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Silicon carbide (SiC) membranes in œnology: a laboratory-scale study

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ABSTRACT

Unfiltered wine is a turbid medium that is not generally accepted by the consumer. Therefore, one or several filtration steps are required before bottling. Silicon carbide (SiC) membranes desirable parameters (porosity, tortuosity fluxes) allow filtering several different types of loaded matrices like wine or residue sediment. An in-depth filtration study was carried out on white and red wines to evaluate membrane efficiency and to optimise their cleaning procedure. Retention rates were studied as a function of wine type, filtration mode, and volumetric concentration factor. Compared to ceramic membranes, SiC membrane permeate fluxes are higher, up to a factor of 10 for red wine. For white wines, equivalent permeate fluxes could be obtained with dead-end filtration. Moreover, SiC membranes appear to be effective in obtaining a clear and brilliant wine and do not modify the concentration of the compounds of interest in wine. Finally, an optimised cleaning protocol has been identified and shown to restore a sufficient permeability to the SiC membranes.

KEYWORDS

vsilicon carbide membrane, wine, filtration performances, fouling, regeneration

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INTRODUCTION

The presence of cloudiness or deposits in wine has always been perceived by consumers as a defect or undesirable trait of the final product (Rayess and Mietton-Peuchot, 2016). The objective of filtration is to produce a clear and brilliant wine over time by removing all particles responsible for sediments and deposits (Ribéreau-Gayon *et al.*, 2012b). The high concentration and variability of the suspended solids limit the suitable filtration technologies: fouling, and retention of wine compounds, have to be carefully managed to achieve an effective filtration. Limpid and stable wine is ensured by several procedures of clarification and stabilization, including traditional practices such as the use of fining agents, enzymes, fining and precoat filtration, as well as new practices such as membrane technologies (Palacios *et al*., 2002; Rayess and Mietton-Peuchot, 2016). Indeed, over the centuries, the various discoveries about the origins of wine have shown that the means of filtration have never ceased to evolve (Hamachi and Mietton-Peuchot, 1999). The wine was first filtered on fabrics and then on industrial filters, which have now been replaced by alluvial, plate or more recently, membrane processes. Moreover, in a cellar, winemakers have to filter liquids ranging from a few $mg.L^{-1}$ of suspended particles up to several tenths of $g.L^{-1}$. The matrices to be filtered present in the cellar are therefore varied and very complex. These rich matrices may cause severe fouling and possibly irreversible modifications of wines organoleptic characteristics. Wine is increasingly filtered on microfiltration membranes, but the performances of currently used technologies limit the efficiency of industrial installations using a high frequency of backwash. In fact, an increase in flow rates has been used to reduce the number of cleaning cycles and/or the size of installations. The microfiltration membranes currently used for wine filtration are between 0.2 and 1.2 µm pores size. Both organic and ceramic membranes consist of a support layer in addition to a very thin filtration layer. The most common membranes installed are polymeric hollow fibre membranes, for their large specific area, or tubular ceramic membranes, of the type titanium oxide or alumina. Silicon carbide (SiC) is increasingly used for membrane manufacturing because they are more stable than synthetic membranes, they have a much longer lifetime, and the cleaning-sterilizing process is better due to high temperature (Peri *et al*., 1988; Békássy-Molnár, 2000). Therefore, these membranes can filter different types of wine matrices with low pressure and minimal fouling. SiC membranes have relevant characteristics such as higher porosity (40 %), lower tortuosity (1.20) (Hofs *et al*., 2011), which could allow them to achieve increased permeate fluxes for filtration of loaded liquids like wine and residue sediments. Moreover, SiC is known to have complex surface chemistry when it comes to its hydrophobic or hydrophilic behaviour. Indeed, as demonstrated by King *et al*., 1999, pure SiC has a hydrophobic behaviour. On the other hand, as oxygen links to the surface of the material, silicon carbide tends to behave closer to that of silica (SiO2), which is hydrophilic. The membranes used in this work are purposely produced with as low levels of silica as possible as this impurity leads to a reduction of the material's chemical resistance. As a consequence, they are primarily hydrophobic rather than hydrophilic. The contact with the wine is expected to create Si–O–C, Si–O and C–O links on the material surface, hence decreasing the hydrophobicity. The chemical cleaning cycles may strip part of the extrinsic oxygen out again. So, one should expect the behaviour of the SiC material of the present study to oscillate between hydrophobicity and hydrophilicity throughout the different phases of the wine clarification processes.

As a result of these characteristics, SiC has become, since the 2010s, a material of choice for the manufacture of mineral membranes used in the filtration of loaded liquids (Zoubeik and Henni, 2016; Fraga *et al*., 2017; Sui *et al*., 2017; Luo *et al*., 2018). Indeed, these membranes are already commonly used in water purification (Zsirai *et al*., 2016) and wastewater treatment (Bakshi *et al*., 2015; He and Vidic, 2016; Kuhn *et al*., 2016).

In the present study, SiC membranes were studied in the filtration of white and red wines coming from different vineyards and cellars. This process was evaluated, in a laboratory scale, in terms of retention efficiency, hydraulic performances, final wine physicochemical characteristics, under different operating conditions (filtration mode, pore size, molecular weight cut off (MWCO), transmembrane pressure (TMP), crossflow velocity, and cleaning procedure).

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MATERIALS AND METHODS

1. Wines, membranes, and pilot plant

One white wine and two red wines with different origins and varieties were chosen for this study. Their characteristics, given in (Table 1), led to different clarification values and fouling agent concentrations. The white wine (WW) was recovered from the cellar shortly after the alcoholic fermentation. The first red wine (RW1) was a wine at the end of vinification and aged in barrels but unfiltered. The second red wine (RW2) was pre-treated (treated with fining agent: Mannostab® and Stabivin® commercialized by Laffort) and pre-clarified (with a pre-filtration 1.0 µm ± 0.4) to facilitate its final filtration. Thus, the membrane impact was studied on a young wine and an aged wine to obtain results on different matrices (different vintage, high and low fouling capacity, suspended matters, anthocyanins, and polyphenols concentration). For each trial fresh wine was used to validate the process efficiency.

Each wine was filtered with two SiC membranes and an oxide ceramic membrane presented below, to study their effectiveness. Each filtration mode was tested in triplicate to ensure the repeatability of the results. The two Saint-Gobain Crystar® SiC membranes used for this study were with pore sizes of 0.25 µm (Crystar® FT250) and 0.60 µm (Crystar® FT600). An oxide ceramic membrane with a pore size of 0.10 µm, commonly used in oenology, was used for comparison. The characteristics of the tested membranes were similar, with a length of 25 cm, an area of 0.047 m^2 and a 6 mm diameter single-channel geometry.

There was a significant difference between the pore size of the membranes used, and the ones compared to, which may play a confounding role in interpreting the experimental results. However, there is not necessarily a correlation between the pore size and the hydraulic performances of the membranes (production flow and/or permeability). This comparison of these three membranes was chosen for several reasons:

- They are membranes with comparable materials (= ceramics)
- For the ceramic oxide membrane, this pore size (0.1 µm) is the closest available to the Crystar® membranes (0.25 µm and 0.60 µm). It is interesting to note that their cut-off thresholds are very close given the differences that can be found between the announced pore size and the real cut-off thresholds.
- All three membranes are marketed and used for similar applications (sterilizing fine filtration)

Finally, Serrano *et al*. (1992) showed that two ceramic membranes with a pore size of 0.2 µm did not retain the yeasts and bacteria of a red and a white wine. Up to 4 logs of viable bacteria are founded in the permeate. Given that the application of this study is a sterilizing filtration, an oxide ceramic membrane with smaller pores (= 0.1 µm) was chosen.

Two pilot plant configurations (Figure 1) were used in accordance with the filtration mode (crossflow or dead-end). For crossflow filtration, the configuration, shown in Figure 1b, allows operation with controlled velocity and transmembrane pressure. The crossflow velocity was kept at 2.5 $m.s^{-1}$ to maintain a turbulent flow while the TMP ranged from 0.7 to 0.95 bar. The volume of the feed tank is 5 L. The system was equipped with pressure sensors at the inlet, the

TABLE 1. Characteristics of the different wines tested

Analysis	White Wine (WW)	Red Wine n°1 (RW1)	Red Wine n°2 (RW2)
Vintage	2018	2010	2015
Initial turbidity	82	545	27
Fouling index (FI)	> 30	> 30	< 30
Tannins ($g.L^{-1}$)	n.a.	2.7	4
Anthocyanins ($mg.L^{-1}$)	n.a.	138	242
CI' (-)	n.a.	1.63	0.9
Total bacteria ($UFC.mL^{-1}$)	$6.0 \cdot 10^2 – 9.70 \cdot 10^3$	$2.0 \cdot 10^3 – 8.75 \cdot 10^3$	$3.33 \cdot 10^2 – 2.40 \cdot 10^3$

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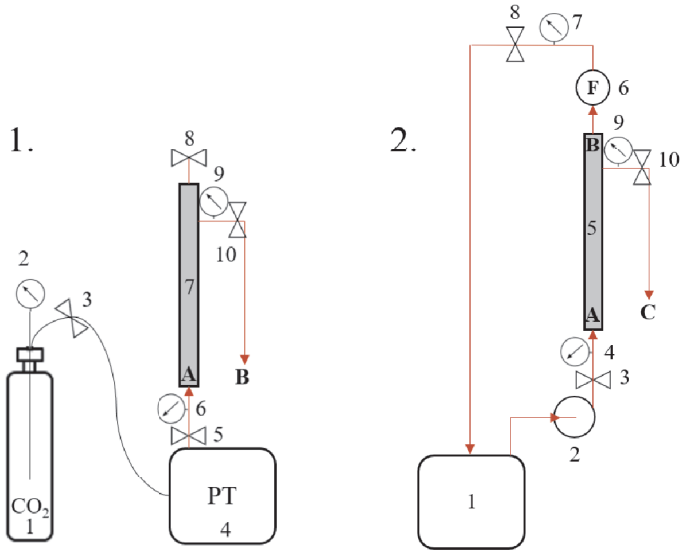


FIGURE 1. Filtration pilots used
(a): Dead-end experimental filtration ; 1: CO_2 bottle ; 2, 6, 9: manometers ; 3, 5, 8, 10: pressure regulation valve ; 4: pressurized feed tank ; 7: membrane module ; A: inlet ; B: permeate and (b): crossflow experimental filtration, 1: feed tank ; 2: centrifugal pump ; 3, 8, 10: pressure regulation valves ; 4, 7, 9: manometers ; 5: membrane module ; 6: flow meter ; A: inlet ; B: outlet ; C: permeate.

outlet, and at the permeate side of the membrane to calculate the TMP. A flow sensor at the membrane inlet allowed the control of hydrodynamic conditions. The tests were performed in dead-end, and crossflow filtration, for the white wine and only in crossflow filtration for the red wines. During dead-end filtration, the feed tank was pressurized with CO_2 to reduce wine oxidation. The membrane was filled with the white wine to purge the air through the upper part of the membrane. The valve number 8 was then closed to increase the pressure up to the desired TMP.

Permeate flow measurement was calculated throughout the time of the experiment. Permeate samples were taken regularly to evaluate retention versus time. At the end of the filtration process step, backwash cleanings were carried out. After a preliminary study, a clean-in-place (CIP) procedure, presented below, was tested and validated. This clean-in-place (CIP) procedure, optimized over time, was a five-step procedure, all with a backwash at a TMP of -1 bar: a flushing with tempered water; a 2 L flushing of basic solution (pH = 12.5) with an addition of hydrogen peroxide solution (0.2 %) at 50 °C; a 2 L flushing with distilled water to recover a neutral pH and a 2 L flushing of acid solution with citric acid (pH = 2.5) at 30 °C. Finally, there was a final flushing before measurement of the membrane's water permeability. If 85 % of the initial water permeability was not reached, the CIP was repeated. Permeability and volumic concentration factor (VCF) were calculated by the following formulae (Equations 1 and 2):

Equation 1. Transmembrane pressure

$$TMP = \frac{Pi + Po}{2} - Pp$$

with TMP = transmembrane pressure (bar), Pi = inlet pressure, Po = outlet pressure and Pp = permeate pressure (bar).

Equation 2. Membrane water permeability

$$Lp0 = \frac{Jwater\ (20°C)}{TMP}$$

with Lp0 = membrane water permeability ($L.h^{-1}.m^{-2}.bar^{-1}$), J = permeate flux ($L.h^{-1}.m^{-2}$)

The VCF calculation depends on the filtration mode. Respectively for dead-end (De) and crossflow (Cf) filtration (Equation 3 and Equation 4):

Equation 3. Volumic concentration factor (VCF) for dead-end filtration. The VCF calculation with Vm = membrane volume, Vi = initial wine volume in the feed tank (L) and Vp = filtered permeate volume (L).

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$$VCF\ De = \frac{Vm + Vp}{Vm}$$

Equation 4. Volumic concentration factor (VCF) for crossflow filtration

$$VCF\ Cf = \frac{Vi}{(Vi - Vp)}$$

The flux of wine ($L.h^{-1}.m^{-2}$) is corrected by the temperature influence on the viscosity of the wines (Yanniotis *et al.*, 2007) and the permeability can be calculated by following the equation (Equation 5):

$$Lp = \frac{Jwine\ (20°C)}{TMP}$$

Equation 5. Membrane wine permeability

2. Wine analyses

The turbidity measured in Nephelometric Turbidity Units (NTU) is correlated to the presence of particles and suspended macromolecules. Their concentration is measured by the incident light scattered at an angle of 90° through the suspension. For each trial, the turbidity measurement of the wine, before and after filtration, was carried out using a turbidimeter (Thermo Scientific Orion AQUAfast AQ3010). The colour was characterised at the optical density (OD) of 420, 520 and 620 nm to study the red wine evolution. These optical densities are the characteristic wavelengths respectively of the yellow, red and mauve colour. For the white wine, only the optical density of 420 nm was measured, this analysis is called oxidation degree. The colour intensity modified (CI') is the sum of the optical densities at 420, 520 and 620 nm measurements with a Perkin Elmer Lambda 25 UV/vis spectrophotometer under 1 mm optical path compared to distilled water. This value represents the entire colour intensity of the wine with (Equation 6 and Equation 7):

Equation 6. Colour Intensity of wine

$$CI = OD420 + OD520$$

Equation 7. Colour Intensity modified of wine

$$CI' = OD420 + OD520 + OD620$$

In wine, the characteristic absorption at 280 nm (OD 280) of the benzene rings of the majority of phenols makes it possible to estimate their quantity present in wines (Flanzy and Poux, 1958; Ribéreau-Gayon, 1970). To measure the index at 280 nm (OD 280), the red wine is diluted 100 times and the absorbance at 280 nm is measured using a Perkin Elmer Lambda 25 UV/vis spectrophotometer and was compared to water with an optical path of 1 cm in a UV-permeable tank (quartz or special plastic). The anthocyanins concentration done only for red wines was measured based on sulphur dioxide discolouration. These measurements were made at 520 nm using a spectrophotometer then compared to water with an optical path of 1 cm. The concentration (in $mg.L^{-1}$) was given by transferring the difference in optical densities to a standard curve established using the formula (Ribéreau-Gayon *et al.*, 2012b) with a slope of 875. For tannin quantification, red wine tannins consist of proanthocyanidin chains that may be polymerized. Heating in an acidic medium causes the breaking of certain bonds and the formation of carbocations that turn into anthocyanidins if the medium is sufficiently oxidized (Bate–Smith Reaction) (Ribéreau-Gayon and Stonestreet, 1965). The concentration (in $g.L^{-1}$) is given by the product of the difference in optical densities and the slope of the calibration curve (19.33).

The membrane retention of microorganisms during the filtration was studied by comparing the concentration of microorganisms in the feed and the permeate. The microorganism concentration in samples was determined by the count of colony-forming units (CFU) in a Petri dish culture. This method was carried out in Petri dishes containing a solid grape juice medium, whose composition is, for one litre of medium: 250 mL of commercial grape juice, 5 g of yeast extract, 1 mL of Tween80®, 20 $g.L^{-1}$ of agar-agar and distilled water to adjust the medium to 1 litre. It was then homogenized, and the pH was adjusted to 5 to optimize the growth of microorganisms. In addition, antibiotics may be added to select microorganism species. Then, the preparation was laid out in Petri dishes. The tested wine samples were diluted in cascade and placed on the boxes in the form of 10 µL drops of each dilution. The Petri dishes were incubated at 25 °C anaerobically for 7 days for yeasts and 10 days for bacteria. After this incubation time, the CFUs were counted on spots with between 2

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and 50 colonies, and populations, in CFU.mL^{-1}, were counted as follows:

Equation 8. Colony Forming Unit

$$[CFU] = \frac{m \times 1000}{v} \times dilution$$

with m = mean of colonies

RESULTS AND DISCUSSION

This part aimed to evaluate the efficiency of SiC membrane in wine filtration. One white wine and two red wines were filtered to optimise the operating conditions of filtration.

1. Statistical data treatment

1.1. Wine filtration repeatability

Obtaining raw materials for the experiments was difficult for several reasons: firstly, to be as representative as possible of what is going on in the field, it was necessary to obtain at least, one white wine and two red wines (young and aged). As the chemical composition of a young and an aged red wine are not the same (Hermosín-Gutiérrez *et al*., 2005), the analytical and hydraulic results during filtration will be different (El Rayess *et al*., 2012), therefore it was necessary to obtain at least two red wines. For the dry white wine, being mostly a product drank soon after bottling, only one young white wine was chosen. However, to filter under the same winemaking conditions as in the field, it was necessary to obtain a dry white wine just out of fermentation and unfiltered. These conditions are only met during a very short period of the year. Moreover, the volumes available for experimentation were limited.

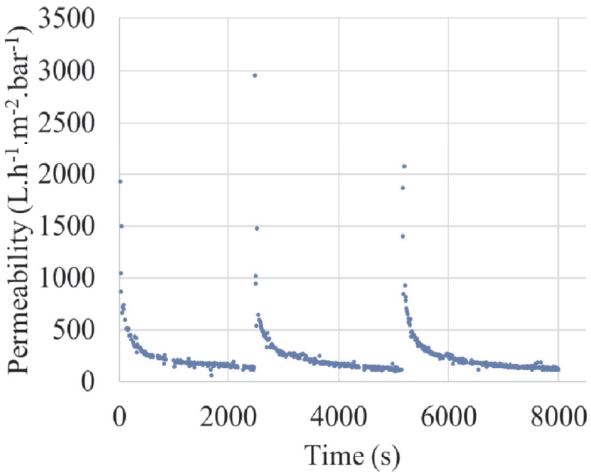


FIGURE 2. Evolution of permeability as a function of time to study experimentations repeatability and robustness
[WW, TMP » 0.8 bars, v = 2.5 m.s^{-1}]

Therefore, to optimize the volume of wine available, and to obtain the maximum amount of relevant results while remaining representative, each filtration mode was tested in triplicate to assure the repeatability of the results. It is shown in Figure 2 by the example of dead-end filtration results on unfiltered white wine under the conditions of 0.8 bar, 2.5 m.s^{-1}.

The microfiltration shows a very satisfactory repeatability during experimentation (length of filtration, stabilization time, and stabilization permeability values). Thus, filtration was considered robust and filtrations were carried out once on each membrane, and on each type of tested wine.

1.2. Wine composition analyses

All the analyses on wine composition: physicochemical and microbiological analyses described in this paragraph were performed in triplicate on each filtration and the results were expressed as mean ± standard deviation. The existence of significant differences between each analysis (feed vs. permeate and/or feed vs. retentate) was estimated by calculating the 95 % confidence intervals (CI) of the difference between means. Following this approach, if the 95 % CI was in a range including the value 0, there was no significant difference between the samples. If it was not, then there was a statistically significant difference between the samples (Knezevic, 2008).

Moreover, this work focused on the potential impact SiC membranes can have on the final product, the results of those findings are presented on the feed and the permeate.

2. Hydrodynamic performances

2.1. White wine

The impact of the filtration process on phenolic compounds and the hydraulic performances were analysed for both SiC and oxide ceramic membranes. The microfiltration process was tested in dead-end (DE) and crossflow (CF) modes for the unfiltered and unfined white wine (WW, Table A). Operating conditions with a TMP of 0.7 bar, without backwash, were applied.

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To evaluate the SiC membrane efficiency, the permeability of the wine was measured as a function of the VCF for 2 different pore sizes (Crystar® 0.25 µm and Crystar® 0.60 µm), and for an oxide ceramic membrane (pore size = 0.10 µm). Results are presented in Figure 3. To evaluate the hydraulic performances for each filtration mode, permeability was plotted as a function of VCF (Figure 3). However, the VCF was found too different in the two types of filtration, because the experimental setup, and the wine volume, were not adapted to reach as high VCFs in crossflow mode as those attained in dead-end mode. Thus, in order to allow a more meaningful comparison between the two filtration modes, the permeability was plotted as a function of the volume of permeate filtered per membrane surface (Figure 4).

In all trials performed, the permeability dropped very quickly during the first minutes of filtration and then became more stable toward the end of the filtration. This observation reflects a significant fouling of the membrane at the beginning of filtration. As expected, the wine concentration process was more progressive and slower in crossflow filtration. Whatever the filtration mode, and for an equivalent filtered volume per unit area (150 $L.m^{-2}$), the Crystar® 0.60 µm membrane had a higher permeability than the Crystar® 0.25 µm and the ceramic 0.10 µm membranes. At the end of the filtration cycles, the SiC membranes showed a more stable permeate flux than the ceramic one. In crossflow filtration, the wine filtration capacity for SiC membranes was between 250 and 300 $L.m^{-2}$ compared to 150 $L.m^{-2}$ for the ceramic membranes tested (Figure 4a,b,c). And for an equivalent filtered wine volume (150 $L.m^{-2}$), SiC permeability was 2.1 and 4.6 times higher than the ceramic membrane, respectively for Crystar® 0.60 µm and Crystar® 0.25 µm (Figure 4).

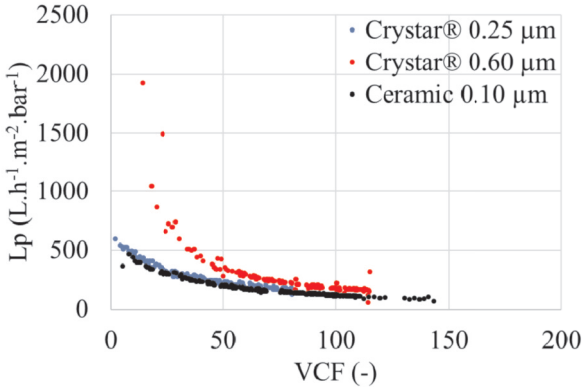


FIGURE 3. Evolution of permeability as a function of VCF
(a): dead-end and (b): in cross flow filtration ; [WW, TMP » 0,8 bars, v = 2.5 $m.s^{-1}$]

During dead-end filtration trails, the wine was concentrated in the membrane channel and during cross-flow filtration, it was concentrated in the feed tank. Therefore, in both filtration modes, the wine was not concentrated in the same volume. That's why, to compare the evolution of fluxes during filtration for each membrane, the permeability as a function of the permeate volume/membrane area was represented in Figure 4. Whatever the membrane, Figure 4 highlights that crossflow velocity leads to an increase of wall shear-stress, hence reducing the fouling and increasing the permeate flux, up to 2 times with Crystar® 0.60 µm. These results highlight the fact that SiC membranes could reach higher productivity than the oxide ceramic membrane tested, for both filtration modes. Furthermore, these results demonstrate the benefit of using dead-end filtration in the case of white wine, seeing a volume of up to 130 $L.m^{-2}$ reached with Crystar® 0.60µm. Dead-end filtration could be preferred due to the significantly reduced energy (no circulation pump, limits on temperature increase, reduction of the passage of wine through the pump) compared to crossflow filtration. The use of backflushes can be

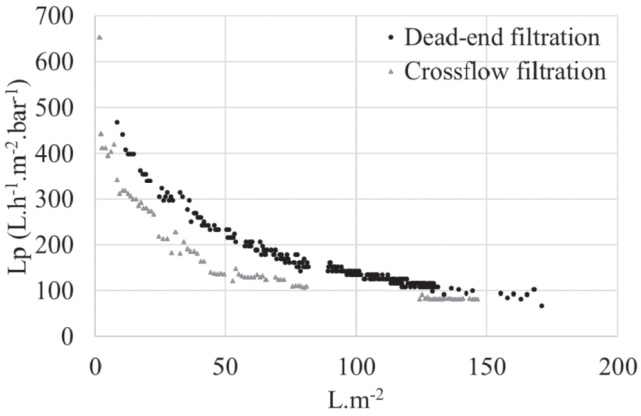


FIGURE 4. Evolution of permeability as a function of permeate volume in both filtration modes for white wine and for each membrane.
(a): Crystar® membrane 0.60 µm, (b): Crystar® 0.25 µm and (c): Ceramic 0.10 µm ; [WW, TMP » 0,8 bars, v = 2.5 $m.s^{-1}$]

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considered when reaching the filtration limit values to partially recover membrane permeability. The differences in performance between SiC and the ceramic membranes may be explained by the different microstructure of the materials and their specific surface chemistries. Indeed, SiC membranes have a very high porosity (40 %) and a lower tortuosity (= 1.2) compared to all other oxide ceramic membranes used in oenology (alumina, titanium dioxide, zirconium dioxide, etc.), therefore, having significantly higher water permeability (up to 7 times depending on pore size). In addition to their high porosity and low tortuosity, SiC membranes have very low surface charges at typical wine pH (3.4), which grants them a better resistance against material adsorption and thus fouling.

2.2. Red wines

The microfiltration process was first tested for the two red wines (RW1 and RW2, see Table 1) only in crossflow filtration (CF) mode with a TMP value set to 0.7 bar. The permeability and membrane resistance evolutions along the filtration cycles are presented in Figure 5.

For both red wines, permeability decreased as permeate volume increased, as usual. However, the filtration behaviour for the two wines turned out to be very different indeed. RW2 seemed to induce more fouling than RW1. In both cases, SiC membranes behaved in the same way, the

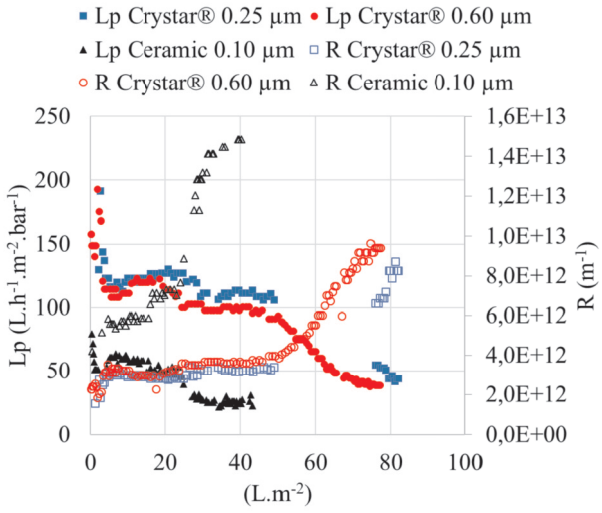


FIGURE 5. Evolution of permeability and membrane resistance as a function of permeate volume per filtration area in crossflow filtration. (a) the red wine n°1 and (b) the red wine n°2 ; [RW1 and RW2, TMP » 0,8 bars, v = 2.5 m.s^{-1}]

permeate flux was clearly impacted by fouling. The oxide ceramic 0.10 µm fouled much earlier than SiC membranes and, as a result, filtration could not be completed. For a fouling resistance of 1.10^{13}m^{-1}, the permeate volume produced by the oxide ceramic membrane were 110 and 25 L.m^{-2} for RW1 and RW2, respectively (Figure 5). At the end of the filtration cycles, the permeate volumes produced by the SiC membranes were around twice that produced by the ceramic oxide membrane. The resistance obtained for Crystar® 0.60 µm, at the end of filtration, was higher than the value obtained for Crystar® 0.25 µm: 8.5 and 1.5 times, respectively, for RW1 and RW2.

For both red wines, the membrane Crystar® 0.25 µm showed the lowest resistance: 4 and 10 times lower for RW2 and RW1 (Figure 5) respectively, when compared to oxide ceramic 0.10 µm.

For all the 3 wines tested, fouling was less pronounced and fluxes were higher for SiC membranes compared to the oxide ceramic (up to 10 times higher permeate flux with Crystar® 0.25 µm). In addition, Crystar® 0.25 µm had a significantly higher permeability than Crystar® 0.60 µm for red wines, despite the lower pore size. This is most likely explained by the size of the particles present in the wine. Indeed, at this stage of vinification, the particles and molecules present in wine range between 0.1 µm and 10 µm, and a vast majority of them (yeasts, bacteria and colloidal macromolecules) are close to the size of the membrane pores, which increases the pore blocking propensity. According to Table 2, which shows different permeate fluxes obtained with different membranes, and comparable pore sizes (Escudier *et al.*, 2000), SiC membranes appear to perform better by 1.5 to 2.5 times for red wine. SiC membranes have shown a flux of between 100 and 180 L.h^{-1}.m^{-2} on a raw white wine, compared to tubular alunina/zirconia membranes which have fluxes of 128 to 250 L.h^{-1}.m^{-2} on fined white wines, which are known to significantly increase the filterability of the wine.

Moreover, the example of RW1 illustrates the non-correlation between pores size and hydraulic performances as discussed in the chapter Material and Methods. Indeed, the pore size of the Crystar® 0.60 µm is larger than Crystar® 0.25 µm membrane; yet the production flows of the latter are higher.

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TABLE 2. Comparison of permeability obtained with different membranes in crossflow filtration (based on Escudier *et al.,* 2000).

Membrane	Pore diameter (µm)	Wine type	Permeate flux ($L.h^{-1}.m^{-2}$)
Tubular alumina	0.20	Raw red wine	30 76
Tubular alumina/zirconia	0.20	Fined red wine	14-85
	0.20	Fined white wine	128–250
	0.20	Red wine	80-115
Carbon/zirconia tubular	0.06	Red wine (no additional information)	83
	0.14		100
This study	0.25	Fined red wine	35–100
Tubular Silicon Carbide	0.25	Raw white wine	100
	0.60	Raw white wine	180

Figure 5 shows the important variation of initial permeability for the different membranes studied. Before the wine filtration trial, SiC membrane permeabilities were between 9700 and 11800 $L.h^{-1}.m^{-2}.bar^{-1}$ for both pore sizes (Figure 6), hence 7 times higher than that of the ceramic membrane. The graph also highlights that the optimized chemical cleaning implemented was efficient for all membranes, even after many filtration cycles. The first cleaning product used was sodium hydroxide combined with hydrogen peroxide, respectively at 2.0 % and 0.2 %, at high temperature (pH = 12.5; 50–55 °C). The mixture of sodium hydroxide and hydrogen peroxide produces a powerful oxidant called sodium peroxide and can generate a significant exothermic reaction causing the dissolution of organic compounds. The chemical cleaner injected inside the membrane, during backwash mode, with a pressure of 1 bar, effectively allowed removal of the membrane fouling. After a rising step with water at neutral pH, a second cleaning with citric acid (pH = 2; 30 °C), also in backwash mode, was performed. Finally, after another rising with water to neutralize the pH, the membrane permeability measurement was performed. The choice of cleaning in backwash mode is explained by the fact that in microfiltration, the pore size is relatively large, so in-depth fouling can take place. This cleaning procedure was effective regardless of the wine treated, the membrane type, the filtration mode and conditions. After all filtration cycles, except one, a sufficient permeability recovery (85 %) was obtained for the SiC membranes (Figure 6), proving the effectiveness of the protocol.

3. Impact of membrane filtration process on wine composition

3.1. Turbidity measurement

Turbidity is one of the most important elements for measuring the efficiency of a microfiltration process. The measurement of "clarity" evaluates the visual quality of the product, which is of key importance to wine consumers. The required specifications were: < 0.2 NTU for white wine (WW) and < 1 NTU for red wines (RW1 and RW2). To monitor the performance of the process over the entire filtration cycle, the turbidity of different permeate samples were

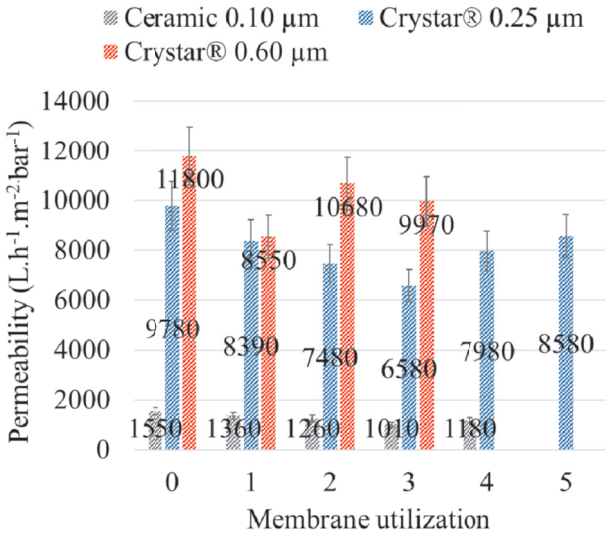


FIGURE 6. Evolution of permeability after chemical backwashes.
0: initial permeability of membranes. Values are the mean ± standard deviation of measure of permeability at different pressures (from 0.5 to 1.5 bar).

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TABLE 3. Evolution of turbidity during the filtration for each membrane and filtration mode for white wine and both red wines.

Wine	Filtration Mode	Sample	Turbidity (NTU)		
			Crystar® 0.25 µm	Crystar® 0.60 µm	Oxide Ceramic 0.10 µm
White wine (WW)	Dead-end	Feed	78	54.8	97.1
		Permeate	0.11–0.07	1.12–0.96	0.37–0.55
	Crossflow	Feed	64	88	67
		Permeate	0.10–0.10	1.50–0.33	0.23–0.14
Red wine n°1 (RW1)	Crossflow	Feed	547	548	418
		Permeate	0.55–0.50	0.95–4.80	1.20–0.86
Red wine n°2 (RW2)	Crossflow	Feed	19	21	31
		Permeate	0.9–0.5	1.40–1.05	0.30–5.60

measured throughout the trials. The obtained values are shown in Table 3.

Results show that only Crystar® 0.25 µm reached a turbidity lower than or equal to 0.2NTU for white wine, regardless of the filtration mode and the VCF. This means that the cut-off threshold of this membrane is sufficient to stop the wine particles responsible for turbidity. Therefore, in light of the results (retention rate and production flow) compared to the oxide ceramic membrane and Crystar® 0.60 µm, membrane Crystar® 0.25 µm is the most relevant candidate for the rest of the study. The two other membranes allow stable and good results, but not enough to reach the specifications defined for these tests at a VCF of 120. Crystar® 0.60 µm appears to give the highest permeate turbidity, which seems consistent with its larger pore size and pore size distribution. In the case of red wines, the tests on RW1 and RW2 with Crystar® 0.25 µm were conclusive. Turbidity values for permeates were below the desired target. For the other membranes, the turbidity values of the permeate appeared above the desired value. Thanks to its superior turbidity retention and permeate flux performances, Crystar® 0.25 µm was the most relevant candidate for complementary investigations at the pilot scale.

3.2. Colour characteristics

The membrane process was studied to evaluate its eventual impact on wine colour characteristics. A significant change in the chromatic characteristics of wine could reflect an oxidation effect in white wine, and a modification or retention of a compound of interest in red wine. Permeate refers to the mean of samples collected respectively for a VCF equal to 1 and higher than 100. For the case of white wine (Figure 7a), the only absorbance at 420 nm was measured. For the case of red wines, the three absorbances representative of the colour of a wine were quantified. The results are presented in Figure 7b.

Results showed all OD420 nm values were below 0.1, thus indicating no important oxidation of white wine by the filtration process, whatever the membrane material or the pore size (Figure 7a). However, Figure 7a shows that white wine is significantly more oxidized in cross-flow filtration mode than in dead-end, and more oxidized by the oxide ceramic membrane. Unlike the dead-end filtration unit, the cross-flow filtration unit is not inert. So, the use of the centrifugal pump can provide oxygen to the wine which causes its oxidation. For the red wines, results were similar for RW1 and RW2. Statistically, there is no significant difference between ODs and CI' between the feed and the permeates for the two red wines. Whatever the membranes and the wine, the microfiltration process had no significant impact on the colour characteristics of the wine.

3.3. Population of microorganisms count

Suspended particles in wine, among them microorganisms, have a fundamental role in winemaking and a high impact on wine clarification. They are responsible for the fermentation or alteration of wine and need to be removed at the end of the vinification process to avoid the development of wine defects due to an uncontrolled growth of microorganisms. The main microorganisms present in wine (*Saccharomyces cerevisiae* and *Oenococcus*

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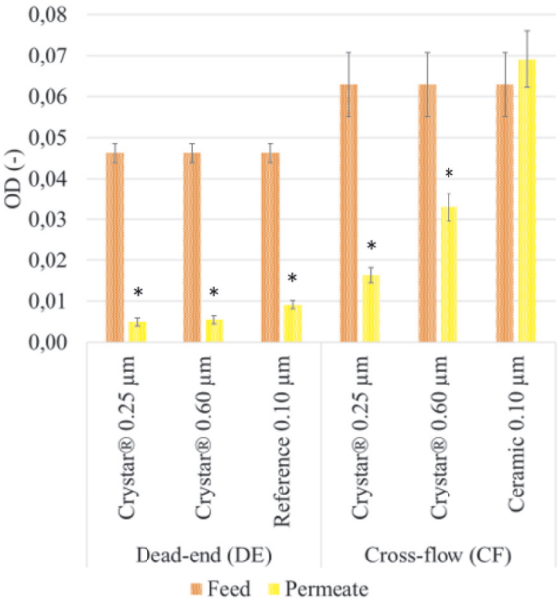


FIGURE 7. (1): Oxidation degree for white wine, (2): evolution of colour characteristic during filtration for each membrane for red wine n°2.
Permeate = mean of samples collected respectively for a VCF equal to 1 and highest concentration; CI' = intensity colour modified. Values are the mean ± standard deviation of triplicate on each sample.

oeni) were counted before and after filtration on several permeate samples to check the retention efficiency. The obtained results are presented in Table 4.

Considering these results, wine filtration with SiC membranes, as well as with oxide ceramic 0.10 µm, was efficient to remove bacteria from wine. These results are encouraging because if these membranes can completely stop bacteria, they are also likely able to stop yeasts, which are larger in size. Indeed, yeasts are unicellular eukaryotic micro-organisms with an ovoid form and size range between 2.0 and 10.0 µm, whereas bacteria are smaller cells with a size range between 0.5 and 1.0 µm (Ribéreau-Gayon *et al*., 2012a). In the case of dead-end filtration, which allowed us to reach a VCF greater than 100, log removals close to 6 log were obtained with the membrane Crystar® 0.25 µm, as no bacteria were detected in the permeate during the filtration process.

3.4. Phenolic compounds quantification

To study the impact of membrane microfiltration on the retention of phenolic compounds, anthocyanins, tannins and absorbance at 280 nm (OD 280) (Figure 8) were measured before and after filtration on several permeate samples throughout the filtration process. Due to the low VCF attained in the trials, the phenolic compounds in the permeate samples did not vary substantially.

Phenolic compounds can react with each other through tannin-anthocyanin linkages. Physicochemical interactions may also occur through tannin-tannin and anthocyanin-anthocyanin self-association. But these various mechanisms are not yet all known. Therefore, the quantities of phenolic compounds can vary significantly among different red wines. The older the red wine, the more interactions exist between tannins and anthocyanins, making the detection of some compounds more difficult because they are not free yet in the wine. Because RW1 was older than RW2, it had lower amounts of free anthocyanins, tannins and a lower abs. For both SiC membranes studied, there was no significant difference in phenolic compounds before and after filtration. However, there appears to be a slight decrease in anthocyanins and tannins through the ceramic

TABLE 4. Microorganisms count during filtration for each membrane for white wine.

Wine	Filtration mode	Sample	Bacteria (CFU.mL^{-1})		
			Crystar® 0.25 µm	Crystar® 0.60 µm	Ceramic 0.10 µm
White wine (WW)	Dead-end	Feed	9700	400	4330
		Permeates	< 1/10 mL	< 1/10 mL	< 1/10 mL
	Crossflow	Feed	600	1760	1770
		Permeates	< 1/10 mL	< 1/10 mL	< 1/10 mL
Red wine n°1 (RW1)	Crossflow	Feed	5230	8750	2000
		Permeates	< 1/10 mL	< 1/10 mL	< 1/10 mL
Red wine n°2 (RW2)	Crossflow	Feed	333	2400	2200
		Permeates	< 1/10 mL	< 1/10 mL	< 1/10 mL

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membrane in RW2 (Figure 8a,b). This result correlates with the absorbance at 280 nm (OD 280) shown in Figure 8c. This retention has already been mentioned in several works, stated that phenolic compounds have an impact on membrane fouling, and decrease the permeation fluxes (Susanto *et al*., 2009), particularly by adsorption on ceramic membranes. This conclusion was determined by the intense colouration of deposits observed on membrane surfaces Belleville *et al*., 1992; Belleville *et al*., 2006;) identified by membrane washing with acidified methanol (Santos and Jorge, 1995). No phenolic compound retention was observed with SiC membranes; thus, they seem to not affect these compounds of interest.

CONCLUSION

Wine filtration with SiC membranes was demonstrated to be efficient in treating white and red wines. This process showed its capacity to remove bacteria with a similar removal efficiency as traditional oxide ceramic membranes, with 0.10 µm pore size, for both types of wine, and each filtration mode (dead-end and crossflow filtration). In terms of hydraulic results, whatever the filtered wine or the filtration mode, SiC membranes exhibited the best performance, with a greater fouling resistance and superior permeate fluxes. Compared to the data available in the state of the art, SiC membranes had up to 2.5 times higher flows compared to oxide ceramic membranes. Considering also the turbidity reduction performance in addition to the permeate fluxes (productivity), Crystar® FT250 (0.25 µm) seemed to be the best candidate and most suitable for filtering wine under optimized conditions (no organoleptic modifications and efficient retention of microorganisms). Regarding the regeneration (chemical cleaning) of membranes, the established protocol (chemically enhanced backwashes with base and acid solutions) was shown to be effective, as seen by the permeabilities, each time, recovering up to the desired efficiency. For wine, especially red, there are specific products for cleaning membranes (acid + base possibly combined with oxygen peroxide) and remove high content and diverse fouling compounds, In this case, the addition of hydrogen peroxide to the sodium hydroxide cleaning step was more effective than if was not added to wash solution. Followed by an acidic cleaning, the complete procedure (sodium hydroxide + hydrogen peroxide and

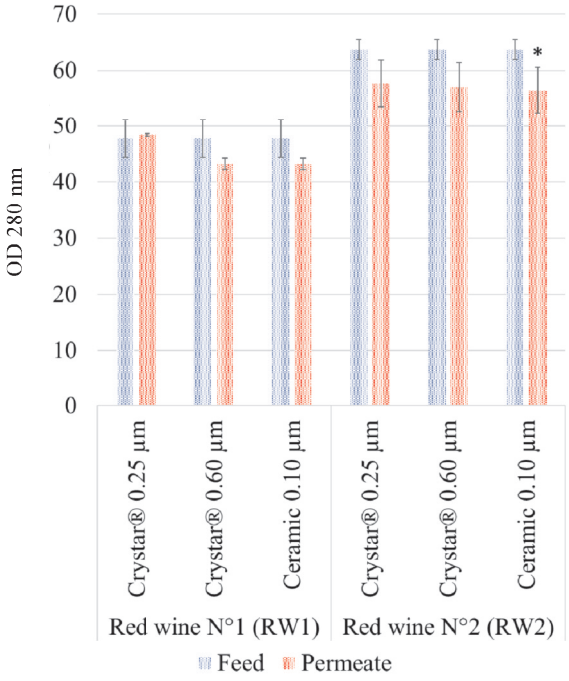


FIGURE 8. (a): Quantity of anthocyanins before and after filtration for each membrane and each filtration mode for both red wines (b): Quantity of tannins before and after filtration for each membrane and each filtration mode for both red wines obtained, (c): absorbance at 280 nm (OD 280) before and after filtration for each membrane and each filtration mode for both red wines.
Permeate = mean of samples collected respectively for a VCF equal to 1 and highest concentration. Values are the mean ± standard deviation of the triplicate on each sample, the asterisk on this graph indicates that the mean value significantly differs from the feed value (significance level 95 %).

acid) seemed to be effective on this membrane material. Finding the best-adapted regeneration protocol to the membrane material used is essential for the wine filtration process stability in the long term. Thereafter, the use in backwash (time, pression, concentration, etc.) of these cleaning products have been optimized during the industrialization of the membrane process and will be the subject of a forthcoming paper. Finally, the results of the physicochemical analyses gave satisfactory results, whatever the wine or the cut-off. Indeed, unlike ceramic oxide membranes, which seem to slightly retain some phenolic compounds, SiC membranes have no significant impact on the retention of the major compounds of interest (anthocyanins, tannins, polyphenols) of the wine, and they do not impact

the colouring component either. Due to the small membrane surfaces involved in these tests, no sensorial analysis was performed. The feasibility and interest of SiC membranes having been demonstrated, however, tests on an industrial scale and further analysis (sensorial analysis, HPLC, GC-MS, etc.) are in progress and will be the subject of a forthcoming paper.

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