ESRF	**Experiment title: In-situ structural organization of colloids submitted to simultaneous ultrasound waves, shear flow and pressure, during cross-flow membrane separation processes.**	**Experiment number**: SC 3483
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Report:

Membrane separation processes are used to concentrate, purify or remove solute from solution. They have gained a prominent place in food, pharmaceutical, water purification and treatment of liquid fluent streams and are effective for a broad range of applications.

Cross-flow ultrafiltration is one of the most popular developments in membrane technology for separating and/or concentrating colloidal particles. Such a process is mainly limited by the accumulation of matter on the membrane surface which leads to two phenomena: concentration polarization and membrane fouling. The events leading to the formation of a concentrated layer close to the membrane surface are taking place at a length scale of nanometers. A better understanding of the mechanism of process requires an accurate characterization technique that is non-destructive and which can provide real-time, *in-situ* observation of the concentrated layer during filtration. Therefore, a dedicated "SAXS Cross-flow Filtration Cell" was developped at the Laboratoire Rhéologie et Procédés (Grenoble) to measure *in-situ* the concentration and structural organization of colloids in the concentrated layer during filtration, as decribed in details in precedent work [1].

Among numerous fouling control techniques, ultrasound (US)-relative approach has gained a great attention. By now, a number of reports claim the effectiveness of US application in membrane cleaning and fouling control [2]. Therefore, the "SAXS Cross-flow Filtration Cell" has been upgraded by coupling an ultrasonic system in an approprate way, which led to the novel ''SAXS Cross-Flow US-coupled Filtration Cell'' (Fig.1). Developped at the Laboratoire Rhéologie et Procédés, it allows, on one hand, applying ultrasonic waves (20 kHz, from 0.6 to 2.9 $W.cm^{-2}$) close to the membrane; on the other hand, getting access to, in real time, *the in-situ* structural organization of the concentrated layer at nano-scales by SAXS measurements [1,3].

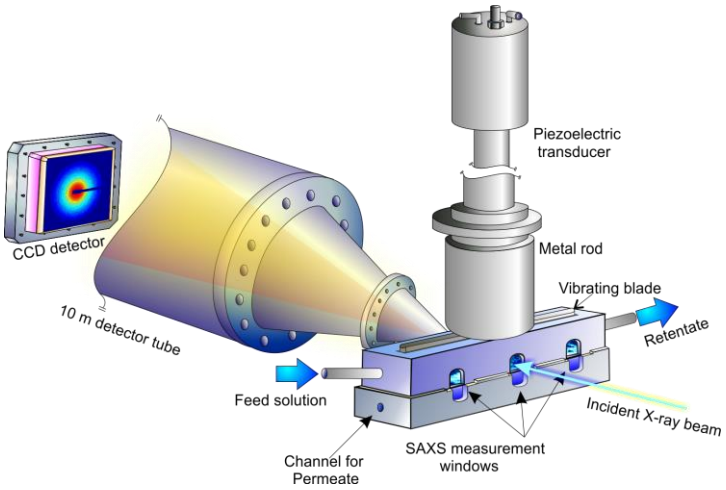

Fig.1 "SAXS Cross-Flow US-coupled Filtration Cell" during in-situ SAXS measurement

The process investigated in our study is a complex one in which colloidal particles are simultaneously subjected to compression and shear flow and ultrasound, induced by transmembrane pressure, cross-flow rate and ultrasonic force, respectively. Several colloids of various characters (nature, size, form, physico-chemical property) have been investigated to widen the explored range and to deepen understanding of this process:

(1) Laponite diserpsions [1,3]: synthetic clay consisting of disc-shape particles of 1 nm × 30 nm, which form an attractive network containing some micro-sized aggregates. Three dispersions have been studied with different feed concentration with or without peptizer (tspp, $Na_4P_2O_7$).

(2) Natural swelling gels [4,5]: which consist of diocthaedral platelets, organized by repulsive interactions in suspensions. They can exhibit liquid-crystal feature with strong oriental order in suspensions. Two of them have been investigated: Na-Wyoming montmorillonite (0.75 nm in thickness, 100 nm in mean diameter) and Austria Nontronite (0.76 nm in thickness, 350 nm in mean length and 54 in mean width).

(3) Skim milk [6]: suspension of casein micelles (spherical deformable particles with broad size distribution and mean size of 200 nm in diameter), organized by repelling interaction with interparticle free volume.

(4) Nanocrystal suspensions [7]: two types of them have been investigated: 1) starch nanocrystals (SNC), consisting of round-shape crystals, a polydisperse system with unconnected clusters; 2) cellulose nanocrystals (CNC), consisting of crystals (10 nm in thickness × 270 nm in length), organized by attractive network which can also exhibit liquid-crystal feature.

Evolution of concentrated layer during ultrasonic assisted cross-flow ultrafiltration

In Fig.2 the evolution of concentrated layer during ultrafiltration of Laponite dispersions with or without US is presented. At the transient state, colloidal matter accumulated to the membrane progressively (Fig.2a). In addition, the accumulated layers followed an exponential shape over distance z at any given time during filtration. The application of US led to a disruption of the concentrated layer until its removal (Fig.2b), which resulted in an significant increase of permeate flux, indicator of filtration performance. More details and discussions can be found in our previous paper [3], including the kinetic analyse of profile evolution and analyse of concentration profiles at steady state.

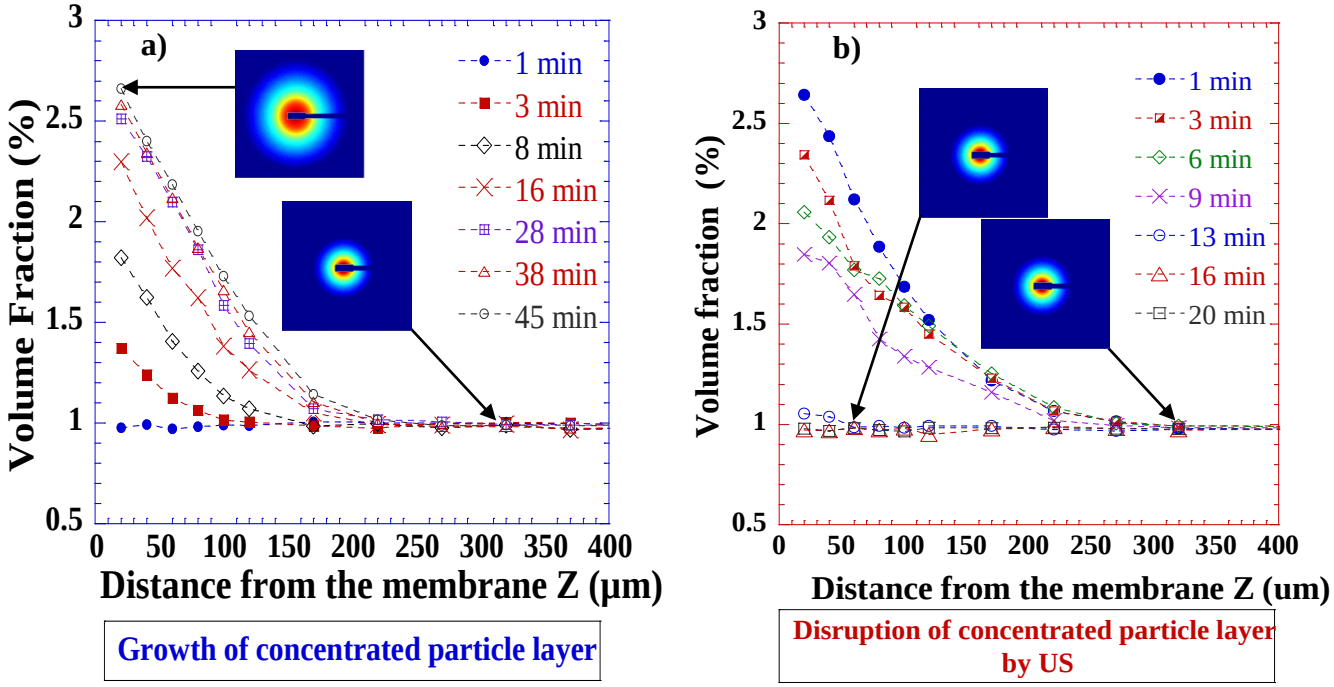

Fig.2 Evolution of concentration profiles within the concentrated particle layer over time during ultrafiltration of Laponite dispersions (Φv = 1 vol%, with tspp 6%, I = 10^{-3} M, pH 10). T = 25±1°C, transmembrane pressure (TMP) = 1.1×10^{5} Pa, cross-flow rate (Q_v) = 0.3 L.min^{-1}. a) Growth of concentrated layer without US. b) Disruption of concentrated layer under US (20 kHz, 2 W.cm^{-2}).

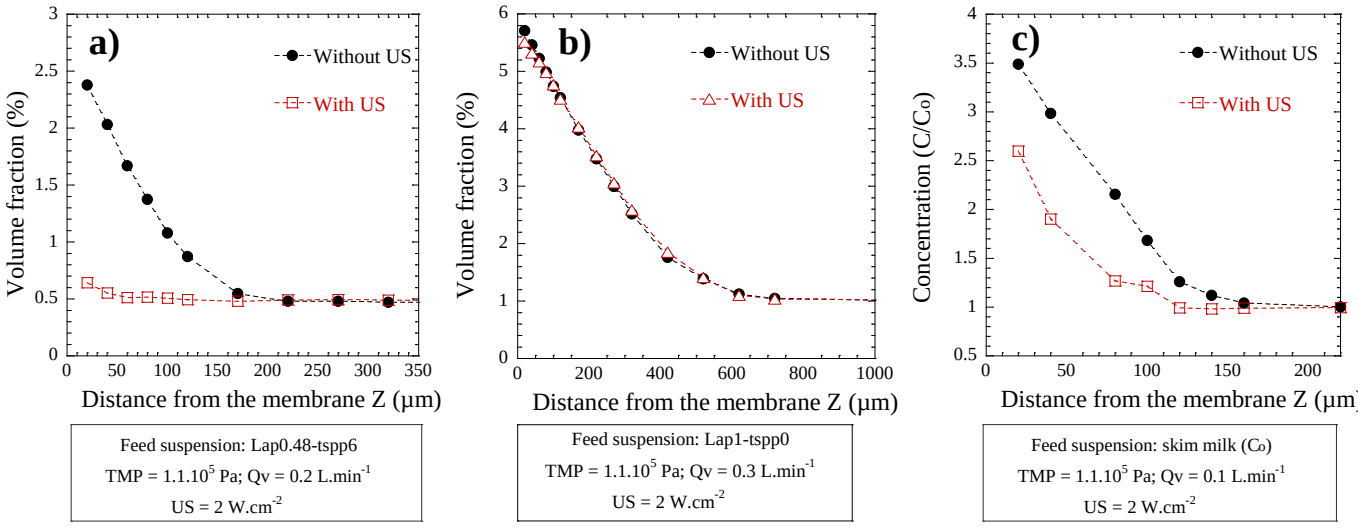

Fig.3 Concentration profiles of different suspensions from the membrane surface to the bulk at steady state during ultrafiltration, deduced from in-situ SAXS measurements. T = 25±1°C.
a) Lap0.48-tspp6 (Φv = 0.48 vol%, with tspp 6%, I = 10^{-3} M, pH 10).
b) Lap1-tspp0 (Φv = 1 vol%, without tspp, I = 10^{-3} M, pH 10).
c) Skim milk suspension at standard concentration of casein micelles Co = 27g/L.

Effect of US on concentrated layer during ultrasonic assisted cross-flow ultrafiltration

As mentioned before, colloids of different structure properties have been investigated in this study. The application of US has induced an intensificaiton of process performance for all of them but with different mechanisms related to the concentrated layer. Generally, they were identified by three groups, as shown in Fig. 3: the applied US induced a removal of accumulated particle layer, as in the case of Laponite with tspp

and SNC; it led to a partial disruption of concentrated layer, as in the case of skim milk and CNC; or no change of concentrated layer was detected by the employed SAXS measurement but a great increase of permeate flux as usual in the case of Laponite without tspp and two natural swelling clays. Fig.3 presents three representatives of each group, which is extracted from our previous paper [8].

Particle orientation during ultrasonic assisted cross-flow ultrafiltration

Particle orientation was also obverved for several colloids during the investigated process. Fig.4 presents an example which is CNC during this process. Under the same operating conditions, the evolution of concentration profile and anisotropy magnitude profile of the concentrated layer were plotted as well as the related SAXS patterns during filtration. This anisotropic feature of SAXS patterns of CNC is thought to result from a particle alignement close to the membrane surface, as discussed in our previous paper [7].

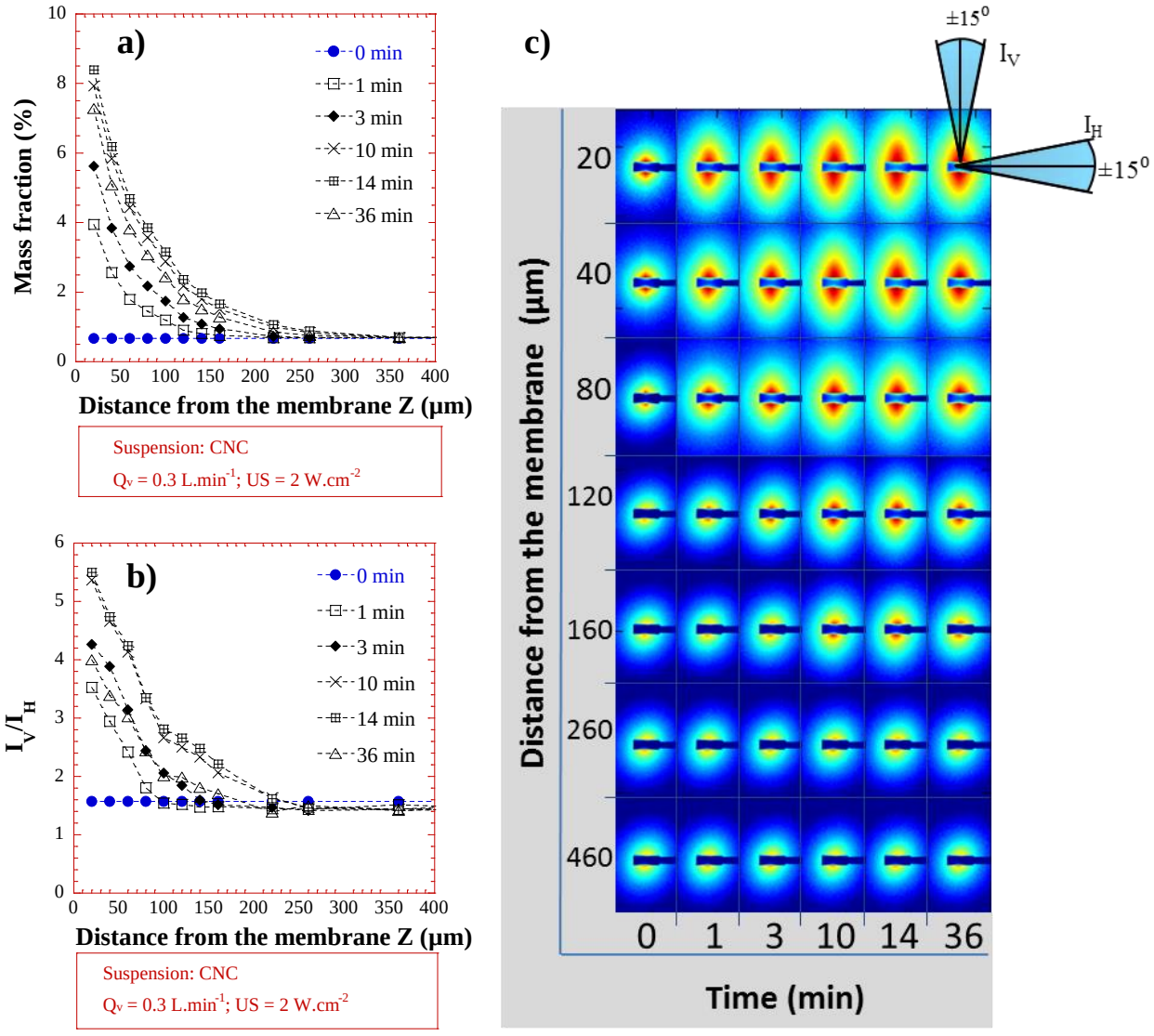

Fig.4 Results of SAXS measurements during ultrafiltration of CNC (Φ_m = 0.7 %). For the same filtration step: a) *Evolution of concentration profile over time. b) Evolution of the anisotropy magnitude (I_V/I_H) profile. c) SAXS patterns of CNC samples of different positions z from the membrane surface.*

References

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**** results from this proposal SC-3483***