

4 The characteristics of the membrane

4.1 Wettability of the membrane

4.1.1 Permeability of the membrane

Microporous membranes are widely used because they make it possible to transfer fast materials between a liquid phase and a gas phase, hence hydrophobic materials must be used in order to avoid pore wetting.

The efficiency of the membrane contactors is linked to the degree of filling of the pores by the gas phase, so the place of the transfer of material is located at the opening of the pores on the liquid phase side; this makes it possible to limit the resistance to the transfer of material induced by the membrane. When the solvent has penetrated, the transfer of material is much smaller (the diffusion coefficient in a liquid is of the order of $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ whereas in a gas it is $10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$).

The water penetration pressure (WPP) ΔP_e , is the minimal pressure that must be applied in order to force the liquid to penetrate inside dried membrane pores. This pressure depends on the maximum pore size and the hydrophobicity of the membrane. The relation between the membrane's largest allowable pore size and operating conditions is given by the LAPLACE equation (83):

$$\Delta P_p = \frac{-4 * B * \gamma_{LV} * \cos \theta}{d_{max}} \quad (83)$$

ΔP_p	<i>Water penetration pressure [bar]</i>
B	<i>Geometric factor determined by the pore structure [negligible]</i>
γ_{LV}	<i>Liquid / vapour surface energy [$\text{mN} \cdot \text{m}^{-1}$]</i>
θ	<i>Liquid–solid contact angle [$^\circ$]</i>
d_{max}	<i>Largest pore diameter [m]</i>

Therefore, the pressure on the liquid side must be maintained to avoid bubbling of the gas phase on the liquid side. The hydrophobic microporous membrane is not penetrated by the solvent; the transfer of material takes place by diffusion of the gas through the pores and then an absorption reaction with the solvent at the surface of the membrane. The pressure difference between the two sides of the membrane must be less than 1 bar.

However, the temperature and the composition of the solution are not included in the previous equation (83) and these parameters can have significant effects on the liquid–solid contact angle and the liquid surface tension. The liquid can penetrate into the pores if the transmembrane pressure drop exceeds P_p (P_p : water penetration pressure). Nevertheless, as far as the membrane presents a pore size distribution, the penetration is not uniform through all porosity. Indeed, the biggest pores are the first wetted. As the pressure is further increased,

more and more pores become wetted (Gabino, Belleville, Preziosi-Belloy, Dornier, & Sanchez, 2007).

Once than the entire porosity has become wetted, the liquid flux across the membrane and obeys DARCY's law:

$$N = K.P \quad (84)$$

N Molar flow [$\text{mol.m}^{-2}.\text{h}^{-1}$]

K Permeation coefficient

P Total pressure [Pa]

4.1.2 Hydrophobicity

As a reminder, the hydrophobicity is defined simply by the contact angle of a drop of water, when it is on a flat surface, must exceed 90 degrees. Beyond 150 °, the surface is then considered super hydrophobic. A contact angle of 180 ° means that the drop of water is completely spherical, pushing the contact zone to a single point (Moonzur & Rahman, 2015).

To describe quantitatively the wetting, we must consider the surface energies γ_{SL} , γ_{LV} and γ_{SV} , linked to the solid/liquid, liquid/vapor and solid/vapor interfaces, and then compare the energy of the "wet" system with the energy of the "dry" system. If the spreading parameter S defined by:

$$S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \quad (85)$$

is positive, the drop totals completely: one is in the case of total wetting. If it is negative, the wetting is partial and the drop joins the solid with a contact angle θ_e .

The contact angle θ_e can be obtained by balancing the interfacial tension forces applying at the contact line (Figure 46) (Callies Reyssat, 2007). The projection of these forces on the plane of the substrate gives the YOUNG relation:

$$\gamma_{LV} * \cos\theta_e = \gamma_{SV} - \gamma_{SL} \quad \text{so} \quad \cos\theta_e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (86)$$

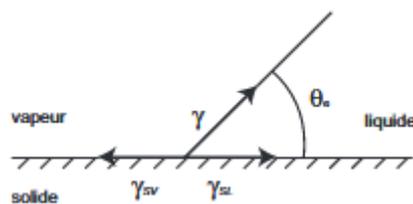


Figure 46: Angle contact

We speak of total wetting if $\theta_e = 0^\circ$, of partial wetting if θ_e has a non-zero finite value and of quasi-zero wetting if θ_e tends towards 180° . If one considers the case of water, one speaks of hydrophilic substrates if $\theta_e \leq 90^\circ$ and of hydrophobic substrates if $\theta_e \geq 90^\circ$. When $\theta_e \geq 120-130^\circ$, we speak about super hydrophobic substrate.

Asperities on the surface give a certain roughness (lotus effect). A super hydrophobic surface, as found on the lotus leaf, is characterized by a contact angle (given by the YOUNG-DUPRÉ law) between the surface and the water equal to or greater than 150° . That is, only 2 to 5 % of the surface of a drop of water is in contact with the surface. In other words, this makes it possible to have an extremely low surface wetting.



Figure 47: A drop water on a plane surface without asperities and an exemple of a suer hydrophobic surface

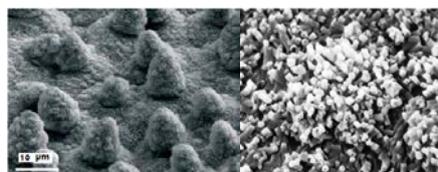


Figure 48: Microscopic view of an hydrophobic surface

4.2 Fouling of the membrane

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.

The membranes allow the retention of bacteria, viruses, yeasts etc...However, fouling is a recurring problem which limits the performance of the filtration units or membrane separation. It is linked to the accumulation of materials in the vicinity of the membrane, which is accompanied by a reduction in the volume of wine treated and/or an increase in the pressures to be applied. Two types of fouling are distinguished: irreversible fouling and reversible fouling. This corresponds to the part of flux recovered after backwashing (hydraulic cleaning). The irreversible clogging is eliminated by chemical washing (acid washing, alkaline and / or use of oxidant such as chlorine).

4.2.1 The fouling mechanisms

The flow of a solvent through the membrane is described by the DARCY law (equation (87)), where the flux is proportional to the transmembrane pressure.

$$J = \frac{\Delta P}{\mu_{(20^{\circ}C)} \cdot R_m} \quad (87)$$

J Flow of permeate [L.h⁻¹.m⁻²]
 ΔP Transmembrane pressure [Pa]
 μ Wine viscosity at 20°C [Pa.s⁻¹]
 R_m Membrane resistance [m⁻¹]

An additional resistance R_c is added to the resistance of the membrane when a clogging phenomenon appears. This phenomenon is described by the relation of series resistances (equation (88)):

$$J = \frac{\Delta P}{\mu_{(20^{\circ}C)} \cdot (R_m + R_c)} = \frac{J_0 \cdot \Delta P}{(R_m + R_c)} \quad (88)$$

Different mechanisms are the origin of fouling: concentration polarization, adsorption, pore blocking, and deposit formation.

All of the different mechanisms are illustrated in Figure 49.

The concentration polarization phenomenon's is linked to the accumulation of solutes in the vicinity of the membrane under the effect of the wine flux. The accumulation of solutes generates a concentration gradient and a backscattering flow proportional to the concentration gradient is created in opposition to the convective flux. When the concentration becomes very high, a gel may form, in particular in the presence of a high concentration of macromolecules or a deposit in the presence of colloids (Aimar, Bacchin, & Maurel, 2010). 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 adsorption of compounds present in wine on the surface of a membrane material is explained by physical-chemical interactions of ionic, hydrophobic type. Adsorption is all the more important as the material of the membrane is hydrophobic (Mallevalle, Odendaal, & Wiesner, 1996).

The blocking of pores is linked to the presence of compounds whose size is close to that of the pores of the membrane. The penetration of these compounds into the pores greatly reduces the local fluxes at the pores, thereby causing a large amount of clogging.

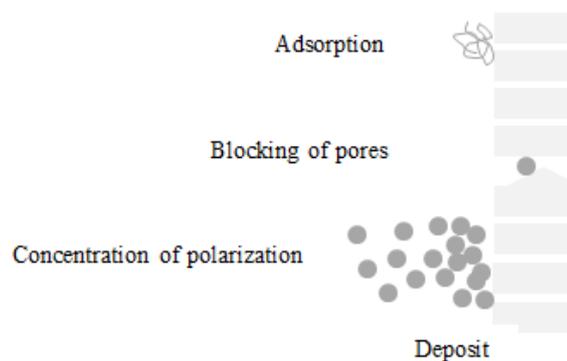


Figure 49: Different fouling mechanisms

Bacchin et al. (2002) displayed in an operating diagram (Figure 50) 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.

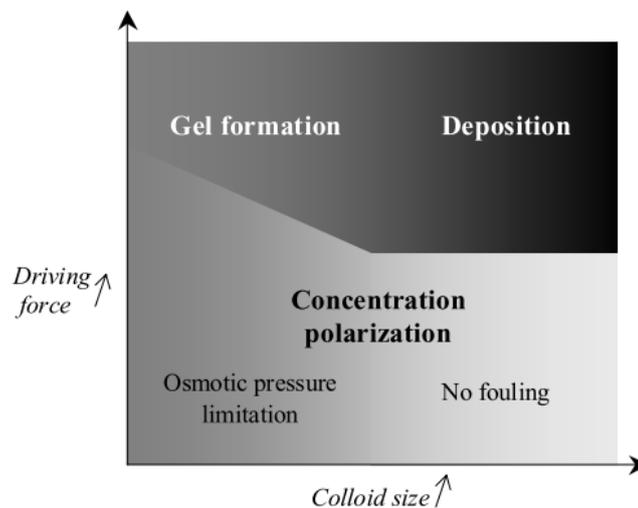


Figure 50: Diagram showing fouling mechanisms as a function of colloid size (or surface repulsion) and driving force (transmembrane pressure or permeate flux) (Bacchin et al., 2002)

When the size of particles is or becomes bigger than that of the pores, they can no longer pass through the membrane and then accumulates on its surface until forming a deposit commonly called "cake". It is more or less porous depending on the size of the particles and acts as a second membrane. The resistance of this deposit is proportional to the amount of material deposited on the membrane.

$$R_c = \alpha * M \quad (89)$$

R_c Cake resistance

α Specific resistance of the deposit [$\text{m}^{-1} \cdot \text{kg}^{-1}$]

M Amount of material deposited per volume of permeate [$\text{kg} \cdot \text{m}^{-3}$]

The term α denotes the specific resistance of the deposit, it is therefore specific to each deposit. The deposition is characterized by a compressibility factor n :

$$\alpha = \alpha_0 * \Delta P^n \quad (90)$$

a_0 Constant

n Factor of compressibility

ΔP Pressure between the membrane and the liquid [Pa]

Pore blockage and cake filtration essentially relate to porous membranes used in ultrafiltration and microfiltration.

4.2.2 Parameters influencing membrane fouling

It is well known that several parameters play a key role in membrane fouling. The control of fouling requires the implementation of technological solutions to compensate the decrease of productivity. The parameters influencing membrane fouling, summarized in Table 18, cover hydrodynamics and operating conditions, membrane characteristics as well as the fluid characteristics.

Table 18: 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...), pH, ionic strength, suspension concentration, suspension size and viscosity

* Pore size: pore dimension (diameter); ** porosity: quantity of pores

4.2.3 Membrane cleaning

Membrane cleaning is an essential step for maintaining the performance of a membrane process. Standard procedures for cleaning a fouled membrane with food compounds as proteins involve cycles of alkaline and acid solutions circulating through the system (Gabino et al., 2007). Alkaline cleaning is generally used to remove organic and colloidal molecules whereas acidic cleaning is useful in removing inorganic compounds. It is important to notice that chemical cleaning agents can modify the characteristics of membranes in particular the hydrophobicity which is fundamental for the membrane contactor. The traditional method to evaluate the hydrophobicity of a solid surface is the contact angle measurement. Therefore for a porous material, this method does not always provide adequate information. The wettability

of membranes can be better defined by a critical surface energy combined with operating pressure conditions rather than by contact angle measurements, because under operating conditions, the circulating liquids exert a pressure on either side of the membrane affecting the contact angle and the wetting conditions.

The membrane stability to cleaning agent was studied by measuring the WPP as well as the process performance after several cycles of cleaning.

Note: Users have noted that we must be very careful to clean the membranes, especially when using cleaning products incompatible with the membrane material, it affects the effectiveness of the membrane contactor, a reduction in gas transfer is observed.

Conclusion

This report brings together information needed to understand and control the theory of gas exchange in wine, but also to put into practice and verify this theory using a membrane contactor.

This separation process is already used in various fields such as the environment, industry or the agri-food industry. Since a few years it is used in the wine industry, it is a process which improves and facilitate the adjustment of dissolved gases. It is also an interesting process on the economic plan especially concerning the consumption of the gases compared, requires less manpower, less expensive cleaning because less water consumption to traditional techniques.

However, to date there is only one manufacturer and supplier of hydrophobic membranes for the design of MC. American industrial "Membrana" has this monopoly. But for the moment it is a product that is not officially authorized by the European Union. Hence, the interest of the MO₂VE project that could give rise to a new French hydroponic membrane that would have the same capacity and performance as that of the main competitor and which would be authorized by the EU and so it would develop a whole new business. It is said that the future is sparkling, or also the certain interest for this process.