HARVESTING *CHLORELLA VULGARIS* BY MEMBRANE FILTRATION

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Abstract - For membrane processes, pumping usually costs most. In classical Rayflow filtration, operating conditions must be optimized to limit membrane clogging. In this article, we study the use of dynamic filtration, where the shear rate is independent of the feed rate, as an interesting alternative to achieve flow and high final concentrations and reduction of energy cost from pumping. The tests were carried out in standard Rayflow filtration under similar operating conditions. Conventional tangential filtration assays, microfiltration (PES 0.05 microns) or ultrafiltration (40 kDaPAN), show a constant and linear reduction of the flow and the ability to reach maximum concentrations of microalgae of about 90g/L.

Key words - dewatering; harvesting, filtration, microfiltration, ultrafiltration, treatment of waste water by microalgae.

1. Introduction

Harvesting is a critical step of microalgae exploitation as it can represent 20 to 30% of the overall process cost [1-4]. For centrifugation, the standard technique used for niche markets [5-7], should be excluded for mass markets because too much expensive and energy consuming in favour of flocculation or membranes processes for instance according to the dewatering rate needed [7].

Membrane separation processes could be now a possible alternative to centrifugation for their energy consumption to be between 0.2 and 3 kWh/m^3, and mainly due to pumping [8] which is much lower than centrifugation consuming between 1 and 10 kWh/m^3 [9]. Furthermore, this method of separation would achieve concentrations *as high as* centrifugation, of the order of 150 g/L [10]. In the field of filtration medium, sand bed filtration showed some effective microalgae retention during pretreatment of sea water in the presence of algal blooms [11]. However, it does not seem to be applied to the microalgae harvestings in ceretention is both dependent on the initial concentration of cell and time, and limited to relatively large size cells (>20 microns). Thus, the filtration media is limited to screening cells that are larger than 40μm.The process is relatively simple and requires only the use of cloth sieve to achieve separation at low pressure gradients (slight over pressure or vacuum) with draining tables or rotating drums. However, to maintain filtration rates, it is necessary to implement a scraping of the cake to limit the increase of the specific resistance of the cake in the time. It may also be necessary to provide a pre-filter layer to improve the operation [12]. In terms of performance, it seems possible to achieve solids concentrations of about 50 to 300$g_{MS}.L^{-1}$ (~5 to 30%DM) for energy cost of between 0.3 and 2$kWh.m^{-3}$ [13].

Unlike the previous case, the membrane separation relates to filter media whose cut-off threshold is lower than one micrometer. Membrane processes are mainly used to separate molecules or ionic species in solution: this is the case of ultrafiltration, nanofiltration, reverse osmosis or electro-dialysis. However, they may also allow the separation of particles or micro-organisms in suspension in a liquid by the use of microfiltration membranes (slightly less than one micrometer pore size). For membrane processes, pumping usually costs most. In classical cross flow filtration, optimized operating conditions must be implemented to limit membrane clogging [14]. First, given the size of the cells, microfiltration seems most appropriate. Thus, a membrane is used for the membrane vinylidine fluoride PVDF 0.1microns. With this membrane, it can be expected to have very high initial flow ($600L/h^{-1}m^2$), however once it is stabilized to only 140 $L.h^{-1}m^2$, or a loss of 75% of the flow initial [14]. This loss of high flows often gets between 75 and 80% [15] to a PVDF membrane but with 0.22μm cut-off. This loss of flow is often the characteristic of the micro under going clogging due to mechanical blockage of the pores. This is why the use of ultrafiltration was privileged.

And in similar conditions for the same filtration and stabilization time an ultrafiltration membrane Polyacrylonitrile (PAN) 40kDa, provides a starting flow certainly to $270L.h^{-1}m^2$, however, its stabilized flow is $120L.h^{-1}m^2$ which approximates the results of 0.1μm PVDF, and this implies a loss of only 55% of the flow compared to 75% of the PVDF [9, 14, 17]. From the comparison of different filtration membranes [14], the intrinsic resistances of microfiltration membranes are very low compared with ultrafiltration membranes, where higher flow at the start of experiment. Then, the resistance due to clogging is either lower or equivalent ultrafiltration compared with microfiltration membranes where the weakest builds up in ultrafiltration, which may be decisive for the cleaning step.

The sizes of microalgae filtering are a few microns, the interesting membranes will be the 0.05μm PES (polyethersulfone) and PAN 40 kD, using a microfiltration membrane justifies originally by the initial willingness to use an anti-clogging specific membrane separation system.

2. Experimental

2.1. Strain & growth conditions

Chlorella vulgaris is a eukaryotic unicellular green fresh water alga. It' cells are spherical or ellipsoidal with a mean diameter of around 4–5μm. The strain used in the study was *C. vulgaris* 211–19 (SAG, Germany), chosen forits ability to assimilate both ammonium (NH_4^+) and nitrateions (NO_3^-), with a preference for ammonium, The strain was, therefore, grown in two media. The first one, with NH_4^+ ions as nitrogen source, was adapted from the autotrophic Sueoka's medium described by Harris. The nutrient concentrations in the mediagiven in Table 1 were adjusted so as to reach a biomass concentration of $2g_{DM}L^{-1}$ (DM, dry matter) in a batch culture without mineral limitation.

Table 1. *Ionic composition of the two culture media of Sueoka (mg.L^{-1}).*

Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}
230	28.7	243.9	13.9	6.8	493.1	-	610	54.6	69.8

All of cultures are added Hutner's solution as nutrient matter.

2.2. Membrane processes

For these tests, the cultures used were those from the scobalite. The test procedures were on the filtration systems in Figure 1 and Figure 2 in particular with a permanent temperature control:

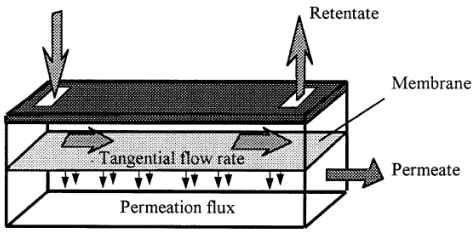

Figure 1. *Schematic diagram of filtration system of Rayflow*

The experiences were implemented with module below:

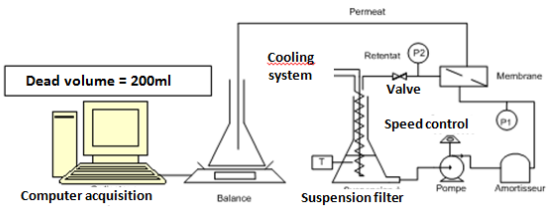

Figure 2. *Schema of filtration experimentals in lab*

The protocol was been accomplished step by step below:

Installation of the membrane, and rinsing with demineralized water for an hour in light filtration (PTM=0.05 to 0.1 bar). After draining the system, measuring the permeability osmosis water. Emptying the circuit and supply of the suspension to be filtered at the desired flow rate (including the modulus Rayflow since the flow rate affects the tangential speed at the membrane).

For the determination of optimal conditions of filtration tests, each membrane was tested by a pressure rise in steps of 0.1 bar. After power is a given pressure, waiting for the stabilization of the stream with total recycling of the permeate. At steady flow, the pressure of a bearing increased. As soon as the flow limit is reached, the manipulation ends. This type of test is used to determine the optimal operating pressure. Then, to the rise in concentration of test: after rising to the previously determined optimum pressure by pressing the pressure valve against present on both circuits, waiting for the stabilization of the stream with total recycling of the permeate. Once the flow is stable, the concentration factor increases by withdrawing the permeate. Upon completion of handling, rinsing of the water network and the measurement of permeability were necessary to do.

The system is a vector tangential filtration one (Rayflow 100 Orelis) equipped with a flat rectangular membrane of 100cm². In its geometrical conditions (ℓxLxe: 7.5cmx14.5cmx0.5mm), there is a correspondence between the Reynolds number and the internal speed as R_e= 1000 to v_{in}= 1m/s. In this "standard" system, the shear rate at the membrane is dependent on the speed in the internal module (thus the pumping rate) of (1) and the trans-membrane pressure (TMP) is calculated according to (2) [9]:

$$\gamma = \frac{8}{e} v_{internal} \quad (1)$$

$$TMP = \frac{P_{in} + P_{out}}{2} - p_f \quad (2)$$

In where:

γ: the shear rate, s^{-1};

$V_{internal}$: the flow velocity in the module, $m.s^{-1}$;

e: the internal thickness of the module, m;

TMP: the trans-membrane pressure, bar;

p_{in}, p_{out}: input and output pressure of the module, bar;

p_f: the filtrate side pressure, bar.

The volume of the permeate flux density (J) is calculated from the equation (3) [9]:

$$J = \frac{D}{\delta} . \ln \frac{C_m - C_p}{C_o - C_p} \quad (3)$$

Where:

J: The permeate flux to the instantaneous temperature T (Ji, T) is expressed as L/h.m², is defined as the permeate flow rate (Q_p) filtration unit are of the membrane (S_f);

C_o, C_m and C_p represent the solute concentrations, respectively in the solution, to the wall and in the permeate, $g.L^{-1}$;

D: the diffusion coefficient;

δ: the thickness of the boundary layer, m;

D/δ: the mass transfer coefficient (k).

2.3. Choice of membranes

The bibliography on microalgae crop showed that for many strains, the use of ultrafiltration (UF) membranes hydrophilic, polyacrylonitrile (PAN), for example, was to be preferred because it limited adhesion agents adhesive and gave stabilized flow comparable to those of microfiltration membranes (MF) [15]. However, the MF membranes with higher initial flux, a tangential MF membrane 0.05µm was tested. No PAN membrane was available, the choice is oriented towards a polyethersulfone membrane (PES), relatively hydrophilic, and widely spread on an industrial scale. Finally, the two membranes are tested:

- AUF with PAN membrane 40kDa (IRIS 3038, Orelis Environment -Novasep);

- An MF with PES membrane to 0.05microns (Nadir MP 005, Alting).

2.4. Analysis

Cell concentration is expressed on a DM basis. The stability of the PBR operation was monitored by checking the constancy of the cell concentration in the PBR, and by assay of the total chlorophylls and carotenoids.

Biomass dry weight was determined by gravimetry. The sample was filtered through a rinsed glass fiber filter (WhatmanGF/F), pre-dried, and weighed. The filter (sample filtered) was dried for 24h at 105ºC, cooled in a desiccator, and weighed again. Measurement was computed as the average of a triplicate, and the experimental error was estimated as the average absolute deviation of the experimental values.

3. Results and discussion

3.1. Ultrafiltration of Chlorella vulgaris on PAN membrane 40kDa

Primarily crop test, it is necessary to first define suitable operating conditions, which will give relatively high permeation flux and limited membrane clogging. For this purpose, the tests for rising of the trans-membrane pressure (TMP) are made at different speeds in order to select a speed and a working pressure. The results are given in Figure 3. For lower traffic speeds $1ms^{-1}$, limit the flow remains relatively low, less than $60L.h^{-1}.m^2$. However, the flow limit for a speed of $2ms^{-1}$ is significantly higher and amounted to $100L.h^{-1}.m^2$, and changes in flows with TMP deviate slightly from linearity up a value of 0.3bar which indicates a moderate blockage. Under these conditions, it is retained as operating conditions a speed of $2ms^{-1}$, maximum acceptable speed for Rayflow module and a pressure of 0.3 bar.

- FC: Factor of concentration

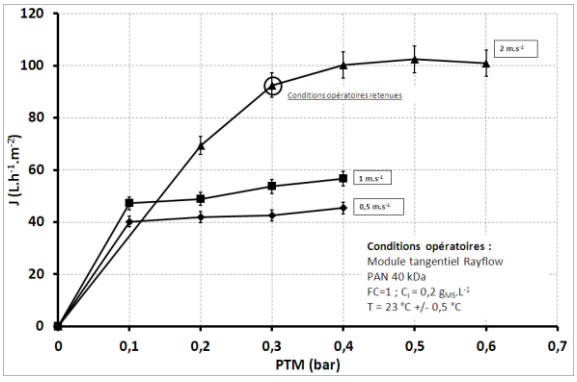

Figure 3. *Ultrafiltration of Chlorella vulgaris suspension concentration ($0.2g_{MS}.L^{-1}$, total recycling); evolution of permeate flux as a function of TMP for various flow velocities in the tangential modulus Rayflow*

To evaluate the performance of the membrane in concentrations of conditions close to those that could be obtained by PBR high concentration, *Chlorella vulgaris* suspension was grown in batch mode at concentrations of levels ranging from 0.32 to $0.55g_{MS}.L^{-1}$ (maximum value has been reached on the PBR Scobalite in batch mode). Following these cultures, a volume of 100L was withdrawn from the reactor and then centrifuged (3600g, 20 DRAVX Roussel et Robatel) to recover a volume of 10L of concentrated harvest (FC = 10). Monitoring the over flow has verified the absence of cells. Thus, three trials have been carried out at different initial concentrations (3.2; 4.8 and $5.5g_{MS}.L^{-1}$)

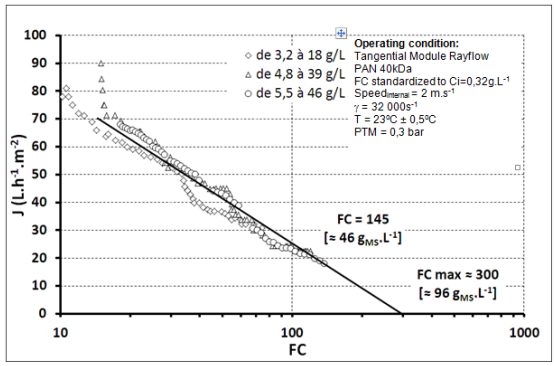

Figure 4. *Ultrafiltration of Chlorella vulgaris suspension; evolution of the permeate flux versus the logarithm of the factor of concentration in the tangential modulus Rayflow*

The results are shown in Figure 4 which carries the permeation flux J as a function of the logarithm of the mass of the cell concentration factor. It shows that, regardless of the initial concentration of cells, the permeate flux drops linearly with the logarithm of the concentration factor and that although the tests are different, the three curves on the tests are quite similar. Referring to Equation 3, we can estimate the maximum concentration reached by extra polating the average right at zero flow. Thus, these tests show that this concentration is here equal to about $96g_{MS}.L^{-1}$, a factor of concentration of the order of 300.

3.2. Microfiltration of Chlorella vulgaris on PES membrane 0.05µm

A similar study was carried out on the microfiltration membrane PES 0,05µm. Figure.5 allows to establish suitable conditions for the concentration of the suspension of *Chlorella vulgaris*. The limits are slightly higher flow for this membrane, but the difference with the flux of the UF membrane cannot be considered significant since the cell concentration was lower. However, similar gaits are served for speeds of 0.5 and $1m.s^{-1}$ whose performances are close, and a flow limit higher than $2m.s^{-1}$. Unlike the PAN membrane, at this speed of 2 ms^{-1}, the flow limit is reached at 0.2 bar. This calls for the same reasons mentioned above work up to 0.1 bar.

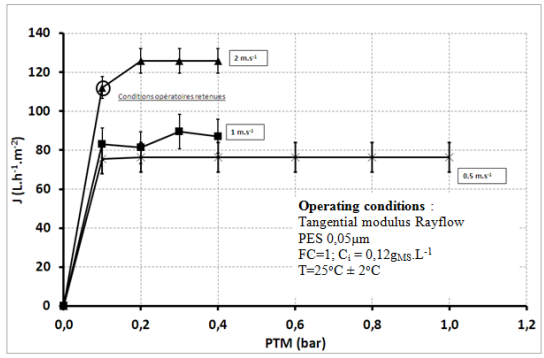

Figure 5. *Microfiltration of Chlorella vulgaris suspension constant concentration ($0.12g_{MS}.L^{-1}$, total recycling); evolution permeate flux as a function of TMP for various flow velocities in the tangential modulus Rayflow*

Concentration mode (Figure 6), the decrease of the flow quickly becomes linear with the logarithm of the concentration factor. However, the flow obtained

concentration equivalent biomass are lower; in this case (for example FC = 10 in Figure 4, the cell concentration is of the order of $3.2 g_{MS}.L^{-1}$ for a neighbor flux of $80 L.h^{-1}.m^2$ while in Figure 6, FC = 10 at a concentration of about $1.2 g_{MS}.L^{-1}$, the flow is already lower at $70 L.h^{-1}.m^2$). This reflects a lower adequacy of microfiltration to this type of separation. However, the value of the maximum concentration that could be achieved by extrapolating flow at zero remains the same order of magnitude as that obtained with the PAN membrane with $84 g_{MS}.L^{-1}$.

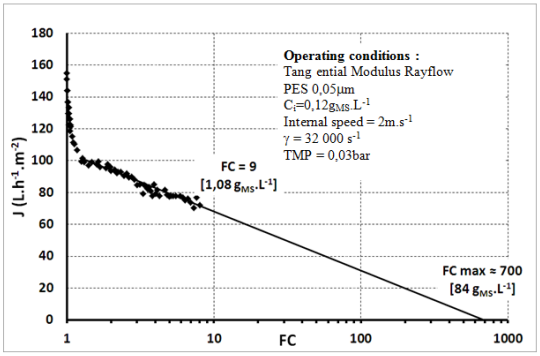

Figure 6. *Microfiltration of Chlorella vulgaris suspension; evolution of the permeate flux versus the logarithm of the factor of concentration in the tangential modulus Rayflow*

4. Conclusions

For both types of membrane, the flow rate was set to $2 ms^{-1}$ (same shear rate at $32\,000 s^{-1}$) and the critical flow of $110 L.h^{-1}.m^2$ and $90 L.h^{-1}.m^{-2}$ respectively were obtained at 0.1 bar to 0.3 bar and PES membrane for the PAN membrane. In all cases, the retention of the cells was complete.

The tests of concentration on the two membrane materials show a linear decrease of the flow with the logarithm of the factor of concentration. Given the initial value of the concentration of microalgal cells, the maximum achievable estimated concentrations are similar both cases and are respectively 84 and $96 g_{MS}.L^{-1}$ to the PES membrane and the PAN. These results confirm the information obtained in the literature review for the single-stage tangential filtration. They are promising, since even without a high permeation flow control (backwash for example), these concentrations are of the order of magnitude of those required for wet post-treatment (60-100 $g_{MS}.L^{-1}$). Its highest concentration in performance ($>60 g_{MS}.L^{-1}$) is to be determined the best positioning for this technology particularly in case of insertion in double concentration stage process for obtaining biomass concentrations above $100 g_{MS}.L^{-1}$. However, the result of this conventional tangential filtration is sufficient in comparison with one of reference.

Acknowledgements

The author thanks the French Professors (PhD's Prof., GEPEA, University of Nantes) and Alexis Paszkier (Engineer, Grand University of Technology and Science in Paris) and colleagues at College of Technology – University of Danang for their contribution to advice, guides and strains.

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(The Board of Editors received the paper on 02/26/2015, its review was completed on 03/30/2015)