



HAL
open science

A facile approach to modify cellulose nanocrystal for the adsorption of perfluorooctanoic acid

Chaimaa Gomri, Belkacem Tarek Benkhaled, Arnaud Chaix, Christophe Dorandeu, Joel Chopineau, Eddy Petit, Karim Aissou, Didier Cot, Marc Cretin, Mona Semsarilar

► To cite this version:

Chaimaa Gomri, Belkacem Tarek Benkhaled, Arnaud Chaix, Christophe Dorandeu, Joel Chopineau, et al.. A facile approach to modify cellulose nanocrystal for the adsorption of perfluorooctanoic acid. Carbohydrate Polymers, 2023, 319, pp.121189. 10.1016/j.carbpol.2023.121189 . hal-04169683

HAL Id: hal-04169683

<https://hal.umontpellier.fr/hal-04169683v1>

Submitted on 25 Jul 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

A Facile Approach to Modify Cellulose Nanocrystal for the Adsorption of Perfluorooctanoic acid

Chaimaa Gomri ^a, Belkacem Tarek Benkhaled ^a, Arnaud Chaix ^a, Christophe Dorandeu^b, Joel Chopineau^b, Eddy Petit ^a, Karim Aissou^a, Didier Cot^a, Marc Cretin ^a, Mona Semsarilar ^a.

^a Institut Européen des Membranes-IEM (UMR 5635), Univ Montpellier, CNRS, ENSCM, 34095 Montpellier, France

^b ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France.

Abstract

Cellulose-based materials are a sustainable alternative to polymers derived from petroleum. Cellulose nanocrystal (CNC) is a biopolymer belonging to this family; it is commonly known for its important physical and chemical properties and ability to form a film. Modifying CNC *via* electrostatic interaction provided by cationic polymers is a facile and promising technique to enlarge the application of CNC. Herein, we report the preparation of films, from blends of negatively charged CNC and positively charged poly (trimethyl aminoethyl methacrylate) (PTMAEMA). The interaction between CNC and PTMAEMA was verified by using a quartz crystal microbalance with dissipation monitoring (QCM-D), as well as by measuring the particle size and ζ -potential of the casting mixture. To favor the application of the nanocomposite film in water treatment, the film was supported on WhatmanTM paper, and adsorption tests were conducted using perfluorooctanoic acid (PFOA) as a model compound for the family of persistent fluorinated pollutants known as PFAS (per- and polyfluoroalkyl substances).

Keywords

Cellulose Nanocrystal (CNC); Perfluorooctanoic acid (PFOA); Adsorption; Poly (trimethyl aminoethyl methacrylate) (PTMAEMA); Reversible Addition-Fragmentation chain Transfer (RAFT).

25 **1. Introduction**

26 Cellulose is an abundant crucial raw material able to meet the increasing demand for biodegradable and biocompatible
27 materials. Cellulose has been used for many decades in the clothes and paper industries. In recent years, the
28 exploitation of crystalline cellulose, also called cellulose nanocrystals “CNC”, increased thanks to their important
29 mechanical properties and modifiable surface, while being eco-friendly (Trache, Hussin, & Thakur, 2017).

30 Commercial application of CNC depends on their quality which is defined by the extraction technique used. Several
31 approaches can be applied to extract CNC from raw cellulose, such as the oxidation method, mechanical treatment,
32 and acid hydrolysis. Extraction by acid hydrolysis requires the use of a strong acid which can be mineral or organic
33 (Trache, Hussin, & Thakur, 2017). Using sulfuric acid for extraction leads to incorporating a negative surface charge
34 due to the presence of sulfate groups (Gomri et al., 2022). The number of sulfate groups incorporated depends on the
35 acid concentration and the hydrolysis time. These negatively charged sulfate groups endow cellulose with considerable
36 reactivity that would allow surface modification via noncovalent interaction. Many researchers emphasize the
37 outstanding properties of the modified CNC via noncovalent interaction with other materials such as polymers,
38 surfactants, counter ion salts, and metals (Trache, Hussin, Haafiz, et al., 2017).

39 For instance, Engkagul et al. developed a nanocomposite film based on CNC combined with the cationic poly[(2-
40 (methacryloyloxy)ethyl) trimethylammonium chloride] (PMETAC). It was shown that the incorporation of CNC into
41 PMETAC increased the material's mechanical properties, assuming this is directly related to the pronounced
42 electrostatic interaction between the two components (Engkagul et al., 2021). Surface functionalization of negatively
43 charged CNC in an aqueous medium with positively charged polymer results in stable suspension. In another example,
44 Khandal et al. showed how a noncovalent modification of CNC with negatively charged polyethyleneimine (PEI)
45 could be efficient, leading to the formation of a stable suspension with interesting rheological behavior (Khandal et
46 al., 2019).

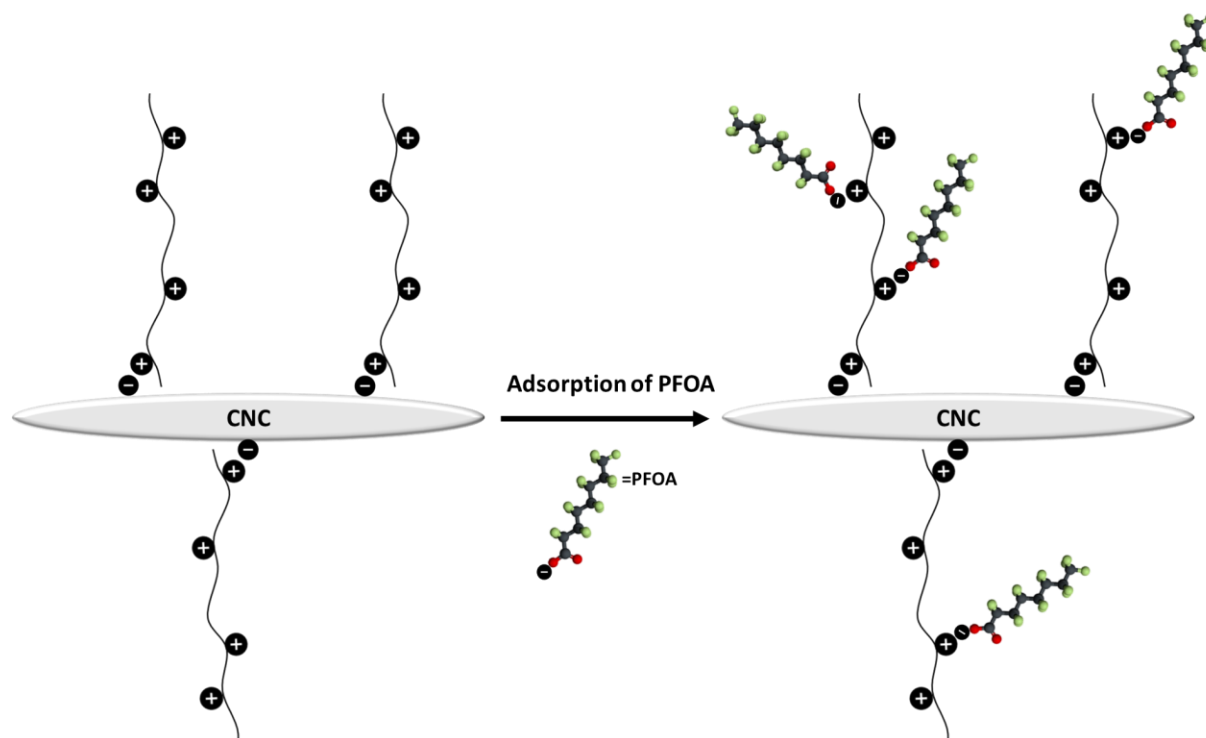
47 The use of CNC in material science is limited since it disperses poorly in polymer matrices. To overcome this issue,
48 Bondeson & Oksman modified CNC with a surfactant (acid phosphate ester of ethoxylated nonylphenol) to enhance
49 its mixing in polylactic acid (PLA). The surfactant covered the surface of the CNC, hindering the formation of
50 aggregates brought about by the formation of hydrogen bonds between CNCs (Bondeson & Oksman, 2007).

51 One practical application of modified CNC is their use as an adsorbent for water pollutants. Ranjbar et al. modified
52 CNC with a positively charged surfactant (CTAB) to remove Congo red from an aqueous medium. The adsorption
53 capacity of the developed material was as high as 244 mg g⁻¹, assuming that the adsorption process is governed by
54 electrostatic attraction, hydrogen bonding, and hydrophobic attraction (Ranjbar et al., 2020). Cationic dyes such as
55 methylene blue and malachite green were adsorbed using hybrid nanocomposite material based on CNC (Cr(OH)₃-
56 NPs-CNC). The maximum adsorption capacities for both pollutants were respectively 106 mg g⁻¹ and 104 mg g⁻¹
57 (Nekouei et al., 2017). Besides organic dyes, modified CNC was applied to remove other contaminants such as arsenic
58 (Dong et al., 2020), heavy metals (Hu et al., 2018), polyphenols (Asante et al., 2020), antibiotics (Liu et al., 2020),
59 etc.

60 Currently, the pollutants of increasing concern to researchers are per- and polyfluoroalkyl substances (PFAS). PFAS
61 are organic compounds that are fully or partially fluorinated. The strong bond between carbon and fluorine endows
62 PFAS with high thermal and chemical stability enabling their extensive use in many fields (Lu et al., 2020). These
63 pollutants have been increasingly detected in the aquatic systems presenting a real threat regarding their toxicity. Two
64 main processes are used to remove PFAS from water: separation and degradation. Adsorption is a separation method
65 commonly used to remove PFAS and has shown its efficiency (Wanninayake, 2021). Thus, green adsorbents such as
66 activated carbon, biochar, polysaccharide-based materials, and aminated sorbents are promising for PFAS remediation
67 (Militao et al., 2021).

68 In this study, we use a facile approach to modify CNC with positively charged poly(trimethylaminoethyl)
69 methacrylate (PTMAEMA) to remove PFAS. For that PTMAEMA was first synthesized using Reversible Addition-
70 Fragmentation chain Transfer (RAFT). The attachment of the PTMAEMA to CNC and the interaction between them
71 were investigated using a quartz crystal microbalance with dissipation monitoring (QCM-D). Film based on
72 PTMAEMA and CNC was prepared using Whatman™ filter paper as a support to increase the mechanical stability
73 of the final adsorbing surface. The resulting nanocomposite film was used to remove perfluorooctanoic acid (PFOA)
74 from an aqueous solution. PFOA was used as a model compound from the PFAS family. The adsorption capacity of
75 the developed composite film was evaluated using high-performance liquid chromatography coupled with mass
76 spectroscopy (HPLC-MS).

77 In the present work, the assumption is that, due to the nature of CNC (presence of surface negative charge), functional
78 polymer chains could be easily attached to their surface using electrostatic charges. The surface of the CNC is modified
79 using a well-defined functional polymer via ionic-interactions, so the functional material could be used for adsorption
80 and removal of pollutants as illustrated in figure 1.



81

82 **Figure 1. Illustration of the adsorption of PFOA onto non-covalently modified CNC**

83 **2. Materials and methods**

84 **2.1. Materials**

85 Cellulose nanocrystal was kindly provided by CelluForce Inc. All reagents were purchased from Sigma-Aldrich and
86 used without further purification. Dimethylamino ethyl methacrylate” DMAEMA” was used as the monomer, 4-
87 Cyano-4-(phenylcarbonothioylthio)pentanoic acid was used as the RAFT agent and recrystallized 2,2’-
88 azobisisobutyronitrile (AIBN) was used as the initiator. Tetrahydrofuran (THF) was used as solvent for the
89 polymerization. Hexane was used for the precipitation of the polymer. Iodomethane was used to quaternize the amine
90 of the polymer. CDCl_3 was used as a NMR solvent, and Whatman™ paper was used to support the developed material.

91 **2.2. Synthesis of Poly (trimethyl aminoethyl methacrylate) “PTMAEMA.”**

92 Poly (dimethylamino ethyl methacrylate) was first synthesized by reversible addition–fragmentation chain transfer
93 (RAFT). 2-(Dimethylamino) ethyl methacrylate (5 g, 31.80 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic
94 acid (0.13 g, 0.4 mmol) and azobisisobutyronitrile (0.015 g, 0.09 mmol) were dissolved in tetrahydrofuran (5 mL) in
95 a round-bottomed flask. The sealed reaction vessel was purged by bubbling nitrogen. The reaction mixture was stirred
96 for 24 h at 70 °C. The resulting polymer (monomer conversion = 94 %, $M_n = 2499$, $M_w = 2623$, and $\mathcal{D} = 1.05$) was
97 purified by precipitation in hexane. The degree of polymerization was calculated using ^1H NMR spectroscopy by
98 comparing the integral of the signals corresponding to the aromatic protons of the RAFT agent (7.5-8 ppm) with
99 signals corresponding to CH_2 of the polymer backbone (3.87 ppm; 4.52 ppm). To quaternize the amine, the synthesized
100 polymer was dissolved in water and placed into an ice bath, then CH_3I was added dropwise, and the mixture was kept
101 under stirring for 2 h. The final product was then freeze-dried. Quaternization was confirmed using ^1H NMR by
102 comparing the integral of the signals corresponding to the proton of the amine before and after the modification. The
103 obtained yield was 100%.

104 **2.3. Investigation of CNC and PTMAEMA interaction.**

105 To investigate the interaction of CNC and PTMAEMA, nanocomposite films were prepared using different
106 concentrations of PTMAEMA, as shown in Table 1. First, 0.4 g of CNC was dispersed in 15 mL of deionized water
107 and sonicated for 30 min. Then 5mL of aqueous PTMAEMA solution with different concentrations was mixed with
108 CNC solution and stirred for 24h at room temperature. The mixtures were poured into a stainless mold and dried at
109 room temperature.

Samples references	CNC	CNC:PTMAEMA 1	CNC:PTMAEMA 2	CNC:PTMAEMA 3	CNC:PTMAEMA 4
PTMAEMA: CNC (Molar Ratio)	0	1	0.5	0.25	0.1

110 **Table 1. Composition of the nanocomposite films**

111 **2.4. Preparation of supported CNC/PTMAEMA film**

112 To test the efficiency of CNC/PTMAEMA film in removing perfluorooctanoic acid (PFOA) from an aqueous solution;
113 CNC and PTMAEMA were deposited consecutively on cellulose filter paper (Whatman™) by spin coating to ensure
114 a homogeneous deposit since the blend of CNC and PTMAEMA was too viscous. First, the cellulose filter paper was
115 soaked for 24 h in NaOH solution, rinsed, and then dried at room temperature. Then, 0.5 mL of CNC aqueous solution
116 (2% w/v) was spin-coated (100 rpm-120 s) on cellulose filter paper (diameter = 4.7 cm) and dried for 15 min at 70 °C
117 in the oven. At the second step, 0.5 mL of PTMAEMA aqueous solution (2% w/v) was spin-coated (100 rpm, 120 s)
118 on the cellulose filter paper coated with CNC. These steps have been repeated two times to ensure proper blending of
119 CNC and PTMAEMA. The obtained composite film was cut into pieces (20 mg) and used for the PFOA adsorption
120 experiments.

121 **2.5. PFOA adsorption experiments**

122 Adsorption experiments were conducted at room temperature. 20 mg (1 cm²) of the composite film was placed in a
123 beaker containing 50 mL PFOA (aq.) solution of 10 ppm (pH = 6.5). The solution was stirred for 6 days, and samples
124 were taken at different time intervals. The adsorption kinetics were analyzed by pseudo-first order model and pseudo-
125 second order model by fitting the experimental data into their linear form consecutively (Eq. 1) and (Eq. 2):

126
$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (Eq.1)$$

127
$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (Eq.2)$$

128 Where q_e is defined as the equilibrium adsorption capacity, K_1 (min⁻¹) is the constant of the pseudo-first order model,
129 and K_2 (g mg⁻¹ min⁻¹) is the constant of the pseudo-second order model.

130 A concentration ranging from 1 to 100 ppm of PFOA was used to investigate adsorption isotherms based on Langmuir
131 and Freundlich model. Langmuir model considers monolayer adsorption of the adsorbate and homogeneous
132 distribution of the adsorption site. The following equation presents the linear form:

133
$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (Eq.3)$$

134 Where C_e is the concentration at the equilibrium, q_e is the quantity adsorbed at the equilibrium, q_m is the maximum
135 quantity adsorbed, and K_L is the Langmuir constant.

136 Freundlich model considers the binding sites of the adsorbent heterogeneous, and the adsorption is multilayer. The
137 following equation presents the linear form:

$$138 \quad \ln(q_e) = \ln K_f + \frac{1}{n} \ln C_e \quad (Eq.4)$$

139 Where K_f is a Freundlich constant, and $\frac{1}{n}$ is the heterogeneity factor.

140 **2.6. Characterization**

141 Particle size and ζ -potential were measured using Anton-Paar Litesizer 500 at 20°C. Samples were prepared at a
142 concentration of 2 w/v %.

143 FT-IR analysis was made on a Thermo Nicolet Nexus FTIR spectrometer with a diamond ATR attachment. Samples
144 were subjected to 32 scans in the range of 4000 cm^{-1} and 650 cm^{-1} , with a resolution of 4 cm^{-1} .

145 Thermogravimetric analysis (TGA) was conducted using TA instruments SDT Q600 by heating the sample to 700 °C
146 under nitrogen with a 10°C/min ramp.

147 Transmission Electron Microscopy (TEM) images were obtained using JOEL 1400 flash. Samples were prepared at
148 0.1% (w/v) and placed on a carbon-coated copper grid for 60 seconds, then ammonium molybdate was added for 20
149 s to stain the samples. The grid was then dried using a vacuum hose.

150 Proton nuclear magnetic resonance (NMR) analysis was conducted on a Bruker Advance spectrometer 400 MHz at
151 room temperature using CDCl_3 as solvent.

152 Size exclusion chromatography (SEC) was performed on TDA 305, Malvern Instruments Worcestershire, UK. The
153 instrument was equipped with a two-column set-up with a particle size of 5 μm , and containing a refractive index
154 detector (RI, concentration detector). The eluent was tetrahydrofuran (THF) with a flow rate of 1.0 mL min^{-1} .
155 OmniSEC software (version 10, Malvern Panalytical, Malvern, UK) was used to analyze the data.

156 X-ray diffraction (XRD) analysis was performed on an X'pert Pro (PAN Analytical). The analysis was done in the 2 θ
157 range from 4° to 60°. The crystallinity index was calculated using deconvolution method. Crystalline peaks were
158 extracted using a software (OriginPro; Peak deconvolution). Gaussian function was used for the curve fitting.
159 Crystallinity index was calculated by dividing the area of all crystalline peaks on the total area (Schroeder et al., 2010).

160 Atomic force microscopy (AFM Nano-Observer, CSI Instruments) was used in tapping mode to characterize the surface
161 morphology of unblended and blended CNC films. Silicon cantilevers (PPP-NCH, Nanosensors) with a typical tip
162 radius of ~5 nm was used. The resonance frequency of the cantilevers was about 235 kHz.

163 Scanning electron microscopy (SEM, Hitachi S-4800) was used at an accelerating voltage of 5 kV to acquire top view
164 and cross-section images of unblended and blended CNC films.

165 The contact angle was measured using the Digidrop instrument (GBX scientific LTD, Dublin, Ireland). 5 μ L of
166 deionized water was deposited onto the films. The contact angle was measured using Digidrop software based on the
167 recorded image.

168 Quartz crystal microbalance with dissipation monitoring (QCM-D) E1 was provided by Biolin Scientific (Västra
169 Frölunda, Sweden). The instrument was equipped with a quartz crystal sensor with a silica-coated surface resonating
170 at 5 MHz. The sensor was coated with CNC, and the flow chamber was fed by an aqueous solution of PTMAEMA.

171 QCM-D provides information on the adsorption kinetics, adsorbed mass, and elastic properties of the layer adsorbed
172 at the sensor's interface. The quartz crystal oscillates at a constant frequency. By varying the mass of the crystal, the
173 resonance frequency of the oscillation changes. This change in frequency could be converted to the adsorbed mass
174 using the Sauerbrey equation (see experimental section for details).

$$175 \quad m = C(\Delta f \times n^{-1}) \quad (Eq.5)$$

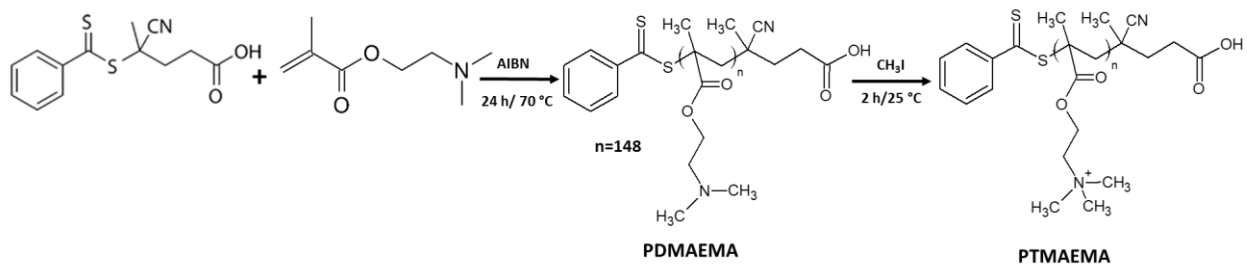
176 Where C is a sensitivity constant ($C = -0.177 (mg m^{-2})Hz^{-1}$). Δf (Hz) corresponds to the change in resonance
177 frequency, and n is the overtone ($n = 1, 3, \dots, 11$). In this experiment, results from the fundamental overtone have
178 been exploited.

179 QCM-D also provides information about viscoelasticity, thickness, and water content of the adsorbed layer by
180 measuring the dissipation (D). Dissipation measure is based on the time the oscillating crystal takes to stop when the
181 experiment is finished.

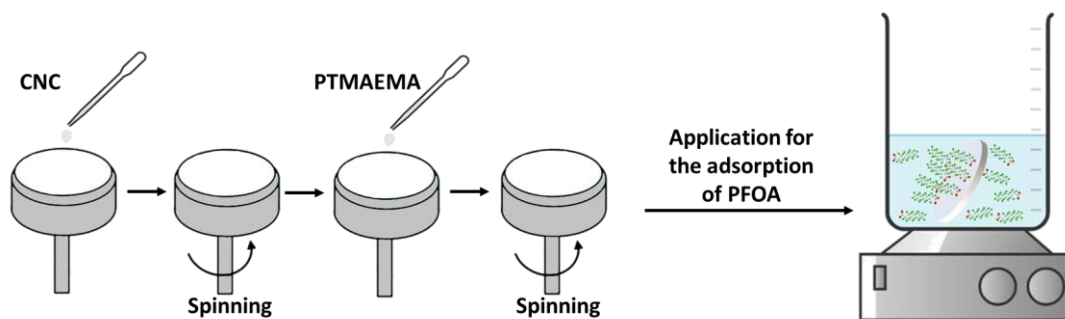
182 PFOA adsorption was evaluated by High-performance liquid chromatography coupled to mass spectroscopy (HPLC-
183 MS). The instrument was equipped with Waters-Xselect HSST3 100mm \times 2.1 mm column with 2.5 μ m particle size.

184 The mobile phase consists of Buffer A (water + 0.1% formic acid) and Buffer B (acetonitrile + 0.05% formic acid)
185 with a constant flow rate of 0.25 mL min⁻¹.

I- Synthesis of poly (trimethyl aminoethyl methacrylate) “PTMAEMA” by RAFT polymerization.



II- Preparation of nanocomposite film based on CNC and PTMAEMA for the adsorption of PFOA.



186

187 **Figure 2. Schematic illustration of the preparation of the nanocomposite film and its application for the adsorption of**

188

PFOA

189 3. Results and discussion

190 3.1. Structural characteristics of CNC

191 CNC is mainly isolated from cellulose fibers through acid hydrolysis. This acid treatment hydrolyzes the disordered
192 regions but retains the crystalline regions with a rod-like morphology (Figure 3.a). When sulfuric acid is used for
193 extraction, it introduces negatively charged sulfate esters groups on the surface of the CNC. These negative charges
194 endow CNC with a good dispersity in water but compromise its thermo-stability (Habibi et al., 2010). Acid
195 concentration directly impacts the size of CNC particles so that increasing acid concentration reduces their diameter,
196 length, and width; it also impacts the percent of sulfate groups inserted (H. Zhang et al., 2019). Because of this, the
197 CNC used in this work was thoroughly analyzed. Elemental analysis, indicated 0.75% of sulfur atoms, and the TGA
198 analysis indicated a good thermally stable microcrystalline cellulose, since the main degradation occurred between
199 260°C-400°C (Figure 3.c) (H. Zhang et al., 2019).

200 FT-IR analysis (Figure 3.b) showed a large band at 3271 cm^{-1} corresponding to O-H stretching vibration. The band at
201 2892 cm^{-1} corresponds to the stretch of C-H. The peak at 1644 cm^{-1} is attributed to O-H bending vibration related to
202 water present in CNC due to its hydrophilic nature. The intensity at 1428 cm^{-1} is associated with CH_2 bending vibration.
203 Band related to C-C forming the cycle appeared at 1159 cm^{-1} , and the broad peak at 1061 cm^{-1} is attributed to the
204 stretching vibration of C-O (H. Zhang et al., 2019) (Hemmati et al., 2018) (Oyewo et al., 2019).

205 The XRD profile of CNC is presented in figure 3.d. The result shows three main peaks at $2\Theta=34.7^\circ$, 22.7° and 15.8° .
206 Each peak is related to respectively following crystalline planes (110), (200), and (004), as described by (Sun et al.,
207 2016). By using the deconvolution method (Figure S1), the obtained crystallinity index is 36.26%.

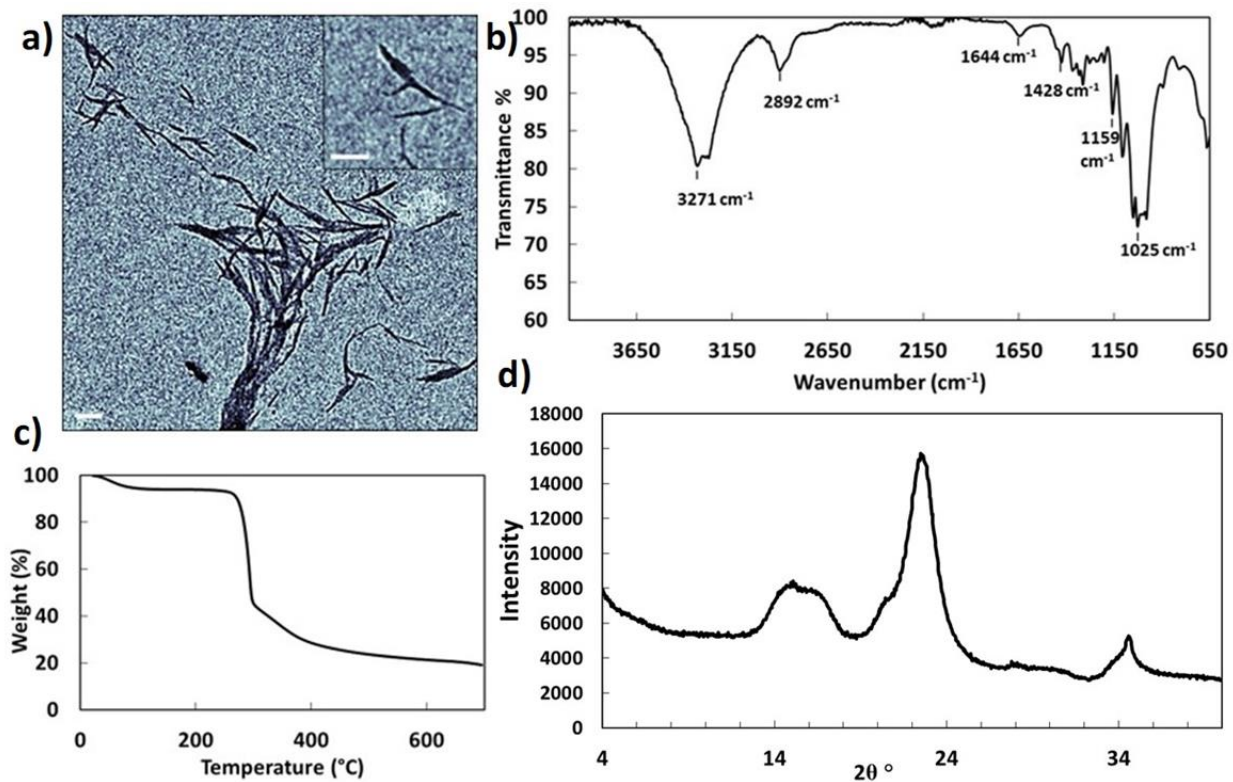


Figure 3. a) TEM image, scale bars= 1 μm , b) FTIR pattern, c) TGA, and d) XRD pattern of CNC

3.2. Characterization of synthesized PTMAEMA

The controlled polymerization of DMAEMA was performed *via* RAFT polymerization with a conversion rate of 94% resulting in an average molecular weight of 11 500 g mol^{-1} and dispersity index (D) of 1.05 (Figure 4.a). The amine groups of PDMAEMA were then quaternized using iodomethane to provide permanent positive charge. The modification was confirmed by NMR. As seen in figures (4.c and d), there is a clear shift of the peak corresponding to the proton of $\text{N}-(\text{CH}_3)_2$ from 2 to 3 ppm. The FTIR analysis of PTMAEMA (figure 4.b) showed a band at 3440 cm^{-1} related to water adsorption due to the hydrophilic nature of the polymer (Yin et al., 2017). Peaks at 3000 and 2950 cm^{-1} correspond to the C-H bond in CH_2 and $-\text{N}(\text{CH}_3)_3$. The band at 1722 cm^{-1} corresponds to the C=O stretching and the characteristic peak of the C-N at 1138 cm^{-1} .

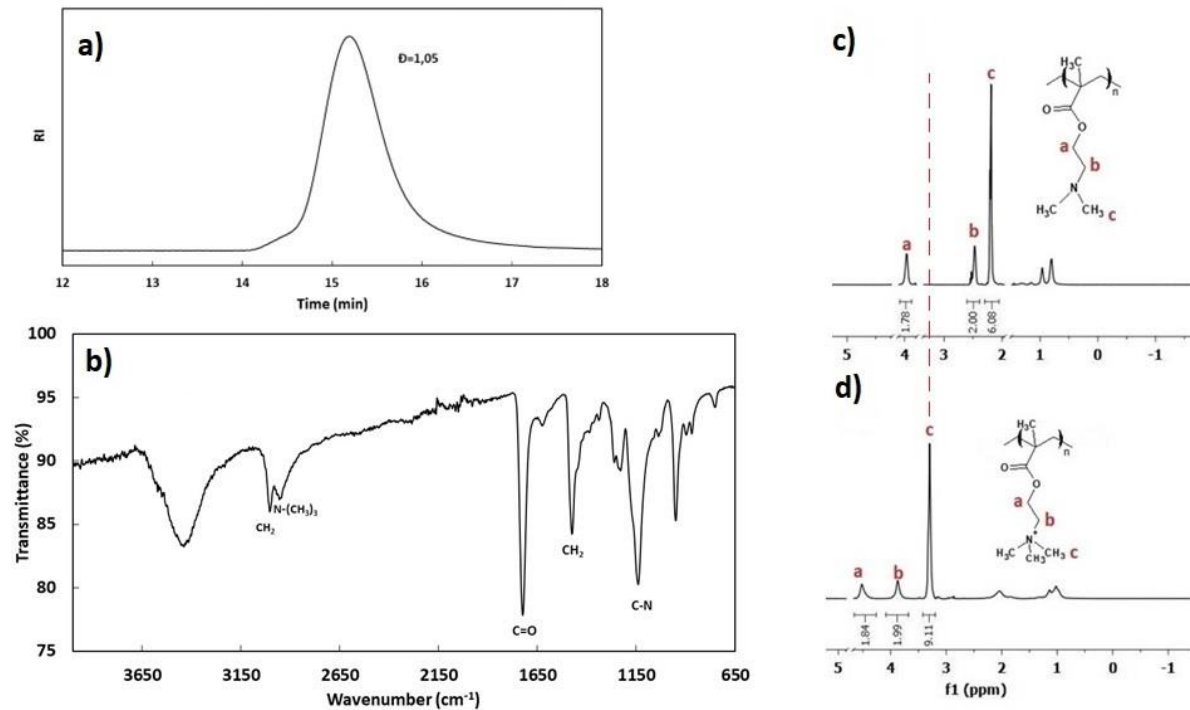


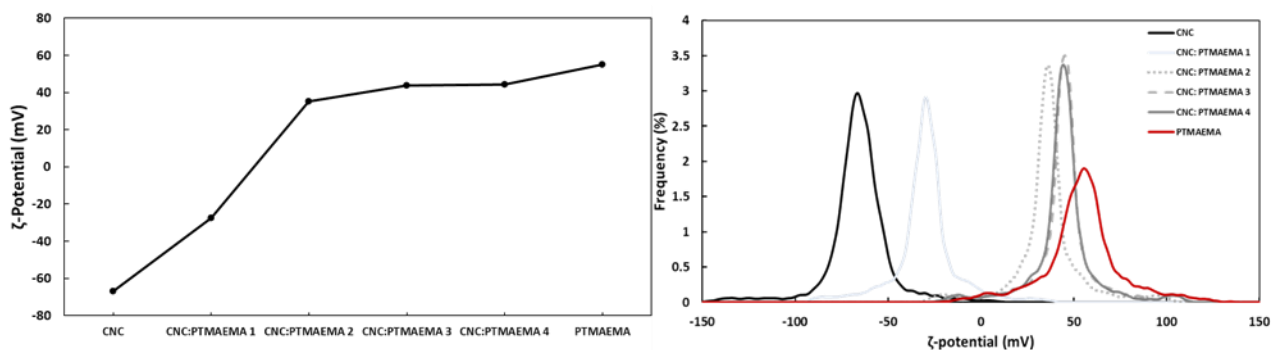
Figure 4. a) SEC trace for PDMAEMA in THF, b) FTIR pattern of PTMAEMA, c) NMR spectra of PDMAEMA (before quaternization), and d) PTMAEMA (after quaternization)

3.3. Investigation of the interaction between CNC and PTMAEMA

To investigate the interaction between CNC and PTMAEMA, the ζ -potential of an aqueous dispersion of CNC with different PTMAEMA concentrations was measured. The obtained results are presented in figure 5. The initial ζ -potential value of aqueous dispersion of CNC before adding PTMAEMA was -67 mV. As PTMAEMA was added, the ζ -potential value increased until it reached a positive value of 44 mV. This ζ -potential value (> 30 mV) indicates the formation of stable dispersions of CNC and PTMAEMA as reported by Rowen and co-workers (Engkagul et al., 2021). Besides the stability, this positive value indicates that the PTMAEMA chains are attached to the CNC surface via strong electrostatic interactions, covering the surface of CNC crystals.

The TEM image analysis has been carried on 100 bare CNC particles before and after modification (figure S2). Before modification CNC presented a diameter of 11 nm and length of 153 nm at dry state (aspect ratio of 13.9), these dimensions remain unchanged after the CNCs have been modified with the charged polymer chains (figure S3). However, the DLS analysis (figure S4.a), suggests that 60% of particles forming CNC dispersion were about 1.23 μm . When adding an equivalent molar ratio of PTMAEMA, the size was reduced to 0.48 μm (figure S4.b). This is most

235 probably due to the attachment of the PTMAEMA chains to the surface of CNC providing enough same charge
236 repulsion between the CNC particles, thus preventing aggregation. Lower amounts of added polymer (molar ratio of
237 0.1) resulted in formation of big aggregates (9.17 μm), suggesting that the surface of the CNC would need to be
238 completely covered with the polymer as fewer positive charge result in large aggregates.

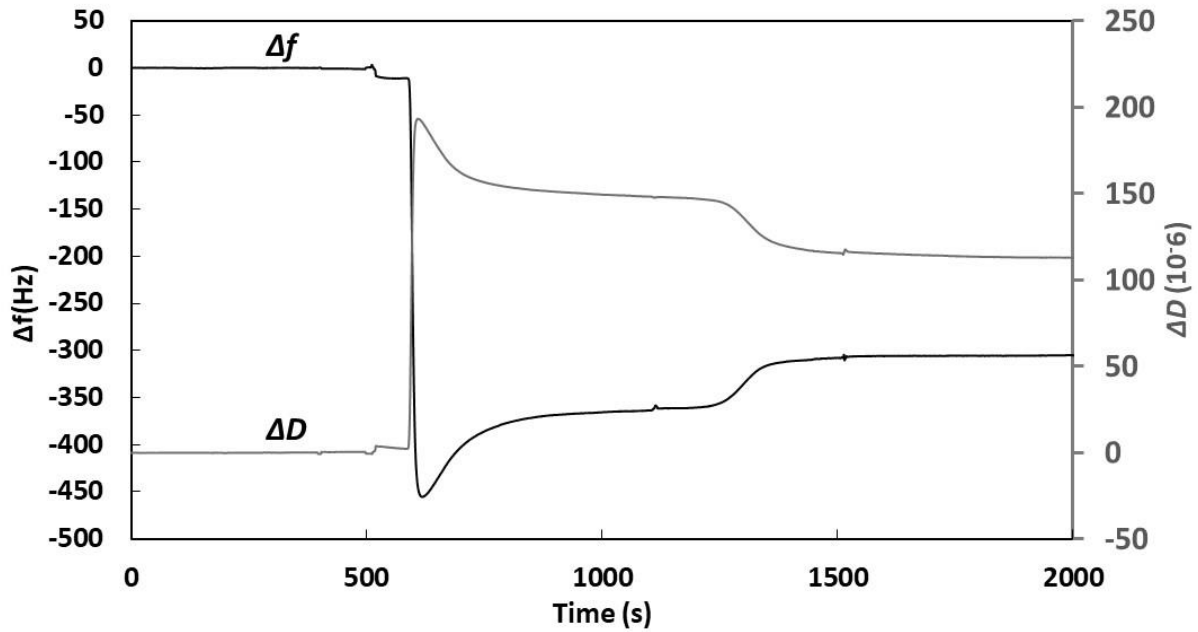


239

Figure 5. ζ -potential of the different CNC: PTMAEMA samples

240

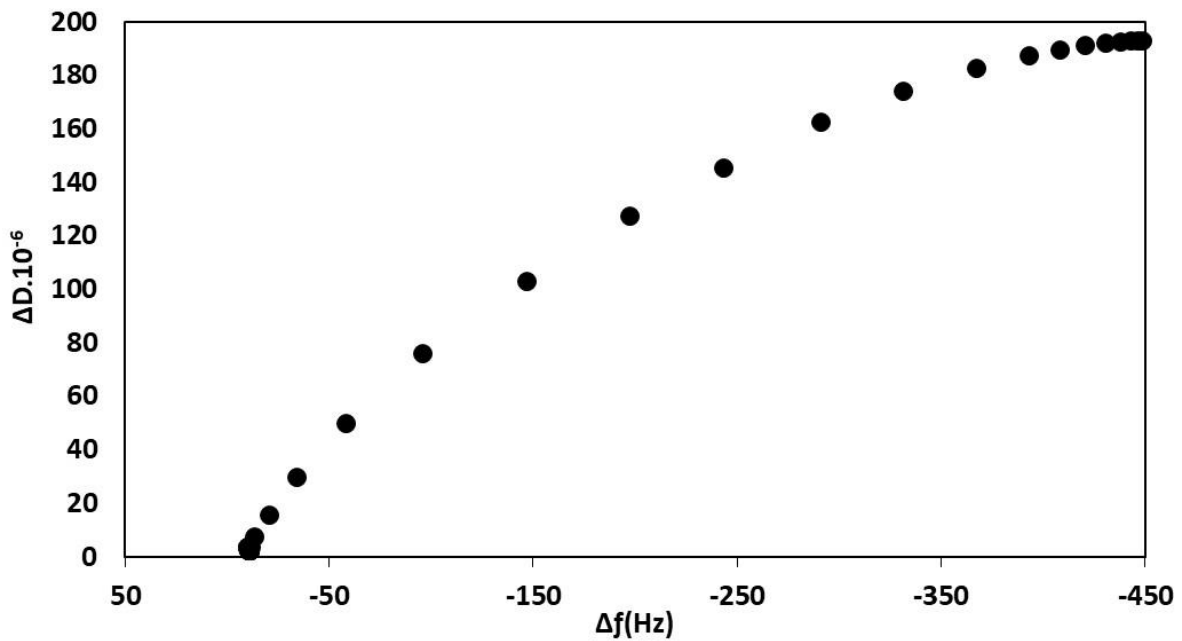
241 To investigate the interaction between anionic CNC and cationic PTMAEMA, silica quartz crystal sensors were
242 prepared following the same procedure as Engström et al. (Engström et al., 2021). CNC layer was deposited on clean
243 QCM-D crystal by spin coating (3000 rpm for 120 s). Then the sensor coated with CNC was equilibrated overnight
244 in water to ensure a stable baseline. For the experiment, an aqueous solution of PTMAEMA at 2 w/w % was
245 introduced into the flow chamber with a constant flow rate of 0.1 mL min⁻¹. After reaching the equilibrium, deionized
246 water was introduced into the chamber to remove the loosely attached polymer. The recorded frequency variation was
247 300 Hz which can be estimated, following the Sauerbrey model (Eq. 5), to an adsorbed mass of 53 mg m⁻² (figure 6).
248 This value highlights the strong electrostatic interaction between anionic CNC and cationic PTMAEMA. Moreover,
249 the equilibrium was reached after only 3 minutes. The ratio $\frac{\Delta D}{\Delta f}$ gives information about the rigidity and the softness of
250 the adsorbed polymer, which is related to the amount of water entrapped in the layer (Kontturi et al., 2008). The value
251 obtained here was 0.38. Based on the result reported by Engström (Engström et al., 2021), the adsorbed polymer can
252 be described as viscoelastic. The adsorption of PTMAEMA on the CNC surface was investigated by presenting the
253 variation of the dissipation as a function of frequency (so-called $D - f$ plot) before the rinsing step (figure 7). When
254 adding PTMAEMA, frequency and dissipation both increase forming a curve implying a slight change in conformation
255 of PTMAEMA on the CNC surface.



256

257 **Figure 6. QCM-D analysis of the frequency (Δf) and dissipation (ΔD) observed for the fundamental overtone**

258 **from adsorption of the aqueous solution of PTMAEMA on CNC.**



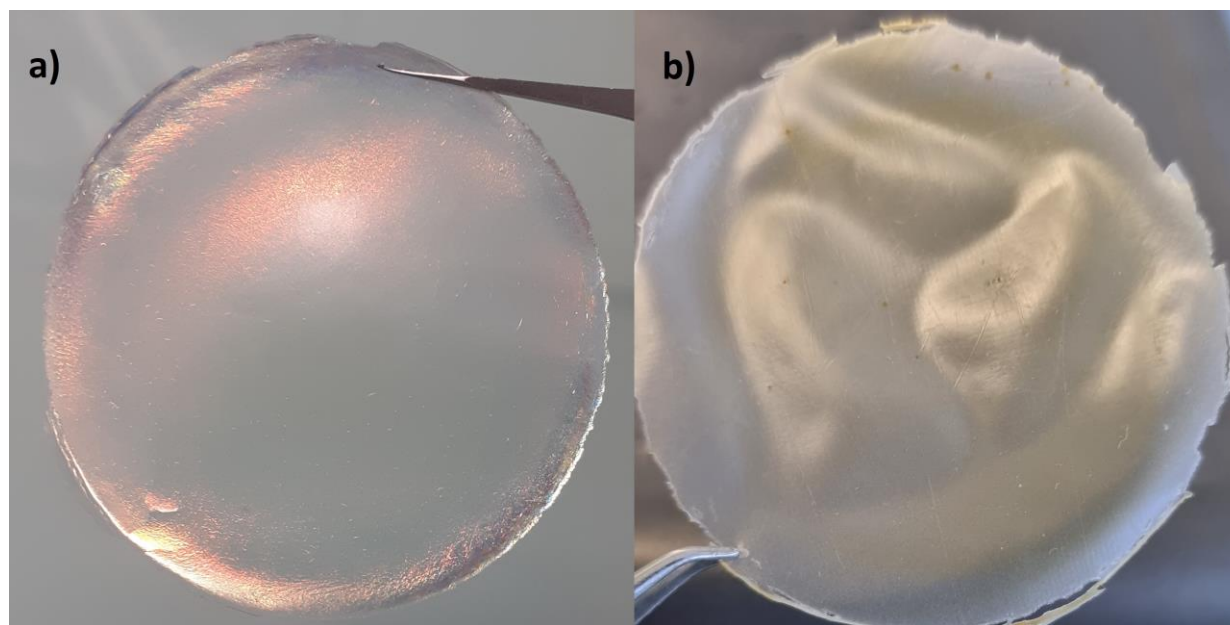
259

260 **Figure 7. Variation of the dissipation as a function of frequency**

261 CNC is known for its ability to form an iridescent well-structured film (figure 8). The SEM image presented in figure

262 9 shows the free surface of a neat CNC film formed by nano-rods having a high degree of alignment. Conversely, the

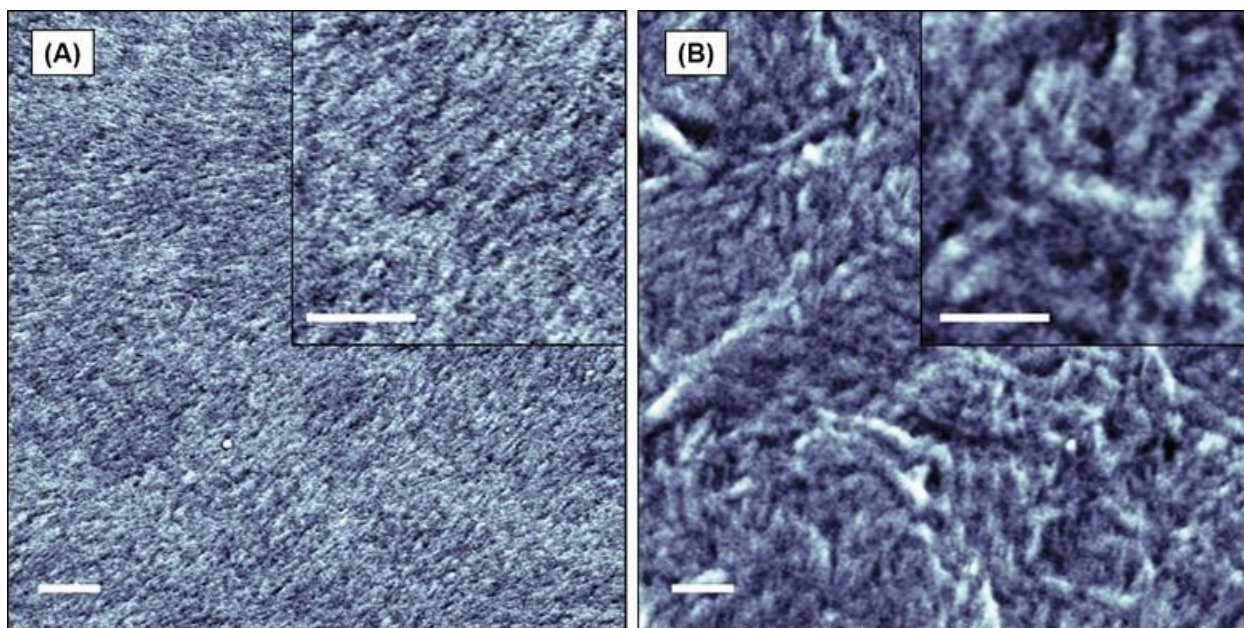
263 degree of nano-rod alignment is decreased within CNC films blended with PTMAEMA due to the electrostatic
264 interactions between CNC and PTMAEMA (see Figure 9b). It is noteworthy that the high degree of nano-rod
265 alignment on the top surface of the neat CNC film is associated with a lower surface roughness ($R_{\text{rms}} = 15.9 \text{ nm}$) than
266 that of the CNC: PTMAEMA 1 composite ($R_{\text{rms}} = 53.8 \text{ nm}$), as revealed by the AFM topographic images presented in
267 figure 10. In addition, the cross-sectional SEM image of the neat CNC film revealed the presence of a typical stacked
268 layered structure that is not clearly observed within the CNC: PTMAEMA 1 composite (see Figure 11). This behavior
269 is in accordance with the disappearance of the iridescent properties within the CNC: PTMAEMA (1:1) composite.
270 The XRD scans of the CNC/PTMAEMA nanocomposite films (figure S5) showed that by adding PTMAEMA, the
271 diffraction peaks of CNC get broadened even at low concentrations of PTMAEMA, indicating that the polymer covers
272 the surface of CNC which hinders the appearance of well-defined CNC crystalline peaks. To evaluate the effect of
273 PTMAEMA on the hydrophilicity of the film, the contact angle of the films was measured, as presented in figure 12.
274 As expected, CNC film was hydrophilic with a contact angle of 58° . Enhancing the concentration of PTMAEMA
275 slightly decreased the contact angle value to 45° . This decrease, although very small is directly related to the
276 hydrophilic nature of PTMAEMA.



277

278

Figure 8. Films made of a) CNC and b) CNC blended with PTMAEMA

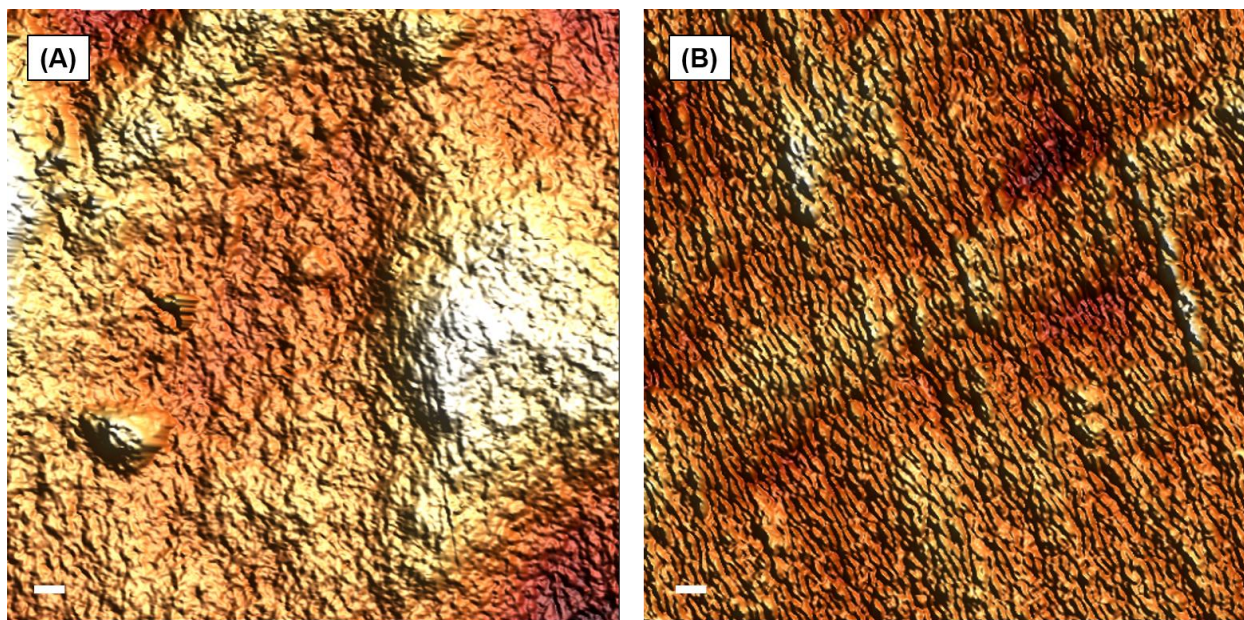


279

280 **Figure 9. SEM images showing the representative top surface of (a) CNC and (b) CNC: PTMAEMA 1 films.**

281

Scale bars: 500 nm.

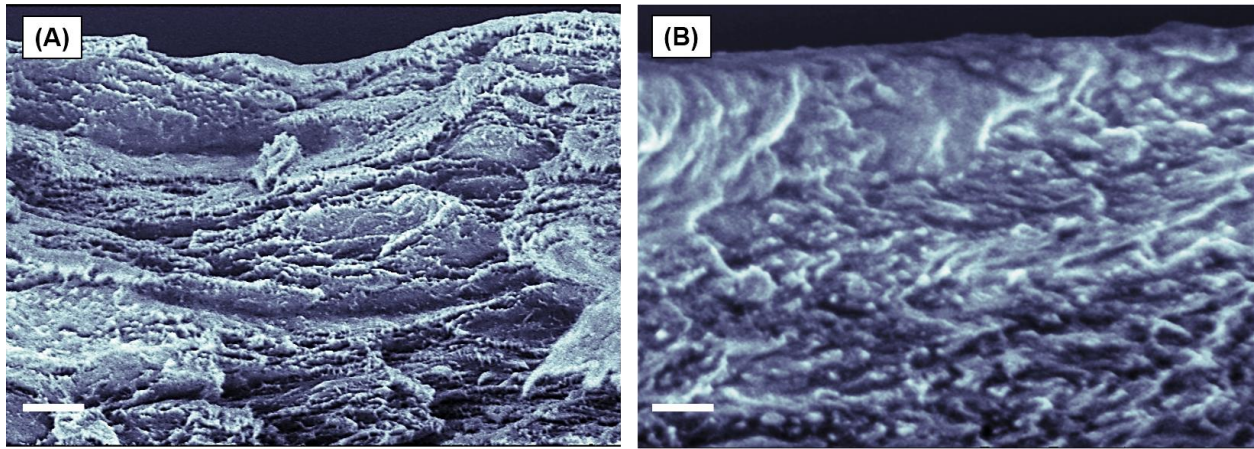


282

283 **Figure 10. AFM topographic views showing the representative top surface of (a) CNC and (b) CNC:**

284

PTMAEMA 1 films. Scale bars: 500 nm.



285

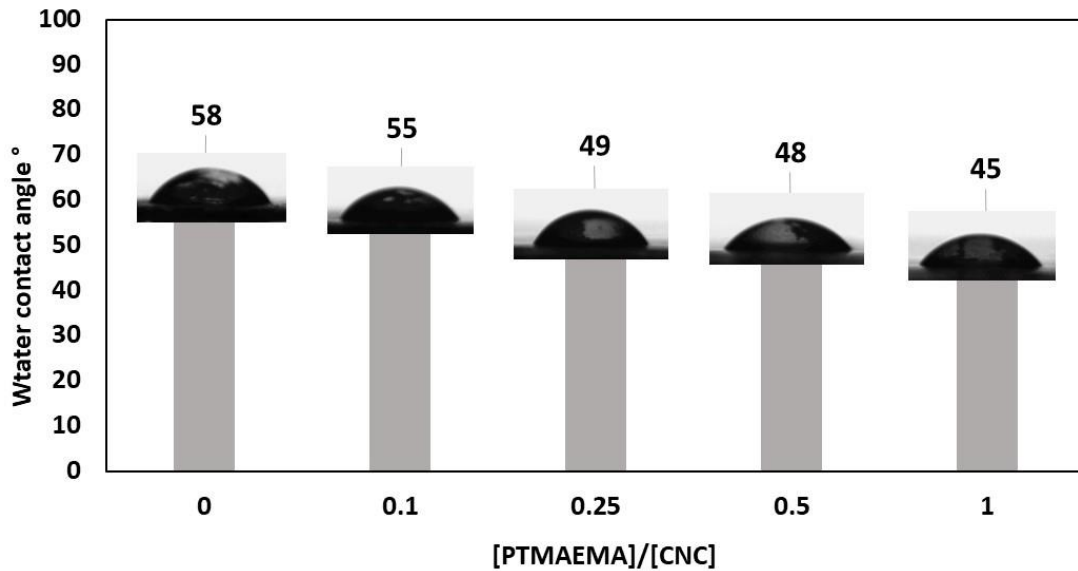
286

Figure 11. Cross-sectional SEM images showing the representative top surface of (a) CNC and (b) CNC:

287

PTMAEMA 1 films. Scale bars: 500 nm.

288



289

290

Figure 10. Variation of water contact angle as a function of the variation of the molar ratio of [PTMAEMA]:

291

[CNC] between 0 and 1.

292

3.4. Evaluation of the stability of CNC/PTMAEMA based nanocomposite films.

293

In the previous paragraph we showed by QCM-D that the interaction between CNC and PTMAEMA is strong, that

294

even after rinsing the coated sensor with water, PTMAEMA was still adsorbed on CNC. But this interaction doesn't

295

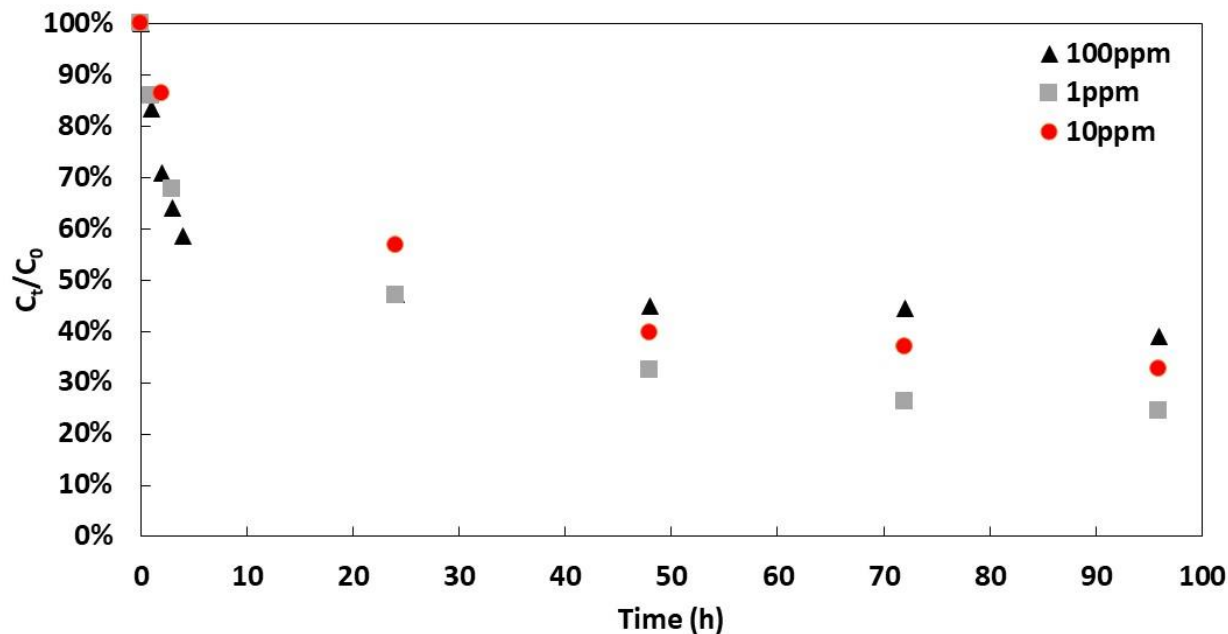
keep the developed nanocomposite film from disintegrating when in water. This is because of the hydrogen bond that

296 is formed between water and the hydroxyl group of CNC. To overcome the disintegration of the film, Whatman™
297 paper was used as support. First, Whatman™ paper was soaked in aqueous solution of NaOH to activate it and favor
298 its interaction with CNC. Then CNC and PTMAEMA were deposited on the cellulose filter paper consecutively by
299 spin-coating. The deposition was confirmed by infrared (figure S6), a new peak that characterizes the carbonyl group
300 of PTMAEMA appeared at 1722 cm^{-1} . To evaluate the efficiency of the developed material in removing PFOA,
301 adsorption experiments were conducted in batch. Adsorption test on bare Whatman™ paper was conducted as the
302 control. As expected, no PFOA was adsorbed to the support Whatman™ paper.

303 The developed nanocomposite material showed great stability in an aqueous environment. The coated Whatman paper
304 was still recoverable even after being placed in water for one week. Figure S7 presents the FTIR spectra of the
305 modified Whatman™ paper after the adsorption of PFOA. The peak characterizing PTMAEMA was still present
306 confirming that the material kept its integrity in water. Furthermore, we have the appearance of new peaks
307 characterizing the adsorbed PFOA. The main advantage of this material is that its adsorption efficiency can be easily
308 upgraded by carrying out a new deposition of the polymer. A small amount of polymer is needed for the coating,
309 guaranteeing good results in the adsorption of PFOA. This material can be easily manufactured which makes it a good
310 candidate to be used on a large scale.

311 **3.5. Adsorption of PFOA onto CNC/PTMAEMA based nanocomposite films.**

312 For a better understanding of the adsorption mechanism, the adsorption kinetic was investigated. Figure 13 represents
313 the variation of C_t/C_0 as a function of time (h) for different concentrations of PFOA. For all the concentrations, the
314 equilibrium is reached after 48 hours of the films being in contact with the PFOA solution. The adsorption efficiency
315 of 100, 10 and 1 ppm of PFOA were 61%, 67%, and 76% respectively. Thus, increasing the concentration of PFOA
316 led to a decrease in the removal efficiency.



317

318 **Figure 11. Variation of C_t/C_0 as a function of time (h) for different concentrations of PFOA.**

319 To define the kinetic order and adsorption parameters, experimental data were fitted into equations (1) and (2). The
 320 experimental results are presented in figure S8 and summarized in table 2. The pseudo-second order model was more
 321 suited for the presented adsorption kinetics since the correlation coefficient was higher than the value obtained from
 322 the pseudo-first order model ($R^2= 0.99$). The pseudo-second order model assumes that the rate-limiting step is
 323 chemisorption, and the adsorption rate depends on adsorption capacity (Sahoo & Prelot, 2020), which correlates well
 324 with the results obtained in figure 13, since for all the different concentrations the equilibrium is reached after 48
 325 hours.

q_e experimental (mg g ⁻¹)	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
	q_e (mg g ⁻¹)	K_1 (h ⁻¹)	R^2	q_e (mg. g ⁻¹)	K_2 (g mg h ⁻¹)	R^2
12.54	10.55	0.0372	0.95	13.42	0.0081	0.99

326

Table 2. Adsorption kinetic parameters of PFOA

327 A concentration ranging from 1 to 100 ppm of PFOA was used to investigate adsorption isotherms based on Langmuir
 328 and Freundlich model. Based on the correlated coefficient “ R^2 ” obtained for each model in table 3, Freundlich isotherm
 329 best fitted the adsorption data, implying multilayer adsorption and the adsorption sites have different binding energies.

330 With $1/n$ being 0.854 (less than 1) implies a chemisorption process (Sahoo & Prelot, 2020). Langmuir isotherm did
331 not fit as good as Freundlich isotherm, but it still can illustrate the maximum sorption which is 303.03 mg g^{-1} .

332

Langmuir model			Freundlich model		
$q_m (\text{mg g}^{-1})$	$K_L (\text{L g}^{-1})$	R^2	$K_F (\text{L g}^{-1})$	$1/n$	R^2
303.03	0.0146	0.75	5.08	0.8542	0.99

334

335 **Table 3. Isotherm parameters of Langmuir and Freundlich model for the adsorption of PFOA**

336 Comparing the obtained results to a similar study (D. Zhang et al., 2016) performed using granulated activated carbon
337 (GAC) ($K_2=4.72 \text{ g mg h}^{-1}$) with the same initial concentration of PFOA (10 ppm), shows that the sorption rate obtained
338 with modified CNC is higher (as sorption rate is inversely related to the rate constant “ K_2 ”). Moreover, the maximum
339 sorption indicated by the Langmuir model for modified CNC is 303.03 mg g^{-1} while for GAC is 52.8 mg g^{-1} (D. Zhang
340 et al., 2016).

341 4. Conclusion

342 Modification of CNC surface is of such importance, since it broadens its application in different fields of science and
343 technology, also enhances its compatibility with other materials. As hypothesized, CNC can be easily and efficiently
344 modified via noncovalent interaction with oppositely charged moieties such as polymers. This modification is
345 advantageous compared to covalent modification since it can be performed at large scales (industrial level). Herein
346 we reported the modification of negatively charged CNC with a positively charged polymer (PTMAEMA). The
347 collected data suggest that CNC and PTMAEMA interact with each other *via* strong electrostatic interactions, which
348 results in formation of a stable suspension as well as a homogeneous film. For application in the adsorption of PFOA
349 in an aqueous environment, Whatman™ paper was used to support the CNC- PTMAEMA film. The sorption kinetic
350 best fitted the pseudo-second order model with a constant rate $K_2=0.0081 (\text{g mg h}^{-1})$. The obtained results indicate
351 that as assumed, the simple approach described here, is a viable pathway to prepare cheap and environmentally friendly
352 material from CNC for efficient elimination of toxic PFAS from water.

353 5. REFERENCES

354 Asante, B., Sirviö, J. A., Li, P., Lavola, A., Julkunen-Tiitto, R., Haapala, A., & Liimatainen, H. (2020). Adsorption of
355 bark derived polyphenols onto functionalized nanocellulose: Equilibrium modeling and kinetics. *AIChE*

356 *Journal*, 66(2), 1–10. <https://doi.org/10.1002/aic.16823>

357 Bondeson, D., & Oksman, K. (2007). Dispersion and characteristics of surfactant modified cellulose whiskers
358 nanocomposites. *Composite Interfaces*, 14(7–9), 617–630. <https://doi.org/10.1163/156855407782106519>

359 Dong, F., Xu, X., Shaghaleh, H., Guo, J., Guo, L., Qian, Y., Liu, H., & Wang, S. (2020). Factors influencing the
360 morphology and adsorption performance of cellulose nanocrystal/iron oxide nanorod composites for the
361 removal of arsenic during water treatment. *International Journal of Biological Macromolecules*, 156, 1418–
362 1424. <https://doi.org/10.1016/j.ijbiomac.2019.11.182>

363 Engkagul, V., Rader, C., Pon, N., Rowan, S. J., & Weder, C. (2021). Nanocomposites Assembled via Electrostatic
364 Interactions between Cellulose Nanocrystals and a Cationic Polymer. *Biomacromolecules*, 22(12), 5087–5096.
365 <https://doi.org/10.1021/acs.biomac.1c01056>

366 Engström, J., Reid, M. S., Brotherton, E. E., Malmström, E., Armes, S. P., & Hatton, F. L. (2021). Investigating the
367 adsorption of anisotropic diblock copolymer worms onto planar silica and nanocellulose surfaces using a quartz
368 crystal microbalance. *Polymer Chemistry*, 12(42), 6088–6100. <https://doi.org/10.1039/d1py00644d>

369 Gomri, C., Cretin, M., & Semsarilar, M. (2022). Recent progress on chemical modification of cellulose nanocrystal
370 (CNC) and its application in nanocomposite films and membranes-A comprehensive review. *Carbohydrate*
371 *Polymers*, 294(June), 119790. <https://doi.org/10.1016/j.carbpol.2022.119790>

372 Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose nanocrystals: Chemistry, self-assembly, and applications.
373 *Chemical Reviews*, 110(6), 3479–3500. <https://doi.org/10.1021/cr900339w>

374 Hemmati, F., Jafari, S. M., Kashaninejad, M., & Barani Motlagh, M. (2018). Synthesis and characterization of
375 cellulose nanocrystals derived from walnut shell agricultural residues. *International Journal of Biological*
376 *Macromolecules*, 120, 1216–1224. <https://doi.org/10.1016/j.ijbiomac.2018.09.012>

377 Hu, Z. H., Omer, A. M., Ouyang, X. K., & Yu, D. (2018). Fabrication of carboxylated cellulose nanocrystal/sodium
378 alginate hydrogel beads for adsorption of Pb(II) from aqueous solution. *International Journal of Biological*
379 *Macromolecules*, 108, 149–157. <https://doi.org/10.1016/j.ijbiomac.2017.11.171>

380 Khandal, D., Riedl, B., Tavares, J. R., Carreau, P. J., & Heuzey, M. C. (2019). Tailoring cellulose nanocrystals
381 rheological behavior in aqueous suspensions through surface functionalization with polyethyleneimine. *Physics*

382 *of Fluids*, 31(2), 021207. <https://doi.org/10.1063/1.5046669>

383 Kontturi, K. S., Tammelin, T., Johansson, L. S., & Stenius, P. (2008). Adsorption of cationic starch on cellulose
384 studied by QCM-D. *Langmuir*, 24(9), 4743–4749. <https://doi.org/10.1021/la703604j>

385 Liu, J., Liu, D., Liu, S., Li, Z., Wei, X., Lin, S., & Guo, M. (2020). Preparation and Characterization of Sulfated
386 Cellulose Nanocrystalline and its Composite Membrane for Removal of Tetracycline Hydrochloride in Water.
387 *Energy and Environmental Materials*, 3(2), 209–215. <https://doi.org/10.1002/eem2.12055>

388 Lu, D., Sha, S., Luo, J., Huang, Z., & Zhang Jackie, X. (2020). Treatment train approaches for the remediation of per-
389 and polyfluoroalkyl substances (PFAS): A critical review. *Journal of Hazardous Materials*, 386(December
390 2019), 121963. <https://doi.org/10.1016/j.jhazmat.2019.121963>

391 Militao, I. M., Roddick, F. A., Bergamasco, R., & Fan, L. (2021). Removing PFAS from aquatic systems using natural
392 and renewable material-based adsorbents: A review. *Journal of Environmental Chemical Engineering*, 9(4),
393 105271. <https://doi.org/10.1016/j.jece.2021.105271>

394 Nekouei, F., Nekouei, S., Keshtpour, F., Noorizadeh, H., & Wang, S. (2017). Cr(OH)₃-NPs-CNC hybrid
395 nanocomposite: a sorbent for adsorptive removal of methylene blue and malachite green from solutions.
396 *Environmental Science and Pollution Research*, 24(32), 25291–25308. [https://doi.org/10.1007/s11356-017-](https://doi.org/10.1007/s11356-017-0111-2)
397 0111-2

398 Oyewo, O. A., Mutesse, B., Leswif, T. Y., & Onyango, M. S. (2019). Highly efficient removal of nickel and cadmium
399 from water using sawdust-derived cellulose nanocrystals. *Journal of Environmental Chemical Engineering*,
400 7(4), 103251. <https://doi.org/10.1016/j.jece.2019.103251>

401 Ranjbar, D., Raeiszadeh, M., Lewis, L., MacLachlan, M. J., & Hatzikiriakos, S. G. (2020). Adsorptive removal of
402 Congo red by surfactant modified cellulose nanocrystals: a kinetic, equilibrium, and mechanistic investigation.
403 *Cellulose*, 27(6), 3211–3232. <https://doi.org/10.1007/s10570-020-03021-z>

404 Sahoo, T. R., & Prelot, B. (2020). Adsorption processes for the removal of contaminants from wastewater: The
405 perspective role of nanomaterials and nanotechnology. *Nanomaterials for the Detection and Removal of*
406 *Wastewater Pollutants*, 161–222. <https://doi.org/10.1016/B978-0-12-818489-9.00007-4>

407 Schroeder, L. R., Gentile, V. M., & Atalla, R. H. (2010). Nondegradative preparation of amorphous cellulose. *Journal*

408 *of Wood Chemistry and Technology*, 6(1), 1–14. <https://doi.org/10.1080/02773818608085213>

409 Sun, B., Zhang, M., Hou, Q., Liu, R., Wu, T., & Si, C. (2016). Further characterization of cellulose nanocrystal (CNC)
410 preparation from sulfuric acid hydrolysis of cotton fibers. *Cellulose*, 23(1), 439–450.
411 <https://doi.org/10.1007/s10570-015-0803-z>

412 Trache, D., Hussin, M. H., Haafiz, M. K. M., & Thakur, V. K. (2017). Recent progress in cellulose nanocrystals:
413 Sources and production. *Nanoscale*, 9(5), 1763–1786. <https://doi.org/10.1039/c6nr09494e>

414 Trache, D., Hussin, M. H., & Thakur, V. K. (2017). *Recent progress in cellulose nanocrystals: sources and production*.
415 1763–1786. <https://doi.org/10.1039/c6nr09494e>

416 Wanninayake, D. M. (2021). Comparison of currently available PFAS remediation technologies in water: A review.
417 *Journal of Environmental Management*, 283(September 2020), 111977.
418 <https://doi.org/10.1016/j.jenvman.2021.111977>

419 Yin, J. J., Wahid, F., Zhang, Q., Tao, Y. C., Zhong, C., & Chu, L. Q. (2017). Facile Incorporation of Silver
420 Nanoparticles into Quaternized Poly(2-(Dimethylamino)Ethyl Methacrylate) Brushes as Bifunctional
421 Antibacterial Coatings. *Macromolecular Materials and Engineering*, 302(6), 1–8.
422 <https://doi.org/10.1002/mame.201700069>

423 Zhang, D., Luo, Q., Gao, B., Chiang, S. Y. D., Woodward, D., & Huang, Q. (2016). Sorption of perfluorooctanoic
424 acid, perfluorooctane sulfonate and perfluoroheptanoic acid on granular activated carbon. *Chemosphere*, 144,
425 2336–2342. <https://doi.org/10.1016/j.chemosphere.2015.10.124>

426 Zhang, H., Qian, Y., Chen, S., & Zhao, Y. (2019). Physicochemical characteristics and emulsification properties of
427 cellulose nanocrystals stabilized O/W pickering emulsions with high -OSO₃- groups. *Food Hydrocolloids*,
428 96(May), 267–277. <https://doi.org/10.1016/j.foodhyd.2019.05.023>

429