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Effects of ultrasound on colloidal organization at nanometer length scale during cross-flow ultrafiltration probed by *in-situ* SAXS

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ABSTRACT

Effects of ultrasound (US) on the structural organization within concentrated particle layers during cross-flow ultrafiltration of Laponite dispersions have been characterized for the first time by *in-situ* time-resolved small-angle X-ray scattering (SAXS). A novel 'SAXS Cross-Flow US-coupled Filtration Cell' has been developed to, on one hand, apply ultrasonic waves close to the flat membrane by embedding in the feed compartment a thin titanium vibrating blade connected to a 20 kHz ultrasonic generator and on the other hand, to monitor *in-situ* the colloidal organization of the concentrated layer by SAXS. Thanks to this cell, concentration profiles have been measured as a function of the distance z from the membrane surface with a 20 μm accuracy and simultaneously linked to the permeate flux, cross-flux and transmembrane pressure. *In-situ* ultrasonication leads to a significant increase of permeate flux arising from the break-up of the concentrated layer. Results also suggest that ultrasonication could be considered as an additional force of an effective range on the order of micrometers or smaller. It is capable to completely remove the particles from the membrane surface when the feed dispersions are dense and aggregated, and is more efficient than classical procedures based on an increase of the cross-flow flux.

1. Introduction

Membrane separation processes are used to concentrate, purify or remove solute from solution. It is currently a proven technology within many important areas, such as food and dairy industries, water purification and treatment of liquid fluent streams. Cross-flow ultrafiltration is one of the most popular developments in membrane technology. Although it presents numerous advantages (large active area per unit volume, easy to operate, multiple configurations and modularity), this technology is mainly limited by the accumulation of particles on the membrane surface which leads to two phenomena: concentration polarization [1] and membrane fouling [2]. Several techniques have been developed trying to overcome these limitations but all of them present drawbacks [3–5].

Ultrasound (US) is an efficient tool in several areas of industrial process engineering. It is based on ultrasonic waves propagation within the liquid, leading to the combined effect of cavitation, acoustic streaming, *etc.* [6]. The application of ultrasound in conventional membrane filtration has been investigated and various studies report process enhancement. Research has often been carried out during membrane cleaning process [7–11] but online ultrasonication has also been applied in both cross-flow [8,10,12–15] and dead-end filtration [16]. In most of these studies, the ultrasound devices are ultrasonic water baths, in which the loss of acoustic power is reported to be very high, about 90% [17]. In order to have a better control of US, Simon et al. [16], Juang et al. [18] and Mirzaie and Mohammadi [19] used an ultrasonic probe system to transmit ultrasonic waves directly to the feed medium in a dead-end filtration operation. Kyllonen et al. [13] also developed a membrane module integrated with several sandwich type ultrasonic transducers to apply ultrasound in cross-flow filtration with little loss of ultrasonic efficiency. Using a different approach than that developed by Kyllonen et al. [13], the present study proposes a new ultrasonic-assisted cross-flow membrane filtration module that can apply ultrasonication directly on the feed side of the membrane at a very close distance (8 mm).

To understand the mechanism of ultrasonic enhancement of membrane filtration, different approaches have been used. Due to its ease of measurement, the evolution of permeate flux is the most obvious measurement to carry out and is directly linked to filtration performance. However it does not provide any

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information on mechanisms occurring within the concentrated particles layer (including reversible concentration polarization layer and irreversible fouling layer) in the feed. Filtrate concentrations close to the membrane surface as well as mass transfer coefficients within the concentrated layer under ultrasonication have been estimated using theoretical and modeling approaches [14,20] whereas Scanning Electron Microscopy (SEM) has been used to characterize 'offline' the fouling cake formed during filtration with and without ultrasound [6,19]. Still, to our knowledge, no real time observation of the concentrated layers during cross-flow filtration under ultrasonication has ever been reported.

To reach such goal, small-angle X-ray scattering (SAXS) measurements were carried out at the European Synchrotron Radiation Facility (ESRF, ID02 High Brilliance SAXS/WAXS/USAXS Beamline). A novel 'SAXS Cross-Flow US-coupled Filtration Cell' has been especially developed at the 'Laboratoire Rhéologie et Procédés', which allows characterizing, *in-situ*, the induced structures and concentration profiles in the vicinity of the ultrafiltration membranes at nanometer length scales over time, when feed dispersions are simultaneously subjected to a transmembrane pressure, cross-flow over the membrane and ultrasonication. The colloidal dispersions filtered are synthetic aqueous clay Laponite, already used in our previous work [21]. In these previous experiments, the dispersions were studied by *in-situ* SAXS during ultrafiltration, but without the ability to apply ultrasound. The Laponite dispersions used here, consisting of nanometric platelets, with shear-thinning rheological behavior for the volume fractions and physico-chemical conditions studied in the present paper.

This work combines macroscopic results with simultaneous observations at nanometer length scale during ultrafiltration. To the best of our knowledge, it is the first time that the effect of ultrasound on cross-flow filtration is determined by *in-situ* characterization of the concentration profiles and structural organization within concentrated particles layer over time.

2. Materials and methods

2.1. Sample preparation

Laponite XLG, manufactured by Laponite Industries, was employed in this paper. Laponite XLG dispersions were prepared under high shear in demineralized water at 20 °C at a fixed ionic strength of 10^{-3} M NaCl. Suspended Laponite particles are in the form of roughly circular discs with a diameter of 25–30 nm and thickness of 1–2 nm [22]. Dispersions to be filtered were prepared at initial volume fractions of $\Phi_v = 0.48\%$ and 1%, corresponding to mass fraction of 0.0121 and 0.0253, respectively. The dispersions were then aged in closed vessels for 12–26 days before the filtration experiments. The pH value of the dispersions remained stable during this aging time and equal to 10 during the measurement, which indicates that there is no further dissolution of material since the pH was always above 9 [23]. The structure and rheological properties of these dispersions evolve with time [23,24]. Consequently, the time t_p that elapsed between the end of preparation and the investigations will always be indicated in this paper. A peptizer, tetrasodium diphosphate $Na_4P_2O_7$ (tspp) was added to the dispersions with a concentration of 6% (percentage with regard to dry clay mass), the peptizer concentration is denoted as C_p. The effect of this peptizer on the structure, rheological behavior, osmotic pressure and frontal filtration performance of the Laponite dispersions has been studied in previous works [24–26]. A reduction in attractive force between the particles takes place while adding this peptizer, which leads to a transformation of the flow properties from yield stress gels to shear-thinning fluids, as those investigated dispersions in this study.

2.2. Rheometric measurements

The rheological behavior of the dispersions was studied with a shear rate controlled rheometer (ARG2, TA Instrument) with a stainless steel cone and plate geometry (diameter 49 mm, angle 4°21′). In order to avoid interfacial effects, the surfaces of the apparatus were covered with sand-paper with a roughness of 200 μm. Measurements were carried out at a temperature of 25 ± 1 °C. The atmosphere around the sample was saturated with water to prevent evaporation during the measurement [27].

2.3. 'SAXS Cross-Flow US-coupled Filtration Cell' and filtration procedure

2.3.1. Filtration setup and procedure

Previously, a 'SAXS Cross-Flow Filtration Cell' was developed to measure *in-situ* the concentration and structural organization of colloids as a function of time at different distances z from the membrane surface [21]. This cell is made of transparent polycarbonate and contains a flat polyethersulfone ultrafiltration membrane (100 kD, PleyadeRayflow × 100, Rhodia Orelis). The design of this filtration cell was modified in order to combine an ultrasound system: a thin titanium vibrating blade was embedded in the feed compartment and placed above the flat membrane at a distance of 8 mm. This blade is connected to a sonotrode consisting of a piezoelectric transducer attached to a metal rod, which generates ultrasonic waves at a 20 kHz frequency and at an applied amplitude of 1.6 μm (SODEVA TDS, France). The input electric power stretches from 2 W to 10 W, corresponding to power intensity from 0.57 W cm^{-2} to 2.86 W cm^{-2} (the input power per unit area of the blade surface). What will be indicated in the following sections refers to the input electric power; about 70% of it is transmitted to effective ultrasonic power. The feed channel is 100 mm long in tangential flow direction and 4 mm × 8 mm (width × height) in the flow section. Three windows of 3 mm × 5.5 mm × 0.3 mm (width × height × thickness) are opened into the wall located upstream, in the middle and downstream in the feed compartment with a distance of 43 mm from each other (Fig. 1a). The filtration cell was mounted in a motorized stage, which allows monitoring by SAXS the concentration and structural organization of suspensions at different distances from the membrane as well as at different positions along the membrane.

As shown in Fig. 1b, during filtration, the feed suspensions, denoted as retentate, are pumped (Mono pump LF series) from a high pressure resistant vessel (Millipore) to the filtration cell and the cross-flow flux is quantified constantly by a magnetic flow meter (Optiflux 6300C, Krohne). The pressure is applied via purified compressed air, and is monitored by two pressure gauges (FP 110 FGP Sensors & Instrument) at both the inlet and outlet of the filtration cell. The filtration temperature is maintained at 25 °C by a thermostatic bath (Thermo &Scientific SC 150 A25, HAAKE) and it is verified constantly by two sensors (YC-747D with K thermocouples) at both inlet and outlet of the filtration cell. The permeate flux J_v is monitored by measuring the mass variation in the reservoir vessel every 5 s with an accuracy of 0.001 g (Balance Precisa 400 M).

2.3.2. SAXS measurement conditions and analysis

SAXS measurements were carried out at the ID02 High Brilliance SAXS/WAXS/USAXS Beamline [28], at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The incident X-ray beam of wavelength (λ) 0.1 nm, was collimated to 20 μm