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# Cellulose as a Natural Emulsifier: From Nanocelluloses to Macromolecules

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## Abstract

During the last decade, cellulose structural features have been revisited, with particular focus on its structural anisotropy (amphiphilicity) and interactions determining its recalcitrance to dissolution. Evidences for cellulose amphiphilicity are patent, for instance, in its capacity to adsorb at oil–water interfaces, thus being capable of stabilizing emulsions. This behavior is observable in all its forms, from cellulose nanoparticles to macromolecules. This chapter is divided into two main parts; first, the fundamentals of emulsion formation and stabilization will be introduced, particularly focusing on the role of natural emulsifiers. Secondly, the emerging role of cellulose as a natural emulsifier, where the ability of cellulose to form and stabilize emulsions is revisited, from cellulose nanoparticles (Pickering-like effect) to macromolecules (i.e., cellulose derivatives and native molecular cellulose).

**Keywords:** Nanocelluloses, regenerated cellulose, cellulose derivatives, native molecular cellulose, amphiphilicity, oil–water interface, emulsifiers, adsorption, emulsions, stabilization

## 1. Introduction

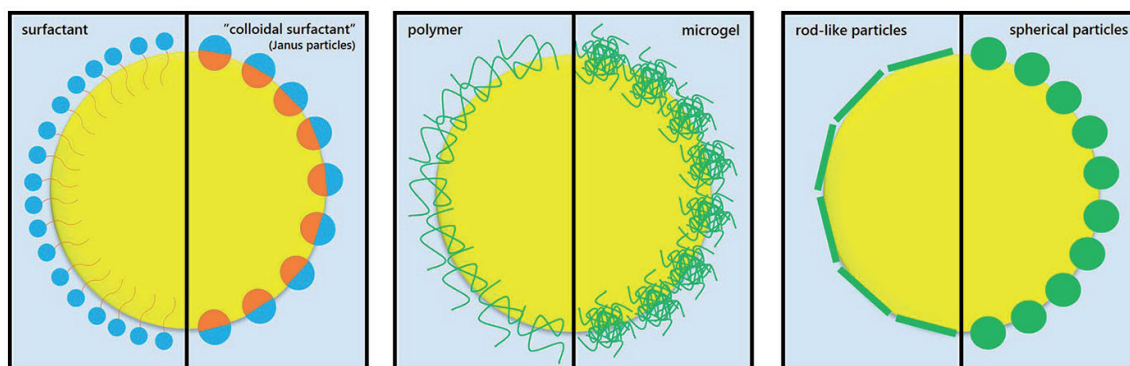
Every year, hundred billion tons of cellulose are produced by nature from various biomass sources, making this biopolymer an ultimate platform for developing sustainable applications on an industrial scale [1]. The increased environmental awareness due to global climate changes has pushed cellulose science to advance rapidly, and thus cellulose is expected to continue playing a central role in the emergent bio-economies and biorefineries. Cellulose extraction and purification rely on fairly simple, scalable, and efficient isolation techniques, and cellulose can be further modified and shaped into different colloidal and macroscopic forms, showing very different features [2–5].

Emulsions are among the most important colloids in everyday life, and have multiple uses, from technical applications, such as paints and coatings, to life science applications, such as foods, pharmaceuticals, and cosmetics. Emulsions can encapsulate and protect sensitive ingredients, adjust appearance, taste and sensorial properties, and facilitate application, spreading and drying. They can also serve as an intermediary for efficient oil extraction, polymerization reactions, and the production of microcapsules and lightweight foams [6]. Their structural and

functional properties are vast and therefore, the emulsifiers and stabilizers must be carefully selected according to the needs. With the growing global demand for sustainable and “clean-label” products, industries are actively seeking to replace synthetic emulsifiers by new alternatives. Finding natural ingredients, with minimal modification requirements (without compromising environment and human health) and still being capable of achieving a competitive performance to the optimized synthetic options is highly desirable but challenging. In this respect, cellulose has the potential to become a key star player in emulsion systems. In addition to its natural, non-toxic, biodegradable, and renewable nature, it is also a versatile source of natural emulsifiers. From cellulose derivatives, used since the early 20th century, to the more recently explored native forms of cellulose, including nanocelluloses, and the native cellulose itself, either molecular or in the form of polymeric particles and microgels, all its different morphological forms have shown an intrinsic amphiphilic character by self-assembling at oil–water interfaces.

## 2. Emulsion formation and stabilization by natural polymers and particles

Emulsions are multiphasic systems of at least three main components, the oil phase, the water phase, and the emulsifier. One of the phases is dispersed into the other in the form of droplets that are stabilized by a key compound, an emulsifier. Depending on the dispersed phase, we can have either oil-in-water (o/w) or water-in-oil (w/o) emulsions, and the type of emulsion formed mainly depends on the solubility properties of the emulsifier. According to Bancroft’s rule, o/w emulsions are formed when the emulsifier has a preference for water whereas the opposite applies for w/o emulsions [7]. When an emulsion is formed, a large interfacial area is created between the two phases, generating an increased energy in relation to the interfacial tension between oil and water. Therefore, emulsions seek to minimize the energy used to create such large interfacial area and break down over time by the combination of different instability mechanisms, such as, creaming, flocculation, coalescence and Ostwald ripening [7]. The role of the emulsifier is to reduce the interfacial tension and form a “protective layer” through its adsorption on the droplets surface, thus facilitating not only the formation of the droplets but also preventing/minimizing their re-association. Amphiphilic molecules and insoluble particles have both been employed as emulsifiers (**Figure 1**). Small surfactant molecules are usually good emulsifiers. Nevertheless, they are often not particularly well suited to provide long-term stability; this is because they are in dynamic equilibrium with the bulk medium. In this case, often, a stabilizer is required to achieve sufficient kinetic stability for the required shelf-life of a certain product. Polymers



**Figure 1.**

*Emulsifiers: Surfactants, polymers and particles. Differences in scaling are not considered.*

are often applied as stabilizers in oil-in-water (o/w) emulsions, and they can act either via the reinforcement of the stabilizing layer, co-acting with the emulsifier at the interface, or via the viscosity enhancement of the continuous phase, thus reducing droplet mobility [8]. Certain amphiphilic polymers and particles may act as both emulsifiers and stabilizers. Good examples are surface-active polysaccharides, such as gum Arabic, pectin, galactomannans and modified starches and celluloses [8–11]. These polymers provide strong steric repulsions driven by the entropic penalty when polymer segments from two droplets start to entangle, since conformational rearrangements are hindered due to their high molecular weight [12].

Another type of stabilization is provided by insoluble particles, often called Pickering stabilization; rigid particles, Janus particles and microgels, have been described as Pickering emulsifiers [13–15]. The amphiphilicity of a typical Pickering emulsifier (rigid particles) is usually described in terms of surface wettability, which is measured by the three-phase contact angle of a particle adsorbed at an oil–water interface. Both o/w and w/o emulsions can be formed depending on the particle wettability and whether the particles are predominantly hydrophilic or hydrophobic [13]. In agreement with Bancroft’s rule, the interface tends to bend towards the more poorly wetted liquid, and this becomes the dispersed phase. Pickering particles adsorb irreversibly at the oil–water interfaces due to the high-binding energy per particle, forming an effective mechanical barrier against coalescence; they may also inhibit lipid oxidation due to the thick interfacial layers formed [10, 11]. This is an important feature in what concerns food and pharmaceutical applications where polyunsaturated lipids are involved. Their double bonds are prone to oxidation leading to the deterioration of the products by the formation of rancid flavors and, eventually, toxic by-products [16]. The most widely used bioparticles are derived from biopolymers, such as cellulose, chitin and chitosan, starch and modified starches, lignin and proteins [17–21]. Bioparticles may vary widely in shape, size, aspect ratio and morphology, implying that their mechanistic behavior considerably deviates from that of both the solid sphere and the flexible polymer [22]. Nevertheless, particles with an irregular shape and higher aspect ratios have been found to have a greater ability in stabilizing emulsions and foams (and at lower concentrations) compared to synthetic particles of spherical shape [19].

A special type of particles that display some similarities to surfactants and polymers are known as Janus particles. These are amphiphilic particles, composed of two or more regions with distinct physicochemical properties, that can self-assemble in bulk media and readily adsorb to fluid interfaces, remarkably lowering the interfacial tension; for this reason, they are also called “colloidal surfactants” [14, 23, 24]. They can be synthesized in geometrically different shapes and chemical compositions with high uniformity and precision [14]. Polysaccharides, such as, alginates, chitosan, pectin, cellulose and heparin, have been used to produce bio-based Janus particles [25, 26].

Another interesting type of emulsifying particles are microgels, which are soft deformable gel-like particles made up of aggregated or cross-linked polymer networks [22]. These microgels can swell in aqueous solvents and rearrange at the oil–water interface, resulting in thick and mechanically resilient layers. Owing to the amphiphilic character of their polymeric constituents, most microgels are inherently surface active at oil–water and air–water interfaces and, as rigid particles, they also irreversibly adsorb at the interfaces [22]. Synthetic microgels offer an additional feature that arises as a direct consequence of their combined polymeric and particulate character. They have the potential to effectively stabilize water-in-water emulsions, which are mixed solutions of thermodynamically incompatible polymers, producing two immiscible aqueous phases, and where the effective thickness of the interface is defined on a length scale considerably greater than the



molecular dimensions of a conventional emulsifier [22, 27]. However, microgels based on physical cross-linking of biopolymers are rather novel and much of their behavior at interfaces remains unclear [15]. Two examples of natural ingredients that exhibit microgel-like characteristics are casein micelles (in their native form) and whey proteins and gelatinized starch granules (upon heat treatment). However, in order to mimic the special features of the synthetic microgels, these traditional food-grade microgels need more pronounced long-term structural stability under conventional processing and storage conditions, which typically requires the introduction of additional covalent cross-links within the aggregated biopolymer-based entity [22].

### 3. Cellulose: a versatile source of emulsifiers

#### 3.1 Physicochemical characteristics of cellulose and the various morphological forms

Cellulose is a polysaccharide composed of glucose monomers, the anhydro-glucose units (AGUs), linked by  $\beta$ -(1–4) glycosidic bonds. These  $\beta$ -linked AGUs adopt the  $4C_1$  chain conformation, which is the conformation with the lowest free energy of the molecule. Consequently, the three polar hydroxyl groups in each AGU are located on the equatorial positions of the rings, and the hydrogen atoms of the non-polar C–H bonds are located on the axial positions [1]. This structural anisotropy is what gives cellulose its amphiphilic nature [28]. Due to the large number of hydroxyl groups within a cellulose molecule, both intra- and intermolecular hydrogen bonding occur and various types of supramolecular semi-crystalline structures can be formed. It is believed that intramolecular hydrogen bonding is responsible for the single-chain conformation and stiffness, while the intermolecular hydrogen bonding would be responsible for the sheet-like arrangement of the native polymer [1]. However, the stacking of these sheets into the three-dimensional crystalline supramolecular structures must involve hydrophobic interactions, as it was shown through molecular dynamic simulations, and moreover was observed, many years ago, in native cellulose biosynthesis [1, 29, 30].

Hydrophobic interactions between cellulose molecules make, in combination with favorable packing conditions (and thus a low energy) in the crystalline state, cellulose insoluble in water [31]. Solubility can be achieved by ionizing cellulose, which occurs at extreme pH's. Solubility in water can also be aided by addition of co-solutes that weaken hydrophobic interactions. Derivatization of cellulose is also found to generally enhance solubility strongly, which can be referred to packing constraints in the solid state. Thus, to make cellulose soluble in aqueous solutions, the crystalline packing has to be disrupted, and this can be achieved, for example, by chemical modifications via etherification reactions in alkaline media, resulting in water-soluble cellulose ethers [32, 33]. These cellulose derivatives keep the amphiphilic properties of cellulose, as can be seen from their association with surfactants and their adsorption at the air–water and oil–water interfaces [34–39].

A fairly simple way of converting cellulose into a versatile class of new materials is through a dissolution-regeneration process. The regeneration of cellulose occurs when a coagulant (“anti-solvent”) gets in contact with a cellulose solution or dope, leading to a solvent exchange and subsequent aggregation of the cellulose chains. The organization of the molecules in the regenerated materials (e.g., fibers, films, foams, particles) and their properties are strongly influenced by the dissolution state of cellulose (molecular cellulose, partially dissolved, crystalline or amorphous aggregates), as well as the nature of the coagulant used [40, 41].

Cellulose can also be shaped into micro- and nanoparticles of different colloidal structure. Acid or mechanical treatments are usually applied to deconstruct the cellulose fibers into crystalline or semi-crystalline nanocelluloses [20, 42–44]. Partial decomposition of cellulose fibers, by acid treatment and cellulase-catalyzed hydrolysis, yields powdery microcrystalline cellulose (MCC), such as commercial Avicel®, with DP values between 150 and 300 [45]. Avicel® still contains both amorphous and crystalline portions. On the other hand, nanocrystalline cellulose (NCC) is obtained by strong acid hydrolysis. During the chemical process, the more readily accessible amorphous regions are completely disrupted deliberating rod-like crystal sections, whose sizes are dependent on the time and temperature of the reaction. The dimensions of the isolated NCC are also found to be strongly influenced by the degree of crystallinity of cellulose, which, in turn, is dependent on the natural source. Cotton, wood and Avicel® usually yield highly crystalline nanorods (90% crystallinity) with a narrow distribution of sizes (5–10 nm in width and 100–300 nm in length), whereas sources, such as tunicin (extracted from the tunicates), bacteria and algae, yield crystals with higher polydispersity and larger dimensions [42]. NCC forms stable suspensions in water by application of a mechanical force, typically sonication. Its surface properties are determined by the mineral acid and the reaction conditions used during its extraction. NCC prepared with hydrochloric acid (HCl) is weakly negatively charged, while it exhibits a strong repulsive character if prepared with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), since approximately one tenth of the glucose units is functionalized with the anionic sulfate ester groups. Thus, NCC prepared with H<sub>2</sub>SO<sub>4</sub> give suspensions with higher colloidal stability than NCC prepared with HCl.

Micro- and nanofibrillated (MFC/NFC) celluloses are obtained by extruding wood pulp suspensions through mechanical devices (high-pressure homogenizers), which results in fiber delamination and delamination of the fibrils, usually being tens of nanometers wide and lengths ranging from several nanometers to several micrometers (i.e., 5–60 nm in width and 100 nm to several micrometers in length) [42]. This type of nanocelluloses are usually less crystalline than NCC, since they still own part of the amorphous domains, and have higher aspect ratios [5, 46]. In aqueous solutions, the fiber-like morphology and high aspect ratio, typically drive gel-like behavior due to entanglements between the microfibrils.

### 3.2 Nanocelluloses at interfaces

Several researchers have demonstrated the ability of cellulose particles to self-assemble at oil–water interfaces and to stabilize o/w emulsions without the aid of classical surfactants [47–49]. It is believed that the amphiphilic character of nanocellulose resides in its crystalline organization at the elementary “brick” level, and thus, cellulose nanocrystals have both hydrophilic and hydrophobic edges that are preferentially wetted by water and oil phases, respectively [49]. The wettability properties of cellulose particles may be tuned by surface hydrophobization, due to the presence of many reactive hydroxyl groups, and w/o emulsions can be formed [50–52]. Most of the particles from biological origins, such as cellulose, chitosan, or starch, show an irregular shape and are polydisperse in size and morphology. However, this structural anisotropy may be very beneficial for emulsion formation and stability. Particles with high aspect ratios are capable of stabilizing biphasic systems at lower concentrations compared to systems containing spherical particles [53]. Particles with such a well-defined shape are usually derived from inorganic materials, like silica and these have been extensively studied because of their availability in different sizes with narrow size distributions and chemical surface tunability. However, their lack of biocompatibility and biodegradability restricts

their use in food and pharmaceutical applications [54]. For this reason, the study and characterization of materials from biological origins have gained increasing attention, and many efforts have been made in the food and pharmaceutical industries in order to develop new food-grade particles [19, 55]. It was early noticed that MCC particles have the ability to stabilize conventional o/w emulsions, and multiple emulsions systems of w/o/w type, with the aid of a hydrophobic surfactant for the stabilization of the internal w/o interface [56, 57]. These MCC particles form a network around the emulsified oil droplets that provides a mechanical barrier against coalescence, and, beyond that, the non-adsorbed particles may act as thickener agents in the continuous aqueous phase. MCC particles have also the ability to reduce lipid oxidation, one of the major concerns among food manufacturers due to its negative effects on food quality [55]. More recently, nanocelluloses, such as MFC/NFC and NCC, have been increasingly in focus for having a better performance than MCC, owing their smaller sizes and more regular shapes [58]. NCCs with low aspect ratios (shorter) have a dense organization at the interface and cover better the oil surface, while NCCs with high aspect ratios (longer) typically form a network around the droplet with relatively low coverage. Therefore, shorter NCCs have better emulsification efficiency and long-term stability, since higher droplet coverage usually means smaller droplet size [59, 60]. On the other hand, long nanofibrils (NFC) with a high aspect ratio also tend to form bigger droplets resultant from a lower surface coverage, but the fibers protrude in the continuous phase forming a strong network that is able to physically hinder droplet coalescence [59]. As mentioned, the colloidal stability of NCC is controlled by their surface charge resulting from the acid hydrolysis with various acids (e.g.,  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ). The higher the charge density the better their colloidal stability, but their ability to efficiently stabilize emulsions is reduced. Thus, the anionic charges on the surface of the nanocrystals control their tendency to be dispersed in water in relation to being adsorbed at the oil–water interface and, therefore, the particle polarity must be confined to a limited range. A surface charge density lower than ca.  $0.03 \text{ e/nm}^2$  is ideal for the effectiveness of NCC as an emulsifier and stabilizer, usually achieved by  $\text{HCl}$  hydrolysis. NCC with sulfate groups, resultant from the hydrolysis with  $\text{H}_2\text{SO}_4$ , possess a high surface charge density (e.g.,  $0.123 \text{ e/nm}^2$ ), and the charges may undergo desulfation or may be screened by salt addition, to tune their amphiphilicity [49, 61]. Nanocellulose-stabilized emulsions are generally thermally stable, but in the presence of charges their stability against pH and ionic strength may decrease [58, 62]. NCC are able to form stable o/w high internal phase emulsions (HIPEs) containing volume fractions of oil as high as 0.9, at very low NCC concentrations ( $< 0.1 \text{ wt.}\%$ ) [61]. Hydrophobized nanocellulose has been also explored to form w/o HIPEs [51]. Double emulsions of both o/w/o and w/o/w have been prepared by using a combination of native and hydrophobized NCC and NFC [63, 64]. Apart from the outstanding physical stability against coalescence, nanocelluloses also afford oxidative stability and lipid digestion control due to the dense interfacial layer formed [60].

### 3.3 Cellulose derivatives at interfaces

Cellulose derivatives produced by etherification reactions are generally water-soluble and surface-active. Therefore, cellulose ethers are a major class of commercially important water-soluble polymers, from construction products, ceramics, and paints to foods, cosmetics, and pharmaceuticals [32, 33, 65, 66]. Cellulose ethers are commonly made by reacting alkali cellulose with the appropriate reagents to substitute the hydroxyl groups of the AGU monomers by either alkyl, hydroxyalkyl or carboxyalkyl groups [66]. Methyl cellulose (MC), ethyl



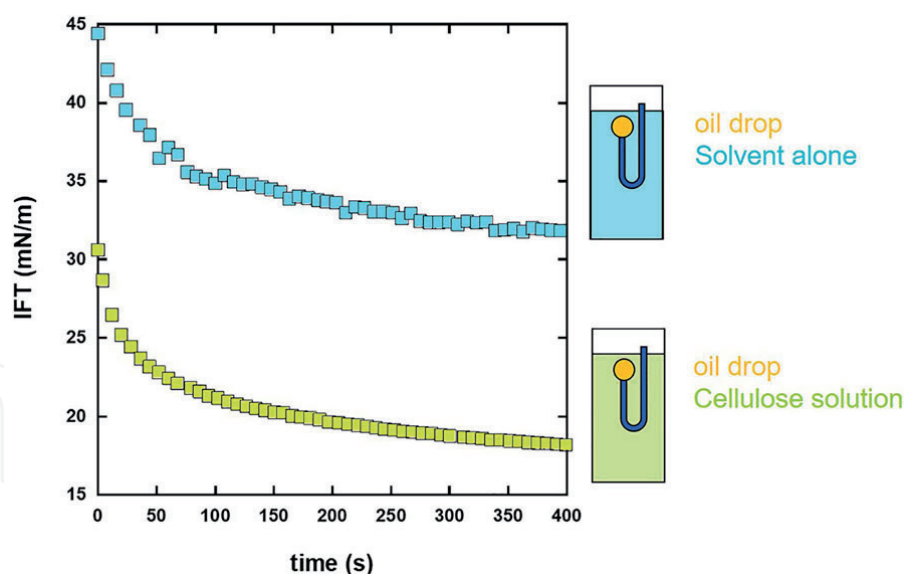
cellulose (EC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), and their derivatives, are common products of those reactions. Their functionality and solubility in water depend on the type of substituent, degree and pattern of substitution, and molecular weight [33, 67]. The non-ionic cellulose ethers, such as, MC, HPMC and EHEC and their hydrophobically modified versions, have been mostly used to produce o/w emulsions due to their water-solubility [68–71], but EC can be used to stabilize w/o emulsions [72]; this change-over from MC to EC illustrates the subtle role of polarity and illustrates the applicability of Bancroft's rule. The emulsion stabilization due to cellulose ethers is the result of the combined effects of: a) reduction of the interfacial tension, arising from the balance between polar and non-polar groups; b) adsorption of thick layers, forming a physical barrier with strong steric repulsion; and c) the viscosity increase of the continuous phase, constraining droplet dynamics [7, 71, 73]. Cellulose derivatives often show a dual effect, as stabilizing and emulsifying agents [73]. However, carboxymethyl cellulose (CMC) which is an anionic polymer, cannot efficiently stabilize emulsions by itself due to its highly polar character. However, it can assist emulsion stabilization by controlling the viscosity of the continuous medium [5, 16]. In general, cellulose ethers provide good stability against droplets aggregation due to the strong steric repulsions between the adsorbed polymer layers of two approaching droplets, and due to the increased viscosity of the systems. One of the main advantages of using non-ionic polysaccharides, such as the cellulose ethers in this specific case, is their high stability against environmental stresses, such as, pH, ionic strength, and temperature. This is particularly important in food and pharmaceutical applications, where complex environments are encountered. Cellulose ethers also provide good oxidative stability to the core materials and delay lipid digestion of o/w emulsions, provided that the physical barrier and thickened aqueous phase slows down the diffusion of pro-oxidants and lipases [71, 74]. Lipid digestion is even further reduced using cellulose ethers when compared to calcium-caseinate, a common food emulsifier. Additionally, the thermo-gelling ability of cellulose ethers, in particular HMC, makes it possible to obtain emulsions with high consistency during gastric digestion, contributing to slow down the gastric digestion and increase fullness and satiety perceptions [71].

### **3.4 Molecular and regenerated cellulose at interfaces**

The behavior of molecularly dissolved cellulose at interfaces is expected to resemble that of typical cellulose derivatives or any semiflexible amphiphilic polymer that shows interfacial activity, i.e., the tendency to adsorb at oil–water interfaces and reduce the free energy between the two phases. However, due to its dissolution limitations, the properties of molecularly dissolved cellulose and its potential in emulsions formation and stability are clearly much less explored. Nevertheless, recent studies have confirmed the stated hypothesis. Molecular dynamics simulations indicate that molecularly dispersed cellulose gradually assembles at the oil–water interface eventually surrounding the oil droplet [75]. Experimentally, molecular cellulose dissolved in  $\text{H}_3\text{PO}_4$  (aq.) was found to adsorb at the oil–water interface and decrease the interfacial tension (IFT) between the two phases (**Figure 2**).

The decrease in IFT is similar in magnitude to that of the non-ionic cellulose derivatives MC and HPMC, for the same polymer concentration (0.1 wt.%) and same type of oil (liquid paraffin) [34]. Yet, cellulose-stabilized emulsions formed in  $\text{H}_3\text{PO}_4$  (aq.) were found to be short-lived, as oil was separating from the emulsions and floating to the top within 24 h. However, by subsequently adding water to the dispersions during emulsification, the properties of the emulsions changed

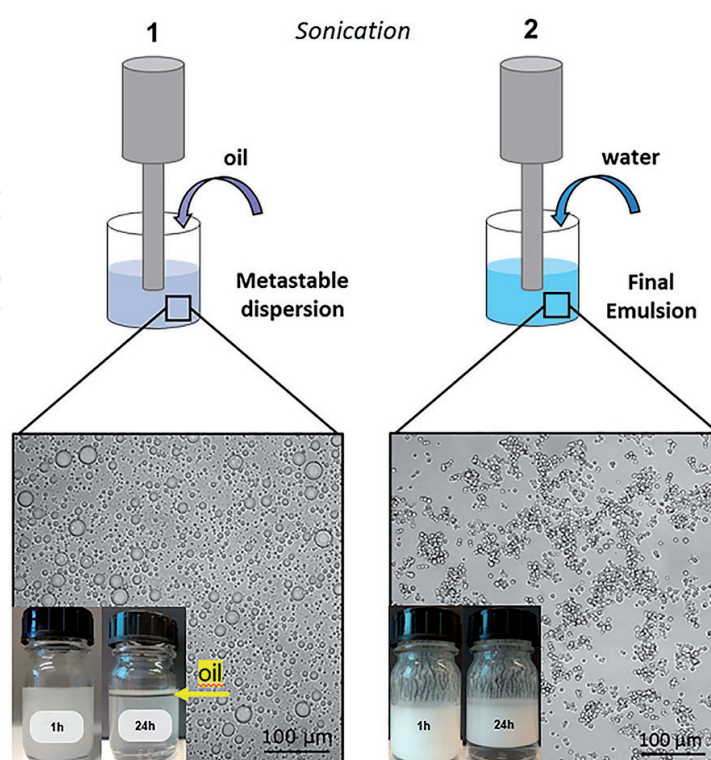




**Figure 2.**  
Effect of dissolved cellulose on the interfacial tension oil-aqueous medium.

dramatically, and there was no evidence of oil separation over one year of storage (**Figure 3**). This effect was attributed to a decrease in cellulose solvency in  $\text{H}_3\text{PO}_4$  (aq.) by the addition of an anti-solvent (water), which promoted a greater affinity for the oil–water interface, leading to the outstanding stability against macroscopic phase separation of the oil.

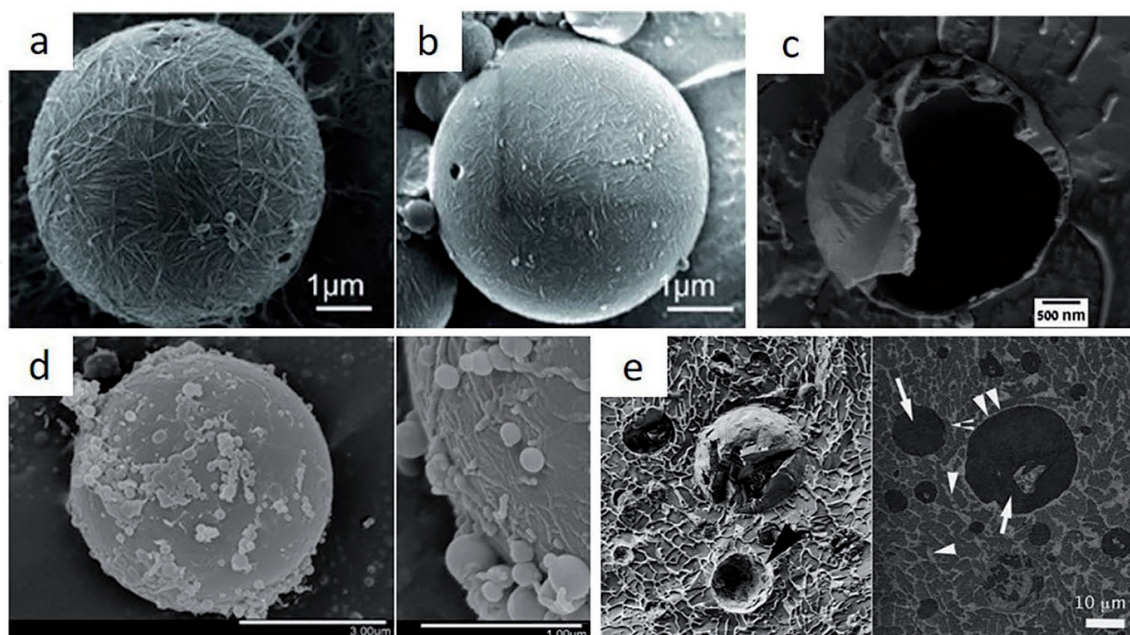
There are two ways of using native cellulose to stabilize o/w emulsions without the need of further modifications. One, is by following the dissolution-regeneration-emulsification approach, resulting in Pickering emulsions of solid or soft cellulose particles (microgels), since the oil is either dispersed in a water suspension of cellulose particles or in a water suspension of cellulose microgels, respectively [76–83].



**Figure 3.**  
Two step emulsification procedure for cellulose dissolved in phosphoric acid solvent.

Another way, is to follow the dissolution-emulsification-("in situ")regeneration approach, where the oil is directly dispersed in the cellulose solution, and regeneration takes place at the oil–water interface ("in situ") [34, 84]. This way, the oil droplets seem to be stabilized by a "cellulose film" with a smooth appearance, contrasting with the rough networks and particulate appearances of Pickering emulsions (**Figure 4**) [7, 84]. Another fundamental difference between the two described approaches is related to the existence of dissolved cellulose during the oil emulsification, which acts as a polymeric surfactant by decreasing the IFT, and possibly contributing for a reduction in droplet size. Overall, the emulsions produced by both methods display very good stability against droplet coalescence which can be referred to the irreversible adsorption of cellulose onto the droplet surfaces [34, 78, 79, 85]. Soft cellulose microgels also impart an outstanding stability against flocculation because of the thick viscoelastic layers formed at the interface [15]. The mechanism behind droplet stabilization in emulsions prepared with cellulose particles is similar to that operating for nanocelluloses as described above, i.e., a combination of Pickering adsorption and network stabilization, often showing gel-like characteristics upon a concentration increase of cellulose [79, 82–84].

Moreover, the resulting emulsions are remarkably stable against environmental changes, such as, pH, ionic strength, and temperature, which makes them good candidates for target delivering [80, 82, 86]. Cellulose regenerated particles have also been shown to improve the physical stability of emulsions stabilized by sodium-caseinate, a milk-protein commonly used as a food emulsifier, promoting adsorption of the protein and thickening the continuous phase [87]. Very little has been done regarding the stabilization of w/o emulsions since cellulose particles are better wetted by water than oil. However, it has been suggested that the presence of a water–oil interface when regenerating cellulose affects the conformation of the cellulose molecules and so the way they reassemble. Therefore w/o emulsions are possible to form, but they have poorer stability compared to o/w emulsions [78]. More recently, a "hydrophobic" cellulose microgel was developed to stabilize w/o emulsions, by coagulating cellulose in the presence of a coagulant and sunflower



**Figure 4.** Different morphologies of cellulose-stabilized emulsions. Particle-stabilized emulsions by longer NCC (bacterial cellulose) (a), shorter NCC (b), and regenerated cellulose (dissolution-regeneration-emulsification approach) (d). Emulsions prepared from molecular solutions of cellulose (dissolution-emulsification-"in-situ" regeneration approach) (c and e). Reprinted (adapted) with permission from Ref. [49, 77, 80, 84].

oil [88]. The resultant microgels were more easily dispersed in oil than water, and stable emulsions w/o emulsions were formed. The simplicity and versatility of the dissolution-regeneration approaches open many new possibilities for the functionalization of cellulose and its applicability in both o/w and w/o emulsions.

#### 4. Conclusions

The list of emulsion formulations having a remarkable impact in our lives is vast, and therefore, it is not surprising that natural molecules have been emerging as important players to partially or completely replace the available non-sustainable options. The future leading role of cellulose as an effective stabilizing agent is unquestionable and opens a new era of sustainable, biocompatible, and value-added functional materials. Surfactant-free emulsions have recently been developed using all forms of cellulose (crystalline, fibrillated, molecular and regenerated), providing a strong support for the vision of cellulose as an amphiphilic molecule, capable of acting as a polymeric surfactant and a Pickering stabilizer. Structural differences and mechanisms of emulsion stabilization between the different cellulose forms have been presented in this chapter. In general, and given the right conditions, cellulose coatings are a powerful mechanical barrier against coalescence, lipid oxidation and lipid digestion. Non-adsorbed cellulose forms a 3D network in the continuous phase, that constrains droplet movements and enhances kinetic stability. The colloidal assembly of cellulose particles when liquid interfaces of notably different polarities are present might serve as a template for the synthesis of new functional microcapsules. The dissolution-regeneration process is highlighted as an important approach of making cellulose-based emulsions, whose hydrophilic-lipophilic balance can be simply tuned by playing with solvent quality and regeneration coagulant(s). Furthermore, the exceptional stability against environmental stresses (pH, ionic strength and temperature) makes the cellulose regenerated coatings potential candidates for target delivery in complex conditions.

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#### Conflict of interest

The authors declare no conflict of interest.

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