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► To cite this version:

Candice Rey, Nicolas Hengl, Stéphane Baup, Mohamed Karrouch, Alain Dufresne, et al.. Velocity, stress and concentration fields revealed by micro-PIV and SAXS within concentration polarization layers during cross-flow ultrafiltration of colloidal Laponite clay suspensions. *Journal of Membrane Science*, 2019, 578, pp.69-84. 10.1016/j.memsci.2019.02.019 . hal-02048008

HAL Id: hal-02048008

<https://hal.science/hal-02048008v1>

Submitted on 22 Oct 2021

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1 **Velocity, stress and concentration fields revealed by micro-PIV and SAXS**
2 **within concentration polarization layers during cross-flow ultrafiltration of**
3 **colloidal Laponite clay suspensions.**

4
5 C. Rey^{1,2}, N. Hengl^{1*}, S. Baup¹, M. Karrouch¹, A. Dufresne², H. Djeridi³, R. Dattani⁴, F. Pignon^{1*}

6
7 ¹Univ. Grenoble Alpes, CNRS, Grenoble INP*, LRP, 38000 Grenoble, France

8 ²Univ. Grenoble Alpes, CNRS, Grenoble INP*, LGP2, 38000 Grenoble, France

9 ³Univ. Grenoble Alpes, CNRS, Grenoble INP*, LEGI, 38000 Grenoble, France

10 (* Institute of Engineering Univ. Grenoble Alpes)

11 ⁴ESRF, The European Synchrotron, CS 40220, 38043 Grenoble Cedex 9, France

12

13 **Abstract**

14 This study focuses on bringing a better understanding of the mechanisms involved in the formation of
15 the concentration polarization and fouling phenomena during the cross-flow ultrafiltration process of
16 colloidal Laponite clay suspensions. New cross-flow ultrafiltration cells were designed to perform
17 firstly time resolved *in-situ* small angle X-ray scattering (SAXS) and secondly time resolved *in-situ*
18 micro particle image velocimetry (micro-PIV) at the vicinity of the membrane surface during the
19 filtration. These two methods have allowed to access to the concentration profiles and the velocity
20 field as a function of the distance z from the membrane surface with respectively 20 μm and 30 μm
21 accuracy, within the concentration polarization layers. The results obtained show an increase of the
22 volume fraction related to a decrease of the velocity within the layers formed during the process. The
23 correlation of these results with the rheological behavior of the suspensions permitted to access to the
24 calculated stress field within the concentrated layers during the cross-flow ultrafiltration process.
25 Three different regions near the membrane surface have been emphasized with different shear
26 stress/shear rate behaviors. The important role of the rheological behavior and inter particle interaction
27 in the dynamic evolution in space and time of the accumulated layers has been highlighted.

28 *Corresponding authors at: CNRS, Univ. Grenoble Alpes, LRP, F-38000 Grenoble, France

29 Email addresses: frederic.pignon@univ-grenoble-alpes.fr (F. Pignon); nicolas.hengl@univ-grenoble-
30 alpes.fr (N. Hengl)

31 **Key words:** *cross-flow ultrafiltration, micro-PIV, velocity field, shear stress, concentration*
32 *polarization layer*

33

34 **1. INTRODUCTION**

35 Membrane separation processes are commonly used in several industrial applications, like bio and
36 agro industries, waste and water treatments, and more recently biorefinery. Ultrafiltration process
37 permits concentrating or separating colloidal suspensions, for several applications like food,
38 pharmaceuticals, cosmetics, chemical, nuclear, and automotive industries among others.

39 Although it presents numerous advantages, the stability of the crossflow ultrafiltration process is
40 governed by the increase of particle concentration at the membrane surface due to simultaneous effect
41 of the shear involved by the flow and the pressure forces generated by the transmembrane pressure
42 (TMP). These two external forces in competition with internal colloidal forces lead to the formation of
43 two phenomena named concentration polarization and fouling of the membrane, which decrease the
44 filtration performance [1-5]. [This phenomenon of concentration polarization layers was evidenced in](#)
45 [ultrafiltration processes as well as in others processes like microfiltration processes \[6\] reverse](#)
46 [osmosis \[7\] as well as direct contact membrane distillation systems \[8\] used for treating very high](#)
47 [salinity produced water. In ultrafiltration processes,](#) these concentrated layers have a thickness of tens
48 to few hundreds micrometers depending on the filtration conditions and the inter-particles interaction
49 within the filtrated suspension and can generate a decrease of the permeate flux of 50 %. Thus, it is of
50 primary interest to characterize the particles organization and interactions within these accumulated
51 layers (hundreds of micrometers thick) and to understand the mechanisms involved in the
52 concentration phenomena during the ultrafiltration process.

53 [Several previous works have investigated the formation of the concentrated layer during this filtration](#)
54 [process and showed an increase of the concentration near the membrane surface in relation with the](#)
55 [decrease of the permeation flux \[9-11\]. Some experimental investigations have probed the deposit](#)
56 [formation at different length scales by means of different approaches. Specific *in-situ* monitoring](#)
57 [techniques have been developed and have been reviewed by Chen et al. \[12\]. To understand the](#)
58 [mechanisms of cake formation and fouling mechanisms, some techniques are more dedicated to](#)
59 [characterize the particle deposition, thickness of deposit and cake layer formation. In a general way,](#)
60 [the whole of the characterization techniques used can be separated in two domains of length scales](#)
61 [probed: at micrometric and nanometric length scales.](#)

62 [Firstly, at micrometric length scales some optical non invasive methods like optical, confocal or](#)
63 [fluorescence microscopy, have been implemented by means of direct observation through or above the](#)

64 membrane to characterize the organization of the deposited particles [13-15]. The increase of the
65 concentration inside the concentration polarization layers has been optically investigated by
66 holographic interferometry [16] during a microfiltration process. This optical method has allowed
67 quantifying the increase of concentration in the vicinity of the microfiltration membrane before
68 reaching a “pseudo steady state” after 20 minutes of filtration. Others techniques like, nuclear
69 magnetic resonance (NMR) have been put in operation to investigate the phenomena during the
70 filtration of colloidal silica suspensions using a single tubular microfiltration membrane [17]. The
71 authors are able to reach the concentration polarization profile in the filtration device and show that
72 the axial component of the flow is driven by the shear induced cross-flow filtration. Another example
73 of concentration polarization investigation is reported by Donogh et al. [18] using two different non-
74 intrusive techniques for different filtration processes. The authors observed a similar phenomenon for
75 different pore sizes and a good match between literature value and measured value concerning the
76 thickness of the concentration polarization layer in each processes for radioactively labelled protein
77 suspensions. More recently, a new optical method using a laser sheet has been developed and
78 validated to characterize *in-situ* the cake formation in a narrow channel, to obtain the mechanisms of
79 cake growth and better understand the relationship between deposit structure and process performance
80 [19-21]. New microfluidic devices in poly-dimethyl siloxane have also been developed for dead-end
81 and cross-flow filtration, which allow direct observation of clogging dynamics in microchannels (20
82 μm) wide by micrometric particles (5 μm) [22-23]. The results allow distinguishing different clogging
83 behaviors according to filtration conditions and considering the different interaction (particle - particle
84 and particle - wall) colloidal interactions. At larger length scales, direct optical observation of the
85 surface of a single hollow fiber membrane have been performed during cross-flow filtration of
86 monodisperse polymer model particles with varying surface charge densities [24]. Some recent
87 measurement by fluid dynamic gauging have investigate *in-situ* the thickness and cohesive strength of
88 cake fouling layers formed during cross-flow microfiltration of a softwood kraft lignin model system
89 [25].

90

91 Secondly, at nanometer length scales, some *ex-situ* or *in-situ* scattering techniques, like small-angle
92 neutron scattering (SANS) as well as small angle x-ray scattering (SAXS) have been used to probe the
93 structural organization of colloids during the filtration processes. Thanks to the development of a
94 filtration cell dedicated to neutron scattering, *in-situ* SANS measurements have allowed monitoring
95 the *in-situ* development of the fouling layer inside the membrane pores [26]. The mechanisms of cake
96 collapse in dead-end filtration have been studied and elucidated by filtration of aqueous dispersions of
97 latex particles aggregated by CaCl_2 . *Ex-situ* SANS experiments on filtered cakes in different pressure
98 conditions have allowed to show that the mechanisms of cake collapse are made of very small relative

99 motions of the particles, which leave the local coordination of the latex particles unchanged but allow
100 large voids to be reduced [27]. In the same manner SANS and transmission electron microscopy have
101 been linked to determine the process by which the particles move and reorganize during cake collapse
102 [28]. Combination of static light scattering , SANS and local birefringence techniques have been used
103 to quantify the inner structure, structural orientation and organization of deposited colloid fouling
104 layers on the membrane surface during dead-end filtration of Laponite clay dispersions [29]. Some
105 developed dead-end filtration cells, simultaneously applying a transmembrane pressure and a magnetic
106 field have allowed to simultaneously characterize by SAXS, the structure of particle deposit during
107 ultrafiltration, manipulate the particle orientations and enhance the filtration performance [30]. On the
108 same principle custom made ultrafiltration dead-end cells have allowed get access to the *in-situ*
109 structural organization of casein micelle suspensions by SAXS and the corresponding spatial and
110 temporal *in situ* concentration profile evolution during dead-end filtration [31-32].

111 On the bases of these dead-end ultrafiltration cells, dedicated to SAXS measurements, some others
112 cross-flow ultrafiltration cells and ultrasound coupled cross-flow ultrafiltration cells have been
113 designed to perform *in-situ* SAXS. Thanks to these cells, concentration profiles and structural
114 organizations have been explored as a function of the distance z from the membrane surface, for
115 different colloidal systems, in different cross-flow filtration / ultrasound conditions [33-36].

116 Apart from these structural characterization of the deposited particles near the membrane surface,
117 some measurements or numerical modelling have been done to access to the velocity fields in
118 filtration processes [37-39]. Nevertheless some important information like the velocity field near and
119 inside the concentrated layer formed during crossflow ultrafiltration and the corresponding local shear
120 stresses are still missing to overcome the phenomena involved during the filtration. This knowledge is
121 necessary to develop the theoretical models and improve the understanding of stability of the
122 ultrafiltration process and the related mechanisms responsible of the concentration polarization
123 phenomena. The objective of this study is to use *in-situ* scattering techniques and develop micro-PIV
124 investigations to get access to concentration profiles, velocity fields and deduce the corresponding
125 calculated shear stresses inside the accumulated layer during membrane separation processes.

126 New cross-flow ultrafiltration cells were designed to perform firstly time resolved *in-situ* small angle
127 X-ray scattering (SAXS) and secondly time resolved *in-situ* micro particle image velocimetry (micro-
128 PIV) at the vicinity of the membrane surface during the filtration. The SAXS measurement performed
129 *in-situ* during ultrafiltration of Laponite clay suspensions allowed characterizing the structural
130 organization at the nanometer length scales and concentration profiles measured as a function of the
131 distance z from the membrane surface with 20 μm accuracy. These structural and concentration
132 information's have been linked to the permeate flux, cross-flow and transmembrane pressure registered
133 simultaneously. In the same manner, the micro-PIV measurements have allowed to establish the

134 velocity field evolutions and corresponding shear rate as a function of the distance z with $30\ \mu\text{m}$
135 accuracy, within the concentration polarization layers and during filtration time. These concentration
136 and shear rate evolutions in space and time, were then correlated to the rheological behavior of the
137 suspensions, in order to calculate the corresponding stress field evolutions within the concentration
138 polarization and fouling layer during the cross-flow ultrafiltration process.

139

140 **2. MATERIALS AND METHODS**

141 **2.1 Sample preparation**

142 The clay used in this study was Laponite XLG which comes from Laporte Industries. It is a synthetic
143 disk-shaped Laponite $30\ \text{nm}$ in diameter and $1\ \text{nm}$ in thickness. The particles have a density of $2.53\ \text{g}\cdot\text{cm}^{-3}$.
144 The suspension was prepared by mixing the Laponite powder with demineralized water at $20\ ^\circ\text{C}$
145 with a fixed ionic strength of $10^{-3}\ \text{M}$ NaCl and $\text{pH} = 10$, following the protocol used by Jin *et al.*
146 [34]. Suspensions to be filtered were prepared at a volume fraction of $1\ \text{vol}\%$. The suspension aged in
147 closed bottle during 12 to 26 days before the filtration experiments. As shown before the structure and
148 the rheological behavior evolves during the aging time and the value of the yield stress increases for
149 increasing aging time [33, 40-43]. Changes were observed in the viscoelastic properties and structural
150 characteristics of the gels over time. This is due, in part, to the osmotic swelling caused by repulsion
151 between the double layers and also to the progressive organization of the particles into fractal
152 aggregates over larger length scales as already studied in details [40]. Ruzicka and co-workers [42] are
153 able to identify the presence of two distinct arrested states. While repulsion is felt almost immediately
154 after samples are prepared, attraction, due to its anisotropic nature and to the presence of an effective
155 repulsive barrier, develops on a much longer time scale. More recently [43] this aging dynamics was
156 studied as a function of solid content, salt, concentration and pH, and discuss in term of the edge to
157 face or face to face contact between the particles. Consequently, to pass over this aging phenomena,
158 the time t_p that has elapsed between the end of the preparation and the different structural or filtration
159 investigations will always be indicated in the following. For the different kinds of measurements
160 (rheometric behavior, cross-flow ultrafiltration) the results will be compared at the same t_p time.

161 The interaction can be controlled by the addition of a peptizer which reduces the positive charges and
162 change the global charge of the particles to be repulsive. The peptizer used in the present study is the
163 tetrasodium diphosphate $\text{Na}_4\text{P}_2\text{O}_7$ (tspp) and has a molecular weight of $446\ \text{g}\cdot\text{mol}^{-1}$. The effect of the
164 peptizer on the rheological behavior and the structure has already been studied in previous works [34,
165 40]. The reduction of the interaction leads to a change in the rheological properties from yield stress
166 fluids to shear thinning fluids behavior with the addition of peptizer. Several suspensions were
167 prepared for the rheometric measurements denoted $L(i)\text{-Cp}(0\ \text{or}\ 6)$, with i corresponding to the volume

168 fraction content, and 0 or 6 corresponding to the C_p concentration in peptizer equal respectively to 0%
169 or 6% of the mass fraction of dry clay.

170 2.2 Rheometric measurements

171 Rheometric measurements were carried out using a shear rate controlled rheometer (ARG2, TA
172 Instrument) with a cone – plate geometry of 49 mm in diameter and with an angle of $4^{\circ}21'$ in the same
173 conditions as [34]. In order to avoid interfacial effect, the surface of the plate geometry has been
174 covered with sand paper with a roughness of 200 μm . Measurements were performed at a fixed
175 temperature of 25 ± 1 °C. An evaporation proof system has been added on the top of the geometry to
176 ensure the saturation of the atmosphere of the sample.

177 2.3 SAXS cross-flow filtration: cell and filtration procedure

178 A SAXS coupled to cross-flow filtration cell was designed to measure *in-situ* concentration profiles
179 and structural organization of the colloidal suspensions during the time of filtration (**Fig. 1 a, b**). This
180 information is obtained as a function of the distance z from the membrane surface. The cell was made
181 of transparent polycarbonate and the membrane was a flat sheet of polyethersulfone of (100 x 4) mm
182 (100 kD, Pleyade, Orelis environnement). The filtration cell is composed of two polycarbonate pieces
183 with a retentate channel for the upper part and the permeate channel for the lower part. The retentate
184 channel was 100 mm long in x cross-flow flow direction and the flow section was 7.4 mm z high for 4
185 mm y large. Three windows of observation were positioned at the entrance, the middle and the outlet
186 of the cell at 43 mm of each other. These windows had a dimension of (3 x 5.5 x 0.3) mm,
187 respectively, in width, height and thickness. The permeate channel was 100 mm long in x cross-flow
188 flow direction and the flow section was 10 mm z high for 4 mm y large. The membrane is strengthen
189 between these two upper and lower parts of the cell. The $z_c = 0$ position of the filtration cell,
190 correspond to the edge of the membrane in contact with the permeate lower part of the filtration cell.
191 During the filtration, the feed suspension was pumped (Mono pump LF series, Axflow) from a high
192 pressure tank (Millipore). Pressure was applied to the rig via purified compressed air and the retentate
193 pressure P was measured at the inlet and outlet of the cell with a pressure gauge (FP 110 FGP Sensors
194 & Instrument). Cross flow flux was continuously measured (Optiflux 6300C flowmeter, Krohne). The
195 permeate flux was recovered and weighed during the time with an accuracy of 0.001 g every 5 s
196 (balance Precisa 400 M). During the filtration the temperature was monitored by a cryo thermostat
197 (Thermo & Scientific SC, 150 A25, HAAKE) and fixed at 25 °C. Filtration procedure with several
198 steps was performed for the Laponite suspensions as described by **table 1** for each system. To
199 emphasize the phenomenon about the formation of the concentration layer during the ultrafiltration
200 process, only the last filtration step at $0.06 \text{ L}\cdot\text{min}^{-1}$ concerning these two kinds of suspension will be
201 presented in detail.

202

2.3.1 *In-situ* SAXS cross-flow filtration: conditions and analysis

203 SAXS experiments were performed at the European Synchrotron Radiation Facility (ESRF, Grenoble,
204 France), at the ID02 TRUSAXS beamline. The incident X rays beam had a wavelength of 0.1 nm and
205 was highly collimated with a corresponding Full Width at Half Maximum (FWHM) (20 μm (FWHM)
206 vertically and 400 μm (FWHM) horizontally) to reach a high spatial resolution in the vertical
207 direction. The sample-to-detector distances were fixed to 2 m and 10 m. The SAXS measurements
208 covered the following scattering vector range: $2 \cdot 10^{-2} \text{ nm}^{-1} \leq q \leq 2 \text{ nm}^{-1}$, $q = (4\pi/\lambda) \sin(\theta/2)$ and θ is the
209 scattering angle. The corresponding ($\lambda = 2\pi/q$) length scale range is $3.14 \text{ nm} \leq \lambda \leq 314 \text{ nm}$. The
210 filtration cell was mounted on motorized stages. A rotational stage was used to align the incident beam
211 parallel with the membrane surface. A vertical translation stage allowed moving the filtration cell in
212 front of the beam, in order to probe the structure at different vertical position. The incident beam
213 passed through the sample in the filtration cell and the two-dimensional scattered intensity patterns
214 were recorded on a high-resolution CCD detector (**Fig. 1 a, b**).

215 The analysis of the SAXS patterns registered in the cross-flow cell is the same which has already been
216 described in preceding works [33, 34]. Four different zones were defined by measuring the transmitted
217 X-ray signal as a function of the distance z_c through the SAXS cross flow filtration cell. The
218 description of these zones has allowed to define the minimal distance z_c above which the scattered
219 intensity is not influence by the X-ray beam partially crossing the polycarbonate permeate channel and
220 the membrane. The detection of this minimal z_c position for which the scattered intensity can be
221 properly registered (without influence of the polycarbonate permeate channel and the membrane) is
222 fixed at zero ($z_c = 0$). Thanks to a new design of the windows of observation and also with the use of
223 the angular motion stage, the minimal distance above this z_c position for obtaining exploitable SAXS
224 data was reduce to 20 μm . To clarify the location of the zero position corresponding to the edge of the
225 membrane surface, the description according to (Fig. 1 c) is the following: four areas are defined
226 depending on the vertical distance in the filtration cell. A first zone Z1 correspond to the permeate
227 channel in polycarbonate matter. The X- ray beam is totally absorbed in this region. A second area Z2
228 is defined as being the membrane since a transmitted signal is received. This means that the X- ray
229 beam starts to pass through the membrane, positioned onto the permeate channel. The signal increases
230 for increasing vertical distance. In the third area Z3 the signal received is provided by the sample but
231 is still affected by the membrane signal. This area measures a determined thickness depending on the
232 beam width, here 20 μm . When the scattering intensities received are constant, any influences from
233 the membrane are detected and the area Z4 corresponding to the measure area is configured. So this
234 area Z4 starts from 20 μm above the membrane surface in our experiments and the $z_c = 0$ position is
235 fixed at the bottom of the area Z3 (Fig. 1 c).

236 Scattering patterns were normalized to an absolute intensity scale after applying standard detector
237 corrections and then azimuthally averaged to obtain the one-dimensional intensity profiles denoted by
238 $I(q)$. Before the filtration experiments the cell was filled with demineralized water and the normalized
239 background scattering associated was systematically subtracted to the scattering of suspensions during
240 filtration experiments [33, 34].

241 An initial investigation of 5 suspensions of known volume fractions was performed in a flow through
242 capillary cell 2 mm in diameter. This step allowed establishing the calibration curve of the absolute
243 intensity as a function of the volume fraction. The results of the scattered intensity as a function of
244 volume fractions allowed us to define the following linear relationship $I(q = 0.6 \text{ nm}^{-1}) = 0.192 \phi_v$ [34].
245 This equation has been established in the linear zone of the scattered intensity (q^{-2} power law decay)
246 corresponding to the form factor of the dispersions, which indicates that it was not affected by the
247 increasing mutual particle interaction (described by the structure factor of the dispersions) and
248 therefore valid at high dispersion concentrations [33]. Indeed, the size of the Laponite clay is 30 nm in
249 diameter and 1 nm in thickness. This size corresponds to q range, which defines the form factor of the
250 scattering curve. This form factor does not vary with particle concentration. But at smaller q vectors,
251 (larger distances than the particle sizes) the aggregation phenomena could change the scattering
252 intensity as a function of the particle concentration (in a q vector range which is attributed to the
253 structure factor) [33]. To properly extract the concentration from the scattering intensity, the analysis
254 as to be done in the q range corresponding to the form factor, to determine the volume fraction as a
255 function of the distance from the membrane.

256 Then, with the obtained calibration curve, the volume fraction of any Laponite suspension could be
257 determined by introducing the corresponding absolute scattered intensity at a scattering vector $q = 0.6$
258 nm^{-1} . This method has already been used [33-36] to determine the evolution of the volume fraction of
259 the dispersions as a function of the distance z from the membrane. In other words, the concentration
260 profiles in the accumulated layers during filtration were determined by this method. The scattering
261 intensity for all the volume fractions reached within the concentrated particles layers at scattering
262 vector $q = 0.6 \text{ nm}^{-1}$ were in the q range where the scattering intensity is not affected by neither the
263 structure factor nor the possible anisotropy of the SAXS pattern, as already discussed in a precedent
264 work [33]. Following these results, *in-situ* SAXS measurements during Laponite clay suspensions
265 filtrations were performed.

266 **2.3.2 *In-situ velocity field measurements during cross-flow ultrafiltration process***

267 Some relevant precedent work have proposed a methodology to predict pressure and velocity field in
268 hollow fiber network of a filtration module [39]. The results were focalized on the effect of geometry
269 of the module and the membranes, the membrane permeability as well as the operating filtration

270 conditions. The effects of shear forces induced by crossflow velocities on ex situ dead end filtration
271 formed alginate fouling layer, were studied by crossflow experiments using multi slice multi echo
272 imaging (MSME). The flow velocity measurements were performed to gain more insight into the
273 hydrodynamics in the fouled membranes [39]. Nuclear magnetic resonance imaging (MRI) combined
274 with MSME flow velocity measurements allowed further characterization of alginate layer structure
275 and was used to elucidate the influence of Ca^{2+} on the fouling layer structure for alginate filtration
276 within ceramic hollow fiber membranes. However, until now not any direct *in-situ* measurements of
277 the flow field within the accumulated layers near the membrane surface during cross flow
278 ultrafiltration, have been reported. Consequently, in this goal, a new cell was designed using Plexiglas
279 (PMMA) to allow a complete visualization of the flow field along the feed channel. Micro-PIV
280 technique was used to quantify the velocity field near the membrane surface during the filtration of
281 Laponite suspensions. The dimensions of the feed channel were the same as for the cell used for
282 SAXS filtration coupled experiments, The retentate channel was 100 mm long in x cross-flow flow
283 direction and the flow section was 7.4 mm z high for 4 mm y large. The design of the cell allows
284 performing micro-PIV measurements all along the length of the channel in the cross-flow flow
285 directions (**Fig. 1d**). Then velocity profiles have been characterized in the same conditions and at the
286 same x positions as those used for SAXS experiments. Micro-PIV measurements were performed with
287 high-resolution camera synchronized with a pulsed laser. The laser used was a Nd:YAG pulsed with a
288 wavelength of 532 nm and a power of 50 mJ/pulses (New Wave Solo). A specific lens was used to
289 generate the thickness of the laser sheet depending on the flow and geometric characteristics. The
290 thickness of this laser sheet was 1 mm. The laser sheet has been positioned in the middle of the canal
291 in the y direction. Although the camera has a resolution of 2657 x 4000 pixels (Hisense 11M) with a
292 cadency of 15 Hz, a visualization area of 2657 x 2000 pixels was used to optimize the storage size of
293 the pictures. Polystyrene fluorescent particles 5 μm in diameter (microParticle GmBh), with an
294 absorbance and emission wavelength of 532 nm and 640 nm, respectively, were included in the
295 filtrated Laponite suspension. Fluorescent particles were used in order to inhibit reflection
296 phenomenon near the wall and surface membrane. The choice of tracers was the most suitable for our
297 experiments and the Stokes number was 8.6×10^{-4} . The concentration in polystyrene fluorescent
298 particles has been optimized to avoid any change in filtration performance or rheological behavior of
299 the Laponite suspensions, and simultaneously permit suitable signals detected by the camera to get
300 reliable correlation functions and velocity measurements.

301 The optical device was composed of a Canon 65 mm MPE lens linked to a filter (LaVision) with a
302 range of 545 to 800 nm. The device is parameterized in order to the field of view be focused in the
303 middle of the channel thickness in the y direction, corresponding to the laser sheet position. PIV
304 processing requires a careful selection of interrogation window size to take into account robustness
305 and accuracy for the calculation of the velocity especially in regions of high gradients. Adaptive PIV

306 approach leads to obtain the optimal local interrogation window size and shape based on flow
307 gradients and image quality. The interrogation window size is varied according to the local flow
308 gradient and the correlation value. Couples of images have been taken during the filtration time with a
309 time laps between the first and the second image of couples corresponding of 150 μs in average,
310 taking into account the order of magnitude of the velocity (about $0.06 \text{ m}\cdot\text{s}^{-1}$) to a particles
311 displacement of 8 pixels on average, according to literature about that parameter [38]. Taking into
312 account the order of magnitude of the velocity (about $0.06 \text{ m}\cdot\text{s}^{-1}$) the time lap chosen corresponds to
313 150 μs in average. This time must be small enough to obtain a valid measure of the velocity and a
314 certain length of displacement in the window of measure is required to quantify the velocity field. If
315 the time laps are too high, particles will not be detected by the software from one picture to the other,
316 and if the time laps are too small, the particles will not move enough and any displacement will be
317 detected.

318 Commercial software “DynamicStudio” (Dantec) was used to extract the mean velocity fields from the
319 recorded image frames. The processing principle is based on cross-correlation analysis of the particle-
320 image patterns in small sub-domains between two successive image frames. To convert the pixel space
321 into physical space, a calibration was performed using a specific target. Adaptive PIV processing
322 requires a careful selection of interrogation window size to take into account robustness and accuracy
323 for the calculation of the velocity especially in regions of high gradients. Adaptive PIV approach leads
324 to obtain the optimal local interrogation window size and shape based on flow gradients and image
325 quality. The interrogation window size is varied according to the local flow gradient and the
326 correlation value.

327 The number of image frames (200 pairs of images) allowed a good convergence for statistical values
328 of the velocity field. Due to high spatial-resolution of the camera, the measurements of the mean
329 velocity components allowed an accurate quantification of the velocity gradients and the strain rate
330 tensor each 30 μm of distance above the membrane surface. An example of velocity profile obtained
331 by this method is presented in **Fig. 1e**.

332

333 **3. RESULTS AND DISCUSSIONS**

334 **3.1 Rheometric measurements**

335 From rheometric measurements, the flow curves (viscosity and shear stress as a function of the shear
336 rate) are presented in **Figure 2** as a function of volume fraction and tspp content. The rheological
337 behavior of the Laponite suspensions without tspp from 1 vol% to 3 vol% exhibits a shear thinning

338 behavior: the viscosity decreases while the shear stress increases with an increasing shear rate. The
 339 yield stress behavior of the suspensions above a certain volume fraction is emphasis on (**Fig. 2b**) at
 340 low shear rates 0.1 s^{-1} , the stresses reach a plateau value corresponding to the yield stress of the
 341 suspensions. When the peptizer is added to the suspensions interparticular interactions are turned to
 342 globally repulsive via linking to positive charges on the surface of the particles [40]. As discussed
 343 before, the effect of this peptizer on the structure, rheological behavior, osmotic pressure and dead-end
 344 filtration performance of the Laponite dispersions have been studied in details in our precedent works
 345 [29, 33, 40]. The diphosphate anion binds the positive surface charge of the edges of the platelets. This
 346 has the consequence to reduce the strength of edge-face and edge-edge attractions between the
 347 particles. The result of this reduction in attractive forces between the particles is a partial disruption of
 348 the network. As a consequence, the yield stresses measured for the same volume fractions are reduced
 349 when the peptizer is added to the suspensions (**Fig. 2b**). For example, at 2 vol% the yield stress
 350 without peptizer (L2-Cp0) is equal to 105 Pa and with peptizer (L2-CP6) the yield stress is reduced to
 351 33 Pa (respectively open and closed square symbols in Fig 2b).

352 **3.2 Method for calculation of the shear stress profile within the accumulated layers,** 353 **during cross-flow ultrafiltration**

354 In the aim to calculate the stresses reach within the concentrated layers during the cross-flow
 355 ultrafiltration process, an analysis of the rheometric flow curves (**Fig. 2**) has been made. This will
 356 allow relating the shear rate to the shear stress by rheological laws. From the shear rate measured by
 357 micro-PIV within the concentrated layers during the cross-flow ultrafiltration process, these equations
 358 will allow to calculate the corresponding shear stress within the concentrated layers. The linear
 359 regression of the experimental rheometric data (**Fig. 2b**) gives power law (eq. 1) or Herschel-Buckley
 360 (eq. 2) laws depending on the volume fraction and peptizer content:

$$361 \quad \tau(\phi) = K(\phi) \cdot \dot{\gamma}^{n(\phi)} \quad (\text{eq. 1})$$

$$362 \quad \tau(\phi) = K(\phi) \cdot \dot{\gamma}^{n(\phi)} + \tau_s(\phi) \quad (\text{eq. 2})$$

363 Where ϕ is the volume fraction (vol%), $\tau(\phi)$ is the shear stress (Pa), $\dot{\gamma}$ the shear rate (s^{-1}), $K(\phi)$ is the
 364 consistency, $n(\phi)$ the shear thinning index, and $\tau_s(\phi)$ is the yield stress.

365 From the fitted laws, the expressions of K and n and τ_s as a function of the volume fraction are
 366 deduced (eq. 3 to 8).

367 For Laponite suspensions with peptizer, the expressions for K , n and $\tau_s(\phi)$ are the following:

$$368 \quad K(\phi) = 64318 \times \phi^{2.396} \quad (\text{eq. 3})$$

369
$$\mathbf{n}(\phi) = 500 \times \phi^2 - 30 \times \phi + 0.65 \quad (\text{eq. 4})$$

370
$$\tau_s(\phi) = 1.046 \times 10^6 \times \phi^{2.69} \quad (\text{eq. 5})$$

371 For Laponite suspensions without peptizer, the expressions for \mathbf{K} , \mathbf{n} and $\tau_s(\phi)$ are the following:

372
$$\mathbf{K}(\phi = 1) = 0.968 \quad (\text{eq. 6})$$

373
$$\mathbf{n}(\phi = 1) = 0.39 \quad (\text{eq. 7})$$

374
$$\tau_s = 1.592 \times 10^9 \times \phi^{4.27} \quad (\text{eq. 8})$$

375 From the velocity profiles ($\mathbf{V}(z)$) obtained by micro-PIV the following expression (eq. 9) gives access
376 to a calculation of the corresponding shear rate:

377
$$\dot{\gamma}(z) = \frac{dV}{dz} \quad (\text{eq. 9})$$

378 With z the distance from the membrane surface (m), and \mathbf{V} the measured velocity ($\text{m}\cdot\text{s}^{-1}$).

379 For each filtration condition during time and distance z from the membrane surface, it is then possible
380 to calculate the shear stress within the concentration polarization (eq. 10), thanks to the knowledge of
381 i) the value of the volume fraction measured by SAXS, ii) the value of the calculated shear rate
382 deduced from the micro-PIV (eq. 9) and iii) the rheological laws (ϕ) (eq. 3 to 8). It is important to
383 notice here that one assumption is made which consider that rheological behavior of concentration
384 polarization and gel layers of Laponite in the cross-flow experiment is equivalent to those of bulk
385 Laponite suspensions having same particle concentration. It will be difficult to verify this assumption
386 as any direct measurements with a specific probe, introduce in the flow, will modify the measuring
387 stresses.

388
$$\tau(\phi, z) = \mathbf{K}(\phi) \cdot \dot{\gamma}(z)^{\mathbf{n}(\phi)} + \tau_s(\phi, z) \quad (\text{eq. 10})$$

389 For Laponite suspensions without peptizer, the rheological behavior is shear thinning only for 1 vol%.
390 For higher volume fractions, the expression of the shear stress (eq. 10) can be replace only by the
391 expression of the yield stress corresponding to this kind of suspension, because $\mathbf{n}(\phi > 1) = 0$ and
392 $\dot{\gamma}(z)^{\mathbf{n}(\phi > 1)} = 0$. So for $\phi > 1$ vol%, (eq. 10) equals (eq. 8).

393 **3.3 *In-situ* Concentration profiles during cross-flow ultrafiltration: SAXS analysis,**
394 **relaxation phenomena and lowering of the membrane**

395 **a) SAXS Analysis.** To investigate the accumulation phenomena during cross-flow ultrafiltration,
396 different filtration condition steps have been explored. In a first step, under a transmembrane pressure
397 of 1.1×10^5 Pa a cross-flow of $0.3 \text{ L}\cdot\text{min}^{-1}$ has been applied and the structural organization and

398 concentration profiles deduced by SAXS have been recorded during time (**Fig. 3a**). In a second step,
399 under the same pressure conditions the cross-flow has been reduced to $0.06 \text{ L}\cdot\text{min}^{-1}$ in order to
400 emphasis the phenomena in a regime for which critical conditions (limiting flux) are reached as shown
401 previously in details in previous works [33]. The corresponding concentration profiles (**Fig. 3b**)
402 deduced from the SAXS measurements (**Fig. 3c and d**) show a continual increase in concentration as
403 a function of z and filtration time. On (**Fig. 3c**) are plotted the scattering intensities $I(q)$ as a function
404 of the q vector for different distances registered in-situ inside the crossflow ultrafiltration cell as a
405 function of distance z , at filtration time $t = 94 \text{ min}$ of step 2. This curve show the increase of the whole
406 scattering intensity curve at decreasing distances z toward the membrane in relation with the increase
407 of particle concentration. The corresponding Kratky plot representation ($q^2 \cdot I(q)$) is plotted in (**Fig.**
408 **3d**). Kratky plot is another way to represent scattered intensities, emphasizing the variation of
409 scattering intensities (slopes and local maximum) as a function of q vectors. Peaks can be observed at
410 a certain q_{max} wave vector which correspond to a maximum of scattering intensity. This q_{max} position
411 correspond to a mean inter-particle distance $d = 2\pi/q_{\text{max}}$ [29, 33] Fig. 3d show that the q_{max} position is
412 increasing at decreasing z distances which **emphasizes** the fact that inter-particle distances d decreases
413 as concentration increase toward the membrane surface.

414 **b) Lowering of the membrane.** In a third step, to explore the relaxation phenomenon during time and
415 the dynamic of the change in structural organization and concentration evolution, the cross-flow was
416 stopped and the pressure was released. In this arrested state, the SAXS measurements were
417 continuously registered as a function of the distance z_c and time (**Fig. 4 a**). Thanks to this relaxation
418 step, a specificity of our experimental setup was emphasized. In our experimental set-up the
419 membrane is not supported by any porous rigid media, which has induced an effect of lowering of the
420 membrane in the permeate channel due to the effect of transmembrane pressure. **Fig. 4 a** compares the
421 scattering intensities inside the accumulated layers just before and after the time when the cross-flow
422 was stopped and the pressure was released. A sudden jump in the scattering intensity in the upper
423 distances has been highlighted. This sudden increase of the corresponding calculated concentration
424 profile is due to the fact that without transmembrane pressure, the membrane has now the ability to de-
425 stress and recover its initial flat form, which allowed now to let appear in front of the beam from $z_c = 0$
426 position, the whole concentration profile from its surface. In this relaxed configuration the $z_c = 0$
427 position correspond to the distance z from the membrane surface as the membrane is not lowered
428 anymore. Many measurements on different samples have allowed checking this phenomenon of
429 lowering of the membrane under pressure and de-stress of the membrane when the transmembrane
430 pressure is released. All the measurements gives the same sudden change of the concentration profile
431 which is shift $350 \mu\text{m}$ above the $z_c = 0$ position. In order to take into account this lowering of the
432 membrane, all the results presented thereafter, under transmembrane pressure, will be plotted as a

433 function of the distance z from the membrane surface named z (μm) in the graphs, where $z = z_c + 350$
434 μm .

435 The consequence of this observation is twofold: firstly it has allowed us to evidence that the first
436 layers deposited near the membrane surface during filtration reach higher concentration levels and
437 better orientated states than initially detected (**Fig. 3**). Secondly, it has allowed us to define the
438 effective z distance from the membrane surface ($z = z_c + 350 \mu\text{m}$). In order to take into account this
439 lowering of the membrane, all the concentration profiles in the next figures were shifted by $350 \mu\text{m}$
440 from the measured z_c position. It is important to notice that this phenomenon of lowering of the
441 membrane has been emphasized also in micro-PIV measurements performed with an equivalent set-
442 up, so that the concentration profiles and the velocity profiles deduced by micro-PIV can be related
443 one to each other as they are finally registered in the same membrane position conditions.

444 **c) Description of the relaxation phenomena.** During the relaxation, the concentration profiles
445 evolves (**Fig. 4 a**) from a gradient of concentration with an exponential trend as a function of z ,
446 towards a flat concentration profile near the membrane surface on time scales of about half an hour.
447 This relaxation phenomena could be interpreted as a diffusion process of the concentrated particles
448 accumulated near the membrane surface (hundreds of micrometers) towards the lowest concentrated
449 layers in the upper part of the accumulated layers on distances of thousands of micrometers length
450 scale.

451 Regarding the scattering patterns evolutions (**Fig. 4 b**) at relaxation time $t = 2 \text{ min}$ the scattering
452 patterns are anisotropic near the membrane surface at $z = 20 \mu\text{m}$ and become more and more isotropic
453 at increasing distances z . This anisotropy of the scattering pattern is induced by a parallel orientation
454 of the particles along the membrane surface during the filtration under the effect of transmembrane
455 and shear flow forces as already described [33]. After cessation of flow and release of the pressure this
456 orientation slowly disappear, for example the scattering patterns at position $z = 20 \mu\text{m}$ becomes more
457 and more isotropic at relaxation times 9, 20 and 30 minutes. This decrease in anisotropy is also visible
458 as a function of distance z for a certain relaxation time. Finally, at relaxation time $t = 30 \text{ minutes}$, all
459 the scattering patterns are isotropic for each distance z , denoted a complete relaxation of the
460 orientations in relation with a flattening of the concentration profile. The concentration is almost the
461 same around 3 vol% from $z = 0$ to $1200 \mu\text{m}$.

462

463 **3.4 Concentration profiles deduced from *in-situ* SAXS,**

464 **Laponite suspension with peptizer:** After one step of filtration at $0.3 \text{ L}\cdot\text{min}^{-1}$ (step 1) during 80 min
465 **Fig 5 a** shows the results of accumulation during step 2 at a flow rate of $0.06 \text{ L}\cdot\text{min}^{-1}$, for a Laponite

466 suspension with peptizer (L1-Cp6). The volume fraction increases near 350 μm above the membrane
467 surface and by further distance from this reference at increasing filtration times. At the beginning of
468 this step 2, the volume fraction near 350 μm above the membrane is around 1.8 vol% (**Fig. 5 a**). After
469 94 min of filtration, the volume fraction reaches 5 vol% near the membrane and the thickness of the
470 concentrated layer formed during the process reaches 950 μm . The SAXS patterns show an increase of
471 the oval shape for closer distances from the membrane surface than for further distances. This non
472 circular shape in the vertical direction means that a horizontal orientation within the colloidal particles
473 aggregated at the membrane surface is induced by the increase of the concentration during the cross-
474 flow filtration. Above a distance of 1000 μm where no particles accumulation is detected, the SAXS
475 pattern shows a circular shape, meaning that there is no preferential orientation.

476 **Laponite suspension without peptizer:** After one step of filtration at 0.3 $\text{L}\cdot\text{min}^{-1}$ (step 1) during 70
477 min and then one step at 0.2 $\text{L}\cdot\text{min}^{-1}$ during 57 min (step 2), **Fig 5 b** shows the results of accumulation
478 during step 3, at a flow rate of 0.06 $\text{L}\cdot\text{min}^{-1}$, for the Laponite suspension without peptizer. The
479 concentrated layer is thicker and the volume fraction reaches a higher value than for Laponite without
480 peptizer. As for a suspension of Laponite with peptizer, the SAXS patterns after 81 min of filtration
481 (Fig. 5b) show an increase in the orientation for closer distances from the membrane surface during
482 the process. It is worth noting that the concentrated layer is thicker for the suspension without peptizer
483 due the ease of the particles to create aggregates. This observation confirms the role played by the
484 interparticular interactions and the rheological behavior in the build up of the concentrated layers.

485 3.5 Velocity field deduced from the *in-situ* micro-PIV

486 A first set of experiments was conducted to characterize the permeation flux evolutions as a function
487 of cross-flow conditions at increasing transmembrane pressures. The goal is to evaluate if the limiting
488 flux is reached or not. In this first experiment, a constant cross-flow is maintained and an increasing
489 transmembrane pressure was applied for the dispersions with and without peptizer. For each
490 transmembrane pressure applied, the permeation flux was recorded until reaching a steady state value
491 after an average value of 25 minutes. The steady state permeation flux J is plotted in **Figure 6** for the
492 different cross-flow conditions investigated in this article. For all these conditions the limiting flux is
493 reached for a higher permeation flux of about 6 $\text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ for the higher cross-flow conditions ($Q = 0.3$
494 $\text{L}\cdot\text{min}^{-1}$) compared to about 2.5 $\text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ for the lower cross-flow conditions ($Q = 0.06 \text{L}\cdot\text{min}^{-1}$). In the
495 following some measurements of the shear velocity field have been performed for all these cross-flow
496 conditions, and give the same features. In order to keep concise presentation, only the results at ($Q =$
497 $0.06 \text{L}\cdot\text{min}^{-1}$) are presented. The same phenomena are observed during the filtration step 1 with a flow
498 rate of $Q = 0.3 \text{L}\cdot\text{min}^{-1}$ for the Laponite suspension with peptizer, and the filtration step 1 and 2 for the
499 Laponite suspension without peptizer. The velocity profiles show the reduction of the velocity near the
500 membrane surface for increasing time of filtration and show the formation of the concentrated layers

501 during the time of filtration and as a function of the flow rate. Indeed, when the flow rate is decreased,
502 the velocity profiles show a higher area with any measurement of flow than for a high flow rate.

503 **Suspensions of Laponite with peptizer:** Because of previous filtration steps to highlight the effect of
504 the hydrodynamic condition on the formation of the concentrated layers, the velocity profile at the
505 beginning of the filtration step 2 at $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$, does not show any velocity at the surface of the
506 membrane and an area of no velocity of $700 \mu\text{m}$ above the membrane surface (**Fig. 7 a**). The
507 corresponding permeation flux measured in-situ (**Fig. 7 b**) continuously decreases and stabilizes
508 around $2.5 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^2$ at time $t = 22 \text{ min}$ until the end of the experiment. For increasing filtration times,
509 PIV results show an increasing thickness of the area of no velocity near the membrane surface. At the
510 end of this filtration step, any velocity is detected over a distance of about $900 \mu\text{m}$ above the
511 membrane instead of $700 \mu\text{m}$ at the beginning of this step. This is important to notice that the velocity
512 profile starts to stabilize since 90 minutes of filtration whereas 22 minutes are enough to show a
513 stabilization of the permeate flux. the stabilization of the upper flowing layers (from time $t = 22 \text{ min}$ to
514 $t = 140 \text{ min}$) will affect not to much the permeation flux as the corresponding changes in concentration
515 are lower than the one in the more concentrated stagnant layer. This emphasis the fact that the most
516 important resistance inducing a flux reduction is due to the stagnant concentrated layer near the
517 membrane surface. This result agrees with SAXS experiment results which show an increasing volume
518 fraction near the membrane surface for increasing filtration times. [We can conclude that the reduction](#)
519 [of the velocity is linked to the increase in volume fraction, which conduct to an arrested state of the](#)
520 [suspensions in the most concentrated layers near the membrane surface.](#)

521 **Suspensions of Laponite without peptizer:** in the same way, for the last filtration step3 with a low
522 flow rate of $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$ (**Fig. 7 c**) the same phenomenon is observed. The region of no velocity
523 has grown for increasing filtration times, even if the permeate flow J has reached a permanent state
524 (**Fig 7 d**). At the end of the filtration, a concentrated layer of $2100 \mu\text{m}$ (higher than the one reported
525 with t_{sp}) is formed at the membrane surface.

526

527 **3.6 Shear rate fields within accumulated layers during cross-flow ultrafiltration**

528 **Figures 8 a) and b)** show shear rate profiles calculated from velocity PIV measurements during the
529 time of filtration of a suspension of L1-Cp6 (**Fig. 8 a**) and for a suspension of Laponite without
530 peptizer L1-CP0 (**Fig. 8 b**) during, respectively, the step 2 and the step 3 of filtration at $0.06 \text{ L}\cdot\text{min}^{-1}$
531 flow rate, corresponding to a limiting flux previously described (**Tab. 1 and Fig. 6**).

532 These shear rate profiles exhibit three different evolutions as a function of the distance z from the
533 membrane surface. Firstly, a zero value corresponding to the area of no velocity near the membrane

534 surface is observed as shown in **Fig. 7**. Secondly, an increase in the shear rate as a function of z is
535 reported (Fig 8a and b) which corresponds to the increase in the velocity until reaching a maximum.
536 Thirdly a decrease in the shear rate until reaching a lower value corresponding to an area where the
537 velocity field reaches middle of the cell in z position is noted. For higher filtration times, the observed
538 phenomena are the same with a difference in the thickness of the area of no flow; a change in the
539 maximum value and position of the shear rate, which is in accordance with the fact that the
540 concentrated layer becomes thicker for increasing filtration times and decreasing flow rate, in
541 agreement with the previous SAXS and micro-PIV results.

542 For the suspension with peptizer, **Figure 8 a** shows a high shear rate of about 140 s^{-1} near $700 \mu\text{m}$
543 above the membrane surface at the beginning of the filtration step ($t=0 \text{ min}$), which corresponds to the
544 shear of the suspension at the initial filtered concentration ($\phi = 1 \text{ vol } \%$). Indeed, at $700 \mu\text{m}$ above the
545 membrane surface, fig. 5a shows for time $t = 0 \text{ min}$ of this filtration step, that the concentration is the
546 initial value of the suspension, which means that any increase in concentration is detected at this
547 distance on z direction. The shear properties of Laponite suspension correspond to a shear thinning
548 behavior with a shear thinning index $n = 0.4$ according to eq. 4. After 60 and 90 min filtration, the
549 maximum value of the shear rate decreases and is positioned at increasing z levels. This evolution is in
550 accordance with the formation of a higher concentrated and thicker layer during the filtration process
551 as shown in **Figures 5 and 7**.

552 For the suspension without peptizer, for the same filtration conditions the maximum of the shear rate
553 profile is positioned at higher z position ($1500 \mu\text{m}$ above the membrane surface) than with peptizer,
554 and the shear rate maximum value (60 s^{-1}) is lower than with peptizer. This is in accordance with the
555 fact that the filtration of the Laponite suspension without peptizer forms a thicker and more
556 concentrated layer than without peptizer, as shown in **Figures 5 b and 7 c**. Nevertheless, at increasing
557 filtration times the maximum value of the shear rate increases, contrary to the case with peptizer. This
558 emphasises a more complex phenomenon certainly related to the more complex thixotropic
559 rheological of the Laponite dispersions without peptizer. One way to better understand these
560 evolutions is to link the shear rate, velocity and concentration profiles to the rheological behavior of
561 the suspensions as a function of their volume fraction.

562 **3.7 Shear stress fields within accumulated layers during cross-flow ultrafiltration**

563 To understand the concentration polarization phenomena, we will take advantage of the combined
564 results obtained by SAXS and micro-PIV on the same suspensions in the same filtration procedures
565 which have allowed to get access to the velocity shear rate and concentration profiles as a function of
566 the distance z from the membrane surface. Combining all these results with the rheological behavior of
567 the suspensions, we had the opportunity to calculate the shear stresses inside the concentrated layers as

568 described in part 3.2 of this article. The only assumption made is that the rheological behavior of
569 concentration polarization and gel layers of Laponite in the cross-flow experiment is equivalent to
570 those determined by rheometric measurements for Laponite suspensions having the same particle
571 concentration.

572 **Figure 9 a** shows the shear stress profiles calculated for increasing filtration times as a function of the
573 distance z from the membrane surface of a Laponite suspension with peptizer during the last step 3 of
574 filtration at $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$. This result shows that the stress near $350 \mu\text{m}$ above the membrane
575 increases during the filtration time due to the formation of the concentrated layer. For the 3 different
576 times of filtration presented, the shear stress profile has the same behavior: a first area where the stress
577 value decreases in link with firstly the decrease in volume fraction at increasing z and secondly in link
578 with the area of no flow measured by micro-PIV (**Fig. 7 a**) and (**Fig. 8 a**). The values of shear stress
579 calculated for this area correspond to the yield stress value. **Figure 10 a** locate the calculated shear
580 stress in the concentrated layers during the filtration, on the shear stress/shear rate flow curve of the
581 suspension as a function of the volume fraction. The stresses reach in this decreasing part of the shear
582 stress (**Fig. 9a**) are located in the yield stress domain of the flow curve of the suspension. After this
583 first area of decreasing stress, the evolution of the shear stress profile reaches a plateau with a constant
584 value for increasing filtration times. In this area above $z = 1000 \mu\text{m}$, the volume fraction of the
585 suspension reaches the initial filtered suspension 1 vol% and the shear rate stabilizes towards its lower
586 value.

587 **Figure 9 b** shows the calculated shear stress profiles during the last filtration step3 for a suspension of
588 Laponite without peptizer. The shear stress profiles show the same behavior during the time of
589 filtration for L1-Cp0 suspensions and L1-Cp6 suspensions. Nevertheless, near the membrane surface,
590 the stress has a higher value than with peptizer (from 500 Pa to 8000 Pa depending on the filtration
591 time) and decreases until reaching a plateau at a constant value around 10 Pa, for the 3 different
592 filtration times. As previously seen for a suspension of Laponite with peptizer, the shear stress
593 measured near the membrane surface (before the plateau) corresponds to the stresses obtained when no
594 flow is measured by micro-PIV in the concentrated layer, and thus corresponds to the yield stresses.
595 **Figure10 b** shows the location of the stress calculated from the velocity profiles in the concentrated
596 layer, on shear stress/shear rate flow curve of the suspension without pepetizer as a function of the
597 volume fraction measured by rheometric measurements. It appears that the stress obtained for a
598 suspension of Laponite without peptizer has a higher value than for a suspension of Laponite with
599 peptizer in accordance with the change in the rheological behavior due to the modification in
600 interparticular interactions. Starting from the same volume fraction of 1 vol % and following the same
601 filtration procedure in the same conditions, the changes observed in the concentration, velocity and
602 stresses profiles in the concentrated layers for the suspensions with and without peptizer, are linked to

603 the change in the rheological behavior. One of the principal change in this behavior is the sol/gel
604 volume fraction transition. Without peptizer the sol/ gel transition is around 1 vol%, while with
605 peptizer, the sol/gel transition is between 1 and 2 vol%. This has a huge consequence on the way the
606 particles concentrate near the membrane surface submitted simultaneously to shear, pressure and
607 colloidal forces. Another interesting point is that as already shown in previous papers [33, 34] the
608 osmotic pressure of the Laponite suspensions with and without peptizer follows the same dependence
609 with the volume fraction, same equation of state. The differences emphasized in these results for the
610 suspensions with and without peptizer reinforce the precedent conclusions [33], namely that the
611 pertinent parameter which control the filtration performance is the hydrodynamic/rheological behavior
612 of the suspension and even though the osmotic pressure evolution is an important parameter of the
613 filtration, it is not the most important parameter in this kind of colloidal suspensions.

614 **3.8 Concentrated layers behavior: relationship with rheological behavior of the** 615 **suspensions**

616 In this section we will analyze the effect of the rheological behavior on the formation of the
617 concentrated layer and the influence on the hydrodynamic field, structural organization and the stress
618 field applied near the membrane surface. From the whole data and calculations obtained in this article,
619 **Figures 11 and 12** summarize and compare on the same figure the volume fraction (red empty circles
620 curve), calculated shear stress (black full circles curve) and calculated shear rate (blue full triangles
621 curve) as a function of the distance z from the membrane surface. For each suspension with peptizer
622 (**Fig. 11**) and without peptizer (**Fig. 12**) these profiles have been plotted for three different filtration
623 times, in the same cross-flow and transmembrane pressure conditions. The calculations have been
624 done from the SAXS and micro-PIV measurements performed mostly at the same filtration time. For
625 example for the results presented in Fig. 11, the calculations are done from the volume fractions
626 deduced from SAXS experiments (Fig. 5a) at filtration time ($t= 0$ min, $t = 59$ min and $t = 94$ min) and
627 the calculated shear rates and shear stress from the micro-PIV measurements (Fig. 7 a) at the related
628 filtration times ($t = 0$ min, $t= 60$ min, $t = 90$ min). *These two set of data from SAXS and micro- PIV
629 experiments are recorded at namely the same filtration times. The largest difference of recording times
630 between the SAXS and micro-PIV data is 5 minutes. As the phenomena of accumulations are slower:
631 the whole accumulation phenomena is on the order of 100 minutes, this small difference of 5 minutes
632 in recording times will negligibly affect the calculation of the shear stress. Consequently, the
633 conclusions on the whole concentration phenomena and trend of the calculated shear stress as a
634 function of z or filtration time, will not be affected by this difference of recording times.*

635 These combined results and calculations allow to highlight three different regions (A, B, C) from the
636 membrane surface to the feed channel, with different specific behaviors in terms of rheological and
637 filtration accumulation.

638 **Laponite suspensions with peptizer (L1-Cp6): Figures 11 a), b) and c)** exhibit the three different
639 regions (A, B, C) at different times of filtration, respectively $t = 0$ min, $t = 60$ min and $t = 90$ min. At
640 the beginning of step 2 of filtration at $Q = 0.06$ L.min⁻¹, the volume fraction is the same as the volume
641 fraction measured at the end of the previous filtration step 1 at $Q = 0.3$ L.min⁻¹, as shown in **Figures 3**
642 **a) and b).**

643 In the first region called A which extends up to $500\ \mu\text{m}$, the velocity and shear rate are close to zero,
644 corresponding to a suspension at rest. This means that the calculated stress, which corresponds to the
645 yield stress, is not high enough to give rise to a flow inside the concentrated layer. This region matches
646 with the fouling layer, with a decreasing stress while the volume fraction decreases, in agreement with
647 the rheometry measurements (**Fig. 10 a**). At the beginning of the second region called B, the shear rate
648 and corresponding calculated shear stress start to increase until reaching a maximum value of 7 Pa
649 when the shear rate maximum is about $135\ \text{s}^{-1}$. In this region B the shear flow forces are sufficiently
650 high, compare to colloidal interactions and pressure forces, to initiate the flow of the suspension. This
651 region B can be assimilated to the concentration polarization layer. The third region called C appears
652 when the shear rate starts to decrease until reaching a minimum value. In this region C, the volume
653 fraction is constant and equal to the initial volume fraction $1\ \text{vol}\%$, the shear rate decreases with the
654 corresponding shear stress until reaching the conditions where the suspension is circulating in the feed
655 channel. This region C is out of the concentration phenomena and corresponds to the flowing layer
656 above the concentration polarization layer (region B).

657 After 60 and 90 mins of filtration corresponding to **Figures 11 b) and c)**, the same phenomena are
658 observed but over a higher z distance range due to accumulation of particles. The values of the
659 calculated shear stresses near the membrane surface increases when increasing the volume fraction for
660 fixed distances depending on the filtration time. Near $350\ \mu\text{m}$ above the membrane surface, the stress
661 reaches 200 Pa after 60 min of filtration (**Fig. 11 b**) and 300 Pa after 90 min of filtration (**Fig. 11 c**) in
662 the fouling layer (region A). When the shear rate increases (region B), the required stress to involve a
663 flow is about 40 Pa at 60 min and 90 min of filtration. This critical stress value to initiate the flow has
664 the same value because this phenomenon appears when the volume fraction is between 1 and $2\ \text{vol}\%$,
665 corresponding to the sol/gel volume fraction transition for a suspension of Laponite with peptizer. The
666 value of the shear rate and shear stress far away from the membrane ($z = 2000\ \mu\text{m}$), are the same at
667 time $t = 60$ min and $t = 80$ min which shows that this region of the flowing suspensions is not
668 influenced anymore by the concentrated lower layers.

669 **Laponite suspensions without peptizer (L1-Cp0):** In the case of Laponite suspensions without
670 peptizer the three regions A, B and C are also well identified but extend on higher z distances from the
671 membrane surface (**Fig. 12 a**). In the first region A corresponding to the fouling layer, the calculated
672 stress decreases as a function of z as a consequence of the decrease in volume fraction, and the stress

673 corresponds to the yield stress of the suspensions. When the filtration time increases (**Fig. 12 b and 12**
674 **c**), the thickness of the fouling layer (region A) increases within higher values of shear stress due to
675 the increase of volume fraction during the time of filtration. The stress level can reach high values at
676 time $t = 80$ min of filtration, as high as 5000 Pa for a corresponding volume fraction of 20 vol% at $z =$
677 $350 \mu\text{m}$. It is interesting to underline that in this region A, the volume fraction decreases until reaching
678 the initial volume fraction of 1 vol% at $z = 1150 \mu\text{m}$ for filtration time $t = 35$ min (**Fig. 12 b**) and at $z =$
679 $1360 \mu\text{m}$ for filtration time $t = 80$ min (**Fig. 12 c**), then the stress becomes flat and corresponds to
680 the yield stress 5 Pa of the Laponite suspensions.

681 In the region B the maximum shear rate obtained in this concentration polarization layer is higher at
682 the end of the filtration than at the beginning (almost 80 s^{-1} instead of 60 s^{-1} at the beginning) because
683 the velocity profiles associated show more brutal changes for increasing filtration times. Indeed, the
684 thickness of the concentrated layer increases for increasing filtration times and the mean flow velocity
685 is more important for larger distances from the membrane surface. Therefore, during the time of
686 filtration when the particles leave the accumulated layer to be introduced in the flow, the velocity that
687 they will adopted will be more important on shorter distances during the time of filtration.

688 The change between region A and B is not only related to the static yield stress of the suspension but
689 also to the shear history of the suspension of this thixotropic system. Consequently, for the two
690 different filtration times the limit between these two regions A and B is pushed towards higher z
691 values, at increasing filtration times. At 0 min filtration time this limit is at $z = 1030 \mu\text{m}$ and shifts to $z =$
692 $1400 \mu\text{m}$ at $t = 35$ min until $z = 1700 \mu\text{m}$ at $t = 81$ min. It is then necessary to take into account the
693 complex relationships between the restructuring level of the Laponite suspensions and the stresses
694 applied by the upper flowing layers which are higher at increasing z distances.

695 Another interesting point is that in this region B, the maximum value of the shear rate reached without
696 peptizer, is lower than for a suspension of Laponite with peptizer, in agreement with the fact that for
697 the same volume fraction 1 vol%, the viscosity of the suspension without peptizer is higher than the
698 one with peptizer. The required stress to involve a flow at the interface between the fouling and the
699 concentration polarization layers is weaker for a Laponite suspension without peptizer than when the
700 peptizer is added. This is mostly explained by the difference of the sol/gel volume fraction transition
701 that depends on the presence of the peptizer. When the peptizer is mixed to the suspension, the sol/gel
702 volume fraction transition is higher than without peptizer and according to the rheometric
703 measurements, the yield stress is more important for increasing volume fractions.

704 These observations emphasize the fact that for the same filtration conditions, same cross-flow and
705 same transmembrane pressure, the stresses inside the concentration polarizations layers adjust their
706 values in order to find an equilibrium between the external forces imposed by the cross-flow (which

707 tend to disrupt the structure) and the resistance forces (which tend to build up the structure related to
708 internal forces of the suspension). In the particular case of this thixotropic colloidal suspension these
709 internal colloidal forces are a complex combination of the colloidal interaction between the particles,
710 the history of the previous shear and pressure forces applied, which could have disrupted the structure of
711 the suspensions and weaken the interparticle forces as a function of time. These time-dependent
712 evolutions (break-down and build-up) of the structure are highly dependent on the volume fraction of
713 the particles and also on the modification of the surface forces between the particles (with peptizer or
714 not) as already shown [33] Consequently during the filtration process, under a constant cross-flow and
715 transmembrane pressure, starting from an initial volume fraction, the final equilibrium concentration
716 polarization layer reached is the consequence of the way the particles (starting from a certain
717 structuring state) start to accumulate and concentrate during time. It has been previously shown that
718 the concentration of the particles within the accumulated layers follow an exponential trend as a
719 function of distance z from the membrane surface as well as a function of filtration time [34]. Each
720 layer of the Laponite suspension at each volume fraction has a certain "destructuring" or restructuring
721 time. It is then a complex combination of this restructuring time (at each sublayer with a given volume
722 fraction) in competition with the destructuring time imposed by the cross-flow, which at the end, result
723 in a certain stabilized concentration polarization layer. These time- and spatial-dependent phenomena
724 are well emphasized in **Figures 11 and 12**, for which in the same filtration conditions (cross-flow and
725 transmembrane pressure) the two different suspensions (with and without peptizer) in terms of
726 interparticle interactions and consequently rheological behavior, give rise to different equilibrium
727 concentration layers. Nevertheless, it is important to claim that the mechanisms involved for these two
728 different suspensions are the same with the existence of the three same behaviors associated to the
729 three regions A, B and C.

730

731 **CONCLUSIONS**

732 This work combines *in-situ* SAXS, *in-situ* micro-PIV and rheological measurement to bring a better
733 understanding of the time and spatial-dependent behavior of the concentrated layer near the membrane
734 surface during the ultrafiltration process of Laponite suspensions. The structural and kinematic
735 evolutions of the concentrated layers have been linked to the rheological behavior evolutions of the
736 filtered suspensions.

737 The results of SAXS experiments performed *in-situ* during the filtration process have allowed
738 highlighting the exponential increase of the volume fraction as a function of the distance z from the
739 membrane surface as well as a function of the filtration time. The obtained results revealed the
740 importance of the level and the type of electrostatic interactions between the particles in the

741 mechanism of formation of the concentrated layers. The Laponite suspensions without peptiser,
742 namely in attractive particle interactions, give rise at equilibrium to a thicker and more concentrated
743 layers than the suspensions with peptisant in repulsive particles interactions.

744 The original micro-PIV characterization performed within the accumulated layers during the crossflow
745 ultrafiltration of colloids allowed giving access to the velocity field as a function of the distance z
746 from the membrane surface. Thanks to rheometric measurements, the rheological behaviors were
747 investigated for each concentration reached in the accumulated layers and revealed by *in-situ* SAXS
748 experiments. The integration of the *in-situ* shear rate fields obtained from the velocity field by micro-
749 PIV into the rheological laws gives access to the calculated *in-situ* stress field of the concentrated
750 layers.

751 These measurements allowed revealing certain mechanisms of flow in link with the rheological
752 behavior evolutions of the suspensions, induced by the simultaneous effect of velocity and pressure at
753 the vicinity of the membrane surface during the filtration process. It thus was highlighted several
754 specific flow regions with well-identified behaviors. Firstly, a region A has been identified at the
755 nearest vicinity to the membrane surface, for which there is no velocity, corresponding to a suspension
756 at rest. Secondly a region B for which the shear rate and corresponding calculated shear stress start to
757 increase until reaching a maximum. In this region the shear flow forces are sufficiently high compare
758 to colloidal interactions and pressure forces, to initiate the flow of the suspension. This region B can
759 be assimilated as the concentration polarization layer. These two first regions A and B had a thickness
760 of about a few hundreds of micrometer. Their thickness evolves according to the time of filtration and
761 the operating conditions, the history of shear flow involved and the physico-chemical conditions of
762 the suspensions. This original information has led to the stress level required to involve a flow
763 between regions A and B during the filtration process and for different physico-chemical conditions of
764 the suspensions, which highlights the important role played by the rheological behavior in the
765 formation of the concentrated layers. Lastly, a third region C is defined in which the suspension
766 reaches the conditions where the suspension is circulating in the feed channel without being affected
767 by any concentration phenomenon. The concentration of the suspension is constant and corresponds to
768 the initial filtered concentration, with a decreasing shear rate until reaching the maximum velocity
769 value between 2000 and 2500 μm above the membrane towards the center of the cell.

770 From a fundamental point of view, obtaining the stress levels inside the concentrated layers, related to
771 the concentration profile, the cross-flow and the rheological behavior of the filtered suspensions,
772 improves the understanding of the phenomena involved in the formation of the concentrated layers and
773 fouling phenomena. From an industrial point of view, this work allows to improve the efficiency of
774 ultrafiltration since it gives a better understanding of the formation of these phenomena.

775

776 **ACKNOWLEDGEMENTS**

777 We would like to thank Theyencheri Narayanan and Michael Sztucki (ESRF, Grenoble) for their kind
778 help in scattering experiments and fruitful discussions, Jean-Jacques Lasserre (Dantec Dynamics) for
779 his help and productive discussions, William Chèvremont for his helps in stress calculations.
780 Mohamed Karrouch, Eric Faivre, H el ene Galliard, Didier Bl es es and Fr ed eric Hugenell (Laboratoire
781 Rh eologie et Proc ed es, Grenoble) and Jacques Gorini (ESRF, Grenoble) for technical assistance. We
782 gratefully acknowledge the ESRF for the SC 4177 beam time allocation. This work was supported by
783 the Labex TEC 21 (Investissements d'Avenir - grant agreement n o ANR-11-LABX-0030). LRP and
784 LGP2 are part of PolyNat Carnot Institut (Investissements d'Avenir - grant agreement no. ANR-11-
785 CARN-030-01) and of program (ANR-15-IDEX-02).

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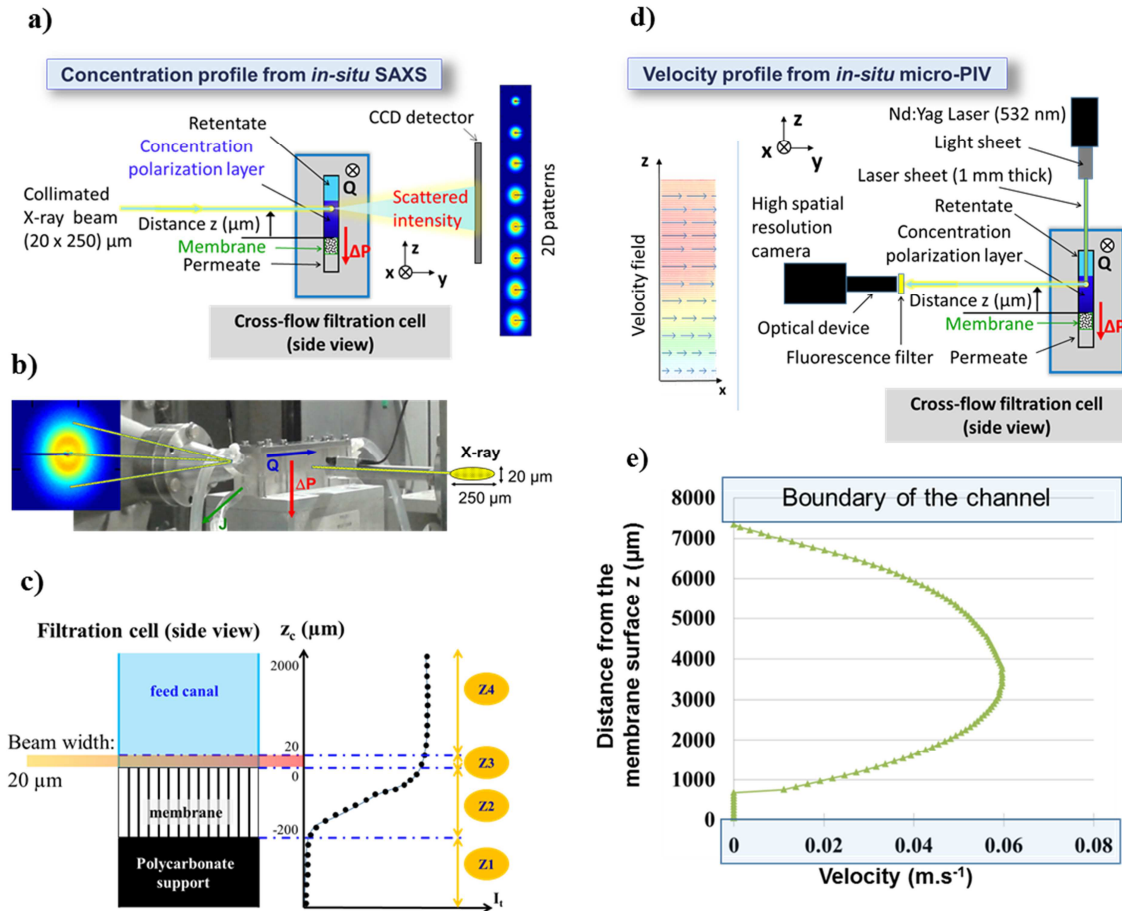
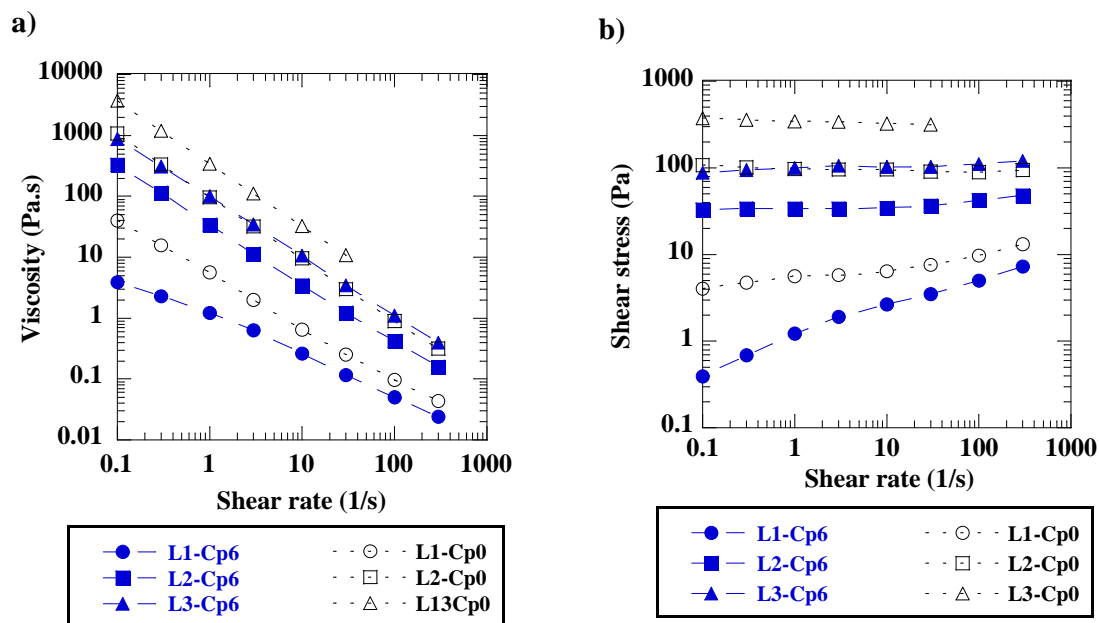


Fig. 1: Scheme of the *in-situ* a) b) and c) SAXS and d) micro-PIV measurements under cross-flow ultrafiltration process e) example of velocity profile inside the whole filtration channel for a laponite suspensions with peptizer, L1-Cp6, $t_p = 12$ days, $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$, $\text{TMP} = 1.1 \times 10^5 \text{ Pa}$, $T = 25 \text{ }^\circ\text{C}$.

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Fig. 2: Steady-state flow curves of Laponite dispersions (10^{-3} M NaCl, pH = 10) at different volume fractions and different peptizer concentrations. $T = 25 \pm 1$ °C, $t_p = 12$ days. a) viscosity and b) corresponding shear stress as a function of the imposed shear rate.

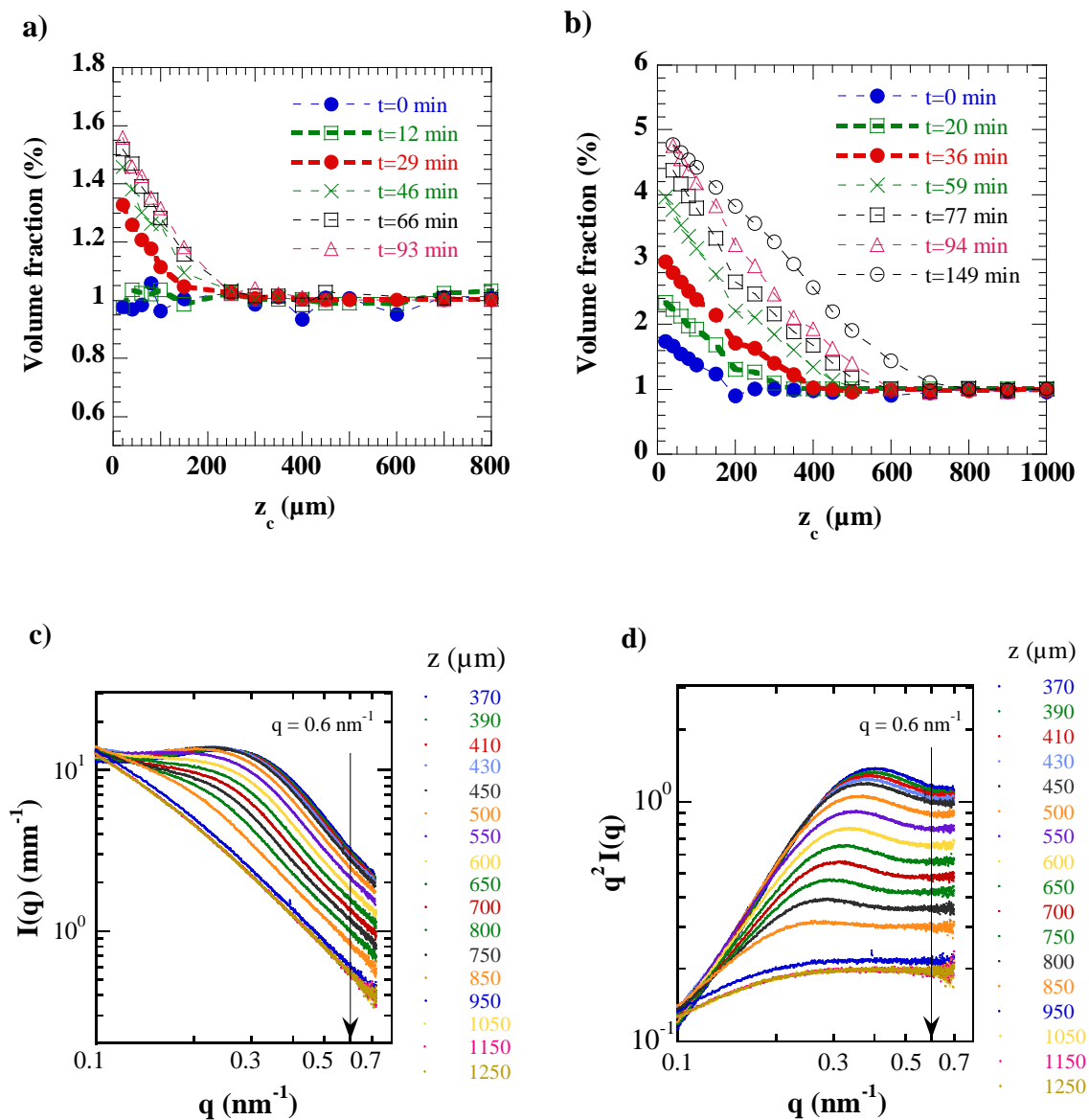


Fig. 3: Concentration profiles (volume fraction as a function of z_c) deduced from *in-situ* SAXS measurements in the middle window: during the cross-flow ultrafiltration of Laponite suspensions with 6% tspp, $t_p = 12$ days, $\text{TMP} = 1.1 \times 10^5$ Pa, $T = 25 \pm 1$ °C
 a) step 1 $Q = 0.3 \text{ L}\cdot\text{min}^{-1}$, b) step 2 $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$, c) corresponding scattering intensities $I(q)$ of the concentration profile (volume fraction as function $z = z_c + 350 \mu\text{m}$) at $t = 94$ min, 6% tspp and d) kratky plot representation ($q^2 I(q)$) of the scattering intensity (same profile).

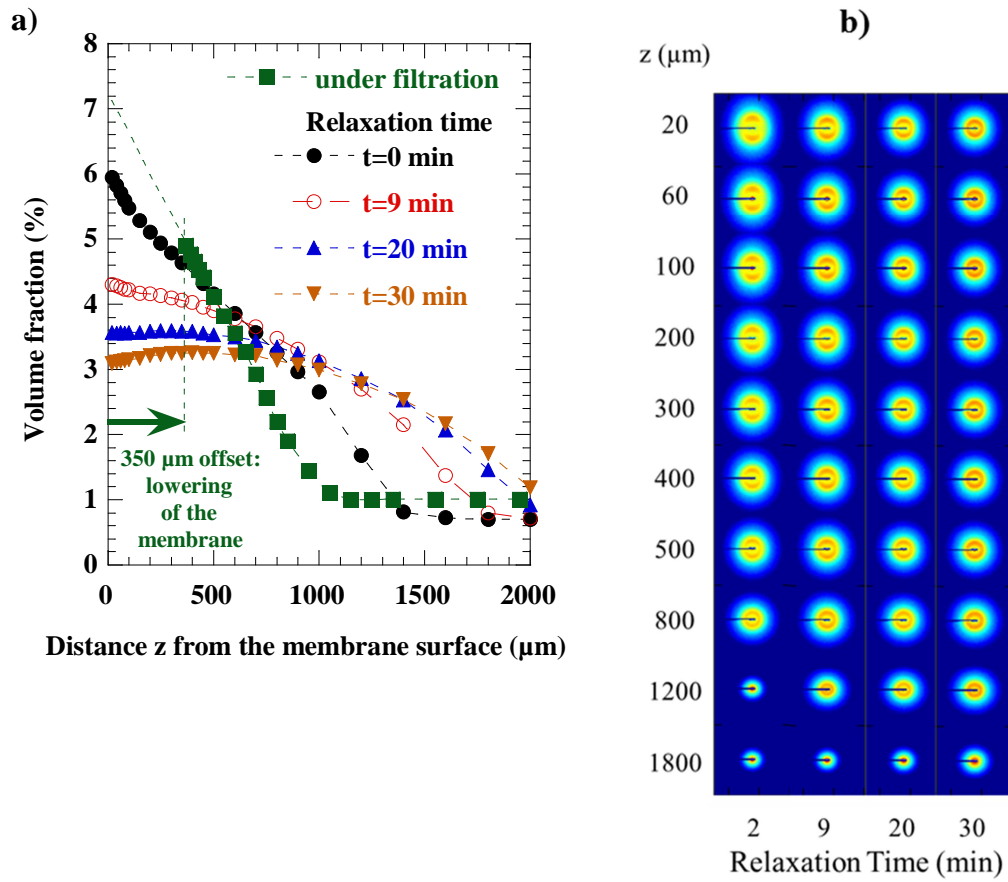


Fig. 4: a) Concentration profiles deduced from *in-situ* SAXS in the middle window during relaxation step (TMP = 0, $Q = 0$) of Laponite suspensions with 6% tspp, and b) corresponding 2D-SAXS patterns during relaxation. Sample distance = 2 m, $t_p = 12$ days, $T = 25 \pm 1$ °C.

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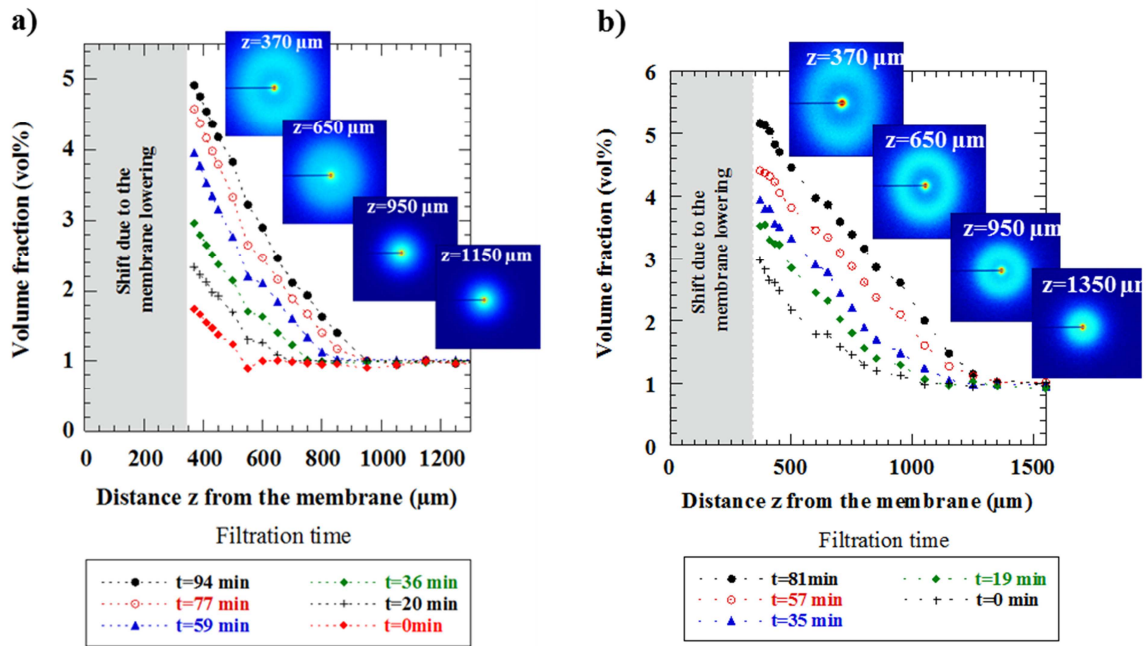
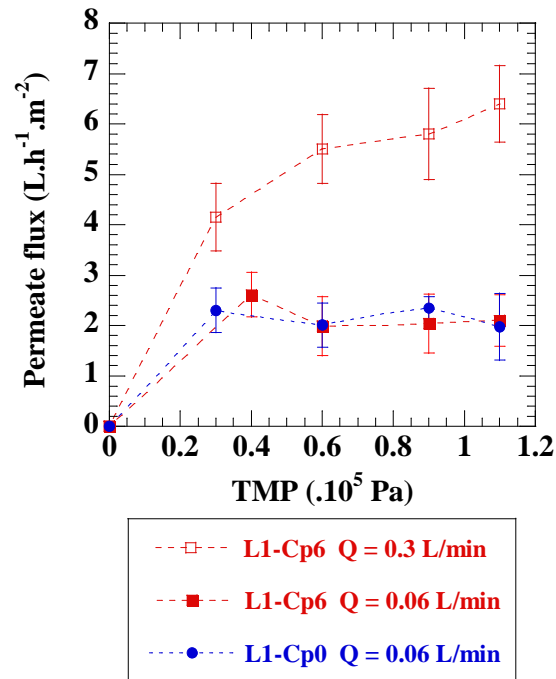


Fig. 5: Concentration profiles and SAXS pattern obtained by *in-situ* SAXS measurements in the middle window during the ultrafiltration process with lowering correction of a) Laponite suspensions with tspp (L1-Cp6) and b) Laponite suspensions without tspp (L1-Cp0). x position is the middle of the channel, $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$, $t_p = 12 \text{ days}$, $\text{TMP} = 1.1 \times 10^5 \text{ Pa}$, $T = 25 \pm 1 \text{ }^\circ\text{C}$.

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Fig. 6: Steady states J permeation flux as a function of transmembrane pressure conditions for different cross-flows measured during ultrafiltration of Laponite suspensions, $t_p = 12$ days, $T = 25 \pm 1$ °C.

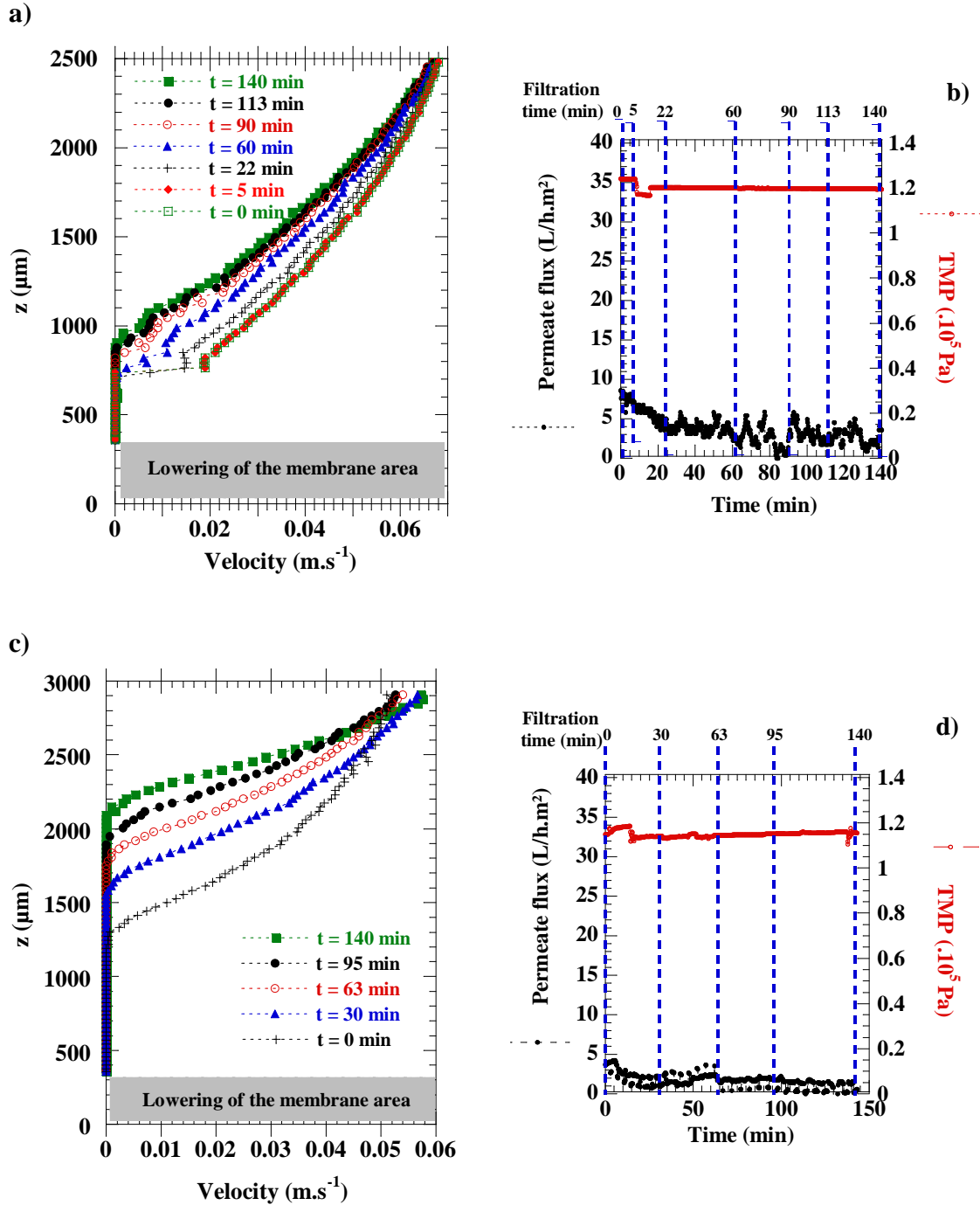


Fig. 7: Velocity profiles in the middle window and associated permeate flux for a Laponite suspension as a function of the distance z from the membrane surface (with lowering correction) during cross-flow ultrafiltration. a) and b) with peptizer (L1-Cp6), c) and d) without peptizer (L1-Cp0). x position is the middle of the channel, $t_p = 12$ days, $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$, $\text{TMP} = 1.1 \times 10^5 \text{ Pa}$, $T = 25 \pm 1 \text{ }^\circ\text{C}$.

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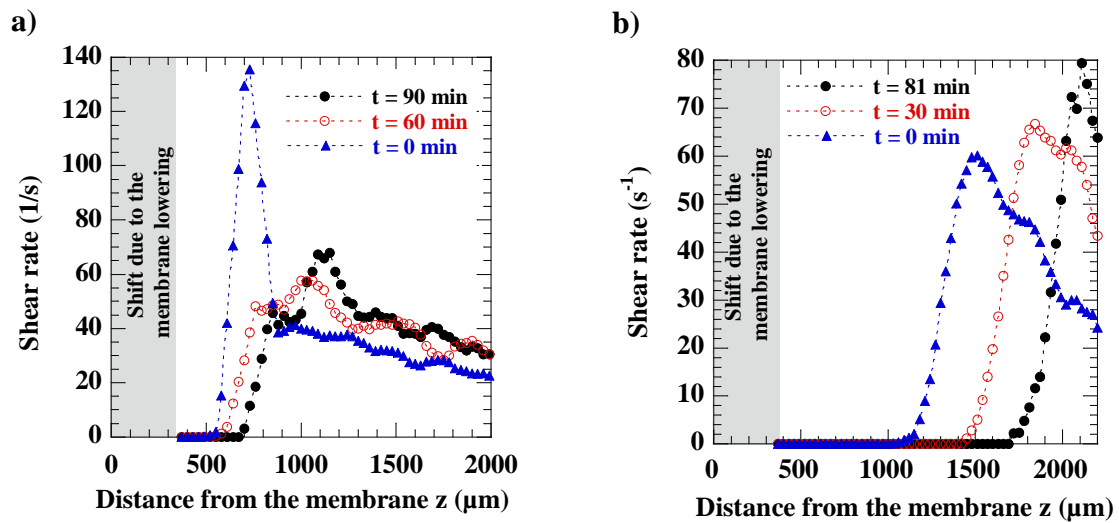


Fig. 8: Shear rates profiles in the concentrated layer formed during cross-flow ultrafiltration process as a function of the distance z from the membrane surface (with the lowering correction) during the last step of filtration. a) Laponite with peptizer (L1-Cp6), b) Laponite without peptizer (L1-Cp0). $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$, $t_p = 12 \text{ days}$, $\text{TMP} = 1.1 \times 10^5 \text{ Pa}$, $T = 25 \pm 1 \text{ }^\circ\text{C}$, middle window.

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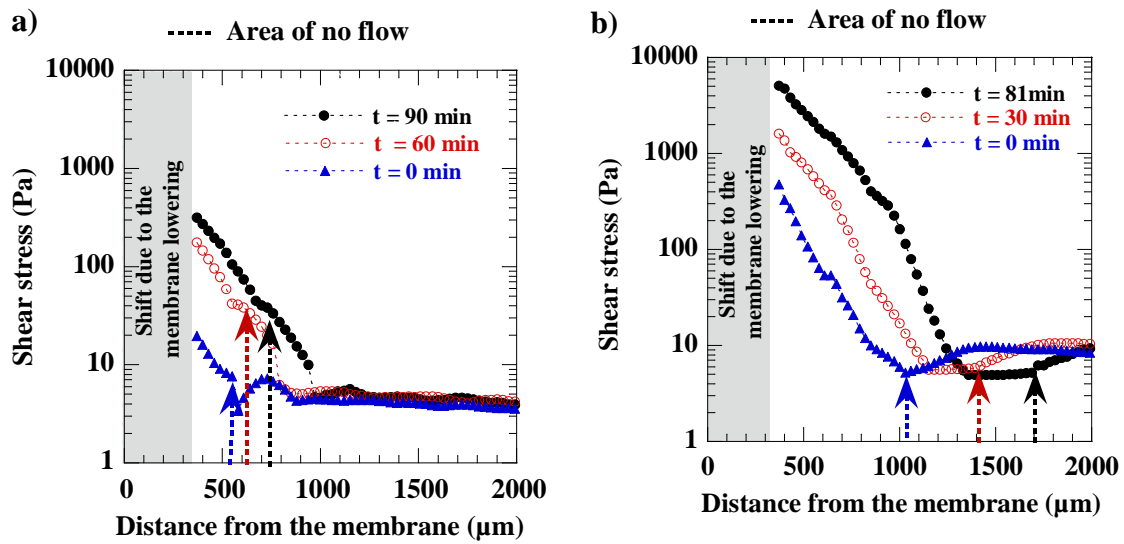


Fig 9: Shear stress profiles in the concentrated layer formed as a function of the distance z from the membrane surface (with the lowering correction) during the time of filtration. a) Laponite with peptizer (L1-Cp6), b) Laponite without peptizer (L1-Cp0). $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$, $t_p = 12$ days, $\text{TMP} = 1.1 \times 10^5 \text{ Pa}$, $T = 25 \pm 1 \text{ }^\circ\text{C}$, middle window.

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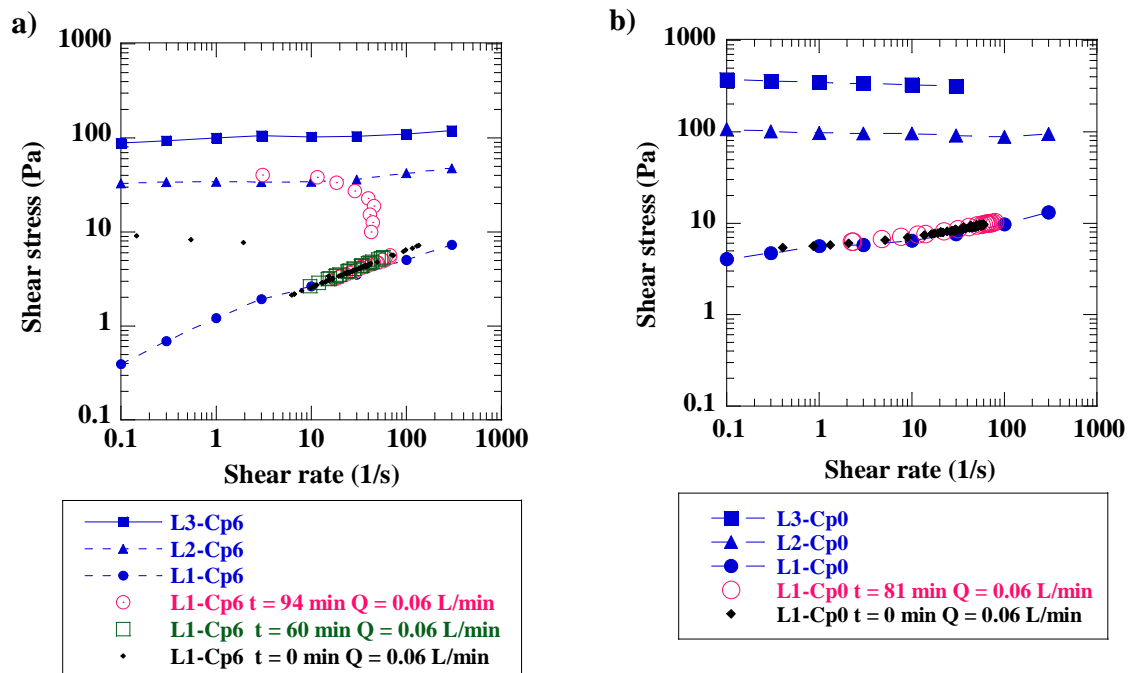


Fig 10: Rheological behavior obtained by rheometric measurements and with shear stresses calculated in the concentration polarization layer deduced from SAXS and micro-PIV experiments. a) Laponite with peptizer (L1-Cp6), b) Laponite without peptizer (L1-Cp0). $t_p = 12$ days, $T = 25 \pm 1$ °C.

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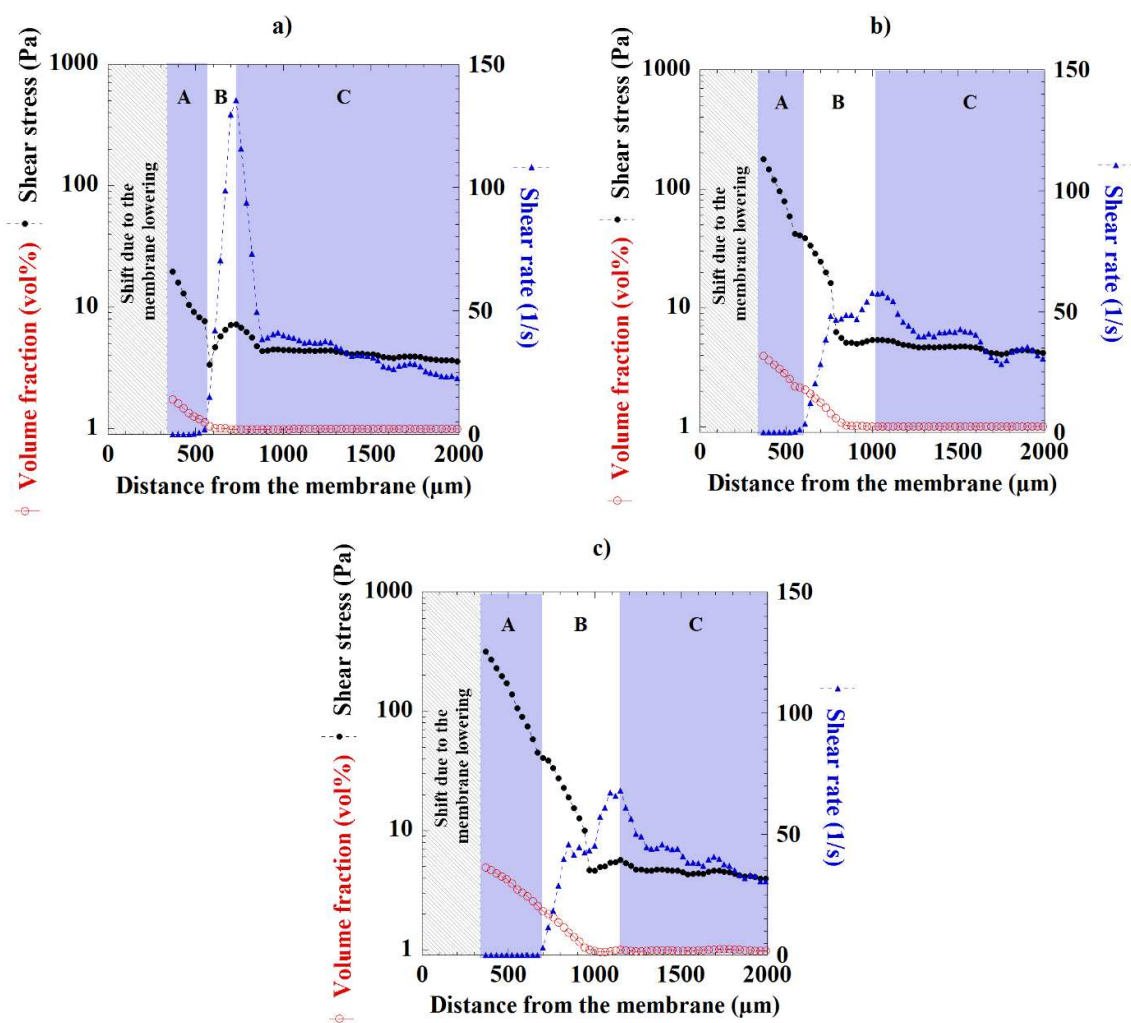


Fig. 11: Behavior regions A, B and C in the concentrated layer formed from Laponite suspensions with peptizer as a function of the distance z from the membrane surface (with the lowering correction) during cross-flow ultrafiltration, for the last step of filtration, Step 2, $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$. At filtration time a) $t = 0 \text{ min}$, b) $t = 60 \text{ min}$, c) $t = 90 \text{ min}$. L1-Cp6, $t_p = 12 \text{ days}$, $\text{TMP} = 1.1 \times 10^5 \text{ Pa}$, $T = 25 \pm 1 \text{ }^\circ\text{C}$, middle window.

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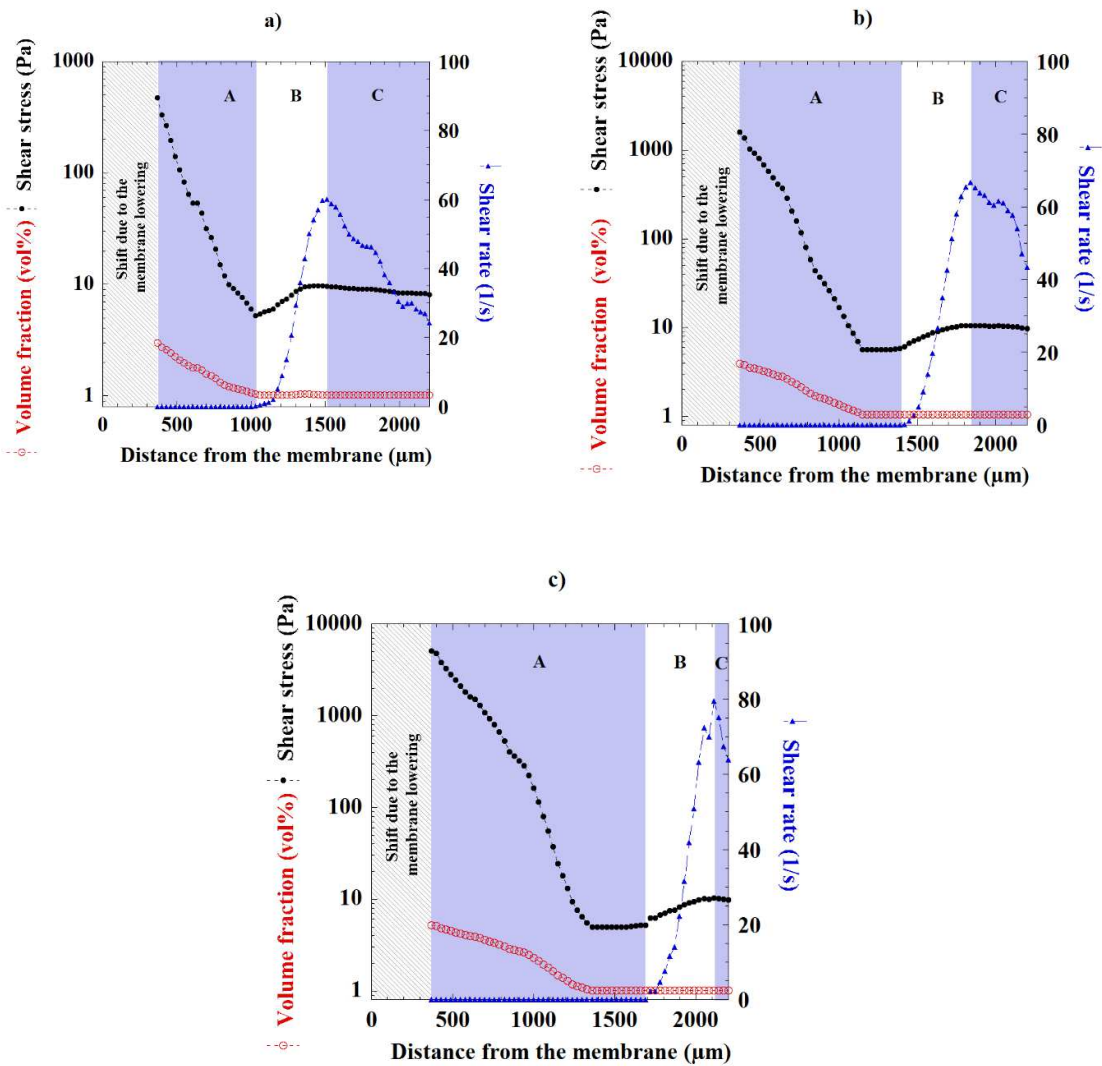


Fig. 12: Behavior regions A, B and C in the concentrated layer formed from Laponite suspensions without peptizer as a function of the distance z from the membrane surface (with the lowering correction) during cross-flow ultrafiltration, for the last step of filtration, Step 3, $Q = 0.06 \text{ L}\cdot\text{min}^{-1}$. At filtration time a) $t = 0$ min, b) $t = 35$ min, c) $t = 81$ min. L1-Cp0, $t_p = 12$ days, $\text{TMP} = 1.1 \times 10^5 \text{ Pa}$, $T = 25 \pm 1 \text{ }^\circ\text{C}$.

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Suspension	Flow rate (L.min ⁻¹)	Transmembrane pressure (x 10 ⁵ Pa)	Time (min)	N° of filtration step
L1-Cp6	0.3	1.1	80	1
	0.06	1.1	149	2
	0	0	30	3
L1-Cp0	0.3	1.1	70	1
	0.2	1.1	57	2
	0.06	1.1	141	3

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959 *Table 1: description of the filtration procedure for suspensions of Laponite with peptizer (L1-*
960 *Cp6) and without peptizer (L1-Cp0).*

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