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Cross-flow microfiltration applied to oenology: A review

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ABSTRACT

The cross-flow microfiltration applied to wine filtration has become a legitimate alternative to conventional filtration processes. However, membrane fouling which affects the operating costs and the plant maintenance, limits the widespread application of this technique. The aim of this review is to provide a better understanding of the development of the cross-flow microfiltration in wine industry, as well as the complexity of wine composition and its consequences on membrane fouling. This review covers also the impact of the operating conditions and the membrane characteristics on fouling mechanisms. Strategies to limit fouling as well as the latest innovations and commercial proposal are discussed in this paper.

Contents

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1. Introduction

Filtration as a means of wine clarification goes back to ancient times. After alcoholic and malolactic fermentations, the crude wine is a complex medium presenting a turbid aspect. This latter is not well accepted by the consumer and wine needs to be clarified. Three groups of compounds have been identified in a crude wine according to compounds sizes as shown in Fig. 1:

- *Solutes* (size less than 1 nm) include ions, salts, organic acids and phenolic compounds.
- *Colloids* (size range between 1 nm and 1 μm) contain polysaccharides, proteins, polymerized phenolic compounds and colloidal aggregates.
- *Particles* (size higher than 1 μm) include microorganisms (yeast and bacteria chains), cell debris, colloidal aggregates and potassium tartrate crystals.

When wine is cloudy, or when a deposit remains at the bottom of the bottles, it is perceived as a sign of product deterioration. Indeed, limpidity of wine is the first visual quality a consumer expects from wine. It must be a permanent quality during all the storage period (even in tank or bottle) whatever the storage condition is (aeration, lighting, temperature, etc.). The key roles of filtration are to provide limpidity and also microbiological stabilization of wines.

Wine limpidity is assessed by measuring turbidity which is expressed by Nephelometric Turbidity Unit (NTU). Table 1 summarized the wines turbidity and its correlation with the visual aspect of the wines. After filtration, the turbidity of wines must be less than 2 NTU.

Stabilization could be divided into physico-chemical and microbiological stabilization. Physico-chemical stabilization (not insured by filtration) prevents the formation of organic and inorganic hazes and deposits after packaging. Microbiological stabilization by microfiltration is guaranteed by eliminating yeasts and bacteria that can destroy or modify a wine's taste. Wine stability is defined as a state or a condition such as the wine will not, for some definite period of time, exhibit undesirable physical, chemical, or organoleptic changes [1]. These undesirable changes that denote wine instability were listed by: browning or other color deterioration, haziness or very slight cloudiness, cloudiness, deposits and undesirable taste or odor [1,2]. Many examples of colloidal instability had been identified in wines, for example the protein and polyphenols instability, iron and copper cloudiness, pectin and yeast polysaccharides haziness [1,2].

Table 1
Correlation between wine turbidity (NTU) and visual aspect of wine [2].

	Brilliant	Haziness
White wine	<1.1 NTU	>4.4 NTU
Rosé wine	<1.4 NTU	>5.8 NTU
Red wine	<2.0 NTU	>8.0 NTU

Early, wineries were equipped with diatomaceous earth filters. This technique showed quickly its limits in terms of wine quality, wine loss and its implementation especially in cooperative cellars (non-automated process). In the mean time, cross-flow microfiltration (CFMF) was widespread used in food industry and biotechnology. It appeared as a promising process to replace the traditional filtration methods.

The first wine filtration tests using membrane goes back to 1960 in California and to 1964 in France. The first trials of cross-flow microfiltration have been conducted in oenology at the beginning of the 80s. The used membranes at the time migrated from other industries and were not specific to wine [3,4]. This resulted in affecting the organoleptic quality of wines and increased temperatures during the process. In the mid-80s, ultrafiltration (UF) and CFMF of wine have been the focus of large interest and research effort [5,6]. The ultrafiltration technique was unsuitable for wine filtration due to the loss of wine quality [6]. From 1990, large progress on wine CFMF was realized by the constructors especially on organic membrane [7,8]. The development of membrane materials associated with a better understanding of the compounds involved in the membrane fouling led to the selection of membranes suitable for wine filtration [7,8].

Nowadays, this technique is well accepted in wine industry and becomes to be widely used in cellars. Despite the progress made, however, the large-scale development of CFMF is still hampered by the technological and economical barriers induced by membrane fouling.

The purpose of this paper is to provide an overview on the CFMF process applied to oenology in order to highlight the application, the problems and the progress of this technique in oenology sector. Given the complexity of wine composition, wine compounds which are susceptible to have an impact on membrane fouling are presented. The implement and the application of the CFMF in oenology are then discussed. This section will be followed by a summary of the fouling mechanisms that hamper the development of this technique in oenology. The review will also deal with the role of wine chemistry in fouling phenomena as well as the impact of the operating parameters. To conclude, strategies to limit fouling are revised as well as the latest progress and propositions to improve CFMF at the industrial scale.

2. Wine's composition

Wines are alcoholic drinks obtained from the fermentation of grapes. Their composition is determined by the composition of the grape, which depends on genetic characters, on vine growing conditions, on grape ripeness at harvest, and on wine-making practices. These latter involve a series of successive operations, the sequence of which varies considerably depending on the wine type. Wines' composition depends also on yeast and bacterial strains and their metabolism. The average composition of wines (white and red) is shown in Table 2.
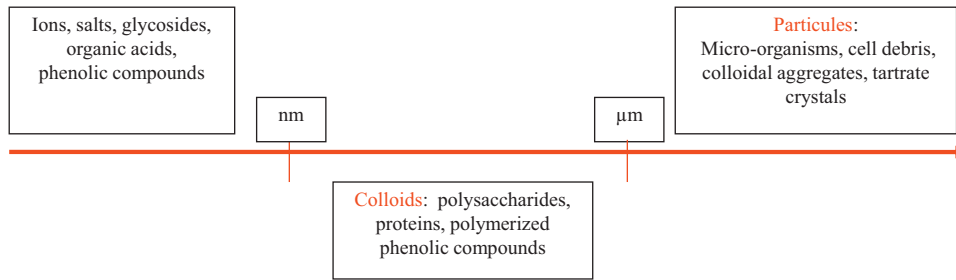
Fig. 1. Crude wine compounds classified according to their sizes.

Table 2
Average composition of wines [2,9].

	Concentration (g.l^{-1})	
Water	750 – 900	
Ethanol	69 – 121	
Glycerol	5 - 20	
Organic acids	3 – 20	
Minerals	0.6 – 2.5	
Nitrogen compounds *(amino acids and proteins)*	0.5 – 5	
	White wine	Red wine
Phenolic compounds	0.1 – 0.3	1.5 – 6
Polysaccharides	0.4 – 0.7	

In the following paragraphs, colloids and particles will be only presented due to their implication in the fouling phenomena during CFMF.

2.1. Wine colloids

2.1.1. Phenolic compounds

The phenolic compounds in wine include a diverse group of naturally occurring compounds, known as polyphenols. Phenolic compounds in grapes and wine could be divided into non-flavonoid compounds and flavonoid compounds as shown in Fig. 2 [2,9]. Flavonoid group contains anthocyanins and tannins which are the most abundant phenolic compounds in the red wines. Contrariwise, little quantities of tannins are found in white wines while anthocyanins are completely absent. Grape flavanols, also called flavan-3-ols (tannins) as they are hydroxylated in the 3rd position, are found as monomers but also as oligomers and polymers with different degrees of polymerization [10,11]. Non-flavonoid group includes phenolic acids such as benzoic acids and hydroxycinnamic acids and stilbenes such as resveratrol [2,9]. In white wine, the most important phenolic compounds are the hydroxycinnamic acids and of minor quantities, the flavan-3-ol monomers.

Major changes in phenolic compounds occur during wine elaboration and ageing. These changes are mostly related to their chemical reactivity and less to specific enzymes. Phenolic compounds can react with each other as tannin–anthocyanin linkage. Physicochemical interactions may occur between phenolic compounds themselves as tannin–tannin and anthocyanin–anthocyanin self-association [2,9]. It may occur also between phenolic compounds and other wine compounds such complexes of tannin–proteins or tannin–polysaccharides [2,9–13]. These interactions and associations modify the average size of these compounds and no data concerning these latter is available in the literature.

It should be noted, however, that grape phenolic compounds besides their antioxidant properties are very important constituents of wines since they contribute to color, astringency and
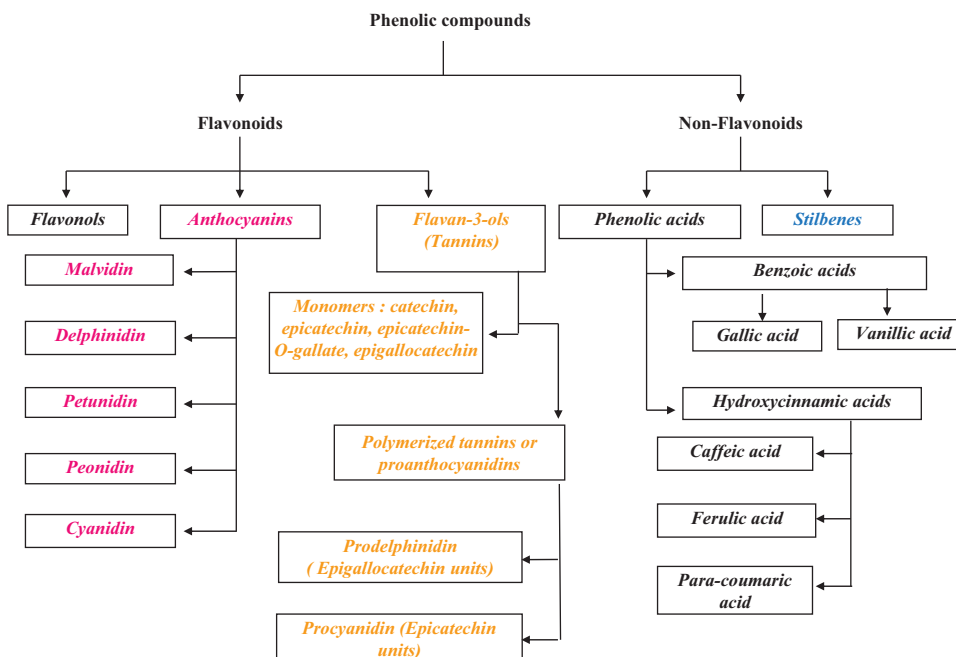

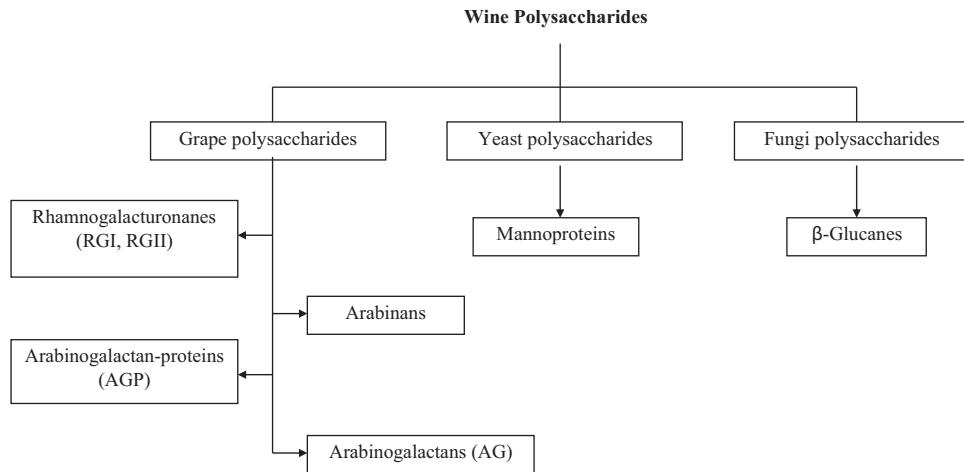**Fig. 2.** Summary of wine's phenolic compounds.

Fig. 3. Main wine polysaccharides classified according to their origin.

bitterness, oxidation reactions, interactions with proteins and ageing behaviour of wines [2,10,12,14].

2.1.2. Polysaccharides

Polysaccharides constitute one of the main groups of macro-molecules found in wine and contribute to increase its viscosity and the stability of the colloidal system [2,9]. Their presence in wines is due to the contribution of the cell walls of either micro-organisms during alcoholic fermentation or grape berries after hydrolysis of pectic chains by pectolytic enzymes during grape maturation or during winemaking [9,15–18]. The polysaccharides may be divided into 3 groups depending on their origin (Fig. 3):

- *Grape polysaccharides*: they include pectin, which are chains formed almost exclusively of galacturonic acid (homogalactur-onane), and pectic substances such as arabinanes, arabinogalac-tanes, arabinogalactan-proteins (AGP) and rhamnogalacturonans (RG-I, RG-II) with a molecular weight ranging between 40 and 250 kDa [15–18]. Pectin are rarely found in wines because of the activity of endogenous or commercial enzymes.
- *Yeast polysaccharides*: their concentration increase during fermentation due to the lysis of yeast cell. This group is represented by mannoproteins (10–450 kDa) and less by mannanes [19,20]. Nowadays, mannoproteins can be added to the wine at doses ranging from 15 g/hl to 25 g/hl in order to inhibit potassium bitartrate precipitation. The added mannoproteins are highly gly-cosylated with molecular masses ranging between 30 and 40 kDa [21].
- *Fungi polysaccharides*: the best-known molecule of this group is beta-glucane deriving from *Botrytis cinerea* and accidentally from *Pediococcus*. This molecule has a molecular weight of 1000 kDa, and is known to be a possible cause of problems in the filtration of wine [9].

2.1.3. Proteins

Together with amino acids and peptides, proteins constitute the main components of nitrogenous fraction of musts and wines [22,23]. In this group, proteins will be only presented due to their negative effect on wine filtration. In the literature, some studies show that wine proteins are a mixture of grape proteins and proteins from autolyzed yeast [22]. Others refer that these macro-molecules come only from grapes [24]. Red wines hardly contain any free proteins, as they are precipitated by tannins. White and rosé wines, on the other hand, may have variable protein concentrations of up to a few hundred (10–500) mg/l, mainly originating from grapes [2]. Some of these proteins have been identified. They are pathogenesis-related proteins involved in the defense mechanism of plants against fungal attacks [22,24]. Among these proteins, the most abundant are chitinases and thaumatin-like proteins with low molecular masses ranging between 20 and 30 kDa. Instability of proteins in white wines is one of the most common non-microbial defects of commercial wines [21]. Denaturation of proteins in white wines may result from unfavorable storage conditions, leading to their aggregation [22]. The denatured protein can subsequently precipitate to form an amorphous sediment or deposit or flocculate and thus produce a suspended and unattractive haze in the bottled wine that reduces its commercial value, making it unacceptable for sale [22–25].

2.2. Wine particles

Suspended particles in wine play a major role in winemaking and especially in wine clarification. This group includes microor-ganisms (yeast and bacteria chains), cell debris, colloidal aggregates and tartrate crystals. They are retained by the filters but may be found accidentally in the final wine.

2.2.1. Yeasts

Yeasts are unicellular eukaryotic micro-organisms with an ovoid form and size range between 2 and 10 μm. They carry out the alcoholic fermentation which is the anaerobic trans-formation of must sugars into alcohol. 16 yeast genera are associated with winemaking. *Saccharomyces cerevisiae* is the pre-dominant yeast in winemaking [26]. Other yeasts, such as species of *Brettanomyces*, *Kluyveromyces*, *Schizosaccharomyces*, *Torulaspora*, *Zygosaccharomyces* and *Saccharomycodes*, may be present during the fermentation or ageing of the wine [26–28]. Wine alcoholic fermentations can be divided into two types: uninoculated (spon-taneous or natural fermentations) with unpredictable results and directly inoculated by adding a selected yeast strain. At the begin-ning of vinification, the yeast population is 10^5–10^6 yeasts per milliliter of must to reach 10^7–10^8 yeasts per milliliter during alco-holic fermentation [25,26]. A few weeks after the completion of fermentation, the yeast viable population is less than a few hun-dred cells per ml. Because of their size, yeasts settle easily and are partially removed by settling and racking operations.

2.2.2. Bacteria

Few species of bacteria are able to grow in wines. This is due to acidic pH (3.0–3.8) and ethanol concentration of these wines. Two distinct types of bacteria may play an important role on the final
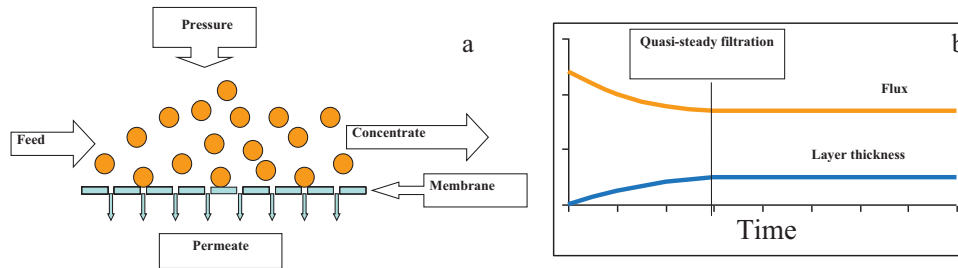
Fig. 4. (a) Principle of cross-flow microfiltration and (b) representation of the quasi-steady filtrate flow.

quality of wines. These bacteria are lactic acid bacteria and acetic acid bacteria [25,26].

Lactic acid bacteria belong to the group of Gram-positive microorganisms. They are small cells (size between 0.5 and 1 μm) round shaped or slightly elongated forming pairs or chains. At the beginning of the alcoholic fermentation, there are 10^3–10^4 bacteria per ml. After the end of the alcoholic fermentation, the number of bacteria may reach 10^6–10^8 bacteria per ml and perform the so-called malolactic fermentation [26]. This latter is the transformation of malic acid into lactic acid leading to a slight deacidification and a possible improvement of the organoleptic quality of wine [9,26]. The main specie of lactic acid bacteria in wine, responsible for carrying out the malolactic fermentation, is *Oenococcus oeni*.

The presence or growth of acetic acid bacteria (Gram-negative) is undesirable since it has generally been related to wine spoilage, mostly by increasing the acetic acid and thus, the volatile acidity. The main specie found in wines is *Acetobacter* and it may reach 10^8 bacteria per ml in contaminated wines.

2.2.3. Tartrate crystals

Tartaric acid and its salts (potassium bitartrate and calcium tartrate) are normal constituents of musts and wines. Musts are usually saturated with potassium bitartrate. The formation of alcohol during fermentation acts to decrease the solubility of potassium bitartrate and calcium tartrate, thus, producing a supersaturated solution in the wine [2]. This may result in crystallization of tartrate salts when the wine is bottled and stored at low temperatures [9,21]. Such crystallization is considered undesirable and generally do not meet with consumer acceptance. Consequently, winemakers employ various treatment methods before bottling a wine to prevent this problem. The most extensively used methods are cold stabilization, ion-exchange process and electro-dialysis.

2.2.4. Colloidal aggregates

Colloidal aggregates are the result of the agglomeration of the macromolecules of wines. This resulted in instability and it is responsible for most physico-chemical disorders and deposits in wines. Phenolic compounds, polysaccharides and proteins are the main constituents of these macromolecules as well as traces of many other compounds. The exact composition of these aggregates, the mechanisms involved and the parameters influencing the aggregations are not completely known yet and lack much information about this topic.

3. CFMF principle and its applications in oenology

In CFMF, the fluid to be filtered flows parallel to the membrane surface and permeates through the membrane by mean of a pressure drop. The shear exerted by the feed solution flowing parallel to the membrane surface can sweep the deposited particles towards the concentrate or retentate side so that the cake layer remains relatively thin (Fig. 4a). In the case of CFMF, a cake layer will be built

up gradually. After some time, a quasi-steady state is reached and a quasi-steady filtrate flow is obtained for a long time as shown in Fig. 4b. This fact is due to the equilibrium between the transport of particles to the cake layer and the back transport of particles into the feed stream.

The liquid amount that passes through the membrane is called permeate while the retained molecules and solvent constitute the retentate which is concentrated progressively during filtration cycles (Fig. 4a). Today this operation mode is a standard operation in many food industries (milk, cheese, wine, vinegar, beer, juice, vegetable oils, etc.)[29].

The permeate flux is governed by the so-called general filtration equation (Darcy's law) given as:

$$J = \frac{\Delta P - \Delta \Pi}{\mu \cdot R_h}$$

where J (m^3/m^2/s) is the permeate flux, ΔP (Pa) the applied pressure, $\Delta \Pi$ the osmotic pressure, μ (Pa s) the solvent viscosity and R_h (m^{-1}) the hydraulic resistance. In wine CFMF, the membranes used have 0.2 μm as average pore size. Thus, they retain only colloids and particles while the solutes and salts pass through the membrane. Therefore, $\Delta \Pi$ could be considered as negligible in this case and Darcy's law could be given as:

$$J = \frac{\Delta P}{\mu \cdot R_h}.$$

3.1. Wine final filtration

In order to have a limpid wine before bottling, the wine makers implement successive solid–liquid separations using traditional technologies such as centrifugation, filtration on sheets, diatomaceous earth filtration and the use of exogenic additives. Diatomaceous earth filtration is the most used technique to clarify wines. Nowadays, diatomaceous earth is classified as dangerous substances due to the presence of crystalline silica. Massive exposure may cause eye and airways irritations [30]. Diatomaceous earth has also a negative impact on environment. After uses, it cannot be disposed but it must be transported to waste disposal sites to be treated. So, restrictions for environment and health force the oenology sector to search for alternative techniques to traditional filtrations, and cross-flow microfiltration could represent this alternative. Indeed, this technology can substitute in a one step procedure to the conventional processes which imply several filtration steps on diatomaceous earth previous to the final microbial stabilization obtained by dead end filtration on membranes. In addition to a great simplification of the wine processing line, crossflow microfiltration offers a number of additional advantages such as elimination of earth use and its associated environmental problems as well as the combination of clarification, stabilization and sterile filtration in one single continuous operation.
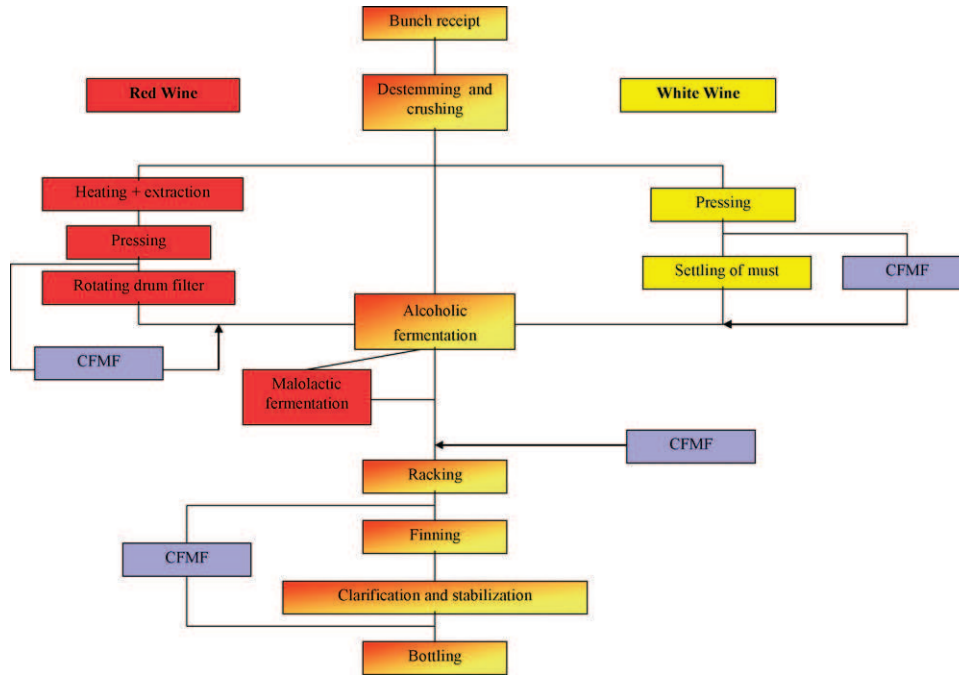
Fig. 5. The processes of red and white wines making and the uses of CFMF as alternative technique.

Besides the technological advantages of cross-flow filtration in winemaking, there are also some economic and operational benefits to consider:

- Elimination of labor costs and saving time (cross-flow filters are highly automated).
- Elimination of sheets and kieselgur which reduces purchasing and storage costs, improve hygiene and work safety and reduce wastes.
- Reduction of wine loss and energy costs by substitution of several treatments in a single operation.
- Reduction/elimination of clarifying agents.
- Possibility of data recovery (high process automation).

3.2. Other applications

CFMF, even though it is used as final filtration before bottling, also allows to carry out other processes needed in wine making without compromising the organoleptic wine features. Fig. 5 illustrates the location of CFMF in the scheme of winemaking as an alternative technique for conventional processes. It may be used in white wine making to replace the step of settling of must which consists in separation of suspended materials by decantation but several developments are needed to achieve this purpose. Also, it avoids excessive sulfur dioxide utilization to inactivate wild micro-organisms inside fresh musts in order to carry out a controlled fermentation with selected yeast [31]. It can be used in the red winemaking to substitute the rotating drum filter in order to decrease the turbidity of the red must [32]. CFMF allows also the elimination of suspended material (colloid, particles and micro-organisms) during or after the fining phase. It may be used in sweet wines making to stop alcoholic fermentation without using excessive amount of sulfur dioxide.

Note that, the clarification of musts is a quite different problem and remains a challenge in oenology, especially after flash-release, because it is not yet adapted to the industrial scale. Even, the pore sizes used for must clarification should not be the same used for wine clarification before bottling. Indeed, membranes with pore size $0.2\,\mu m$ decrease hugely the turbidity (<2 NTU) of the must while conventionally the turbidity of the must should range between 50 and 150 NTU. In other hand, membranes will be quickly and completely fouled while filtering musts because these latter are highly loaded with particles and their turbidity may exceed 2000 NTU.

4. CFMF fouling mechanisms in oenology

Conventionally, the development of cross-flow microfiltration in oenology sector has long been hampered by significant fouling of the membrane despite definite advantages of membrane usage. The consequence of this is a reduction in permeation rates, affecting the economic viability of the process, and a risk of excessive retention of some components, which may affect the product quality.

Fig. 6 shows a curve of typical flux decline in time during wine CFMF process. This typical curve can be divided into three parts. First part (I) is characterized by a rapid initial drop from the flux of pure water filtration. It is followed by a long term gradual flux decrease in part II and ended with a steady-state flux in the third part (III) [33].
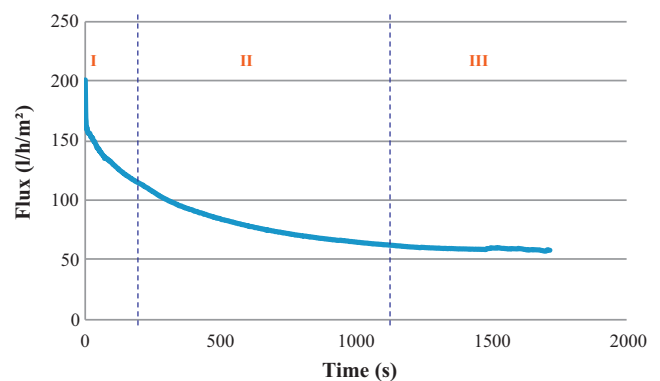

Fig. 6. A schematic presentation of red wine filtration at 800 mbar with multichannel ceramic membrane ($0.2\,\mu m$) (personal data).
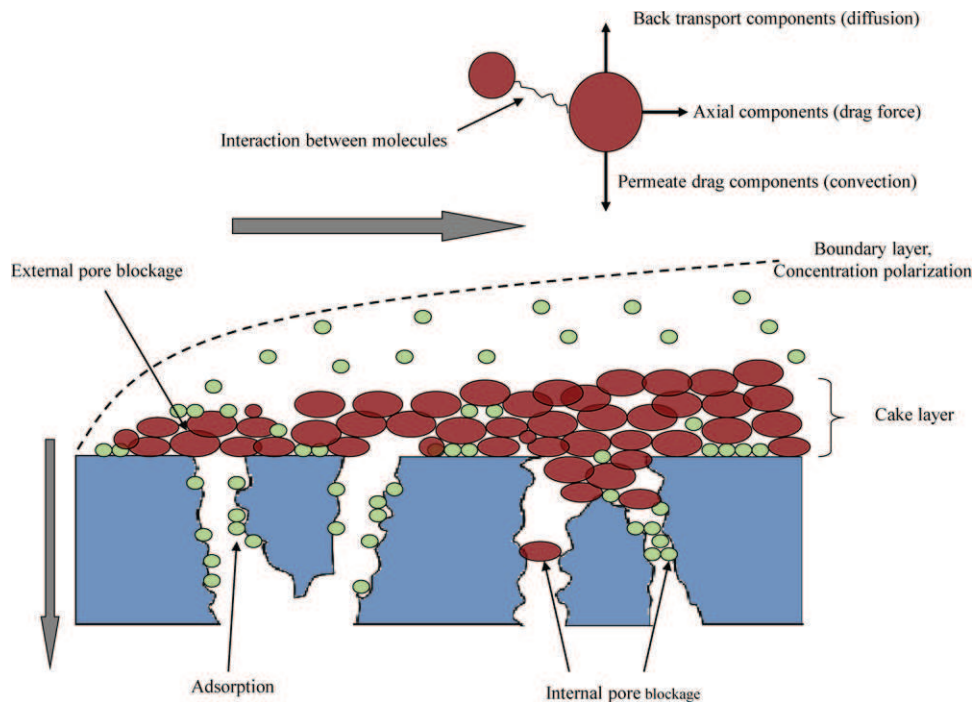
Fig. 7. Schematic description of fouling mechanisms during filtration of wine.

For biological fluids such as wine, membrane fouling can be attributed to three different mechanisms [33–39] illustrated in Fig. 7: (i) concentration polarization and subsequent cake layer formation, (ii) adsorption of solutes on to the membrane surface and pore walls, and (iii) blockage of pores.

Membrane fouling could be divided according to its localization relative to the membrane structure [40,41]:

- *Internal fouling* is caused by the adsorption and deposition of small particles and macromolecules within the internal structure of the pores.
- *External fouling* is caused by the deposition of large macromolecules and particles on the top surface of the membrane.

In microfiltration of complex fluids as wine, the model of concentration polarization is no longer applicable because the fluid contains macromolecules and particles which have low diffusion coefficient [40]. Therefore, back diffusion of components from the membrane surface into the bulk solution is slow and cannot counterbalance the convective mass transport towards the membrane. This results in the precipitation of the feed solution components at the membrane surface and the formation of a deposit layer on the membrane surface, which adds an additional hydrodynamic resistance to the membrane flux.

When the concentration of molecules at the surface increases, the molecules reaches its solubility limit and precipitates on the membrane surface to form solid gel [35,36]. In the field of oenology, the solid gel is well known and identified while filtering wines containing high quantities of pectic substances and where no pectolytic enzyme were added to these wines.

The cake layer formation mechanism was also identified during CFMF of wines [42–45]. The retained particles (yeast, bacteria, colloid aggregates, etc.) accumulated on the membrane surface in a growing cake layer.

Pore blocking is one of the most frequently used mechanisms in explaining flux decline in membrane filtration. This mechanism was identified during CFMF of red wines and model wine-like solutions of polysaccharides and polyphenols through scanning electron microscopy observation of membrane surfaces [46].

Membrane fouling may be induced also by the adsorption of wine macromolecules and colloids to the membrane surface or within the membrane pores. This mechanism was reported by several studies during CFMF of wines or synthetic solutions imitating wine composition [43,44,46–49]. The implication of wine components in adsorption mechanism will be developed gradually later in this review. Adsorption mechanism involves several forces which are:

- *Short range forces*: hydrophobic interactions, chemical bonds, dipole–dipole interactions, dipole induced dipole interactions, ion–dipole interactions and H-bridges.
- *Long range forces*: London van der Waals forces, electric double layer attraction/repulsive forces, steric repulsion forces and bridging.

Bacchin et al. [50] displayed in an operating diagram (Fig. 8) the links between the driving force (transmembrane pressure), the colloid size and the fouling mechanisms. If the driven force is high enough, it can give rise to an irreversible fouling (gel formation and deposit). They concluded that the transition between reversible and irreversible fouling and its effect on flux is increasingly sharper as the colloid size increases.

4.1. Mathematical description of fouling

Modeling the flux during filtration provides better identification of membrane fouling. It provides also predictive tools for successful scale up or scale down of microfiltration systems. Many empirical and theoretical models have been proposed to describe the membrane fouling phenomena. Four filtration models or blocking laws, originally developed for dead-end filtration, have been proposed to describe the initial flux decline: standard blocking model, intermediate blocking model, complete blocking model and cake filtration model [51,52]. For tangential mode, theoretical research has focused on various mechanisms by which the tan-
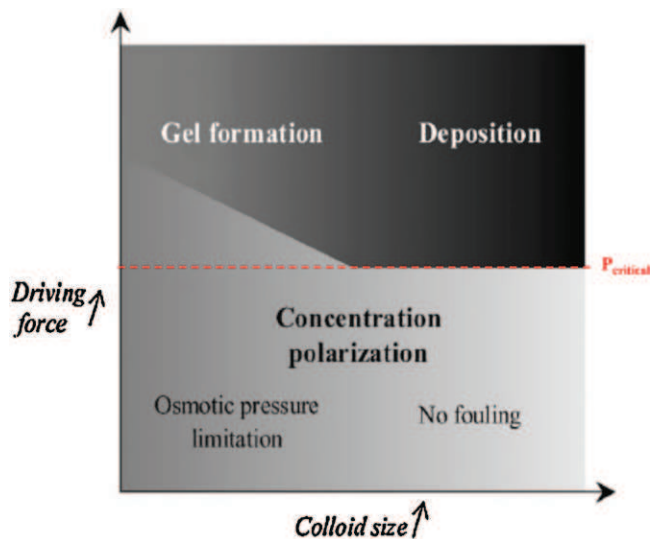
Fig. 8. The effects of the driving force (transmembrane pressure) and the colloid size on the fouling mechanisms [50].

gential shear stops the cake growth, leading to different models (Brownian diffusion, inertial migration, shear-induced diffusion, and surface transport models) for predicting the permeate flux [36,40]. Resistance-in-series model is the simplest and the most applied for wine filtration [44–46,48,53–56]. The Darcy law, which can be used to estimate the flux decline of CFMF, is the earliest form of a resistance-in-series model

$$J = \frac{\Delta P}{\mu \cdot R_t}$$

where R_t is the total resistance including the intrinsic membrane resistance (R_m) and the resistance caused by fouling (R_f). According to this model, the flux is inversely proportional to the total resistance, the latter being the sum of individual resistances. Later, it was modified and developed by many researchers, and many different models were obtained. The more used models classified fouling resistance into reversible resistance and irreversible resistance and it is calculated as:

$$R_t = R_m + R_{rev} + R_{irrev}$$

where R_t is total resistance, R_m is membrane resistance, R_{rev} is reversible resistance and R_{irrev} is irreversible resistance. Other models classified total resistance into membrane resistance, adsorption resistance, pore blocking resistance, concentration polarization resistance, internal fouling resistance, external fouling resistance and resistance of the cake layer [35,57].

These different resistances are conventionally measured through a series of filtration experiments, as shown in Fig. 9, comprising: pure-water filtration, the complex liquid filtration, and pure water filtration following cake removal. However, such experiments are not always practical and, in any case, assume complete decoupling of all resistances.

4.2. Fouling by wine components

Wines show considerable variation in filtration performance due to the complex mixture of suspended and colloidal matter that comes from components naturally present in the grape juice, those developed during fermentations and those introduced during fining treatments.

Membrane fouling during filtration of biological origin solutions such as wine, results from a combination of several mechanisms: adsorption on membrane material, internal fouling of the pores
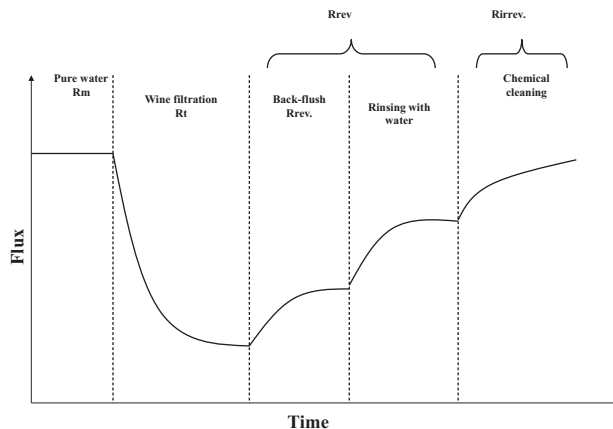

Fig. 9. Schematic representation of the filtration protocol used to determine resistances-in-series adapted to wine filtration from [57].

(pore blocking) by macromolecules and small particles, and external pore fouling by particles and retained species forming a cake [40]. The impact of these different mechanisms and the transition from one to another depend on the composition of the fluid to be filtered, hydrodynamic conditions, characteristics of the membrane, the physico-chemical interactions that occur between wine constituents and the surface membrane, and the physicochemical interactions between the constituents themselves [58–60]. For the following, fouling by wine components will be divided into 2 parts: fouling by wine colloids and fouling by wine particles.

4.2.1. Fouling by wine colloids

The colloidal state in wines is not accurately defined at this time. A wide range of unrelated substances with very different origins and chemical compositions are able to form colloidal dispersions. Colloids in wine are pectic substances, yeast polysaccharides, proteins, and molecular aggregates resulting from the association of small solutes such as polyphenol aggregates. The colloid dispersions in wine during filtration may be stable or unstable depending on several physico-chemical parameters (pH, surface interactions, hydrodynamic conditions, etc.). Vernhet et al. [44] showed that the macromolecular compounds present in wines induce a sharp and irreversible fouling. The importance of this fouling is dependent on the composition of wine colloids and their complexes and aggregates; there is a lack of information concerning their composition, size distribution and volume fraction.

In the following part, a special attention will be made to the general knowledge on colloids given the limited information available on wine colloids. It is also essential for understanding and explaining some fouling behaviours.

The phenomena of adsorption, adhesion and aggregation in liquid media result from a complex balance between the interactions that occur between the different colloids, surfaces and solvents. The interactions involved in these phenomena are:

- Interactions of Lifshtitz–van der Waals.
- Electrostatic repulsion related to the recovery of electrical double layer surrounding two charged constituents in the solution.
- Polar interactions or acid–base Lewis character.
- Forces associated to Brownian motion.

A major characteristic of colloidal systems is to have properties very changeable depending on their volume fraction or concentration. Five different phases appear relative to the concentration and the degree of destabilization as shown in Fig. 10 [50,60]
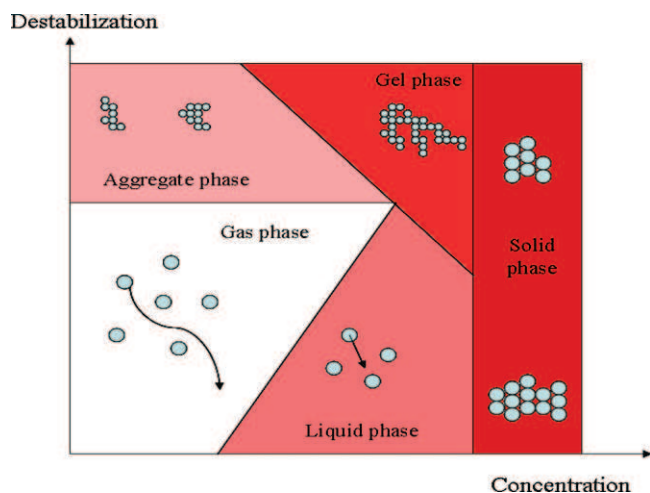
Fig. 10. Schematised phase diagram of a colloidal dispersion [60].

- "*Gas*" *phase*: diluted dispersion of stable particles having a free and random motion.
- "*Liquid*" *phase*: network of stable colloids interacting by repulsion then moving from and towards equilibrium position.
- *Aggregate phase*: diluted suspension of aggregate.
- *Gel phase*: network of colloids interacting by attraction characterized by elastic behaviour.
- *Solid phase*: solid structure where colloids are in contact.

The transition may occur between these phases when the dispersion is unstable and the volume fraction of colloids in the medium increases. An irreversible transition can take place and leads to solid structures when the colloids come into contact with the van der Waals interactions. During filtration, the volume fraction of retained compounds increases from within the suspension to the surface of the membrane, which can cause aggregation and eventually membrane fouling.

The stability of colloidal solutions defined by their ability not to aggregate over time is explained by D.L.V.O. theory which consists into 2 antagonistic effects: a repulsive effect that tends to keep particles dispersed and an attractive effect that promotes aggregation of particles. According to this theory, the stability of colloidal suspensions is determined by the balance between attractive energy of van der Waals and electrostatic repulsion. In wine, electrical charges play a secondary role in colloidal stability while macromolecular colloids as polysaccharides have the most important role. In fact, wine polysaccharides are known as "protective colloids" [2]. This protective effect is attributed to a coating of the colloid particles that prevents them from agglomerating. This was highlighted by the effect of mannoproteins on wine protein stability [61] and on tartaric stability [62]. This protective effect is not only specific to mannoproteins but also to pectic polysaccharides. When decomposing the pectic polysaccharides by adding pectolytic enzymes, the system becomes unstable and colloids (as proteins, tannins, ferrous phosphate, ferric ferrocyanide and copper sulfide) tend to flocculate. Therefore, wine clarification becomes easier to process.

4.2.1.1. Fouling by wine's polysaccharides. Several studies [5,43,44,46–49,63–66] have reported the incidence of wine polysaccharides on the performance of microfiltration membranes. They have demonstrated their negative effect on the permeation flux. Feuillat et al. [5] pointed out while filtering 2 red wines on 0.2 μm ceramic membrane, big losses in polysaccharides up to 66%.

The researchers noticed that the membrane fouling by a given wine is not directly related to its total polysaccharides content but rather to the composition, structure of these polysaccharides and the balance between different groups of polysaccharides [47,65]. At wine pH, wine polysaccharides are essentially basic (donor of electron pair, H$^+$ acceptor) and hydrophilic macromolecules. They are adsorbed in very small quantities due to unfavorable acid/base interactions. The adsorbed compounds are essentially arabinogalactan type II (AG-II) and mannoproteins [47]. While studying the effects of membrane surface properties on wine polysaccharides adsorption, it was shown that polysaccharides adsorption was negligible under static conditions and shown to be governed by membrane polarity. It decreased as surface polarity increased due to hydrophilic repulsion between surface and the hydrophilic macromolecules. However, it is well known that these results cannot be extrapolated to dynamic conditions during membrane filtration.

A recent study [49] had provided evidence that different membrane materials (polypropylene (PP) and polyethersulfone (PES)) exhibit different levels of adsorption of typical foulants in wine such as polysaccharides. In contradiction with [47], it was shown that larger amounts of polysaccharides were adsorbed to PES than to PP membrane. To notice that, PES membrane presents hydrophilic character while PP membrane has hydrophobic character.

The results of a study [65] on an organic membrane (PES) with synthetic solutions show that the effects of polysaccharides on fouling are not similar, due to the nature of polysaccharides fraction involved in the fouling. It was shown that the pectic polysaccharide of low molecular weight (rhamnogalacturonan type II: RG-II) have no noticeable effect on the permeation flux, whereas mannoproteins play a crucial role in reducing the fluxes. It was shown that mannoproteins have the most pronounced fouling effect among the polysaccharides in wine. Their impact on the flow is dependent on their concentration. This effect results from their natural abundance and their high molecular weight. But their effect is reduced by sealing the presence of pectic polysaccharides, suggesting that the performance of the membrane will depend on the balance between the polysaccharides from the grapes and those from yeast.

Vernhet et al. [46] tested the effect of wine polysaccharides on three organic membranes (M1 and M2 made from PES + PVP with different amount of polyvinylpyrrolidone (PVP) and M4 made from polyvinylchloride (PVC)). They showed that the polysaccharides adsorption was negligible in static membranes for the three membranes. They related these results to membrane wetting and conditioning with the synthetic wine that promotes hydrophilic repulsion between materials and polysaccharides. By filtering wines enriched with polysaccharides, no significant differences were observed between the three membranes in terms of amount and nature of the deposited polysaccharides. A specific deposition of arabinogalactan-proteins type II (AGP-II) and mannoproteins was noticed on the surface of the membrane. Scanning electron microscopy observations revealed the presence of aggregates within the most external pores of the membranes, partially blocking these pores and leading to more or less regular surface deposits. Membrane fouling by polysaccharides is considered to be related to their accumulation on membranes, mostly at the pores entrance and on surface. The adsorption of polysaccharides is quantitatively very low because of unfavorable acid/base interactions with membrane (polysaccharides are hydrophilic and basic, donor of electron pair, molecules).

Belleville et al. [66] have shown while filtering a wine on mineral membrane that the RG-II presents an abnormally high fouling power even if it has a low molecular weight. It could be explained

by its preferential adsorption in the positive charged membrane given its negative charge at pH of wine. Also, they have shown that an insoluble polysaccharide fraction (predominantly a linear arabinan) induces a significant reduction in filtration rate.

4.2.1.2. Fouling by wine polyphenols. Several studies have reported the involvement of wine phenolic compounds in the membrane fouling during cross-flow microfiltration [3,43,46–49,55,64,66–68].

Poirier et al. [3] has repeatedly pointed out that the phenolic compounds of wine may play a role in membrane fouling while filtering a wine on alumina membrane. He also highlighted the adsorption of dye on the membrane, which could partly explain the obtained poor permeate fluxes. Other studies [64,66] have shown that the colloidal deposit on an alumina membrane showed an intense red color, and therefore it was not exclusively composed of polysaccharides but also probably contain polyphenols. According to Czekaj et al. [55], while filtering two white wines having the same initial turbidity, the different polyphenol concentrations of the 2 wines may explain the different performances observed during filtration.

The involvement of wine polyphenols in the membrane fouling has been identified by washing the fouled membrane with acidified methanol [43]. Significant increases in permeability were obtained. This fact can be attributed to the elimination of the layers of phenolic compounds because the other wine constituents are insoluble in this solvent. HPLC analysis of methanol extracts of fouled membrane revealed that during cross-flow microfiltration, polyphenols interact with the membrane material. It is worth to notice that polyphenols are amphipathic molecules with hydrophobic aromatic rings and hydrophilic phenolic hydroxyl groups. So their adsorption involves both hydrophobic effects and the formation of hydrogen bonds. The preferential adsorption of phenolic compounds with low polarity suggests the predominance of hydrophobic interactions.

Phenolic compounds have a much more important affinity for membranes than the polysaccharides and there are both quantitative and qualitative differences between the different materials tested. To better understand the impact of phenolic compounds on membrane fouling, some studies were investigating the relationship between the polarity of surfaces and adsorption of flavan-3-ols and procyanidins monomers [47,49]. The overall results show that flavan-3-ols and procyanidins mainly react as acidic compounds (acceptor of electron pair or donor of H$^+$) due to their hydroxyl (OH) groups of phenolic nuclei and highlight the importance of the formation of H bonds in their physico-chemical reactivity. They also note that once the number of nuclei phenols is greater than two, the affinity of compounds to surfaces is greatly increased regardless of the polarity of the latter.

Polyphenol adsorption under static conditions increased with the polarity of the membrane and the ability of its surface to act as hydrogen acceptor (basic character) in hydrogen bonding which strengthens the interaction [47]. There is a direct relationship between membrane polarity and the amount of adsorbed or deposited polyphenols. The adsorption of polyphenols seems to be governed by two mechanisms depending on membrane material: polar interactions (van der Waals interactions and electron donor–acceptor interactions) and hydrogen bonds [49].

4.2.1.3. Fouling by wine proteins. In the general case, membrane fouling by proteins has been extensively studied. Many authors have studied the fundamental mechanisms involved in membrane fouling by protein suspensions, which may be grouped as follows [40,52,69,70]:
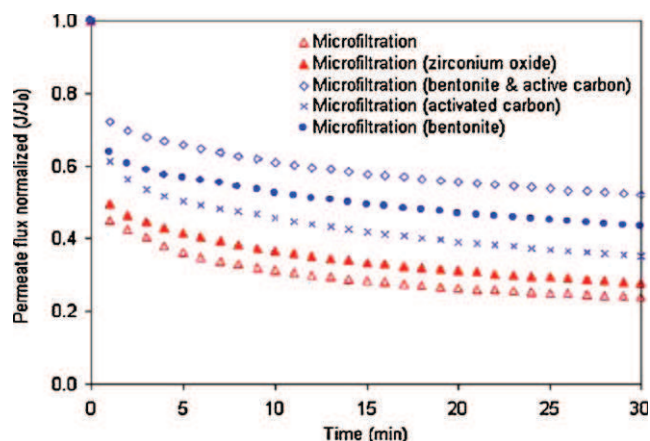

Fig. 11. Influence of protein content on the wine permeate flux during microfiltration using different treatments [71].

- The formation of a gel layer due to concentration polarization.
- Adsorption of species on the membrane surface and inside the pore structure.
- Deposition and pore blocking after the formation of protein aggregates due to denaturation.

During winemaking, heat-unstable soluble proteins may become insoluble and precipitate causing the formation of undesirable hazes or deposits in white wines after bottling during the storage or when different white or rosé wines are blended.

In wine filtration, the effect of wine proteins on membrane fouling was a little studied. This is due to their elimination before filtration by fining with bentonite (flocculation and sedimentation) [2]. Therefore, it is considered that proteins do not play an important role in membrane fouling. If wines are not finned, it was shown that the presence of proteins affected negatively the fluxes.

Salazar et al. [71] showed that the utilization of hybrid process comprising an adsorption step with zirconium oxide in a packed column followed by wine cross-flow microfiltration increases the permeate flux in Pinot Noir wine microfiltration increased by 15–20% (Fig. 11). Moreover, the protein stabilisation of the wine was better with the hybrid process than with conventional microfiltration and did not affect the color or phenolic compounds of the wine. It was shown also when fining with bentonite, the permeate flux increases by 75% due mostly to the elimination of proteins; when the wines are treated with bentonite and active carbon, an enhancement in permeate flux ($\approx$90%) is observed due to the reduction of protein and polyphenol amounts (Fig. 11).

Recently, El Rayess et al. [72] also showed the negative effect of wine proteins on permeate fluxes. They observed a strong decrease of the fluxes when 0.25 g/l of yeast extract (containing 300 mg/g of equivalent BSA proteins and no manoproteins) is added to the wine-like solution. Fouling was more important when the quantity of yeast extract is doubled. To point out this suspected "protein effect" on solution filterability, proteins were removed by fining with bentonite. Permeate fluxes obtained with the fined solutions were 25% higher than those containing 0.5 g/l of yeast extract.

4.2.2. Fouling by wine particles

Suspended particles, as defined here, are elements with a linear dimension superior to 1 μm and have a negligible osmotic pressure (Π) as compared to the transmembrane pressure for microfiltration. The amount of particles in wine and their effect on membrane fouling will depend on the step of winemaking process (cf. Fig. 4) at which the wine will be filtered and on the techniques used for
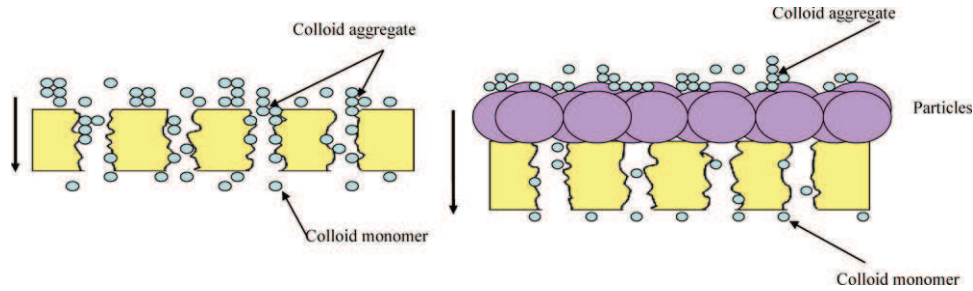
Fig. 12. Proposed mechanisms for microfiltration membrane fouling by colloids with and without particles [75].

the elaboration of wine like centrifugation, flash-release, racking, etc.

In the general case, several studies have investigated the effect of particles and yeast on membrane fouling [45,73–77]. It has been shown that in the cross-flow microfiltration of particles, a deposit cake layer tends to form on the membrane and this usually controls the performance of the filtration process.

Yeast cells have been shown to form compressible cakes under transmembrane pressure within the range 0–4 bar [77]. It was also shown that large particles in crude wine were only implied in reversible fouling while the removal of these particles did not modify the irreversible fouling [44]. During their experiments on cross-flow microfiltration of wine containing yeasts, Boissier et al. [45] proved that the increase in the total resistance related to yeast deposition is due to the compaction of the cake layer on the surface of the membrane. The same authors [45] found also that fouling is governed by fines particles (lactic bacteria and colloidal aggregates) more than yeast. The scanning electronic microscopy observations showed that these fines particles formed a coherent and adherent cake on the membrane surface. It must be noticed that the lactic bacteria concentrations are too high comparing those found in wines after malolactic fermentations or aged wines.

Czekaj et al. [54] studied the effect of particles and macromolecular aggregates of wine on the membrane fouling. They concluded that the removal of large particles, aggregates and high macromolecular weight fraction from the wine, led to a change in fouling behaviour. They observed a reduction in the final total resistance (20 times lower).

Other works have investigated the effect of yeast and colloidal solutions (essentially proteins) on membrane fouling [74–76]. They showed that yeast cells would then lead to a less compact deposit at the membrane surface and enhance permeate flow compared to solutions containing only colloids. In fact, external cake of rejected particles plays an important role in filtration processes. It may act as a secondary or dynamic membrane which screens the first membrane from the more strongly fouling species of smaller size (Fig. 12). However, it is depending on the yeast or particles concentration, on the membrane characteristics as well as on the hydrodynamic conditions [74,75].

4.3. Parameters influencing membrane fouling

It is well known that several parameters of the CFMF process play a key role in membrane fouling. The control of fouling requires the implementation of technological solutions to compensate the decrease of productivity. This could be achieved through a judicious choice of the membrane material and an optimal choice of operating conditions used for filtration. The parameters influencing membrane fouling, summarized in Table 3, cover hydrodynamics and operating conditions, membrane characteristics as well as the fluid characteristics.

4.3.1. Operating conditions

4.3.1.1. Transmembrane pressure. Darcy's law indicates that the flow rate of a liquid through a porous membrane is directly proportional to the applied pressure gradient. In fact, studies showed that this law is valid for free colloidal solutions or solutions containing large particles. Tarleton and Wakeman [78] found that the permeate flux is not proportional to the hydraulic pressure gradient during filtration and only small increases in flux are observed for increases in pressure when feeds contain a high proportions of particle fines. Jaffrin et al. [79] showed, while filtering red wine and white wine, that an increase in transmembrane pressure increases the fluxes of the both filtrations. The results highlight also that the flow rate was not proportional to the applied pressure. Same observations were found by Vernhet el al. [44] and Cassano et al. [56]. This can be explained by the high amount of colloids and fine particles in the crude wines.

Poirier et al. [3] revealed that the permeate flux of wine increases when the transmembrane pressure passes from 1 to 3 bar, then it remains almost identical when the pressure rises till 9 bar. Song and Elimelech [34] showed that if the applied pressure is smaller than a pressure which is named as "critical pressure", the particles brought to the membrane surface by permeate flow can be transported back into the bulk suspension by diffusion and flow out of the filter. If the applied pressure is higher than the "critical pressure", the particles in suspension have higher free energy than those on the membrane surface and tend to deposit and stick on the surface. This critical pressure can be visualized on Fig. 8. Below a given pressure, there is no fouling or a totally reversible fouling while above this pressure, the fouling will switch to irreversible fouling.

4.3.1.2. Permeate flux. When operating at a constant pressure, the flux increases with the increasing of the transmembrane pressure to reach a given value called "limiting flux". Limiting flux represents the maximum stationary permeation flux which can be reached when increasing the transmembrane pressure with a given solution or suspension [80].

It has been suggested that, in some membrane filtration systems, there may be a "critical flux" below which fouling does not occur. Field et al. [81] defined the critical flux as a flux below which a decline of flux with time does not occur; above it fouling is observed. Howell [82] described the critical flux as a flux below

Table 3
Summary of the parameters influencing membrane fouling.

|	Parameters
Operating conditions	Transmembrane pressure, permeate flux, cross-flow velocity and temperature
Membrane characteristics	Pore size, porosity, hydrophilicity/hydrophobicity character and surface free energy
Fluid characteristics	Physico-chemical interactions (electrostatic, polar, etc.), pH, ionic strength, suspension concentration and suspension size
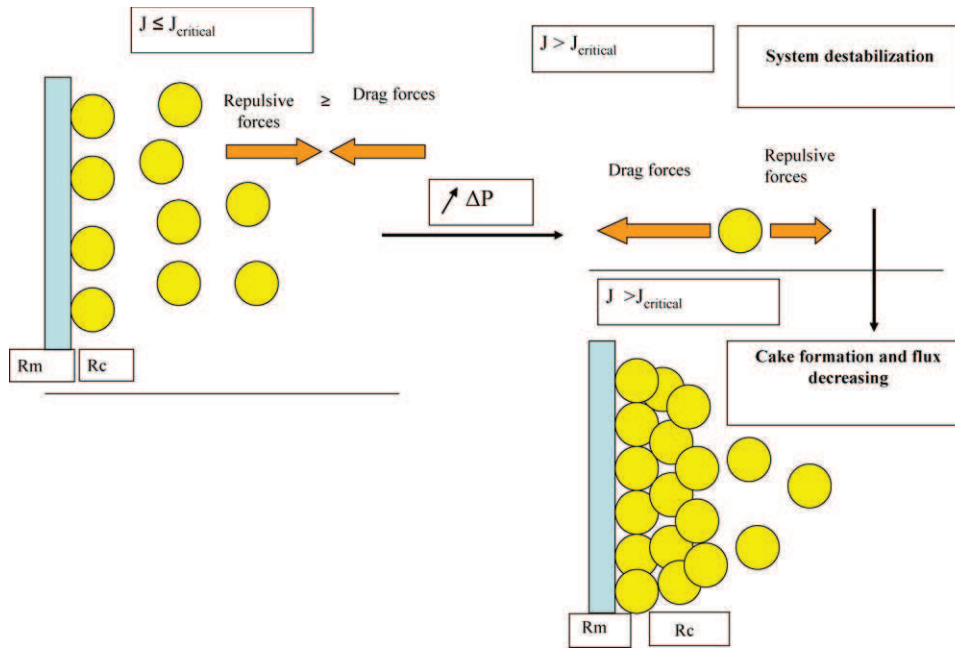
Fig. 13. Summarizing of membrane fouling state depending on the system forces.

which there is no fouling by colloidal particles. In the case of wine filtration, this definition cannot be adopted because the adsorption of wine colloids on membrane materials almost always occurs, even in static conditions. The following definition could be the most appropriate for wine filtration; the critical flux is the flux above which an irreversible deposit appears at the membrane surface.

For colloidal suspensions, this critical flux phenomenon is generally explained by a balance of particle–particle or particle–membrane repulsive forces and permeate drag forces. Above a given value of flux (critical flux), the repulsive forces are overcome by the permeate drag forces, allowing the formation of a deposit on the membrane surface which creates an additional resistance to the permeate flow (Fig. 13).

In the literature, many researchers have been studying the critical flux, but only one paper can be found about critical flux concerning wine filtration [45]. The aim of this work was to evaluate, under different hydrodynamic conditions, the properties of the deposited layers formed by yeast and fine particles (lactic bacteria and colloidal aggregates). They found that fouling by yeast cells in synthetic solutions can be avoided by maintaining the permeate flux under 2×10^{-4} m s^{-1}. They also found, when filtering solutions containing yeasts and wine macromolecules, that macromolecules enhance the hydraulic resistance by fouling internally the yeast cell cake formed at the membrane surface.

4.3.1.3. Cross-flow velocity. Several studies have revealed cross-flow velocity to be a major influence on membrane fouling [3,42,79,83]. The cross-flow velocity affects the mass transport of particles away from the membrane surface, and thus the resultant cake layer thickness, by increasing the shear stress and so shear-induced diffusion. So, an increase in cross-flow velocity improves the permeate flow rate.

For wine filtration, Mietton-Peuchot et al. [42] observed that increasing in cross-flow velocity from 0.8–1.6 to 2.5 m s^{-1} does not affect significantly the permeate flux. Jaffrin et al. [79] also showed that for both wines studied (red and white wines); there is no systematic variation of fluxes with fluid velocity. Those both observations are in contradiction with the theory. In opposition, Poirier et al. [3] and Lüdemann [83] found that increasing flow velocities improved flux rate. This improvement of permeate flux seems to be linearly with the increasing of the flow velocity [83]. But, it must be noticed that the used white wine was finned with bentonite, so it is impoverished in total colloids especially proteins and the amounts in colloidal particles/aggregates were lower.

The most used cross-flow velocity in wine cross-flow microfiltration is 2 m s^{-1}. It insures satisfying shear stress and preserves the wine quality. In fact, any increase in cross-flow velocity induces a rise in the temperature of the wine and can alter the organoleptic characteristics of the wine.

4.3.1.4. Temperature. The permeate flow in Darcy's law is inversely proportional to the viscosity (μ). The viscosity increases with solute concentration and decreases with temperature. So temperature impacts on membrane filtration through its influence on permeate fluid viscosity. A possible method for analyzing the influence of temperature on R, would be to do two series of flux measurements: one in which the viscosity of the feed liquid is increased by adding viscosity increasing solutes and one in which the viscosity of the feed liquid is increased by lowering the temperature. The temperature effect can then be separated from the viscosity effect.

A rise in temperature will affect positively the permeate flow. In other hand, it is well known that wine temperature should not exceed 25 °C, in order to not modify the organoleptic characteristics. Recently, Romat and Reynou [84] tested the impact of temperature on wine viscosity. The results are shown in Table 4. The results showed an increase in wine viscosity when decreasing the temperature. This observation is more important for sweet wines.

Table 4
Variation of dynamic viscosity of 3 different wines with temperature [84].

Sample	Dynamic viscosity (mPa s)			
	20 °C	15 °C	10 °C	4 °C
Water	1.00	1.14	1.30	1.56
Bordeaux dry white wine	2.53	2.58	3.02	3.67
Bordeaux red wine	2.22	2.64	3.12	3.86
Bordeaux sweet white wine	3.84	4.52	5.41	6.88

Table 5
Main membranes used in microfiltration of wine.

	Material	Pore size	Properties	References
Organic membrane	Cellulose acetate	0.2 μm	Hydrophilic	Urkiaga [86], Czekaj [55], El Rayess [72]
	Cellulose acetate	0.45 μm	Hydrophilic	Urkiaga [86]
	Polypropylene	0.2 μm	Hydrophobic	Boissier [50], Ulbricht [49]
	Polypropylene	1.2 μm	Hydrophobic	Arrigada-Carrazana [87]
	Polypropylene	5 μm	Hydrophobic	Urkiaga [86]
	Polyethersulfone	0.2 μm	Hydrophilic	Ulbricht [49], Urkiaga [86]
	Polyethersulfone + polyvinylpyrrolidone	0.2 μm	Hydrophilic/polar	Cameira Dos Santos [43], Vernhet [44,47,46,65]
	Polysulfone	0.2 μm		Czekaj [55], Cassano [56]
	Polyvinylidene difluorure	0.2 μm	Hydrophobic	Arrigada-Carrazana [87], Czekaj [55], Jaffrin [79]
	Polyvinylchloride	0.2 μm	Hydrophobic	Vernhet [47]
Ceramic membrane	Zirconium oxide	0.2 μm	Hydrophilic	Salazar [71]
	Alumina	0.2 μm		Belleville [64,66]
	Titanium oxide	0.45 μm	Hydrophilic	Vernhet [88]
	Titanium oxide + zirconium oxide	0.2 μm		

The decrease in temperature does not only affect the viscosity but it decreases the Brownian movement of particles and favours the attraction between particles.

Lüdemann [83] showed, while filtering a fined white wine with a cross-flow microfiltration pilot, that an increase of the filtration temperature not only yields higher flux rates but also has a positive effect on back-flushing. This observation could be explained by an alteration of the colloidal systems in the wine and the reduction of the viscosity.

Jaffrin et al. [79] found that the total resistance decrease linearly when temperature increases. The rate of decrease is larger for the red wine. They related this fact also to the changes in the colloidal system of the deposited layer.

4.3.2. Membrane characteristics

It is well known that membrane characteristics such as pore size, porosity, surface free energy, charge, roughness, and hydrophilicity/hydrophobicity, have a direct impact on membrane fouling. There is a wide variety of membrane materials proposed for the tangential filtration of wines. They are divided into organic membranes and ceramic membranes. Table 5 reports the main membrane materials used in wine filtration as mentioned in the literature.

Pore size and pore size distribution on membrane fouling are likely to be one of the parameters affecting membrane performance. A narrow pore size distribution is preferred to control membrane fouling in cross-flow microfiltration. The effects of pore size and pore size distribution on membrane fouling are strongly related to the feed solution characteristics and in particular the particle size distribution. Poirier et al. [3] tested 3 average pore sizes (0.2, 0.45 and 1.2 μm) for wine filtration and they found similar membrane performances in term of permeate flux. Also, Peri et al. [6] performed wine filtration with membranes having average pore diameter less than 0.2 μm (0.2 μm, 0.02 μm and 0.005 μm). It was concluded that membrane with average pore diameter of 0.2 μm showed the best results in term of permeate flux and wine quality. Chang et al. [85] found while investigating the effect of pore size on flux from alcohol-distillery wastes, that the flux produced from 0.05 μm pore size to be higher than that from 0.4 μm membrane. In general, a membrane with a higher porosity will have a better distribution of the permeate flux on the porous surface and should lead to less fouling.

During filtration of activated sludge, Fang and Shi [89] tested the effects of membrane roughness and porosity on fouling behaviours by testing in parallel four microfiltration membranes with nominal pore sizes ranged between 0.2 and 0.22 μm. They observed that the track-etched membrane, with its dense structure and uniform cylindrical pores, featured the lowest resistance due to pore fouling. In contrast, the other three membranes presented a sponge-like microstructure and trend to more pore fouling due

to their highly porous network. In protein microfiltration, Ho and Zydney [90] demonstrated that membrane having straight trough (non-interconnected) pores showing a more rapid flux decline than membranes with an interconnected pore structure since the filtrate can flow under and around any surface blockage through the interconnected pores. They also showed that the initial rate of flux decline varied inversely with the surface porosity for track-etch membranes with well-defined cylindrical pores.

Kuiper et al. [91] noticed that beer filtration through slits gives a much higher flux than through circular pores. The difference in flux is approximately a factor 4–5. They attributed this observation to the fact that slit cannot be blocked completely by a spherical particle and particles have less membrane surface to adhere to. And, if a colloid layer grows on the inside of the pores, the flow resistance of a slit decreases much less than that of a circle.

In membrane science, materials always show different fouling behaviours due to their free surface energy and their hydrophilicity/hydrophobicity character. In general, membrane fouling occurs more readily on hydrophobic membranes than on hydrophilic ones because of the attractive hydrophobic interaction between foulants and membranes. As a result, much attention has been given to reduce fouling by modifying hydrophobic membranes to relatively hydrophilic. Recent experience [49,86] in wine filtration had indicated that membranes with the same pore structure and sizes but made from different membrane polymer (cf. Table 5) had shown quite different filtration performance. Researchers have mentioned that the polysaccharides and tannins adsorption take part in irreversible fouling of membranes during the cross-flow microfiltration of wine. This adsorption is dependent on the membrane surface properties, especially its surface free energy, and could be minimized by the development of adequate materials. Belleville et al. [64,66] showed that the small chain of acidic polysaccharides (rhamnogalacturonans) were adsorbed on the alumina membrane and adsorption was attributed to electrostatic interactions between positively charged alumina and negatively charged polysaccharides at wine pH. Vernhet et al. [47] concluded that polysaccharides adsorption is governed by membrane polarity: it decreased as surface polarity increased due to hydrophilic repulsion between surface and the hydrophilic macromolecules. They also observed a direct relationship between the adsorption of polyphenols and membrane polarity. Polyphenols adsorption increased as the polarity and the basic component of the membrane surface free energy increased.

Ulbricht et al. [49] showed that the adsorption of polysaccharides and polyphenols occurs more on polar polyethersulfone (PES) membranes than on non-polar polypropylene membranes. In fact, polar interactions were much stronger with polyethersulfone membrane than with polypropylene membrane and hydrogen bonds towards the additive PVP in PES may further increase adsorp-

tion tendency. It is worth to notice that the polyphenol compound used by Ulbricht et al. [49] is tannic acid which not represents the true polyphenol groups in the wine.

So, the apolar character of the PP membrane results in a different behaviour of membrane fouling by wine macromolecules, which remains very limited. The total lack of polar bonds is therefore a decisive factor in sealing materials by the macromolecules of wine. Therefore, it is interesting to further study on the PP membranes (or other apolar material) which may enhance permeate fluxes during cross-flow microfiltration and results in longer service life.

4.3.3. Fluid characteristics

It is well admitted that membrane fouling depends on the hydro-dynamic conditions and membrane characteristics as well as on the composition and the characteristics of the fluid to be filtered. Fluid characteristics (pH, particles size, interactions, etc.) will strongly impact the physico-chemical interactions that occur between the fluid constituents and the membrane surface as well as the physico-chemical interactions between these constituents [92,93].

As mentioned before, wine is a complex medium containing solutes, colloids and large particles. The main difficulties with a fluid such as wine are related to the unawareness of the whole particulate fraction and colloids which constitutes the fluid. It lacks information on the composition of the colloids, their stability, their size distribution and volume fraction that may represent. These parameters vary from one product to another, due to the type of cultivar, the climate, the techniques used for winemaking and the storage conditions.

Many fluid characteristics have an impact on wine filtration. These characteristics include pH, ethanol content, physico-chemical interactions and particle size.

It was shown that improvement of the permeation flux of water is obtained by increasing the repulsive forces between colloidal particles. This increase of repulsive forces is achieved by changing the pH of the solution which affects the surface charge of colloidal particles [94]. A feature of most of the colloidal compounds is that they generally have a charge. The overall charge of the main fractions of polysaccharides in wine and different fractions of phenolic compounds was determined. Generally, the wine has a pH range between 3 and 4 and the overall charge is neutral [95]. The polysaccharide fractions are negatively charged in hydro-alcoholic model solution at pH 3.5 but there are important differences in the absolute value of their negative charge density which is a function of pH. For mannoproteins, the charge density varies only slightly depending on the pH in the range tested (pH 2–9). Most of the mannoproteins present in wine are neutral. Instead of mannoproteins, pectic polysaccharides have a very significant increase of net negative charge in the pH range tested. This charge is due to the carboxylic groups of uronic acids. Thus, electrostatic interactions that can develop between these polysaccharides and other macromolecules, as well as between themselves, are very dependent on the pH of wine.

The determination of the charge of phenolic compounds was only performed in hydro-alcoholic model solution at pH of 3.5. All the studied tannins exhibit negligible surface charges at wine's pH because the hydroxyl groups of tannins are not dissociated at this pH.

The interactions between molecules and surfaces as well as molecules themselves will depend on pH, but also on the physico-chemical properties of macromolecules. As mentioned in paragraph 4.2.1, there is considerable heterogeneity within each group of wine colloids (polysaccharides, proteins and polyphenols) and neither the structures nor the mechanisms involved in the formation of instabilities are known. So nowadays, little informations are available and the colloidal system remains little explored.

The alcohol content plays an important role in membrane filtration. Ethanol is considered as a wetting agent. It was shown when wetting membranes with ethanol before filtrations, higher fluxes are obtained due to pore activation and reduction of surface tension but there is no significant effect on fouling propensity [96]. Nowadays, there are no studies concerning the effect of ethanol content in wine on membrane filtration.

Particle size has been identified in literature to play a role in membrane fouling. Depending on the relative size of colloidal particles and membrane pores, fouling may occur due to either accumulation of particles on the membrane surface and build-up of a cake or penetration within the membrane pores. As a general rule, a reduced particle size in the feed resulted in lower overall flux levels. Boissier et al. [45] have shown that yeast alone always formed reversible deposits while fine particles induced very low permeate fluxes and formed an irreversible deposit.

The crude wine is a very polydispersed medium system containing particles with size range between 0.1 μm and 100 μm. This very high polydispersity made the determination of the size distribution impossible. Another factor affecting the size distribution measure is the wavelength used (633 nm), especially for colloidal particles of red wine.

5. Membrane cleaning

In general, there have been many attempts to reduce membrane fouling and enhance the permeate flux during the CFMF of wine. Till now, few studies [97–100] are referenced in the literature concerning the cleaning of the membranes by mechanical or chemical techniques in enology. So, a summary of different cleaning techniques will be proposed in following.

5.1. Hydraulic and mechanical techniques

Various hydraulic and mechanical methods have been investigated to reduce the resistance caused by concentration polarization in order to improve the efficiency of the separation process and decrease operating cost. There are a number of non-chemical membrane cleaning techniques available, including back-flushing, cross-flushing and back-shocking [101–103]. In most previous work using these techniques, the flushing pulses have been applied to the feed space. Although these techniques, applied in a non-continuous way, can be successfully used to clean some foulant layers off membranes and (partially) restore the flux, they seem to be inefficient in the removal of adhesive foulants [55].

The cross-flushing is the simplest technique to be implemented. The permeate outlet is temporarily closed which cancels the permeate flux and hence the contribution of particles on the membrane. The shear stress erodes the deposit formed. The effectiveness of this method is limited to a little adhering deposit to the top surface of the membrane.

Back-flushing or back-washing is the common practice to minimize fouling. Filtrate is pumped back through the membrane into the feed channel to give a periodic backwash to lift deposited material off the membrane surface. The efficiency of this technique is limited to remove the deposits or cakes at the membrane surface. If the deposits adhere strongly or if pore fouling has occurred, it may be fairly ineffective.

Back-pulsing methods are relatively novel methods in comparison with the other methods. The principle of these methods is reversing the feed pressure at high frequency to force the fluid in reverse direction through/into the membrane. Back-pulsing is similar to the more familiar technique of back-flushing which is common commercially. However, in back-flushing, flow reversal through the membrane occurs for a few seconds once every sev-
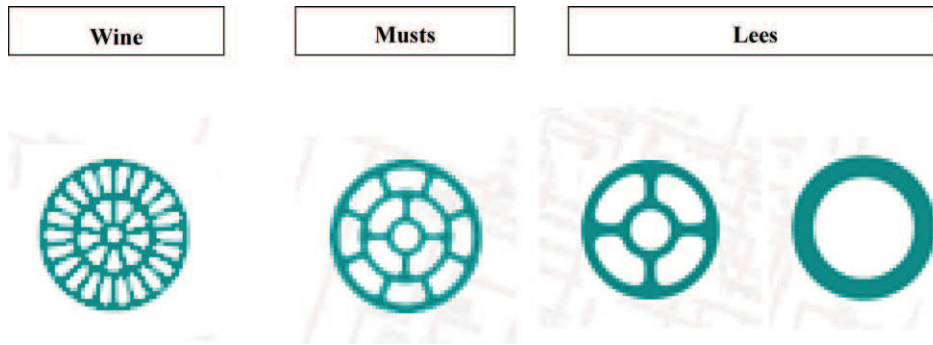
Fig. 14. Different configurations of ceramic membranes adapted for different types of wine.

eral minutes, while in back-pulsing, flow reversal occurs every few seconds or less and reverse pressure pulses are applied for very short periods of time.

Some researchers used the ultrasound waves to enhance the permeate flux [103,104]. The passage of ultrasounds waves through a suspension can cause many phenomena, including particle dispersion, viscosity reduction and changes in particle surface properties. Ultrasound waves can weaken the deposit and makes it more sensitive to the action of the shear stress. The application of the ultrasonic fields depends on the suspension concentration. Increasing the suspension concentration reduces the filtration rate enhancements possible with an ultrasonic field by attenuating the sound waves.

The use of an external electric field is a promising approach towards improving the permeate flux in cross-flow filtration. A superimposed electric field induces a force on charged biopolymers in order to reduce the surface layer on the membrane. Electrical field treatment can reduce membrane fouling by microbial inactivation and the enhancement of particle coagulation. Park [97] showed, while testing electric field on microfiltration in the wine-brewery industry, that the membrane resistances in the electro-microfiltration at 24 V were reduced by 85.1%. He showed also when the electric field was increased to 8 V, 15 V and 24 V the permeate velocities were increased by 60.0%, 95.5% and 133.3%, respectively. This effectiveness of this technique is limited by the cross-flow velocity. It was noted that high cross-flow velocities do not guarantee a reduction in fouling [105].

Several studies on the use of gas bubbling have been reported to enhance ultrafiltration performance resulting in higher permeate fluxes [106]. In this technique, gas/air is dispersed in the liquid stream to generate two-phase flow which produces very high turbulences along the membrane surface. This high turbulence on the membrane surface reduces the deposition of solid particles on membrane surface and resultantly, the permeate flux increases. This technique is limited in wine filtration according to the gas used. Gases not containing oxygen can be used because wine quality is degraded with contact with oxygen.

Various researchers have used different turbulence promoting techniques in order to control the fouling on membrane surface. These techniques include: use of turbulence promoters, dynamic filtration, pulsating flows, jet flows and vortex waves [105–111].

5.2. Chemical techniques

Chemical cleaning is performed when the various hydraulic and mechanical cleaning techniques cannot restore flux. Cleaning agents divided into different categories:

- Acid (HNO_3, H_2SO_4, HCl, citric acid, etc.) – for dissolving mineral and salts.

- Base (NaOH) – for dissolving protein and other organic foulants.
- Oxidizing agents (H_2O_2, NaOCl) – for biological foulants.
- Surfactants, detergents (Ultrasil, Froclean, etc.) – for organic foulants.
- Enzymes (protease, alpha amylase, polygalacturonase) – for severe fouling.

In wine industry, sodium hydroxide is the most used in the range of 1–5% depending on fouling level and membrane material. Reagents containing chloride molecules are banned in the food industry.

In wine filtration, enzymes are used to reduce membrane fouling and enhance permeate flux more than as cleaning technique. Several enzyme preparations are available on the market and all have pectolytic activity (hydrolysis of pectin). It was shown that breaking the pectin molecules into smaller components will expose some of the positively charged particles as proteins and leads to an electrostatic aggregation of oppositely charged and flocculation of the cloud. Humbert-gauffard et al. [98] tested the efficiency of a commercial enzyme preparation in wines in relation to filterability by measuring the V_{max}. They showed that adding 5 g/l of B-glucanase will increase the filterability of white wine by 55% and red wine by 40%. Several other studies have indicated the positive effect of pectolytic enzymes on wine filterability [99,100].

6. Innovations and commercial proposal

Many modifications have been made on tangential filters since the mid of 80s. The first CFMF of wine were realized with filters equipped with ceramic membranes. The results obtained were not satisfactory: flows per m^2 were too low, the ratio filtration area over volume occupied by the membranes was low, and there was a significant loss in the quality of filtrated wines. Between 1990 and 2000, the filters were developed and set up, and equipped with organic membranes. Large progress of optimization was realized by the constructors, despite the inconvenience of organic membranes due to their fragility. This type of membranes was privileged because the ratio filtration area over volume occupied by the membranes was favourable (hollow fibres). The margin of progress has been made on the choice of membrane materials and their consistency with the physico-chemistry of wine.

In 2000, new ceramic hollow fibres membranes were developed specially for wine filtration in order to optimize the ratio filtration surface on membrane volume. The advantage of these membranes (other than the advantages due to the membrane material) is that their shape can be adapted to the type of liquid (wine or must) to filter as shown in Fig. 14.

After the development of membranes, manufacturers oriented their research into the filter design. All filters on the market are completely automated and equipped with a back-flush or back-

Fig. 15. Flavy FX tandem filter.

and the loss of wine is only 0.1% or 0.05% of the volume of filtered wine, resulting in improved overall productivity.

This same manufacturer offers with its "Flavy Leestar" a solution for the filtration of tank residues. The original idea based on the use of a filter membrane with tangential tubular stainless steel, capable of withstanding abrasive and viscous fluids (such as bentonite and activated carbon) with a large solid content. This design is especially dedicated to cooperative cellars (from 80,000 hl) to marketers and bottlers, which process high volumes.

"Oenoflow XL" series (Pall) are equipped with proven PVDF membrane which offers approximately 145% more filter area. The XL modules have at least twice the area of typical competitive hollow fibre membranes allowing the manufacturing of more compact and economical systems. In addition to increased surface area modules, the "Oenoflow XL" series incorporates a new and evolved flow distribution by a system which they named "Dynamic Solid Control". With this new function, the system gradually, but continuously, modifies the percentage of the solids present in the recycling loop upstream of the separation membrane, which will oppose the stabilization of a gel layer. The system "Oenofine XL" is another design proposed by the same manufacturer which allows the stabilization and clarification of wine protein in one step, without going through the settling phase usually performed after treatment with bentonite. In fact, this design has the same characteristics of "Oenoflow XL" in addition with a small dosing skid of a proprietary activated bentonite, located upstream of the hollow fibre membranes. This system will provide in single step protein stabilization and wine clarification and will enable wineries to

pulse technique. Nowadays, several manufacturers propose filters with organic membrane. The most original concepts will be presented in following.

"Flavy FX tandem" (Bücher Vaslin) combines two filters dedicated and adapted to different filtration (Fig. 15). The first filter performs the filtration of the crude wine while the second concentrates the retentate from the first filter. Each filter has specific hydrodynamic parameters and equipped with adapted membrane to each type of filtration. Thanks to this operation by successive stages, fouling is significantly reduced by decreasing the concentration factor in the recycling loop. The dead volumes are reduced
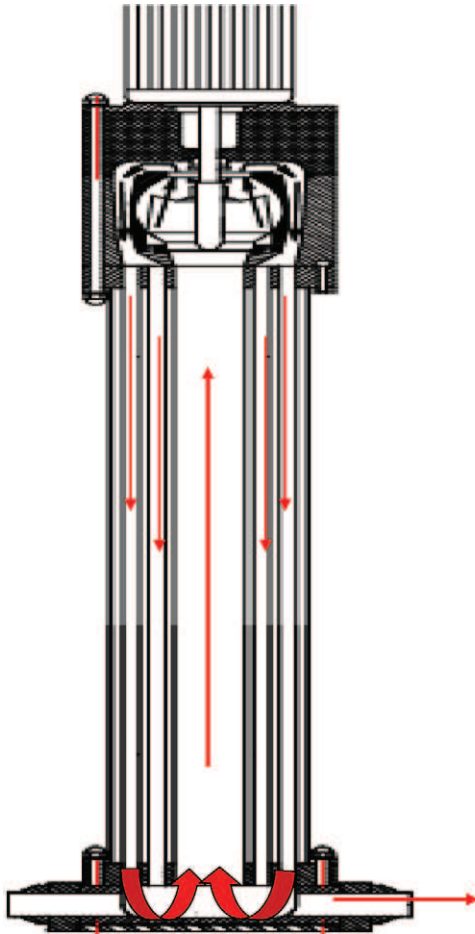

Fig. 16. Tangential Integrated System (TIS).

reduce bentonite consumption, eliminate settling time after bentonite fining, and reduce wine waste and lees volumes.

An original concept has also been developed for ceramic membrane for example "VINI-TIS" (SIVA). The Tangential Integrated System (TIS) is an autonomous module which integrates the membranes, the circulation loop and the pump, creating a tangential flow (Fig. 16). The TIS simplify the realisation of the systems, reduces the costs of manufacturing and its implantation is easy, due to its low space requirement. Due to its higher compactness, the TIS reduces also the dead volumes.

The "VINI-TIS" units can also be used for the filtration of musts and lees. This versatility is possible because the TIS is an autonomous module in which the membranes can be changed easily, and because the large range of geometries of the ceramic membranes, make it possible to adapt to the load and viscosity of the products that need to be filtered.

7. Conclusion

In the wine industry, cross-flow microfiltration presents many advantages compared to the traditional techniques and becomes to be widely used. When cross-flow microfiltration for must clarification remains a challenge, this technique for wine clarification still suffers from the poor permeates fluxes due to the fouling of the membrane by wine compounds. Membrane fouling depends on the composition of the wine, the operating conditions and the membrane type. Despite the progress and the research made to understand and resolve the problem of fouling, there is still relatively little fundamental knowledge about the problem. The lack of information concerns:

- The physico-chemical interactions between wine molecules themselves and between these molecules and the membrane.
- The individual impact and contribution of wine compounds on fouling.
- Mechanisms causing membrane fouling by wine compounds.
- Methods or index to predict the degree of membrane fouling.

In oenology, it will also be interesting to test new type of filtration as the dynamic filtration or new membrane types as microsieves because the configurations and the principles of the conventional filters reach their limits.

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