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Application of membrane processes for the filtration of extra virgin olive oil

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Abstract

The oil extracted from olive paste is a turbid and opalescent must and contains impurities that can compromise its quality since they facilitate hydrolysis, fermentation and rancidity. Although filtration of this oil removes these otherwise damaging substances, it can also cause small changes in the oil. In this paper membrane cross-flow filtration is proposed as a different and innovative filtration process for extra virgin olive oil. The preliminary results reported here show that the removal of damaging substances through membrane filtration can be achieved in a single step, without the addition of filter aids (therefore reducing oil loss). Membrane filtration also does not alter the chemical composition of the oil.

Keywords: Extra virgin olive oil; Membrane; Microfiltration; Ultrafiltration

1. Introduction

Extra virgin olive oil (EVOIL) is obtained from pressing only the *Olea europea* (olive) fruit. It is one of the earliest vegetable oils used by man and the only one that can be consumed without refining. European legislation states that EVOIL must be exclusively obtained through mechanical and physical processes, such as pressing, washing, decantation, centrifugation and filtration that do not modify its characteristics (EU regulations no. 2568/91). The must extracted from the olive paste is still turbid and opalescent and contains impurities such as water in emulsion, pieces of fruit or stone and mucilage that can compromise the quality of EVOIL since they facilitate hydrolysis, fermentation and can cause the oil to become rancid. The filtration process removes these otherwise damaging substances (Peri, 1983).

The must is usually treated by a filter-press, where the oil flows under pressure through the filtration panel (made of filter aids). Two filtration steps (removal of large-size solids and making the oil brilliant) are usually necessary.

The basic disadvantage of this process lies in the fact that all the oil retained in the filtration panels is lost and additionally, traces of the filter aids (used in the formation of the filtration panels) can be found in the oil (Peri, 1983). Furthermore, disposal of these panels can be problematic.

It is therefore necessary to study different and innovative filtration processes for the olive oil industry that are safer for the product, environment and consumer. The application of cross-flow filtration, using membranes to remove the various undesired substances could be an interesting and valuable alternative to traditional filtration (Cuperus, 1998).

To our knowledge, membrane filtration has never been applied to EVOIL but has been extensively used on seed oil (Ochoa, Pagliero, Marchese, & Mattea, 2001; Pioch, Largueze, Graille, Ajana, & Rouviere, 1998) to substitute in part the refining process. Membrane processes reduced the waxes, phospholipids (Lin, Rhee, & Koseoglu, 1997), suspended particles and impurities found in seed oil (Subramanian, Nakajima, & Kawakatsu, 1998; Subramanian, Nakajima, Rimura, & Maekawa, 1998). This technology can also remove trace amounts of heavy metals including copper, manganese

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and iron, which are sometimes present in the oil (Snape & Nakajima, 1996).

The aim of this work is to verify the potential applications of membrane cross-flow filtration technologies for EVOIL. Various commercial micro (MF) and ultra (UF) filtration membrane were used. They were of a different chemical nature and structure and were tested under different operating parameters to identify the optimal process conditions required to obtain brilliant EVOIL of an improved quality.

2. Materials and methods

2.1. Extra virgin olive oils

Crude oil used in this work was supplied by Carapelli Firenze S.p.A and was filtered on non-woven before the membrane tests, in order to remove the large particles and suspended solids that can damage the membrane surface.

2.2. Membrane

Various types of commercial membrane (polymeric or ceramic, flat or tubular, single or multichannel) were used for MF and UF experiments. Their main characteristics are reported in Table 1. The ceramic membrane had an asymmetric structure formed by a selective meso or microporous internal layer, deposited onto the surface of a macroporous ceramic (α-Al_2O_3) support.

Both Accurel and Celgard membrane were polymeric, asymmetric and free-standing while Osmonics-Desal membranes were formed by a selective PTFE layer supported by a thicker macroporous non-woven.

2.3. MF and UF units and procedures

Fig. 1 shows the scheme of the laboratory pilot plant used for UF and MF tests on the crude EVOIL. The plant is equipped with a 5 l feed tank and interchangeable modules for flat (channel height: 2 mm) or tubular membrane (Table 1). It can work in a pressure operating range of 100–1000 kPa, temperature up to 60 °C and a recirculation rate from 1 to 6 $\mathrm{m\,s^{-1}}$. Precautions were adopted in order to avoid loss of the EVOIL properties due to its continuous recirculation though the plant. These included for example, the selection of proper construction materials of the plant and a prolonged pre-rinse with the same EVOIL used for the membrane filtration tests. The plant also worked under nitrogen atmospheres and was fitted with a cryostatic bath, which controls the temperature. The tests were carried out according to the total recycling mode (recycling both permeate and concentrate stream to the feed tank). The duration of each test normally varied from one to three hours. Permeate and concentrate samples were taken and an average sample was analysed.

After each test, the membrane module was removed and washed with water and detergents. The use of a different plant was necessary for these operations in order to not pollute the olive oil plant. The module was first rinsed with pure water for 30 min, and then submitted to cleaning procedures using an Ultrasil 110 solution at (1% w/w) and a NaOH solution at (1% w/w). Ultrasil 110 is a liquid alkaline cleaner and belongs to a family of products (P3-ultrasil) developed by Henkel-Ecolab for membrane and membrane filtration plant cleaning. These solutions were circulated for 60 min at a temperature of 60 °C, a recirculation rate (v_R) of 5 $\mathrm{m\,s^{-1}}$ and a pressure of 400 kPa. After each cleaning treatment the water permeability of the membrane was measured under the following conditions: $T = 25$ °C, $v_R = 2\ \mathrm{m\,s^{-1}}$, $P = 400$ kPa. After a final rinse with pure water for 20 min the membrane was dried in an oven at 120 °C, to completely remove any residue water, to be ready for further EVOIL tests.

2.4. Analytical testing

Free acidity, peroxide value and UV absorption characteristics were determined following the analytical methods described in EEC Regulations 2568/91 (EEC, 1991) and its later modifications. Free acidity, given as a percentage of oleic acid, was determined by titration of a solution of oil dissolved in ethanol–ether (1:1) with ethanolic potash. Peroxide value, expressed in milliequivalents of active oxygen per kilogram of oil ($meqO_2$/kg), was determined as follows: a mixture of oil and chloroform–acetic acid was left to react in darkness with a solution of potassium iodide, the free iodine was then titrated with a sodium thiosulphate solution. The K_{232} and K_{270} extinction coefficients were calculated from absorption at 232 and 270 nm respectively, with a UV spectrophotometer (Lambda 2 Perkin Elmer) using a 1% oil in cyclohexane solution.

The sensory evaluation (panel test score) for the olive oil sample was also carried out using a panel of ten assessors (panelist) trained in the fundamental tastes (sweet, salt, sour and bitter) and on the four defects of virgin olive oil (bitter, marc, wined and rancid). Each panelist had to evaluate the intensity of the olive oil's sensory characteristics and give a score ranging from one to nine according to the qualities and defects found in every sample. Therefore, the final sensory values for the tasting samples (the experimental response) were derived from the average of the single scores. For the sensory analysis an olive oil is classified as extra virgin when it gets a score equal or superior to 6.5, while it is classified as virgin if its score is equal or superior to 5.5.

Table 1
Membrane used in the cross-flow filtration tests

Manufacturer	Trade name	Membrane type	Nominal porosity for MF and MWCO for UF	Process	Membrane surface (m^2)	Configuration	Filtration length (mm)	Number of channels	Channel diameter (mm)	Composition skin and support layer	Chemical nature	Pressure (kPa)	Permeate flux (l/m^2 h)
Orelis (France)	Kerasep	K15	15 kD	UF	0.059	Tubular multichannel	400	19	2, 5	TiO_2 on Al_2O_3	Hydrofilic	400	3.2
		K300	300 kD	UF								400	13.3
Orelis (France)	Carbosep	M14	0.14 μm	MF	0.0075	Tubular monochannel	400	1	6	TiO_2 on carbon	Hydrofilic	400	13.9
		M1	150 kD	UF								400	2.3
Tami (France)	Tami	T50	50 kD	UF	0.0132	Tubular trichannel	400	3	3, 5	TiO_2 on Al_2O_3	Hydrofilic	400	4.9
		T150	150 kD	UF								400	6.8
		T300	300 kD	UF								400	20
Hoechst (Germany)	Celgard	2500	0.21 μm	MF	0.0066	Flat sheet	–	–	–	Polypropylene	Hydrofobic	200	9.1
Akzo Nobel (Germany)	Accurel	PP1E	0.1 μm	MF	0.0066	Flat sheet	–	–	–	Polypropylene	Hydrofobic	200	45.6
Osmonics-Desal (USA)		K150	0.1 μm	MF	0.0066	Flat sheet	–	–	–	PTFE	Hydrofobic	200	47
		K750	1 μm	MF								200	577

Permeate obtained at constant temperature ($T = 30$ °C), and recirculation rate ($v_R = 2\ m\,s^{-1}$) for different commercial membrane.

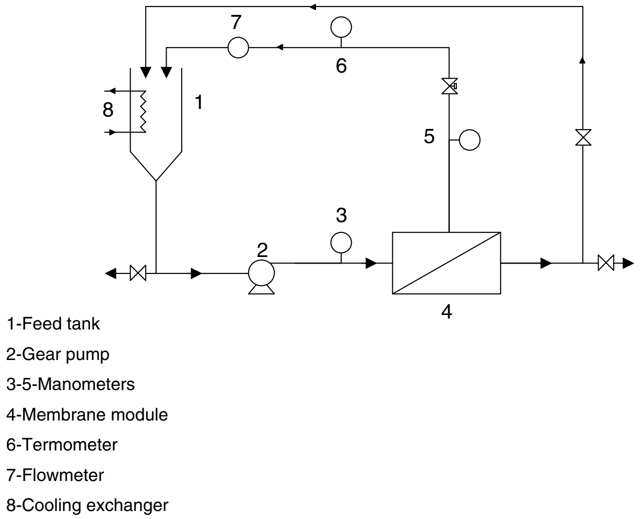

Fig. 1. Scheme of the cross-flow membrane filtration plant.

3. Results and discussion

The efficiency of the membrane filtration process (quality of the permeate oil and flux) depends not only on membrane characteristics but also on the operating parameters applied. In cross-flow filtration the continuous flow over the membrane surface reduces the deposition of impurities in comparison to dead-end filtration and the permeate flux is therefore generally more stable over time.

Results of the experiments conducted to verify the effect of membrane characteristics and the operating conditions (temperature, pressure, recirculation rate) on the permeate flux, are reported below.

3.1. Effect of membrane characteristics (chemical, material and porosity)

Permeate fluxes obtained for the different membrane are listed in the last column of Table 1. The data refers to the samples taken after 60 min operating time. It can be seen that polymeric membrane give much higher fluxes (under the same operating conditions and with membrane of the same porosity) than ceramic membrane. The highest fluxes are observed for the polymeric membrane (PP1E, K150, K750). However, the permeate oil was slightly turbid and showed very similar characteristics to traditional filtered oil. The specific fluxes obtained for some of the hydrophilic membrane were too low (even at high pressure) and for this reason these membrane were excluded from the experiments (M1, K15). Attention was then focused on a limited number of selected membrane that provided not only higher fluxes but also good flux stability over time and a permeate with high organoleptic characteristics.

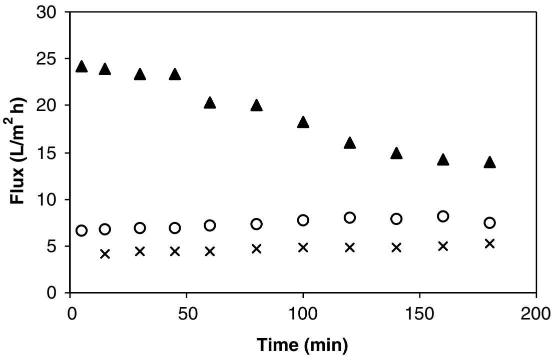

Fig. 2. Effect of MWCO and running time on permeate flux of TAMI ceramic membranes. Operating conditions: $P = 400$ kPa; $v_R = 2\ \mathrm{m\,s^{-1}}$; $T = 30$ °C. MWCO: 50 kD (×), 150 kD (○), 300 kD (▲).

Fig. 2 shows the trends of the permeate flux as a function of operating time for three membrane (with the same material and structural characteristics but different Molecular Weight Cut-Off, MWCO). The permeate flux is higher for the membrane with a 300 kD MWCO but the flux of this membrane decreases more rapidly over time. Membrane with higher MWCO are usually characterised by a higher fouling tendency and pore clogging, since it is easier for the fluid particles to penetrate into the pores and plug them.

3.2. Effect of the temperature on the permeate flux

Fig. 3 shows the variation of the permeate flux as a function of the temperature for the polymeric and ceramic membrane. As can be seen, an increase in temperature leads to an increase in the flux. This is due to a decrease in the EVOIL viscosity as the temperature rises. For example, by increasing the temperature from 20 to 50 °C, the flux of the polymeric membrane increases from ≈10 to 24 l/m^2 h. In both the cases the

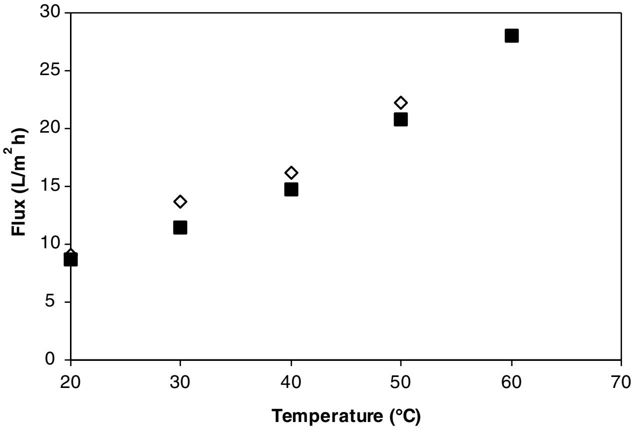

Fig. 3. Effect of feed temperature on the permeate flux for polymeric membrane Celgard 2500 (◇); and ceramic membrane Kerasep 300 kD (■). (Operating conditions $P = 400$ kPa; $v_R = 2\ \mathrm{m\,s^{-1}}$; $t = 90$ min.)

permeate flux increases with the temperature. From an applicative point of view, operating at high temperatures is very positive for flux efficiency, since it enhances the mass transfer and thus increases the permeate rate (Cheryan, 1986). However, a higher temperature can only be applied when the quality of the oil, in terms of its thermolabile components, is not significant (for example in refined oil). However, for EVOIL it is of paramount importance to preserve the oil nutritional components (phenols or vitamins), improve the organoleptic quality and limit the formation of oxidized species. For these reasons it was decided to operate at a maximum temperature of 30 °C.

3.3. Effect of the pressure on the permeate flux

Fig. 4 shows the results obtained for the ceramic (Fig. 4(A)) and polymeric membrane (Fig. 4(B)) at different transmembrane pressure (TMP), this represents the difference in pressure between the concentrated side and the permeate side. The initial high operating pressure guarantees an initial greater flux. However, while at 200 kPa the flux remains constant for the entire duration of the test, at 400 and 600 kPa a different behaviour is observed and in particular at the highest pressure, a strong flux decrease over time occurs. This fact is probably linked to the fouling phenomenon, which occurs at higher pressure (Schäfer, Fane, & Waite, 2000). The increase of the flux for all the pressure conditions during the first 50 min of the process is connected to the increase in temperature (from 22 to 30 °C). Although a very similar flux trend for both the polymeric and ceramic membrane can be seen, the flux decrease over time is higher for the polymeric membrane (Fig. 4(B)). For this type of membrane the permeate after ≈100 min working time at 600 kPa is lower to the flux measured at 200 kPa. The optimal working conditions (to obtain high flux and its stability over time) seem to be therefore 400 kPa for the ceramic membrane and 200 kPa for the polymeric one.

3.4. Effect of the recirculation rate on the permeate flux

Generally speaking, in the MF and UF of solutions with a low viscosity the use of high recirculation rates reduces the polarisation phenomena (Cheryan, 1986). By lowering the mass transport resistance a higher and more stable flux is generally obtained. This was not found to be true in our case where a more viscous fluid (EVOIL) is treated. This is clearly shown in Fig. 5, where even though the recirculation rate increases, practically no difference is observed in the flux values.

An increase in the recirculation rate is normally used to reduce the thickness of the polarisation layer. However, in our case the effect of this operating parameter is not so important since the high viscosity of EVOIL leads to $Re < 2100$ (i.e. viscous or laminar flow) even at the highest recirculation rate (6 m/s) used for the tests. As reported in literature (Cheryan, 1986) the mass transfer coefficient, which controls the permeate flux is connected to the density and viscosity of the treated fluid using the dimensionless number of Sherwood, Reynolds and Schmidt (Perry & Green, 1997). According to this, the higher the feed fluid viscosity is, the lower both the mass transfer coefficient and the permeate flux are.

Based on the results obtained, the optimal operating conditions for the cross-flow filtration of EVOIL using a ceramic membrane are: temperature of 30 °C (to facilitate the flux and not alter the oil), pressure of 200 or 400 kPa and recycling rate of 2 m s^{-1} (to guarantee a discrete and stable flux). By working in these conditions, it is possible to considerably reduce the fouling phenomenon of the membrane. This is demonstrated in Fig. 6 where the flux, after the initial 4–5 h of operation, remained stable over time. This behaviour of the membrane will be further examined in Section 3.6.

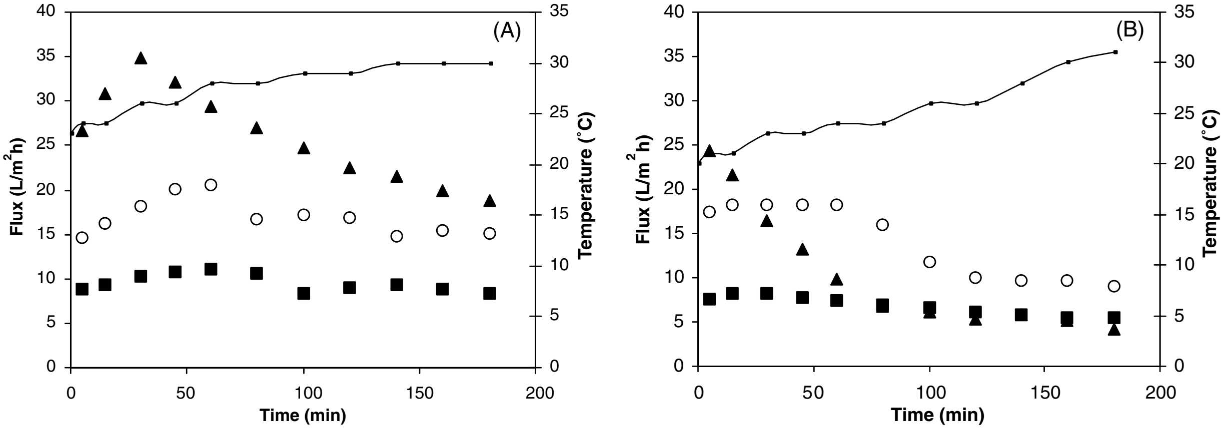

Fig. 4. Effect of TMP: (■) 200 kPa; (O) 400 kPa; (▲) 600 kPa, temperature (—) and running time on permeate flux, at different (A) ceramic membrane, Tami 300 kD and (B) polymeric membrane: Celgard 2500. (Recirculation rate = 2 m s^{-1}.)

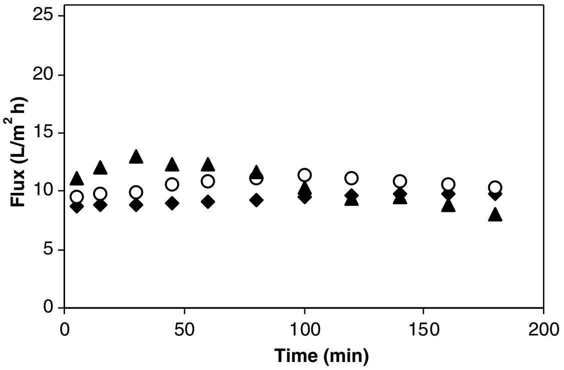

Fig. 5. Effect of recirculation rate on permeate flux: (◆) 1 m s^{-1}, (○) 2 m s^{-1}, (▲) 6 m s^{-1}. Operating conditions: $P = 400$ kPa; $T = 30$ °C; ceramic membrane Kerasep 300 kD.

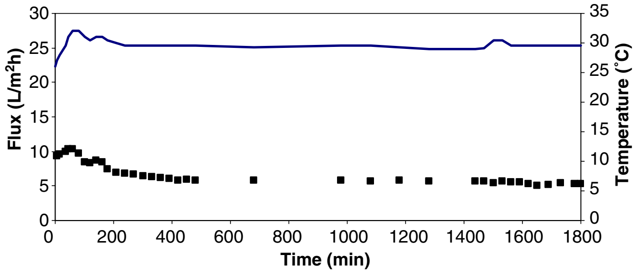

Fig. 6. Permeate flux as a function of running time and temperature (—). Operating conditions: $P = 400$ kPa; $v_R = 2$ m s^{-1}; ceramic membrane Kerasep 300 kD.

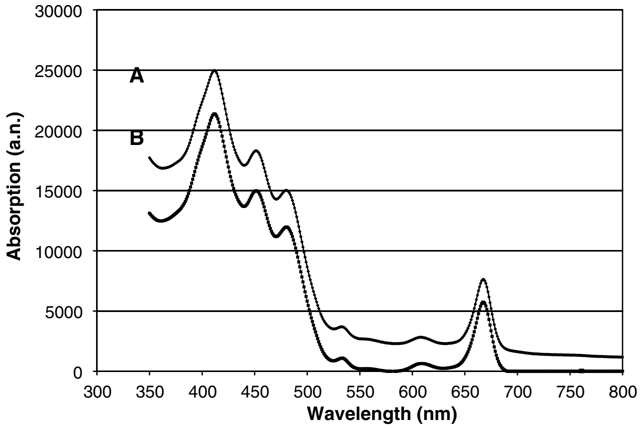

Fig. 7. Absorption spectrum of extra virgin olive oil: crude (A) and membrane filtered (B).

3.5. Extra virgin olive oil quality

Table 2 compares the results for the analytical testing of membrane filtered oil with those obtained for two types of crude oil filtered using the traditional method. One of the crude oils was taken after the first filtration step (which removes the larger particles) and the other type was taken after the second filtration step, which serves to retain the finer particles and makes the EVOIL brilliant. As can be seen, membrane filtration (especially with membrane Kerasep 300 kD and Celgard 2500) does not significantly alter the high quality of EVOIL (in terms of acidity, peroxide values and the visible–UV absorption spectra). The values are in fact very similar to those obtained through traditional filtration. Membrane treatment can remove all the absorbing visible light spectrum substances (Fig. 7), which render the oil turbid. In addition membrane treatment does not affect the composition of the final oil, in terms of pigment carotenoids (peak at 450 nm) and chlorophyll (peak at 670 nm). EVOIL using the proposed membrane technology retains its colour and pleasant aroma. Thus, this product is similar to the crude oil since aroma, colour and natural antioxidants are preserved during filtration.

3.6. Cleaning and fouling control

As shown in Fig. 6, by operating with cross-flow filtration membrane it was possible to maintain a stable flux over a long period of time (when operating in bland conditions). Bland conditions also limit pore occlusion, therefore allowing us to work with membrane with a lower porosity than 300 kD and not a very high TMP. However, the high viscosity of EVOIL favours the polarisation phenomena that in turn lead to a lowering of the permeate flux. Therefore, the polarisation layer is more stable and tends to clog the pores over time, causing the permeate flux to decrease. Washing the membrane is very important in order to restore the initial

Table 2
Analytical testing for crude, filtered bv traditional and membrane-filtered oil

Sample	Oleic acid %	Peroxide values (meq O_2/kg)	UV-Absorption			Panel test scores
			K_{232}	K_{270}	Δk	
Crude oil	0.42	7.5	1.98	0.13	−0.002	7
Celgard 2500	0.42	8.2	1.98	0.13	−0.002	7
Desal K150	0.42	8.3	1.97	0.13	−0.002	7
Carbosep M14	0.41	8.5	1.98	0.13	−0.002	7
Kerasep 300 kD	0.42	8.7	1.99	0.13	−0.002	7
First filtration	0.43	9.0	1.98	0.13	−0.002	7
Second filtration	0.42	8.9	1.95	0.13	−0.002	7

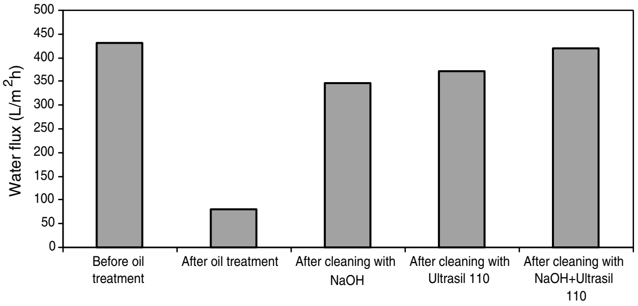

Fig. 8. Water permeability recovery for Kerasep 300 kD ceramic membrane (operating conditions: $T = 25$ °C; $v_R = 2$ m s^{-1}; $P = 400$ kPa).

membrane flux. Organic solvents cannot be used as they could contaminate the EVOIL, damage the PP membrane (Chi-Sheng Wu & Lee, 1999; Ebert & Cuperus, 1999) and could be dangerous when used under pressure. A water solution was therefore used for membrane cleaning. After the cleaning treatment, water was completely removed from the membrane pores. Fig. 8 shows the water flux of the membrane module after membrane filtration of oil and after cleaning with different solutions. Cleaning with a 1% (w/w) Ultrasil 110 solution gives a recovery of about 86% of the initial water permeability of the membrane. A more complete regeneration (97%) of the membrane permeability is obtained using a 1 % (w/w) Ultrasil 110 and NaOH solution.

4. Conclusions

This work clearly demonstrates the usefulness of membrane processes in the EVOIL treatment. The membrane process, carried out directly after the crushing process, gives a good level of clarification without using filtering aids, absorbents and other filtration coadjuvants. The retentate oil phase (volume around 1/20 of the initial volume) could be submitted to a classical filtration step or to a refining step. During membrane filtration polarisation gel tends to form on the membrane surface and its control is of paramount importance on the mass transport. The fouling seems to be better controlled by initially filtering olive oil in order to remove large particles that can foul the membrane surface.

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