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Layered organization of anisometric cellulose nanocrystals and beidellite clay particles accumulated near the membrane surface during cross-flow ultrafiltration: In situ SAXS and ex situ SEM/WAXD characterization

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1 Layered organization of anisometric cellulose
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5 SEM / WAXD characterization

6
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18

19 **Abstract**

20 The structural organization of the concentration polarization layer (CPL) during the cross-
21 flow membrane separation process of anisometric aqueous suspensions of colloidal cellulose
22 nanocrystals and beidellite clay particles has been characterized by *in situ* time-resolved small-
23 angle X-ray scattering (SAXS). Dedicated cross-flow filtration cells were implemented on the
24 ID02 TRUSAXS beamline at the European Synchrotron Radiation Facility (Grenoble, France).
25 From the analysis of the scattered intensities and structure factors of particles in the CPL, both
26 the concentration profiles $\phi(\Delta z, \Delta t)$ and anisotropic structural organization have been
27 characterized as a function of filtration time (Δt) and distance from the membrane surface (Δz).
28 Remarkably, a coupling between concentration and anisotropy was revealed and modeled using
29 either a simple or stretched exponential trend for rod- or disk-like systems, respectively. Using
30 a simple filtration model, the time evolution of the deposit thickness, membrane resistance and
31 specific resistance of the deposit, deduced from an analysis of the normalized concentration
32 profiles, allowed directly predicting the rapid decay of permeate flux associated to the
33 exponential growth of concentration and anisotropic organization inside the CPL. *Ex situ*
34 scanning electron microscopy (SEM) observations and wide-angle X-ray diffraction (WAXD)
35 analyses performed on dried deposits parallel and perpendicular to the membrane surface
36 revealed well-defined layered structures from nanometer to micrometer length scales.

37

38 **Keywords:** cross-flow ultrafiltration, concentration polarization layer, SAXS, anisotropic
39 colloids, cellulose nanocrystals, clay particles, permeation flux.

40

41 **Introduction**

42 Membrane separation processes are widely used in industrial applications (bio-industries,
43 agro-industries, or sludge treatment) for concentrating and purifying nanoparticle dispersions.¹
44 Under the action of the transmembrane pressure and cross-flow velocity, the particles
45 accumulate near the membrane surface in the so-called concentration polarization layer (CPL)
46 and their concentration can rise above the sol-gel transition, leading to a catastrophic loss in
47 permeability. Consequently, an accurate understanding of the structural organization of colloids
48 in the CPL in parallel with the filtration properties is of considerable interest to improve the
49 efficiency of the filtration. Depending on the transmembrane pressure and cross-flow
50 conditions, a transition from stable to unstable filtration performance has been identified and a
51 limit has been proposed in the literature.^{2,3} The authors have identified a critical flux, which
52 determines the transition from a reversible CPL to an irreversible deposit formation. Colloidal
53 interactions and osmotic pressure have been identified as pertinent parameters and have been
54 introduced in models to describe this transition.⁴⁻¹² It has only been recently possible to access
55 the evolution of the concentration within the CPL as a function of time, distance from the
56 membrane surface and filtration conditions by combining dedicated cross-flow ultrafiltration
57 cells and *in situ* small-angle X-ray scattering (SAXS) measurements.¹³⁻¹⁶ Thanks to this unique
58 method, it is now possible to finely investigate the colloidal concentration profile as well as the
59 anisotropic organization at the micrometer scale and relate these quantities to the permeate flux
60 reduction during cross-flow ultrafiltration.

61 In this work, we studied the mechanisms involved in the sol-gel transition that takes place
62 during the cross-flow ultrafiltration of anisotropic colloidal suspensions. From a filtration point
63 a view, the questions raised are the following: *i*) what are the sol/gel phase-transition
64 mechanisms involved during the ultrafiltration processes when anisotropic colloids are
65 simultaneously submitted to shear flow and pressure near the membrane surface? *ii*) Which link

66 can be established between the permeation flux and the space- and time-dependent evolutions
67 of the deposit formation (accounting for thickness, concentration, particle orientation and
68 specific resistance)? Finally, we evaluated the extent to which a prediction of the permeate flux
69 could be achieved by a direct analysis of the dynamic evolution in space and time of the colloids
70 accumulated near the membrane surface, using *in situ* SAXS data.

71 To answer these questions, two types of anisometric particles (rod- and disk-like) have been
72 considered. The rod-like system consisted of cellulose nanocrystals (CNCs),¹⁵ prepared by
73 strong acid hydrolysis of native wood cellulose microfibrils. Their average dimensions are
74 typically 10 nm in width and 100-200 nm in length (Fig. 1A) and thanks to the presence of
75 charged sulfate groups at their surface, they can form chiral nematic (cholesteric) organizations
76 in aqueous suspension.^{17,18} CNCs are particularly attractive building blocks for the design of
77 innovative biobased materials and with numerous potential applications such as
78 environmentally-friendly nanocomposites, paper coating or biomedical products.¹⁹⁻²¹ CNCs
79 display outstanding mechanical properties such as a modulus as high as 120-150 GPa and a
80 strength up to 6 GPa and are now commercially available in large quantities. The disk-like
81 system is composed of natural beidellite clay particles (Fig. 1B) which are subhedral lamellae
82 (typically 1 nm-thick and 300-500 nm-wide). Like other swelling clays like montmorillonite,
83 beidellite is a ubiquitous mineral on the Earth's surface and subsurface and is largely used for
84 industrial (drilling fluids, anti-settling agents, ointments, cosmetics, and health)
85 applications.^{17,22,23}

86 The space and time dependence of particle concentration and structural organization within
87 the accumulated layers of CNCs or beidellite particles deposited near the membrane surface,
88 have been characterized by *in situ* SAXS experiments during cross-flow filtration and linked to
89 the filtration properties of the dispersions. Specific analyses of concentration, anisotropy and
90 principal orientation direction of the particles, have allowed to link these different parameters

91 and to provide a straightforward prediction using a simple filtration model of the rapid decay
92 of the permeate flux at the initiation of the deposit growth and its corresponding specific
93 resistance. The comparison of these results obtained on the two studied systems, namely CNCs
94 and beidellite clay particles, is used to bring some highlights on the potential links between
95 filtration parameters (thickness, resistance and permeate flux) and physical features (colloidal
96 volume fraction, orientation, shape and aspect ratio).

97 The organization built during cross-flow ultrafiltration was consolidated via dead-end
98 ultrafiltration, followed by air-drying of the deposits. The structure of the solid deposits was
99 characterized *ex situ* using wide-angle X-ray diffraction (WAXD) and scanning electron
100 microscopy (SEM) both parallel and perpendicular to the membrane surface, which allowed
101 evaluating the degree of orientation of the constituting particles in the textured materials.

102 **Materials and Methods**

103 **Materials**

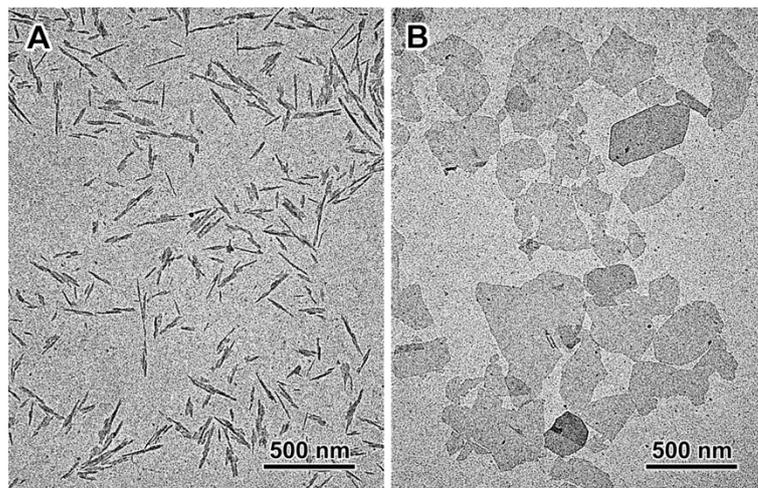
104 Cellulose nanocrystals (CNCs) were purchased from UMaine Development Center
105 (University of Maine, USA) as a suspension in water with a stock concentration of $c = 12.2$
106 wt%. Suspensions at $c_0 = 0.7$ wt% were prepared by diluting the stock suspension with
107 deionized water, followed by 2 h of vigorous stirring. CNC aggregates were fragmented by
108 using a sonication probe (Branson Digital sonifier) applying a minimum of 2 kJ per gram of
109 CNCs.²⁴ Considering the CNC density (1.6 g cm^{-3}), the final suspension had a nominal volume
110 fraction of $\phi_0 \simeq 0.0044$.

111 Natural beidellite (SBId-1) clay powder was purchased from the Idaho Source Clays
112 Minerals Repository of the Clay Mineral Society (Purdue University). Beidellite suspensions
113 were purified of extra minerals and centrifugation was used for size fractionation (the detailed
114 sample preparation has been described by Paineau et al.^{17,23}). The dilute suspension had an ionic

115 strength of 10^{-4} M and a concentration of about $c_0 = 0.8$ wt%, corresponding to a volume
116 fraction of about $\phi_0 = 0.0031$ (beidellite density 2.6 g cm^{-3}).^{23,25}

117 **Transmission Electron Microscopy (TEM)**

118 Droplets of dilute CNC or beidellite aqueous suspensions were deposited onto glow-
119 discharged carbon-coated copper grids and allowed to dry. The specimens were observed with
120 a JEOL JEM-2100-Plus microscope operating at an accelerating voltage of 120 kV. Images
121 were recorded with a Gatan Rio 16 camera equipped with the GMS acquisition software. In
122 Figure 1A, the TEM image of the CNC is presented, revealing elongated objects constituted of
123 rod-like crystallites of a few units.²⁴ In Figure 1B, the TEM image of beidellite clay particles
124 reveals a typical platelet shape exhibiting irregular faceted contours.^{23,25}



125

126 **Figure 1.** TEM images of the CNCs (A) and beidellite clay particles (B) used in this study.

127 **Small-Angle X-ray Scattering (SAXS)**

128 SAXS measurements were performed at the TRUSAXS ID02 beamline (ESRF, Grenoble).²⁶
129 Measurements were performed at room temperature with a sample-detector (RayoniX MX170)
130 distance of 10 m and an X-ray wavelength $\lambda = 0.095$ nm, covering a range of scattering vector
131 amplitude, q , of $(0.01-0.5) \text{ nm}^{-1}$. Thanks to the pinhole collimation setup available at ID02, all
132 the measurements were acquired by using a vertical beam cross-section at the sample position

133 of about 30 μm , hence corresponding to the maximum resolution of the membrane distance Δz .

134 The two-dimensional scattering patterns were corrected and normalized to absolute scale.

135 A temperature-controlled flow-through capillary cell (diameter = 1.85 mm) was used to
136 measure the absolute scattered intensity of dispersions at rest at $T = 22\text{ }^\circ\text{C}$. Sample and
137 background scattering were measured at the same position of the capillary, thus allowing a very
138 reliable subtraction. The normalized background scattering of the flow-through capillary cell
139 and cross-flow ultrafiltration cell filled with distilled water were systematically subtracted prior
140 to data analysis. Then, scattering intensities as a function of q were obtained by azimuthally
141 averaging isotropic scattering patterns. In the case of anisotropic signals (Fig. 3A), scattering
142 intensities along a defined scattering angle ψ (either $\psi = 0$ or $\pi/2$) were obtained by azimuthally
143 averaging such patterns around the angle of interest over a narrow sector of $\pm 0.044\text{ rad}$ ($\pm 2.5^\circ$).

144 **Preparation of textured solid deposits**

145 The protocol used to prepare air dry deposit is the following. In a first step, a cross-flow
146 ultrafiltration identical of the one performed under *in-situ* SAXS at cross-flow flux $Q = 0.06$
147 L min^{-1} and transmembrane pressure $\Delta P = 1.1 \times 10^5\text{ Pa}$ was achieved during 2 h. The deposits
148 were further consolidated by continuing the filtration in dead-end ultrafiltration, i.e. the cross-
149 flow was arrested while ΔP remained unchanged. This second step of dead-end ultrafiltration
150 was applied for about 20 h to consolidate the structural organization induced during the first
151 step. Then, the suspensions were gently removed from the filtration cell and tubing by using
152 compressed air ($\Delta P = 0.1\text{ bar}$) and the gel-like deposits were extracted from the filtration cell.
153 Finally, as a third step, samples were dried at ambient conditions for several days for further *ex*
154 *situ* structural analyses.

155 **Wide-Angle X-ray Diffraction (WAXD)**

156 Strips of solid specimens were cut with a razor blade and fixed on 0.2 mm collimators in
157 such a way that the plane of the film was oriented parallel or perpendicular to the X-ray beam.
158 The specimens were analyzed in a Warhus vacuum chamber using a Philips PW3830 generator
159 operating at 30 kV and 20 mA (Ni-filtered $\text{CuK}\alpha$ radiation, $\lambda = 0.1542$ nm). Two-dimensional
160 patterns were recorded on Fujifilm imaging plates read with a Fujifilm BAS 1800-II bioimaging
161 analyzer.

162 **Scanning Electron Microscopy (SEM)**

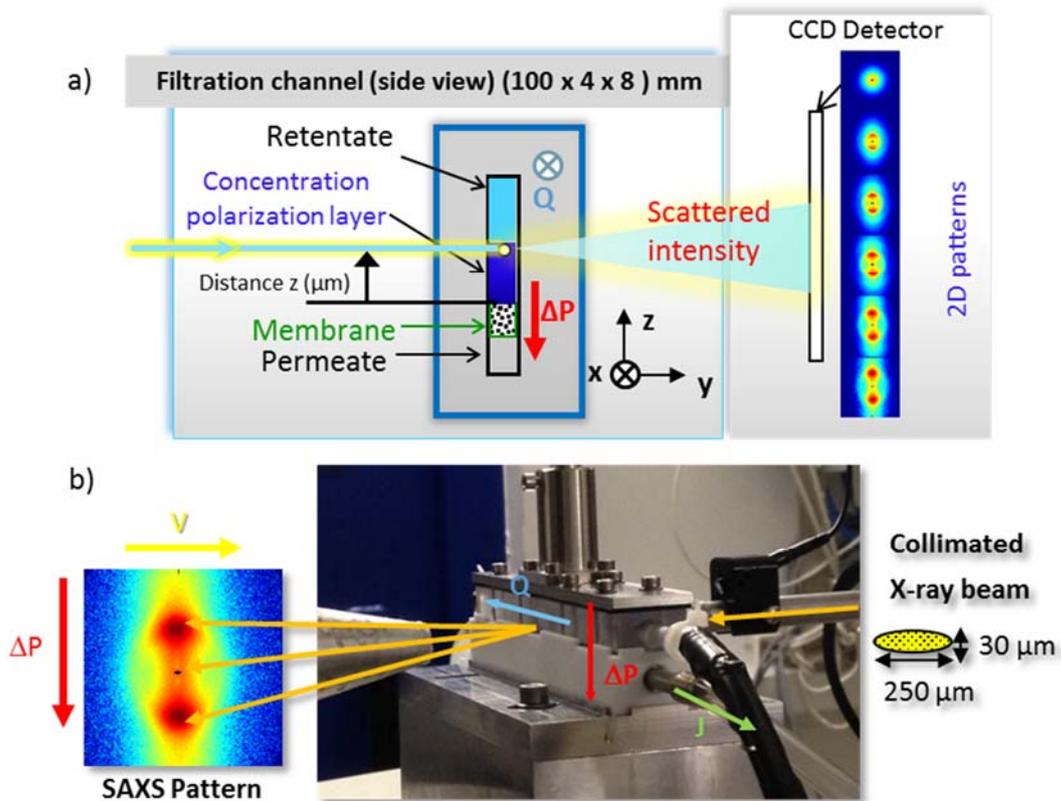
163 The solid deposits were fractured at room temperature and the fragments were fixed on
164 metallic stubs covered with carbon tape. The fracture surfaces were coated with Au/Pd in a
165 Baltec MED 020 sputter coater and the various surfaces were observed in secondary electron
166 mode with a FEI Quanta-FEG 250 microscope operating at an acceleration voltage of 2 kV.

167 **Cross-Flow Ultrafiltration under SAXS**

168 A tailored cross-flow ultrafiltration cell was employed for SAXS experiments. It consisted
169 of a PTFE channel for the permeate and a polycarbonate upper channel for the retentate (Fig. 2).
170 The polycarbonate block exhibited a 500 μm -thick window in the center of the upper channel
171 to minimize X-ray absorption. The two channels were separated by a flat polysulfone
172 ultrafiltration membrane (100 kD, Pleyade Rayflow x100, Orelis Environnement, membrane
173 resistance $R_m \sim 5 \times 10^{12} \text{ m}^{-1}$) placed on a rigid, perforated substrate to avoid pressure-induced
174 deformations. The length of the retentate channel was 100 mm along the tangential flow (Q)
175 direction, with a section of 8 mm in height and 4 mm in depth (along the X-ray beam direction).

176 The transmembrane pressure, ΔP , was measured at the entry of the cell with a pressure gauge
177 (FP 110 FGP Sensors & Instrument) and set to $\Delta P = 1.1 \times 10^5$ Pa. Pressure was applied to the
178 rig via purified compressed air. The feed suspension was pumped (Mono pump LF series,
179 Axflow) from a high pressure resistant vessel (Millipore, France) to the ultrafiltration cell.^{14,15}
180 The feed cross-flow rate was imposed at $Q = 0.06 \text{ L min}^{-1}$ and measured with a magnetic flow

181 meter (Optiflux 6300C, KROHNE, France). The permeate flux, J_p , was continuously recovered
 182 in a recipient and its mass was registered with a computer every 10 s with a scale of 0.001 g of
 183 accuracy (Precisa 400M). During SAXS measurements, the cell was mounted on a motorized
 184 sample stage, which enabled *i*) aligning the membrane plane parallel to the X-ray beam and *ii*)
 185 vertically translating the cell across the incident beam in order to follow the evolution of the
 186 colloidal structure as a function of membrane distance Δz .



187
 188 **Figure 2:** a) Schematic description, and b) picture and of the SAXS cross-flow ultrafiltration cell
 189 positioned on the ID02 TRUSAXS beamline at the ESRF. The arrows define the corresponding
 190 directions of the cross-flow Q , transmembrane pressure ΔP , permeate flux J , velocity v , related to the
 191 X-ray beam propagation and scattered intensity recorded on the CCD detector. The retentate flows in
 192 the upper channel (polycarbonate), which has a 500 μm -thin window in the center to minimize X-ray
 193 absorption. The solvent passes through the ultrafiltration membrane and reaches the permeate channel
 194 (PTFE). The membrane is supported by a grid with a honeycomb structure, preventing any pressure-
 195 induced deformation of the membrane and CPL.

196

197 *In situ* SAXS measurements were performed during the whole filtration process, in order to
198 follow the evolution of both colloidal concentration and particle orientation. The analysis of the
199 anisotropy (in this case related to the preferential orientation of the colloids) was performed by
200 using the MATLAB-based Small-Angle Scattering Evaluation Tool (SASET) software.²⁷
201 Specifically, the model-free Principal Component Analysis (PCA) method was chosen, which
202 provides values from 0 (for isotropic suspensions) to 1 (in the case of completely aligned
203 systems). The anisotropy and direction of maximum scattering (ψ_0) were calculated via PCA in
204 the (0.045 - 0.5) nm⁻¹ q -range. The determination of the colloidal volume fraction was
205 performed by exploiting specific properties of both CNCs and beidellite particles. These are
206 both negatively charge-stabilized colloids, that show well-defined scattering structure-factors
207 of interaction [$S(q)$] even at moderately low volume fraction.^{18,22,23,28}

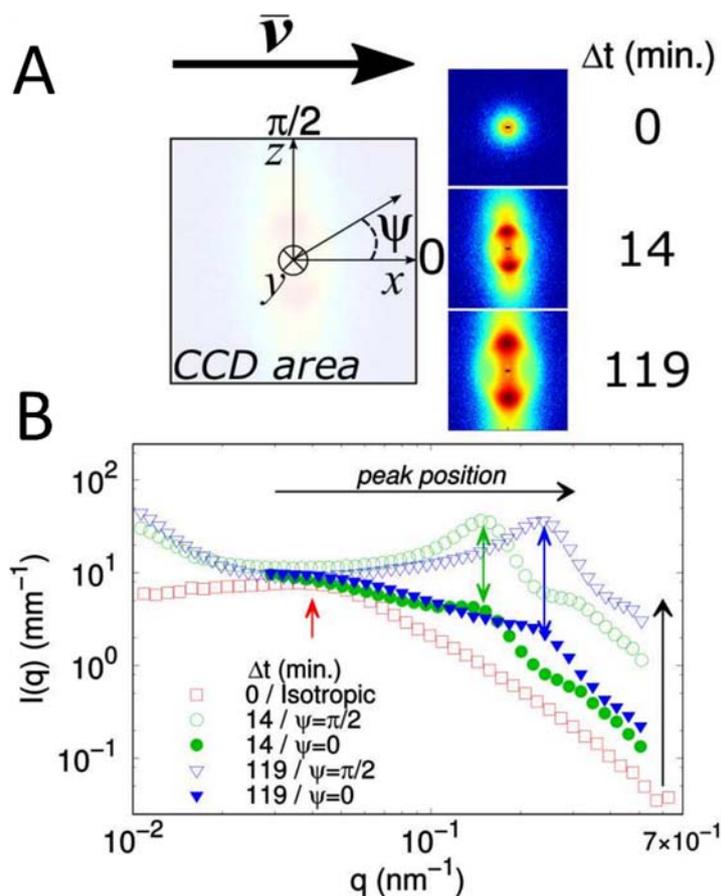
208

209 **Results and Discussion**

210 **Structure Factor and Calibration of Cellulose Nanocrystal Scattering Intensity**

211 In order to analyze the scattering intensities [$I(q)$] in the cross-flow ultrafiltration cell, a
212 calibration curve has to be established. It relates the absolute $I(q)$ of cellulose nanocrystals to
213 the volume fraction in the suspension via the peak position of their structure factor $S(q)$. Thanks
214 to this calibration procedure, *in-situ* scattering intensities measured in the cross-flow
215 ultrafiltration cell at different filtration times and distances from the membrane surface, allowed
216 calculating the volume fractions $\phi(\Delta z, \Delta t)$ of the filtered suspension near the membrane surface.
217 In this aim, several CNC samples at different volume fractions were first measured by SAXS
218 in static conditions in flow-through cell, in order to obtain the calibration curve, which uniquely
219 defines the particle concentration as a function of the peak position of $S(q)$ (Supporting
220 Information Fig. S1).²⁸ Due to the strong repulsive electrostatic interactions between CNCs in

221 aqueous suspensions,¹⁸ scattering intensities from CNC suspensions exhibited a visible
 222 structure factor even at the lowest concentration $\phi_0 \approx 0.0044$ (Fig. 3B, $\Delta t = 0$). Hence, during
 223 cross-flow measurements, the effective ϕ of CNC colloids was extracted through the evaluation
 224 of the peak position of $S(q)$ at each position Δz and time step Δt (Δt was set to 0 when the
 225 transmembrane pressure ΔP was applied).
 226



227
 228 **Figure 3:** (A) Left: example of scattering pattern in the xz plane of the CCD detector. The scattering
 229 angle ψ is null in the direction of the velocity field of the retentate. Right: representative evolution of
 230 the scattering pattern of CNC under filtration at $\Delta z = 30 \mu\text{m}$ and $\Delta t = 0, 14$ and 119 min. (B) Scattering
 231 intensities I as a function of q . The isotropic pattern at $\Delta t = 0$ min was azimuthally averaged, whereas
 232 data at $\Delta t = 14$ and 119 min were averaged around two directions of interest. Arrows point out the shift
 233 of the peak position as a function of time.
 234

235 Selected scattering patterns are shown in Figure 3. At $\Delta t = 0$, the scattering pattern is
 236 isotropic and the azimuthally averaged $I(q)$ exhibits a peak at about $q \simeq 0.04 \text{ nm}^{-1}$. In contrast,
 237 during filtration, scattering patterns close to the membrane display a significant anisotropy
 238 (Fig. 3B). The maximum scattering direction is alongside $\psi \sim \pi/2$, demonstrating that CNC
 239 nanorods are preferentially oriented parallel to the membrane surface (xy -plane) with their main
 240 axis in the direction of the flow. Scattering curves at $\psi = 0$ and $\pi/2$ are shown in Figure 3B. The
 241 peak positions shift as a function of time, reflecting how the colloidal concentration increases
 242 during the filtration process. Interestingly, the q -positions of the peaks at $\psi = \pi/2$ are
 243 systematically consistent with the broader ones at $\psi = 0$. In the hard-sphere model (as an
 244 approximation of a repulsive potential), the q -value corresponding to the peak of $S(q)$ is related
 245 to the interparticle distance via the relation $2\pi/q_{peak}$. Therefore, as the peak positions at $\psi = 0$
 246 and $\pi/2$ are matching, the average interparticle distances along both z - and x -directions are also
 247 comparable. Thanks to this, the effective volume fraction can be reliably deduced from q_{peak} ,
 248 even in the case of an anisotropic scattering pattern. This important information allowed us to
 249 retrieve actual colloidal concentrations in the ultrafiltration cell through the q -positions of the
 250 peaks of $I(q)$ regardless the anisotropic feature of the scattering pattern.

251 Ultrafiltration of Cellulose Nanocrystal Suspensions

252 In Figure 4A, the concentration of CNCs as a function of the distance from the membrane,
 253 $\phi(\Delta z, \Delta t)$, is reported for different time steps. Distinctly, an increase of concentration is observed
 254 from the first few minutes of filtration. At each time step, the concentration profiles
 255 systematically follow a single exponential decay:

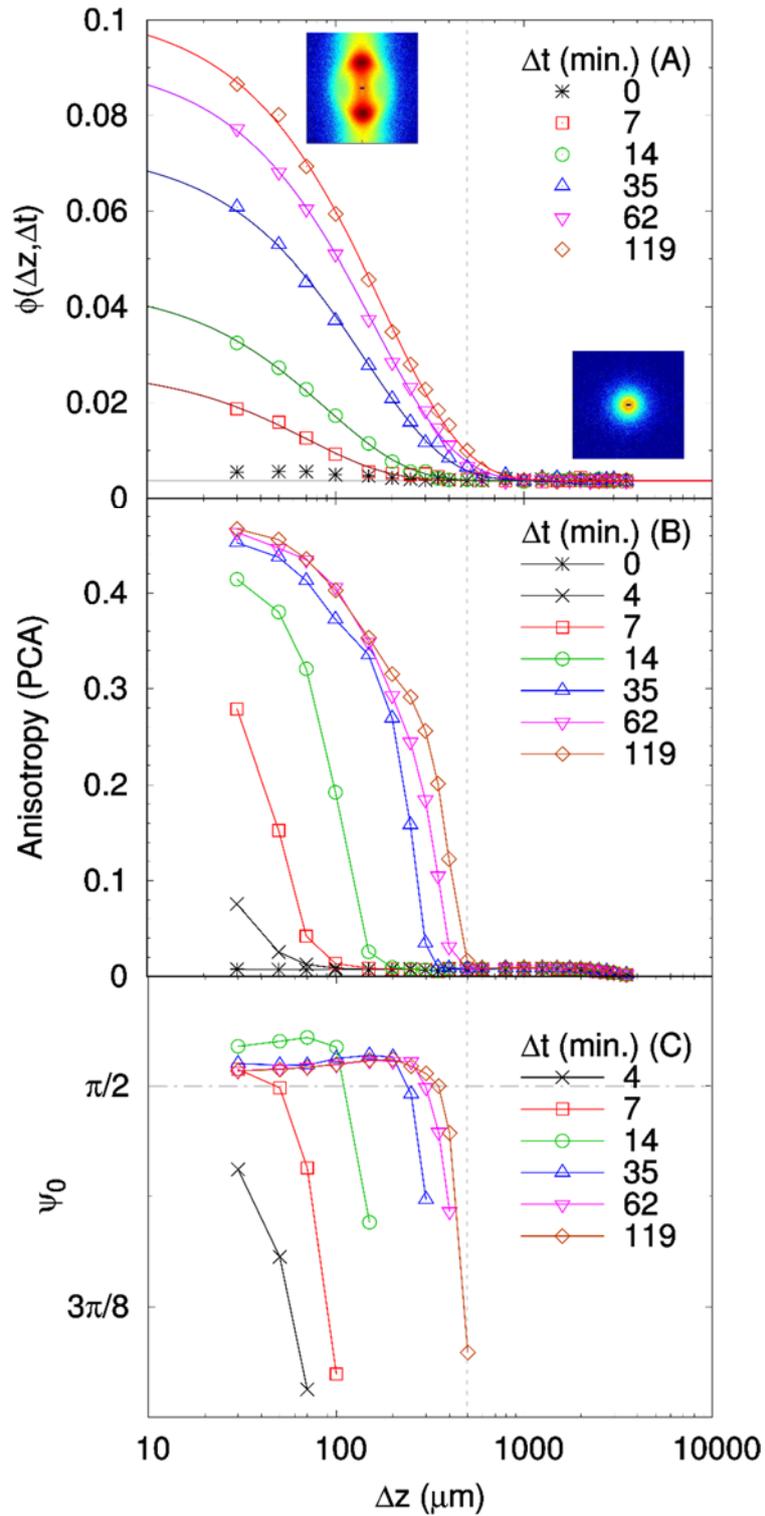
$$256 \quad \phi(\Delta z, \Delta t) = \phi_0 + \phi(0, \Delta t) e^{-\frac{\Delta z}{\zeta_c(\Delta t)}} \quad (1)$$

257 where $\zeta_c(\Delta t)$ is the time-dependent characteristic length of the exponential decay (Supporting
 258 Information Table S1) and $\phi(0, \Delta t)$ is the time-dependent colloidal volume fraction at the

259 membrane position ($\Delta z=0$). Both quantities were determined by data fitting (Figure 4A). Such
260 an exponential concentration profile is consistent with the solution of the particle mass balance
261 equation given by:

$$262 \quad D(x, t) \frac{\partial \phi(x, z, t)}{\partial z} + \tilde{J}_p(x, t) \phi(x, z, t) = 0 \quad (2)$$

263 where $\tilde{J}_p(x, t)$ and $D(x, t)$ are the permeate flux and average diffusion coefficient of the particles
264 within the concentrated layer at the cell position x and time t .²⁹ Equation 2 is obtained under a
265 few assumptions, including *i*) much smaller average particle dimensions compared to the
266 concentrated-layer thickness; *ii*) much smaller permeate flux compared to cross-flow velocity;
267 *iii*) negligible convection on the x -axis within the concentrated-layer; and *iv*) zero particle-
268 transport at the membrane surface ($\Delta z = 0$). Essentially, CNC concentration profiles in Figure
269 4A describe well-defined concentrated layers with their flowing particles that obey a “model”
270 particle mass-balance for hard-spheres dispersions. Moreover, this description is valid for each
271 observed Δt . One could note that, within the framework of this model, the obtained
272 characteristic length, ζ_c , can be used to extrapolate information about the diffusion coefficient,
273 as $\zeta_c(t) = D(x, t) \tilde{J}_p(x, t)$. However, in the experiments reported in this work, the measured $J_p(t)$
274 is the total permeate flux, which is averaged over the full x -axis. Another interesting feature
275 highlighted by these *in-situ* measurements is that the deposited layers undergo no compaction
276 of the deposit all along the concentration phenomena. Indeed, the measured concentration
277 profiles show regular accumulation of particles from the membrane surface $\Delta z = 0$ until
278 increasing Δz positions and this for each Δt filtration time. That is to say that, at each filtration
279 time, all the layers accumulated above the membrane surface concentrate regularly.



280

281 **Figure 4:** Concentration (A), anisotropy (B) and maximum scattering direction (C) profiles of the
 282 growing CNC deposit as a function of Δz at different time steps. Solid lines in panel (A) refer to the
 283 fitting performed with Eq. 1. The two-dimensional scattering patterns in (A) corresponds to $\Delta z = 30 \mu\text{m}$
 284 at $\Delta t = 0$ (right) and 119 min (left). The vertical dotted line highlights the coupling between
 285 concentration and anisotropy and marks the edge of the deposit. Note that ψ_0 is not defined for isotropic
 286 scattering patterns.

287 If a compaction of the deposited layers would appear at a certain filtration time, this regular
 288 particle accumulation from the membrane surface would exhibit a change in the single
 289 exponential decay features highlighted on these concentrating phenomena. This change has not
 290 been observed, as the single exponential decay persisted all along the concentration phenomena.
 291 Consequently, no occurrence of compaction of one part of the deposited layers has been
 292 evidence in the studied filtration conditions.

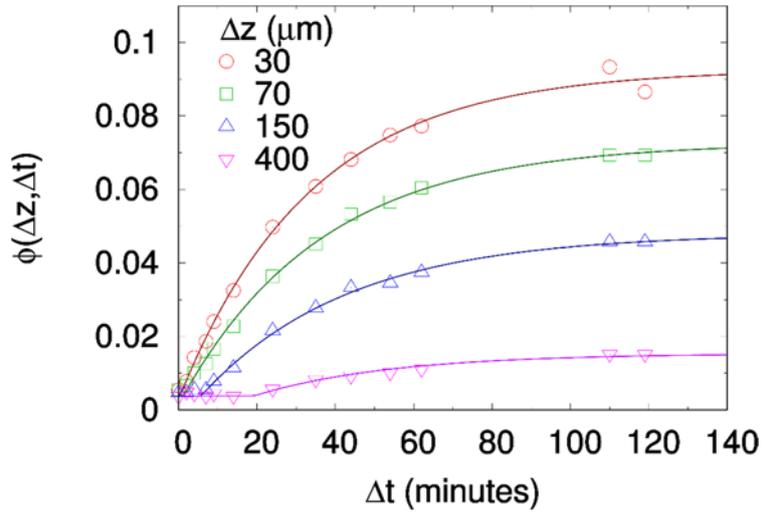
293 Anisotropy parameters and maximum scattering direction, ψ_0 , calculated via PCA are
 294 presented in Figures 4B and 4C, respectively. Although the concentration profile continuously
 295 decreases as a function of Δz , a sharp fall in both anisotropy and ψ_0 is observed. Such a behavior
 296 can provide a direct observation of the edge of the structured CPL, which systematically
 297 corresponds to a threshold in volume fraction of $\phi \sim 0.01$. Below this value, the trend of the
 298 anisotropy values seems strongly linked to the concentration profile and the formation of a
 299 concentrated, oriented layer of a few tens of micrometers is already visible after 4 min of
 300 filtration. However, ψ_0 is stabilized at about 1.6 rad after 14 – 35 min. In the steady state, the
 301 average orientation of CNC nanorods is then slightly tilted with regard to the membrane plane.
 302 This deviation may be associated to the shape of the deposit in the xz -plane, which likely results
 303 from a different rate of colloidal accumulation alongside x .^{14,29}

304 Concentration profiles, $\phi(\Delta z, \Delta t)$, plotted as a function of time are shown in Figure 5. Also
 305 in this case, these curves can be described by a single exponential increase:

$$306 \quad \phi(\Delta z, \Delta t) = \phi_0 + \phi^\infty(\Delta z) \left[1 - e^{-\frac{(\Delta t - t_0)}{\tau_c(\Delta z)}} \right] \quad (3)$$

307 where $\phi^\infty(\Delta z) \equiv \phi(\Delta z, \Delta t \rightarrow \infty)$ is the limiting volume fraction that the deposit can achieve at a
 308 given Δz . The value $\tau_c(\Delta z)$ is the characteristic time of the exponential increase, whereas $t_0(\Delta z)$

309 depicts the moment when any variation from ϕ_0 start to be detectable. The $\phi^\infty(\Delta z)$, $\tau_c(\Delta z)$ and
 310 $t_0(\Delta z)$ values were obtained from the fits shown in Figure 5.



311
 312 **Figure 5:** Concentration profiles of the growing CNC deposit as a function of Δt at different distances
 313 from the membrane. Solid lines refer to the fitting performed with Eq. 3.

314 Ultrafiltration of Beidellite Suspensions

315 Like CNC nanorods, beidellite platelets are electrostatically stabilized in aqueous
 316 suspensions. Above the liquid/gel transition ($0.005 < \phi < 0.0075$),²² the strong repulsive
 317 interaction is responsible for the observation of the scattering structure factor $S(q)$ (Fig. 6).

318 Approximating the repulsive interaction as a hard-sphere potential allows determining the
 319 interparticle distance as $d = 2\pi/q_{max}$, where q_{max} is the peak position of $S(q)$. The interparticle
 320 distance was then used to determine the effective colloidal volume fraction, ϕ , from the swelling
 321 law $\phi(d)$ as described by Paineau and coworkers.^{23,25}

322 Unfortunately, at low ϕ , below the gel transition, no interaction peak was observed. In these
 323 cases, effective ϕ values were calculated by fitting scattering curves along ψ_0 and $\psi_0 - \pi/2$. The
 324 analysis was performed by using a monodisperse scattering form factor for disks, given by:

$$325 \quad F(q, \psi, \theta, \phi) = \phi V \Delta \rho^2 \left\{ 2 \frac{\sin[qa \cos(\gamma)/2] J_1[qR \sin(\gamma)]}{qa \cos(\gamma) / 2 \quad qR \sin(\gamma)} \right\}^2 \quad (4)$$

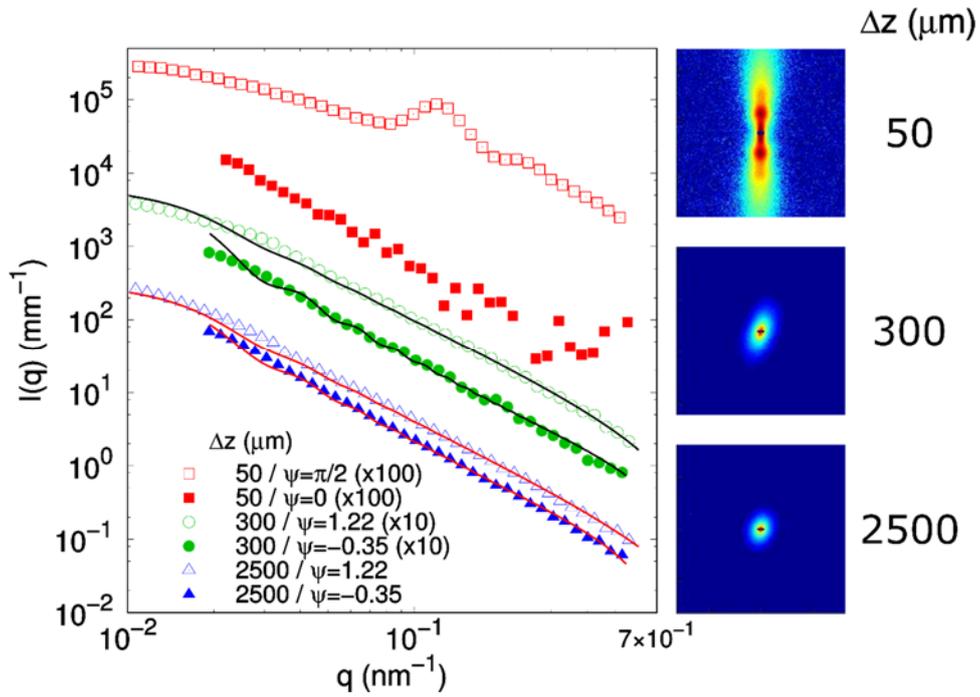
326 where:

$$327 \quad \cos(\gamma) = \cos(\psi) \cos(\theta) + \sin(\psi) \sin(\theta) \cos(\varphi) \quad (5)$$

328 and using the Maier-Saupe orientation distribution function (ODF)³⁰ to perform the orientation

329 averaging:

$$330 \quad I(q, \psi) = (2\pi N)^{-1} \int_0^{\pi/2} d\theta \int_0^\pi d\varphi F(q, \psi, \theta, \varphi) e^{m \cos(\theta)^2} \sin(\theta) \quad (6)$$



331
 332 **Figure 6:** Example of scattering intensities, $I(q)$, and respective two-dimensional patterns of beidellite
 333 sample at $\Delta t = 18$ min and $\Delta z = 50$ (squares), 300 (circles) and 2500 μm (triangles). $I(q)$ curves were
 334 obtained by integrating the scattering patterns along ψ_0 and $\psi_0 - \pi/2$ over a sector of ± 0.044 rad ($\pm 2.5^\circ$).
 335 Data at $\Delta z = 50 \mu\text{m}$ display a peak due to the presence of $S(q)$. Solid lines refer to the fitting performed
 336 with Eq. 6, with $m = 1.49$ (circles) and 0.70 (triangles).

337 In Equations 4, 5 and 6, R and a are average radius and thickness of platelets (286 and 0.85
 338 nm, respectively^{22,23}). θ and φ are polar and azimuthal angles, where θ is null when the normal
 339 to the platelet surface is parallel to z . J_1 is the Bessel function of order 1. $\Delta\rho$ is the difference
 340 between scattering length density of beidellite and water and V is the average platelet volume.

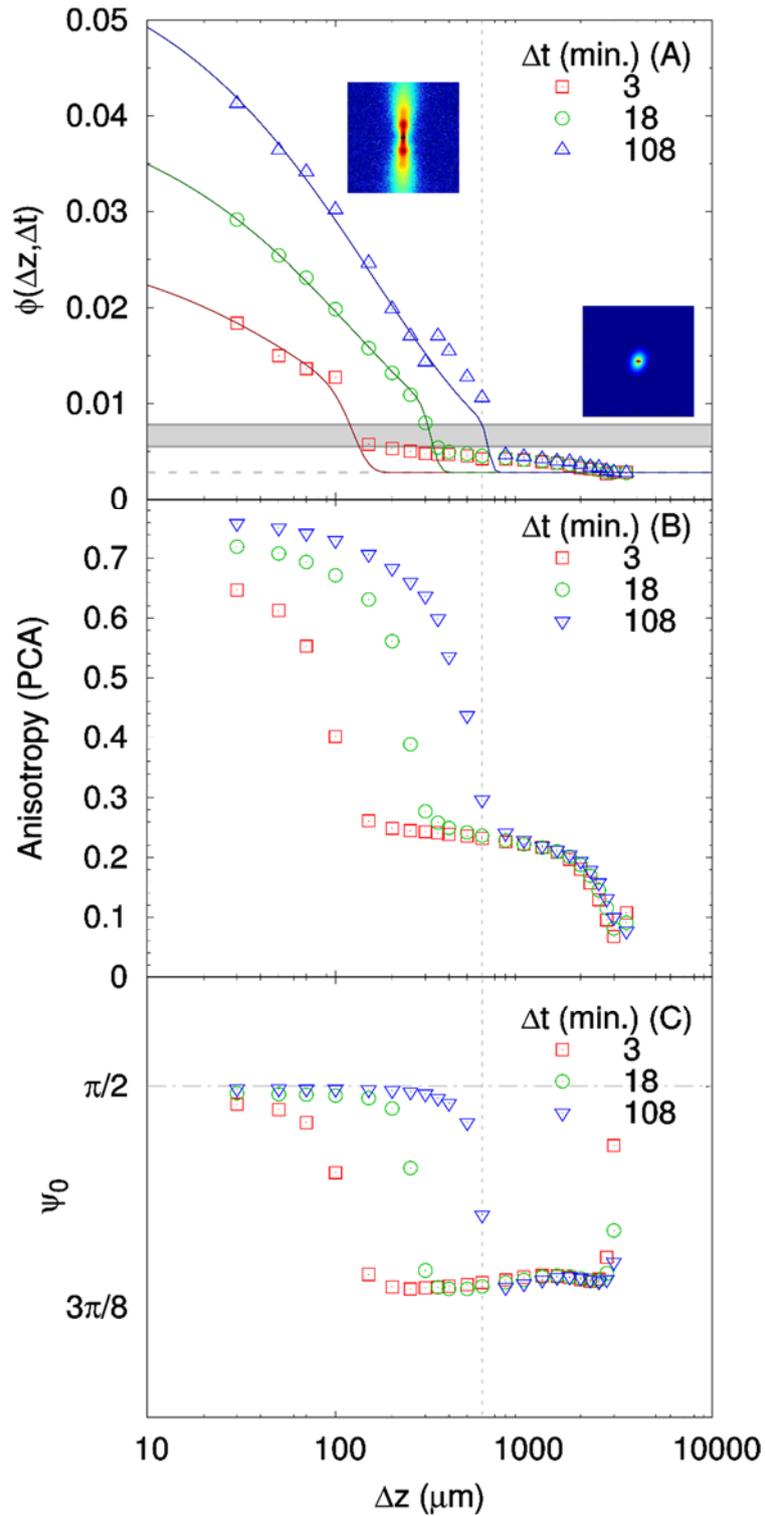
341 Finally, m and N are the width parameter and normalization factor of the ODF, respectively.
 342 Selected fit curves are shown in Figure 6. Note that Equation 6 is valid only when the ODF
 343 maximum is centered at $\pi/2$. Nevertheless, curve pairs at $(\psi_0, \psi_0 - \pi/2)$ were treated as $(\pi/2, 0)$ in
 344 order to be fitted.

345 The platelet concentration profile at different time steps during filtration is reported in Figure
 346 7A, as a function of the distance from the membrane. A very fast increase in volume fraction
 347 was detected already after 3 min of filtration. At each time step, $\phi(\Delta z)$ behavior exhibits two
 348 distinct regimes. Far from the membrane, ϕ is slowly increasing as Δz decreases. Then, when
 349 the concentrations reach the gel transition value, there is a sharp jump in ϕ . In this region,
 350 presumably describing the thick deposit, the concentration smoothly increases as much as Δz
 351 approaches 0. The concentration profile within this concentrated layer has been described by a
 352 heuristic stretched exponential decay:

$$353 \quad \phi(\Delta z, \Delta t) = \phi_0 + \phi(0, \Delta t) e^{-\left[\frac{\Delta z}{\zeta_b(\Delta t)}\right]^\omega} \quad (7)$$

354 where $\zeta_b(\Delta t)$ is the time-dependent characteristic length of the decay (Supporting Information
 355 Table S1) and $\phi(0, \Delta t)$ is the time-dependent colloidal volume fraction at $\Delta z = 0$. At each Δt the
 356 stretching factor was $\omega = 0.64$. In Figure 7A, the transition between the two regimes has been
 357 simulated by a using a smooth step-function, but just as a guide for the eyes. The fits shown in
 358 Figure 7A were performed using $\zeta_b(\Delta t)$, $\phi(0, \Delta t)$ and ω as free parameters, in analogy with
 359 Equation 1, where ω is a global parameter which remain constant at every Δz .

360 Anisotropy parameters and maximum scattering direction, ψ_0 , calculated via PCA are shown
 361 in Figures 7B and 7C. The strong link between concentration and orientation is qualitatively
 362 very similar to the one observed for CNC. Also in this case, the edge of the CPL is well-
 363 described by the upturn of orientation degree and angle. In contrast, now the edge is clearly
 364 visible even in the concentration profile region related to the sol/gel transition.



365

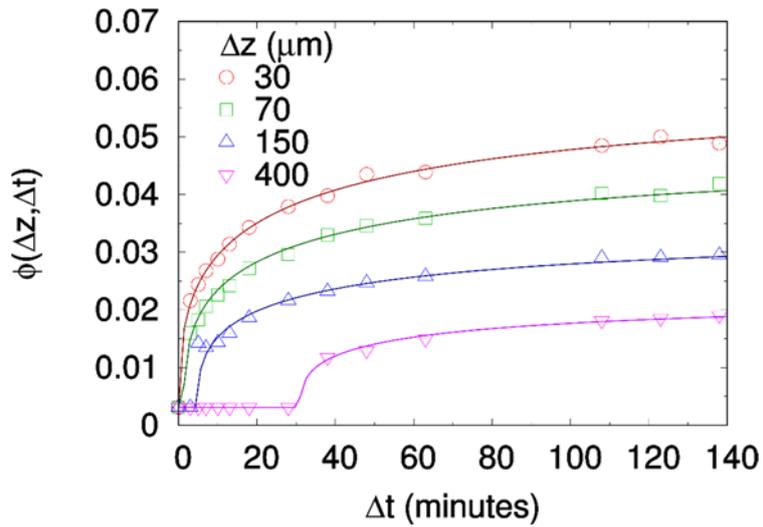
366 **Figure 7:** Concentration (A), anisotropy (B) and maximum scattering direction (C) profiles of the
 367 growing beidellite deposit as a function of Δz at different time steps. Solid lines in panel (A) refer to the
 368 fitting performed with Eq. 7. The two-dimensional scattering patterns in (A) corresponds to $\Delta t = 18$ min
 369 at $\Delta z = 50$ (right) and $2500 \mu\text{m}$ (left). The vertical dotted line highlights the coupling between
 370 concentration and anisotropy and marks the edge of the deposit. The horizontal band marks the
 371 concentration of the sol-gel transition.²²

372 Anisotropy and orientation angles are defined also in the bulk region close to the deposit.
 373 Such values correspond to the average orientation of platelets flowing in the retentate.²⁵
 374 Compared to CNC, ψ_0 is stabilized at $\pi/2$ rad since the first stages of filtration. This is most
 375 likely due to the much higher aspect ratio of the beidellite platelets when compared to the
 376 cellulose rods.

377 Plotting the concentration profiles, $\phi(\Delta z, \Delta t)$, as a function of time (Fig. 8) results once again
 378 in an exponential increase:

$$379 \quad \phi(\Delta z, \Delta t) = \phi_0 + \phi^\infty(\Delta z) \left\{ 1 - e^{-\left[\frac{(\Delta t - t_0)}{\tau_b(\Delta z)}\right]^\beta} \right\} \quad (8)$$

380 where $\tau_b(\Delta z)$ is the characteristic time of the exponential increase and $\beta = 0.42$ is the exponential
 381 stretching factor. These fittings allowed to extract the values $\phi^\infty(\Delta z)$, $\tau_b(\Delta z)$ and $t_0(\Delta z)$ values
 382 for the beidellite CPL. β is a global parameter which remain constant at every Δt .

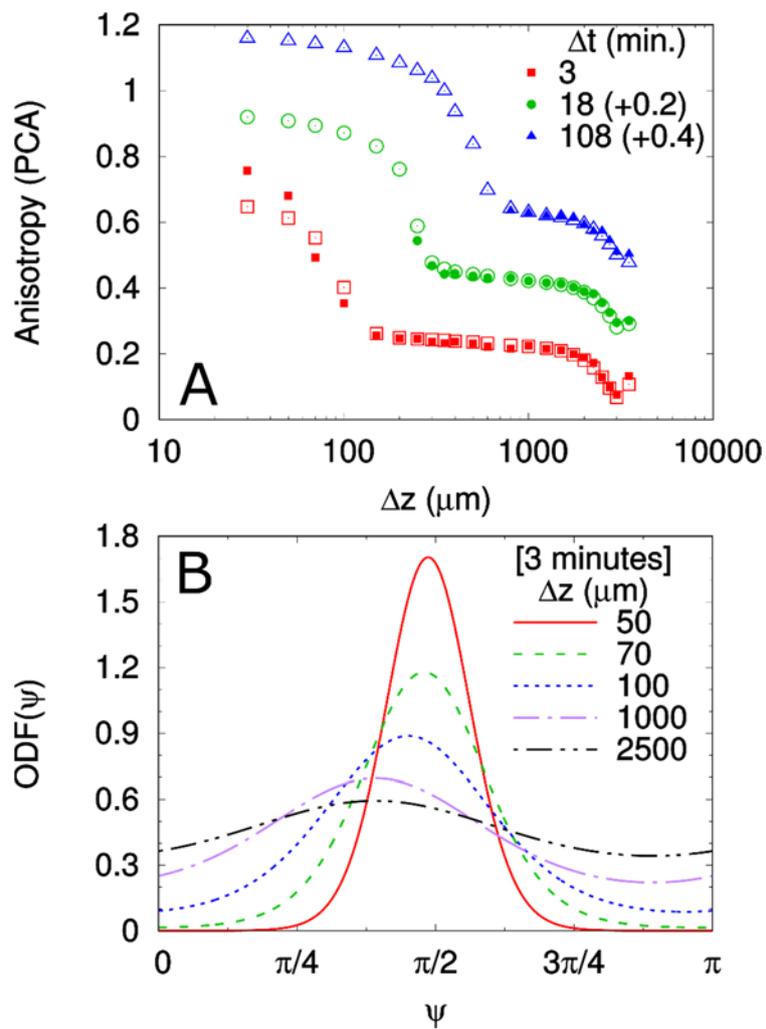


383
 384 **Figure 8:** Concentration profiles of the growing beidellite deposit as a function of Δt at different
 385 distances from the membrane. Solid lines refer to the fitting performed with Eq. 8.
 386

387 Even if the PCA method for the determination of the anisotropy is a very powerful tool, it
 388 remains qualitative in terms of comparison among different systems. In fact, PCA results

389 depend on the chosen q -range, particle size and aspect ratio. Therefore, it was very interesting
 390 to observe how the partial curves of the ODF width, m , decrease as a function of Δz : specifically,
 391 $Anisotropy \propto \ln(m + 1)$ (Fig. 9A). The reason of this simple relationship was not investigated
 392 in the frame of this work. Nevertheless, it gives the opportunity of “mapping” anisotropy values
 393 to a quantitative ODF description, even when the scattering model of Equation 6 cannot be
 394 applied, as shown in Figure 9B.

395



396

397 **Figure 9:** Beidellite system: (A) Comparison between anisotropy values calculated via PCA (empty
 398 symbols) and the function $\alpha \ln(m + 1)$ from the Maier-Saupe ODF ($\alpha \approx 0.294$) (full symbols); (B) Plots
 399 of Anisotropy Maier-Saupe ODF as a function of ψ at $\Delta t = 3$ min and at different distances from the
 400 membrane.

401

402

Comparison between CNC and Beidellite Systems

403

In the previous sections, the concentration profiles of CNC and beidellite CPLs have been

404

reported and described by heuristic exponential functions in both space and time scale. Such

405

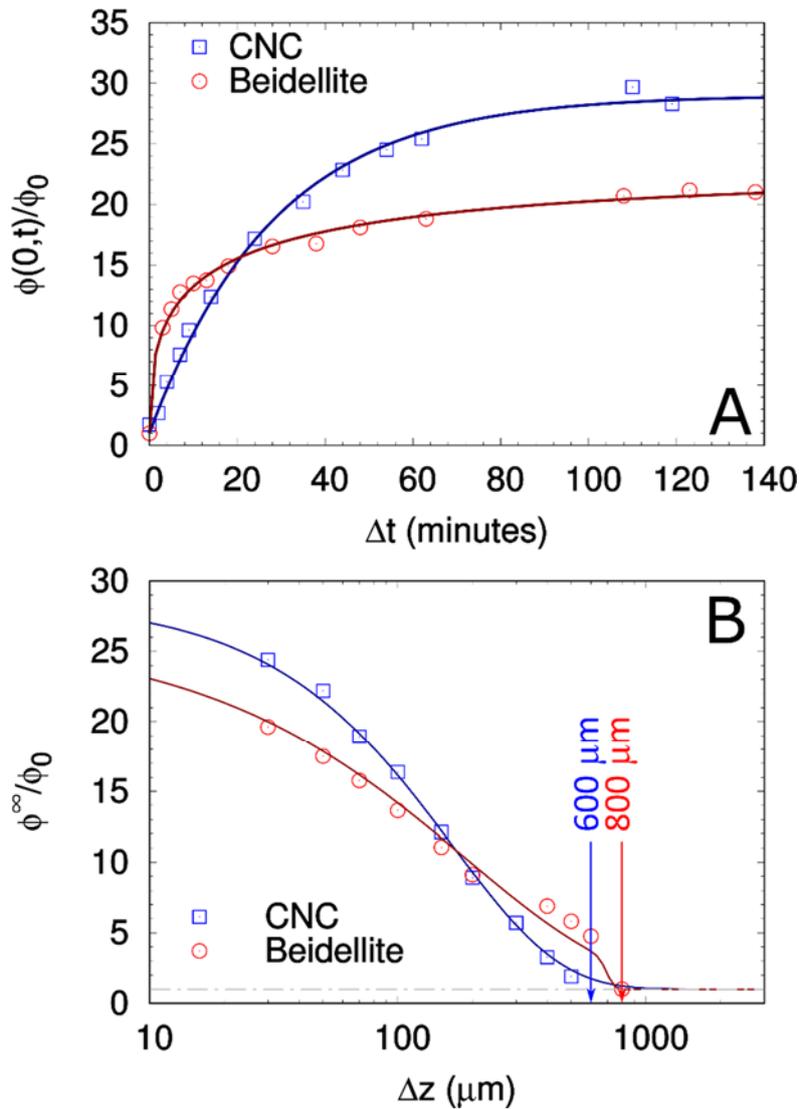
fittings allowed the extrapolation of curves of interest for cross-filtration processes, i.e. the

406

time-dependence of the colloidal concentration at the membrane, $\phi(0, \Delta t)$ (Fig. 10A), and the

407

concentration profile in the steady state, $\phi^\infty(\Delta z)$ (Fig. 10B).



408

409

Figure 10: (A) Normalized concentration profiles, extrapolated at $\Delta z = 0$, as a function of Δt . Data for

410

CNC and beidellite systems were obtained by fitting with Eqs. 1 and 7, respectively. Solid lines

411

correspond to fits in agreement with Eqs. 3 and 8. (B) Normalized concentration profiles, extrapolated

412

at $\Delta t \rightarrow \infty$ (steady state), as a function of Δz . Data for CNC and beidellite systems were obtained by fitting

413 with Equations 3 and 8, respectively. Solid lines correspond to fits in agreement with Equations 1 and
414 7.

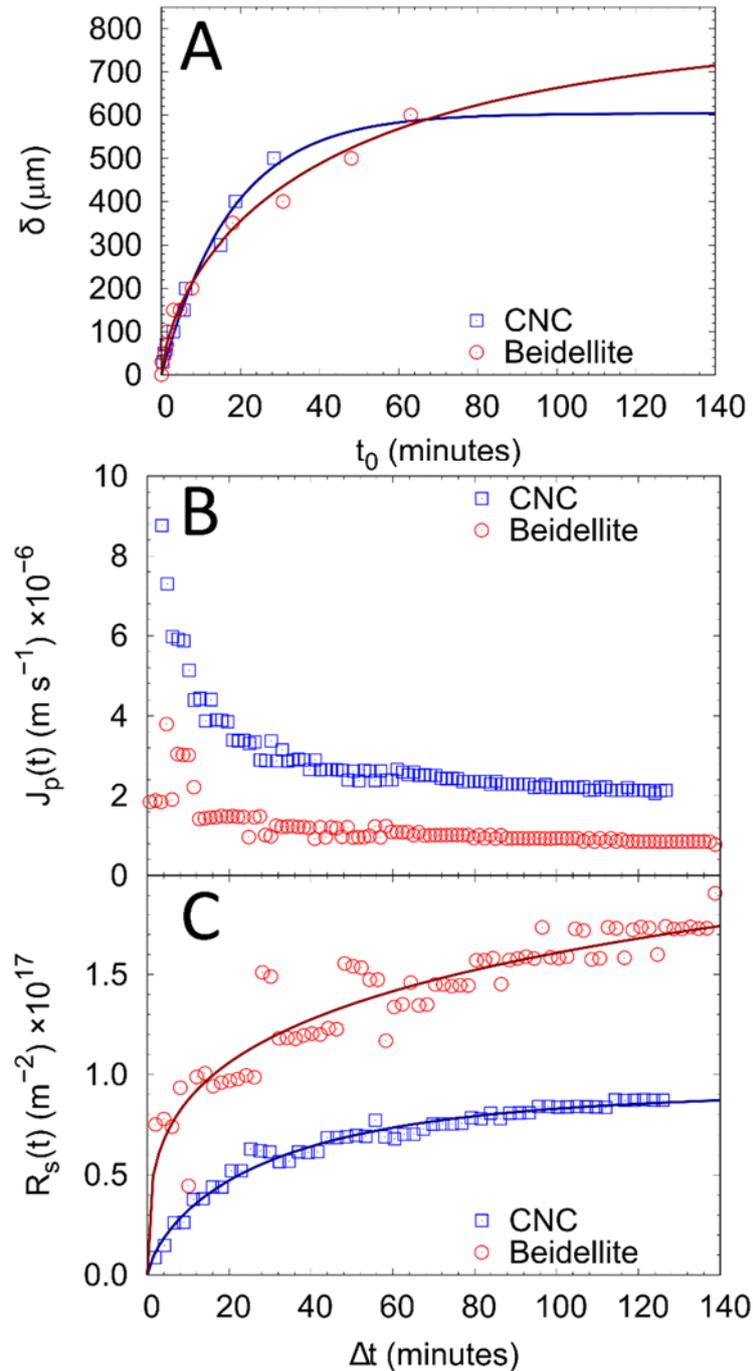
415

416 In Figure 10A, $\phi(0, \Delta t)$ data are normalized by the initial concentrations. Curves were fitted
417 using the same exponential functions in Equations 3 and 8 for CNC and beidellite systems,
418 consistently with all the profile configurations at any Δz . From this plot, one can observe that
419 beidellite concentration reaches half the asymptotic concentration within the first 6 minutes.
420 Then, during the following about 2 h of observation, it slowly converges to the asymptotic limit,
421 up to about 20 times the initial concentration. The CNC system instead shows a more
422 continuous increase, which is slower at the beginning but then rapidly converge to
423 concentrations about 30 times higher than the initial one.

424 The concentration profile in the steady state, $\phi^\infty(\Delta z)$, is displayed in Figure 10B. Equations
425 1 and 7 were used to fit such curves, once again in agreement with all the profile configurations
426 at any Δt . Beidellite concentration profile is flatter compared to the CNC one, simultaneously
427 exhibiting a thicker deposit but with lower relative concentrations close to the membrane. The
428 apparent discrepancies between the values $\phi^\infty(0)$ (steady state at the membrane position) are
429 just an artifact of the representation. In fact, in Figure 10A, the asymptotic value is not fully
430 reached, especially in the beidellite plot, whereas in Figure 10B, there is a significant difference
431 between 0 and 10 μm . The extrapolated $\phi^\infty(0)$ values are 0.10 and 0.06 for CNC and beidellite
432 systems, respectively.

433 Another interesting set of values is the lag time t_0 as a function of Δz . It provides the time series
434 of the positions at which the measured colloidal volume fraction starts increasing as compared
435 to the bulk concentration ϕ_0 (Figs. 5 and 8), i.e. the position of the upper boundary of the CPL.
436 Therefore, the time-dependent effective thickness of the deposit, $\delta(t)$, can be defined as the
437 inverse of function $\delta(t) \equiv [t_0(\Delta z)]^{-1}$. In Figure 11A, $\delta(t)$ values are reported alongside a tentative
438 extrapolation in the long time range. This was performed by applying Eqs. 3 and 8 for CNC

439 and beidellite deposits, respectively. In the case of CNC deposit, despite the absence of points
 440 after the first 30 minutes, the asymptotic limit of $\delta \approx 600 \mu\text{m}$ matches with the steady state
 441 concentration profile, $\phi^\infty(\Delta z)$ (Fig. 10B).



442

443 **Figure 11:** (A) Effective deposit thickness $\delta(t)$ as a function of time $t_0 \equiv \Delta t$. Solid lines for CNC and beidellite
 444 systems were obtained by fitting the curves with Equations 3 and 8, respectively. (B) Permeate flux for CNC
 445 and beidellite systems. (C) Specific resistance values as a function of time. Solid lines are just a guide for the
 446 eyes.

447 One can observe that in this case the limit thickness is achieved after about 30 min. Further
448 CNC cross-filtration does not significantly increase the size of the deposit layer, but strengthens
449 it in terms of both concentration and orientation degree (Fig. 3). On the other hand, the thickness
450 of the beidellite CPL exhibits a slower but persistent increase as a function of time. The fitted
451 curve matches the experimental data within the first 60 minutes (which is about the maximum
452 measured lag time t_0 , Figs. 5 and 8), so it is reasonable to extrapolate it toward the asymptotic
453 value of about $\delta \approx 800 \mu\text{m}$ (Fig. 9B). Hence, in contrast to CNC deposit, the beidellite layer
454 needed additional time ($\Delta t > 140 \text{ min}$) to reach steady state. Such a conclusion was not evident
455 during cross-flow filtration. Indeed, the observation of 2D scattering patterns and permeate
456 fluxes, $J_p(t)$, from both CNC and beidellite experiments showed very weak differences after
457 about 2 h of filtration, qualitatively indicating that the steady state was reached.

458 Another interesting point is that the permeate flux $J_p(t)$ of the CNC suspension is higher than
459 that of the beidellite suspension all along the filtration time (Fig. 11B), while the asymptotic
460 value of the thickness of the CNC deposit ($\delta \approx 600 \mu\text{m}$) is lower than the one of beidellite ($\delta \approx$
461 $800 \mu\text{m}$) (Fig. 10B). Furthermore, the equilibrium volume fraction at the membrane surface of
462 CNC suspension [$\phi^\infty(0) = 0.10$] is higher than the one of beidellite suspensions [$\phi^\infty(0) = 0.06$].
463 This means that a thinner deposit, even with a higher equilibrium volume fraction at the
464 membrane surface, can induce a higher permeate flux. This observation highlights the
465 complexity of the relationships between the permeation flux and the deposits properties
466 (thickness, equilibrium volume fraction, concentration profile). Hence, the permeability
467 property of the deposits is highly dependent of both the nature of filtered particles (their size,
468 shape, aspect ratio, colloidal interaction), and their structural organization inside the deposits
469 (orientation level, inter particle distance, porosity).

470 Some of these properties can be enclosed in a single time-dependent function such as the
471 specific resistance of the CPL, $R_s(t)$. It is the resistance parameters per thickness units and is
472 defined by the expression:²⁹

$$473 \quad J_p(t) = \frac{\Delta P}{\mu[R_m + \delta(t)R_s(t)]} \quad (9)$$

474 where ΔP is the applied transmembrane pressure, μ is the solvent viscosity and R_m is the
475 membrane resistance (respectively $R_m = 5.20 \cdot 10^{12} \text{ m}^{-1}$ and $R_m = 4.94 \cdot 10^{12} \text{ m}^{-1}$ during CNC and
476 beidellite experiments). As $\delta(t)$ can be extrapolated in the full time-range, the time-evolution of
477 the specific resistance can be simply calculated from the measured permeate flux (Fig. 11C).
478 These results describe the behavior of $R_s(t)$ in the first minutes after the application of pressure.
479 However, this simplified model does not consider the effect of osmotic pressure within the
480 deposit, which would decrease the effective pressure⁸ in Eq. 9. Nevertheless, a lower effective
481 pressure would result in a scaling factor, with negligible effects on the slopes of $R_s(t)$. Another
482 limitation is that $\delta(t)$ has been calculated at one x -position in the cell, while the measured
483 permeate flux is the averaged over their full extension of the membrane. However, all the other
484 pertinent physical quantities, such as concentration, orientation and colloidal shape, are
485 incorporated in the time-dependent specific resistances $R_s(t)$.

486 In conclusion, the effective functions of $J_p(t)$ not only depend on CPL thickness and particle
487 volume fraction, but parameters like the colloidal aspect-ratio and microstructure (anisotropy
488 degree and orientation angle with respect to the membrane surface of anisotropic colloids) have
489 to be considered. The calculated specific resistance well describes how the physics of these
490 systems is reflected in the filtration parameters. In particular, it is interesting to compare Figures
491 10A and 11C, as the specific resistance of the beidellite CPL is systematically higher than the
492 CNC system, whereas CNC cake exhibits a higher equilibrium volume fraction. Given that both
493 colloids are stabilized by repulsive electrostatic forces, it can be suggested that the shape and

494 orientation degree of these particles have a pivotal role in the trend and magnitude of the
495 specific resistance, i.e. on the permeate flux. In CNC fouling layers, despite the equilibrium
496 volume fraction of $\phi^\infty(0) = 0.10$, the equilibrium degree of orientation (anisotropy of about 0.5)
497 of these rod-like colloids allows water to pass through the CPL more easily than in beidellite
498 system. In this latter case instead, the clay platelets showed a lower volume fraction along with
499 a higher anisotropy degree, both resulting in a stronger specific resistance to water. From these
500 results, it can be proposed that, in these cases, the differences between the filtration parameters
501 (e.g. CPL thickness, permeate flux, specific resistance) are mainly ascribed to the shape and
502 aspect ratio of the charged-stabilized colloids, which in turn govern the two main features of
503 the microstructure: volume fraction and degree of orientation. Finally, differences in specific
504 resistance seems more linked to the orientation degree rather than to concentration, even though
505 these two parameters are in both cases strongly correlated. This also seems to be confirmed by
506 the fact that the beidellite system shows a strong degree of orientation in the first minutes as
507 compared to the CNC system, where the CPL does not show the same level of anisotropy even
508 at the final stage.

509

510 **Structural Organization of Dry Deposits at higher Length scales**

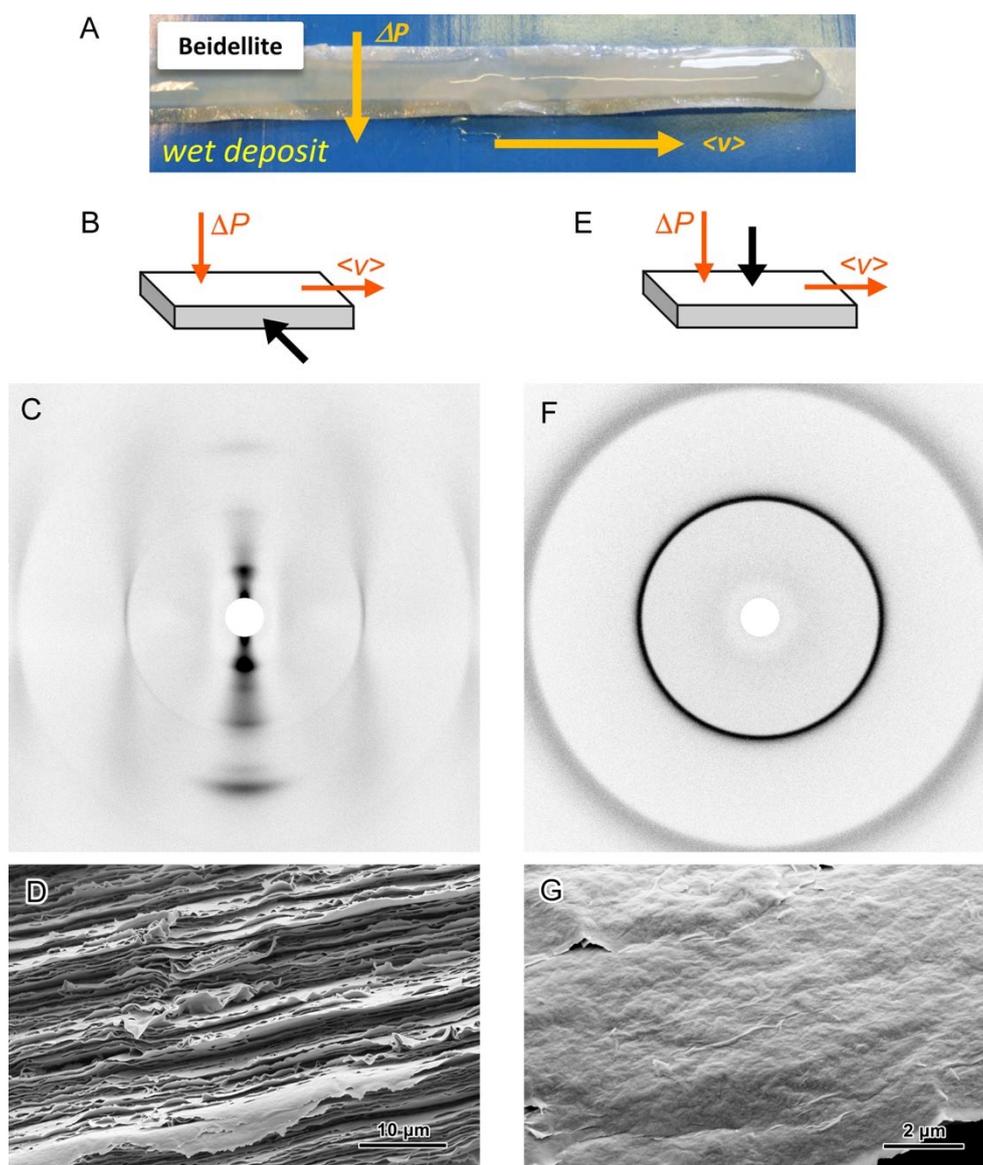
511 With the aim of understanding in more details the structural organization on a larger range
512 of lengthscales (from nano- to micrometer), additional ultrafiltration measurements have been
513 performed. One protocol has been developed in order to apply in a first step the same conditions
514 of cross-flow ultrafiltration as the one achieved during *in situ* SAXS measurements, follow by
515 a second step of dead-end filtration. The latter step was used to consolidate the structural
516 organization reached during this first step. Figures 12 and 13 show WAXD patterns and SEM
517 images of dry beidellite and CNC deposits, respectively. These *ex situ* techniques offer the
518 possibility to characterize the structural organization along directions parallel or orthogonal to

519 the film plane. While *in situ* SAXS experiments provided structural information in a parallel
520 geometry, that is in the *xz-plane*, orthogonal observations in the *xy-plane* allowed to access to
521 the structural organization along the velocity (*x*) and transmembrane pressure directions (*y*). In
522 the case of beidellite films analyzed in parallel geometry (Figs. 12B-D), the WAXD pattern
523 exhibit aligned narrow ark reflections, which reveals a strong orientation parallel to the flow
524 direction (Fig. 12C) and the corresponding SEM image show a well-defined layered structure
525 (Fig. 12D). In contrast, the orthogonal WAXD pattern contains rings (Fig. 12F) that, along with
526 the SEM image of one beidellite layer (Fig. 12G), correspond to an isotropic in-plane
527 orientation of the clay platelets. These observations confirmed that during the cross-flow
528 ultrafiltration, under the simultaneous effect of shear flow and transmembrane pressure,
529 beidellite platelets aligned in the direction of the flow and parallel to the membrane surface.
530 Particles are stacked along a direction perpendicular to the membrane surface, forming a well-
531 defined layered structure along the transmembrane pressure direction.

532 The case of dry CNC deposits is more complex as the WAXD patterns suggest a lower
533 degree of orientation of the particles (the description of the reflections in terms of a mixture of
534 two cellulose allomorphs, namely cellulose I and II, is provided in Supplementary Information
535 (Fig. S2). Indeed, a careful examination of the SEM images shows that the film is not
536 homogeneous and contains domains with different organizations. Figures 13D and 13H
537 correspond to a domain where the CNC are parallel to the flow direction and seem to form a
538 layered structure parallel to the membrane. In another region of the film (Figs. 13E and 13I),
539 the fracture surface reveals a layered texture with CNC arches that recalls the patterns observed
540 in chiral nematic arrangements of CNCs. Such an arched organization is observed when the
541 fracture plane is oblique with respect to the helicoidal axis of the cholesteric phase.^{29,31} The
542 WAXS patterns in Figure 13C and 13G are thus likely the superimposition of patterns from
543 highly oriented domains (yielding aligned narrow diffraction arks) and less oriented or chiral

544 nematic regions (yielding diffraction rings). In static conditions, CNCs undergo a phase
545 separation into a lower anisotropic phase and an upper isotropic phase providing that the volume
546 fraction exceeds the initial critical concentration ϕ_i of about 0.05. Above a second critical
547 volume fraction ϕ_a of about 0.09, a fully anisotropic chiral nematic phase is obtained, due to
548 the intrinsic chiral character of the rods. The presence of cholesteric domains in the dry deposits
549 is consistent with the high concentration reached upon drying that most probably becomes
550 higher than the second critical concentration. However, the presence of helicoids implies that
551 the nematic organization induced during cross-flow filtration was at least locally suppressed
552 during the dry deposit formation in the second consolidation step or upon pressure release,
553 leading to a relaxation of the organization from nematic to chiral nematic.

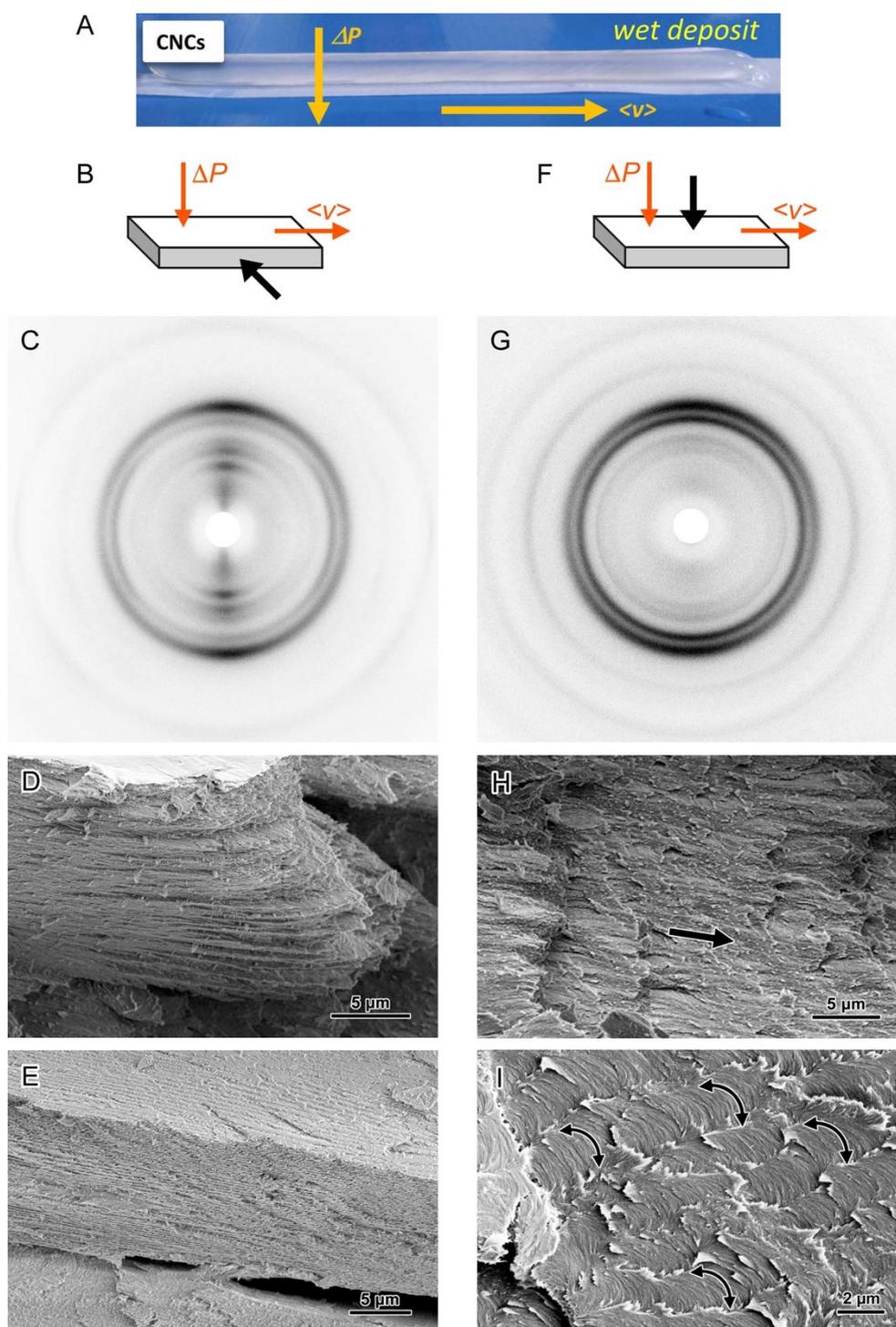
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556

557 **Figure 12:** A) Photograph of the beidellite wet deposit ($\phi_0 = 0.0031$, 10^{-4} M) obtained by 2 h of cross-
 558 flow ultrafiltration ($Q = 0.06$ L min^{-1} , $\Delta P = 1.1 \times 10^5$ Pa) followed by 18 h of dead-end ultrafiltration.
 559 Texture analyses of the dry deposit parallel (B-D) and perpendicular (E-G) to the plane of the film.
 560 B and E schematically describe the direction of observation (black arrows). C and F are the WAXD
 561 patterns of the film. D and G are SEM images of the deposit after a longitudinal fracture (D) of one
 562 beidellite layer seen in planar view (G).

563



564

565 **Figure 13:** A) Photograph of the CNC wet deposit ($\phi_0 \approx 0.0044$) obtained by 2 h of cross-flow
 566 ultrafiltration ($Q = 0.06 \text{ L min}^{-1}$ $\Delta P = 1.1 \times 10^5 \text{ Pa}$) followed by 22 h of dead-end ultrafiltration. Texture
 567 analyses of the dry deposit parallel (B-E) and perpendicular (F-I) to the plane of the film. B and E
 568 schematically describe the direction of observation (black arrows). C and G are the WAXD patterns of
 569 the film. D, E, F and I are SEM images of the deposit after a longitudinal fracture (D,E) or in planar
 570 view (H,I). The arrows indicate the orientation of the CNCs.

571 Conclusion

572 A SAXS study of the concentration polarization layer of either rod- or disk-like charge-
573 stabilized colloids was reported, presenting results in time- and space-scales which were not
574 previously accessible. The spatial resolution and minimal distance from the ultrafiltration
575 membrane of 30 μm , allowed to observe colloidal deposition within the first 2-4 min of the
576 filtration process. The rod-like cellulose nanocrystals system showed a remarkably regular and
577 continuous exponential increase of the colloidal concentration, as a function of both membrane-
578 distance and time. Beidellite clay disk-like particles exhibited a similar behavior, although
579 heuristic stretched-exponential functions had to be used in order to fit the data. Furthermore,
580 the formation of the beidellite concentration polarization layer is clearly affected by the sol-gel
581 transition. Despite these differences, both systems displayed a clear connection between
582 concentration and degree of orientation within the deposit. Both simple and stretched
583 exponential descriptions of concentration profiles were used to extrapolate other characteristics,
584 such as the concentration at the membrane ($\Delta z = 0$) as a function of time, the concentration
585 profile as a function of membrane distance in the steady state ($\Delta t \rightarrow \infty$) and the effective
586 thickness of the concentration polarization layer as a function of time. The latter was
587 successfully used to propose a very simple description of the time-dependence of the specific
588 resistances of both CNC and beidellite fouling cakes, which are directly calculated from the
589 rapid decay of the measured permeate fluxes, including the first few minutes of ultrafiltration.
590 The originality of the structural parameters acquired by the *in situ* SAXS measurements during
591 cross-flow ultrafiltration, allowed discussing in details the potential links between filtration
592 parameters (thickness, resistance and permeate flux) and physical features (colloidal volume
593 fraction, orientation, shape and aspect ratio). It opens up new perspectives in characterization
594 methods at the nanometer lengthscale to better understand the concentration polarization layers
595 phenomena. WAXD analyses and SEM observations of dried deposits obtained after cross-flow

596 followed by dead-end ultrafiltration, allowed to demonstrate that under ultrafiltration, the
597 nanosized platelets assembled into a well-defined layered ultrastructure over micrometer
598 distances. The chiral nematic organization of the CNC deposits have also been evidenced on
599 distances of few tens of micrometers. The characterizations presented in this work demonstrate
600 that ultrafiltration methods can be used to efficiently control the concentration polarization layer
601 of anisotropic nanoparticles, both in terms of both colloidal concentration and orientation which
602 could be extended up to a lengthscale of a few tens of micrometers.

603 **List of Symbols**

604	a :	Beidellite platelet thickness (m)
605	c :	Weight percent concentration
606	D :	Diffusion coefficient (m s^{-2})
607	d :	Interparticle distance (m^2)
608	q :	Scattering vector (m^{-1})
609	$F(q)$:	Scattering form factor (m^{-1})
610	$I(q)$:	Scattering intensity (m^{-1})
611	Jp :	Permeate flux (m s^{-1})
612	m :	Maier-Saupe orientation parameter
613	N :	Normalization factor
614	Q :	Cross-flow rate (L min^{-1})
615	R :	Beidellite platelet radius (m)
616	Rm :	Membrane resistance (m^{-1})
617	Rs :	Specific resistance (m^{-2})

618	$S(q)$:	Scattering structure factor
619	V :	Particle volume (m^3)
620	v :	Retentate velocity (m s^{-1})
621	β :	Stretching parameter (time-dependent concentration profile)
622	ΔP :	Transmembrane pressure (Pa)
623	Δz :	Distance from the membrane plane (m)
624	$\Delta\rho$:	Scattering contrast density (m^{-2})
625	δ :	Thickness of the concentration polarization layer (m)
626	ζ :	Characteristic length of the exponential decay (concentration profile) (m)
627	θ :	Polar angle in spherical coordinates
628	μ :	Solvent viscosity (Pa s)
629	τ :	Characteristic time of the exponential increase (concentration profile) (s)
630	ϕ :	Volume fraction
631	ϕ_0 :	Initial (retentate) volume fraction
632	ϕ^o :	Equilibrium volume fraction
633	φ :	Azimuthal angle in spherical coordinates
634	ψ :	Azimuthal scattering angle in the plane (CCD detector)
635	ω :	Stretching parameter (length-dependent concentration profile)
636		
637		
638		

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