Vignolini, *Adv. Mater.*, **29**, 1701469 (2017), http://doi.org/10.17863/CAM.12529

[75] R. J. Moon, S. Martini, J. Nairn and J. Simonsen, *Chem. Soc. Rev.*, **40**, 3941 (2011), http://doi.org/10.1039/c0cs00108b

[76] D. Klemm, F. Kremer, S. Moritz and T. Lindstron, *Angew. Chem. Int. Ed.*, **50**, 5438 (2011), http://doi.org/10.1002/anie.201001273

[77] E. Lam, K. B. Male, J. H. Chong and A. C. W. Leung, *Trends Biotech.*, **30**, 283 (2012), http://doi.org/10.1016/j.tibtech.2012.02.001

[78] R. Sunasee, U. D. Hemraz and K. Ckless, *Expert Opin. Drug Deliv.*, **13**, 1243 (2016), http://doi.org/10.1080/17425247.2016.1182491

[79] O. M. Vanderfleet and E. D. Cranston, *Nature Rev. Mater.*, **6**, 124 (2021), http://doi.org/10.1038/s41578-020-00239-y

[80] R. Sunasee, in "Comprehensive Glycoscience", edited by J. J. Barchi, 2nd ed., Elsevier, Oxford, UK, 2021, pp. 506-537, http://doi.org/10.1016/B978-0-12-409547-2.14946-7

[81] A. S. Dorcheh and M. Abbasi, *J. Mater. Process. Technol.*, **199**, 10 (2008), http://doi.org/10.1016/j.jmatprotec.2007.10.060

[82] V. Rahmanian, T. Pirzada, S. Wang and S. Khan, *Adv. Mater.*, **33**, 2102892 (2021), http://doi.org/10.1002/adma.202102892

[83] H. Zhu, X. Yang, E. D. Cranston and S. Zhu, *Adv. Mater.*, **28**, 7652 (2016), http://doi.org/10.1002/adma.201601351

[84] L. Zhu, L. Zhong, X. Wu and M. Li, *ACS Nano*, **12**, 4462 (2018), http://doi.org/10.1021/acsnano.8b00566

[85] J. Qin, L. Chen, C. Zhao and W. Lin, *Mater. Sci.*, **52**, 8455 (2017), https://link.springer.com/article/10.1007%2Fs10853-017-1065-y

[86] Y. Lv, L. Li, Y. Zhou and M. Yu, *RSC Adv.*, **7**, 43512 (2017), http://doi.org/10.1039/C7RA07908G

[87] Q. Yao, B. Fan, Y. Xiong and C. Jin, *Sci. Rep.*, **7**, 1 (2017), http://doi.org/10.1038/srep45914

[88] K. De France, T. Hoare and E. Cranston, *Nanocellul. Chem. Mater.*, **29**, 4609 (2017), http://doi.org/10.1021/acs.chemmater.7b00531

[89] Y. Li, C. Guo, R. Shi and H. Zhang, *Carbohyd. Polym.*, **223**, 115048 (2019), http://doi.org/10.1016/j.carbpol.2019.115048

[90] N. Lavoine and L. Bergström, *J. Mater. Chem. A*, **5**, 16105 (2017), http://doi.org/10.1039/C7TA02807E

[91] T. Pirzada, Z. Ashrafi, W. Xie and S. Khad, *Adv. Funct. Mater.*, **30**, 1907359 (2020), http://doi.org/10.1002/adfm.201907359

[92] C. A. García-González, M. Alnaief and I. Smirnova, *Carbohyd. Polym.*, **86**, 1425 (2011), http://doi.org/10.1016/j.carbpol.2011.06.066

[93] Y. Wang, S. Yadav, T. Heinlein and V. Konjik, *RSC Adv.*, **4**, 21553 (2014), http://doi.org/10.1039/c4ra02168a

[94] Y. Si, J. Yu, X. Tang and J. Ge, *Nat. Commun.*, **5**, 5802 (2014), http://doi.org/10.1038/ncomms6802

[95] A. Tripathi, G. N. Parsons, O. J. Rojas and S. A. Khaan, *ACS Omega*, **2**, 4297 (2017), https://doi.org/10.1021/acsomega.7b00571

[96] Y. Fei, M. Liang, L. Yan and H. Zou, *Chem. Eng. J.*, **392**, 124815 (2020), http://doi.org/10.1016/j.cej.2020.124815

[97] A. Sharma, H. Rana, S. Goswami and Anjana, *J. Polym. Environ.*, **30**, 1 (2022), https://link.springer.com/article/10.1007/s10924-021-02185-4

[98] R. R. Choudhury, S. K. Sahoo and J. M. Gohil, *Cellulose*, **27**, 6719 (2020), https://link.springer.com/article/10.1007/s10570-020-03253-z

[99] X. Sun, L. Yang, Q. Li and H. Liu, *Chem. Eng. J.*, **241**, 175 (2014), http://doi.org/10.1016/j.cej.2013.12.051

[100] K. Singh, T. Sinha and S. Srivastava, *Int. J. Miner. Process.*, **139**, 51 (2015), http://doi.org/10.1016/j.minpro.2015.04.014

[101] C. Dong, F. Zhang, Z. Pang and G. Yang, *Carbohyd. Polym.*, **151**, 230 (2016), http://doi.org/10.1016/j.carbpol.2016.05.066

[102] C. Zhou, Q. Wu, T. Lei and I. Negulescu, *Chem. Eng. J.*, **251**, 17 (2014), http://doi.org/10.1016/j.cej.2014.04.034

[103] H. Ma, C. Burger, B. S. Hsiao and B. Chu, *Biomacromolecules*, **13**, 180 (2012), http://doi.org/10.1021/bm201421g

[104] L. Jin, Q. Sun, Q. Xu and Y. Xu, *Bioresour. Technol.*, **197**, 348 (2015), http://doi.org/10.1016/j.biortech.2015.08.093

[105] H. Qiao, Y. Zhou, F. Yu and T. Ma, *Chemosphere*, **141**, 297 (2015), http://doi.org/10.1016/j.chemosphere.2015.07.078

[106] A. Pei, N. Butchosa, L. Berglund and Q. Zhou, *Soft Matter*, **9**, 2047 (2013), http://doi.org/10.1039/C2SM27344F

[107] S. Hokkanen, A. Bhatnagar, E. Repo and M. Silanpää, *Chem. Eng. J.*, **283**, 445 (2016), http://doi.org/10.1016/j.cej.2015.07.035

[108] K. Köse, M. Mavlan and J. P. Youngblood, *Cellulose*, **27**, 2967 (2020), https://link.springer.com/article/10.1007/s10570-020-03011-1

[109] M. E. González-López, C. M. Laureano-anzaldo, A. A. P. Fonseca and J. R. R. Ortiz, *Environ. Chem. Eng.*, **9**, 105029 (2021), http://doi.org/10.1016/j.jece.2021.105029

[110] R. E. Abou-Zeid, K. Ali, R. Khiari and S. Kamel, *J. Renew. Mater.*, **9**, 601 (2021), http://doi.org/10.32604/jrm.2021.014005

[111] K. Ali, M. Hassan and M. Elnashar, *Int. J. Environ. Sci. Technol.*, **14**, 2009 (2017), https://doi.org/10.1007/S13762-017-1298-Y

[112] K. Ali, M. I. Wabah, A. Abouzeid and S. Kamel, *Int. J. Environ. Sci. Technol.*, **16**, 5569 (2019), http://doi.org/10.1007/s13762-018-1936-z

[113] W. Li, L. Zhang, D. Hu and H. Gao, *Int. J. Biol. Macromol.*, **187**, 922 (2021), http://doi.org/10.1016/j.ijbiomac.2021.07.181

[114] H. Zhao, X.-K. Ouyang and L.-Y. Yang, *J. Mol. Liq.*, **324**, 115122 (2021), http://doi.org/10.1016/j.molliq.2020.115122

[115] H. Ren, Z. Gao, D. Wu and C. Luo, *Carbohyd. Polym.*, **137**, 402 (2016), http://doi.org/10.1016/j.carbpol.2015.11.002

[116] D. Allouss, Y. Essamlali, O. Amadine, A. Chakir and M. Zahouoily, *RSC Adv.*, **9**, 37858 (2019)

[117] N. Maaloul, P. Oulego, M. Rendueles, A. Ghobal and M. Díaz, *Environ. Sci. Pol. Res.*, **27**, 23447 (2020), https://doi.org/10.1007/s11356-018-3812-2

[118] X. Ma, C. Liu, D. P. Anderson and P. R. Chang, *Chemosphere*, **165**, 399 (2016), https://doi.org/10.1016/j.chemosphere.2016.09.033

[119] H.-R. Yang, S. S. Li, X. Chan and Z. Xiao, *Sep. Purif. Technol.*, **278**, 119607 (2021), http://doi.org/10.1016/j.seppur.2021.119607

[120] Q. Liu, Y. Wu, X. Jiang, F. Lin, X. Liu *et al.*, *Int. J. Biol. Macromol.*, **140**, 1 (2019), https://doi.org/10.1016/j.ijbiomac.2019.08.116

[121] X. Luo, X. Lei, N. Chai, X. Xie and Y. Xue, *ACS Sustain. Chem. Eng.*, **4**, 3960 (2016), https://doi.org/10.1021/acssuschemeng.6b00790

[122] Q. Liu, R. Qin, J. Xue and L. Xiang, *Int. J. Biol. Macromol.*, **189**, 722 (2021), http://doi.org/10.3390/polym17070920

[123] S. Liu, S. A. Qamar, M. Qamar and M. Bilal, *Int. J. Biol. Macromol.*, **181**, 275 (2021), http://doi.org/10.1016/j.ijbiomac.2021.03.147

[124] B. Li, Q. Zhang, Y. Pan and H. Xiao, *Int. J. Biol. Macromol.*, **163**, 309 (2020), http://doi.org/10.1016/j.ijbiomac.2020.06.280

[125] Y. Ding, C. Song, W. Gong and J. Yao, *Cellulose*, **28**, 7227 (2021), https://link.springer.com/article/10.1007/s10570-021-03979-4

[126] N. Mohammed, N. Grishkewich, R. M. Berry and K. C. Tam, *Cellulose*, **22**, 3725 (2015), http://doi.org/10.1007/s10570-015-0747-3

[127] J. Wu and M. P. Andrews, *ACS Appl. Nano. Mater.*, **3**, 11217 (2020), http://doi.org/10.37934/jrnn.5.1.4364

[128] J.-T. Xu, X. Q. Chen, W. H. Shen and Z. Li, *Carbohyd. Polym.*, **256**, 117493 (2021), http://doi.org/10.1016/j.carbpol.2020.117493

[129] X. Xu, X.-K Ouyang and L.-Y. Yang, *J. Mol. Liq.*, **322**, 114523 (2021), http://doi.org/10.1016/j.molliq.2020.114523

[130] C. Tang, P. Brodie, Y. Li and K. C. Tam, *Chem. Eng. J.*, **392**, 124821 (2020), http://doi.org/10.1016/j.cej.2020.124821

[131] S. Ma, M. Zhang, J. Nie and T. Luo, *Carbohyd. Polym.*, **208**, 328 (2019), http://doi.org/10.1016/j.carbpol.2018.12.081

[132] D. Li, X. Tian, Z. Wang and Q. Wei, *Chem. Eng. J.*, **383**, 123127 (2020), http://doi.org/10.1016/j.cej.2019.123127

[133] B. Li, Y. Pan, Q. Zhang and H. Xiao, *Cellulose*, **26**, 9163 (2019), https://link.springer.com/article/10.1007/s10570-019-02687-4

[134] L. Qiao, S. Li and K. Du, *Biochem. Eng. J.*, **153**, 107412 (2020), http://doi.org/10.1016/j.carbpol.2005.12.009

[135] L. Qiao, S. Li, Y. Li and K. Du, *J. Clean. Prod.*, **253**, 120017 (2020), http://doi.org/10.1016/j.jclepro.2020.120017

[136] A. Qiao, M. Ciu, R. Huang and R. Su, *Carbohyd. Polym.*, **272**, 118471 (2021), http://doi.org/10.1016/j.carbpol.2021.118471

[137] S. Dutta, B. Gupta, S. Srivasta and A. K. Gupta, *Mater. Adv.*, **2**, 4497 (2021), http://doi.org/10.1039/D1MA00354B