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IMPACT OF THE PHYSICO-CHEMISTRY OF THE WINE ON MEMBRANE FILTRATION PERFORMANCE

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Abstract. During the process of wine making, operation of cross-flow microfiltration allows a one-step clarification and sterilization of wine, with lower waste compared to the conventional processes of clarification and sterilization. Indeed, these processes are sources of voluminous waste (earth, Kieselguhr, additives), when discharges are becoming more and more restricted by environmental and health rules. Nevertheless, cross-flow microfiltration of wine presents a major drawback: membrane fouling causes a significant decrease in the flow rates, due to excessive retention of some wine components which could lead ultimately to the alteration of the quality of wine. The aim of this work was to study the impact of some specific wine components (phenolic compounds and yeast extract), as well as some physico-chemical parameters (pH) in regard to membrane fouling. Studies were performed using one red wine and synthetic wines, using cellulose acetate membranes (0.2 μm) operated in the dead-end mode under 2 bar pressure. The simultaneous presence of the both species of phenolic compounds (anthocyanins and tannins) in the synthetic wine was shown to be the main cause of fouling, whereas the presence of one specie leads only to standard blocking type behavior. An important decrease in the flow rates was also observed when yeast extract was added to the liquid. This yeast extract was shown to contain 300 mg/g of proteins and to be free of mannoproteins. The influence of these proteins on fouling was demonstrated while pre-treating the synthetic wine with bentonite, which was able to adsorb proteins, and in this case, no fouling was observed. It was also shown that, when decreasing the pH, the flow rate was enhanced. For all experiments, a fouling index or cake specific resistance, according to the type of fouling, was calculated in order to be used as a reference to estimate the filterability of a given wine, according to its composition in some targeted molecules. Finally, the experiments of the actual red wine exhibited complete rapid fouling of the membrane, probably due to the presence of high concentration of phenolic compounds.

Key-words. microfiltration membrane, polyphenols, proteins, yeast extract, fouling, wine

INTRODUCTION

The crude wine, after fermentations (alcoholic and malolactic), is a complex medium containing many different compounds in solution (small molecules such as organic acids, salts, glycosides, phenolic compounds,...), components of colloidal size (ranging between 1 nm and until a few hundreds of nm: polysaccharides, polymerized phenolic compounds and proteins) and particles (molecular aggregates, micro-organisms, residues of vegetable and microbial cells, crystals of potassium hydrogenotartrate,...) [1,2]. However, strict qualitative and healthy specifications are established by the distributors: absence of haze, brightness, microbiological stability, tartaric stability, low oxygen content...

To answer these requirements, the wine makers are used to implement successive solid-liquid separation using traditional technologies such as centrifugation, filtration on plates, diatomaceous earth filtration and the use of exogenic additives. However, restrictions for environment and health preservation lead the viticulture sector to look for alternative techniques to traditional filtrations: cross-flow microfiltration could represent this alternative. Indeed, this technology can substitute 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 [1,2]. In addition to a great simplification of the wine processing line, cross-flow 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 [3,4].

Unfortunately, the development of cross-flow microfiltration in wine industry is still hampered by the occurrence of significant fouling phenomena upon the microfiltration membranes. This has caused difficulties in obtaining an economical flux rate, as well as good product quality [3,4].

Membrane fouling during cross-flow microfiltration of biological fluids results from a complex interaction between macromolecular adsorption or deposition, internal fouling and cake formation by the retained species [2,5]. The respective impact of these different fouling mechanisms strongly depends on the composition of the fluid to be filtered, on the membrane characteristics, on the hydrodynamic conditions as well as on the physico-chemical interactions between the fluid components and the membrane surface and between these components themselves [2,5].

Theory

Filtrations of low concentrated suspensions (concentration in particles lower than 1% in volume), realized at constant pressure, are shown to follow laws described by simple mathematical equations. In this study, two laws, more particularly suitable for the wine filtration, will be considered [6,7]:

- i) Cake filtration i.e. deposit of particles larger than the membrane pore size onto the membrane surface. The thickness of the cake increases along time and the cake resistance is proportional to the thickness of the cake. A filtration governed by cake filtration law is modelled by the following equation: $t/V = kV + 1/q_0$ where t is the duration of filtration, V is the volume filtered at t , k is a constant, q_0 is the initial flow.
- ii) Standard blocking i.e. deposit of particles smaller than the membrane pore size onto the pore inner walls, thus reducing the pore size. The equation, which characterizes this law, is following: $t/V = k_1 t + 1/q_0$ where t is the duration of filtration, V is the volume filtered at t , k_1 is a constant, q_0 is the initial flow.

The slopes k and k_1 characterize the fouling phenomenon: a low value of this constant indicates a good filterability of the wine.

The aim of this work was to study the impact, of some wine components (phenolic compounds and yeast extract), as well as some physico-chemical parameters (pH, calcium content) on fouling of microfiltration membranes. The results obtained must enable the determination of the elements (components or parameters) playing a determining role in the fouling of membranes during wine microfiltration.

MATERIALS AND METHODS

Wine and model solutions

As the crude wine is a complex medium, studies were first carried out using “synthetic wines”, to determine more easily the effect of some wine components on fouling. Then, experiments were carried out on a real red wine.

Synthetic wine or model solutions

The effect of some wine components on the microfiltration membrane fouling was studied by using 2 synthetic wines: synthetic white wine (named as S.W.) and synthetic red wine (named as S.R.). S.W. is made of ethanol 12% (v/v); glucose 0.5 g.l⁻¹; fructose 0.5 g.l⁻¹; tartaric acid 5 g.l⁻¹; malic acid 4 g.l⁻¹; citric acid 0.6 g.l⁻¹; potassium hydrogenophosphate 2 g.l⁻¹; magnesium sulphate 0.2 g.l⁻¹; ammonium sulphate 0.2 g.l⁻¹. The synthetic red wine has the same composition as S.W. with addition of 0.25 g.l⁻¹ anthocyanins and 0.5 g.l⁻¹ tannins. The initial pH of the solutions is 2.3 and it is adjusted to 3.7 (closed to the usual pH of wine) with a 5N NaOH solution.

Red wine

The red wine used in the present study was elaborated in 2007 at the cooperative cellar of Rabastens from Duras, Fer de Servadou and Syrah grape varieties. To increase the extraction of polyphenolic compounds (anthocyanins and tannins), the flash-release process was used. This process consists of sending a de-stalked, drained and heated (> 85°C) harvest to a vacuum chamber. The juice will instantly vaporize due to the low pressure and the grape skin and the seeds will be deconstructed [7,8]. After alcoholic and malolactic fermentations, the wine was centrifuged at the cellar in order to remove microorganisms and particles (size greater than 0.65 µm). When received, the wine was analyzed and maintained at 4°C until use.

Microfiltration experiments

The experiments were carried out in an Amicon cell manufactured by the Amicon-Millipore company. This cell is a polyethylene cylinder, having an internal diameter of 40.7 mm, containing 60 ml of solution. Its lid is provided with a valve to slacken the pressure. The membrane lays on a fine plastic grid. The maximum pressure of operation is of 5.2 bars. This cell allows a dead-end or pseudo-tangential filtration. All filtration experiments are carried out in the dead-end mode.

Filtrations are carried out on samples of 500 ml of solution. The membranes used are cellulose acetate microfiltration membranes (flat sheet type) with 0.2 μm pore diameter, filtration area of $1.3 \times 10^{-3} \text{ m}^2$. Gaseous pressurized nitrogen ensures the driving force allowing the passage of the liquid through the pores of the membrane (air was not convenient because it can modify the physico-chemical properties of the wine by oxygenation). The pressure was maintained at 2 bars for all experiments. A balance, connected to a computer for the acquisition of the data, makes it possible to measure the effective flow-rate by measuring the cumulative liquid mass. Filtrations are carried out at room temperature (22- 24°C).

A compaction procedure for the membranes preceded all filtrations to insure reproducibility of the membrane initial state, and thus eliminating “membrane effect”. This compaction is carried out by circulating osmotic water through the membrane. This circulation is done in 3 steps. The first consists in circulating the liquid at 3 bars pressure during 10 minutes. Then, the liquid is circulated at 2 bars pressure during 5 minutes and at the third step, the liquid is circulated at 1 bar pressure during 5 minutes.

Analytical methods

Spectrophotometric analyses were carried out on an Agilent 8453 UV/VIS spectrophotometer. The Bradford’s method was used to evaluate the proteins concentration by absorbency at 595 nm. Total polyphenols in wine were estimated by the Total Polyphenol Index (TPI) using the absorbency at 280 nm and under 1 cm optical path. Total polysaccharides were determined using the modified Usseglio-Tomasset method based on the precipitation of the polysaccharides with ethanol [9]; this method is also used to determine mannoprotein concentrations. Total anthocyanins were determined according to Ribéreau-Gayon method using the sodium bisulphite [7]. Total tannins were also determined according to Ribéreau-Gayon method by transforming the proanthocyanidins into antocyanidins [7]. Colour Intensity (IC) is the sum of optical densities at 420 nm, 520 nm and 620 nm [7]. Tartaric acid concentration was determined by colorimetric method using ammonium metavanadate. % of alcohol, malic acid, glucose and fructose concentration were determined on the wine by FTIR spectroscopy (Fourier Transform Infra Red spectroscopy). Total and free SO_2 were determined by iodine. Table 1 shows the composition of the wine.

Table 1. Concentration of wine components and comparison with colloids concentrations quoted in the literature. * Components expressed in g/l H_2SO_4

	TAV	pH	Total ac.*	Tartaric ac.*	Malic ac.*	Volatile ac.*	Total SO_2	Free SO_2
Wine	11.9	3.65	4.18 g/l	4.2 g/l	0.1 g/l	0.33 g/l	37 mg/l	30 mg/l
	Proteins		Total Polysacch.	Total tannins	Total Anthocyanins		IPT	IC
Wine	621 mg/l		360 mg/l	3.42 g/l	984.4 mg/l		72.7	13.52
Literature	15-230 mg/l		2 - 4 g/l	1 - 4 g/l	100 - 500 mg/l			

RESULTS AND DISCUSSION

The results of filtrations are represented by graphs of normalized fluxes (J/J_0) according to time which allows us to eliminate the J_0 variations between the membranes (J_0 is the flux obtained by filtering osmosed water). The law(s), which suit to each filtration, is (are) determined by a graph $t/V = f(t)$ or $t/V = f(V)$ according to the type of fouling.

Effect of phenolic compounds

Phenolic compounds are responsible of the strong decline of filtration flux for S.R. solution compared to the flux of the S.W. solution. Figure 1 enables us to follow the profiles of normalized fluxes obtained by filtrations of six synthetic red wine solutions containing different concentrations of phenolic compounds (S.W. + 0.25 g/l anthocyanins; S.W. + 0.5 g/l anthocyanins; S.W. + 0.5 g/l tannins; S.W. + 1g/l tannins; S.R. = S.W. + 0.25 g/l anthocyanins + 0.5 g/l tannins; S.W. + 0.5 g/l anthocyanins + 1 g/l tannins). The concentrations used are in the range of actual concentrations found in the oenological practices, as quoted in the literature. The profiles of the curves indicate clearly that the solutions containing the two species of phenolic compounds (anthocyanins and tannins) exhibit a more important flux reduction than those containing only one specie of phenolic compound (anthocyanins or tannins). This can be explained by the fact that anthocyanins and tannins may react together to yield to an anthocyanin-tannin complex with bigger molecular size, this condensation being done via ethanal

molecules present in the solution. It is suspected that ethanal is issued from uncontrolled oxidation of ethanol during storage [8,10].

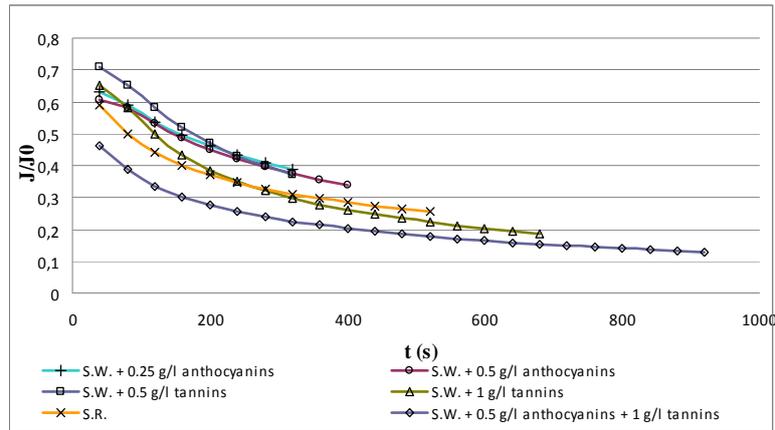


Fig. 1. Incidence of phenolic compounds on normalized fluxes

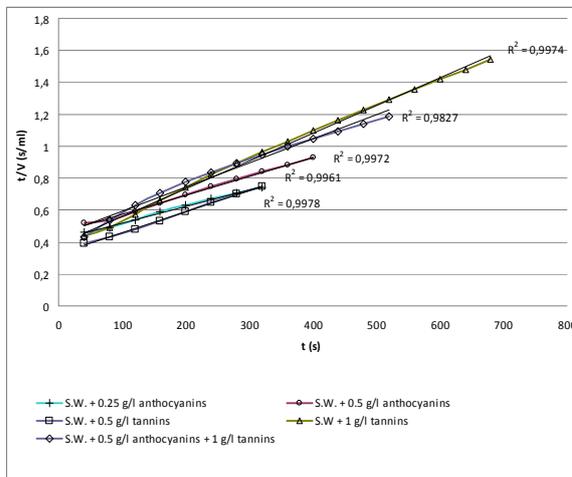


Fig. 2. Standard blocking law

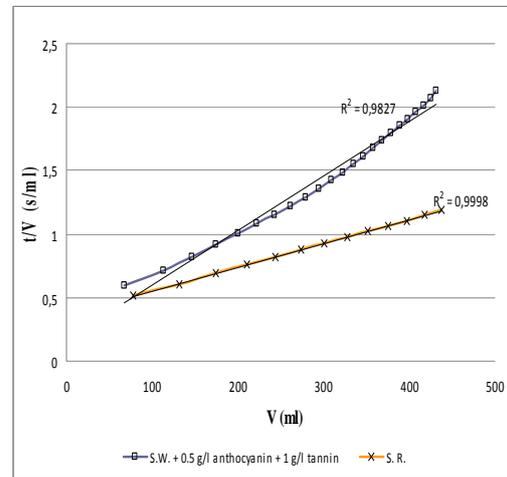


Fig. 3. Cake filtration law

When considering the effect of some species on filtration, it is clearly seen that the flux reduction when doubling the quantity of tannins, while the anthocyanin concentration is maintain, is almost similar than in the case of 2 selected amounts. Indeed, it has been shown that tannins are likely to form metastable colloidal particles at such concentration in the wines. The size of the aggregates depends on the tannin concentration and their degree of polymerization [7,8,11]. The molecules of anthocyanins may also form complexes between themselves, although a hydro-alcoholic solution, and wine in particular, is not a favorable medium for this phenomenon [11]. So increasing the anthocyanin concentration did not show a significant effect on the wine filterability

Figure 2 and 3 show the standard blocking law and the cake filtration law, respectively applied to filtration of these solutions. Such a representation of the results enables us to understand the behavior of the fouling in each solution. We note that filtration of solutions containing only one species agrees with the standard blocking law, while the cake blocking law seems to better describe the filtration of S.R. containing 0.25 g/l anthocyanins and 0.5 g/l tannins. Solution containing 0.5 g/l anthocyanins and 1 g/l tannins seems to be in agreement with the both laws.

As a conclusion of this part, it is pointed out that, when only one specie is present (either anthocyanin or tannin) a progressive blocking of pores seems to be the limiting phenomenon, while, when the two species are present (as in the case of S.R.) the fouling by cake formation is likely to be occurring, because of complexation between anthocyanin and tannin. Nevertheless, for high concentrations of these both products (as in the case of S.W. + 0.5 g/l anthocyanin + 1g/l tannin), the ethanal concentration is probably not sufficient to insure the complexation of all species. So, remaining free anthocyanin and tannin molecules may participate to a progressive inner blocking of the membrane and because both mechanisms are present in this case, this may explain why none of the both laws are suitable here.

Effect of yeast extract

The yeast extract is an autolysate of yeasts *Saccharomyces Cerevisiae* where cell-walls have been eliminated. Such an extract is a good source of amino nitrogen and vitamins, especially vitamin B. The yeast extract is added when fermentations are qualified as “difficult”, or to accelerate the fermentation. These compounds can be also found naturally in the wine after the ageing process or when any fining agent is used.

Three synthetic solutions (S.R., S.R. + 0.25 g/l yeast extract and S.R. + 0.5 g/l yeast extract) were filtrated. A strong flux decrease is observed when yeast extract is added, and fouling is more important when the quantity of yeast extract is doubled. The composition given by the yeast extract provider (OXOID) mentions only inert compounds, with respect to fouling (amino-acids, vitamins and minerals). Therefore, specific yeast extract analyses were carried out at the laboratory: no mannoproteins (a compound usually found in cell walls and known for its strong effect for membrane fouling) were found. However, analyses revealed the presence of 300 mg/g of equivalent BSA proteins (bovine serum albumin).

Filtration behaviour of these solutions was found to obey perfectly the cake filtration law. Cake formation on the surface of the membrane is probably due to anthocyanins-tannins complexation, but mainly to tannin-proteins complexation and to protein aggregation. Indeed, tannins have the capacity to complex with proteins by hydrogen bonding or hydrophobic interactions, yielding stable complexes [7,11].

To point out this suspected “protein effect” on solution filterability, proteins were removed by addition of bentonite. Indeed, bentonite is a widely used fining agent in oenology for the stability in respect to protein breakage. At usual pH of wine, bentonite is a negatively charged clay on which positively charged proteins, at the same range of pH, adsorb [7,8]. Thus, large neutral particles are formed, which flocculate then settle when their size allows it. 0.4 g of bentonite were been added to 1 L. of S.W. + 0.5g/l yeast extract. After 24 hours, 0.25 g/l of anthocyanin and 0.5 g/l of tannin have been added to the clear liquid phase (C.L.) which is free of proteins. Phenolic compounds, positively charged, have been added after fining because they can adsorb on bentonite [7,8]. This solution (C.L + 0.25 g/l anthocyanins + 0.5 g/l tannins) is filtered. In this case, we can observe (figure 4) that the fluxes curves of S.R. and C.L + 0.25 g/l anthocyanins + 0.5 g/l tannins are similar, which illustrates clearly the fouling effect of proteins issued from yeast extract addition.

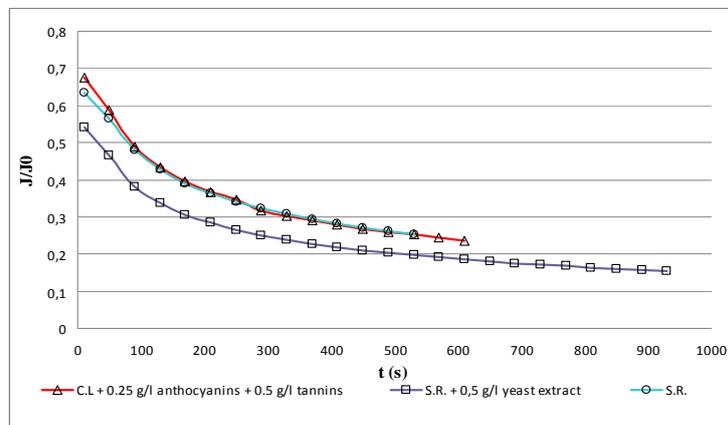


Fig. 4. Effect of fining on the filtration

Influence of pH

The charge of colloids in the wine, especially proteins and anthocyanins, depend directly on the pH of wine [8,11]. Two pH were selected (3.3 and 3.7) to evaluate the influence of pH on filterability of two solutions (S.R. and S.R. + 0.5 g/l of yeast extract).

It is observed that lowest pH (3.3) leads to an improvement of the filterability, for the two solutions (S.R. and S.R. + 0.5 g/l of yeast extract), and that all the filtrations are found to obey the cake filtration law. For the S.R. solution, decreasing the pH to 3.3 induces the modification of anthocyanins into its flavylium form (AH^+), which is evidenced by an increase of the red coloration of the liquid. The presence of AH^+ ions was checked by measuring the optical density at 520 nm (wavelength at which these ions present the highest absorbance). Flavylium forms are not likely to aggregate because their positive charge is responsible of repulsive forces between molecules [7,8,10].

For S.R. + 0.5g/l yeast extract, a flux increase is observed when decreasing pH. Indeed, the pH of the solution determines the type and the total charge of proteins, thus modifying the electrostatic interactions. The pH influences dramatically the rate of aggregation of proteins: when the pH values are close to the isoelectric point of proteins (usually close to 4 for proteins present in the wine), the very anisotropic distribution of charges may create dipoles [12]. In this case the protein-protein interactions can be highly attractive, favoring aggregation, and thus membrane fouling. When decreasing the pH of the solution, the number of the charged groups on the protein surface is increased and repulsive forces are predominant, preventing from protein aggregation [13]. This phenomenon is accounting for the significant improvement in the case of filtration of SR + 0.5 g/l of yeast extract.

Wine filtration

The evolution of the normalized flux obtained during filtration of the red wine presents a very important flux decline, much more important than observed for synthetic solutions. This decline is particularly important in the first minutes of filtration and flux tends rapidly towards zero while progressing in filtration, indicating total fouling of the membrane by specific wine components. By analyzing the wine, the results presented in table 1 revealed very high concentrations of colloidal compounds, compared to those usually present in the literature. We suspect that it is due to one step (“flash-release”) of the specific wine making process of the wine we have used in this study. We can also note the low total polysaccharides content which is due to the use of the pectolytic enzymes (degrading the pectic substances). Indeed, this type of wine was not well adapted for the procedure (dead-end filtration) of our study, and choice of a more suitable wine is under progress.

CONCLUSION

The present work was conducted with the aim to determine the effect of wine components and of some physico-chemical parameters on the fouling of microfiltration membrane. We tried also to define the type of fouling which governs each filtration. It was demonstrated that the simultaneous presence of the 2 species of phenolic compounds has a synergistic detrimental incidence on the membrane fouling, than the presence of one single species. Adding yeast extract, a widely used agent in oenology, lead to increased fouling, due to the presence of proteins in the yeast extract. The pH has also an incidence on solution filterability: improvement in flux filtration was found in the case of low pH.

Additional analyses, like particle size distribution, zeta potential... are still needed to monitor the particle distribution evolution, their charge, and the formation of aggregates along the time. These analyses will provide better understanding of the specific fouling phenomena related to wine processing.

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