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Silicon carbide (SiC) membranes in œnology

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ABSTRACT

In a winery, clarification and stabilization steps by crossflow microfiltration are limited by fouling phenomenon which reduces production flows and can alter the aromatic potential of wines, forcing professionals to use several successive filtration steps. The objectives of this industrial-scale study are to (i) introduce SiC membranes at different vinification steps (ii) evaluate the hydraulic and retention performances of SiC membranes and (iii) carry out a comparative study between SiC membranes and polymeric hollow fibers commonly used in the wine industry. It appears that SiC membranes are able to filter diverse matrices with very satisfactory production flow and retention efficiency. This particular process was optimized by developing an efficient regeneration protocol. The clarification and stabilization of the matrices by SiC membranes allowed (i) the production of clear and brilliant wines, (ii) the retention of wine microorganisms, (iii) higher production flows than hollow fibers, while conserving wines interest compounds, (iv) and the filtration of matrices that cannot be processed by hollow fibers.

1. Introduction

The presence of a cloudiness or deposits has always been perceived by different consumers as a defect or alteration of the wine. Over the centuries, the various discoveries on the origins of wine have shown that the means of filtration have constantly evolved [30]. Wine was first filtered with tissues, then industrial filters appeared, and nowadays filtered by alluvial filtration, by plates, or more recently on filtration membranes. Filtration is not only intended to avoid the presence of a cloudiness altering the visual quality of a wine, but also to ensure the microbiological and organoleptic stability of a wine, sometimes replacing certain techniques or process used in the cellar. More generally, the nature of the materials to be eliminated and their concentrations vary according to the purpose of the filtration [37] but also according to the stages of vinification. The main challenge of filtration in œnology is to fulfill these two objectives while respecting the intrinsic characteristics of the wine: filtration must remain neutral with respect to the organoleptic properties of the wine. Global warming is having an increasingly marked influence on vine phenology, grape composition and eventually affects vinification, microbiology, wine chemistry and

sensory aspects of the wine [29]. It also constitutes a major challenge in adapting œnological practices and implementing new techniques [18]. The combination of these new conditions tends to lead to a difficult problem for professionals to manage, which is to produce “zero defect” wines adapting to the increasing emergence of lower doses of bisulfite (SO₂) in wines while controlling the increase in pH due to global warming, allowing spoilage microorganisms to develop and lead to organoleptic deviations [1]. It was therefore essential to find solutions to adapt to these new challenges, one of them being microfiltration, which limits wine losses to 0.1 to 0.5% by volume [12]. In addition to a great simplification of the wine processing chain, microfiltration offers a number of other advantages, such as the elimination of diatomaceous earth which is known to be harmful to the user and the environment. With low-filtering and/or complex matrices (lees, barrel aging, treated wine, fined wine, etc.) inducing higher membrane fouling, loss of flow, detrimental to the winemaker, is sometimes observed, and can cause macromolecular retentions; [4,5] which have a negative impact on wine quality. Indeed, membrane fouling leads to the formation of adsorbed layers or deposits that may be difficult to remove during the regeneration phase of the membranes. Consequently, these limitations can

Abbreviations: CIP, clean in place; PES, polyethersulfone; PP, polypropylene, PVDF, polyvinylidene fluoride; TMP, transmembrane pressure; SiC, silicon carbide; VCF, volumic concentration factor.

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sometimes lead to additional operating costs, increased water usage and effluent generation. It appears necessary to develop a membrane that can ensure, in very few operations, the stabilization of wines in terms of clarity, the microbiological and organoleptic levels by reducing the use of chemical inputs (SO₂), and is capable of resisting fouling while offering high production flows. Currently, membranes (ceramic or polymeric) are mainly used just prior to bottling, where the wine is the least loaded, and give low fluxes. Indeed, one of the explanations is that they have a low porosity ($\leq 30\%$) [21,27] which limits the efficiency of industrial installations (production rate) and forces them to use high backwash frequencies during the filtration cycles. This fouling is mainly caused by the adsorption of wine macromolecules such as phenolic compounds, polysaccharides (including mannoproteins) or proteins on some membrane materials (alumina, PP, PVDF, PES) [5,6,15,16,33]. Polymeric membranes are the most common membranes used in oenology because they are less expensive than ceramic membranes [2]; El Rayess *et al.*, 2011). The pore diameters of wine microfiltration membranes are mostly close to 0.20 μm , allowing clarification (turbidities ~ 1 NTU) and microbiological stabilization. However, although in theory, microfiltration membranes should stop all yeasts and bacteria in the wine, in practice they do not manage to eliminate all germs [23]. Indeed, at the end of microfiltration (0.2 μm), wines contain on average $8 \cdot 10^2$ FCU.mL⁻¹ of viable yeasts and $1 \cdot 10^4$ FCU.mL⁻¹ of viable bacteria [10]. Today, the most demanding accepted commercial threshold is less than 1.333 FCU.L⁻¹ (1 FCU per 750 mL). Despite this threshold, the incidence of up to $1 \cdot 10^2$ FCU.mL⁻¹ remains low overall in oenological terms [10]. Ceramic membranes have better chemical stability, mechanical strength and thermal resistance, so ceramic membranes can be used in extreme conditions of pH and temperature [9,28] and also to perform clean-in-place (CIP) at extreme pH [14]. These properties allow for better cleaning control and their hydrophobicity allows for a decrease in membrane fouling [3]. In addition, it is possible to use significantly higher TMPs (high production flows) mechanical backwash cleaning systems at higher pressures. Titanium dioxide and alumina membranes are the most commonly used and exhibit good performances. They are easy to use, their surface is smooth, and the material is inert with respect to the fluids they process [31]. Moreover, the robustness of ceramic membranes is undeniable when filtering fined wines with finning product residues [20], there is no need to rack (remove finning product gently from the bottom of the tank so as to eliminate the deposits) after flocculation in the bottom of the tank.

So, in this context, crossflow microfiltration could have many advantages in replacing all the clarification and stabilization steps in winemaking. Indeed, it could replace and eliminate the succession of different stages to obtain the desired clarity and stability. Thus, the rate of discharge of pollutants is eliminated (diatomaceous earth), the loss of wine and the sulfites amount are reduced and the need for manpower is reduced. However, some limitations still need to be overcome by optimizing the process, in particular a higher permeability. Membrane fouling can have several origins [9] in wine filtration, but the increase in fluxes is not proportional to the increase in applied pressure [30,38]. Indeed, since wine contains charged colloids, fouling is due to these molecules [7,8,13]. In order to limit fouling phenomena, it has been previously described that it is preferable to regulate a filtration process on the basis of a constant permeate flow rather than a fixed transmembrane pressure [22] as the permeate flow is a key element in limiting fouling. There is also a correlation between flow velocity, permeate flux and membrane fouling [19]: the higher the flow velocity, the higher the permeate flux. In order to avoid fouling, the tangential velocity must be high ($1\text{--}2.5$ m.s⁻¹) to obtain a turbulent regime [16,22,34].

This study is based on industrial-scale trials with the objectives of (i) positioning SiC membranes at different points in the wine production chain and in particular on matrices for which existing membrane processes have limitations or are not used (very high fouling), (ii) studying the hydraulic and retention performances of SiC membranes, (iii)

Table 1

Technical characteristics of the membranes and modules used.

	SiC pilot	Hollow fibres pilot
	Membranes	
Material	SiC	Polyethersulfone
Pore diameter (μm)	0.25	0.20
Channel internal diameter (mm)	3	1.5
pH resistance	0–14	2–12
	Module	
	<i>old</i>	<i>new</i>
Number of membranes	19	14
Number of modules	1	6
Length of membranes (mm)	1 030	1 030
Filtration surface (S) (m ²)	5.7	3.9
Filtration mode	Constant flow	72 (for 6 modules)
Used filtration type	Tangential	
Permeate flow (min–max) (hL.h ⁻¹)	2–16	36–72

carrying out a comparative study between SiC membranes and polymeric hollow micro-filtration fibers commonly used in the wine industry and positioning their performances with respect to production data, (iv) treating matrices that cannot be processed by hollow fibers. To do this, wines were filtered in parallel on the two types of membranes. The polymeric hollow fibers (PES) have a similar pore size (0.20 μm) to the SiC membranes used (0.25 μm). The microstructure of the SiC membranes was analyzed (porosity, granulometry, tortuosity, etc.) and laboratory scale tests confirmed the potential of these membranes [36]. In order to study the impact of SiC membranes on wine, classical physicochemical analyses are carried out on wines before and after filtration (tannins, anthocyanins, polyphenols, chromatic characteristics, polysaccharides and mannoproteins).

2. Material and methods

2.1. Membranes and microfiltration plants

All the matrices in this study were filtered with Crystar® SiC membranes with a pore size of 0.25 μm (Crystar® FT250) and some with hollow fiber membranes (0.20 μm) in order to compare their efficiency. The polymeric hollow fiber membranes were chosen because they are widely represented in the wine industry, installed in the cellar and used for final sterilizing filtrations. The other technical characteristics (length, surface, etc.) of the tested membranes are presented in Table 1.

The microfiltration pilot equipped with SiC membranes (Fig. 1) was installed in the cellar of Vignobles Ducourt (Ladaux, France) and operated automatically.

This pilot has a pump that allows backwashing during the filtration cycles. The parameters to be set are the maximum and minimum filtration flow rate, the minimum and maximum transmembrane pressure (TMP), the volume to be filtered and the frequency of backwashing. These parameters depend essentially on the quality of the wine and whether it is easy, medium, or difficult to filter. It is important to note that these three qualities are important feedback from the winery in which the pilot is positioned. It is indeed in this context that the wines are filtered on the industrial pilot of the winery equipped with polymeric membranes. In production, only backwashes can be carried out by the pilot. Once the filtration cycle is completed, the pilot launches a chemical cleaning (CIP). In production, the pilot fills up completely with wine located in the feed tank (Fig. 1) which allows continuous feeding of the pilot. The feed pump delivers the wine or oenological matrix to be treated to the strainer (inlet pre-filter) and then to the microfiltration module, the wine then circulates in the loop via the circulation pump. The permeate flow rate is automatically adjusted according to the parameters set up by the operator. The filtered wine is then collected in a

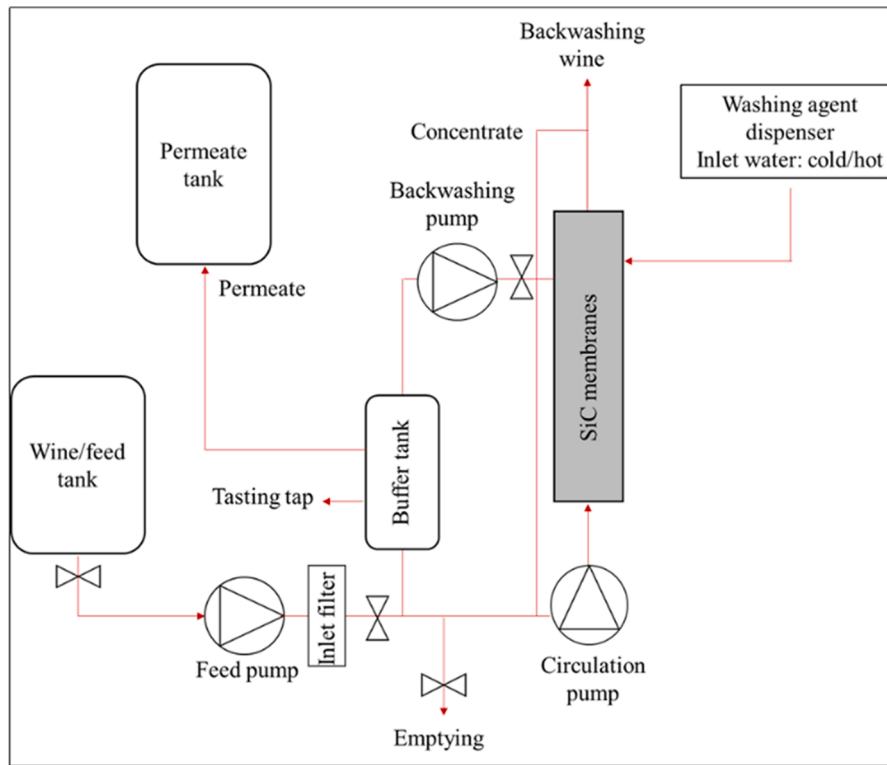


Fig. 1. Pilot of SiC membranes (Crystar® 0.25 µm).

Table 2

Filtration operating parameters set according to wine filterability for CrystarFT250 membranes and hollow fibre 0.2 µm.

Filterability	Hollow fibres 0.20 µm (72 m ²)			Crystar FT250 (5.7 m ²)		
	TMP_{max} (bar)	Q_{max} (L.h ⁻¹)	J_{max} (L. h ⁻¹ . m ⁻²)	TMP_{max} (bar)	Q_{max} (L.h ⁻¹)	J_{max} (L. h ⁻¹ . m ⁻²)
Easy	0.7	5 400	75	0.7	1 600	280
Medium	0.7	4 200	59	0.7	1 400	245
Difficult	0.7	1 800	25	1.2	1 200	210
Very difficult				1.6	≥ 1 000	175
Unfilterable with hollow fibre 0.2 µm						

separate tank (permeate tank) (Fig. 1). Backwashing consists of injecting filtered wine (permeate) in the reverse direction of filtration at high pressure (1.5–2 bar), the wine can be returned either to the circulation loop or to the feed tank.

These two crossflow microfiltration pilots are from the same manufacturer and operate with the same parameters. The major differences are (i) the number of membrane modules; the SiC pilot has one while the hollow fiber pilot has six and (ii) the concentration for the hollow fiber pilot is in the pilot itself (a volume of 200 L) while for the SiC pilot the concentration of the retentate can be in the pilot volume (\approx 25 L) or in the feed tank depending on the connections. Both pilots can operate in automatic mode, they have a sub-pressure chamber allowing backwashing during the filtration cycles. All the valves are pneumatic and open/close automatically according to the different stages (filtration, backwashing regeneration, etc). The configuration of these pilots allows them to operate at constant flow. Before each filtration, TMP (minimum; maximum) and flow rates (minimum; maximum) are set according to the filterability of the wines (Table 2).

The values for the hollow fibers are imposed and used in the winery and those for the SiC membranes were determined from laboratory scale experiments [36]. It is important to note that while the maximum

Table 3

Presentation of the different filtered matrices.

Filterability	Matrices	Denomination	Characteristics
Very easy	Dry white wine*	DWW1	End of vinification, fined and racked before bottling
Very easy	Dry white wine	DWW2	End of vinification, fined and racked before bottling - filtration with new module
Easy	Standard red wine	RW	End of vinification, fined and racked before bottling
Medium	Sweet white wine*	SWW	End of vinification, fined and racked before bottling; 15 g.L ⁻¹ of sugar
Medium	Red wine (bottom of barrels)	RWB	End of maturation, fined and racked before bottling, with a strong deposit at the bottom of barrels.
Medium to difficult	Standard red wine	RWF	End of vinification, fined and racked before bottling but with a high residue of fining agent at the bottom of the feed tank
Difficult	Sweet rosé wine	SRW	End of vinification, fined and racked before bottling but with a bottom of the feed tank with a high residue of bentonite; sweet wine with 15 g.L ⁻¹ of sugar
Difficult	Grape Juice	GJ	Unfermented white grape juice, pre-filtered (0.2 µm); high sugar concentration (220 g.L ⁻¹) - filtration with new module
Very difficult	Lees	L1	Fresh lees of standard red wine, very lightly decanted
Very difficult	Lees	L2	Fresh red wine sediment very rich in colouring matter, very lightly decanted - filtration with new module

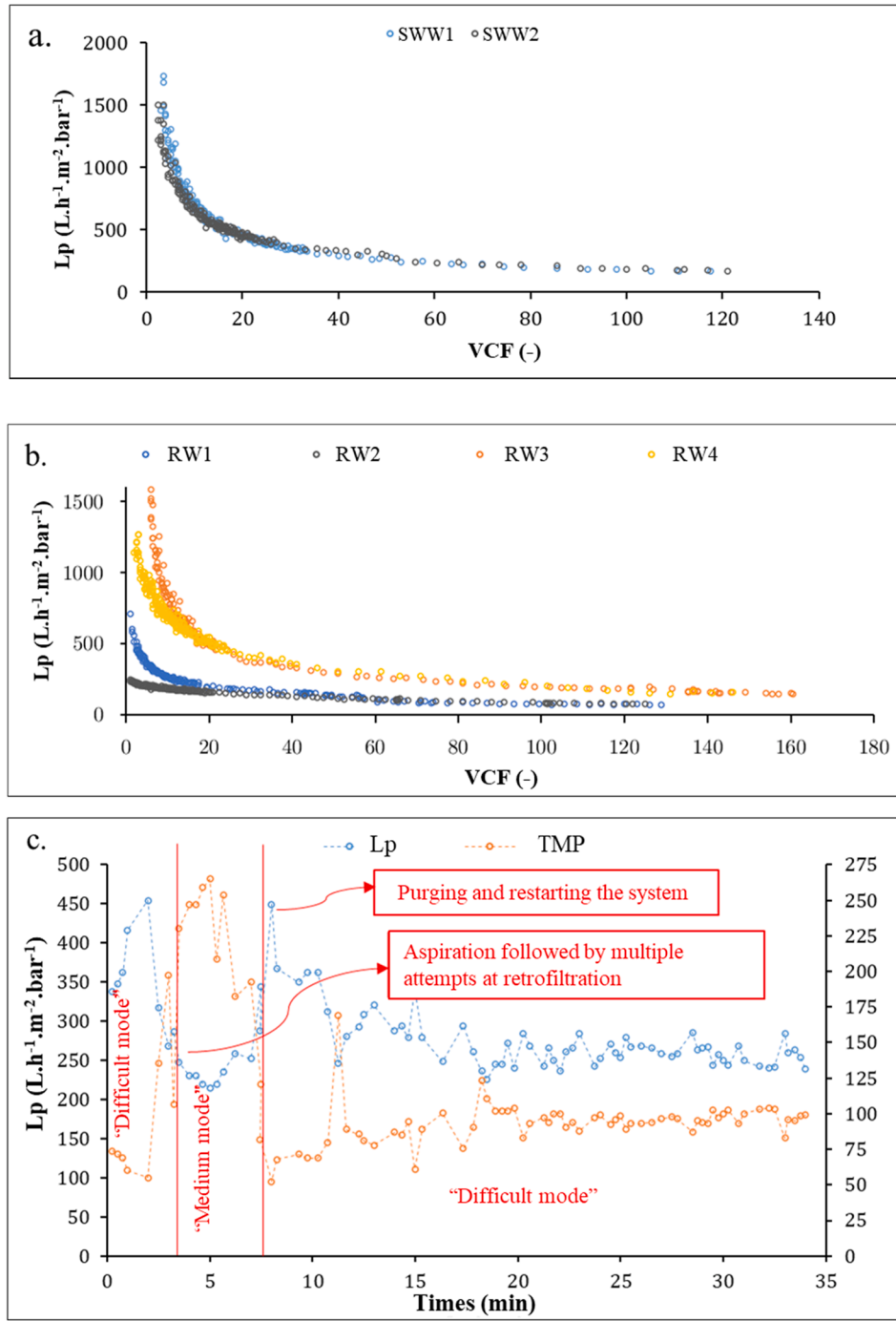


Fig. 2. Permeability as a function of volume concentration factor for (a) two sweet white wines filtered with the “easy mode” [hollow fibres 0.2 μm ; $J_{\text{max}} = 75 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$]; (b) four clean red wines filtered with the “medium mode” [hollow fibres 0.2 μm ; $J_{\text{max}} = 59 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$]; (c) for the wine filtered with the “difficult mode” with hollow fibres 0.2 μm].

filtration rates are higher with the hollow fiber pilot, the membrane surface area is almost 10 times higher (72 m^2 versus 5.7 m^2 or even 3.9 m^2 for the new module). Moreover, the notion of filterability is a feed-back from the operator with regard to the matrices he has to filter throughout the year (at least 7 different matrices representing about 20 000 hL). During filtration, the default “set point” priority is to maintain the maximum flow rate set, up to the maximum TMP imposed. Moreover, during filtration, the retentate was concentrated not in the feed tank but in the pilot circulation loop. Once the maximum TMP is reached, the flow rate strongly decreases and, once the minimum flow rate is reached, an evacuation is automatically carried out to empty the

concentration loop to refill with (less concentrated) fresh wine. By emptying the loop, the pilot discharges a highly concentrated wine which is either returned to the feed tank to be filtered again or discharged to a decantation tank to try to recover as much of the supernatant as possible to be filtered again during another filtration.

2.2. Filtered matrices

The matrices were selected to be as representative as possible of what can be commonly filtered in a winery and throughout the wine production process. They are represented in Table 3 and are ordered by

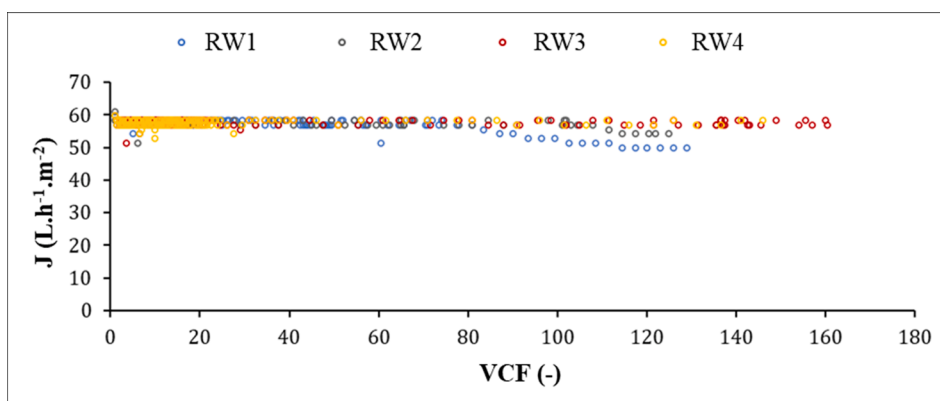


Fig. 3. Variation of permeate flux as a function of volume concentration factor for four clean red wine (RW5) filtered with the “medium mode” with hollow fibre 0,2 μm .

filterability according to the filter medium installed on site i.e. hollow fiber 0.2 μm .

The matrices marked with an asterisk are those whose filtration runs were done in parallel on SiC membranes and hollow fibre. It should be noted that matrices such as lees are never filtered without prior treatment with microfiltration hollow fibers (0.2 μm) because they foul too easy, or on specific membranes with large diameters and therefore very low specific surface areas. All the filtrations in this section (excluding lees) are carried out with a aim of a final sterilizing filtration before bottling. Filtration of the lees is carried out to clarify them in order to recover a maximum of product for blending. These different matrices of origin explain the different levels of filterability. Throughout these different filtrations, the membrane process was optimized, and a new module was installed during the last three filtrations (DWW2, L2 and GJ). This module had fewer membranes (14) and therefore the filtration area was reduced (3.9 m^2), allowing to overcome the feed pump limitations.

2.3. Analysis

In order to study the filtration performance but also the impact of SiC membranes on the physicochemical characteristics of the wine, several analyses are performed on the wine upstream of the filtration (feed) and the filtered wine (permeates). The analyses performed are the measurement of turbidity (AQUAfast AQ3010, Thermo Scientific™), fouling index (CI), chromatic characteristics by measuring the CIELab (NomaSense Color P100 colorimeter, NomaSense), total polyphenol indices (TPI), anthocyanin concentration, tannin concentration, enumeration of wine microorganisms on solid medium, mannoproteins and polysaccharides [32].

3. Results

3.1. Reference filtration with polymeric hollow fiber membranes: Flow and retention

The positioning of new SiC membranes in the wine production chain can only be done with a good knowledge of the existing ones. The monitoring of the pilot plant equipped with hollow fiber 0.2 μm (PES) allowed us to present a “state of the art” of the hydraulic performance of these membranes on wines with very different filterabilities. Wines filtered in “easy mode” (dry or sweet white wines and clean dry rosés (fined and racked)) are filtered thanks to the fining and racking operations carried out, which make it possible to obtain a wine that is less loaded with particles in suspension and therefore easily filterable. Fig. 2 shows the permeability (L_p) as a function of VCF for two sweet white wines (SWW1 and SWW2) filtered in “easy” mode.

For the two sweet white wines (SWW1 and SWW2), the hydraulic behavior is almost identical. Indeed, Fig. 2a describes a decrease of the permeability during the filtration, this decrease is very important at the beginning of the filtration, up to a VCF of 10 (from 70 to 85 %, respectively for SWW2 and SWW1). Then, it becomes slower and more progressive until the end of the filtration (from 90 to 95%, respectively for SWW2 and SWW1). For these two sweet white wines, the permeability stabilized at around 180 $\text{L.h}^{-1} \text{m}^{-2} \text{bar}^{-1}$. Two other wines (dry whites) were filtered with this “easy mode”, and in the case of these four wines, the rise in TMP remains low compared to the maximum value set, since it does not exceed 0.4 bar at the end of filtration, and is therefore much lower than the maximum transmembrane pressure (0.7 bar). In terms of flow, whatever the wine filtered, the permeate flow set for filtration (74 $\text{L.h}^{-1} \text{m}^{-2}$), remains constant over the entire filtration as time and VCF increase. Therefore, the choice of “easy mode” is suitable for these types of matrices since fouling remains limited.

The “medium mode” is generally reserved for clean red or white wines (fined and racked) or for wines usually filtered in the “easy mode” but which may present some difficulties in doing so (low fining product residues, particles, etc.). As for the white wines presented above, Fig. 2b shows an immediate drop in permeability for all the red wines (up to –74% for a VCF of 29.5 in the case of RW3), reflecting very rapid fouling. For the four red wines, the permeability is stabilized between 130 and 150 $\text{L.h}^{-1} \text{m}^{-2} \text{bar}^{-1}$. For two wines (RW1 and RW2), the strong fouling caused the maximum TMP (0.7 bar) to be reached and consequently the filtration set point (59 $\text{L.h}^{-1} \text{m}^{-2}$) to be disregarded, forcing the pilot to reduce the permeate flow (Fig. 3).

On these two wines (RW1 and RW2), this phenomenon is observed in a similar way but at different VCF. Indeed, Fig. 3 shows a decrease in permeate flux of between 9% and 16% at VCFs of 84.5 and 106.5 respectively for RW1 and RW2, illustrating once again the complex differences between matrices that initially appear similar (fined and racked red wines). Thus, controlling the filtration in “medium mode” on these two wines regulates the TMP to obtain a constant permeate flow rate, up to the defined maximum TMP (0.7 bar). Once this maximum TMP is reached, the permeate flow rate decreases below the set point (59 $\text{L.h}^{-1} \text{m}^{-2}$) as fouling continues. The filtration unit therefore has no choice but to continue to filter what remains in the tank at a lower flow rate and therefore over a significantly longer period. Thus, the choice of this mode, even if relevant, may sometimes not be sufficient to ensure full filtration at the set point. Unfortunately, as demonstrated in this study, the fouling index (CI) or turbidity measured upstream only gives a rough indication of the filterability of the wines and does not allow a classification in terms of industrial filtration. The “difficult mode” is used for all matrices that foul easily and cannot be filtered with the other two modes. Often, these are highly decanted lees, or wines with a high presence of fining agent residues at the bottom of the tank. In our case, it

Table 4

Turbidity evolution before and after filtration for all wines filtered with hollow fibre membranes 0.2 μm ; with DWW1 and DWW2 = dry white wine 1 and dry white wine 2.

Filtration mode	Wine	Turbidity (NTU)			Retention rate (%)	
		Feed	Start permeate	End permeate	Start of filtration	End of filtration
Easy	SWW1	6.8 \pm 0.1	0.5 \pm 0.0	0.7 \pm 0.1	92.19	99.83
	SWW2	6.5 \pm 0.2	0.4 \pm 0.1	0.7 \pm 0.2	94.04	99.91
	DWW1	10.3 \pm 0.1	0.5 \pm 0.1	0.8 \pm 0.2	95.49	99.91
	DWW2	5.1 \pm 0.1	0.6 \pm 0.0	0.6 \pm 0.0	92.14	99.91
Medium	RW1	27.2 \pm 0.2	0.3 \pm 0.0	0.2 \pm 0.0	98.90	99.99
	RW2	22.3 \pm 0.2	0.3 \pm 0.1	0.2 \pm 0.0	98.67	99.99
	RW3	3.1 \pm 0.1	0.4 \pm 0.0	0.4 \pm 0.0	86.27	99.93
	RW4	17.6 \pm 0.2	0.4 \pm 0.1	0.6 \pm 0.0	97.57	99.98
Difficult	RW5	10.3 \pm 0.1	0.5 \pm 0.1	0.8 \pm 0.2	95.49	99.83

is a red wine tank bottom loaded with fining product and lees residues (RW5). Fig. 2c shows the permeability and transmembrane pressure as a function of time and not as a function of VCF as in the previous figures. This choice was made because the filtration time being very short, the maximum VCF is very low ($\text{VCF} \approx 7$): the objective being to recover what is possible. Therefore, the variations are not very visible. This red wine (RW5) was first filtered with the “difficult mode”, therefore with an imposed flow rate of 25 $\text{L.h}^{-1}.\text{m}^{-2}$ for 2 min then with the “medium mode” with a flow rate of 59 $\text{L.h}^{-1}.\text{m}^{-2}$ for 5 min and finally with a return to the “difficult mode” until the end of the filtration because the performances obtained with the “medium mode” were not conclusive (too fast and important increase of TMP). The large variations in permeability and transmembrane pressure visible in Fig. 2c reflect the different transitions from “medium mode” to “difficult mode” and the various problems encountered. As in the other cases, these results show a significant decrease in permeability and an increase of TMP that diminishes as the filtration progresses. In spite of this, the permeate flow set point imposed was respected and maintained because the maximum pressure of 0.7 bar was not exceeded, but the filtration time was short (35 min).

The turbidities before and after filtration are presented in Table 4. In order to study the retention efficiency of the hollow fiber membranes in a representative way, the turbidity values indicated after filtration are those measured at the end of filtration for all the filtered wines. Table 4 highlights the retention performance during filtration. Whatever the type of wine and the filtration mode (easy, medium or difficult), permeate turbidities in line with the target of 1 NTU for red wines but above the target value of 0.1 NTU for white wines - nevertheless acceptable (for Vignobles Ducourt) of 0.7 ± 0.2 NTU are observed. It should be noted that the retentions are calculated in relation to the turbidity values. Retention rates vary from 92.19% to 99.99%, between the beginning and the end of filtration, and are always higher than 99.8% at the end of filtration whatever the matrix.

3.2. SiC membranes filtration: Flow and retention

3.2.1. Flow

In order to evaluate the efficiency of SiC membranes and to be able to compare the influence of the material, porosity and tortuosity on the filtration efficiency and the wine permeability, the production flow and the evolution of the TMP are represented as a function of the VCF for the three filtration modes (Fig. 4).

Thus, the variations in permeability and the occurrence of fouling between the three types of wine are comparable. For ease of reading, the hydraulic performance of all filtered wines is not shown. Fig. 4a describes filtration for a dry white wine that has been fined (Gecoll® Supra 30 g.hL^{-1}) and racked, said to be very easily filtered (DWW1). Fig. 4b describes the filtration of a standard red wine but with a high level of fining product removal (RWF). This strongly reduces the filterability and makes it moderately filterable (“medium mode”). Finally, Fig. 4c shows the filtration of a sweet rosé wine (SRW) with a sugar concentration of 15 g.L^{-1} fined (Gecoll® Supra 30 g.hL^{-1}) and racked. This wine has a non-negligible sugar concentration, which makes it more viscous, increasing the pressure drop and therefore less easy to filter. In addition, the bottom of the tank contains a high level of a particularly fouling oenological stabilizer: bentonite. The single platelets of bentonite can have a minimum size of 0.1 μm and therefore induce deep fouling. Finally, the permeabilities for RWF and SRW at identical VCF are compared in Table 5a and the performance obtained with the other wines is summarized in Table 5b.

In all the tests carried out on these wines, the Fig. 4 shows that the permeability of the SiC membranes drops very quickly at the beginning of filtration (up to 87% for a VCF of 1.60 in the case of SRW - “difficult”) and then tends towards stability until the end of filtration. These observations, as in the laboratory scale tests [36], reflect a rapid and significant fouling of the membranes at the beginning of filtration. However, if the trend of the curves is similar, the membranes do not clog up as quickly and strongly for the three types of wines filtered. As observed, the fouling and the drop in permeability are in line with the filterability of the wines advertised and are the most important in the case of sweet rosé wine (SRW). For a VCF of 1.77 the permeability is 209 $\text{L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$, while it is 414 and 711 $\text{L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$, respectively for red wine with fining product residues (RWF) and dry white wine (DWW1). This greater fouling for the SRW results in an evacuation of the circulation loop at a VCF of 1.88 and a very rapid increase in TMP (up to 1.6 bar), even exceeding the limit set at the outset (0.7 bar) by more than two times. This does not pose a mechanical problem for the ceramic membranes - but could lead to more difficult cleaning of the membranes, due to increased fouling. This strong decrease in permeability can be explained by the presence of bentonite affecting the filterability of a wine. The rapid increase in TMP is also observed in the case of RWF with fining product residues. Furthermore, these results show that the Crystar® 0.25 μm SiC membranes can filter without any apparent difficulty with high and stable permeate fluxes (Table 5a) for wines classified as moderately to hardly filterable by the winery for the 0.20 μm hollow fiber membranes (RWF and SRW). Indeed, for maximum VCF of 85 and 67.4, the permeability of the Crystar FT250 membranes is 170 and 272 $\text{L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ respectively for the RWF and the SRW (Table 5). Bentonite has a very high fouling capacity for the hollow fiber, but also a risk of fouling the hollow fiber channels. The service life of these membranes is then strongly affected. Concerning bentonite filtration, Moulin et al. [26] conducted a study on the hydraulic performance of hollow fiber membranes in ultrafiltration on solutions with different bentonite concentrations. Two membrane module geometries were also compared: coiled and straight hollow fibers. With a coiled geometry, generated Dean vortices, for 1 bar of TMP, flows of 170 $\text{L.h}^{-1}.\text{m}^{-2}$ are obtained with a 3.27 g.L^{-1} bentonite solution. This study highlights (i) the difficulty of filtering bentonite with ultrafiltration membranes, (ii) that the coiled geometry allows a significant reduction in membrane fouling thanks to the implementation of a Dean vortex creating a shear stress on the membrane surface, allowing the resuspension of particles. These results therefore suggest the difficulty of filtering bentonite on hollow fiber membranes in microfiltration.

Finally, with these filtration operating parameters [$Q_{\text{max}} = 1\ 400\text{--}1\ 600\ \text{L.h}^{-1}$; $\text{TMP}_{\text{max}} = 0.7\text{--}1.6\ \text{bar}$; $\text{BW} = 5\ \text{min}$], these results underline that the Crystar FT250 membranes can filter three types of wines from very high to low filterability while maintaining a constant flow

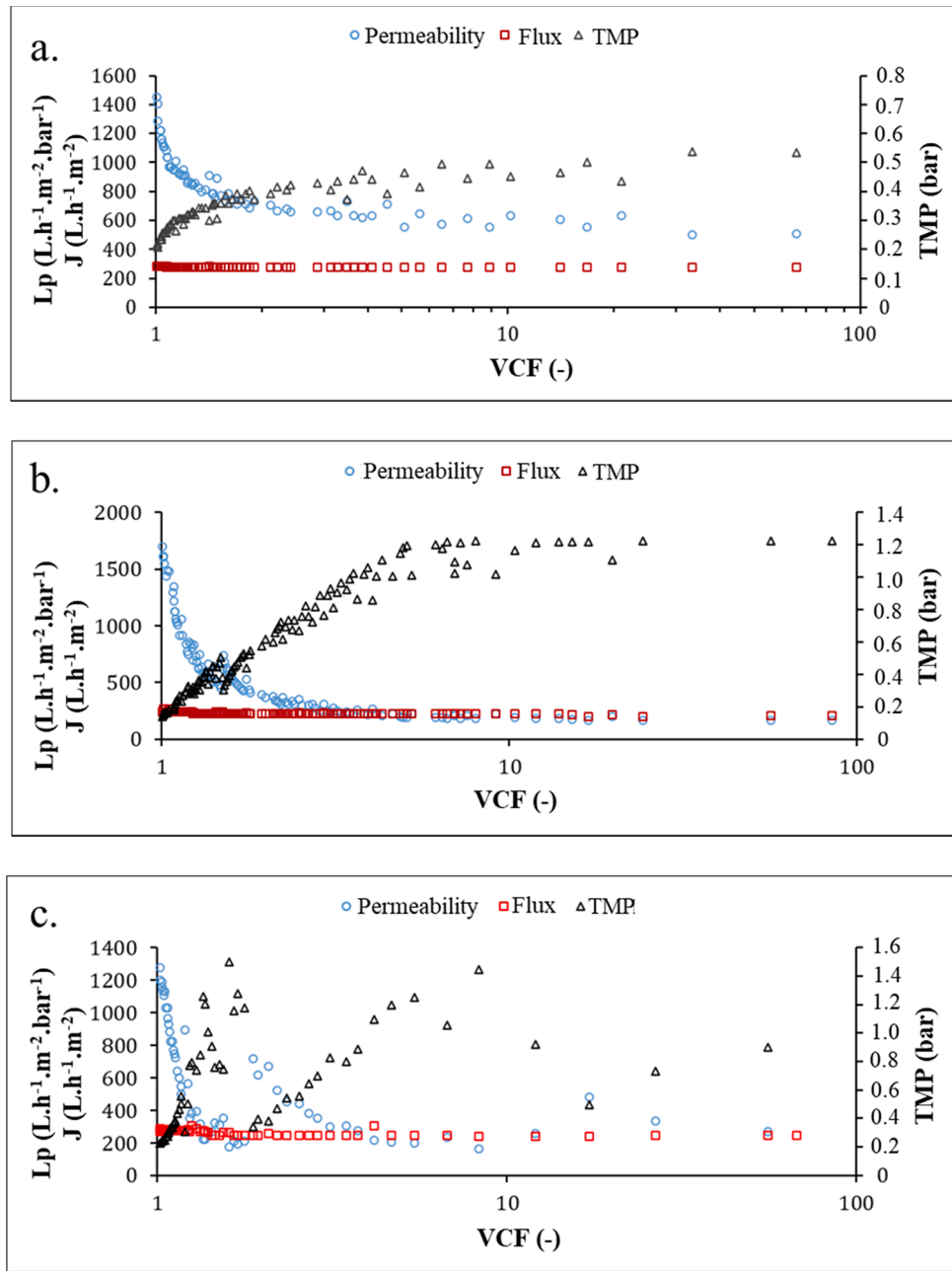


Fig. 4. Variation of permeability and flow as a function of volume concentration factor for three types of wine: (a) dry white wine (DWW1); (b) red wine with a high fining product residue in the tank (RWF) and (c): sweet rosé wine with a high bentonite residue in the tank (SRW) with Crystar FT250.

Table 5

Variation of permeability as a function of volume concentration factor for (a) RWF and SRW (b) other wines filtered by Crystar FT250 membranes.

(a) VCF (-)		Permeability ($\text{L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$)			
RWF	SRW	RWF "medium mode"		SRW "difficult mode"	
1.80	1.77	414		716	
10.40	12.05	195		261	
85	67.35	170		272	

(b) Mode	Wines	Mean flow ($\text{L.h}^{-1}.\text{m}^{-2}$)	Lp_{max} ($\text{L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$) at VCF = 1	Lp_{min} ($\text{L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$)	Filtered volume (hL)
Easy	RW	164	1 469	337	10
Medium	SWW	257	1 539	246	40
Medium	RWB	200	776	116	23
Easy	DWW2	408	2 895	250	30

from the beginning to the end of the filtration (32.5 hL for the DWW1 ; 33.6 hL for the RWF and 22.5 hL filtered for the SRW), without presenting too much membrane fouling that could limit their hydraulic performances. These performances were also observed on the other wines that were filtered and are presented in Table 5b. Thus, whatever the filtration mode of the wines, the hydraulic performance of the SiC membranes was maintained over the filtration cycle at set values increased by 74%, 75% and 90% respectively for the "easy", "medium" and "difficult" modes, compared to the reference values obtained with 0.2 μm hollow fiber membranes.

3.2.2. Retention

The physicochemical analyses are carried out on the feeds and on the filtered wine. The results obtained on the filtered wine are referred to as "Permeates" and are the values representing the first and last volumes of permeate respectively. This allows us to observe if there is a difference in

Table 6

Variation in turbidity and CI of filtered wines, the order of the wines is presented according to the chronological order of filtration with CrystarFT250 ; with nd = CI too high.

Wines	Samples	Turbidity (NTU) \pm 5 %	CI (-)
RW	Feed	4,00	681
	Permeate	0,01–0,07	12–17
SWW	Feed	35,00	nd
	Permeate	0,73–6,61	8 - nd
RWF	Feed	32,10	nd
	Permeate	0,00 – 6,7	12 – 257
DWW1	Feed	7,66	nd
	Permeate	0,02 – 0,00	6–6
SRW	Feed	12,73	nd
	Permeate	0,40 – 0,30	6 – 9
RWB	Feed	18,19	nd
	Permeate	0,30–0,10	16–15
DWW2	Feed	19,8	nd
	Permeate	0,0 – 0,5	14 – 11

Table 7

Results of CIELab measurements before and after filtration on the different filtered wines with CrystarFT250.

Wines	Samples	CIELab			
		L	a	b	ΔE
RW	Feed	7.1	32.4	9.7	
	Permeate	7.8 – 7.6	33.3 – 32.3	10.6 – 9.8	1.6 – 0.6
SWW	Feed	77	3.5	4.7	
	Permeate	77.5 – 77.4	3.8 – 3.8	4.4 – 4.6	0.7 – 0.6
RWF	Feed	10.1	36.5	13.9	
	Permeate	10 – 10	36.8 – 36.8	13.9 – 14.2	1 – 1
DWW1	Feed	76.6	4	5	
	Permeate	76.6 – 76.8	4.1 – 4	5 – 5	0.01 – 0.2
SRW	Feed	73	8.8	6.7	
	Permeate	73.2 – 73.1	9.1 – 9	6.7 – 6.7	0.7 – 0.7
RWB	Feed	8.7	35	12.1	
	Permeate	8.2 – 7.8	34.1 – 33.1	11.1 – 10.4	1.4 – 2.6
SWW2	Feed	77.3	4	4.9	
	Permeate	77.5 – 77.4	3.9 – 3.9	5 – 5.2	0.2 – 0.3

the efficiency of the membrane process between the beginning and the end of the filtration, and is representative of what is found in the permeate collection annex tank as the filtration proceeds. For turbidity, the required specifications are those imposed for hollow fiber: less than or equal to 0.1 NTU for white wines, less than or equal to 1 NTU for red wines, and the fouling index must be less than or equal to 30 whatever the type of wine. The results are presented in Table 6.

The results show that Crystar FT250 membranes achieve the turbidity and fouling index targets ($NTU \leq 0.1$ and $1 NTU$; $CI \leq 30$) except for SWW and RWF wines. This increase in turbidity and CI at the end of filtration may be due to a technical problem: a loosening of the back plate due to backwashing hence decreasing the gaskets seal and tightness. This gasket issue allowed a few drops of highly concentrated wine to pass into the permeate at the end of filtration and consequently increased the turbidity and CI above the required values. On wines (DWW1; SRW; RWB) that were filtered later, this problem was solved and turbidity and CI returned to values in line with the objectives. These values confirm the results obtained in experiments carried out on Crystar FT250 membranes at the lab scale [36] and show that these membranes can be used prior to bottling, achieving the turbidity and CI targets set. The chromatic characteristics of the wines presented (Table 7) show that all ΔE are between 0 and 1 (except for RWB).

This means that the observer does not notice any difference between the unfiltered wine (feed) and the filtered wine (permeates). Crystar FT250 membranes therefore do not alter the chromatic profile of the wines whatever the type of wine filtered. For RWB, the ΔE is slightly higher and greater than 1 (1.4–2.6), this is due to the deposits present in the wines, particularly at the bottom of the barrels, modifying the

chromatic aspect of the wine once these have been removed by filtration. These ΔE values are nevertheless low and are not considered to alter the color (retention of phenolic compounds). This is confirmed by the measurement of total anthocyanins, total tannins and total polyphenols. As with the color profile, filtration should not alter the phenolic composition of a wine. The results obtained (Fig. 5) on all the wines being similar and in order to facilitate the reading for total anthocyanins and total tannins, only the example of two red wines with different filterabilities are presented. Because these are not present in white wines and very little present in rosé wines, we look at standard red wine (RW) and red wine aged in barrels with deposit (RWB).

For the determination of total polyphenols, the results are presented for the two red wines mentioned above and the sweet rosé wine (SRW) (Fig. 6).

It should be noted that the concentrations of phenolic compounds in wines can vary significantly depending, for example, on the grape variety, the sanitary state of the harvest, the maceration time and/or the oenological treatments applied to the harvest (e.g. thermovinification, enzymes, etc.) which can significantly vary the anthocyanin or tannin content [11,25]. Moreover, as the tannin determination is entirely done by the handler it is possible to find concentrations slightly above or below the average values. The results obtained show that there is no retention of phenolic compounds (total anthocyanins or total tannins) by the Crystar FT250 membranes during filtration. These results are correlated and confirmed with the total polyphenol assays (Fig. 6). The main microorganisms present in the wine (yeasts and bacteria) were counted before and after filtration on feed and permeate samples (at the beginning and the end of filtration) in order to verify the efficiency of retention by the membranes (Table 8).

Filtered wines are wines at the end of the vinification process, i.e. with completed fermentations and sulfites. Consequently, it is normal to observe concentrations of viable non-homogenous microorganisms, sometimes very low or even zero in the feed. These results underline that Crystar FT250 membranes are effective in removing yeast and bacteria from a wine. In the case of yeast, regardless of the concentration (from 24 to $1.5 \cdot 10^4$ FCU.mL⁻¹), there is a total retention of yeast in the permeates. This is valid throughout the filtration process since the permeate values represent the first and last volumes of wine filtered. In the case of the RWF, 2 FCU.mL⁻¹ are observed at the end of filtration in the permeate. This slight passage of yeast corresponds to one of the above-mentioned filtrations with a gasket leakage issue. As for bacteria, they are less present in the filtered wines but, whatever the concentration observed upstream of filtration (from 14 to $4.2 \cdot 10^2$ FCU.mL⁻¹), without taking into account the concentration effect (VCF), there is a total retention of bacteria in the filtered wines. Thus, the cut-off of Crystar FT250 membranes is effective for removing microorganisms prior to bottling for any type of wine and allows up to 4 log retention. For comparison with the literature, the efficiency of two ceramic crossflow microfiltration membranes (0.2 μ m) on a white wine and a fined red wine were compared (Table 9). As for the retention rates of wine microorganisms, none of the tested crossflow microfiltration membranes were able to retain 100% of the total yeasts and total bacteria of a white or red wine by letting pass in the permeates up to $1.1 \cdot 10^2$ UFC. mL⁻¹ and $1.25 \cdot 10^4$ FCU.mL⁻¹ for yeast and bacteria respectively [33].

Studies have shown that some ceramic (alumina) and polymeric (PP and PES) membranes can cause a loss of up to 66% of polysaccharides [5,13,30,37]. A loss of polysaccharides can negatively affect the organoleptic balance of a wine as they play a major role in the perception of fat and the aromatic stabilization of wines. They come from the grape berry, yeast (glucans and mannoproteins), fungi and certain bacteria. This is why two different assays were carried out: all the polysaccharides on the one hand and mannoproteins on the other, as these are the molecules with the most important fouling effect among the polysaccharides in wine (thesis [35]). The results obtained by HPLC are presented in Fig. 7. Thus, SIC membranes seem to resist well to the

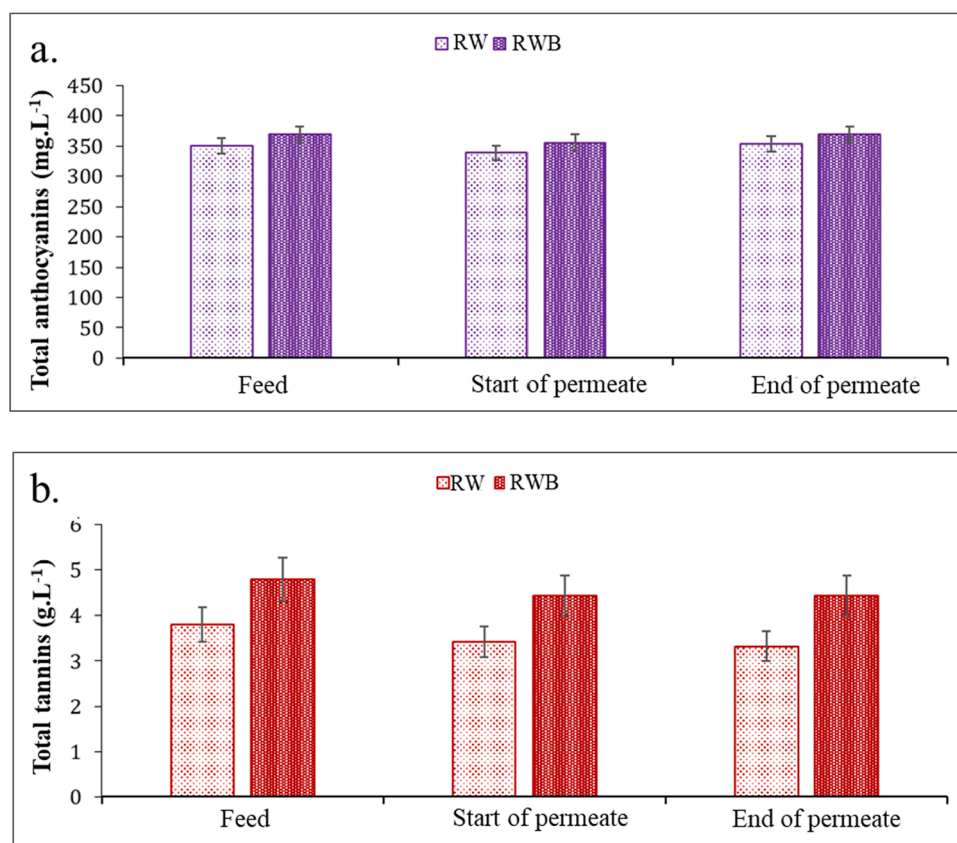


Fig. 5. Variation in the concentration of (a) anthocyanins and (b) tannins before and after filtration for two wines with different filterability (RW) and (RWB) with CrystarFT250.

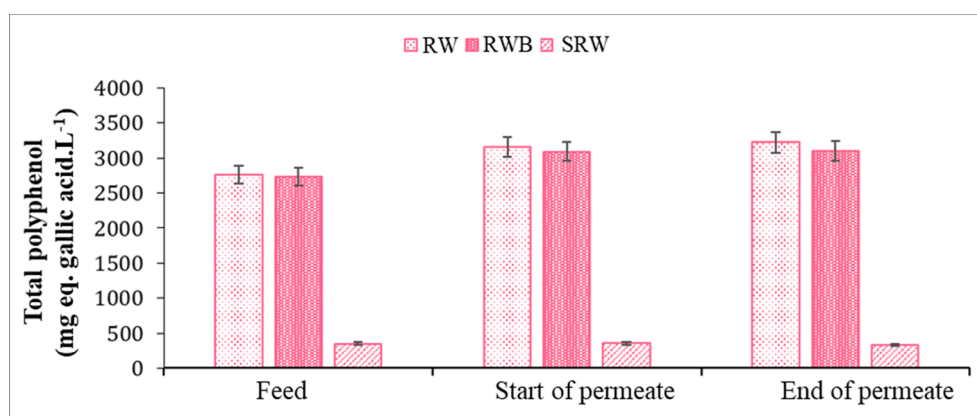


Fig. 6. Variation of the total polyphenol index (TPI) before and after filtration for three types of wine (RW, RWB and SRW) with CrystarFT250.

membrane fouling that can be induced by mannoproteins and confirm the results obtained here, with sweet rosé wine (SRW).

These analyses on sweet rosé wine (SRW) show that there is no retention of either total polysaccharides or mannoproteins by the Crystar FT250 membranes. Crystar FT250 membranes seem to have a neutral behavior towards polysaccharides including mannoproteins. The veracity of these results could be questioned by the bentonite treatment because even if it does not directly affect the polysaccharides it can do so indirectly. Indeed, a treatment with sodium bentonite will mainly precipitate the unstable proteins of a wine and a treatment with calcium bentonite (respectively the high proportion of sodium ions or calcium ions) will mainly precipitate the coloring matter. In any case, if the concentration of protein or coloring matter is too highly affected by

the treatment, the colloidal equilibrium of the wine will be modified and consequently impact the polysaccharide equilibrium. In this study, this does not seem to be the case as the polysaccharide concentrations are in the known range of wine (200 – 1 000 mg.L⁻¹). These results provide an interesting conclusion as fine filtration with Crystar FT250 membranes does not seem to affect the aromatic balance of a wine by retaining polysaccharides.

3.3. Lees and grape juice filtration

3.3.1. Lees

In this study, the lees recovered are very lightly decanted red lees (1–2 weeks), which are therefore still very difficult to filter. As in this

Table 8

Enumeration of microorganisms before and after filtrations for the different filtered wines with CrystarFT250; with nd = not available and below 1 = limit of detection (less than 1 in 10 mL).

Wine	Sample	Total yeasts (UFC.mL ⁻¹)	Total bacteria (FCU.mL ⁻¹)
RW	Feed	1.5•10 ⁴	20
	Permeate	Less than 1	Less than 1
SWW	Feed	2.0.10 ⁵	Less than 1
	Permeate	nd	Less than 1
RWF	Feed	24	14
	Permeate	Less than 1 – 2	Less than 1
DWW1	Feed	36	Less than 1
	Permeate	Less than 1	Less than 1
SRW	Feed	30	Less than 1
	Permeate	Less than 1	Less than 1
RWB	Feed	51	4.2.10 ²
	Permeate	Less than 1	Less than 1
DWW2	Feed	Less than 1	Less than 1
	Permeate	Less than 1	Less than 1

case, the settling time is significantly shorter than usual, it is not possible to compare the hydraulic performance of the Crystar FT250 membranes because filtration with 0.2 µm hollow fibers is impossible for such poorly settled lees. Two trials were carried out on different lees: one (L1) on classic red wine lees and one (L2) on lees of a thermovinified grape variety (very rich in colouring matter), therefore extremely rich in molecules such as phenolic compounds or polysaccharides. For both tests, a tank of about 10 hL is used, the concentration is done in the feed tank to moderate the increase of the VCF (in comparison with the membrane loop) with a backwash every 2 min and the lees are filtered until the membranes are completely fouled. The hydraulic performance for the first trial (L1) is shown in Fig. 8.

For both tests, the maximum target flow rate is 400 L.h⁻¹ and the maximum TMP set is 1.5 bar. For comparison, the target flow rate in “difficult mode” for wines with Crystar FT250 membranes is 1 200 L.h⁻¹. As for wines, the permeability of Crystar FT250 membranes drops very quickly during the first volumes filtered (from 500 to 54 L.h⁻¹ m⁻² bar⁻¹ for 384 L filtered corresponding to a VCF of 1.52) and then reaches a certain stability which continues to decrease slightly throughout the filtration. This observation reflects a rapid and very important fouling of the membranes, particularly at the beginning of filtration, confirmed by

Table 9

Application of different filtration techniques to white wine after fining with blood albumin (8 g.hL⁻¹) and to red wine after fining with gelatin (8 g.hL⁻¹) [33]; with uncountable = above the detection limit.

		Unfiltered wine	Filtration on a Kieselguhr pre-coat	Crossflow microfiltration		
				Inorganic membrane (0.2 µm)	Inorganic membrane (0.2 µm) with backwash	Organique Membrane (0.4 µm)
Viable yeast (cell.100 mL ⁻¹)	White wine	3.0•10 ⁴	1.4•10 ³	less than 1	10	less than 1
	Red wine	2.0•10 ⁵	4.2•10 ³	16	1.1•10 ²	5
Viable bacteria (cell.100 mL ⁻¹)	White wine	7.2•10 ³	6.5•10 ³	1.3•10 ²	8.5•10 ²	50
	Red wine	Uncountable	1.6•10 ⁴	8.5•10 ³	1.25•10 ⁴	5.0•10 ²

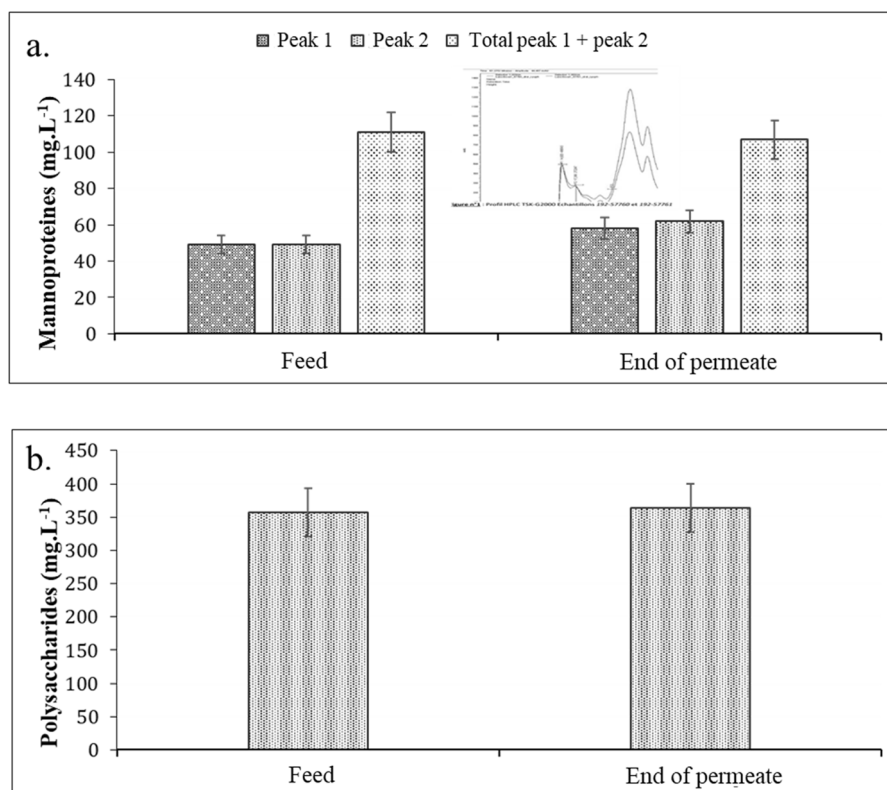


Fig. 7. Determination of (a) mannoproteins and (b) polysaccharides before and after filtration of filtered rosé wine (SRW) by HPLC with CrystarFT250.

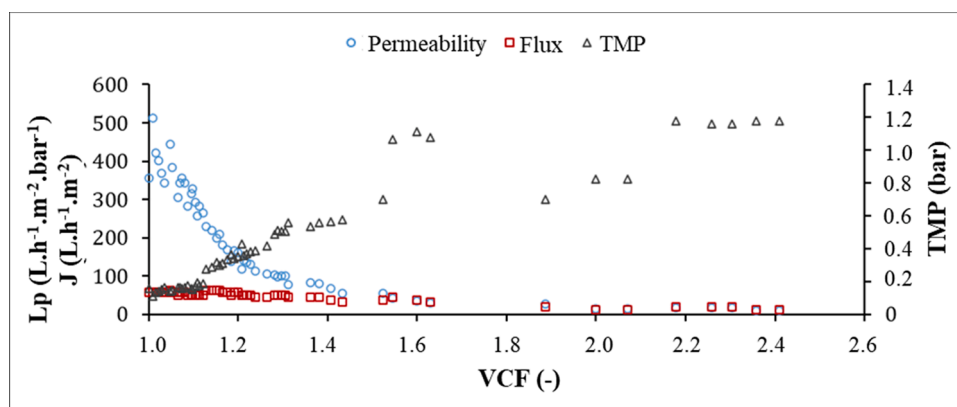


Fig. 8. Variation of permeability and flux as a function of volume concentration factor (VCF) for the first test of weakly settled red lees (L1) with CrystarFT250.

Table 10

Summary of the physico-chemical analyses carried out for the two lees tests (L1 and L2) before and after filtration; with CI nd = not available because membrane fouling before 200 mL; VY = total viable yeast; VB = total viable bacteria; less than 1 = less than 1 FCU.mL⁻¹ in 10 mL.

	L1 Feed	Permeate: Start of filtration step	Permeate: End of filtration step	L2 Feed	Permeate: Start of filtration step	Permeate: End of filtration step
Turbidity (NTU)	557	0.6	23	16 000	0.01	3.8
Retention rate (%)		99.89	99.25		99.99	99.98
IC (-)	nd	37	nd	nd	nd	nd
Anthocyanins (mg.L ⁻¹) ± 4,5 %	422	359	392	nd – overloaded sample	nd – overloaded sample	nd – overloaded sample
Tannins (g.L ⁻¹) ± 10 %	3.63	3.34	3.71			
IPT (-) ± 2,2 %	3 479	3 360	3 371	3 017	2 889	2 926
VY (UFC.mL ⁻¹)	2.6•10 ²	less than 1	less than 1	1.3•10 ⁶	80	less than 1
VB (UFC.mL ⁻¹)	1.6•10 ⁴	2.6•10 ²	70	2.4•10 ²	6.3•10 ²	less than 1

a very rapid increase in the TMP at the set limit (1.2 bar). Then, once the permeability is almost stabilized, a slower fouling process takes place until the end of the filtration. These results are not surprising in view of the particularly fouling initial matrix, which is very dense and highly charged with organic matter, and which also becomes concentrated during filtration. At the end of filtration, for a VCF of 2.40, the permeability to lees of the Crystar FT250 membranes is 15 L h⁻¹ m⁻² bar⁻¹, for a flux of approximately 13 L h⁻¹ m⁻². These production flows are low but nevertheless interesting in view of the starting matrix and especially for the cellar with the aim of limiting the immobilization of these lees. The second test on lees (L2) shows that the flux of Crystar FT250 membranes drops very quickly during the first volumes filtered, then reaches stability with an average flow rate of 65 L h⁻¹, an average flux of 17 L h⁻¹ m⁻² until the end of filtration for a volume of 4 hL filtered (40% reduction in the immobilized volume). In the case of lees, the analysis of chromatic characteristics before and after filtration is not carried out because the appearance of the lees, before and after filtration, is too different to obtain a stable chromatic profile. Moreover, at the time of decantation, a strong red color of the decantate can be observed, which suggests that the organic matter contained in the lees adsorbs the coloring matter: this phenomenon is well known in red wine lees. This slight decrease in total anthocyanins (and consequently in total polyphenol content) corresponds to the loss of coloring matter once the lees are decanted and removed from the wines [24]. The importance in lees filtration is to minimize losses by recovering a clear lees wine free of microorganisms. Regardless of the test (L1 or L2) the results (Table 10) presented show a strong decrease in turbidity after filtration (0.01–23 NTU) and a retention rate of more than 99% (99.89%–99.99%) over the whole filtration.

However, for L1, an increase in turbidity was observed at the end of filtration (23 NTU) in correlation with CI, retention rate and microbial count. These increases suggest leakage and therefore passage of

concentrated lees from the circulation loop into the permeate. If we follow the chronological order of the filtrations, the first lees filtration (L1) is positioned just before the filtration of the two wines with the same leakage concern (SWW and RWF). Concerning L2, a slight increase in turbidity is also observed but, (i) the turbidity upstream at this stage of filtration is significantly higher (36 000 NTU) and (ii) this test was not carried out in a temperature-controlled tank. Therefore, the temperature rise during filtration (28 °C) may have impacted the retention efficiency of the Crystar FT250. Nevertheless, the retention (99.98%) at the end of filtration by the Crystar FT250 membranes (36 000 to 3.8 NTU) remains quite satisfactory and confirms the efficiency of the Crystar FT250 membranes with respect to polymeric hollow fiber membranes which cannot be used. These results obtained on turbidity are in correlation with the results obtained on microbiology: abatement reduction of 5 log for yeasts and a total retention for bacteria are observed at the beginning of filtration, then a passage of 6.3•10² FCU.mL⁻¹ is observed in correlation with the slight increase in turbidity for an upstream value that is close to 36 000 NTU. Moreover, these results also highlight a very slight decrease in coloring matter (total anthocyanins) in the permeate (undetectable for L2 because the matrix is too loaded and exceeds the detection threshold of the measuring device). Indeed, the values obtained for the permeates are slightly below the standard deviation calculated for the analyses of total anthocyanins and total polyphenols. This decrease corresponds to the adsorption of anthocyanins by the organic matter of the lees.

3.3.2. Grape juice

Grape juice filtered here is an unfermented lightly decanted white grape juice, which is very high in sugar (220 g L⁻¹). This grape juice is intended for consumption. During its preparation, the grape juice is filtered by tangential microfiltration in order to clarify and stabilize it. For this filtration, the maximum flow rate was set at 1 000 L h⁻¹ and the

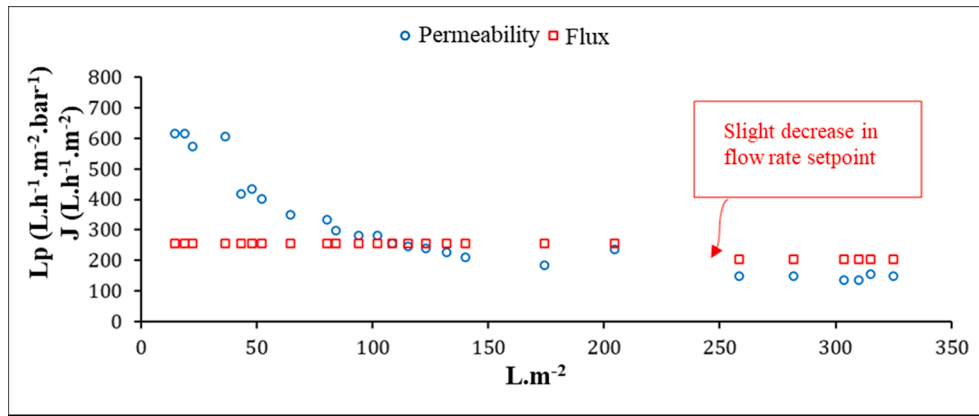


Fig. 9. Variation of permeability and flux as a function of volume filtered per membrane area for the first grape juice test (GJ) with CrystarFT250.

Table 11

Summary of the analyses carried out for the two tests on grape juice (GJ) before and after filtration; with less than 1 = limit of detection of the enumeration method on solid medium; less than 1.10 FCU.mL⁻¹

	Feed			Permeate Start of filtration step				Permeate End of filtration step			
Turbidity (NTU)	1.3			0.06				0.08			
CI (-)	nd			2				0			
VY (UFC.mL ⁻¹)	less than 1			less than 1				less than 1			
VB (UFC.mL ⁻¹)	less than 1			less than 1				less than 1			
CieLab	<i>L</i>			<i>L</i>	<i>a</i>	<i>b</i>	ΔE	<i>L</i>	<i>a</i>	<i>b</i>	ΔE
	76.6	4.7	2.3	76.9	4.6	2.6	0.2	76.9	4.6	2.4	0.4

maximum TMP at 2 bar. The results on hydraulic performance are presented in Fig. 9.

As for all the filtered matrices, the permeability of the Crystar FT250 membranes drops very quickly during the first volumes filtered (from 615 to 281 L h⁻¹ m⁻² bar⁻¹ for 368 L filtered, corresponding to a volume of 102 L filtered per unit of membrane surface area) and then reaches a certain stability until the end of the filtration process. The filtration flux remains constant for most of the filtration (255 L h⁻¹ m⁻²). However, at the end of the filtration, the pilot having reached the maximum TMP imposed, it is forced to lower its production flux slightly (204 L h⁻¹ m⁻²). These results underline the difficulty for SiC membranes to respect the imposed production flow rate (1000 L h⁻¹ \approx 255 L h⁻¹ m⁻²). It should be noted that the hydraulic performance is nevertheless very satisfactory. Indeed, the 0.2 μ m hollow fiber can only filter this matrix in “difficult mode” which corresponds to 25 L h⁻¹ m⁻² due to the high sugar content and the resulting viscosity. These results highlight the advantage of (i) Crystar FT250 ceramic membranes to filter viscous matrices at high TMPs and (ii) an ability to filter highly sugar-laden matrices with high production flows (factor \approx 10). Concerning the physicochemical analyses on white grape juice, only the retention efficiency (by measuring turbidity and CI) and the analysis of chromatic characteristics (by measuring CieLab) are carried out because it is a very clear matrix and comes from a white grape and it is therefore not relevant to assay the phenolic compounds.

The results in Table 11 show that the Crystar FT250 membranes achieve the turbidity and CI targets after filtration (\leq 0.1 NTU and CI \leq 30) throughout the filtration. In addition, the chromatic characteristics before and after filtration remain constant (0.2 < ΔE less than 0.4). Crystar FT250 membranes seem to remain neutral with respect to the chromatic aspect of the matrix. These results confirm all the results obtained upstream and reinforce the effectiveness of Crystar FT250 membranes placed at different stages of the winemaking process to filter matrices with very low filterabilities.

4. Performance comparison

For this comparative study, and due to the very different membrane surfaces on the two pilots, the results obtained show the wine permeability for the two types of membranes (Crystar FT250 and hollow fibers 0.20 μ m) as a function of the volume of wine filtered per unit of membrane surface (Fig. 10).

As a reminder, the backwashing frequency is 2.5 times higher for the hollow fiber membranes (2 min versus 5 min). The Crystar FT250 membranes show significantly better hydraulic performance than the 0.20 μ m hollow fiber membranes. As the filtrations were carried out at constant flow: Crystar FT250 membranes ensure a stable production flow on average 3.85 times higher than 0.20 μ m hollow fiber membranes. For a similar volume filtered per unit area, Crystar FT250 membranes have a 1.85 times and 3.5 times higher permeability for SWW and RWF respectively (Fig. 10 and Table 12). SiC membranes have the particularity of being, compared to other membranes (ceramic and polymeric), more porous (\geq 40%) and especially less tortuous (\approx 1.2). This gives them a much higher initial water permeability (greater than 6000 L h⁻¹ m⁻² bar⁻¹) and explains their higher hydraulic performances.

Furthermore, SiC is known to have a complex surface chemistry regarding its hydrophobic or hydrophilic behavior. King et al., [17] demonstrated that pure SiC has a hydrophobic behavior. On the other hand, as oxygen binds to the surface of the material, SiC tends to behave more like silica (SiO₂), which is hydrophilic. The membranes used in this work are deliberately produced with silica levels as low as possible, as this impurity leads to a reduction in the chemical resistance of the material. As a result, they are mainly hydrophobic rather than hydrophilic. Contact with wine creates Si—O—C, Si—O and C—O bonds on the surface of the material, which reduces hydrophobicity. Chemical cleaning cycles can remove some of the extrinsic oxygen again. It is therefore to be expected that the behavior of the SiC material in the present study will oscillate between hydrophobicity and hydrophilicity during the different phases of the wine clarification processes. Another special point of the SiC membrane is that its isoelectric point (\approx 4) is very close to wine pH. This feature could limit adsorption phenomena

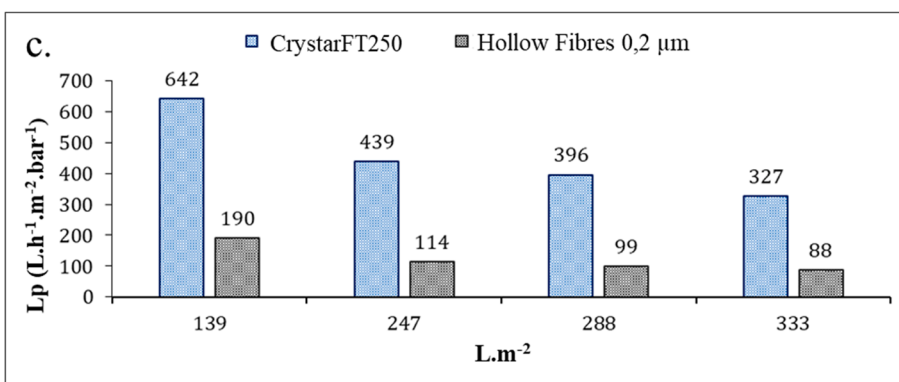
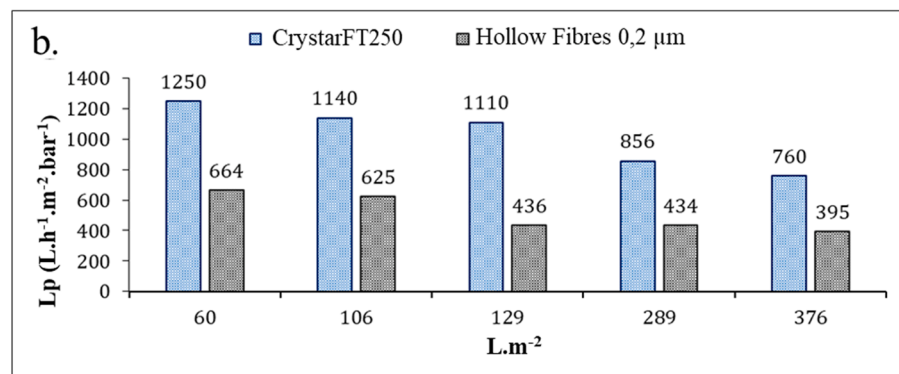
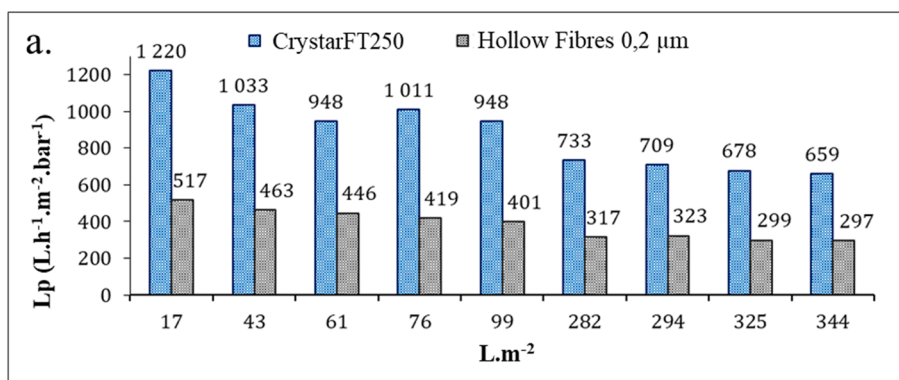


Fig. 10. Comparison of the filtration performance of SiC membranes to hollow fibre membranes for three different types of wine; (a): DWW1; for hollow fibres “easy mode”: 344 L.m⁻² = 248 hL of wine filtered for hollow fibres and 20 hL for SiC membranes; (b): SWW; for hollow fibres “medium mode”: 376 L.m⁻² = 271 hL of filtered wine for hollow fibres and 21.5 hL for SiC membranes; (c): RWF; for hollow fibres “medium to difficult mode”: 33 L.m⁻² = 240 hL of filtered wine for hollow fibres and 19 hL for SiC membranes.

Table 12

Comparison of hydraulic performance between CrystarFT250 membranes and 0.2 µm hollow fibres.

Mode	Wine	CrystarFT250 /Hollow fibre 0.20 µm permeability ratio
Easy	DWW1	2.28
Medium	SWW	1.85
Medium to difficult	RWF	3.5

during the different phases of wine clarification processes. Last but not least, the regeneration of the SiC membrane is efficient as shown on Fig. 11.

5. Conclusion

Crystar FT250 membranes respect the hierarchy of wine filterability (easy, medium or difficult) with permeate flow sets that can be increased (compared to the flux obtained with hollow fibres) by 74%, 75% and

90% respectively for “easy”, “medium” and “difficult” modes. Moreover, the Crystar FT250 membranes can be used to filter matrices that cannot be filtered by polymeric hollow fibres, such as bentonite tank bottoms (270 L.h⁻¹.m⁻².bar⁻¹) or very lightly decanted lees (15–20 L.h⁻¹.m⁻².bar⁻¹), with industrially meaningful permeabilities, in the same way as is currently done in the winery (automatization). For wine lees, making this filtration possible allows the winery to limit immobilization in the tank and faster treatment of the matrices. Except for the two wines that had gasket leakage issues (RWF and SWW), the Crystar FT250 membranes allowed us to obtain turbidity and CI values in line with expectations (WW ≤ 0.1 NTU; RW ≤ 1 NTU and CI ≤ 30). The cut-off of the 0.25 µm Crystar FT250 membranes was found to be effective in fully retaining yeast and bacteria from the wine (up to 4 log reduction). The physicochemical analyses gave very satisfactory results: whatever the type of wine filtered (white, red, rosé) and whatever its filterability, the SiC membranes do not seem to retain phenolic compounds, total polysaccharides or mannoproteins in the wine, nor do they modify its chromatic appearance (0 < ΔE less than 1). For lees, the physicochemical analyses are encouraging: a decrease in turbidity and CI of the permeate was satisfactory in the first part of the filtration cycle. The

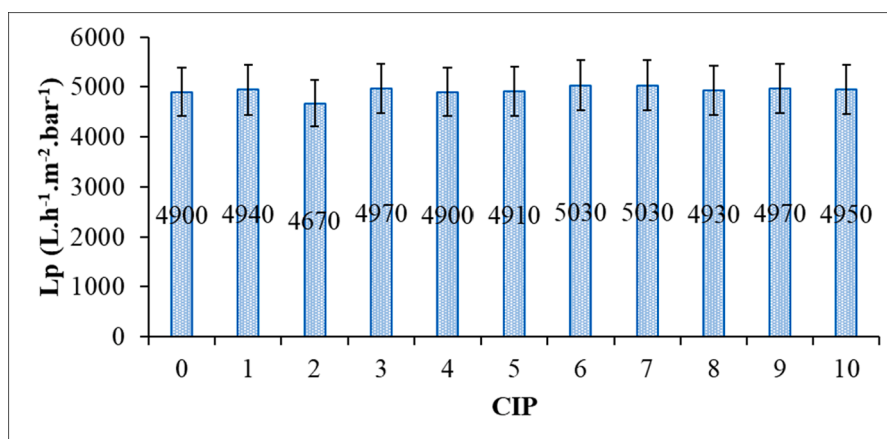


Fig. 11. Variation of the permeabilities after each filtration step.

results show that there is no retention of tannins and a very slight decrease in the concentration of total anthocyanins (and consequently in the TPI), but this is likely due to the adsorption of the coloring matter by the organic matter and not by the SiC membranes. For the lees, a reduction of at least 2 and 5 logs respectively for total bacteria and yeast is also observed. Finally, Crystar FT250 membranes seem to be very efficient for filtering viscous, high sugar matrices such as unfermented grape juice with very satisfactory fluxes and permeabilities (205 L.h⁻¹.m⁻² and 151 L.h⁻¹.m⁻².bar⁻¹) and clearly superior to 0.2 µm hollow fibers (factor ~ 10). Compared to hollow fibers, Crystar FT250 membranes show significantly better performance and filtration efficiency. These membranes allow for (i) the respect of the hierarchy of wine filterability (easy, medium, difficult), (ii) maintaining significantly higher permeate flow set points throughout the filtrations, (iii) filtering up to 3.5 times more wine volume for the same filtration time with 2.5 times less backwashing. These improved performances represent a considerable advantage for professionals in the sector as they allow significant savings in terms of time and energy. It should be noted that the use of SiC membranes brings other advantages such as (i) limiting the fouling of the membranes because the channels have a large diameter, (ii) during the filtration of very fouling products and even if the regenerations did not pose any problem, "stronger" cleanings with more extreme pH could be performed, (iii) limiting the immobilization of volume due to the long settling time. These filtration tests on several matrices on an industrial scale are in agreement with the results obtained in the laboratory [36].

CRedit authorship contribution statement

M. Trevisan: Methodology, Writing – original draft, Writing – review & editing. **R. Ghidossi:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision. **P. Moulin:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] M. Agnolucci, A. Tirelli, L. Cocolin, A. Toffanin, *Brettanomyces bruxellensis* yeasts: Impact on wine and winemaking, *World J. Microbiol. Biotechnol.* 33 (10) (2017) 180, <https://doi.org/10.1007/s11274-017-2345-z>.
- [2] Aptel, P., Moulin, P., & Quemeneur, F. (2002). Micro et ultrafiltration : Conduite des essais pilotes, traitement des eaux et effluents. Club français des membranes.

- [3] F. Arndt, F. Ehlen, S. Schütz, H. Anlauf, H. Nirschl, Influence of operating parameters and membrane materials on fouling of ceramic hollow fibre membranes, *Sep. Purif. Technol.* 171 (2016) 289–296, <https://doi.org/10.1016/j.seppur.2016.07.046>.
- [4] M.-P. Belleville, J.-M. Brillouet, B.T. Fuente, M. Moutounet, Polysaccharide Effects on Cross-Flow Microfiltration of Two Red Wines with a Microporous Alumina Membrane, *J. Food Sci.* 55 (6) (1990) 1598–1602, <https://doi.org/10.1111/j.1365-2621.1990.tb03579.x>.
- [5] M.-P. Belleville, J.-M. Brillouet, B.T. Fuente, M. Moutounet, Fouling Colloids During Microporous Alumina Membrane Filtration of Wine, *J. Food Sci.* 57 (2) (1992) 396–400, <https://doi.org/10.1111/j.1365-2621.1992.tb05502.x>.
- [6] Boulton, R. B., Singleton, V. L., Bisson, L. F., & Kunkee, R. E. (1999). The Fining and Clarification of Wines. In R. B. Boulton, V. L. Singleton, L. F. Bisson, & R. E. Kunkee (Eds.), *Principles and Practices of Winemaking* (p. 279–319). Springer US. https://doi.org/10.1007/978-1-4757-6255-6_7.
- [7] W.R. Bowen, F. Jenner, Theoretical descriptions of membrane filtration of colloids and fine particles : An assessment and review, *Adv. Colloid Interface Sci.* 56 (1995) 141–200, [https://doi.org/10.1016/0001-8686\(94\)00232-2](https://doi.org/10.1016/0001-8686(94)00232-2).
- [8] A. Cassano, A. Mecchia, E. Drioli, Analyses of hydrodynamic resistances and operating parameters in the ultrafiltration of grape must, *J. Food Eng.* 89 (2) (2008) 171–177, <https://doi.org/10.1016/j.jfoodeng.2008.04.015>.
- [9] P. Czekaj, F. López, C. Güell, Membrane fouling during microfiltration of fermented beverages, *J. Membr. Sci.* 166 (2) (2000) 199–212, [https://doi.org/10.1016/S0376-7388\(99\)00261-6](https://doi.org/10.1016/S0376-7388(99)00261-6).
- [10] Ducruet, J., Silvestri, A.-C., & Hippenmeyer, P. (Ecole d'ingénieurs de C. (2006). Comparative study of cross-flow filters in oenology. *Revue suisse de viticulture, arboriculture, horticulture* (Switzerland). <https://agris.fao.org/agris-search/search.do?recordID=CH2007000022>.
- [11] N. El Darra, M.F. Turk, M.-A. Ducasse, N. Grimi, R.G. Maroun, N. Louka, E. Vorobiev, Changes in polyphenol profiles and color composition of freshly fermented model wine due to pulsed electric field, enzymes and thermovinification pretreatments, *Food Chem.* 194 (2016) 944–950, <https://doi.org/10.1016/j.foodchem.2015.08.059>.
- [12] J.-L. Escudier, M. Moutounet, A. Vernhet, décembre 10). Application des membranes dans la filière œnologique [Text], Ref : TIP700WEB - « Agroalimentaire ». (2000) <https://www-techniques-ingenieur-fr.docelec.u-bordeaux.fr/base-documentaire/42430210-operations-unitaires-du-genie-industriel-alimentaire/download/f3270/application-des-membranes-dans-la-filiere-oenologique.html>.
- [13] M. Feuillat, D. Peyron, J.L. Berger, Effects of tangential microfiltration on their chemical composition and organoleptic characteristics, Application to Burgundy wines. (1987) https://pandor.u-bourgogne.fr/ead.html?id=FRMSH021_00019&c=FRMSH021_00019_BOIV_1987_03-04_n673-n674_art01.
- [14] E. Garmsiri, Y. Rasouli, M. Abbasi, A.A. Izadpanah, Chemical cleaning of mullite ceramic microfiltration membranes which are fouled during oily wastewater treatment, *J. Water Process Eng.* 19 (2017) 81–95, <https://doi.org/10.1016/j.jwpe.2017.07.012>.
- [15] C. Güell, R.H. Davis, Membrane fouling during microfiltration of protein mixtures, *J. Membr. Sci.* 119 (2) (1996) 269–284, [https://doi.org/10.1016/0376-7388\(96\)80001-J](https://doi.org/10.1016/0376-7388(96)80001-J).
- [16] M.Y. Jaffrin, B.B. Gupta, A. Chaibi, Effect of physical parameters on the microfiltration of wine on a flat polymeric membrane, *Chem. Eng. Processing: Process Intensification* 32 (6) (1993) 379–387, [https://doi.org/10.1016/0255-2701\(93\)80026-D](https://doi.org/10.1016/0255-2701(93)80026-D).
- [17] S.W. King, R.J. Nemanich, R.F. Davisa, Wet chemical processing of (0001)Si 6H-SiC. Hydrophobic and hydrophilic surfaces, *J. Electrochem. Soc.* 146 (5) (1999) 1910–1917, <https://doi.org/10.1149/1.1391864>.
- [18] C. van Leeuwen, A. Destrac-Irvine, Modified grape composition under climate change conditions requires adaptations in the vineyard, *OENO One* 51 (2) (2017) 147–154, <https://doi.org/10.20870/oenone.2017.51.2.1647>.
- [19] A. Lüdemann, Wine Clarification with a Crossflow Microfiltration System, *American Journal of Enology and Viticulture* 38 (3) (1987) 228–235.

- [20] S. Luque, D. Gómez, J.R. Álvarez, Industrial Applications of Porous Ceramic Membranes (Pressure-Driven Processes) Vol. 13 (2008) 177–216, [https://doi.org/10.1016/S0927-5193\(07\)13006-0](https://doi.org/10.1016/S0927-5193(07)13006-0).
- [21] W.A. Meulenbergh, J. Mertens, M. Bram, H.-P. Buchkremer, D. Stöver, Graded porous TiO₂ membranes for microfiltration, *J. Eur. Ceram. Soc.* 26 (4) (2006) 449–454, <https://doi.org/10.1016/j.jeurceramsoc.2005.06.035>.
- [22] M. Mietton-Peuchot, Milisic, & BEN AIM. Microfiltration tangentielle des boissons. Influence des caractéristiques hydrodynamiques, *Le Lait* 64 (638.639) (1984) 121–128.
- [23] V. Millet, A. Lonvaud-Funel, The viable but non-culturable state of wine micro-organisms during storage, *Lett. Appl. Microbiol.* 30 (2) (2000) 136–141, <https://doi.org/10.1046/j.1472-765x.2000.00684.x>.
- [24] A. Morata, (Ed.). *Red wine technology*, Academic Press an imprint of Elsevier, 2019.
- [25] C. Morel-Salmi, J.-M. Souquet, M. Bes, V. Cheynier, Effect of Flash Release Treatment on Phenolic Extraction and Wine Composition, *J. Agric. Food. Chem.* 54 (12) (2006) 4270–4276, <https://doi.org/10.1021/jf053153k>.
- [26] P. Moulin, P. Manno, J.C. Rouch, C. Serra, M.J. Clifton, P. Aptel, Flux improvement by Dean vortices : Ultrafiltration of colloidal suspensions and macromolecular solutions, *J. Membr. Sci.* 156 (1) (1999) 109–130, [https://doi.org/10.1016/S0376-7388\(98\)00333-0](https://doi.org/10.1016/S0376-7388(98)00333-0).
- [27] J. Mueller, R.H. Davis, Protein fouling of surface-modified polymeric microfiltration membranes, *J. Membr. Sci.* 116 (1) (1996) 47–60, [https://doi.org/10.1016/0376-7388\(96\)00017-8](https://doi.org/10.1016/0376-7388(96)00017-8).
- [28] M. Padaki, R. Surya Murali, M.S. Abdullah, N. Misdan, A. Moslehyani, M. A. Kassim, N. Hilal, A.F. Ismail, Membrane technology enhancement in oil–water separation, A review. *Desalination* 357 (2015) 197–207, <https://doi.org/10.1016/j.desal.2014.11.023>.
- [29] A. Pons, L. Allamy, A. Schüttler, D. Rauhut, C. Thibon, P. Darriet, What is the expected impact of climate change on wine aroma compounds and their precursors in grape? *OENO One* 51 (2) (2017) 141–146, <https://doi.org/10.20870/oeno-one.2017.51.2.1868>.
- [30] Y.E. Rayess, M. Mietton-Peuchot, Membrane Technologies in Wine Industry : An Overview, *Crit. Rev. Food Sci. Nutr.* 56 (12) (2016) 2005–2020, <https://doi.org/10.1080/10408398.2013.809566>.
- [31] C. Ren, H. Fang, J. Gu, L. Winnubst, C. Chen, Preparation and characterization of hydrophobic alumina planar membranes for water desalination, *J. Eur. Ceram. Soc.* 35 (2) (2015) 723–730, <https://doi.org/10.1016/j.jeurceramsoc.2014.07.012>.
- [32] Ribéreau-Gayon, P., Glories, Y., Maujean, A., & Dubourdieu, D. (2012). *Traité d'œnologie—Tome 2*.
- [33] M. Serrano, B. Pontens, P. Ribéreau-Gayon, Etude de différentes membranes de microfiltration tangentielle. Comparaison avec la filtration sur précouche de diatomées, *OENO One* 26 (2) (1992) 97–116, <https://doi.org/10.20870/oeno-one.1992.26.2.1202>.
- [34] F. Springer, R. Ghidossi, E. Carretier, D. Veyret, D. Dhaler, P. Moulin, Study of the Effect of Geometry on Wall Shear Stress and Permeate Flux for Ceramic Membranes: CFD and Experimental Approaches, *Eng. Appl. Computational Fluid Mechanics* 4 (1) (2010) 17–28.
- [35] Trevisan, M. (2020). Microfiltration des vins par membranes en carbure de silicium (SiC) : De la caractérisation à la filtration au chai. [Thèse soutenue en 2020, Aix-Marseille]. <https://www.theses.fr/s197126>.
- [36] M. Trevisan, L. Barthélémy, R. Ghidossi, P. Moulin, Silicon carbide (SiC) membranes in œnology : A laboratory-scale study, *OENO One* 54 (4) (2020) 719–732, <https://doi.org/10.20870/oeno-one.2020.54.4.3856>.
- [37] M. Ulbricht, W. Ansorge, I. Danielzik, M. König, O. Schuster, Fouling in microfiltration of wine : The influence of the membrane polymer on adsorption of polyphenols and polysaccharides, *Sep. Purif. Technol.* 68 (3) (2009) 335–342, <https://doi.org/10.1016/j.seppur.2009.06.004>.
- [38] W. Youravong, Z. Li, A. Laorko, Influence of gas sparging on clarification of pineapple wine by microfiltration, *J. Food Eng.* 96 (3) (2010) 427–432, <https://doi.org/10.1016/j.jfoodeng.2009.08.021>.