



The role of electrostatic interactions of anionic and cationic cellulose derivatives for industrial applications: A critical review

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ARTICLE INFO

Keywords:

Adsorbent
Carboxymethyl cellulose
Cationic cellulose
Cellulosic derivatives
Intermolecular interactions
Ionic bonds
Oxidized cellulose
Thickener
Stabilizer

ABSTRACT

Some of the most popular cellulose derivatives exhibit charged functional groups, either cationic (generally, quaternary ammonium moieties) or anionic (most typically, carboxylate groups). Noticeably, the second most successful cellulosic derivative in the world, in terms of market share, is the salt of a negatively charged polymer: sodium carboxymethyl cellulose. However, many of the applications that have long been proposed by researchers have never proven feasible on a large scale. In light of this, the present review critically discusses the current and potential applications of anionic and cationic cellulose derivatives: (i) coagulation-flocculation or direct flocculation processes, for which the limited molecular weight of cellulose derivatives is a key limitation; (ii) thickening and rheology modification in general, where polymer-water interactions play a major role; (iii) stabilization of colloids or emulsions, in such way that the repulsive electrostatic forces prevent aggregation unlike coagulation-flocculation; (iv) adsorption of cations by anionic cellulose, of anions by cationic cellulose, and adsorption mediated by other mechanisms; (v) encapsulation of bioactive compounds for drug delivery or other purposes; (vi) filtration by means of cellulose-based membranes, and (vii) production of antimicrobial materials by exploiting the interactions between cationic cellulose and the phospholipid bilayer of microorganisms. We highlight the recent trends and, closely related to them, the knowledge gaps in the literature on anionic and cationic derivatives. For instance, the survey remarks on the increasing popularity of anionic or cationic nanocellulose (generally, as nanofibers or nanocrystals), progressively outweighing both conventional fibers and soluble derivatives.

1. Introduction

The fact that cellulose is the most abundant biopolymer on Earth, at least simply considering the lithosphere, has already been repeated to a point of exhaustion. Nonetheless, this high availability underpins the industrial success of some of its derivatives. Cellulose is commonly extracted from cotton, softwood, hardwood, bamboo, and cereal straw, although other kinds of agricultural waste, annual plant crops, the outer layers of fruits and vegetables, many protists, some bacteria, and even certain species of animals are also possible sources of this biopolymer (Alila et al., 2013). Indeed, given the renewable and biodegradable

nature of cellulose, its ubiquitousness, its high density of functional groups, and the traditions of cotton fabric and paper manufacturing, its choice as platform polymer for many different materials is not surprising. For that, cellulose is usually substituted or oxidized on its hydroxyl groups, depolymerized by cleavage on its β 1,4-glycosidic bonds, and/or crosslinked with other polymer chains and/or functional groups (Hasanin, 2022; He et al., 2021; Shokri and Adibkia, 2013).

The most successful cellulose derivatives in 2022 were hydroxypropyl methyl cellulose (HPMC), with a market share as high as 40%, and carboxymethyl cellulose (CMC), accounting for roughly one third of the market (Grand View Research, 2023). Both are commonly obtained

Abbreviations: A-, anionic; Alg, alginate; C-, cationic; CA, cellulose acetate; CHPTAC, (3-chloro-2-hydroxypropyl) trimethylammonium chloride; CMC, carboxymethyl cellulose; CMCA, carboxymethyl cellulose acetate; CNCs, cellulose nanocrystals; CNFs, cellulose nanofibers; DAC, dialdehyde cellulose; DP, degree of polymerization; DS, degree of substitution; EPTAC, epoxypropyltrimethylammonium chloride; GA, glutaraldehyde; HEC, hydroxyethyl cellulose; HNC, hairy nanocrystalline cellulose; HPMC, hydroxypropyl methylcellulose; MC, methylcellulose; MCC, microcrystalline cellulose; MIM, methylimidazolium; PAM, polyacrylamide; PDADMAC, polydiallyldimethylammonium chloride; PEI, polyethyleneimine; PEG, polyethylene glycol; PES, polyethersulfone; PYR, pyridinium; SCMC, Sulfated carboxymethyl cellulose; TEMPO, 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl; ZPP, 3-(6-methoxynaphthalen-2-yl)-2-(4-(pyridin-4-yl) phenyl) acrylonitrile.

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<https://doi.org/10.1016/j.indcrop.2023.116898>

Received 5 April 2023; Received in revised form 12 May 2023; Accepted 15 May 2023

Available online 30 May 2023

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by etherification of cellulose and account for a market size of approximately USD 4.8 billion. HPMC is a neutral derivative, used as water-retention agent, as binder, and as thickener (Espert et al., 2020). Regarding CMC (generally as its sodium salt, CMC-Na), its anionic

character is key to explain how it works as emulsifier and stabilizer, besides being a common thickener and a bulking agent in the cosmetic industry (Wennman et al., 2023). Other well-known anionic derivatives are sodium cellulose phosphate, with both traditional and potential

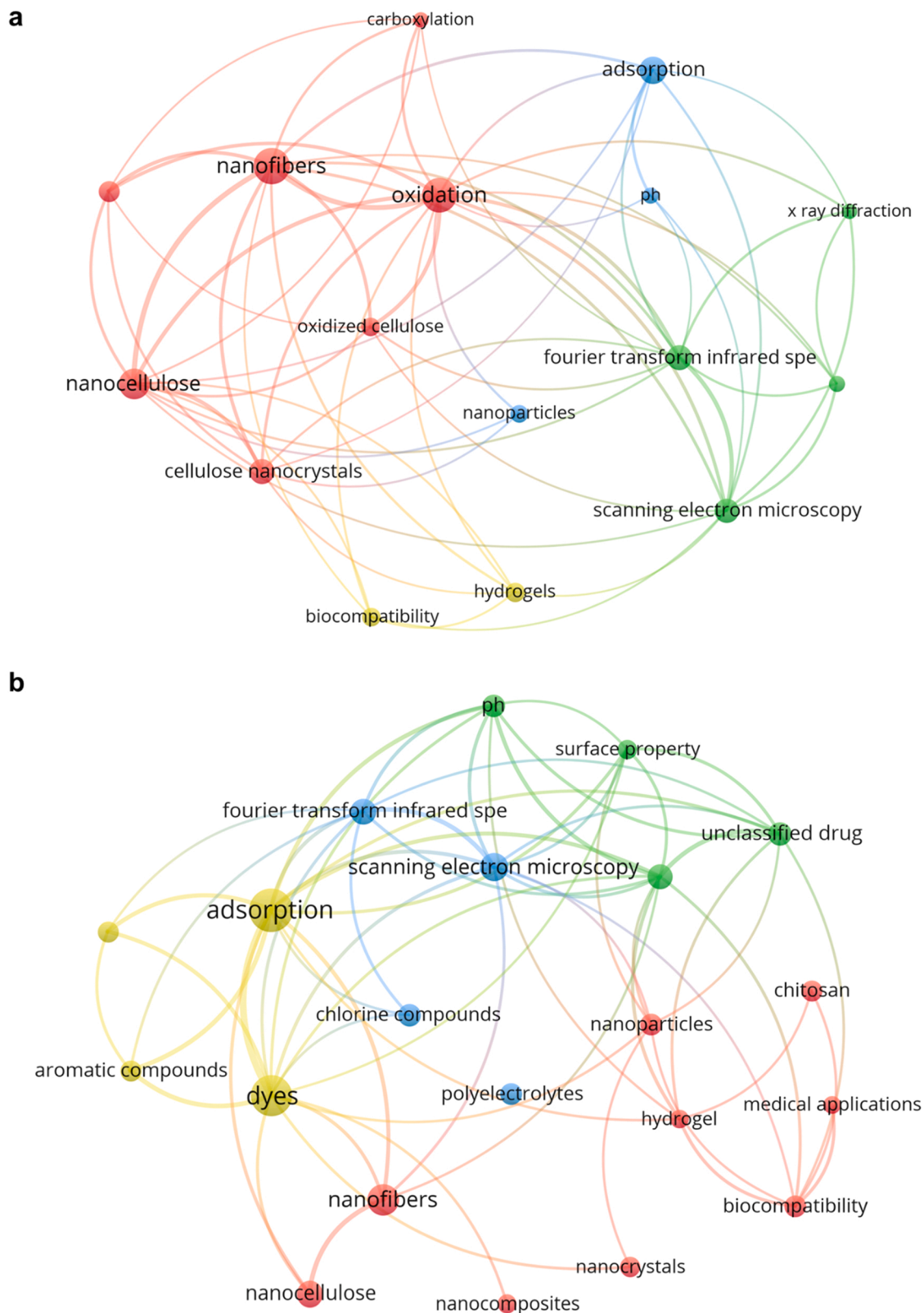


Fig. 1. VOSviewer's co-occurrence diagram relating the explicit and indexing keywords of Scopus-indexed publications on anionic cellulose derivatives (a) and cationic cellulose derivatives (b)..

applications in the pharmaceutical industry (Raghav and Sharma, 2021), and oxidized cellulose, at least in niche areas for medical or cosmetic applications (Surendran and Sherje, 2022).

As of today, the market for cationic cellulosic derivatives is much smaller than that for CMC. Among other reasons, the reagents implied in the manufacturing of carboxylated (anionic) derivatives are generally cheaper than those needed for cationic cellulose. For instance, in March 2023 and in Europe, free-on-board (Hamburg) prices were USD 1220/t for chloroacetic acid, used directly in the manufacturing of CMC, and USD 2970/t for epichlorohydrin, required in the synthesis of cationizing reagents along with tertiary amines (ChemAnalyst, 2023).

Nevertheless, at least two products of the Polyquaternium family of cosmetic ingredients, namely those with numbers 4 and 10, are constituted by cationized cellulose (Cumming et al., 2011). The UCARE™ Polymer JR series from Dow, constituted by cationic polymers with a cellulose backbone, is also worth mentioning (Donnelly et al., 2015).

Fig. 1 shows the diagram of co-occurrence of the main keywords and indexing terms corresponding to the recent research (2013–2023) on anionic (Fig. 1a) and cationic (Fig. 1b) derivatives of cellulose. It was obtained by applying the University of Leiden's VOSviewer software to the exports resulting from two search strings in Scopus. For anionic derivatives, the string was: (TITLE-ABS-KEY (carboxymethylation AND cellulose) OR TITLE-ABS-KEY (carboxyl AND oxidation AND cellulose) OR TITLE-ABS-KEY ("cellulose sulfate" OR "cellulose sulfonate") OR TITLE-ABS-KEY ("cellulose phosphate") AND TITLE-ABS-KEY (applications)) AND PUBYEAR > 2012; resulting in 843 matches. The length of the string is justified by the fact that anionic cellulosic derivatives, unlike cationic ones, are usually not merely referred to by their charge. For cationic cellulose, the string was: (TITLE-ABS-KEY (cationic AND cellulose) OR TITLE-ABS-KEY (cationization AND cellulose) AND TITLE-ABS-KEY (applications)) AND PUBYEAR > 2012; resulting in 560 matches. Only terms with more than 30 appearances were selected. Generic keywords like *article*, *priority journal*, *chemistry* or *procedures* were removed, and so were those forced by the search string in each case. The fact that anionic cellulose derivatives are usually not referred by their ionic character may cloud the real number of scientific documents, and the ratio between both searches must be carefully taken (843 vs 560). However, we consider that the highlighted clusters and keywords are representative of the uses of both classes of cellulose derivatives, this is anionic and cationic.

In Fig. 1a, the main keywords were *nanofibers*, *nanocellulose*, *adsorption*, and *scanning electron microscopy*. Within the red cluster, it is worth to mention that one of the most common treatments leading to cellulose nanofibers (CNFs) is the oxidation of cellulose fibers mediated by the 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) radical. It is a regioselective oxidation, since only the primary hydroxyl groups are converted into carbonyl groups, which are in turn oxidized to carboxylate groups in the presence of secondary oxidizers such as sodium hypochlorite (Isogai and Kato, 1998; Mazega et al., 2023). The high price of TEMPO puts the industrial feasibility of this way to produce anionic cellulose under question, but its regeneration in an alkaline $\text{Br}^-|\text{BrO}^-||\text{Cl}^-|\text{ClO}^-$ system allows for the use of small amounts. Hence, TEMPO is usually (and properly) referred to as the catalyst, but it should not be forgotten that its nitronium cation is the primary oxidizer as well. Against certain preconceptions on this process, a life cycle assessment of our group has recently hinted that this pathway leading to CNFs may be more environmentally friendly than the enzymatic route (Arfelis et al., 2023).

Regarding cationic cellulose, Fig. 1b highlights *scanning electron microscopy* as the most common characterization technique and *adsorption*, usually of *dyes* or of *aromatic compounds*, as a widely reported feature. *Medical applications* and *biocompatibility* are found within the objectives of many research articles, and so is the modification of the surface tension (*surface property*). Cationic nanocellulose, both as CNFs and as cellulose derivatives, both as CNFs and as cellulose nanocrystals (CNCs), were found to be less common than anionic nanocellulose. As for the

synthesis, besides common etherification reaction with an electrophile containing a quaternary ammonium group (Aguado et al., 2018; Chen et al., 2023), the presence of *chitosan* or other *polyelectrolytes* is often related to other methods of cationization. For instance, electrostatic interactions allow for the non-covalent cationization of anionic or even neutral cellulose fibers, CNFs or CNCs with cationic polymers (Aguado et al., 2022; Kaboorani and Riedl, 2015).

As usual, the trends in the scientific literature differ from those of industrial production. As aforementioned, CMC is by far the most successful anionic derivative of cellulose but, given how well-known it is at this point, it seldom becomes the focus of a research article (Tarrés et al., 2018a,2018b). In contrast, oxidized cellulose, and especially oxidized nanocellulose, are highly popular among researchers, but they seem destined to niche markets (Balea et al., 2020). As for cationic cellulosic derivatives, while the cosmetic industry widely uses them as surfactants, anti-static agents, and film forming agents, the long-suggested implementation of cationic cotton in the textile industry remains under question (Farrell and Hauser, 2013).

This review places an inquiry into the overall usefulness of ionic derivatives of cellulose for industrial applications. In this direction, the importance of their electrostatic interactions (ionic, ion-dipole, hydration shells) is unveiled in their actual and potential roles as flocculants, thickeners, stabilizers, adsorbents, encapsulating agents, membranes for filtration, and antimicrobial materials. Within the scope of chemical engineering, this classification by unit operations seems more convenient than by sectors, given that the same process can be shared by multiple players in the market, e.g.: stabilization is common to the food industry and manufacturers of cosmetic products. Notions of basic physical chemistry and surface science, such as the thermodynamics of solvation and the electrical double layer, are applied to explain the differences between anionic and cationic derivatives, and between them and nominally neutral cellulosic materials. Finally, our critical lens seeks to identify the current trends, the perspectives, and what is still missing to fill relevant knowledge gaps.

2. Coagulation and flocculation

2.1. Electrostatic interactions and mechanisms in coagulation-flocculation

Coagulation and flocculation are commonly used processes not only for wastewater treatment, but also for mineral processing, paper manufacturing, food and beverage production, textile manufacturing or the oil and gas industry, among others. The relevance of coagulation and flocculation is doubtless, as these processes contribute to enhancing the efficiency of separation processes, are versatile for many sectors and are useful techniques for industries for regulatory compliance, particularly in terms of environmental regulations and standards.

While coagulation differs from flocculation, these processes are commonly used in succession to disrupt the stabilization of suspended particles. On the one side, coagulation has as main purpose the neutralization of particle charges, while on the other, flocculation is intended to bind together these particles generating aggregates that may behave as single and bigger particles, which are more easily removed from the liquid. As these processes are usually succeeded, they are commonly known as coagulation-flocculation. However, in the recent years, a tendency on replacing coagulation-flocculation by direct flocculation has appeared, particularly due to the lower cost, environmental impact, and technical requirements of the latter, but also due to its higher safety for human health and time effectiveness (Fauzani et al., 2021).

Direct flocculation is mainly driven by a bridging mechanism, between suspended solids and colloidal particles, and charge neutralization. These processes are usually conducted by synthetic polyelectrolytes, which take benefit from their long chains and surface characteristics, which may interact by electrostatic mechanisms. Some examples of synthetic polyelectrolytes used as flocculants are

polyacrylamides (PAM), either cationic or anionic, and polyethylene imines (PEI), but also inorganic salts may be used, such as aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) or ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) (Chatsungnoen and Chisti, 2019; Nyström et al., 2003; Tarrés et al., 2020).

The flocculation effectiveness has been reported to be influenced by chain length and surface charge of flocculants. Another important aspect that must be taken into consideration is the ionic strength of the medium, which may influence the shape and conformation of the flocculant polymer, which is related to persistence length at the same time. Indeed, persistence length plays a major role in electrostatic interactions as, in presence of ions, the effective surface charge of flocculants may be affected and, thus, influencing their neutralization and bridging capacity (Serra-Parareda et al., 2021; Trizac and Shen, 2016). Fig. 1 schematically shows the effect of surface charge and chain length of the flocculant. Highly charged and long chain flocculants (Fig. 1a) will have the ability to generate flocs with multiple suspended particles and colloids, as the surface charge of the particles will be partially neutralized (coagulation) and the repulsion forces within particles will be decreased. In this case, the mechanisms taking place are coagulation-flocculation, this is neutralization and bridging. On the contrary, for long chain but low charge flocculants (Fig. 1b), the amount of particles and/or colloids that will be able to bind will be lower, leading as well to a lower density floc due to the lower degree or lack of local neutralization of their surface charge. This lower density will lead to bigger but weaker flocs, which may disintegrate under any mechanical stress (*i.e.*, agitation). Finally, Fig. 1c represents the mechanism of short chain flocs, which will be able to bind smaller particles and colloids, as well as a reduced amount compared to those from Fig. 1a. Fig. 2.

2.2. Cellulose-based flocculants: the role of surface charge, solubility, and morphology

In the recent years, several efforts have been paid on the search for bio-based flocculants able to replace those coming from non-renewable resources. Such is the case of polysaccharides and their derivatives. Among polysaccharides, cellulose and its derivatives deserve special attention, due not only to their broad range of surface and morphological characteristics, but also to its wide availability and renewable character. Indeed, cellulose-based flocculants can be tailored in terms of surface functional groups while remaining insoluble in water, *e.g.*, carboxyl or quaternary ammonium groups (Aarne et al., 2012; Aguado et al., 2018); exhibit different morphologies (*i.e.*, from micro to nano

domains) while keeping these surface functionalities (Li et al., 2021), or even be functionalized in such way that they can be soluble in water (Granström, 2009). Some relevant cellulose-based flocculants, along with their remarkable features and applications, are provided in Table 1.

As described above, direct flocculation requires highly charged and long polymer chains to conduct the neutralization-bridging process in a single step. The degree of polymerization (DP) of native cellulose can range from hundreds to roughly ten thousand, which would enable flocculation by bridging mechanisms. However, the processes for the extraction of cellulose from the raw materials and most chemical modifications result in significant depolymerization, leading to relatively short chains in comparison to synthetic polyelectrolytes of high molecular weight (Aguado et al., 2017).

In the case of cationic flocculants, they are mostly used for wastewater treatment, sludge treatment, papermaking, and removal of specific dyes and pollutants (Karppinen et al., 2011; Serra-Parareda et al., 2021; Zhang et al., 2016). Depending on the degree of substitution (DS) of quaternary ammonium (most commonly), phosphonium or sulfonium groups, the cellulose chain will become highly charged or medium-to-low charged (Song et al., 2013; Xue et al., 2014; Zhang et al., 2016). The surface charge density of the cationic cellulose will drive the coagulation mechanism, while the DP or chain length will directly influence the bridging process. Cationic cellulose-based flocculants, apart from generating large flocs by the bridging process, can also absorb dyes or other pollutants by confinement flocculation (Koshani et al., 2020).

The use of cationic flocculants is of utmost relevance for the paper-making industry. Retention mechanisms of fines, fibers and other negatively charged constituents during paper formation require the incorporation of cationic polyelectrolytes, such as partially quaternized polyacrylamides (PAM). The use of such cationic polyelectrolytes has a double purpose: on the one hand, retaining finer fibers in the paper wet end, on the other, neutralizing the anionic trash present in industrial waters (Nyström and Rosenholm, 2005; Quim Tarrés et al., 2018a, 2018b). Recently, our group proposed a retention system for anionic cellulose nanofibers in paper production based on the incorporation of non-covalently bonded polydiallyldimethylammonium chloride (PDADMAC) onto cellulose nanofibers, indicating the suitability of the latter to act as retention agent, *i.e.*, generating bridging between negatively charged fibers and nanofibers (Aguado et al., 2022). However, this approach is not based on the introduction of functional groups by chemical modification of cellulose and requires the use of an additional polyelectrolyte. Some researchers have reported the convenience of

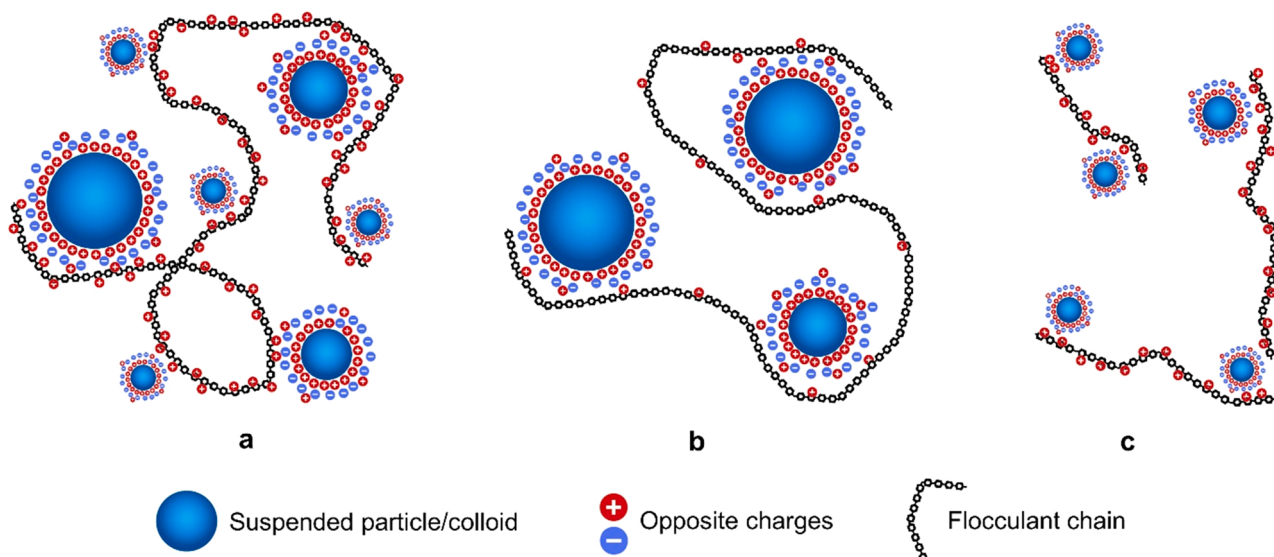


Fig. 2. Schematic representation of long chain and highly charged (a), long chain and low charged (b) and short chain (c) flocculants.

Table 1

Some relevant cellulose-based flocculants that have been reported over the last decade (2013 – 2023): main features and applications.

Application sector	Flocculant	Modification/functional groups	Character	Reference
Wastewater treatment	Diacetyl cellulose/ bentonite	Periodate oxidation + Girard's reagent T (quaternary ammonium)	Cationic	(Grenda et al., 2020)
	Diacetyl cellulose/ bentonite	Periodate oxidation + sodium metabisulfite (sulfonate)	Anionic	(Grenda et al., 2020)
	Cellulose nanocrystals	EPTAC (quaternary ammonium group)	Cationic	(Morantes et al., 2019)
	HNC	Periodate oxidation + Girard's reagent T (quaternary ammonium)	Cationic	(Tavakolian et al., 2019)
	HEC	Acrylamide grafting	Anionic	(Chaouf et al., 2019)
	Cotton linters	Alkaline hydrolysis + acrylamide grafting	Anionic	(Song et al., 2011)
	CMC	Acrylamide grafting	Anionic	(Cai et al., 2013; Feng et al., 2020)
	Dissolved pulp	PAM grafting	Anionic	(H. Zhu et al., 2016)
	Cotton linters	Chlorosulfonic acid and Dimethylformamide (sulfate)	Anionic	(Nourani et al., 2016)
	Cellulose nanocrystals	Fe ²⁺ /H ₂ O ₂ oxidation (carboxylation)	Anionic	(Fan et al., 2019)
Harvesting	Cellulose nanofibers	Dicarboxylation	Anionic	(Suopajarvi et al., 2013)
	Cellulose nanocrystals	Carboxylation	Anionic	(Yu et al., 2016)
	Cyanobacterial blooms	Hydroxyethyl cellulose	CHPTAC (quaternary ammonium)	Cationic
Microalgae	Cellulose nanocrystals	PYR and MIM	Cationic	(Blockx et al., 2019; Verfaillie et al., 2020; Zhao et al., 2022)
	HNC	Periodate oxidation + Girard's reagent T (quaternary ammonium)	Cationic	(Lopez-Exposito et al., 2019)
Papermaking Retention and drainage	Cotton dissolving pulp	CHPTAC (quaternary ammonium)	Cationic	(Li et al., 2015)
	Bleached kraft eucalyptus pulp	CHPTAC (quaternary ammonium)	Cationic	(Aguado et al., 2017)
	Microfibrillated cellulose	β-chloroethyldiethylamine	Cationic	(Diab et al., 2015)
	HNC	Periodate oxidation + Girard's reagent T (quaternary ammonium)	Cationic	(Campano et al., 2019a, 2019b; Chen and van de Ven, 2016)
Cellulose nanofibers	PDADMAC	Cationic	(Aguado et al., 2022)	

microcrystalline cellulose (MCC) to be modified by cationization, incorporating quaternary ammonium groups, and enhancing its solubility in water (Song et al., 2010; Yan et al., 2009). Noticeably, the higher the DS and, thus, the cationic character of the cellulose-based flocculant, the lower the required dosage.

Cellulose ethers containing cationic groups exhibit an expanded chain due to the electrostatic repulsion forces. This positive surface charge, along with the expanded chain, can result in an excellent flocculant for anionic suspended particles and colloids, and even for cyanobacterial blooms harvesting (Koshani et al., 2020; Zhou et al., 2023). As examples, cationic hydroxyethyl cellulose (C-HEC) or cationic cellulose acetate (C-CA) are usually obtained by means of their chemical modification through epoxypropyltrimethylammonium chloride (EPTAC) or (3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC) (Liesiene and Kazlauskas, 2013). However, the flocculation mechanism of these water-soluble cellulose derivatives is usually dominated by charge neutralization rather than by direct flocculation through bridging, due to their low molecular weight (Biggs et al., 2000). In another study, Kono (2017) evaluated the effect of varying the DS (from 0.56 to 1.33) of cationized water-soluble cellulose by means of modifying the addition of EPTAC. The author found that at moderate amounts, the increasing DS promoted the flocculation of dyes, but excess EPTAC could lead to the opposite effect due to the prevalence of repulsive forces (Kono and Kusumoto, 2014).

Aiming at increasing or modifying the reactivity of cellulose before cationization, some researchers opt for the ring opening (C2–C3) of cellulose caused by periodate oxidation. The resulting dialdehyde cellulose (DAC) easily reacts with hydrazides. As an example, Grenda et al. (2020) reacted DAC with Girard's reagent T, a hydrazide containing a quaternary ammonium group on the non-reactive end. Depending on the process conditions, this cationic cellulose-based flocculant was found to be more effective than cationic PAM at removing turbidity of industrial effluents. In a similar approach, Sirviö et al. (2011) prepared DAC through periodate oxidation to be later cationized with Girard's reagent

T. In this case, the authors achieved a slightly higher cationicity than that reported by the Portuguese researchers (4.27 vs 3.9 mmol/g). The authors from the University of Oulu reported excellent flocculation performance of the cationic DAC for ground calcium carbonate (GCC).

Cellulose nanocrystals (CNCs) have been also modified by means of cationization for microalgae flocculation purposes. In a recent study, Zhao et al. (2022) developed cationic CNCs (C-CNCs) by means of incorporating pyridinium (PYR) and methylimidazolium (MIM) groups, as reported elsewhere (Blockx et al., 2019; Verfaillie et al., 2020). C-CNCs achieved efficiencies of 90% without adjusting the pH, value that was increased to 100% when combined with membrane filtration. Regardless of whether the modification of CNCs was conducted by the incorporation of PYR or MIM groups, it was clearly shown that the dosage of CNCs could be decreased at increasing DS. On the other hand, when comparing the flocculation efficiency of either PYR- or MIM-modified CNCs with chitosan, it was found that longer and more flexible chains can lead to dispersion restabilization due to the excess of cationic charges (Li et al., 2004; Renault et al., 2009). In another approach, Morantes et al. (2019) modified CNCs with EPTAC for flocculating SiO₂ suspended in water, reducing the turbidity to 100%.

Regarding CNFs, cationization as pretreatment for nanofibrillation has been a topic of great interest in the recent years (Bansal et al., 2021; Lu et al., 2022; Pedrosa et al., 2022b). Due to their greater surface area and length, CNFs have been reported to exhibit a good performance as flocculant, mainly by bridging mechanisms (Hasani et al., 2008; Korhonen and Laine, 2014). In a recent study, Pedrosa et al. (2022a) reported the feasibility of cationized nanocellulose, using Girard's reagent T, to be used as cationic flocculant. Although the performance of these cationic CNFs was lower than that provided by cationic PAM, the work highlighted the potential of these CNFs to be used as filler retention in papermaking.

In between CNCs and CNFs, hairy nanocrystalline cellulose (HNC) was firstly developed by Yang and van de Ven (2016). These nanosized cellulose structures present both amorphous and crystalline regions,

exhibiting positive charges at the ends of the cellulose crystals in the form of amorphous cellulose nanofibrils. This cationic character has been reported to provide good flocculation performance for mineral fillers, such as clays (Campano et al., 2019b) or calcium carbonate (Chen and van de Ven, 2016), microalgae harvesting (Lopez-Exposito et al., 2019), and dye removal in wastewater treatment (Tavakolian et al., 2019) or papermaking (Campano et al., 2019a). HNC allegedly exhibits a superior colloidal stability, pronounced pH- and ion-responsive behavior, and a much larger hydrodynamic size, mainly due to the presence of densely located protruding polymer chains. This, together with their capacity to generate biomimetic mineralization of some fillers (e.g., calcium carbonate), reveal the potential of HNC to be used as cellulose-based flocculant (Sheikhi and van de Ven, 2017).

Anionic cellulose-based flocculants, while less frequent, also are of great interest for several applications. As in the case of cationic flocculants, anionic cellulose-based flocculants can be also found in the form of cellulose derivatives, or nanostructured cellulose. For instance, acrylamide-modified cellulose was reported as a promising anionic cellulose-based flocculant of Fe(OH)₃, while being highly efficient, non-toxic and biodegradable (Song et al., 2011). Acrylamide modification has also been approached with CMC, particularly for methylene blue, with removal efficiencies above 90% (Cai et al., 2013; Feng et al., 2020). In general, this strategy is claimed to decrease the dependence on non-biodegradable flocculants such as PAM (Koshani et al., 2020). In contrast to acrylamide-grafted cellulose, long-chain acrylamide polymers are highly resistant to hydrolysis. Moreover, they cannot pass through the cell membranes of microorganisms, unlike the acrylamide monomers or oligomers that result from the hydrolysis of acrylamide-grafted cellulose.

Micro and nanostructured cellulose, in their anionic form, have been also reported to provide efficient coagulation and flocculation, particularly for minerals and dyes. Some examples are the use of decarboxylation of cellulose nanofibers, the single-step carboxylation of cellulose nanocrystals, or even grafting acrylamide onto the surface of nanocellulose (Song et al., 2011; Suopajarvi et al., 2013; Yu et al., 2016). As the border between coagulation-flocculation and electrostatic adsorption is diffuse, the use of anionic nanostructured cellulose will be further described in the subsequent sections.

3. Rheology modifiers

3.1. Thickening agents in solution

In terms of market volume, it is not an understatement to say that most applications of cellulosic derivatives involve thickening, i.e., increasing the apparent viscosity of a generally aqueous medium, or of the aqueous phase in heterogeneous systems. Regarding current cosmetic products, pharmaceuticals and foodstuff, derivatives of cellulose (unlike microcrystalline cellulose) usually act as rheology modifiers in solution. Some examples of nominally neutral but water-soluble derivatives are HPMC, methylcellulose (MC) and HEC, working as thickeners in skin care or hair care products, artificial tear products, ice cream, lubricants, inks, paint, coatings, etc. (Chang and Zhang, 2011; Kondo, 1997; Semp et al., 2023). CMC hydrogels are not less common, as their anionic character is translated in the requirement of lower concentrations (for equal DP) to attain a similar gain in viscosity (An et al., 2020). For instance, CMC is commonly used as bulking agent in low-fat, low-calory dairy and bakery products (Tuan Mohamood et al., 2021). Being highly water-soluble, it can become associated with large amounts of water, creating a gel-like texture that mimics the sensation of fat and starch in the human mouth.

Regarding cationic cellulosic derivatives such as Polyquaternium-10 and UCARE™ JR400, their primary purpose belongs to surface chemistry, but thickening is acknowledged as a side benefit (Rodríguez et al., 2001).

The aqueous solubility of the aforementioned neutral derivatives,

whose density of hydroxyl groups is actually lower than that of native cellulose, is not self-evident. An analogy could be established with β -cyclodextrin, whose hydroxypropyl derivative is more water-soluble (Cova et al., 2018), and poly(vinyl alcohol), whose dissolution is easier if not fully hydrolyzed (Ferreira et al., 2022). Briefly put, the high stability in the supramolecular structure of cellulose relies on various intra- and intermolecular interactions, including hydrogen bonding, dipole-dipole interactions, and dispersive forces. Neutral cellulose derivatives, such as MC and HEC, contain functional groups (–OCH₃ and –OCH₂CH₂OH) that hinder the intermolecular hydrogen bonding between cellulose chains (C6 and C3), disrupting the original structure and conferring different properties such as increased solubility in water (Kondo, 1997). When it comes to ionic derivatives, the spacer effect of the functional groups incorporated remains, to which their more thermodynamically favorable solvation adds up to ease solubility.

Cellulose elementary fibrils present good interaction with water, yet they present an insoluble character, due to the fact that the entropy gain by solvation is outweighed by the enthalpy of intermolecular interactions within the fibril (Wohler et al., 2022). As mentioned before, the hydroxyl groups on C6 and C3 are one of the keys for cellulose's high stability on a supramolecular level. The potential for cellulose derivatives being used as rheological modifiers arises from the fact that substituting these hydroxyl groups will tip the thermodynamic scales from an enthalpy-driven phenomenon to an entropy gain capable of making the cellulose fibril spontaneously dissociate, fully solubilizing in water.

Within the broad spectrum of soluble derivatives of cellulose, they all present distinct rheological behavior. The viscosity and gel strength (usually expressed by the storage and loss moduli) of the solution are determined by the shape of and size of the functional groups of the polymer, as well as external factors such as concentration, temperature, and pH (Lopez and Richtering, 2021). The ability of the solution to form a gel-like substance is mainly caused by physical crosslinking between the polymer chains (including dipole-dipole and ion-dipole interactions), in opposition to the parallel arrangements in native cellulose. This explanation can also be applied to the ionic derivatives but, the fashion in which the polymer interacts with its hydration radius and the reach of influence on water molecules should be considered on the basis of the intensity and character of the surface charge. Furthermore, the cross-linking of ionic derivatives may be achieved or enhanced by using counter-ionic divalent or trivalent entities, e.g., CMC hydrogels attained with Ca²⁺ (Tuan Mohamood et al., 2021).

As a paradigm of soluble cellulosic thickeners, sodium CMC displays the following properties in water: pseudoplastic behavior, slightly rheopectic behavior at very low shear rates and slightly thixotropic behavior at high shear rate, and absence of yield stress or requirement of unusually high concentrations to reach it (Edali et al., 2001). The specific viscosity of CMC solutions has been reported to follow piecewise power functions with different exponents: $n = 0.5$ when unentangled (dilute polymer), $n = 1.5$ at medium concentration, and $n = 3.9$ at high concentration (Lopez and Richtering, 2019):

$$\frac{\eta}{\eta_0} = 1 - \alpha(\varphi)^n \quad (1)$$

where η is the apparent viscosity of the suspension, η_0 is the viscosity of the aqueous medium without rheology modifiers, and φ is the mass fraction, volume fraction, mass/volume concentration, or molar concentration of CMC. This piecewise function is qualitatively depicted in Fig. 3a for a hypothetical maximum viscosity of 100 Pa·s at a certain shear rate ($\dot{\gamma}$). Regarding said shear, in general, the behavior of CMC solutions can be satisfactorily fitted to the Ostwald–de Waele relationship:

$$\eta = K(\dot{\gamma})^{m-1} \quad (2)$$

where K and m are the consistency index and the flow behavior index,

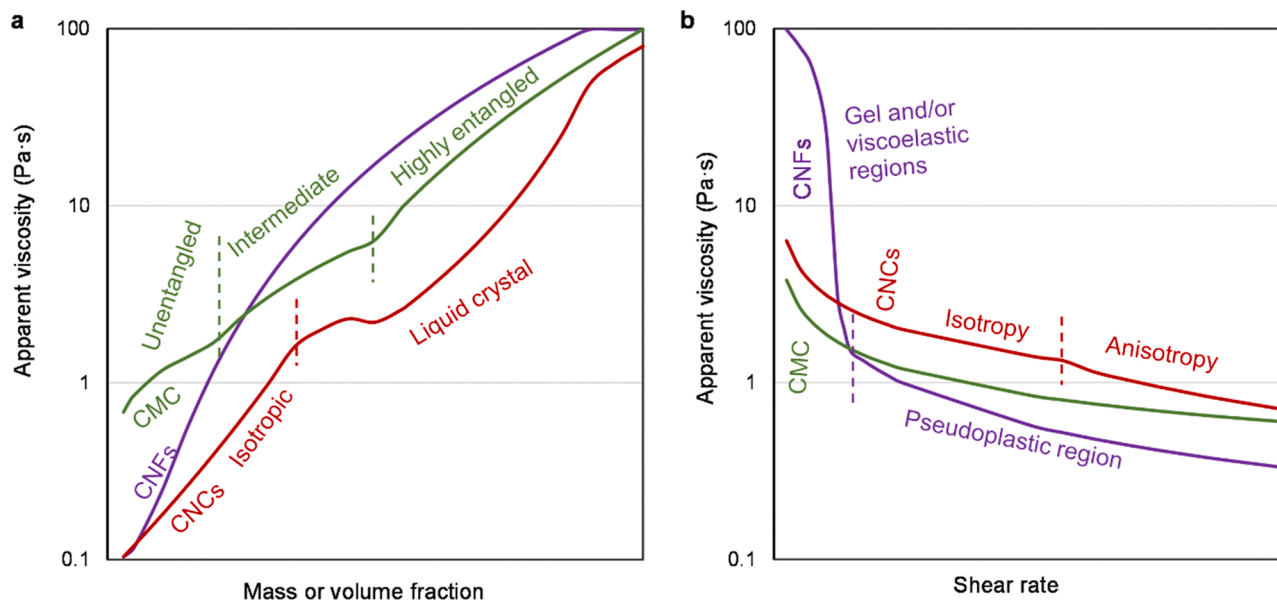


Fig. 3. Generalized evolution of the apparent viscosity of aqueous solutions or suspensions of some popular anionic cellulosic materials with their concentration at constant shear rate (a), and with the shear rate applied at a given concentration (b).

respectively. An example curve with $m < 1$ is plotted in Fig. 3b to highlight the pseudoplastic behavior of sodium CMC solutions. Generally speaking, they can be described as non-Newtonian purely viscous fluids that, for most applications, could be regarded as time independent.

3.2. Nanocellulose-based thickeners

In the recent literature on cellulose-based rheology modifiers, colloidal suspensions of nanocellulose have become more popular than soluble agents (Patoary et al., 2022). Unlike CMC, anionic CNFs have yield stress at relatively low concentration. The minimum concentration for the suspension to display yield stress, often referred to as “gel point”, is highly dependent on the aspect ratio of CNFs (Sanchez-Salvador et al., 2022). In comparison with the so-called CMC gels, anionic nanocellulose gels display higher thixotropy and, as long as the consistency is not too high, can easily become sol-like colloidal dispersions by applying shear stress. The properties of CNF gels have proven useful for foodstuffs such as mayonnaise and cosmetic products like moisturizing creams (Heggset et al., 2020; Meftahi et al., 2022).

All considered, any model for viscosity that ignores solvent-particle interactions (Dörr et al., 2013), such as the Einstein equation (hyperbolic, frequently approximated to linear) and the Batchelor equation (quadratic), are not suitable for nanocellulose dispersions, let alone for highly charged nanocellulose. Those equations consider the concentration or volume fraction of particles as the only variable, keeping the exponents fixed. In contrast, experimentation shows that the relative viscosity of CNF suspensions with the volume fraction (φ) may be fitted to Eq. 1. Once again, the exponent n depends on the charge and dimensions of the CNFs, and it may be as high as 3.7 (Hubbe et al., 2017). Fig. 3a displays this kind of trend, while Fig. 3b shows the shear-thinning behavior of anionic CNFs. While a pseudoplastic region can be observed if the shear rate is high enough, anionic CNF suspensions cannot be deemed purely viscous, as gel and/or viscoelastic regimes may be observed at low shear rates even if the concentration is as low as 0.1 wt% (Liao et al., 2021).

Typically, CNCs are anionic because of the sulfate groups introduced as a side reaction in the sulfuric acid-mediated hydrolysis, which is still the most common route for their production (Petschacher et al., 2022). Their viscosity tends to increase monotonously at low concentrations, as

the nanocrystals are randomly oriented. However, when increasing the concentration, CNC suspensions behave as liquid crystals, whose complex rheological behavior depends on the coexistence of isotropic and anisotropic (aligned with the flow) phases (Buffa et al., 2019). A plausible curve is presented in Fig. 3a. Although usually applied to systems other than cellulosic nanoparticles (Dörr et al., 2013), an Einstein-Roscoe regression could be proposed for randomly oriented CNCs:

$$\frac{\eta}{\eta_0} = (1 - \beta \varphi)^{-\alpha} \quad (3)$$

where α and β depend on intermolecular interactions and on the characteristics of the CNCs. Similarly to other suspensions of cellulosic materials, increasing the shear rate decreases the apparent viscosity, but a change in the slope (Fig. 3b) is observed as nanocrystals become increasingly aligned with the flow (Buffa et al., 2019; Qiao et al., 2016).

3.3. Importance of anionic and cationic functional groups

Carboxylate groups (COO^-), phosphate groups ($-\text{PO}_4^{3-}$) and sulfate groups ($-\text{SO}_4^{2-}$) will not only reduce the interaction in between polymer chains, but also increase the hydration potential of each substituted chain. Carboxylate groups ($-\text{COO}^-$), often found as carboxymethyl groups ($-\text{CH}_2-\text{COO}^-$) substituting hydroxyl groups, are weakly acidic and their charge will increase the electrostatic attraction for water molecules. This leads to the formation of a network structure formed by restricted water molecules, resulting in a thicker hydrodynamic radius. Phosphate groups ($-\text{PO}_4^{3-}$) and especially sulfate groups ($-\text{SO}_4^{2-}$) are more acidic and present higher charge distribution, leading to a more stable network and higher viscosity. However, they can also interact with other groups through hydrogen bonding and the hydration pattern will heavily depend on the DS of the cellulose chains, leading to a more complex behavior. In summary, the rheological aspects of soluble or nanosized cellulosic derivatives with carboxylate, phosphate, and sulfate groups on their surface can differ significantly due to differences in the pH, strength of electrostatic interactions, and ability to form hydrogen bonds or interact with water molecules through hydration (Patoary et al., 2022). Understanding these differences is important for developing cellulose-based materials with tailored rheological properties.

In general, cationic cellulose derivatives contain quaternary ammonium groups ($-N^+(CH_3)_3$) on the cellulose surface, most commonly as $-O-CH_2-CHOH-CH_2-N^+(CH_3)_3$ moieties in substitution of hydroxyl groups. The positive charges will have a similar effect of increasing the hydrodynamic radius but without the possibility of hydrogen bonding (neither as donors nor as acceptors), besides the decrease in surface tension caused by alkylammonium moieties (Cumming et al., 2011; Kaboorani and Riedl, 2015). This results in a network of less restricted water molecules, generating a completely different rheological pattern when compared to the negatively charged derivatives mentioned before.

Aside from that, the main difference on the rheological behavior of cationic and anionic is how the chains interact with water, with the anionic interaction being more enthalpy-driven and the cationic more entropy-driven. The bigger restriction and wider range of influence of negative charge on water molecules not only will result in a bigger hydrodynamic radius, but also in particles that are less susceptible to flow alignment, explaining the substantial difference in rheological behavior of polymers similar in size but opposites in charge. The gel point is achieved at lower concentrations for negatively charged chains, given the fact that flow alignment implies also in aligning a higher amount of water molecules *permanently* bound to the chain. For cationic-charged chains, the water-polymer interaction is mainly electrostatic, and more precisely ion-dipole, which leads to fluid-like behavior caused by the increasing in entropy within the system. In summary, the higher amount of interaction possibilities between the chains and solvent creates a *pathway* where the particles can flow with more ease (Fig. 4). Hindering the solvent interaction capabilities or decreasing the availability for exchanging within the solvent network trapped by the chains will lead to an increase in viscosity (Zheng and Chen, 2023).

4. Stabilization and emulsifying effects

4.1. The need for stabilizing heterogeneous mixtures

Solid particles suspended in a liquid medium in which they are insoluble, unless they are stable by nature (e.g., high zeta potential, high Debye length), tend to undergo sedimentation or flotation, depending on the density of both phases. Similarly, two immiscible liquid phases tend to minimize their interfacial area, even if the droplets of one of them are intensively dispersed in the continuous phase by means of mechanical stress. Right after reducing the size of the dispersed phase by such means, to particles or droplets that are below $1\ \mu\text{m}$ in hydrodynamic diameter, these particles or droplets are expected to follow Brownian motion (Du et al., 2017). However, in *lieu* of specific ways to prevent it, particle size soon begins increasing by diverse phenomena, including coagulation, flocculation, nucleation, and/or coalescence (Maximova and Dahl, 2006). When the size is big enough, gravitational forces outweigh the mechanisms of apparently random motion (Rother et al., 2022), leading to clearly visible phase separation.

It is not less well-known that heterogeneous mixtures are widely produced and consumed in many sectors: protein and carbohydrate hydrocolloids in the food industry (Kasprzak et al., 2018), pharmaceutical and cosmetic emulsions (Kunik et al., 2022), lubricants (Saidi et al., 2020), and coating suspensions (M. Sharma et al., 2020), to name a few. In virtually all those cases, aggregation, coalescence, sedimentation, and/or flotation are prevented by means of a stabilizing agent. From a practical point of view, we deem these heterogeneous mixtures *physically stable* if phase separation is not macroscopically observed after a long enough time-lapse.

Some typical stabilizing agents or stabilizers are lecithin (a natural emulsifier) in many products of the food industry, cetyl alcohol in cosmetics, and sodium dodecyl sulfate (one of the most common ionic surfactants) for multiple applications. These examples are water-soluble, but the use of solid particles for stabilization, and more particularly for emulsification, have gained substantial popularity along the last decade. The first use of solids, instead of soluble surfactants or dispersants, to

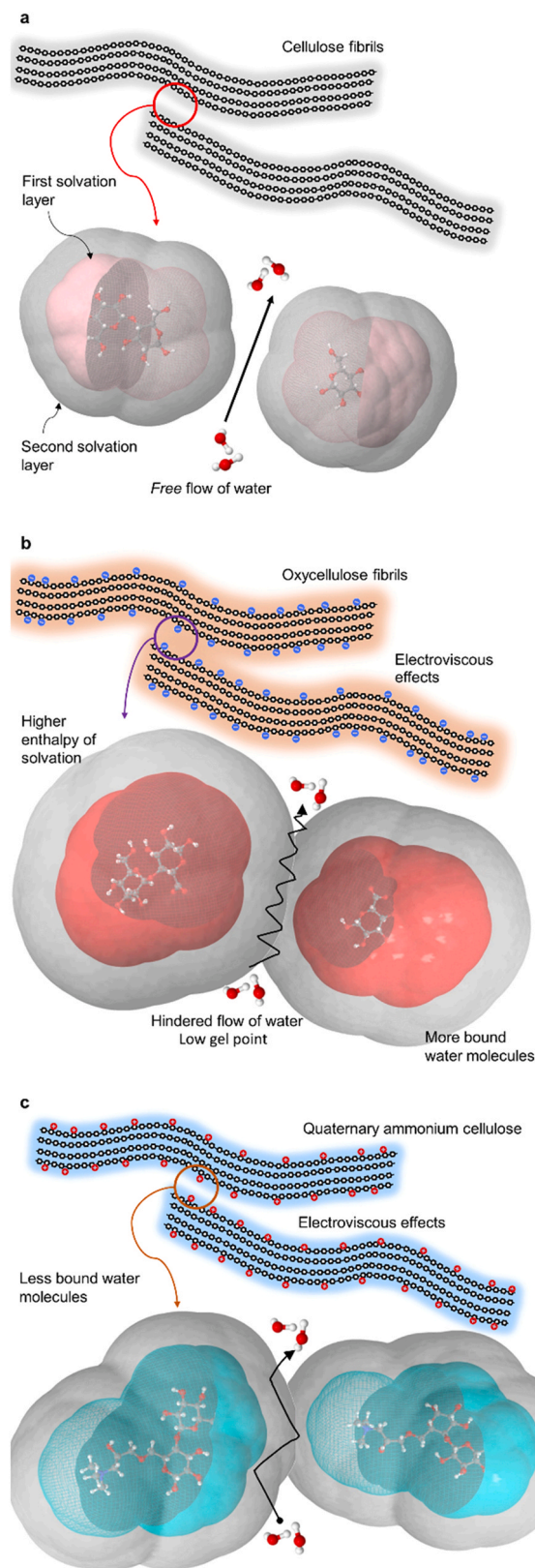


Fig. 4. Qualitative depictions of the first solvation shell (semi-permanent, bound) and second solvation shell (dynamic) in the cases of neutral cellulose (a), cellulose with carboxylate groups (b), and cellulose with quaternary ammonium groups (c), highlighting the ease or hindrance of translational movement for water molecules in relation to the fibrils.

emulsify immiscible phases was attributed to Spencer Pickering (1907), and the resulting systems are thus called “Pickering emulsions” (Lee et al., 2021; Zheng et al., 2022).

Interestingly, a relevant research trend consists of choosing cellulose, frequently in the nanoscale, to stabilize oil-in-water Pickering emulsions (Sanchez-Salvador et al., 2019; Zheng et al., 2022). And, not less interestingly, successful chemical modifications exerted on it include the incorporation of cationic and anionic groups, *i.e.*, accentuating the polar character of cellulose (Goi et al., 2019; Silva et al., 2020). If this incorporation is performed to a large enough extent, the resulting cellulose derivatives will be soluble. In fact, soluble cationic derivatives of cellulose can act not only as flocculants (Section 2), but also as tensioactive agents (Cumming et al., 2011). That said, research on cellulosic materials as emulsifiers or dispersants usually implies insoluble forms of them, and thus Pickering stabilization outweighs *classical* stabilization.

4.2. Mechanisms of pickering stabilization and the usefulness of ionization

The mechanism underlying solid-stabilized emulsions is generally described as: i) physical entrapment, ii) in terms of the rheological yield stress, iii) due to the adsorption of oil droplets onto the solid particles, iv) owing to the hydrophobic effect, or by a combination of such phenomena (Atanase, 2022). Nanocellulose-stabilized emulsions are not an exception. For instance, Goi et al. (2019) attributed the emulsification of 1-octanol in water with TEMPO-oxidized nanofibers to physical trapping within the dense network of fibrils, not finding proof of octanol-cellulose binding. Nonetheless, within the same work, those CNFs became firmly bound to other immiscible liquids with greater oil-water surface tension. In another context, Lee et al. (2021) simulated the interactions between nanocellulose and hydrophobic liquids by molecular dynamics. They concluded that, in the case of emulsifying poly(1-butene) in water, the enthalpy of the nanocellulose-oil binding is key for the reduction of the free energy.

Arguably, physical entrapment and rheological stabilization may refer to the same condition: oil droplets would coalesce if the distance between them became short enough, but the momentum transfer to said droplets is somehow hindered by the presence of the suspended or entangled particles. In these cases, the introduction of charged functional groups in cellulose, and more particularly of anionic groups (Courtenay et al., 2021), contributes to the stability of an emulsion or suspension by promoting gel-like behavior. Section 3 has already covered the role of electrostatic interactions in rheological phenomena.

Likewise, we can also merge those explanations based on adsorption and on the hydrophobic effect. Indeed, the latter implies that oil droplets are adsorbed on the cellulosic stabilizer as well, even if only in the presence of water. In that manner, the entropically favored exclusion of water molecules closes the distance between the surface of the solid stabilizer and that of the oil droplet, favoring relatively strong London dispersion forces between the droplet and certain planes of the cellulosic derivative (Lee et al., 2021; Sanchez-Salvador et al., 2019). More generally, it could be argued that adsorption takes place to a certain extent in all cases of Pickering emulsions, but not always in an irreversible manner. It is generally accepted that the higher the oil/water interfacial tension (γ_{ow}), the higher the desorption energy (E_d):

$$E_d = \pi R^2 \gamma_{ow} (1 + \cos\theta)^2 \quad (4)$$

where R is the Sauter radius of the particle; θ is the angle between the tangent line to the oil/water interface and the tangent line to the solid/water interface. Hence, whenever E_d is not high enough to grant stability by irreversible oil-cellulose binding, coalescence will only be avoided by the creation of a fibrillar network and the subsequent rheological effects. It can be noted that both mechanisms are not mutually exclusive. In a case of irreversible adsorption, once there is an excess of cellulosic

stabilizer, those fibrils, fibers or crystals that are not adsorbed on the surface of oil droplets can further enhance the physical stability of the emulsion by means of their interactions with water.

Fig. 2 depicts both kinds of stabilization mechanisms, highlighting a plausible shape of the DLVO potential curve in each case (Derjaguin and Landau, 1993). In Fig. 2a, there is no significant adsorption of ions on the surface of the droplets and, if the steric repulsion is deemed negligible, coalescence is spontaneous. In Fig. 2b, they are surrounded by nanofibers with higher zeta potential in water, either negative or positive, and their electrical double layer prevents aggregation. Even if two oil droplets collide, for coalescence to take place, the potential energy barrier to be surpassed (following the DLVO theory) is not that of oil, but that of the adsorbed particles (Hatchell et al., 2022). It is easy to see that if these particles are electrostatically repelled, coalescence will not take place. Thence comes the convenience of anionic or cationic functional groups, in a similar fashion that ionic surfactants are extremely successful in very different industries. Fig. 5.

4.3. Amphiphilicity: relevant but not necessary

Although most of the literature on cellulose-stabilized emulsions and dispersions implies insoluble microfibers, nanofibers, or nanocrystals, the most widely used anionic or cationic derivatives at an industrial level are soluble in water. Take cationic cellulose ethers for instance. As abundant as research works on cationic fibers or nanofibers are (Aguado et al., 2022; Sehaqui et al., 2016; Silva et al., 2020), the production of cationic cellulosic derivatives at a large scale is actually directed towards soluble tensioactive compounds of the Polyquaternium family, such as those with number 4 and 10 (Cumming et al., 2011). Among anionic cellulosic derivatives, the most widely used one, CMC, generally fulfills the roles of thickener and emulsifier at the same time (Wenman et al., 2023).

It is known that hydrophobic particles become adsorbed on cellulose macromolecules dissolved in concentrated phosphoric acid (Costa et al., 2019), proving the amphiphilic character of this polysaccharide. This amphiphilicity has been a hot topic during the last decade, at least since the hydrophobic effect was advocated as the main reason behind the insolubility of cellulose in neutral aqueous media (Lindman et al., 2010). Whereas cellulosic materials in general can be deemed *hydrophilic* for most industrial applications, they do have planes or areas excluded from hydrogen bonding at the level of the macromolecule or of the elementary fibril. The essentials go like this: i) all hydroxyl groups are equatorial; ii) for instance, those planes parallel to the one defined by the Miller indices (200), or *axial*, are dominated by C-H bonds, and thus dispersive forces prevail; iii) as hydrophobic planes tend to stack (Medronho et al., 2015), the parallel (cellulose I) or antiparallel (cellulose II) arrangement of polymer chains allow us to speak of whole “hydrophobic surfaces” (Sanchez-Salvador et al., 2019). Arguments *i* and *ii* explain the amphiphilic character of each cellulose chain; argument *iii* extends it to cellulose crystals or cellulosic elementary fibrils.

However, allegations of hydrophobic character at the level of fibers, microfibers, or even nanofibers must be approached critically. Briefly put, increasing the scale and the number of fibril-fibril or fibril-water interfaces decreases the degree of order of the system. Along with it, so does the validity of any reductionist explanation. First, fibril aggregates have structural water (Chen et al., 2022). Then, intermolecular interactions between elementary fibrils, and between them and water, are too dynamic to distinguish hydrophilic from hydrophobic zones *a priori*. That said, molecular dynamics simulations have recently shown that, within an aqueous medium, those cellulose chains in the vicinity of a hydrophobic surface tend to orient their water-repelling parts toward said surface (Kong et al., 2023).

Soluble or not, ionic cellulose derivatives are generally synthesized by etherification, oxidation, or esterification reactions on hydroxyl groups. Since the resulting functional groups are highly polar and/or hydrophilic, it is relevant to formulate the following question: *are*

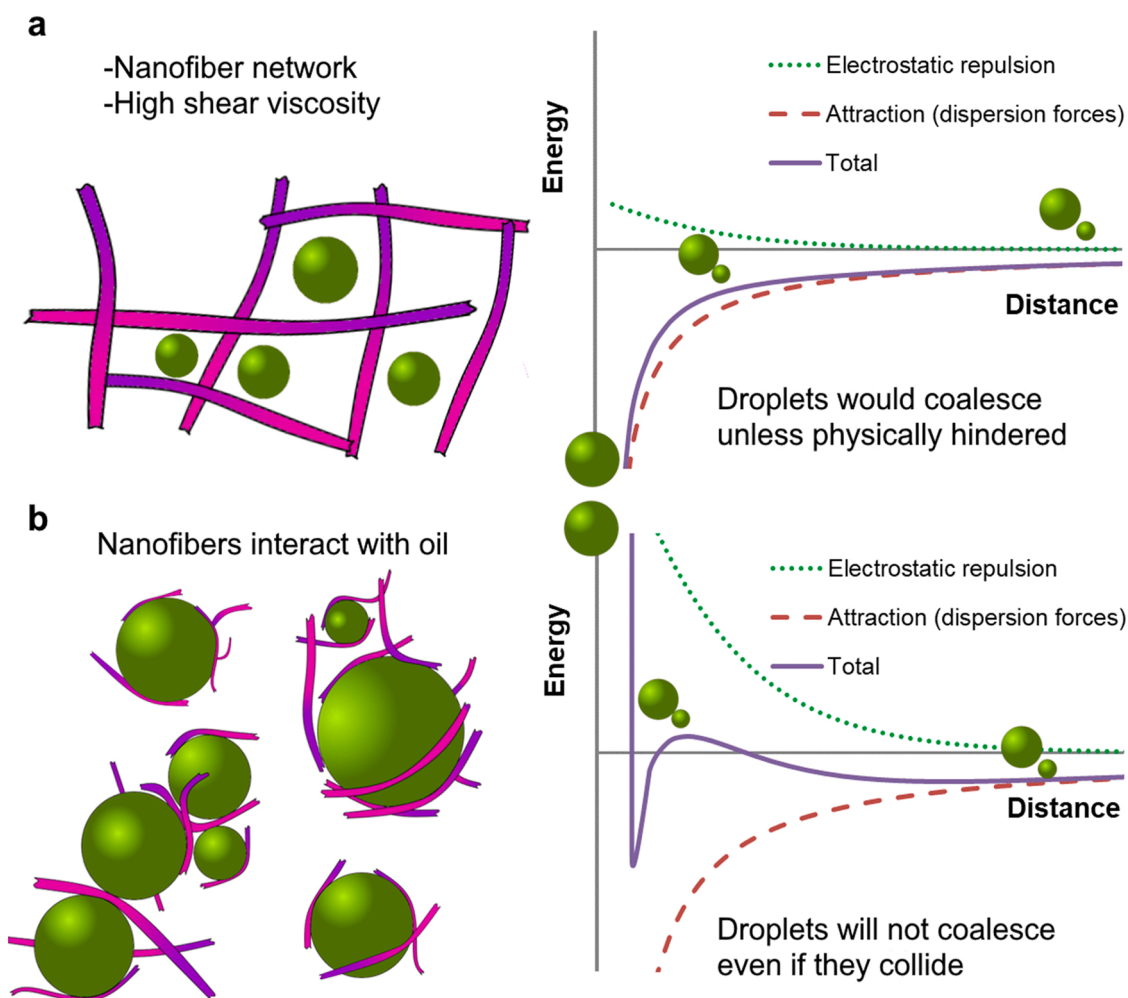


Fig. 5. The ways cellulose nanofibers may stabilize Pickering emulsions: a) physical phenomena in lieu of irreversible adsorption; b) intermolecular interactions at the interface with high desorption energy. For plotting the paradigmatic DLVO curves, steric repulsion was neglected.

anionic and cationic cellulosic derivatives still amphiphilic? After all, the resulting functional groups are usually oriented in an equatorial direction as well. To explore this, we have simulated the solvation of cellobiose, as a simplistic proxy for cellulose, and different derivatives thereof by using the publicly available script AutoSolvate (Hruska et al., 2022) under the specifications made explicit in a previous work of ours (Aguado et al., 2023). Fig. 3 shows the *syn* conformation of cellobiose (Fig. 3a), plus the lowest energy conformations of dimers of some relevant cellulose derivatives that are widely used in the literature for emulsification purposes. Fig. 6.

For example, the most common form of cationic cellulose, presented in Fig. 3b, certainly leaves some areas available for significant dispersive interactions with hydrophobic surfaces. In fact, the aforementioned product Polyquaterrium 10, widely used by the cosmetic industry, can be considered amphiphilic for this reason. However, one of the most popular (if not the most popular) derivatizations directed to synthesize cellulosic emulsifiers is the oxidation of hydroxyl groups towards highly hydrated and relatively voluminous carboxylate groups (Fig. 3c), and the resulting surfaces can hardly be deemed amphiphilic at all. Indeed, Congo Red is known not to adsorb on greatly oxidized cellulose (Isogai et al., 2010). Goi et al. (2019) make a stimulant statement in their work on oil-in-water Pickering emulsions with TEMPO-oxidized cellulose nanofibers: *[T]he reason why TEMPO-oxidized CNFs can emulsify oils better than the other nanocelluloses is not known.* As they correctly pointed out, even highly hydrophilic fibrils do not tend to desorb from oil droplets with very high interfacial tension with water.

All in all, while soluble surfactants (including soluble cellulosic derivatives) are generally amphiphilic, the surfaces of Pickering stabilizers may be highly hydrophilic for oil-in-water emulsions, highly hydrophobic for water-in-oil emulsions, or also amphiphilic. That said, several works indicate that the use of a more amphiphilic derivative may be beneficial for the stability of oil-in-water systems. CMC nanofibers, with a methylene group per substituted unit that oxidized cellulose lacks, outperformed TEMPO-oxidized CNFs for the emulsification of olive oil (Wei et al., 2019). Likewise, for high internal phase emulsions, where the oil fraction is particularly high, Pickering stabilization was enhanced by the esterification of CNCs with octenyl succinic anhydride (Chen et al., 2018). The incorporation of hydrophobic chains onto nanocellulose can even allow for oil-in-water and oil-water-oil emulsions (Heise et al., 2021). A plausible conformation of a dimer of this sort of derivatives in water is represented in Fig. 3d. In this case, the hydrophobic chain diverges from the equatorial direction.

4.4. Anionic versus cationic. Trends and pending issues in the literature

As evidenced in Table 1, the most frequently used cellulosic material to stabilize oil-in-water emulsions is anionic nanocellulose. More precisely, CNFs with carboxylate groups ($-\text{COO}^-$) outweigh the rest for reasons that go from their ease of preparation to their ability to display gel-like behavior even at low consistency. The most common method to obtain them is the TEMPO-mediated oxidation of primary hydroxyl groups in cellulose (Isogai and Kato, 1998), followed by a mechanical

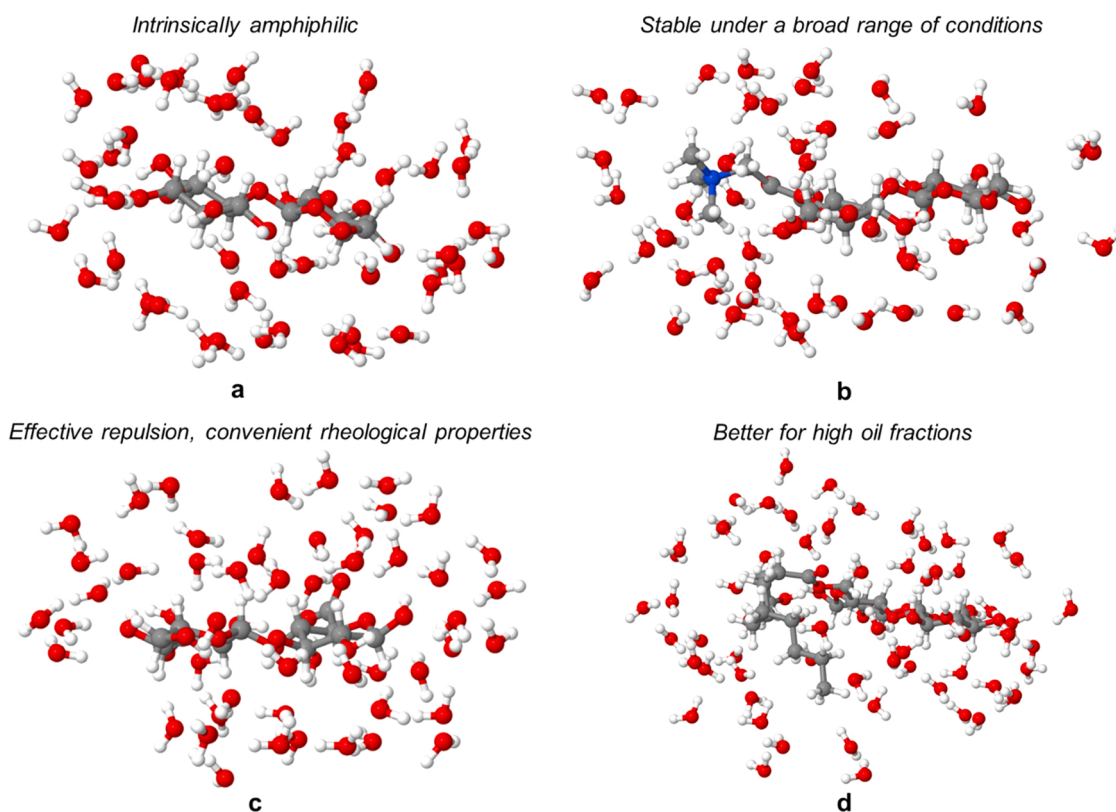


Fig. 6. Solvation clusters, as computed by molecular mechanical simulations, of: a) cellobiose, b) cellobiose cationized with EPTAC (Guo et al., 2022), c) TEMPO-oxidized cellobiose (Aguado et al., 2023), and d) cellobiose esterified with a hydrophobic chain (Chen et al., 2018). The dimer has been chosen as a proxy for cellulose. The angle of view intends to highlight the C–H bonds on the axial plane.

stage that attains nanofibrillation. Alternatives to this regioselective oxidation include, among others, carboxymethylation (Wei et al., 2019), oxidation with persulfate (Filipova et al., 2020), and esterification with dicarboxylic or polycarboxylic acids. As an example of the latter reaction included in Table 1, Luo et al. (2021) esterified cellulose with concentrated oxalic acid, thus exposing the unreacted –COOH end to the surrounding water molecules.

Outside of anionic CNFs (A-CNFs), we can find CNCs that, due to the sulfate groups attached during sulfuric acid-mediated hydrolysis (the most common approach to obtain nanocrystals), attain strongly negative surface charge. Nonetheless, the remarkable ζ -potential (–55 mV) of Yu et al. (2021)'s CNCs was not due to sulfate groups, since they were obtained by a cleaner process, but to their treatment with CMC. A similar method was employed by Ahsan et al. (2019) to provide microcrystalline cellulose (MCC) with negatively charged surfaces.

Finally, cationic cellulosic materials that can work as Pickering emulsifiers are generally produced by reacting cellulose with EPTAC, as in all three cases presented in Table 1. The key advantage of cationic nanofibers lies in their stability, as also indicated succinctly in Fig. 3. Indeed, quaternary ammonium groups have high chemical stability, they are more shielded, and their positive charge is not dependent on proton transfer phenomena. Thus, the properties of cationic cellulose suspensions hardly vary with pH changes or with salt addition (Courtenay et al., 2021). The potentially beneficial and potentially hazardous effects of electrolytes on the stability of nanocellulose-stabilized emulsions have been extensively studied by researchers of Aalto University (Heise et al., 2022; Solhi et al., 2023). However, the resistance of emulsions stabilized by cationic cellulose to changes in pH and in ionic strength is usually outweighed by their drawbacks. These include lower storage modulus, more concentration required to display gel-like behavior, and less effective electrostatic repulsion for a similar degree of substitution.

Most works dealing with nanocellulose as emulsifier were found to employ mechanical means to reduce the size of the dispersed phase to the microscale or even to the nanoscale. Homogenizing stirrers with angular speed over 3000 rpm, such as those of IKA's Ultra-Turrax series, are common for this size reduction. Hence, the role of charged nanocellulose as emulsifier or stabilizer of suspensions is not disaggregating by itself, but to prevent spontaneous (re)aggregation. In fact, even for the same proportions of nanocellulose, oil and water, droplet size and emulsion stability have been found to be highly dependent on the stirring stage (Goi et al., 2019; Souza et al., 2021). If anything, soluble anionic and cationic cellulosic derivatives can work as peptization agents, aiding in the disaggregation by mechanical shear, but extending this claim to Pickering emulsions is audacious.

Table 1 also highlights that, in most works on cellulose-stabilized Pickering emulsions, the dispersed phase is a highly hydrophobic liquid: hydrocarbons (mostly alkanes), triglycerides, and terpene-rich essential oils. The water/oil interfacial tension in these cases is generally above 20 mN/m, likely to be higher than the solid/oil interfacial tension. One possible knowledge gap that comes from surveying the literature is the scarcity of assays with solvents that are poorly miscible with water but whose interfacial tension is relatively low: 1-heptanol, diethyl ether, butyl acetate, acetophenone, or aniline, to name a few. These systems would imply that the energy required for cellulose-droplet desorption is lower (Eq. 4). Also, they have added complexity for a number of reasons: the significant soluble part decreases the dielectric constant of the solvent, they are capable of hydrogen bonding (at least as acceptors), and thus their intermolecular interactions cannot be reduced to dispersive forces. Table 2.

5. Adsorption

Considering the serious health and environmental problems that

Table 2

Anionic and cationic cellulosic materials for the emulsification of hydrophobic liquids. The continuous phase is aqueous in all cases. ζ -potential measurements correspond to conditions of neutral media (pH \sim 7) and low ionic strength. A-: anionic. C-: cationic.

Cellulosic stabilizing agent			Dispersed phase			Reference
Kind of cellulosic material	Charge quantification	Critical concentration	Organic liquid	Disaggregation	Stability	
A-CNFs	0.83 mmol COO ⁻ g ⁻¹	\leq 1 wt% ^a	Palm oil (50 wt%)	Ultra-Turrax, 10000 rpm	Likely high, due to gel behavior	Wang et al. (2018)
	1.8 mmol COO ⁻ g ⁻¹	0.15 wt%	1-octanol, cyclohexane, or hexadecane (20 wt%)	Primix's homomixer, 3000–10000 rpm	At least for one week	Goi et al. (2019)
	1.4 mmol COO ⁻ g ⁻¹	0.01 wt%	Sunflower oil (10 wt%)	Ultra-Turrax, 12000 rpm; then microfluidizer, 200 MPa	Over 6 days	Wei et al. (2019)
	ζ -potential -33 mV	\leq 0.5 wt% ^a	Cinnamon essential oil (30 vol%)	Ultra-Turrax, 10000–12000 rpm	Creaming after 10 days	Souza et al. (2021)
	ζ -potential up to -35 mV	0.15 wt%	Olive oil (10 vol%)	Ultra-Turrax, 12000 rpm	7 – > 30 days, depending on CNF content	J. Luo et al. (2021)
	ζ -potential up to -46 mV	3 g/L	Hexadecane (30 vol%)	Sonication, 17 W mL ⁻¹	Highly stable above 8 g CNFs/L	Courtenay et al. (2021)
A-CNCs	0.73 mmol COO ⁻ g ⁻¹	0.20 wt%	Dithizone-solvated chloroform (3 wt%)	Ultra-Turrax, 4000 rpm	At least for 3 months	Aguado et al. (2023)
	ζ -potential from -30 mV to -60 mV	Dependent on salt	Hexadecane (30 vol%) or styrene (20 vol%)	Sonication, 2 W mL ⁻¹	For more than a year. Salt required	Saidane et al. (2016)
	ζ -potential -33 mV	\leq 0.5 wt% ^a	Cinnamon essential oil (30 vol%)	Ultra-Turrax, 10000–12000 rpm	Creaming after 10 days	Souza et al. (2021)
	ζ -potential -55 mV	1.0 wt%	Clove oil (10 wt%)	Brief stirring (22000 rpm), then HPH	Over a broad range of conditions ^b	Yu et al. (2021)
A-MCC	ζ -potential up to -67 mV	1.0 wt%	Undecane (10 vol%)	Ultra-Turrax, 12000 rpm	3 – > 7 days, depending on preparation	Ahsan et al. (2019)
C-CNFs	ζ -potential up to $+34$ mV	\leq 10 g/L ^a	Hexadecane (30 vol%)	Sonication, 17 W cm ⁻²	Resistant to salt addition and pH changes	Courtenay et al. (2021)
	ζ -potential $+24$ mV and $+37$ mV	\leq 0.5 wt% ^a	Almond oil (30 vol%)	Ultra-Turrax, 20000 rpm	At least for 6 months	Silva et al. (2020)
C-MCC	ζ -potential up to $+70$ mV	\leq 0.25 wt% ^a	Soybean oil (20 vol%)	Ultra-Turrax, 15000 rpm	Certain loss of stability after 24 h ^c	Guo et al. (2022)

^a Results for lower values were not reported.

^b pH, temperature, and ionic strength.

^c Phase separation forced by centrifugation.

heavy metals can cause in water due to their toxicity and incompatibility, several strategies have appeared to properly remove them from water flows. Coagulation-flocculation, as described above, is one of the mostly used methodologies, but there are other approaches that can result in similar or even higher effectiveness, particularly in the case of heavy metal ions. Some examples of harmful heavy metal ions are those from cadmium, mercury, lead, chromium or arsenic, which are known to interfere with the functioning of vital cellular components, including structural proteins or nucleic acids. Others besides the aforementioned, such as copper or nickel, are also known to cause serious environmental problems. Among the strategies to solve the problem with heavy metals in wastewater, adsorption is of great interest due to its high removal efficiency, flexibility in design, and low cost. However, most of the adsorbents usually consist of activated carbon, clays, or other polymers, which are neither biodegradable nor easily regenerated.

Cellulose can serve as an excellent platform to adsorb heavy metals, mainly due to its great capacity to be functionalized, both in terms of surface functional groups and morphology. Some of the surface chemical functionalization for heavy metal ion uptake that have been reported are TEMPO-mediated oxidation (Fiol et al., 2019; Liu et al., 2016), Fe²⁺/H₂O₂ oxidation (Fan et al., 2019), periodate oxidation (Shahnaz et al., 2020), carboxymethylation (Qin et al., 2019), nitro-oxidation (Sharma et al., 2018), esterification (Tang et al., 2020), cationization (Zhao et al., 2021), or phosphorylation (Mautner et al., 2016), among others (Si et al., 2022). However, not only surface characteristics impart an important role on the removal of heavy metals from wastewater, but also morphology. In a recent study, we demonstrated that the use of nanosized cellulose fibers, previously modified by TEMPO-mediated oxidation, exhibited a higher adsorption capacity than fibers with

lower surface area (Fiol et al., 2019). Indeed, this is attributed to the higher availability of functional groups at the surface (COO⁻ groups, in this case) and the reduction of steric effects that may hinder ionic interactions. Cellulose-based adsorbents have been reported to effectively adsorb metal ions such as Cu²⁺, Pb²⁺, Hg²⁺, Cr³⁺, Cr⁶⁺, Fe³⁺, and Ag⁺, among others.

As for other applications, the initial concentration of metal in the solution, together with the pH and conductivity of wastewater, can have an important role on the adsorption capacity of the cellulose-based adsorbents for heavy metals removal (Shahnaz et al., 2020). One useful tool to monitor the adsorption capacity of adsorbents, as well as the affinity between the metal and the adsorbent, is determining the parameters of the Langmuir isotherm (Bhatnagar and Jain, 2005; Hsi and Langmuir, 1985):

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (5)$$

where q_e is the adsorbed metal per gram of adsorbent (mg/g), q_m is the maximum amount of metal that can be adsorbed per gram of adsorbent (mg/g) in equilibrium, C_e is the equilibrium concentration of free metal ions in the solution (mg/L), and K_a is a constant related to the energy of adsorption (L/mg), which reflects the affinity between the metal and the adsorbent. In fact, K_a and q_m can be easily calculated by means of rearranging the isotherm above in its linearized form:

$$\frac{1}{q_e} = \frac{1}{K_a q_m C_e} + \frac{1}{q_m} \quad (6)$$

In Table 3, we have collected the most relevant works on metal ions adsorption with cellulose-based adsorbents, providing information

Table 3
Langmuir isotherm parameters of cellulose-based metal ion adsorbents.

Adsorbent	Modification	Target metal ion (s)	Langmuir parameters		Comments	Reference		
			q _m (mmol/g)	K _a (L/mmol)				
CNF	TEMPO-mediated oxidation	Cu ²⁺	4.85	8.33	K _a not provided K _a not provided R ² of 0.849	(Fiol et al., 2019)		
		Cu ²⁺	1.62	6.35		(M. Li et al., 2019)		
		Zn ²⁺	1.14	24.05				
	Esterification Carboxymethylation	Cu ²⁺	1.32	0.55		(Tang et al., 2020)		
		Cu ²⁺	1.82	-		(Qin et al., 2019)		
Nitro-oxidation	Pb ²⁺	10.96	-	(Sharma et al., 2018)				
Microfibrillated cellulose	Succinylation/Carboxyl	Cu ²⁺	1.88	58.90	R ² of 0.902	(Hokkanen et al., 2013)		
		Zn ²⁺	1.50	59.21				
		Ni ²⁺	0.72	12.32				
		Co ²⁺	1.30	3.55				
Softwood	Citric acid esterification/Carboxyl	Cd ²⁺	1.95	691.00	R ² of 0.923	(Low et al., 2004)		
		Cu ²⁺	0.37	-				
		Pb ²⁺	0.40	-				
Whatman paper	Succinylation/Carboxyl	Cu ²⁺	2.42	196.53	K _a not provided K _a not provided	(Alves-Gurgel et al., 2008)		
		Cd ²⁺	2.22	203.62				
		Pb ²⁺	2.41	1036.00				
Microcrystalline cellulose	Graft polymerization acrylamide and acrylic acid	Cd ²⁺	5.32	4.48	R ² of 0.923	(El-Naggar et al., 2018)		
		Cu ²⁺	0.21	100.97				
		Zn ²⁺	0.13	50.70				
		Fe ³⁺	0.16	22.90				
		Ni ²⁺	0.15	33.45				
		Co ²⁺	0.17	8.25				
		Pb ²⁺	0.10	267.29				
		Incorporated dithiooxamide	Cd ²⁺	0.07			0.10	(Jorgetto et al., 2013)
			Cu ²⁺	0.06			2.43	
		p-aminobenzoic modification	Cd ²⁺	1.72			3.10	K _a not provided
	Cu ²⁺		1.96	4.98				
	Ni ²⁺		1.88	3.67				
	Pb ²⁺		2.01	5.73				
	Zn ²⁺		1.93	4.55				
	Tetrafluorotereph-thalonitrile crosslinking	Pb ²⁺	0.10	190.62	K _a not provided	(Cao et al., 2017)		
Cu ²⁺		0.28	43.18					
Cd ²⁺		0.13	14.89					

regarding the selected cellulose modification (functionalization and morphology), the target ions and, when available, the Langmuir isotherm parameters.

Apart from heavy metals, organic dyes are also considered as pollutants in water, posing a significant environmental problem in many parts of the world. Due to their complex aromatic structure, they can be found in the form of cationic, anionic, or non-ionic species. The mechanism behind the removal of cationic dyes is similar to that described above for cationic metal ions, where the presence of functional groups such as carboxylic is of great importance (Voisin et al., 2017).

However, cationic cellulose-based adsorbents are also of great interest, particularly for the removal of anionic dyes (Jin et al., 2015a). As in the case of heavy metals, the morphology and surface area of the adsorbent also plays a key role, and most of the literature is focused on the use of amino-functionalized CNCs, showing notable uptakes of anionic dyes such as acid red GR, Congo red 4BS or reactive light K-4 G (Jin et al., 2015b, 2015a; W. Zhu et al., 2016). Apart from organic dyes, cationic cellulose-based adsorbents are also of great interest for the removal of other negatively charged contaminants, such as nitrate, phosphate, or sulfate (Sehaqui et al., 2016).

Other strategies for the removal of metal ions encompass the use of packed columns, where the adsorption is performed continuously. In a previous study, Fiol et al. (2021) proposed the use of partially modified TEMPO-oxidized CNF aerogels for continuous uptake of Cu²⁺. It was found that the use of 3D-structured networks is more efficient than calcium alginate beads, as the diffusion of metal ions through highly

charged water is avoided and the surface area is much higher. However, the authors also highlighted the need of partially jeopardizing the adsorption potential to avoid aerogel gelation due to excessive water absorption. Other authors also have reported the use of cellulose-based adsorbents for packed columns; such is the case of Rossi et al. (2018), who demonstrated that subjecting bacterial cellulose to carboxymethylation can result in an efficient Pb²⁺ adsorption, both in batch and in continuous, as well as an excellent sorption/desorption performance. In both cases, the adsorption fitted the breakthrough curves by previously reported models, such as the Yoon-Nelson, the Bohart-Adams or the Thomas models. Comparatively, Fiol et al. (2021) found an adsorption capacity of the adsorbent per volume unite (N₀) of 3.028 mg/cm³ and a breakthrough time of 450 min for Cu²⁺, while in the case of Rossi et al. (2018) the value of N₀ accounted for 2.89 mg/cm³ of Pb²⁺ but the shape of the curve exhibited the presence of Pb²⁺ at the outlet from the very beginning. This is strongly related to the adsorption kinetics, which is defined by the k_{BA} parameter and can be confirmed by other models through the calculation of logistic parameters (Chu, 2020). This kinetics can be affected by the surface area, but also by the ionic strength or other steric effects hindering the adsorption of metal ions onto the cellulose-based adsorbent surface (Fiol et al., 2004). The mechanism behind the adsorption of metal ions has been previously related to thermodynamics, namely entropy, enthalpy, and Gibbs free energy. Lombardo and Thielemans (2019) noted that adsorption onto cellulose surface may be driven by two conflicting mechanisms: (i) the release of water molecules upon binding and (ii) the formation of new

interactions (i.e., electrostatic, coordinate bonds, or Van der Waals forces). In most of the cases, the electrostatic interactions between the cellulose-based adsorbent and the adsorbate (pollutant in the case of wastewater) are predominant in the adsorption process, rather than complex formation or other interactions.

6. Encapsulation

6.1. General purposes and main methods of encapsulation

There are many fields in which the immobilization, binding, or confinement of compounds is necessary, either for their preservation or for their controlled release (Oehme et al., 2011). In this regard, the encapsulation process involves enclosing one material inside another. The encapsulation of active compounds is a technique widely used in the food industry, biomedicine, and even fields such as energy storage (Das and Fernandez, 2020; Li et al., 2017; Sheng et al., 2021). The need to protect sensitive, unstable or reactive compounds from the harsh environment of industrial processing and the aggressive conditions in the stomach, as well as the loss of some compounds during food processing, have increased interest in encapsulation (Fareez et al., 2018; Giampieri et al., 2014; Hong et al., 2019). In the biomedical sector, encapsulation has enabled breakthroughs in three-dimensional cell culture systems (Das and Fernandez, 2020) and controlled drug release (Kumari et al., 2021). In the field of energy storage, encapsulation systems are typically used to prevent leakage, resulting in stable containers (Liu et al., 2015).

The physical and chemical characteristics of these microcapsules are mainly determined by the material selected for wall formation and the technology used, which should be adapted to the specific application. The main encapsulation methods are spray drying, emulsion-based encapsulation, coacervation, and electrostatic coating (Eghbal and Choudhary, 2018; Oliveira et al., 2016; Yang et al., 2015).

The spray drying technique is widely used to encapsulate bioactive materials in the food and pharmaceutical industries. It involves atomizing a solution containing the component to be encapsulated and the wall material, forming small solid particles (Mohammed et al., 2020). The emulsion encapsulation system stabilizes an emulsion where the compound and encapsulating material are present, usually achieved by the addition of surfactants. The emulsion droplets are solidified by chemical or thermal processes, creating a stable capsule (Lu et al., 2016). Coacervation is based on the interaction between two oppositely charged polyelectrolytes in an aqueous medium, forming a complex between the encapsulating materials. The complex can be solidified by crosslinking (Eghbal and Choudhary, 2018). Electrostatic Coating involves spraying simultaneously charged composite and encapsulating material in an aerosol. At this point, the charged particles attract each other and form a capsule around the compound. Usually, these capsules are solidified by heating (Szafran et al., 2012).

Sodium alginate (Alg) is one of the most widely used materials for encapsulating polyphenols and probiotics in the food industry. Alg is a natural polysaccharide derived from marine algae that is biocompatible, non-toxic, and pH-sensitive (Banerjee et al., 2013). However, there are limitations to its use, including high porosity in the resulting microcapsules, instability when exposed to heat, and rapid degradation under gastric conditions (Hu et al., 2018).

Other materials commonly used in the food and biomedical sectors are gelatin and chitosan (Mishra et al., 2021). Chitosan is a cationic polysaccharide known for its bifunctionality, biodegradability, biocompatibility, and antimicrobial properties (Confederat et al., 2021). However, chitosan's low porosity, lower stability, reduced pore size, and low mechanical properties limit its use. Nonetheless, ionization of amine groups at low pH allows for the formation of compounds with other biopolymers (Alirezalu et al., 2021; Mehdizadeh et al., 2020).

6.2. Cellulose derivatives as confiner polymers

Cellulose derivatives are a versatile and biocompatible approach to create protective coatings for a wide range of compounds. Among them, MC and sodium CMC are notable due to their water solubility, while HPMC is known for its film-forming and mechanical properties (Fareez et al., 2018). In recent years, the development of encapsulation systems using CNFs has drawn the attention of many researchers. CNFs possess the essential characteristics of cellulose, but with a higher specific surface area and many hydroxyl groups that allow the creation of multiple binding sites for different compounds such as drugs, probiotics, antioxidants, antibacterial agents, flavors, and fragrances (Gao et al., 2014; Löbmann and Svagan, 2017). Examples of cellulosic materials used for binding specific compounds are displayed in Table 4.

In general, it can be established that the diameter of microcapsules determines their size, which in turn affects their physical properties, such as dimensional stability, wall permeability, and the rate of compound release (Li et al., 2008). Numerous studies have shown that the resulting microcapsule size and morphology depend on the polymer used for encapsulation and the encapsulation method employed (Bile et al., 2015; Freitas et al., 2005; Li et al., 2008). Microcapsules with a larger diameter have a smaller specific surface area and a larger volume, which generally results in a slower release rate. Conversely, microcapsules with a smaller diameter may have a faster release rate due to their larger specific surface area. Therefore, one parameter to be monitored is the encapsulation efficiency of microcapsules, which refers to the amount of compound material enclosed within the polymeric shell. The higher the encapsulation efficiency value, the more compound is protected from degradation and the more control over the release rate. As mentioned earlier, the encapsulation efficiency is a function of the physicochemical properties of the core material, the material used for the manufacture of the polymeric shell, and the method used to obtain the microcapsules. In this sense, hydrophobic compounds generally exhibit higher encapsulation efficiency in hydrophobic materials, while hydrophilic compounds show higher encapsulation efficiency in hydrophilic microcapsules.

Nanocellulose is a promising material to produce microcapsules due to its biocompatibility, biodegradability, high specific surface area, and ability to form stable films and coatings (Wang et al., 2022). Additionally, its barrier or release properties can be modified by functionalization towards neutral, cationic or anionic derivatives. Despite these advantages, one of the challenges associated with the use of nanocellulose in encapsulation is its high tendency to aggregate, which affects the stability and properties of nanocellulose-based microcapsules. To address this challenge, various methods have been reported, including the use of surfactants and surface modifications to grant spacer effects, steric hindrance or electrostatic repulsive forces (Shishir et al., 2018).

In the food industry, the use of nanocellulose for encapsulating compounds has the potential to enhance the stability and prolong the shelf life of food products. Aromas, antioxidants, and nutraceuticals are among the primary compounds that have been identified as suitable materials for encapsulation. The primary motivation is to prevent their degradation or interaction with other food components, as well as to control their release. Numerous studies have demonstrated the potential of nanocellulose for encapsulating compounds in the food industry. For instance, Maleki et al. (2020) encapsulated *L. Rhamnosus* probiotic powder with varying proportions of CNCs. CNCs improved encapsulation efficiency and increased the survival rate of bacteria under gastrointestinal conditions.

The potential use of nanocellulose for agricultural applications, including encapsulating compounds such as pesticides, herbicides, and fertilizers, has gathered considerable interest. The direct release of nanocellulose in the environment offers significant advantages in terms of sustainability, increased effectiveness, and reduced toxicity. For instance, Tang et al. (2019) successfully employed cinnamoyl

Table 4

Some encapsulation methods for active compounds involving cellulose derivatives, sorted by their application, and their main features.

Application	Encapsulation method	Compound	Microcapsule	Additive	Mean diameter (μm)	Encapsulation Yield or Efficiency (%)	Reference
Food Industry	Spray Drying	Calcium citrate and Calcium lactate	CMC	-	13–19	84–91	(Oneda and Ré, 2003)
			HPMC	-	7–489		
	Dripping + Freeze-Drying	Proanthocyanidins	Alg	CaCl ₂ + NaCl	1296	86.5	(Sheng et al., 2021)
			Alg – MC	+ Tween 80	1321	88.8	
			Alg – HPMC	-	1338	92.7	
	Dripping + Freeze-Drying	L. Plantarum	Alg – MC	-	1322	97.1	(Fareez et al., 2018)
			Alg – CMC	-	1312	96.2	
Filtration + Freeze-Drying	Quercetin	Alg – HPMC	-	1338	96.5	(X. Li et al., 2019)	
		TEMPO-CNF	-	Nanopaper	88.8		
Agrochemicals	Dripping + Filtration	Whey protein isolate	Alg – CNF	CaCl ₂	488 – 559	-	(Rungraung et al., 2022)
			Alg – CNC	-	449 – 461	-	
	Dripping + Freeze-Drying	L. Rhamnosus	CNC	-	0.16 – 4.37	82.8–89.5	(Maleki et al., 2020)
			HPMC phthalate	Span 20	12.7	68.0	
Energy	Spray Drying	Gallic acid	Ethyl cellulose	Span 20	15.2	34.9	(Cortesi et al., 2017)
			Polydopamine - CNC	Cinnamoyl chloride	0.08 – 0.11	40 – 93	
			Chitosan - CNF	Tween 80	0.43	90.8	
Biomedical	Injection into hydrogel	Cell aggregates	TEMPO-CNF	-	Nanopaper	-	(Li et al., 2017)
			TEMPO-CNF	-	Aerogel	-	
Biomedical	Dripping + Freeze-Drying	Ocimum basilicum L.	Chitosan – TEMPO-CNF	-	Aerogel	-	(Das and Fernandez, 2020)
			Enzymatic-CNF	DMSO	12	99.14	
	Dripping + Centrifugation	Curcumin	Alg – TEMPO-CNF	CaCl ₂	1250	> 95	(Zhang et al., 2018)
			Alg – TEMPO-CNF	CaCl ₂	1250	> 95	

ZPP: 3-(6-methoxynaphthalen-2-yl)– 2-(4-(pyridin-4-yl) phenyl) acrylonitrile

chloride-modified cellulose nanocrystals for the encapsulation of polydopamine. However, there are several challenges associated with utilizing nanocellulose for agricultural encapsulation, such as developing biocompatible and cost-effective production methods, and ensuring compatibility between the encapsulation materials and target crops and soil conditions.

In the energy sector, researchers have explored the possibility of using nanocellulose for encapsulating phase change materials (PCMs) in thermal energy storage. PCMs can store significant amounts of thermal energy during the melting process and release it during the solidification process, making them an attractive option for thermal energy storage systems. However, their limited thermal conductivity and tendency to leak out of their containment material over time restrict their practical use. Nanocellulose can serve as a porous matrix for PCM encapsulation, enabling enhanced thermal conductivity and long-term stability. Additionally, nanocellulose can be readily functionalized to modify its surface properties and improve compatibility with both the PCM and the containment material (Shchukina et al., 2018; Shen et al., 2023). The potential applications of nanocellulose encapsulation in the energy sector include encapsulating fuel and lubricant additives to boost their stability and performance, as well as encapsulating enzymes for biofuel production. However, challenges such as developing cost-effective production methods and ensuring the compatibility of encapsulation materials with intended applications still need to be addressed in the use of nanocellulose for PCM confinement purposes.

The biomedical sector has shown significant interest in nanocellulose in recent years, particularly as a potential encapsulation material in various applications such as drug delivery, tissue engineering, and wound healing (Klemm et al., 2006). Encapsulation of therapeutic molecules, such as proteins, peptides, and small molecules, has received significant attention in recent studies (Lin and Dufresne, 2014). Nanocellulose-based carriers can protect encapsulated drugs from degradation, enhance their bioavailability, and enable controlled

release over time. In tissue engineering, nanocellulose-based materials have been utilized to encapsulate cells and growth factors, providing a three-dimensional scaffold for cell growth and differentiation, while protecting them from host immune response and improving their survival and function (Patel et al., 2019).

Nanocellulose also holds promise for wound healing applications (Patel et al., 2022). Nanocellulose-based dressings have demonstrated excellent mechanical strength, high water holding capacity, and exceptional biocompatibility, making them ideal for use in wound healing. Encapsulation of growth factors and antibiotics in nanocellulose-based dressings can further enhance their therapeutic effects and promote wound healing. However, utilizing nanocellulose for encapsulation in the biomedical sector presents some challenges, such as developing scalable production methods and ensuring the safety and biocompatibility of encapsulation materials.

6.3. Attractive and repulsive forces in encapsulation

Electrostatic interactions play a crucial role in the encapsulation of compounds, particularly with nanocelluloses (Feng et al., 2023). These interactions arise due to the surface charges present on the encapsulating material and the charges of the encapsulated molecules. Opposite charges attract each other, leading to encapsulation of the molecule within the matrix, while similar charges repel each other, hindering encapsulation. The strength of electrostatic interactions can significantly affect encapsulation efficiency, release kinetics, and stability of the encapsulated molecules (Hartvig et al., 2011). Strong electrostatic interactions result in tighter encapsulation and slower release, whereas weaker interactions can lead to faster release.

Moreover, the pH and ionic strength of the solution can also impact the electrostatic interactions between the encapsulating material and the encapsulated molecules (Teo et al., 2022). Therefore, adjusting the pH, ionic strength, and surface charge of the encapsulating material can

help attain the specific objectives of encapsulation. Overall, electrostatic interactions are a crucial factor in the encapsulation process and require careful consideration for the optimal encapsulation of compounds.

The choice between cationic or anionic nanofibers for encapsulation depends on the charge of the molecules to be encapsulated. Cationic nanofibers might be more effective for encapsulating negatively charged molecules, such as some drugs, polypeptides or nucleic acids, while anionic nanofibers might be more effective for encapsulating phosphonium or ammonium-containing compounds, including some antibiotics and pesticides (Li et al., 2022; Liu et al., 2018; Mendes et al., 2017). In addition to electrostatic interactions, other factors such as the size and shape of the nanofibers, the porosity of the nanofiber matrix, and the compatibility of the nanofibers with the encapsulated molecules can also affect the encapsulation efficiency and release kinetics (Teo and Ramakrishna, 2009). As aforementioned, anionic.

As evidenced from Table 4, the main cellulose derivatives used for encapsulation primarily have negative surface charge, being either neutral or anionic in terms of nominal charge. CMC and hydroxypropyl methyl cellulose phthalate are among the most commonly used anionic cellulose derivatives for encapsulation (Fareez et al., 2018). Moreover, other anionic cellulose derivatives, such as TEMPO-oxidized CNFs, have also been studied for encapsulation systems (Das and Fernandez, 2020; Ibrahim et al., 2022; Mishra et al., 2021).

The negatively charged carboxymethyl groups ($-\text{CH}_2-\text{COO}^-$) of CMC can interact with cationic molecules via attractive electrostatic interactions (Aarne et al., 2012). These carboxymethyl groups form ionic bonds with positively charged groups on the encapsulated molecules, such as amino groups or quaternary ammonium groups (Oneda and Ré, 2003). The strength of these interactions is influenced by pH: at higher pH values, the carboxymethyl groups become more ionized, increasing the electrostatic repulsion between polymer chains, and reducing the strength of interactions with the target compound. Conversely, at lower pH values, the carboxymethyl groups ionize less, allowing for stronger electrostatic interactions. Additionally, CMC can form hydrogen bonds with the compound, further improving encapsulation efficiency. HPMC phthalate, containing phthalic acid groups whose degree of ionization depends on the pH, follow the same principle (Hu et al., 2018; Sheng et al., 2021).

TEMPO-oxidized nanocellulose have large surface area and excellent mechanical properties, making them an attractive material for encapsulation. These anionic nanofibers can interact with other molecules through ionic bonding and electrostatic repulsion, depending on their surface charge. The negative charge of the carboxylate groups on the TEMPO-CNF surface can attract positively charged or zwitterionic molecules, allowing for the formation of stable adducts or encapsulation systems. Moreover, the high surface area and aspect ratio of TEMPO-CNF make it a suitable material for loading and delivering bioactive molecules (Zhang et al., 2018).

In another context, there are cellulose derivatives with cationic character that can be used for encapsulation. Cationic nanocellulose has been applied in various fields including drug delivery, gene delivery, and food packaging. In drug delivery, cationic nanocellulose has demonstrated promising results in encapsulating small molecule drugs, proteins, and peptides, thereby improving drug solubility, stability, and release (Atanase, 2022; Surendran and Sherje, 2022). In gene delivery, cationic nanocellulose has been employed to encapsulate DNA and RNA, exhibiting potential as a non-viral gene delivery vector. In food packaging, cationic nanocellulose has been used as a coating layer to enhance the barrier properties of packaging materials (M. Sharma et al., 2020).

The characteristic functional groups of non-ionic cellulose derivatives, such as ethyl cellulose, MC, and HPMC are neutral and lack any significant ionic character, so their interactions with other molecules are primarily governed by non-ionic interactions such as London dispersion forces. Consequently, non-ionic cellulose derivatives offer versatility for encapsulation as they can interact with a wider range of molecules. Nonetheless, in these cases, the role of repulsive interactions,

useful e.g. to grant a high surface area, is played by comparatively weak steric effects.

7. Membranes

Cellulose derivatives are highly versatile materials that are widely used in various filtration and osmosis processes due to their unique properties and ability to perform well under different conditions. In filtration, an operation based on momentum transfer, cellulose derivatives such as cellulose acetate (CA), nitrocellulose and anionic CNFs are highly effective at trapping and removing particles from liquids and gases, achieved through physical trapping or adsorption on the surface of the material. In contrast, osmosis is a process whereby solvent molecules move from a region of lower solute concentration to a region of higher solute concentration across a semi-permeable membrane. Cellulose derivatives may also be highly effective in producing membranes for reverse osmosis and nanofiltration applications (Fei et al., 2018). These membranes allow water to pass through while selectively rejecting dissolved salts and other impurities, making them highly useful in the treatment of wastewater, desalination of seawater, and other industrial processes (P. R. Sharma et al., 2020; Warsinger et al., 2018).

Water filtration is a widely used method for water purification, with membranes being a key component in separating particles or ions. There are two main types of membranes: microfiltration for particle separation and reverse osmosis for ion separation (Warsinger et al., 2018). These membranes typically operate under pressure, with smaller pore sizes requiring higher pressure. The average pore size of microfiltration and ultrafiltration membranes is greater than 1 nm (Van Der Bruggen and Vandecasteele, 2003), while nanofiltration and reverse osmosis membranes have pore sizes smaller than 1 nm (Geise et al., 2010).

Asymmetric pore structure is a common feature of membranes, which typically consist of three layers. The nonwoven substrate layer provides overall mechanical strength and has the highest porosity (60–70%), while the intermediate porous layer has an even distribution of pores on the surface with relatively low porosity (25–50%). The densely cross-linked barrier layer has a smaller pore size distribution and lower porosity (Lalia et al., 2013). Nanocellulose and neutral or ionic cellulose derivatives of cellulose, have been applied as membrane material for water desalination (P. R. Sharma et al., 2020). In this direction, nanocellulose is particularly attractive for membrane synthesis because it allows for smaller pore size without sacrificing porosity. By reducing fiber diameter, the effective mean pore size can be reduced while maintaining porosity, as the average pore size is generally directly proportional to fiber diameter in the nonwoven layer (P. R. Sharma et al., 2020).

Despite their good properties, there are some limitations to using cellulose and its derivatives as membranes for water desalination. For example, they are highly sensitive to pH and can exhibit reduced activity at high temperatures, low thermal and mechanical resistance, and poor resistance to scaling and chlorine (Shafiq et al., 2018). Chlorine, in particular, can affect the salt rejection capacity of cellulosic membranes, as it can deteriorate the membrane's selectivity, permeability, and overall performance when present at high concentrations (Fujiwara and Matsuyama, 2008). To overcome these limitations, cellulose derivatives can be modified to improve their function as membranes in filtration systems. Proper chemical modifications can improve their resistance to chlorine and scaling, their thermal and mechanical resistance, and their selectivity and permeability (Shafiq et al., 2018).

Some relevant membranes with cellulose derivatives that have been recently reported are presented in Table 5. Neutral derivatives (CA, CTA, CMCA) outweigh the anionic ones (CMC, SCMC, TEMPO-oxidized CNFs), and cationic cellulose is seldom employed for this purpose. CA is one of the most widely used derivatives for the manufacture of membranes due to its excellent film-forming properties and its high permeability to water (Shokri and Adibkia, 2013). CA membranes have a relatively high degree of hydrophobicity, which leads to high fouling

Table 5
Key characteristics of some membranes based on cellulose and intended for pollutant removal.

Cellulose derivative	Additive	Contaminant concentration	Rejection (%)	Water flux (L/m ² ·h)	Pressure (bar)	Reference
CA	Graphene oxide	25000 ppm NaCl	90	85	25	(Ghaseminezhad et al., 2019)
CA	Chitosan	35 g/L NaCl	94	18	60	(El-Ghaffar et al., 2020)
CA/CMCA	PEG	0.1 wt% protein (BSA)	98.7	73.2	Hydrostatic	(Han et al., 2013)
CTA	Activated charcoal	96 ppm uranium	60	363	69	(Villalobos-Rodríguez et al., 2012)
CTA	α-Fe ₂ O ₃ /PAN/ CaCO ₃	100 mg/L Pb ²⁺ and Cu ²⁺	> 90	-	-	(Kumar et al., 2022)
CMC	PES/GA	100 mg/L Na ₂ SO ₄	91.9	47.9	40	(Jabbarvand Behrouz et al., 2021)
		100 mg/L MgSO ₄	68.63			
		100 mg/L NaCl	45.9			
SCMC	GA	1 g/L Na ₂ SO ₄	88.5	39.6	50	(Shao et al., 2014)
TEMPO-CNF	-	Canola oil	98	166	Hydrostatic	(Halim et al., 2019)
Electrospun-CNF	Graphene oxide	50 vol% Red Oil	97	960	Hydrostatic	(Ao et al., 2017)

CMCA: Carboxymethyl cellulose acetate, PEG: Polyethylene glycol, PES: Polyethersulfone, GA: Glutaraldehyde, SCMC: Sulfated carboxymethyl cellulose

resistance and good mechanical strength. However, they have relatively low selectivity for water desalination and can exhibit decreased performance at high temperatures.

Cellulose triacetate (CTA) is another widely used derivative for the manufacture of membranes, and it has better thermal and chemical stability than CA (Shokri and Adibkia, 2013). CTA membranes have a higher degree of hydrophilicity compared to CA membranes, which leads to lower fouling resistance but higher salt rejection. However, CTA membranes can be prone to swelling, which can negatively affect their selectivity.

CMC is a water-soluble, anionic cellulose derivative that is used to enhance the hydrophilicity of membranes. CMC is often used as a modifier for CA or CTA membranes to improve their performance in water desalination (Shokri and Adibkia, 2013). CMC-modified membranes have higher water permeability and lower salt rejection compared to unmodified membranes, but they also have lower fouling resistance.

Nanocellulose, on the other hand, offers attractive characteristics for membrane synthesis due to its unique structural and mechanical properties (P. R. Sharma et al., 2020). CNF membranes have high strength and toughness, as well as high selectivity for water desalination. The pore size of these membranes can be finely tuned by controlling the size of the CNFs used in their manufacture. However, the production of nanocellulose membranes is still relatively expensive, which limits their widespread use.

When producing filtration membranes, it is important to consider several key aspects of cellulose derivatives. One of the most relevant is the molecular weight, as this characteristic determines the membrane's mechanical properties, including tensile strength and flexibility. Additionally, the solubility of the cellulose derivative plays a crucial role in the manufacturing process, affecting how easily the material can be dissolved in the appropriate solvent. The pore size of the membrane is another critical factor, as it determines the effectiveness of the membrane's filtration performance. Thickness is also an important characteristic, as it affects the membrane's performance in various ways. Another crucial aspect to consider is the flux or permeability of the membrane, as this directly impacts its overall performance. Finally, the chemical resistance of the membrane to various solvents and chemicals can significantly affect its durability and lifespan, making it an essential consideration during production.

In addition, membranes made of nanocellulose can be obtained through casting or electrospinning techniques, with the main difference between these processes lying in the arrangement of the nanofibers. However, creating stable adsorbent membranes that exhibit high binding affinity towards a broad spectrum of heavy metals in the aqueous phase is a significant challenge (Pei et al., 2021). One potential solution is to introduce carboxylate functional groups onto the fiber surfaces. Juntadech et al. (2021) proposed modifying an electrospun CA nanofiber membrane using TEMPO-mediated oxidation to capture heavy

metal ions from aqueous solutions. In this case, electrostatic interactions between an anionic cellulosic derivative and a cationic pollutant are evident, but cellulose-based membranes rely less on surface charge than other materials covered in this review. Instead, their usual roles are those of support and size exclusion. Furthermore, although anionic derivatives such as CMC, TEMPO-oxidized CNFs and SCMC have been proven useful in membranes (Table 5), when it comes to water filtration, researchers and manufacturers should consider the increased swelling ability that anionic functional groups imply.

8. Antimicrobial materials

There are many sound and valid reasons to provide cellulosic materials with antibacterial or antifungal properties. Some examples are active food packaging with antimicrobial activity to extend the shelf life of products (He et al., 2020), facemasks (Khan et al., 2021), biomedical and environmental membranes (Rahman et al., 2021), and excipients of cosmetic or hygiene products (Onyszko et al., 2022). This can be extended to wallpapers and writing paper in health centers, and virtually to any paper-based material to be reused, considering that paper, unlike glass or clothes, can be difficult or impossible to wash (Aguado et al., 2019).

Cationic cellulosic derivatives are self-standing antimicrobial materials. Their quaternary ammonium groups primarily target the phospholipid bilayer at the membranes of microorganisms, as depicted in Fig. 4. This causes the phase separation and reorientation of phospholipids, ultimately causing the disruption of the membrane (Xue et al., 2015). When cellulose is cationized with this purpose in mind, the degree of substitution should be high enough to compensate the intrinsic prebiotic effect of cellulose. This may explain why the use of quaternary ammonium-containing hydrazines or hydrazides, following the formation of dialdehyde derivatives with sodium periodate, is quite popular in the literature on cationic cellulose materials for growth inhibition (Otoni et al., 2019; Park and Choi, 2018; Tavakolian et al., 2020). Furthermore, it has been proved that DAC has antimicrobial properties by themselves (H. Luo et al., 2021), and thus even the unsubstituted units contribute to the overall biocide activity. Nonetheless, the all-round most popular method for cationization, i.e., etherification with quaternary ammonium epoxides, has also been commonly and successfully applied for antimicrobial purposes (Chaker and Boufi, 2015; Song et al., 2010). Likewise, although in an arguably less industrially feasible way, antibacterial cationic cellulose derivatives have also been synthesized by silane coupling (Poverenov et al., 2013).

The straightforward antimicrobial activity of cationic cellulosic derivatives has been exploited for different kinds of materials such as films, paper or nanopaper (Chaker and Boufi, 2015; Rol et al., 2019); foams, aerogels, xerogels or cryogels (Otoni et al., 2019), and multipurpose adsorbents or membranes (Yao et al., 2022). In general, contributions opting for cationic nanofibers or nanocrystals outweigh those based on

conventional cellulose fibers whose surface has been cationized. The lower performance of the latter when exposed to microbial cultures is due to their relatively low specific surface area. In contrast, in nanocellulose-based materials including suspensions, films and aerogels, among other possibilities, more quaternary ammonium groups are potentially exposed to microbes per unit of mass (Otoni et al., 2019). According to (Chaker and Boufi, 2015), the maximum mole fraction of anhydroglucose units that can be cationized when fibers are destructured to their constituent fibrils could be roughly estimated as 0.4.

Generally speaking, carboxylated derivatives of cellulose, such as CMC or TEMPO-oxidized CNFs, cannot be regarded as antimicrobial agents. In fact, CMC and anionic nanocellulose have been found to be adequate as carriers for probiotic bacteria (Ebrahimi et al., 2018; Wang et al., 2022). That said, they have also been used to support genuinely bactericide materials, being the substrate of antimicrobial films (He et al., 2020; Pawcenis et al., 2022). In these cases, the antimicrobial activity is not provided by the anionic cellulosic derivatives, but by metal nanoparticles (Ag, Pt, Cu, etc.) or bioactive essential oils. However, the electrostatic interactions involving carboxylate groups are still important in regard to the film forming properties, the stability of the resulting material, and the release rate of the active substance, for the reasons elaborated in Sections 3, 4, and 6. Finally, anionic functional groups can be combined with cationic surfactants or cationic polymers (Abitbol et al., 2014; Kaboorani and Riedl, 2015), enabling the ulterior ionic exchange with the phospholipids of cell membranes.

As for the trends and pending issues in the literature, it is easy to see that most growth inhibition assays are restricted to typical, commonplace microorganisms for research, namely *Escherichia coli* as paradigmatic Gram-negative bacteria and *Staphylococcus aureus* as paradigmatic Gram-positive bacteria (Fei et al., 2018; Jia et al., 2019; Li et al., 2018; Otoni et al., 2019; Salama et al., 2023). Although cellulosic materials are targeted by numerous strains of fungi, antifungal demonstrations of cationic cellulose are less frequent. For instance, Chen et al. (2023) have recently showed that a typical cationization with EPTAC improves the resistance of cellulose from bamboo towards *Aspergillus niger*, *Penicillium citrinum* and *Trichoderma viride*. When it comes to the potential applications of cationic cellulose materials in the food industry, performing tests with foodborne pathogens other than *E. coli* and *S. aureus* is undoubtedly useful. These include *Salmonella enterica*, *Listeria monocytogenes*, *Campylobacter jejuni*, and *Clostridium perfringens* (Gao et al., 2022). Fig. 7.

9. Conclusions, research gaps and future perspectives

This overview has shown the usefulness, versatility and potential of anionic and cationic derivatives of cellulose whose synthesis is commonly reported across the scientific literature, but whose current industrial applications is subjected to challenges and limitations. While the sales of CMC (the most popular anionic derivative) amounted to USD 2.2 billion in 2022, in terms of recent publications it is outweighed, e.g., by TEMPO-oxidized nanofibers, sulfated CNCs, and cationized DAC. Nonetheless, the commercialization of these materials is either non-significant or relegated to niche areas.

Overall, cationic derivatives are more common for coagulation-flocculation or direct flocculation processes, given the usual needs of wastewater treatment plants and paper mills. For instance, most particles with no nominal charge display negative effective charge in aqueous media. Moreover, cationic cellulosic derivatives are often developed by research groups with relation to paper engineering, thus targeting key issues of paper mills. Another application for which cationic cellulose is extremely popular in the literature is the development of antimicrobial materials, taking advantage of the electrostatic interactions between quaternary ammonium groups and phospholipids on the cell membrane of microorganisms.

Anionic derivatives of cellulose, either soluble or nanosized, are generally preferred whenever the purpose relies on strong interactions with the water molecules in the first or second solvation shells. The thermodynamics of hydration and the hydrogen bonding capabilities of carboxylate groups and other anionic functional groups, along with their size (considering the water molecules captured), justify their prevalence for thickening and emulsifying agents. Indeed, these two functions are commonly found together, since the rheological hindrance of the coalescence of immiscible droplets is one of the most common mechanisms for stabilization. In another context, it is easy to see why anionic derivatives are generally preferred for adsorbent materials and membranes intended to capture heavy metal cations. Negatively-charged derivatives are also more common for encapsulation or drug delivery purposes, partially because their more effective repulsive forces are normally translated into a greater surface area.

Regarding the pending issues, a common critique is that researchers frequently opt for the most typical choices, e.g. methylene blue as paradigmatic (and easy to measure) cationic adsorbate, *E. coli* and *S. aureus* to test antimicrobial activity, and oils with high interfacial

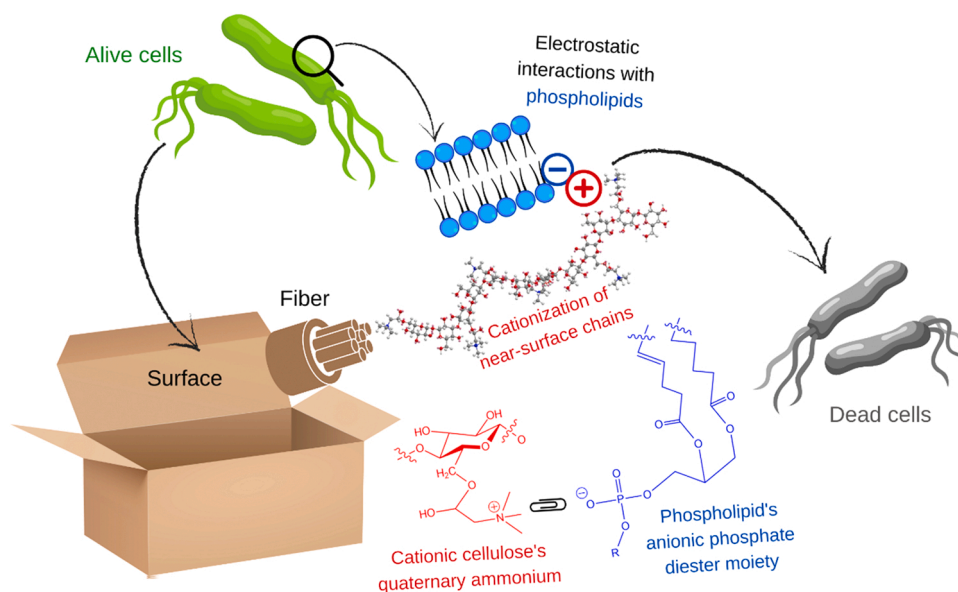


Fig. 7. Representation of the mechanism underlying the antimicrobial activity of the surfaces of cationic fibers. Quaternary ammonium groups bind to the phospholipids at the cell membrane, promoting the separation of the double layer.

tension with water for emulsions. And yet, daring hypotheses are usually more interesting to test. For instance, what is the role of ionic derivatives of nanocellulose when emulsifying partially miscible organic liquids, provided that the stabilization is successful? Moreover, the biodegradability and the so-called “biocompatibility” of cellulosic derivatives is often uncritically assumed, but, for instance, the introduction of quaternary ammonium groups leads to a decrease in biodegradability under normal circumstances. Hence, to what extent can biodegradability be alleged as an advantage of a highly substituted cationic cellulose flocculant over, for example, a cationic PAM of medium molecular weight? Most likely, the truism will remain valid in a qualitative sense, but biodegradability studies are scarce, while said assumed biodegradability drives the motivation of many research lines. In a similar fashion, more toxicity studies may be necessary to regard an anionic nanocellulose-based film as edible or safe for humans, especially when considering all the materials that researchers frequently incorporate for the sake of differentiation from previous works.

A major trend across the literature on ionic derivatives of cellulose is the shift towards nanofibers and nanocrystals. Some of the most well-known processes for the chemical modification of cellulose, such as cationization with quaternary ammonium-containing electrophiles or carboxymethylation, face some challenges when applied to nanocellulose. Said challenges, along with the broad spectrum of possibilities that the diverse kinds of CNFs and CNCs offer, stand as a source of novelty. Precisely, the popularity of nanocellulose derivatives is perhaps the most noticeable pending issue when analyzing the gap between research and large-scale production. This limitation seems to be common to the vast scientific production on nanocellulosic materials, ionic or not, and more works on the feasibility or scalability of some of their most popular production processes are expected over the following years. These methods include TEMPO-mediated oxidation towards anionic CNFs, acid hydrolysis towards anionic CNCs, or periodate oxidation as pretreatment towards either anionic or highly substituted cationic nanocellulose. Works advancing on this direction may not necessarily be explicit about industrial applications, but every attempt of simplifying, assessing, or reducing the cost, the environmental impact, and the risk of these processes will be worth considering.

CRedit authorship contribution statement

Roberto J. Aguado: Conceptualization, Writing – review & editing. **André Mazega:** Writing – original draft; **Quim Tarrés:** Writing – original draft; **Marc Delgado-Aguilar:** Conceptualization, Writing – review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

Acknowledgements

Authors wish to acknowledge the Spanish Ministry of Science and Innovation for the financial support to the project NextPack (PID2021-124766OA-I00). André Mazega Fontes received funding for his PhD thesis by the University of Girona and Banco Santander (PhD grant IFUDG2020). Marc Delgado-Aguilar and Quim Tarrés are Serra Hünter Fellows.

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