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# Shear-enhanced membrane filtration of model and real microalgae extracts for lipids recovery in biorefinery context

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## Abstract

In this work, the hydrodynamic effects of rotating disk filtration (with maximum shear rates of  $16\,000\text{ s}^{-1}$  and  $66\,000\text{ s}^{-1}$ ) were evaluated and compared with the crossflow filtration ( $16\,000\text{ s}^{-1}$ ) in the recovery of lipids from a model solution that simulates the characteristics of *Parachlorella kessleri* aqueous extracts. Four polymeric membranes were tested. The PAN 500 kDa membrane along with the rotating disk filtration presented the best performances for lipid concentration and coalescence. The rotating disk filtration was tested with real microalgae extracts, confirming the total lipid retention and the limited membrane fouling.

*Keywords:* Microalgae, Lipids, Rotating disk filtration, Ultrafiltration, Oil-in-water emulsion

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## 1. Introduction

Satisfying the increasing world energy demand with renewable natural resources has significant environmental benefits, that are of great importance to both researchers and entrepreneurs alike. In this context, a very attractive area of research is the cultivation and harvest of microalgae for biodiesel production. A large variety of microalgae has been characterized with regard to cultivation conditions, biomass productivity, lipid content, and lipid productivity (Chun-Yen et al., 2011). Between the different varieties of microalgae, the *Parachlorella kessleri* species stand out for their high lipid production; in addition, the lipid production of this specific species has been successfully scaled to the semi-industrial level (Ota et al., 2016) with promising results. Several studies concerning the dilution of nutrient media (Li et al., 2013), variation of carbon sources (Hamza et al., 2013), and macronutrient limitation (Ota et al., 2016) have demonstrated that nitrogen limitation is (at the moment) the most widely used method to induce lipid overproduction (Li et al., 2013).

A crucial step in biodiesel production is the cell disruption and lipid extraction from the harvested cells. Since lipids are intracellular compounds, cell disruption is absolutely necessary to increase the amount of lipids recovered (Lee et al., 2012); the extraction efficiency, and the lipid integrity depend on the disruption processes being used (Byreddy et al., 2015). The disrupted microalgae form a mixture composed of the extracted lipids, among other intracellular components, cell debris, and solvent (Halim et al., 2012). The extraction of lipids directly from the wet disrupted microalgae cells reduces the required monetary and time investment associated with drying processes (’t Lam et al., 2018).

The filtration process is an attractive option for the lipid concentration from the wet disrupted cells because it can be automated, and it can treat large volumes (Kumar Patel et al., 2013). Additionally, filtration methods allow for a drastic reduction of the required solvents and chemicals used for extraction (Safi et al., 2014). Operating conditions and feed properties such as the transmembrane pressure (TMP), shear rate, membrane hydrophilicity, initial oil concentration, salinity, and pH all play an important role in membrane separation processes (Chakrabarty et al., 2008; Li et al., 2009). The main drawback of the filtration process is the membrane fouling due to the deposition of microalgae material on the

membrane surface and/or inside the membrane pores (Waghmare et al., 2016; Marcati et al., 2014; Kumar Patel et al., 2013). In recent years, shear-enhanced or dynamic filtration (DF) has emerged as an interesting option that reduces membrane fouling. This technique limits the cake growth at the membrane surface (Rios et al., 2011; Ding and Jaffrin, 2014) by increasing the shear rate. This increase can be produced by generating turbulence using a rotating disk over a fixed membrane, or by rotating (or vibrating) the membrane itself (Jaffrin, 2008).

Rotating disk (RD) is a type of DF module that provides high permeate fluxes at a steady shear rate, with good performance and low energy requirements (Moulai-Mostefa et al., 2007; Jaffrin et al., 2004; Hwang et al., 2016). The aforementioned characteristics make this process a very favorable option for biotechnological applications. For example, a vibrating DF system was used to concentrate lipids from steam exploded biomass by Lorente et al. (2017). A polyethersulfone (PES) membrane with a molecular weight cut off (MWCO) of 5 kDa, and a polyvinylidene fluoride membrane (PVDF, MWCO 100 kDa) were selected to perform the filtration at 5 bar. The flux reached 5 to 65 L h<sup>-1</sup> m<sup>-2</sup>. However, even with the promising results that the RD filtration can provide towards lipid concentration from disrupted microalgae cells, its usage in microalgae biorefining has been generally left unexplored. If a methodology for carrying out lipid concentration from disrupted cells can be established using membrane technology, this process could be used for obtaining different microalgae fractions with minor modifications.

In this work, the performances of the RD technique applied towards the concentration of lipids from microalgae aqueous extracts were evaluated. A model solution (Clavijo et al., 2017) to test the different polymeric membranes was used due to limited access to large volumes of real microalgae culture. Moreover, the large variability inherent to the real products would have limited the comparisons. The membrane with the best separation characteristics was used to compare the performances between crossflow (CF) filtration and RD filtration. Finally the RD filtration was tested with real microalgae aqueous extracts and compared to the CF filtration of the same products.

## 2. Material and methods

### 2.1. Real microalgae extracts

The characteristics of the *Parachlorella kessleri* culture used in this work was grown in autotrophic starving conditions; two aqueous extracts containing dispersed lipids called supernatant (SN<sub>1</sub> and SN<sub>2</sub>) were produced after bead milling and centrifugation of two different biomasses.

### 2.2. Model solution preparation

The model solution is an oil in water emulsion. It corresponds to the supernatant of a concentrated pretreated culture, after bead milling and separation of the cell fragments by centrifugation (Clavijo Rivera et al., 2018; Clavijo et al., 2017). It contains 2%<sub>w</sub> of lipids in an aqueous phase (emulating a fresh water culture medium), with a pH of 7.4 and a conductivity equal to 790 μS cm<sup>-1</sup>. The lipid phase contains 70%<sub>w</sub> of neutral lipids coming from the mixture of vegetable oils and 30%<sub>w</sub> of polar lipids constituted of commercial products. The emulsification was performed with a rotor-stator T-25 ULTRA-TURRAX (IKA). The aqueous phase was mixed with a polar lipid product (15%<sub>w</sub> of the total lipid content) at 80 °C. The vegetable oils were mixed with a second polar lipid product (15%<sub>w</sub> of the total lipid content) at 80 °C. The aqueous and the oil phases were then mixed (24 000 rpm by 30 min) and then, cooled to room temperature during 20 h with gently stirring at 700 rpm.

### 2.3. Filtration modules

The RD module used in this study is described in detail in Refs. (Bouzerar et al., 2000b) and (Bouzerar et al., 2000a). This RD module is equipped with a disk of 15 cm of diameter that rotates inside a cylindrical housing. This disk has eight vanes that are each 2 mm wide by 6 mm tall. The disk can rotate at a maximum speed of 3000 rpm. The pressure is adjusted by operating a valve on the retentate outlet tubing. The peripheral pressure is measured at the top of the cylindrical housing by a pressure sensor. On the cover of the cylindrical housing (in front of the disk), a single circular membrane with dimensions of 8.4 cm of outer radius and 1.2 cm of inner

radius (usable area of 185 cm<sup>2</sup>) can be placed. Fig. 1a presents a cross-sectional view of the module design and its internal circulation path.

The movement of the disk near the fixed circular membrane creates a maximum shear rate ( $\dot{\gamma}_{max}$ ) with turbulent flow, which is calculated as (Bouzerar et al., 2000a; Frappart et al., 2011),

$$\dot{\gamma}_{max} = 0.0296 \cdot \nu^{-\frac{4}{5}} \cdot (k\omega)^{\frac{9}{5}} \cdot R_d^{\frac{8}{5}}, \quad (1)$$

where  $\nu$  is the kinematic viscosity (m<sup>2</sup>s<sup>-1</sup>),  $k$  is the velocity factor,  $\omega$  is the angular disk velocity (rad s<sup>-1</sup>), and  $R_d$  is the disk radius (m).  $k\omega$  is the angular velocity of the inviscid fluid.

The CF module is a Rayflow X100 (Orelis-Novasep). This module consists of two restraining plates that can contain up to two flat rectangular membranes, each with a usable area of 130 cm<sup>2</sup>. Filtration pressure is adjusted with a valve, with one pressure sensor placed at the module inlet and another at the retentate outlet. Fig. 1b presents a schematic representation of this module. The maximum shear rate from the laminar flow on the membrane can be calculated as (Delaunay et al., 2008),

$$\dot{\gamma}_{max} = \frac{4}{e} \cdot v_{max}, \quad (2)$$

where  $e = 0.5$  mm is the chamber thickness, and  $v_{max}$  is the tangential flow velocity obtained in the chamber (m s<sup>-1</sup>). The experimental setup used in this study (the RD and the CF modules) is described in Ref. (Frappart et al., 2011). Table 1 shows the corresponding  $v_{max}$  and  $\dot{\gamma}_{max}$  for the three different setups tested in this work.

#### 2.4. Membranes

Four commercial membranes were selected. These membranes were manufactured by Orelis Environnement (Pleiade range), with differing polymer composition, hydrophilicity, and MWCO. The membranes used were a PES (200 kDa), a polyacrylonitrile (PAN 500 kDa), a PVDF (0.4  $\mu$ m), and another PVDF (1.5  $\mu$ m). Before being used, each membrane was cut, washed, and compacted in order to eliminate membrane preservatives (glycerol), and to ensure a steady water flux. The cleaning procedure involved the membrane rinsing with ethanol and demineralized

water; then, the membrane was submerged for 30 min in demineralized water (refreshed every 10 min). The experimental flux values were adjusted to 30 °C using a correction coefficient related to water viscosity ( $\mu$ ).

### 2.5. Screening of the membranes with the model solution

The permeate flux ( $J$ ) variation versus the TMP was determined by recirculating the emulsion in a closed system at 30 °C.  $J$  was measured for the lowest TMP possible, then the permeate was returned to the feed tank and the TMP was increased with 0.1 bar steps, repeating the same procedure. Once the limiting flux was reached, two additional measurements were performed in order to verify the flux plateau.

#### 2.5.1. Concentration experiment

The concentration experiment was evaluated through the volume reduction ratio (VRR). The emulsion was recirculated at 30 °C, collecting the permeate and returning the retentate back to the feed tank until reaching different VRR. In a batch system concentration, the VRR is defined as,

$$\text{VRR} = \frac{V_0}{V_f}, \quad (3)$$

where  $V_0$  and  $V_f$  are the initial and final emulsion volumes. Samples of instantaneous retentate, permeate, and collected permeate were taken at each of these points. During this experiment the membrane performance was followed through the flux decline, membrane selectivity and total oil mass accumulated on the membrane. Flux decline was calculated as a function of the emulsion permeate flux ( $J$ ) and the initial membrane demineralized water flux ( $J_w$ ) according to the following expression,

$$\% \text{ Flux decline} = \left( 1 - \frac{J}{J_w} \right) \times 100. \quad (4)$$

The membrane selectivity was verified through the retention rate (% R), which is a function of the permeate ( $C_p$ ) and retentate ( $C_r$ ) concentrations,

$$\% \text{ R} = \left( 1 - \frac{C_p}{C_r} \right) \times 100. \quad (5)$$

The total oil mass accumulated on the membrane and non-membrane interfaces during the concentration experiment ( $m_{\text{VRR}}^{\text{Tot}}$ ) was calculated as

$$m_{\text{VRR}}^{\text{Tot}} = (X_0 M_0) - (X_r M_r) - (X_p M_p) - \sum_{i=0}^n (X_r m_r^i + X_p m_p^i), \quad (6)$$

where  $X_0$ ,  $X_r$ , and  $X_p$  are the initial, retentate, and permeate mass fractions of oil in the emulsion ( $g_{\text{oil}}/g_{\text{emulsion}}$ ), respectively. Likewise,  $M_0$ ,  $M_r$ , and  $M_p$  are the equivalent emulsion masses (g).  $m_r^i$ , and  $m_p^i$  are the samples mass (g) taken out of the system for each analysis, and  $i$  represents the sample taken out of the system from a total  $n$  number of samples. The amount of salt contained in the buffer that was used to prepare the emulsion, was subtracted from the different samples before calculating  $m_{\text{VRR}}^{\text{Tot}}$ .

The maximum amount of oil accumulated on the non-membrane interfaces of the RD module was obtained by recirculating the model solution through the system for 7 h, without a membrane in order to reach equilibrium. A sample was taken at each hour of the experiment, and the oil content was quantified by gravimetric analysis. The maximum amount of oil accumulated at the non-membrane interfaces of the RD module was subtracted from Eq. (6). The final amount was divided by the apparent surface area of the membrane ( $\text{m}^2$ ), obtaining the quantity of oil accumulated only on the membrane ( $q_{\text{VRR}}^{\text{mb}}$ ) as,

$$q_{\text{VRR}}^{\text{mb}} = \frac{(m_{\text{VRR}}^{\text{Tot}} - m^{\text{non-membrane}})}{A}. \quad (7)$$

### 2.5.2. Cleaning procedure

The emulsion elimination from the membrane was performed right after the concentration experiment, once the remaining emulsion was expelled out of the filtration module. The cleaning procedure encompasses a cycle of three steps. First, recirculation of demineralized water (40 °C and  $1.0 \text{ m s}^{-1}$ ) for 30 min; second, recirculation of sodium dodecyl sulfate (SDS, 8 mM, 40 °C) for 30 min, and ethanol (25 % in volume) for 60 min; and third, measurement of the demineralized water permeability adjusted at 30 °C. For membranes used with the real microalgae extract, another cleaning step was implemented using a commercial alkaline Ultrasil 110 (Ecolab) solution.



A long rinsing with water was performed after each step. The cleanability of the membrane was evaluated using the flux recovery ratio (% FRR) which relates the permeate flux after the cleaning procedure ( $J_r$ ) and  $J_w$  as,

$$\% \text{ FRR} = \left( \frac{J_r}{J_w} \right) \times 100. \quad (8)$$

The membrane was considered clean when the % FRR was greater than 90 %.

### *2.6. Gravimetric analysis*

The IR-30 Moisture Analyzer (Denver Instrument) was used to determine the emulsion dry matter, and therefore calculate the mass balance. This device is based on heating the sample with infrared light then determining the remaining amount of dry mass. A measuring accuracy of 0.05 g is reported for an initial sample weight from 5 g to 10 g. Glass fiber pads were used to evenly spread the samples. Prior to the sample analysis, a glass fiber pad and a weighing dish of 90 mm in diameter were dried at 105 °C for 5 min, eliminating any trace of moisture. The samples were dried at 105 °C and automatic drying time. To ensure accuracy all samples were replicated three times.

### *2.7. Droplet size distribution*

The droplet size distribution (DSD) of the emulsion was determined with a Mastersizer 3000 laser diffraction particle size analyzer (Malvern). This instrument is equipped with the hydro large volume and small volume wet dispersion units. The device has a detection particle size range of 0.01  $\mu\text{m}$  to 3500  $\mu\text{m}$ . The samples were analyzed (in triplicate) without dilution, using a refraction index of 1.44 and a absorption index of 0.003.

### *2.8. Ultrapure water contact angle*

The ultrapure water contact angle ( $\theta_w$ ) quantifies the wettability of a solid surface. The water used has a resistivity of 15  $\text{M}\Omega\text{cm}$  and  $\text{pH}=8.35 \pm 0.49$  at 25 °C.  $\theta_w$  was measured on the four clean and emulsion-fouled membranes. The Drop Shape Analyzer – DSA30A TRACKER instrument

was used for this purpose in sessile drop mode. Before the  $\theta_w$  measurement, the fouled membranes were removed from the filtration modules immediately after the concentration experiment in order to maintain the fouled surface. The membrane surface was then gently rinsed with demineralized water to eliminate the excess emulsion. Both membrane samples were dried in an oven for 48 h at 35 °C, followed by 24 h in a desiccator. The membranes were then fastened on glass slides using double-sided tape.

The water drops were dosed using a glass syringe (500  $\mu\text{L}$ ) with a disposable stainless steel needle (diameter of 0.5 mm). The approximate volume of each drop was 2.5  $\mu\text{L}$ .  $\theta_w$  was measured 100 ms after drop deposition. The left and right contact angles of each drop were calculated from the digitized image using the DSA software. The profile of the sessile drop was calculated using a tangent method that fits the drop to a general conic equation. The derivative of the equation at the drop baseline is the slope at the three-phase contact point, which is used to determine the contact angle. 12 droplets of the water were deposited on different sections of the same membrane sample, increasing the accuracy of the average value of the contact angle. This technique presents an accuracy of 2° to 5.5° (Diagne et al., 2013).

### 3. Results and Discussion

#### 3.1. Screening evaluation of the membranes with the model solution

##### 3.1.1. Determination of the critical pressure

The limiting flux ( $J_{\text{lim}}$ ) is the maximum steady flux achieved by increasing the TMP (Hurt et al., 2015); the TMP value at which this occurs is defined as the maximum pressure ( $P_{\text{max}}$ ). The critical flux ( $J_c$ ) can be generally defined as the first permeate flux at which a prominent fouling takes place (Hurt et al., 2015), and the corresponding pressure for this flux is called the critical pressure ( $P_c$ ). This  $P_c$  corresponds to the TMP at which the normalized flux ( $J/J_w$ ) begins to decrease, which indicates an increase in membrane fouling. Figs. 2a and 2b feature the average variation of the permeate flux ( $J$ ), and  $J/J_w$  as functions of the TMP taken at 30 °C for the

PAN 500 kDa and PVDF 0.4  $\mu\text{m}$  membranes. The initial  $J_w$  was measured and adjusted at 30 °C.

As can be seen in Fig. 2a, the 0.4  $\mu\text{m}$  PVDF membrane presents a  $J$  which increases with the TMP; for this membrane, a value of  $J_{\text{lim}} = 66 \pm 1$   $\text{L h}^{-1} \text{m}^{-2}$  occurs at  $P_{\text{max}} = 0.6$  bar. For the PAN membrane,  $J_{\text{lim}}$  never reaches a steady value in the range of TMP studied in this work; therefore,  $P_{\text{max}}$  can not be determined. Different fouling behavior of the membranes with similar filtration conditions can be explained considering their pore size distribution and degree of hydrophilicity; these characteristics determine the water and oil droplet permeation. Membrane polarization, attraction/adsorption between the membrane and the oil droplets, oil layer formation at the membrane surface, and the steric effect all play a role in determining the oil droplet retention by the membrane.

Fig. 2b shows that the initial  $J/J_w$  is close to 1.0 for both membranes. This indicates that the permeate flux is nearly the same as the water flux at low TMP, indicating that fouling is very low. However, the  $P_c$  of the 0.4  $\mu\text{m}$  PVDF membrane was detected around 0.4 bar; for the 500 kDa PAN membrane,  $P_c$  was between 0.5 and 0.6 bar. For  $\text{TMP} > P_c$ , the  $J/J_w$  begins to decrease inversely proportional to the TMP for both membranes, indicating that the membrane fouling has begun. The 500 kDa PAN membrane has a slow, gradual decrease, while the 0.4  $\mu\text{m}$  PVDF membrane has a significantly steeper decline. Table 2 presents the average  $J_w$  at 1 bar, the  $J_{\text{lim}}$ ,  $J_c$  along with their variability ( $\sigma$ ),  $P_{\text{max}}$ , and  $P_c$  values of the different membranes used in this study. The initial water contact angle ( $\theta_w^0$ ) of the different membranes was measured following the procedure described in Sec. 2.8. Materials with  $\theta_w < 45^\circ$  are highly-hydrophilic, when  $45^\circ < \theta_w < 90^\circ$ , they have both hydrophilic/hydrophobic properties, and for  $\theta_w > 90^\circ$ , the materials are hydrophobic (Świerczyńska et al., 2016).

The 500 kDa PAN membrane presented relatively high  $P_c$  values along with the lowest  $\theta_w^0$  value ( $75.0 \pm 2.4$ ). This suggest a high degree of membrane hydrophilicity that might limit fouling formation. The 1.5  $\mu\text{m}$  PVDF membrane also presented relatively high  $P_c$  values despite its  $\theta_w^0$  value ( $82.3 \pm 0.7$ ), which indicates hydrophilic/hydrophobic membrane properties. Therefore, the potential accumulation of lipids on the membrane did not have a significant impact on the water permeation and the critical pressure because of the large pore size, that allowed the permeation of water but

also some fine oil droplets. During the screening evaluation the 1.5  $\mu\text{m}$  PVDF membrane presented turbid permeates, while transparent permeates were obtained for the remainder of the membranes. 200 kDa PES and 0.4  $\mu\text{m}$  PVDF membranes presented the lowest  $P_c$  values; therefore, a considerably high membrane fouling was supposed for both cases. For the former membrane, this fouling was mainly due to its small MWCO leading to a high lipids retention and probable adsorption pore blocking or cake formation. In the latter membrane, the fouling was due to its hydrophobic properties ( $\theta_w^0 = 95.1 \pm 1.2$ ) thus a strong adsorption.

### 3.1.2. Concentration experiment

The concentration experiment was carried out just after the critical pressure measurement. The TMP of the concentration experiment was 90 % of the  $P_c$ ; this percentage was selected in order to have the highest permeate flux while avoiding strong membrane fouling. The examples of the evolution of  $J$  and its normalized representation versus the VRR during the concentration experiments for the 500 kDa PAN and 0.4  $\mu\text{m}$  PVDF membranes are presented in Fig. 3.

$J$  and  $J/J_w$  decreased with the VRR; this behavior is similar for all the membranes studied in this work. The 500 kDa PAN and 0.4  $\mu\text{m}$  PVDF membrane presented an initial  $J/J_w$  around 0.9 and 0.7, respectively. At the highest VRR the normalized flux decreased 22 % for the former membrane, and 14 % for the latter membrane. Table 3 shows the % Flux decline, % FRR,  $q_{\text{VRR}}^{\text{mb}}$ ,  $\theta_w^0$ , and water contact angle after the concentration experiment ( $\theta_w^{\text{VRR}}$ ) for all membranes at an average VRR =  $4.3 \pm 0.1$ .

As already observed during previous critical pressure measurements, concentration experiments do not modify the retention behavior of the membrane. Oil retention was higher than 95 % for each membrane. An increased hydrophilicity (lower  $\theta_w^{\text{VRR}}$  value) in comparison with the clean membranes ( $\theta_w^0$ ) was observed for all the membranes. The 200 kDa PES membrane presented a very high % Flux decline along with the lowest % FRR. This suggests a high degree of membrane fouling that is difficult to remove which has a significant impact on the membrane properties. In fact, this membrane presented the greatest increase in hydrophilicity, 28 % that might be due to the adsorption of the polar lipids present in the model solution formulation. These results suggest that the oil droplet

accumulation on the membrane is responsible for the strong fouling of the membrane.

The 500 kDa PAN membrane presented a low value of % Flux decline, and a total % FRR. This membrane behavior suggests the formation of a fouling layer that is easily removed. In fact, a large amount of the oil droplets accumulated on the membrane surface were almost completely eliminated when gently rinsed before the measurement of  $\theta_w$ . The hydrophilic properties of the fouling may also be near from the membrane properties. This led to a very small increase in the membrane hydrophilicity of only 8 %. The large quantity of accumulated matter had a low impact on the filtration performances. This indicates a different structure of the fouling.

The 0.4  $\mu\text{m}$  PVDF membrane presented a % Flux decline between 42 and 45 %, and a % FRR < 90 % that suggests an irreversible membrane fouling. This membrane presented the highest amount of accumulated oil and an increased hydrophilicity of 11 %; this membrane changed from hydrophobic to hydrophilic due to the accumulation of polar lipids. This performance indicated a strong fouling, which was expected due to the initial hydrophobic properties and MWCO of the membrane that led to pore blocking and cake formation.

The 1.5  $\mu\text{m}$  PVDF membrane presented a % Flux decline between 23 % to 85 %, along with a % FRR < 90 %. The lowest quantity of oil accumulated was calculated for this membrane. A turbid permeate was observed for the PVDF 1.5  $\mu\text{m}$  membrane. Because of the MWCO of the membrane, some oil droplets could be accumulated in the pores reducing their size and provoking a fast, irreversible, and internal membrane fouling (pore blocking and pore constriction). A small amount of polar lipids were present on the membrane surface, leading to an increase in the hydrophilicity of only 2 %.

Considering all the previous results, the membrane that presented the best oil separation performances was the 500 kDa PAN membrane. This membrane had a high range of  $P_c$ , and the highest initial hydrophilicity level amongst the membranes included in this study. During the concentration experiment, it presented complete oil retention, the lowest % Flux decline, and was the only one with a % FRR > 90 %. Also, the oil accumulated on the membrane (polar lipids) improved the hydrophilicity. In addition to these experimental observations, other works have demonstrated that this type of membrane (in both crossflow and dynamic

filtration modules) is well suited for microalgae suspensions, as it presents less adsorption of cells or cellular compounds (Rossi et al., 2004; Rossignol et al., 1999; Frappart et al., 2011). The same membranes were tested using the crossflow filtration technique, confirming the classification of the membranes with respect to the flux decline described above (Clavijo et al., 2017).

### 3.2. Influence of the hydrodynamics on the filtration of the model solution

The hydrodynamic impact on the filtration performance was studied using the CF and RD modules along with the previously selected 500 kDa PAN membrane. Three different setups were tested in this work and are shown Table 4. The permeate flux measurements versus the TMP were carried out as described in Sec. 2.5 for the CF filtration and RD filtration at 365 rpm. The results collected were compared with the best result obtained for the RD filtration at 800 rpm, described in the previous section.  $J_{\text{lim}}$ ,  $P_{\text{max}}$ ,  $J_c$ , and  $P_c$  values for the three different setups are also presented in Table 4.

For both RD speeds,  $J$  never reached a steady value in the range of TMP studied in this work, therefore  $J_{\text{lim}}$  and  $P_{\text{max}}$  could not be measured. Only the CF filtration presented  $J_{\text{lim}}$  and  $P_{\text{max}}$  values. It can be seen that  $P_c$  increased with the  $v_{\text{max}}$ . The concentration experiments were carried out just after the  $P_c$  determination, as described in Sec. 3.1.2. The TMP of the concentration experiment was 90% of the  $P_c$ . The three setups presented a similar  $J$  evolution having an average value of  $28 \pm 16 \text{ m s}^{-1}$  at a VRR = 1; after this,  $J$  began to decrease with the VRR. Fig. 4 shows the evolution of the normalized  $J/J_w$  versus the VRR with the 500 kDa PAN membrane during the CF and the RD filtrations.

Membrane fouling can be limited by high shear rates (Zhao et al., 2016; Zhang and Ding, 2015; Goh et al., 2018); therefore, the smallest decrease in the  $J/J_w$  ratio was expected for the RD filtration at 800 rpm since the  $\dot{\gamma}_{\text{max}}$  was more than four times larger than the CF filtration and the RD filtration at 365 rpm. On the other hand, the CF filtration and the RD filtration at 365 rpm had the same  $\dot{\gamma}_{\text{max}}$  value; however, the CF filtration presented a laminar regime while the RD filtration had a turbulent one. This turbulent flow can more efficiently enhance the convection of particles away from the membrane (Frappart et al., 2011; Du et al., 2017; Zhang and Ding, 2015; Abid et al., 2017; Goh et al., 2018). As can be seen in Fig. 4,

the  $J/J_w$  ratio decreased progressively with the VRR for the three different setups. Table 5 presents % Flux decline and  $q_{\text{VRR}}^{\text{mb}}$  measured during the concentration experiment at a  $\text{VRR} = 3.8 \pm 0.3$ .

The retention rate and the cleanability were higher than 97% and 90%, respectively, for all experiments; the latter suggests a totally reversible membrane fouling. The CF filtration presented the highest  $q_{\text{VRR}}^{\text{mb}}$  indicating the presence of a strong fouling on the membrane. As mentioned above, this low performance of the CF filtration can be explained by its laminar regime which allows a large accumulation of droplets on the membrane. The RD filtration at 365 rpm led to a  $q_{\text{VRR}}^{\text{mb}}$  value lower than at 800 rpm but the same flux decline. This may be due to different fouling mechanisms.

### 3.2.1. Effect on the hydrodynamics on the DSD

The applied pressure in the system has a huge impact on the oil droplets (Hong et al., 2003). In particular, coalescence is the joining of two or more (micron and submicron) oil droplets to form a single droplet with a larger diameter than the original (Chakrabarty et al., 2008). The effect of the CF filtration and the RD filtration on the coalescence or division of the oil droplets during the emulsion filtration was followed using the technique described in Sec. 2.7. The droplet size can be represented as a differential distribution, which represents the frequency of each size. The mode is the most repeated droplet diameter and corresponds to the highest point of the differential curve (Flügel, 2010). The evolution of the retentate volume DSD as a function of the VRR is shown in Fig. 5. It was not possible to measure the DSD in the permeates because of the low concentration of oil droplets.

The DSD presented a multimodal distribution, but the DSD during CF filtration changed the least. The major mode diameter during the CF filtration was maintained around  $1.28 \pm 0.01 \mu\text{m}$ . The major mode diameter during the RD filtration at 365 rpm increased with the VRR from 1.59 to 3.93  $\mu\text{m}$ . The volume fraction of the droplets with a diameter around 1.5  $\mu\text{m}$  decreased and the volume fraction of the droplets with a diameter above 4  $\mu\text{m}$  increased with VRR, indicating coalescence. On the contrary, during the RD filtration at 800 rpm the droplets with a diameter around 15  $\mu\text{m}$  disappeared, indicating droplet division. The differences in the two DSD from the RD filtration were due to the different shear rate applied near the membrane. It is possible that the shear rate at 365 rpm

( $16\,000\text{ s}^{-1}$ ), facilitated the oil droplet coalescence, while the higher shear rate at 800 rpm ( $66\,000\text{ s}^{-1}$ ) divided the oil droplets. The laminar flow during CF filtration did not significantly affect the DSD.

The RD filtration offered better performances over the CF filtration because it limited membrane fouling, thus achieving relatively high ranges of  $P_c$  and permeation flux. During the concentration experiment, this RD filtration presented an almost complete retention of lipids and a full cleanability. However, oil droplet coalescence seemed to be favored at 365 rpm, while droplet breakage tended to occur at 800 rpm. This may have an impact on the fouling mechanisms. These results confirm former studies which demonstrated that the RD filtration presents increased performances compared to the CF filtration when applied to microalgae fractionation (Frappart et al., 2011; Lorente et al., 2017).

### 3.3. Filtration of real microalgae extract

Two *Parachlorella kessleri* cultures ( $1\text{ g L}^{-1}$ ) were used to produce two batches of clarified supernatant, SN<sub>1</sub> and SN<sub>2</sub>, dedicated to filtration tests at the pilot scale. The supernatants were filtered using the RD module equipped with a 500 kDa PAN membrane at 800 rpm. The composition of the supernatants, retentates (RET<sub>1</sub> and RET<sub>2</sub>) and permeates (PERM<sub>1</sub> and PERM<sub>2</sub>) are described in Table 6. The variations between SN<sub>1</sub> and SN<sub>2</sub> are due to differences in biomass and pretreatment (Liu et al., 2018).

After critical pressure measurements, the chosen TMP (90 % of the  $P_c$ ) were 0.4 bar and 0.7 bar for SN<sub>1</sub> and SN<sub>2</sub>, respectively. The normalized representation of the permeate flux of SN<sub>1</sub>, SN<sub>2</sub>, and model solution versus the VRR with the 500 kDa PAN membrane in the RD module ( $\dot{\gamma}_{\max}=66\,000\text{ s}^{-1}$ ) and CF module ( $\dot{\gamma}_{\max}=16\,000\text{ s}^{-1}$ ) are presented in Fig. 6. The  $J/J_w$  ratio was used for comparison due to the inherent variability of the individual membrane pieces.

The flux from the RD filtration with the supernatants was two times (SN<sub>1</sub>) or three times (SN<sub>2</sub>) superior to the water flux, which was not the case of the model solution. This means that during the filtration of the supernatants, the membrane permeability and hydrophilicity were strongly enhanced. Additionally, minimal membrane fouling was observed, thus reducing the needed time to reach the highest VRR. These changes in the



membrane properties may be due to the adsorption of some of the polar compounds (possibly proteins or polar lipids) present in the supernatants. Therefore, the calculation of the membrane cleanability was not realistic under such conditions. The  $J/J_w$  values in both cases are higher than those presented by Lorente et al. (2017) ( $J/J_w < 0.2$ ). Their choice of the TMP (5 bar, probably above the  $P_c$ ) coupled with a shear rate that may induce droplets division, and the membrane nature (PES or PVDF), have probably limited the flux performance. These results demonstrate the crucial choice of the filtration operating conditions.

The particle size distribution of the supernatants show that the particle diameter decreases very slightly, without significant changes (not shown). The retention rates of lipids, proteins, polysaccharides, and salts were calculated for the RD filtration at VRR=2. For both supernatants the lipids are totally retained, while the salts have a retention rate between 11 % and 15 %. The retention rates of proteins for SN<sub>1</sub> is 100 %, while for the SN<sub>2</sub> is 78 %. The polysaccharides are retained 48 % for SN<sub>1</sub> and 52 % for SN<sub>2</sub>. These percentages depend on the supernatant and the pretreatment steps. They are not far from the retention rates obtained in CF filtration. Finally, the RD and CF filtrations of supernatants were compared confirming that the RD filtration presents better flux and  $J/J_w$  performance than the CF filtration.

#### 4. Conclusions

This study first evaluated different commercial membranes, filtration regimes, and shear rates using an emulsion that simulates the characteristics of real microalgae extracts. The 500 kDa PAN membrane presented the best performances (oil retention, water permeation and cleanability) and the RD filtration offered better performances than the CF filtration. The performance of the RD module was then evaluated with real microalgae extracts, confirming those results. The importance of the operating conditions was demonstrated. Further investigation will allow finding the best pretreatment and filtration coupling for lipids and hydrophilic compounds separation.

Supplementary Material for this work can be found with the online version of the paper. It includes the preparation and characteristics of the

*Parachlorella kessleri* culture used in this work and the parameters (TMP, fluxes and permeabilities) registered during the filtration of real supernatants.

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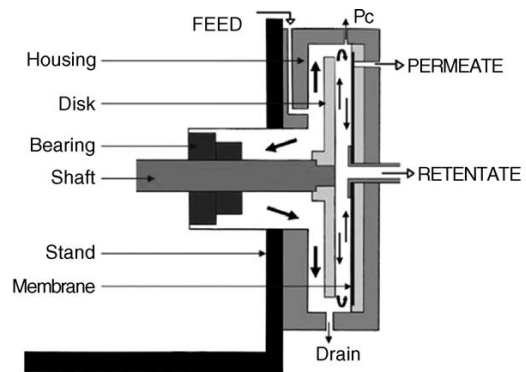
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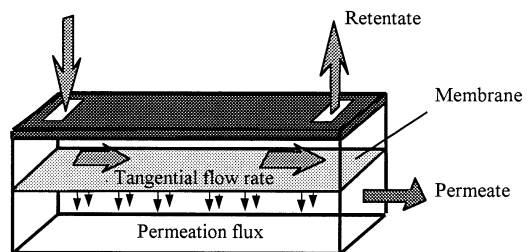


## Figure Captions

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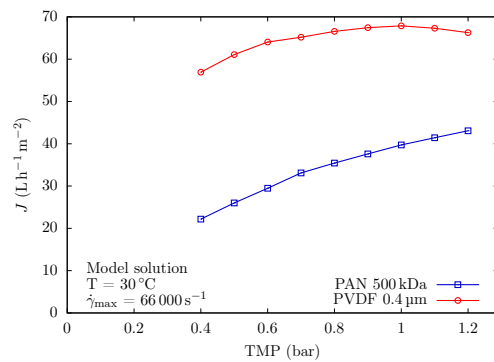


(a) Cross-sectional view of the rotating disk module (Frappart et al., 2006).

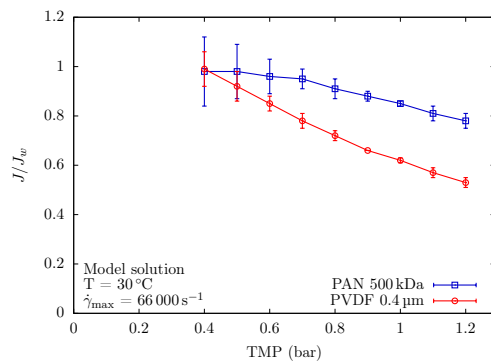


(b) Schematic of the crossflow module.

Figure 1: Filtration modules used in this study.

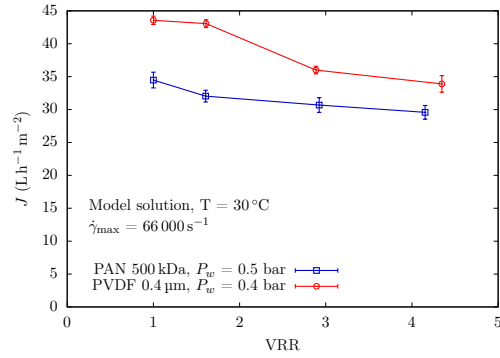


(a) Flux ( $J$ ).

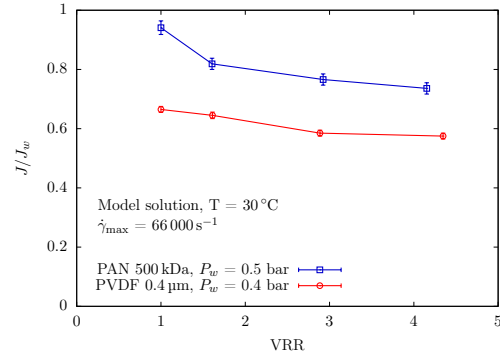


(b) Normalized flux ( $J/J_w$ ).

Figure 2: Flux ( $J$ ) and normalized flux ( $J/J_w$ ) of the model solution permeate versus TMP for the PAN 500 kDa and PVDF 0.4  $\mu\text{m}$  membranes on the RD module with  $\dot{\gamma}_{\text{max}}=66\,000\text{ s}^{-1}$ . The error bars correspond to the standard deviation calculated from three independent measurements.



(a) Flux ( $J$ ).



(b) Normalized flux ( $J/J_w$ ).

Figure 3: Evolution of the permeate flux ( $J$ ) and its normalized representation ( $J/J_w$ ) versus the VRR for the PAN 500 kDa and PVDF 0.4  $\mu\text{m}$  membranes during the RD filtration ( $\dot{\gamma}_{\text{max}}=66\,000\text{ s}^{-1}$ ). The error bars correspond to the uncertainty propagation from three independent measurements.

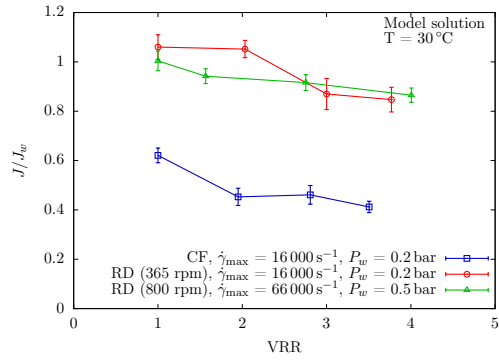
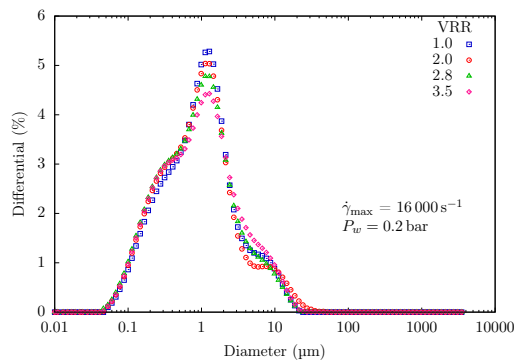
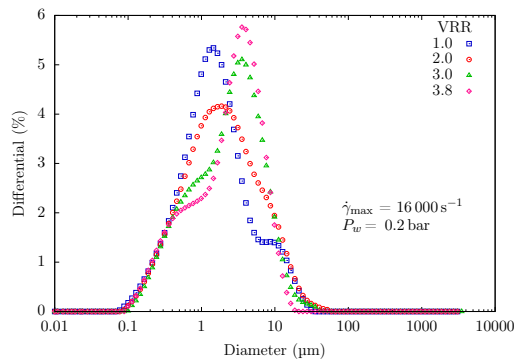


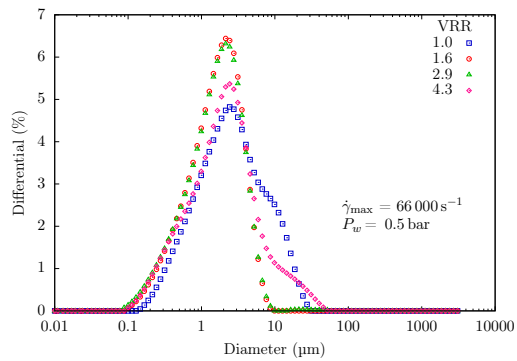
Figure 4: Normalized representation of the permeate flux versus the VRR with the 500 kDa PAN membrane at 30 °C during the RD and the CF filtrations. The error bars correspond to the uncertainty propagation from three independent measurements.



(a) Crossflow filtration.



(b) Rotating disk filtration at 365 rpm.



(c) Rotating disk filtration at 800 rpm.

Figure 5: Volume droplet size distribution as a function of the VRR in the retentate sample using the 500 kDa PAN membrane for the CF and RD filtrations.

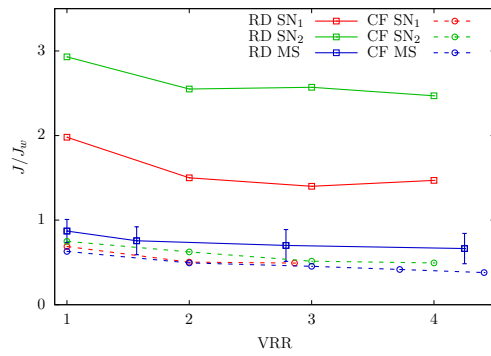


Figure 6: Normalized representation of the permeate flux of the supernatants, SN<sub>1</sub> and SN<sub>2</sub>, and the model solution (MS) versus the VRR with the 500 kDa PAN membrane and both filtration modules; RD module ( $\dot{\gamma}_{\max}=66\,000\text{ s}^{-1}$ ) and CF module ( $\dot{\gamma}_{\max}=16\,000\text{ s}^{-1}$ ) The error bars correspond to the uncertainty propagation from three independent measurements.

## Table Captions

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Table 1: Working parameters selected for both the RD and CF modules. Parameters for the RD module were obtained from Eq. (1), while Eq. (2) was used for the CF parameters.

Module	$v_{\max}$ ( $\text{m s}^{-1}$ )	$\dot{\gamma}_{\max}$ ( $\text{s}^{-1}$ )
RD (365 rpm)	2.5	16000
RD (800 rpm)	5.4	66000
CF	2.0	16000

Table 2:  $J_w$  (1 bar),  $J_{\text{lim}}$ ,  $P_{\text{max}}$ ,  $J_c$ , and  $P_c$  values for the different membranes studied during the RD filtration with  $\dot{\gamma}_{\text{max}} = 66\,000\text{ s}^{-1}$  at  $30\text{ }^\circ\text{C}$ . The standard deviation ( $\sigma$ ) is calculated from three independent measurements.

Polymer	MWCO	$J_w \pm \sigma$ ( $\text{L h}^{-1} \text{m}^{-2}$ )	$J_{\text{lim}} \pm \sigma$ ( $\text{L h}^{-1} \text{m}^{-2}$ )	$P_{\text{max}}$ (bar)	$J_c \pm \sigma$ ( $\text{L h}^{-1} \text{m}^{-2}$ )	$P_c$ (bar)
PES	200 kDa	$96 \pm 2$	$62 \pm 5$	1.0	$36 \pm 4$	$< 0.4$
PAN	500 kDa	$75 \pm 3$	–	–	$29 \pm 8$	0.5–0.6
PVDF	0.4 $\mu\text{m}$	$123 \pm 11$	$64 \pm 20$	0.6	$57 \pm 20$	$< 0.4$
PVDF	1.5 $\mu\text{m}$	$82 \pm 8$	$65 \pm 13$	0.8	$55 \pm 13$	0.5–0.6

Table 3: % Flux decline, % FRR,  $q_{\text{VRR}}^{\text{mb}}$ ,  $\theta_w^0$ , and  $\theta_w^{\text{VRR}}$  at a VRR of  $4.3 \pm 0.1$ , during the RD filtration at  $\dot{\gamma}_{\text{max}}=66\,000\text{ s}^{-1}$ , and  $30\text{ }^\circ\text{C}$ .  $q_{\text{VRR}}^{\text{mb}}$  is reported with uncertainty propagation, while  $\theta_w^0$  and  $\theta_w^{\text{VRR}}$  have standard deviations ( $\sigma$ ) calculated from ten independent measurements.

Polymer	MWCO	Flux decline (%)	FRR (%)	$q_{\text{VRR}}^{\text{mb}}$ ( $\text{g m}^{-2}$ )	$\theta_w^0 \pm \sigma$ ( $^\circ$ )	$\theta_w^{\text{VRR}} \pm \sigma$ ( $^\circ$ )
PES	200 kDa	75–84	20	$134 \pm 19$	$79.4 \pm 0.5$	$57.3 \pm 0.6$
PAN	500 kDa	14–40	100	$378 \pm 15$	$75.0 \pm 2.4$	$69.2 \pm 2.1$
PVDF	0.4 $\mu\text{m}$	42–45	72	$429 \pm 18$	$95.1 \pm 1.2$	$84.5 \pm 0.5$
PVDF	1.5 $\mu\text{m}$	23–85	47	$6 \pm 18$	$82.3 \pm 0.7$	$80.6 \pm 0.7$

Table 4:  $v_{\max}$ ,  $\dot{\gamma}_{\max}$ ,  $J_{\text{lim}}$ ,  $P_{\max}$ ,  $J_c$ , and  $P_c$  values for the 500 kDa PAN membrane at 30 °C during the CF and the RD filtrations. The standard deviation ( $\sigma$ ) is calculated from three independent measurements.

Module	$v_{\max}$ ( $\text{m s}^{-1}$ )	$\dot{\gamma}_{\max}$ ( $\text{s}^{-1}$ )	$J_{\text{lim}} \pm \sigma$ ( $\text{L h}^{-1} \text{m}^{-2}$ )	$P_{\max}$ (bar)	$J_c \pm \sigma$ ( $\text{L h}^{-1} \text{m}^{-2}$ )	$P_c$ (bar)
CF	2.0	16000	$19.7 \pm 4.6$	0.4	$17 \pm 2$	0.2–0.3
RD (365 rpm)	2.5	16000	–	–	$33 \pm 6$	0.3–0.4
RD (800 rpm)	5.4	66000	–	–	$31 \pm 3$	0.5–0.6

Table 5:  $\dot{\gamma}_{\max}$ , % Flux decline and  $q_{\text{VRR}}^{\text{mb}}$  (reported with uncertainty propagation) measured during the concentration experiment with the 500 kDa PAN membrane and both modules at the final average VRR =  $3.8 \pm 0.3$  and 30 °C.

Filtration module	$\dot{\gamma}_{\max}$ ( $\text{s}^{-1}$ )	Flux decline (%)	$q_{\text{VRR}}^{\text{mb}}$ ( $\text{g m}^{-2}$ )
CF	16000	59	$676 \pm 231$
RD (365 rpm)	16000	13	$24 \pm 23$
RD (800 rpm)	66000	14	$378 \pm 15$

Table 6: Composition of the supernatants (SN<sub>1</sub> and SN<sub>2</sub>) of bead-milled *Parachlorella kessleri* cultures before filtration, and composition of the retentates (RET<sub>1</sub> and RET<sub>2</sub>) and permeates (PERM<sub>1</sub> and PERM<sub>2</sub>) sampled at VRR=2 with the RD module at  $\dot{\gamma}_{\max}=66\,000\text{ s}^{-1}$ . The standard deviation ( $\sigma$ ) was calculated from three independent measurements.

	Dry matter (g L <sup>-1</sup> )	Lipids (g L <sup>-1</sup> )	Proteins (g L <sup>-1</sup> )	Sugar (g L <sup>-1</sup> )	Conductivity ( $\mu\text{S cm}^{-1}$ )	pH
SN <sub>1</sub>	2.00 ± 0.10	0.16 ± 0.02	0.38 ± 0.05	0.45 ± 0.04	1049 ± 8	7.6 ± 0.1
RET <sub>1</sub>	2.80 ± 0.05	0.33 ± 0.05	0.62 ± 0.01	0.42 ± 0.01	1231 ± 6	7.6 ± 0.1
PERM <sub>1</sub>	1.44 ± 0.09	0.00 ± 0.00	0.00 ± 0.02	0.22 ± 0.00	1092 ± 6	7.6 ± 0.1
SN <sub>2</sub>	1.34 ± 0.10	0.17 ± 0.03	0.19 ± 0.03	0.32 ± 0.07	993 ± 20	7.2 ± 0.1
RET <sub>2</sub>	1.76 ± 0.04	0.30 ± 0.03	0.23 ± 0.01	0.33 ± 0.01	1119 ± 6	7.3 ± 0.1
PERM <sub>2</sub>	1.00 ± 0.04	0.00 ± 0.00	0.05 ± 0.14	0.16 ± 0.02	947 ± 5	7.3 ± 0.1