

UNIVERSITÀ DELLA CALABRIA



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CICLO

XXIX

TITOLO TESI

Use of submerged membrane technology for the treatment of
Olive Mill Wastewater: fouling study and process performance

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A mio Nonno...

Sommario

L'obiettivo di questo lavoro di ricerca è stato quello di studiare le prestazioni di un sistema a membrane immerse per il trattamento delle acque di vegetazione. A tal fine, è stato costruito un prototipo su scala da banco dalla capacità di 5 L che impiega un fascio di membrane a fibre cave polimeriche per la chiarificazione delle acque. L'approccio allo studio è stato quello di dividere l'indagine su tre fronti: il primo ha previsto lo studio della matrice acque di vegetazione al fine di individuare un metodo di pretrattamento capace di favorire i processi di filtrazione a membrana limitandone il *fouling* (sporcamento); il secondo ha previsto lo studio del *fouling* per adsorbimento di componenti presenti nelle acque su diverse membrane polimeriche, al fine di individuare i materiali più adatti per il processo; il terzo e ultimo ha previsto l'assemblaggio del sistema a membrane immerse e lo studio delle prestazioni in funzione dei parametri di processo. Le analisi chimico/fisiche sulle acque di vegetazione restituiscono range di valori influenzati da diversi parametri relativi alla produzione dell'olio di oliva. Parametri quali periodo di raccolta, maturazione del frutto, clima e terreno possono variare la concentrazione chimica di un composto nelle acque anche più del doppio. Ciò restituisce un refluo che per essere trattato è necessario un processo flessibile a tali variazioni. Una delle proprietà delle acque di vegetazione che non varia è il potenziale Z della soluzione. Le acque di vegetazione post produzione presentano un valore di potenziale di circa -30 mV, il quale definisce una soluzione stabile e l'impossibilità da parte delle particelle in soluzione di intraprendere processi di aggregazione e o flocculazione. Sulla base di questo dato è stato studiato un trattamento che prevedesse la destabilizzazione della soluzione a valori di potenziale Z compresi tra ± 5 mV, in modo tale da favorire l'attrazione tra le particelle in soluzione e la conseguente sedimentazione. Una volta allontanato il deposito di materiale sedimentato dalla soluzione si ottiene un refluo più facile da trattare con i processi di filtrazione a membrane rispetto al refluo originario. L'interazione dei componenti che causano lo sporco con la superficie di membrana è stata studiata su diverse membrane, le quali differivano per materiale di composizione e grandezza dei pori. Al fine di capire il

comportamento dello sporciamento sono stati utilizzati tre diversi sistemi in cui acque di vegetazione e membrane sono state messe a contatto. I tre diversi sistemi miravano a verificare i diversi contributi allo sporciamento dovuto ad adsorbimento di molecole sulla superficie delle membrane e ad intrusione di molecole all'interno dei pori a causa dei pur minimi valori di pressione idrostatica della colonna di liquido con cui viene a contatto la membrana. Mediante misure di permeabilità all'acqua ultrapura delle membrane, prima e dopo contatto con le acque di vegetazione, e analisi morfologica delle superfici delle stesse, mediante microscopia a forza atomica (AFM) è stato possibile definire il grado ed il meccanismo del *fouling* per i diversi tipi di membrana. La realizzazione del sistema a membrane immerse, la sua messa in funzione e lo studio dell'influenza delle condizioni operative sull'efficienza del processo hanno consentito di individuare i parametri che rendono competitivo il trattamento di acque di vegetazione mediante microfiltrazione a fibre cave immerse. E' stato costruito un modulo a membrana con un fascio di circa 50 fibre polimeriche in polietilene, da 0.4 μm di diametro dei pori, dalla lunghezza di 20 cm e alla base del modulo è stato inserito un sistema per la produzione di bolle d'aria connesso ad una linea d'aria a portata regolabile. Il modulo a membrana così completo è stato installato dentro un vasca cilindrica dalla capienza di 5 L e connesso ad una pompa peristaltica regolabile. Il lumen delle fibre cave è occluso dall'estremità immersa nella soluzione (nella quale le fibre sono libere di ondeggiare) mentre è aperto dall'estremità fissata alla base del modulo. La pompa peristaltica crea una depressione all'interno delle fibre che promuove la permeazione dell'acqua attraverso la membrana. Un manometro posizionato lungo la linea di connessione tra modulo a membrana e pompa ha permesso il controllo della pressione transmembrana applicata. L'intento è stato quello di trovare un modo di operare che permettesse al sistema di lavorare in continuo a flusso costante per 8h (equivalente ad una giornata lavorativa). Le condizioni operative studiate includono l'influenza della pressione transmembrana, della frequenza e portata di aria e della frequenza di *back-flushing* sull'andamento del flusso di permeazione nel tempo. Gli studi sono stati condotti con diverse acque di vegetazione che differivano per pH e contenuto in solidi. I risultati hanno confermato la definizione di un sistema flessibile per il trattamento delle acque

di vegetazione. Infatti, il sistema a membrane immerse ha mostrato di poter chiarificare tali acque con efficienza in termini flusso stazionario, qualità di prodotto e riusabilità. E' opportuno sottolineare che le basse pressioni transmembrana impiegate determinano un flusso di permeato attraverso membrane immerse inferiore rispetto a quello di membrane esterne. Tuttavia, il minor consumo energetico e la minore tendenza allo sporramento delle membrane polimeriche immerse rendono queste ultime competitive per il primo stadio di trattamento di acque con elevato carico inquinante come quelle di vegetazione.

Abstract

The objective of this research work was to study the performance of an immersed (or submerged) membrane system for the treatment of vegetative waste water, coming from the production of olive oil (or Olive Mill WasteWater OMWW). To this end, a prototype has been built up on a bench-scale capacity of 5 L, which employs a bundle of polymeric hollow fiber membranes. The approach of the study has been to divide the survey on three fronts: the first aimed at studying the waste water matrix in order to identify a pre-treatment method capable of favoring the membrane filtration processes limiting the fouling (fouling); the second involved the study of fouling by adsorption of the components present in the waters using different polymeric membranes, in order to identify the most suitable materials for the process; the third and final concerned the construction of the immersed membranes system and to the study of its performance as a function of process parameters.

The chemical/physical analysis on the vegetation water evidenced range of values affected by different parameters related to the production of olive oil. Parameters such as the collection period, maturation of the fruit, the climate and soil can significantly vary the chemical concentration of a compound, which can become more than double in certain condition. This means that the effluent to be treated needs a flexible process to cope with such variations. One of the properties of the waste water that does not vary is the Z potential of the solution. The post production vegetation waters have a potential value of about -30 mV, which defines a stable solution, and the inability of the particles in solution to undertake processes of aggregation and or flocculation. On the basis of this finding it has been studied a treatment that provided for the destabilization of the solution to values of Z potential between ± 5 mV, in such a way as to favor the attraction between the particles in solution and subsequent sedimentation. Once removed the deposit of material, is obtained an effluent easier to treat with the processes of submerged membrane filtration compared to the original effluent. The interaction of the components that cause fouling on the membrane surface was studied using different membranes, which differed in composition of material and pore

size. In order to understand the behavior of fouling, three different systems to put in contact vegetable water with membrane surface were used. The three different systems were intended to verify the different contributions to fouling by adsorption of molecules on the surface of membranes and/or the intrusion of molecules within the pores due to the even minimum values of the hydrostatic pressure of the liquid column which is in contact with the membrane. By means of membrane ultrapure water permeability measurements, before and after contact with the waste water, and by morphological analysis of the surfaces of the same membranes, by atomic force microscopy (AFM), it was possible to define the degree of fouling and the mechanism for different types of membranes.

The construction of a system immersed membrane system on a batch-scale was obtained using hydrophilized polymeric hollow fiber membranes. The study of the influence of operating conditions on the efficiency of the process permitted to identify the parameters that make competitive the treatment of vegetable waste by means of immersed hollow fiber microfiltration.

The membrane module was constructed with a bundle of about 50 polymeric hollow fibers of polyethylene having 0.4 μm pore diameter and the length of 20 cm. At the base of the module a system for the production of air bubbles was inserted connected to an air line with adjustable flow. The membrane module was installed inside a cylindrical tank with a capacity of 5 L and connected to an adjustable peristaltic pump. The lumens of the hollow fibers is occluded from the upper and immersed in the solution (in which the fibers are free to sway) while it is open from the end secured to the base of the module. The peristaltic pump creates a depression inside the fibers, which promotes the permeation of water through the membrane. A pressure gauge positioned along the connection line between the module and diaphragm pump measured the pressure downstream the fibers. The intent was to find a *modus operandi* that would allow the system to work continuously at a constant flow for 8 hours (the equivalent of a working day). The operating conditions studied include the influence of the transmembrane pressure, frequency and flow rate of air and the frequency of back-flushing on the progress of the permeation flux over time.

The studies have been conducted with various vegetative waters differing in pH and solids content. Results confirmed that a flexible system for the treatment of vegetative waste water was identified. In fact, the immersed membranes system was efficient in clarifying these waters in terms steady state permeate flux, product quality and reusability. It should be noted that the low transmembrane pressures employed determine a permeate flow through the immersed membranes lower compared to that usually obtained with side-stream membranes. However, the lower power consumption and less tendency to fouling of immersed polymeric membranes makes the latter competitive for the first stage of water treatment with high pollutant load such as the vegetative waste water.

Outlines

The structure of this thesis reflects the problem-solving approach scheme used to perform this study. The objective was to proof the suitability of submerged membrane microfiltration for the treatment of the olive mill wastewater (OMWW). The research was performed on a three stage work scheme in which (i) OMWW were studied and analyzed in order to propose a protocol pretreatment method to limit membrane fouling, (ii) membrane fouling was investigated for different membrane materials and feeds in order to understand fouling mechanism and how to control/limit fouling during operation, and (iii) a submerged hollow fiber membrane system was studied in order to perform the first stage microfiltration of OMWW. These three specific objectives were obtained starting from the interrogative of what affected the efficiency of this technology. Obviously, the most important parameter that affects microfiltration performance in waste water treatment is fouling. For this reason, the need to find a strategy to limit fouling is a key issue to improve the process. For this purpose, OMWW matrix, fouling mechanism and operative conditions for the membrane system were studied. Following this scheme, the first chapter is devoted to OMWW and the attention is focused on their production and chemical composition. In the second chapter general aspects on membrane fouling are reported. Fouling mechanisms and its mathematical representations are discussed. This knowledge was used to analyze the interactions between foulants present in OMWW and membrane surface. In Chapters three and four experimental results about fouling analysis and submerged membrane system, respectively, are discussed. A final section of general conclusion highlights achievements and perspectives.

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Olive Mill Waste Water (OMWW)

1

1.1 Introduction

Olive oil production is an important economic resource for most countries situated in the Mediterranean basin. In tab. 1 the average production and the percentage contribute at the World production of olive oil of most countries situated in this area are reported. The data cover a period of 31 years and show that about 90% of world production of olive oil occurs in the Mediterranean basin while Spain, Italy and Greece are the major producers in the World.

Country	Period 1990-2010		Period 2010-2016	
	Average (t)	% World Production	Average (t)	% World Production
Algeria	5.0	0.2%	9.8	0.3%
Cyprus	5.7	0.2%	5.8	0.2%
Croatia	-	-	3.7	0.1%
France	5	0.2%	4.3	0.1%
Grèce	363.5	13.1%	284.3	9.7%
Italy	580.9	20.9%	402.5	13.7%
Israel	6.2	0.2%	15.3	0.5%
Malta	-	-	0.1	0.0%
Morocco	85.0	3.1%	121.7	4.1%
Portugal	45	1.6%	76.7	2.6%
Spain	1099.3	39.5%	1275.1	43.3%
Tunisia	165.0	5.9%	178.7	6.1%
Turchia	128.5	4.6%	164.0	5.6%
		89.5 %		86.3%

Tab. 1: Last 31 years data of olive oil production for the Countries situated in the Mediterranean basin and percent of world production. World olive oil production 1990-2010: 2784.8 tons. World olive oil production 2010-2016: 2944.5 tons. Data from International Olive Council (www.internationaloliveoil.org)

The production of olive oil generates a high quantity of olive mill waste water (OMWW). This waste is a serious environmental problem because, although in all countries that

produce olive oil the direct discharge of OMWW into receiving natural water bodies and public sewers is strictly forbidden, the most common practice followed from the olive mills was direct disposal of OMWW into nearby aquatic bodies, i.e. rivers, lakes, or even the sea.¹ This practice is today illegal.

The pollution produced from OMWW is a direct consequence of the chemical composition of this waste. OMWW are characterized by a high concentration of organic material with a COD value of 220 g/L and a ratio COD/BOD₅ value between 2.5 and 5 that suggest the polluting nature of this solution. The corrosive action is due to the pH solution value between 3.9 and 5.9 and the high phosphorous and phenolic concentrations generate detrimental effects on ecological balance.

Chemical and biological procedures can treat OMWW destroying the contaminant agents in the solution but they involve high operating costs and sophisticated technologies requiring qualified personnel.

An approach to the study of OMWW was carried out by changing the consideration of OMWW from waste to resource. In this area, the use of a technology based on membrane process could be the keystone to solve the problem OMWW. Membrane process is able to treat OMWW separating contaminant agent from the water, obtaining organic and inorganic materials and pure water. Organic and inorganic materials could be employed to improve olive oil quality, biogas production and compost while purified water could be used in the production of olive oil.

1.2 Olive oil production processes

Olive oil production is a step process that can be performed in two different ways, three-phase and two-phase. These processes generate similar quantity of olive oil, but different quantity and composition of waste. The steps of these processes are reported in Fig. 1. Centrifugation is the crucial step in that it is possible to see the different performance of the three-phase and two-phase processes. In the three-phase process hot water is used for oil extraction and after the oil washing step 1-1.6 m³ of OMWW are produced for each 1000 kg of olives milled. In the two-phase process the centrifugation step isn't supported by hot water and a small quantity of wastewater is produced after the oil washing step.

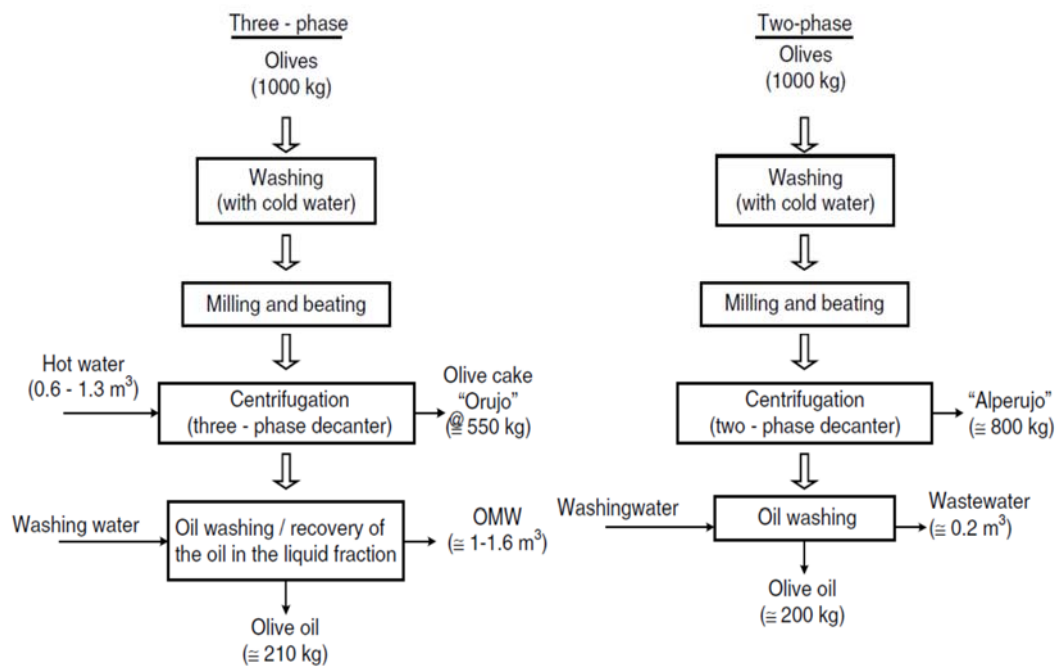


Fig. 1: Three-phase and two-phase olive oil production process

The two-phase extraction system was developed during the 1990s to minimize the volume of the waste produced and is widely adopted in Spain, where approximately 90% of the country's olive mills use this technology. The philosophy is the same as at the three-phase centrifugation system. The difference is that it uses no process water and delivers only two streams: olive oil and a single waste, a combination of olive husk and OMWW, i.e., a very wet olive cake, which is called "alpeorujo." This modified extraction system is less complicated, consumes less energy, and yields higher-quality olive oil than the three-phase decanter. Nevertheless, although it is called "the ecological system," because it reduces wastewater generation up to 80%, the problem remains unsolved, since a new, not yet fully characterized waste is produced with new difficulties in its treatment and disposal.

1.3 Chemical composition

The concentration of the environmental contaminant agents of the OMWW is variable.

Many factors influence this concentration:

- Olives quality
- Soil
- Collection period
- Climate conditions
- Production method used
- Pesticides
- Fertilizers

All these factors have a great interaction on OMWW composition; organic constituents, for example, are phenolic compound, sugars and some organic acid and sugars vary from 1.6-4% w/v depending on the variety of olives, the climatic conditions and the production method used. The high number of parameters that influence the composition of the OMWW combined with the complexity of the matrix, makes the OMWW a wastewater difficult to define, for this reason, the chemical characteristics have very wide ranges. In Tab. 2 the chemical characteristics of the OMWW in their ranges are summarized:

Chemical Characteristic	Range Values
pH	3 – 5.9
COD	100 – 220 g/L
BOD	40 – 100 g/L
Polyphenols	0.5 – 3.6 g/L
Sugars	1.6 – 4.7 g/L
Pectin	0.3 – 1.5 g/L
% (w/w) dry residue	2.3 % - 24%

Tab. 2: OMWW chemical characteristics

1.4 Environmental legislation

As mentioned in the introduction the most common practice followed by all producing Countries olive oil for the disposal of the OMWW is the direct disposal in the natural water bodies. This practice is strictly forbidden due to the detrimental effect on ecological balance of the OMWW. There is no single guideline for safety disposal of OMWW and every producing country follows its own course of action. The three Countries in the world's largest producers of olive oil have in fact three different laws;

Spain promoted the construction of storage ponds to promote evaporation during the summer period. This is a good practice to improve the water quality, but caused odor problems for the inhabitants of the region.

Italy legislation imposes OMWW treatment before their release into the environmental, but at same time, taking in account the potential fertilizing value of OMWW, spreading on land is permitted under controlled conditions.

In Greece, small olive mills serving local communities are extensively widespread. Extensive research is underway in research organizations and universities in order to safely dispose of the produced wastewater within a maximum period of 3 months after the campaign.

1.5 Membrane processes for safety disposal of OMWW

Predominately used treatments applied for the safe disposal of OMWW destroy the potential value of this wastewater. The OMWW possess a high concentration of polyphenols, which have antioxidant and antimicrobial properties. The development of a method capable of recovering these compounds and obtains clean water, which can be reused during production processes, would add value to the entire production cycle of olive oil. An economic and green process for the safe disposal of OMWW could be represented by the use of membrane separation processes. A single separation step is ineffective to separate the organic part of interest and obtain clean water. The most effective system to obtain these results is represented by a membrane integrated system, in which various membranes of different pore size are used in a step by step

process. In literature there are many examples of membrane integrated systems for the disposal of the vegetation water and the recovery of polyphenols, but the common problem to the application of these systems is represented by the fouling of the membranes that decreases over time drastically the OMWW flow treated. The application of a pretreatment method of the OMWW before sending the wastewater to the integrated membrane system could ensure the best performance of the membrane process.

Membrane Fouling

2

2.1 Introduction

Membrane separations become one of the most promising technologies over the past 70 years. The development of this technology began in the mid-twentieth century using reverse osmosis (RO) membranes for desalination purposes and later it became one advanced wastewater treatment technology.

A membrane process provides lower pollutant levels in purifying and/or concentrating waters and wastewaters from pharmaceutical and chemical products, respect to the conventional wastewater treatment, due to their inherent advantages such as selective separation, continuous and automatic operation, easy and well-arranged process conduction, purification without the addition of chemicals, easy scale-up and low space requirement [1]. Especially, microfiltration (MF) and ultrafiltration (UF) membrane applications are receiving increased attention, associated with water quality and cost reduction by improvements in membrane technology [2].

However, as various factors govern the operating cost of a membrane system, such as power requirements, costs of power, labor, materials, membrane cleaning, scale inhibition and membrane life and replacement, some limitations remain in using membranes for water and wastewater treatment [3].

Membrane processes can be performed in either constant permeate flux (flow rate per unit membrane area, L/m²h) with variable transmembrane pressure (TMP) or at constant TMP with variable permeate flux. However the former mode is the common one, hereupon membranes for water treatment and reuse can be divided into low pressure membranes (LPMs) and high pressure membranes (HPMs). LPMs include microfiltration (MF) and loose ultrafiltration (UF) membranes, which are operated at relatively low TMPs, typically less than 100–200 kPa. On the other hand, HPMs such as tight UF (>200 kPa), nanofiltration (NF, ≤10.000 kPa) and reverse osmosis (RO, ≤20.000 kPa) membranes are operated at much higher TMPs.

Membrane fouling represents the limiting factor of this technology, because it causes a rapid decline of permeate flux over time, membrane lifetime and increase the power requirements of the processes. For this reason membrane efficiency and membrane fouling present the significant challenges for membrane and related technologies [4].

In this chapter the different types of fouling plaguing membrane processes and the mechanisms of fouling occurring during the separation processes will be discussed.

2.2 Foulants and fouling mechanisms

Membrane fouling results as a decreasing of membrane process performances. It can cause severe flux decline and affect the quality of the water produced. Depending on the fluids filtered, various foulants can interact with the membrane surface: biological (bacteria, fungi, viruses, biomolecules), colloidal (clays, flocs), organic (oils, humic acids), scaling (mineral precipitates).

In the past three or four decades, substantial experimental effort has been made to investigate the effects of various parameters on flux decline or TMP increase and the mechanisms of membrane fouling. Membrane fouling can increase the TMP of the process when the system works at constant permeate flux or to decrease the permeate flux when the system works at constant TMP.

A typical flux decline for MF and UF membrane processes is a result of the increase of the membrane resistance and the development of another resistance layer, which can be elucidated in terms of pore size reduction, pore blockage and cake layer formation that can be considered as two mechanisms for membrane fouling.

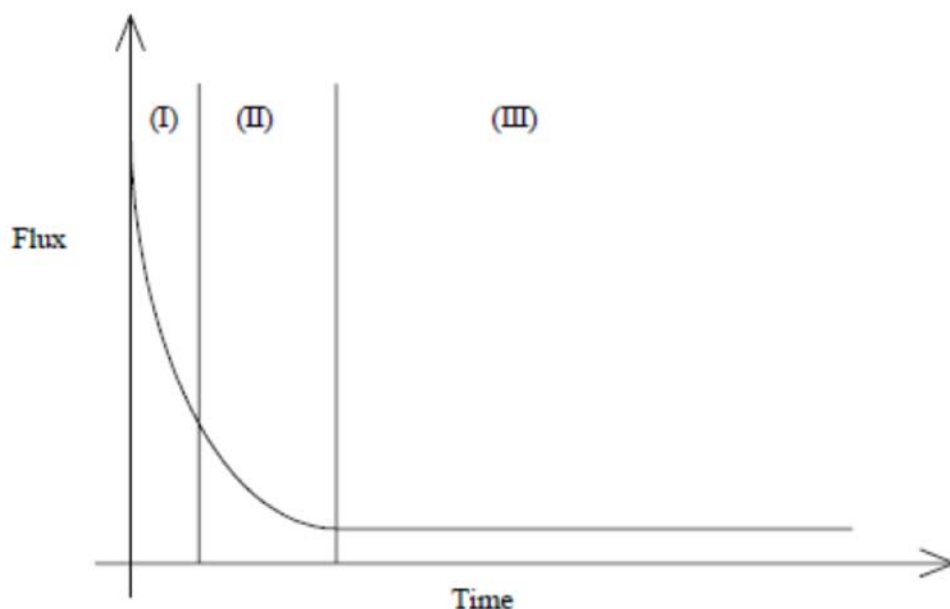


Fig. 2.1: The three stages flux decline [5]

The rapid permeate flux decline (I) can be attributed to membrane pores blocking. In the first stage the high flux value is obtained thanks to opened and clean membrane pores, then the retained particles start to block the membrane pores. The degree of pore blockage depends on the shape and the relative size of particles and pores and generally more complete blockage is due to the similar shape and size of pores and particles [6-8].

In addition, the system resistance changes significantly during the course of filtration, as the pores of the membrane become fouled with impurities, which are carried by the flow. Filter performance thus ultimately deteriorates, via a combination of mechanisms (alluded to above). (i) Particles larger than the pores cannot pass through the membrane. Assuming that such particles follow streamlines (advection-dominated flow with large-particle Péclet number), they will be deposited on top of pores, blocking them. (ii) Particles smaller than the membrane-pore size are deposited (or adsorbed) within the pores, shrinking the pore diameter and increasing membrane resistance. (iii) Once pores are blocked, other particles can form a cake on top of the membrane, adding additional resistance via another porous layer on top [9]. Mathematical models for all three fouling mechanisms have been proposed, based mostly on empirical laws of how membrane resistance relates to total volume of filtrate processed, or net flow rate through the membrane, in the different fouling regimes.[10-15]

Pore blocking is a quick process compared with cake formation since less than one layer of particles is sufficient to achieve the full blocking [7]. Furthermore, flux decline after pore blockage is due to the formation and growth of a cake layer on the membrane surface. The cake layer is formed on the membrane surface as the amount of retained particles increases. The cake layer creates an additional resistance to the permeate flow and the resistance of the cake layer increases with the growth of cake layer thickness. Consequently, the permeate flux continues decreasing with time.

Cake layer resistance (R_c) can be defined by using the cake filtration model:

$$R_c = \hat{R}_c \cdot m_d \quad (2.1)$$

where \hat{R}_c (m/kg) and m_d (kg/m²) are the specific cake resistance of the cake layer on the membrane surface and the mass of deposit per unit surface area of membrane respectively.

By using the Darcy's law and a resistance-in-series-model can be defined the permeate flux:

$$J = \frac{\Delta P}{\mu(R_m + R_c)} \quad (2.2)$$

Where ΔP (Pa) is the transmembrane pressure, μ (Pa·s) is the solution viscosity, R_m (1/m) is the hydrodynamic resistance of clean membrane. This model is able to indicate the proportionality between the increase in hydrodynamic resistance and the mass of deposit on the membrane, but it does not explain the mechanism of fouling. \hat{R}_c value is influenced by different factors such as cell morphology, membrane surface properties, operating pressure and temperature and time.

Another mathematical model was developed by Kosvintsevet al. [17] to describe fouling by physical sieving of low pressure membranes by particles lager than membrane pore sizes. This model describes the permeate volume as a function of permeate time, dominated by pore blocking at constant pressure:

$$V = \frac{1}{\gamma\beta} \ln(1 + \beta t^*) \quad (2.3)$$

Where V (cm³) is the permeate volume, β is the ratio of membrane area fouled with particles to the area of clean pores, n is the number of particles per unit volume of the feed, γ is the ratio of the pore area to the total membrane area and t^* is the dimensionless filtration time:

$$t^* = \gamma \int_0^t \frac{dV}{dt} \quad (2.4)$$

In the strategy of low pressure membranes, Zydney et al. developed a combined mathematical method for pore blocking and cake layer formation to describe the fouling produced by humic acids and proteins [18, 19]. According to this model, the fouling is due at first stage by large particles, proteins aggregates and humic acids. The ratio between the flux (J) during the filtration process and the flux of the clean membranes J_0 (m^3/s) is obtained at constant pressure and varying flux:

$$\frac{J}{J_0} = \exp\left(-\frac{K_b \Delta P C_b t}{\mu R_m}\right) + \frac{R_m}{R_m + R_c} \left[1 - \exp\left(-\frac{K_b \Delta P C_b t}{\mu R_m}\right)\right] \quad (2.5)$$

where K_b (m^2/kg), a pore blockage parameter, is equal to the blocked membrane area per unit mass of aggregates convected to the membrane. This parameter can be measured experimentally. C_b (kg/m^3) is the bulk concentration of large aggregates, R_m ($1/\text{m}$) is the clean membrane resistance, R_c ($1/\text{m}$) is cake layer resistance, μ ($\text{Pa}\cdot\text{s}$) is the solution viscosity and ΔP is the transmembrane pressure (Pa). Both resistances can be measured experimentally. The right-hand side of the equation has two terms that are related to pore blocking and cake formation, respectively. The first term (pore blocking) dominates the early stage of fouling, and the second term (cake filtration) governs fouling at longer times. The impact of solution chemistry on membrane fouling is, however, not included in the model, but was rather considered as a prerequisite for the aggregation of proteins or humic acids.

For particles, smaller than membrane pores sizes adsorptive fouling can be expressed by a modified form of Hagen-Poiseulle capillary filtration model [20]:

$$\frac{J}{J_0} = \left(1 - \frac{\delta'}{r_p}\right)^4 \quad (2.6)$$

where J and J_0 are the permeate flux after the formation of the adsorptive fouling layer and the initial flux, respectively, under a given transmembrane pressure, δ' (m) is the thickness of the adsorption layer that can be measured experimentally and r_p (m) is the membrane pore radius.

The major obstacle is defining theoretically or experimentally the δ' parameter, due to the heterogeneity of membrane surface properties and the complex nature of aquatic NOM (natural organic material).

2.3 Interaction between foulants and membrane

The interaction between foulants and membrane can be attributed at two forces: dispersion interaction and polar interaction.

The dispersion interaction is due to the Van der Waals attractive forces between molecules across water and it is balanced by the electrostatic repulsion between particles and the membrane surface, due to the presence of surface charges.

In order to reduce the attachment of particles on membrane surface, an increase of charge density can be performed. As shown in Fig. 2.2 the height of the energy barrier depends not only on how strong the attractive force is, but also on the magnitude of the repulsive electrostatic interaction.

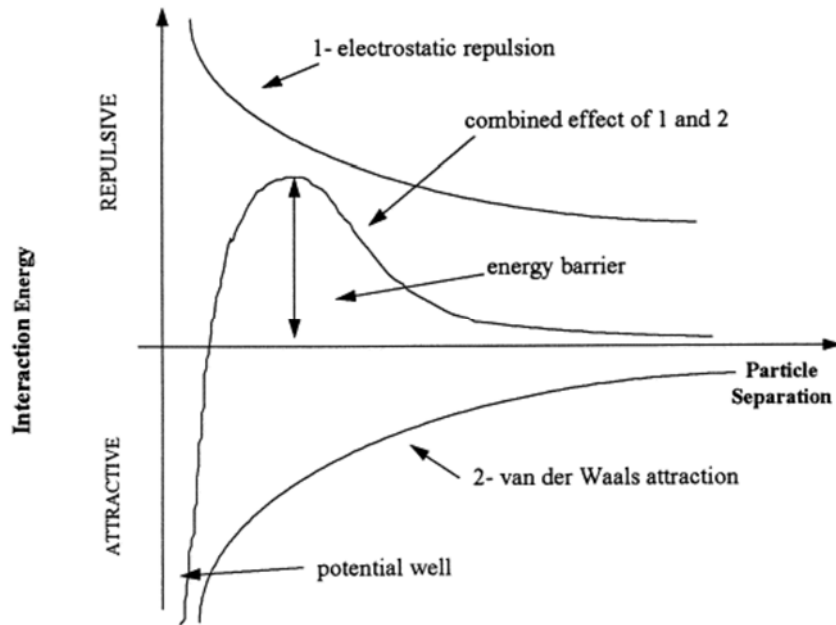


Fig. 2.2: Energy curve of interaction forces [20]

The Hamaker constant can be used to represent the dispersion interaction. This constant is used for macroscopic bodies and represent the strength of van der Waals interaction between two bodies in a medium. A schematic representation of this interaction is shown in Fig. 3:

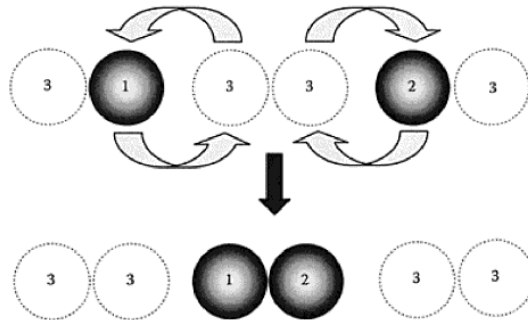


Fig. 2.3: interaction between two macroscopic bodies (1 and 2) in a medium (3) [20].

The Hamaker constant can be calculated using the Lifshitz theory, a simplification of van der Waals theory adapted for macroscopic bodies, that uses the dielectric constants (ϵ) and the refractive indices (n) of the bodies:

$$A \approx \frac{3}{4} KT \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \cdot \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \cdot \frac{3h\nu_e}{8\sqrt{2}} \cdot \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2} [(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2}]} \quad (2.7)$$

The subscripts “1” and “2” denote the two interacting bodies in the medium “3”, A is the Hamaker constant, ν_e is the medium absorption frequency, ε is the dielectric constant that indicates the extent to which a material concentrates electric flux, n is the refractive index, K is the Boltzmann constant, h is the Planck constant and T the absolute temperature [21].

The dispersion interaction is used to define apolar interaction between two particles in an aqueous medium. On the other hand, the polar interaction is strictly connected to the Lewis acid-base theory. These two interactions explain the advantage of hydrophilizing membrane surface to decrease the irreversible fouling attachment to the membrane surface of fouling materials. The strength of the fouling attachment depends on the hydrophilicity of the two interacting surfaces. For example, for two hydrophilic surfaces the polar interaction is repulsive and counteracts the dispersion interaction or apolar interaction. For hydrophobic surfaces, which are additive to the attractive dispersion interactions, the polar interactions would be fairly attractive. Consequently, electrostatic repulsion becomes the dominant factor in balancing the attractive and repulsive interaction which enhances fouling. Therefore, there are in principle at least two possible approaches to make the membrane less vulnerable to the attachment of aquatic contaminants: hydrophilization of membrane surfaces (to enhance thermodynamic stability) and ionization of membrane surfaces (to achieve kinetic stability).

All these models assume that the membrane surface has homogeneous properties. This is not realistic because particles and membrane surface have heterogeneous properties. This means that different parts of the surface have different affinities to the membrane. This heterogeneity can be attributed to different physical and/or chemical origins. For instance, the attachment of particles to membrane pores of various shapes was investigated. It was found that membrane pores with round corners are the least

affinitive to colloidal fouling compared to those with sharp and spiky corners due to enhanced electrostatic repulsion [22]. In another investigation, the surface heterogeneity of nanofiltration and reverse osmosis membranes was studied using chemical force microscopy, a modified technique based on atomic force microscopy (AFM) to obtain the lateral distribution of surface energies/stickiness. It was found that the surfaces of the two membranes used were chemically heterogeneous, and that the heterogeneity became more significant below micron-sized dimensions [23]. This implies that the stickiness of membrane surfaces to foulants can be heterogeneous, rather than uniformly homogenous as considered previously.

2.4 Factors affecting fouling

Membrane properties, solution properties and operation conditions are the most important factors that affecting fouling.

2.4.1 Membrane properties

Membrane properties that affecting fouling are:

- Membrane material
- Hydrophobicity
- Pore size
- Pore size distribution
- Morphology

The wettability of a membrane is its attitude to perform attractive or repulsive interaction with water. This attitude is direct connected to the membrane material and surface roughness. The presence of active groups that have the ability to form hydrogen-bonds with water is the principal characteristic of a hydrophilic membrane. For this reason, hydrophilic membranes possess high wettability and hydrophobic membranes possess low wettability due to the lack of active groups in their surface for the formation of hydrogen-bond with water. The wettability of the membrane can be determined by measuring the contact angle between the membrane surface and a droplet of liquid. In

Fig. 4 is reported the difference in wettability for hydrophobic and hydrophilic membrane:



Fig. 4: Wettability for a hydrophobic membrane (a). Wettability for a hydrophilic membrane (b). [23]

Hydrophobic membranes have the opposite interaction to water compared to hydrophilic membranes as they have little or no tendency to adsorb water and water tends to bead on their surfaces. Particles, which foul membranes in aqueous media, tend to be hydrophobic. They tend to cluster or group together to form colloidal particles because this process lowers the interfacial free energy. Usually, greater charge density on a membrane surface is associated with greater membrane hydrophilicity. Polysulfone, cellulose acetate, ceramic and thin-film composite membranes used for water treatment and wastewater recovery typically carry some degree of negative surface charge and hydrophilic. Thus, fouling can be reduced with use of membranes with surface chemistry which have been modified to render them hydrophilic.

2.4.2 Solution properties

Solution properties that affecting fouling are:

- Solid concentration
- Particles size
- Nature of component
- pH
- Ionic strength

Generally, an increase in the feed concentration is an increase in membrane fouling by the presence of higher foulant concentration and particles can be present in the feed

because of the nature of the feed or through precipitation of soluble feed components. These particles can affect membrane by pore blocking, pore narrowing or cake formation, depending of particle size. Large particles, respect membrane pore size, maintain the process with higher permeate flux and cake thicknesses [24]. Some other factors, such as: pH, ionic strength, and electric charges of particles, are also important. The pH and ionic strength of the feed affect the charge on the membrane, the charge on the particles, conformation and stability of, and thereby adhesiveness of particles/molecules and the size of the cake. For example, a study of the impact of pH of the latex emulsion on membrane fouling showed that the latex emulsion pH should be high enough to prevent the coagulation of latex particles, and hence, to increase the antifouling properties of the latex emulsion. Also, it has been showed that a reduction in pH could decrease the molecular size of NOM and thus enhances adsorption onto membrane, resulting in a significant fouling.

2.4.3 Operating conditions

Salahi et al. investigated the effect of temperature on permeate flux and found that an increase of feed temperature was an increase of permeate flux. Changing the feed temperature from 20 °C to 40 °C lead to an increase in the permeate flux up to 60% and a change in the permeate diffusion rate through the membrane occurs [25].

Another important operating condition is definite by cross flow velocity. The effect of cross flow velocity on permeate flux was studied for many different feed solutions. An increase on cross flow velocity affect the mass transfer coefficient of the solute and the extent of mixing near the membrane surface [26]. The result is an increase in permeate flux supported by a reduction of aggregation of the feed solids in the gel layer, essentially due to increasing diffusion of these components back towards the bulk, leading to an overall reduction in the effect of concentration polarization.

The last operating condition affecting fouling is the TMP. The TMP is the pressure difference between the feed and the permeate stream. An high TMP forces the fluid flowing towards the membrane and an higher permeate flux is obtained, but the higher

flux causes increased concentration polarization of the retained material at the membrane surface [27].

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Low pressure membranes for the treatment of OMWW: fouling evaluation

3

Abstract

A knowledge of fouling mechanism is needed to provide a basis for a suitable selection of design and operation of a membrane process. In this chapter, the fouling behavior on different flat sheet membranes for low-pressure membrane operation was evaluated calculating the flux reduction (FR) of the membranes, before and after the fouling tests. PVDF, PS, PSH and RC membranes were tested in static conditions using Olive Mill Wastewater (OMWW) as feed. Parameters such as membrane material, pore size, solid concentration, particle size, pH, temperature flow rate and pressure were investigated in order to identify membrane fouling behavior. Untreated water and pretreated water were used as feeds for fouling evaluation. The pretreated water was obtained through an acid treatment in order to promote a rapid flocculation of particles in solution. Experiments carried out in static conditions suggested that OMWW fouling by both pretreated and untreated raw waste water exhibited similar effect on the membrane surface. The strong adhesion of organic molecules on membrane surface develops a pore blocking resistance that decrease the clean water flux significantly.

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3.1 Introduction

Led by Spain Italy, Greece and Turkey, the Mediterranean Basin is the most important region where 85%

of the world olive oil being produced. This production generates significant amount of highly

polluted Olive Mill Wastewater (OMWW). For every litre of oil produced, 2.5 L of wastewater is

released resulting in approximately 10 million m³ of OMWW per year. This represents a serious environmental problem due to its high organic loading, acidic pH and the presence of recalcitrant and toxic substances such as phenolic and lipidic compounds.

Disposal on soil is the most commonly practiced way to discharge OMWW. Direct disposal of OMWW to aquatic bodies results in environmental deterioration

due to the large amount of organic loadings. In order to prevent further degradation of the environment,

so far various biological and physico-chemical treatment methods have been practiced.

However, the presence of antibacterial phenolic compounds limited effectiveness of either aerobic or anaerobic biological treatment focused on destruction of the wastewaters toxicity. Though phytotoxic with strong

antibacterial activities, the phenolic compounds have important biological activity that can be employed in pharmaceutical industry. Therefore, a more pragmatic solution towards this problem is, instead of focusing on destructing the phytotoxic compounds, could be to look for alternative valorizing mechanism.

OMWWs have therefore converted the traditional “money-wasting” process of pollution control to a profitable operation through recycling the waste effluent. One possible “green” approach to the problem is represented by membrane technologies. Membrane processes can be applied to the treatment of OMWWs for water reuse and for the recovery of substances of pharmaceutical interest such as polyphenols.

Membrane systems are receiving increased attention for water treatment and other applications. However, a major obstacle to further incorporation of membrane processes in industrial operations is flux decline resulting from fouling. Membrane

replacement due to fouling is the single largest operating cost when membranes are used in water treatment applications. Generally, two distinct types of fouling phenomena are considered: (1) macrosolute adsorption, which refers to the specific intermolecular interactions between the macrosolute and the membrane that occur even in the absence of filtration and (2) filtration-induced macrosolute or particle deposition, which is over and above that observed in a static (nonflowing) system [1].

The aim of the work here reported is the study of micro- and ultra-filtration membranes in a submerged configuration combined in an integrated system for the treatment of water and recovery of high valuable components from agro-food streams. Olive mill wastewaters (OMWW) were used as model streams. Many works about treatment of OMWW with external membrane module configuration plants are reported in literature. As mentioned above, the interest arises from the fact that the olive oil production generates huge amount of waters containing phenolic compounds. These are phytotoxic and regulations prohibits the discharge of water containing more than 1 mg/l of phenolic compounds in the environment. On the other hand, polyphenols are natural compounds with strong antibacterial and antioxidant activities. Therefore, their recovery is regarded as an added value of olive oil industry.

The use of submerged membranes is investigated as an alternative strategy to process fresh waters coming from the olive oil production. The submerged configuration may prevent severe fouling due to cake formation of retained suspended solids contained into the waters.

A screening of different membrane materials is carried out in order to evaluate irreversible fouling. The membranes exhibited different morphological surface properties in terms of pore size, porosity and roughness. Membrane autopsy and analyses of adsorbed components permitted to identify fouling mechanism and possible strategies for membrane functionalization to obtain antifouling surface properties.

In order to study the membrane fouling mechanism due to the OMWWs the following parameters were investigated:

- Membrane properties: pore size, wettability, pore size distribution, roughness and membrane material.
- Solution properties: solid (particle) concentration, particle size and nature of components.
- Operating conditions: pH, temperature, flow rate and pressure.

As introduced in chapter 2, in an aqueous environment a membrane can be attractive or repulsive to water. The composition of the membrane and its corresponding surface chemistry determine its interaction with water, thus affecting its wettability. The wettability of the membrane can be determined by measuring the contact angle between the membrane surface and a droplet of liquid. Hydrophilic membranes are characterized by the presence of active groups that have the ability to form hydrogen-bonds with water and so these membranes are water wettable. Hydrophobic membranes have the opposite interaction to water compared to hydrophilic membranes as they have little or no tendency to adsorb water and water tends to bead on their surfaces (i.e. discrete droplets). This tends to enhance fouling. Hydrophobic membranes possess low water wettability due to the lack of active groups in their surface for the formation of hydrogen-bonds with water. Particles, which foul membranes in aqueous media, tend to be hydrophobic. They tend to cluster or group together to form colloidal particles because this process lowers the interfacial free energy. Usually, greater charge density on a membrane surface is associated with greater membrane hydrophilicity. Polysulfone, cellulose acetate, ceramic and thin-film composite membranes used for water treatment and wastewater recovery typically carry some degree of negative surface charge and hydrophilic.

Thus, fouling can be reduced with use of membranes with surface chemistry which have been modified to render them hydrophilic.

Membrane morphology also has a considerable effect on fouling depending on pore size, pore size distribution and pore geometry especially at the surface of the membrane. These determines the predominant fouling mechanisms such as pore blocking and cake formation. The properties of the feed solution also significantly

influence membrane fouling [2]. Some of the important feed properties are solid and soluble particle concentration, particle properties, pH and ionic strength. Generally, an increase in the feed concentration results in a decline in the permeate flux. This is due to the increase in membrane fouling by the presence of a higher foulant concentration. Particles may be present in the feed because of the nature of the feed or through precipitation of soluble feed component(s). The particles can cause fouling by pore blocking, pore narrowing or cake formation, dependent on the particle sizes. Higher permeate fluxes and cake thicknesses are usually obtained with larger particles. Large particle size is one of the factors that inhibit deposition. In a filtration process, the particle sizes in the feed often cover a wide range. The presence of fine as well as coarse particles results in a lower cake porosity as the fine particles can slide between the large ones, filling the interstices. The range of the particle size distribution plays a major role in the selective deposition at high crossflow. In addition to the particle size, the particle shape affects the porosity of the cake formed on the membrane surface. In general, the lower the particle sphericity, the greater is the porosity. Some other factors, such as: pH, ionic strength, and electric charges of particles, are also important [3]. The pH and ionic strength of the feed affect the charge on the membrane, the charge on the particles, conformation and stability of, and thereby adhesiveness of particles/molecules and the size of the cake. For example, a study of the impact of pH of the latex emulsion on membrane fouling showed that the latex emulsion pH should be high enough to prevent the coagulation of latex particles, and hence, to increase the antifouling properties of the latex emulsion [4]. Also, it has been showed that a reduction in pH could decrease the molecular size of natural organic material (NOM) and thus enhance adsorption onto membrane, resulting in a significant fouling.

The effect of temperature on the permeate flux was investigated and found that at higher temperatures, the permeate flux increased, indicating an effect on lowering the degree of fouling. Changing the feed temperature from 20 °C to 40 °C leads to an increase in the permeate flux up to 60%. This might be due to the fact that changes in the feed water temperature resulted in changes in the permeate diffusion rate through the membrane.

The cross-flow velocity is defined as the superficial velocity of the feed stream travelling parallel to the membrane surface. The effect of the cross-flow velocity on permeate flux has been studied for a wide variety of feed solutions. It is believed that increasing the cross-flow velocity positively affects the mass transfer coefficient of the solute and the extent of mixing near the membrane surface. Consequently, the permeate flux is increased with cross-flow velocity. Higher mixing experienced with larger cross-flow velocity leads to a reduction of aggregation of the feed solids in the gel layer, essentially due to increasing diffusion of these components back towards the bulk, leading to an overall reduction in the effect of concentration polarization.

The control of the transmembrane pressure (TMP) which is the pressure difference between the feed and permeate stream is essential as it greatly affects the permeation rate. At a higher TMP, the force of the fluid flowing towards the membrane is increased, leading to a higher permeate flux. At very low pressure p_1 , the flux is close to clean water flux at the same pressure. As the applied pressure is increased to pressure p_2 , the higher flux causes increased concentration polarization of the retained material at the membrane surface increases. If the pressure is increased further to p_3 which is considered the critical pressure, concentration polarization becomes enough for the retained solutes at the membrane surface to reach the gel concentration, c_{gel} . Once a gel layer has formed, further increase in the applied pressure does not lead to further increase in the permeate flux above this critical value. The gel layer thickness and the density of the retained material at the membrane surface layer, however, increase. This limits the permeate flux through the membrane, and hence, the flux reaches a steady state level (when a balance between accumulation and removal of particles is reached) or it continues to decrease (if particles accumulation rate is larger than their removal rate). It was reported that no fouling was experimentally observed when the process was operated below this critical flux [5].

3.2. Experimental section

3.2.1 Materials

Membranes used in this study are commercial flat sheet membranes made by polyvinylidene fluoride (PVDF), polysulfone (PS), hydrophilized polysulfone (PSH) and regenerated cellulose (RC). PVDF and PS membranes were kindly supplied by Alfa Laval (Soborg, Denmark), PSH and RC flat sheet membranes were purchased from Micro Nadir and Millipore, respectively. The characteristics of the membranes are summarized in Tab. 3.1

Material	Pore Size (nm)	MWCO (kDa)	Manufacturer	Support	pH Range	Structure
PVDF	500		Alfa Laval	Polypropylene (PP)	1-11	Composite Asymmetric
PVDF	200		Alfa Laval	Polypropylene (PP)	1-11	Composite Asymmetric
PS	200		Alfa Laval	Polypropylene (PP)	1-11	Composite Asymmetric
PS	100		Alfa Laval	Polypropylene (PP)	1-11	Composite Asymmetric
PS		100	Alfa Laval	-	1-11	Integrally Asymmetric
PSH		100	Micro Nadir	-	2-12	Integrally Asymmetric
RC		30	Millipore	-	3-12	Integrally Asymmetric

Tab. 3.1: Membranes characteristics.

Sulfuric acid and sodium hydroxide (Sigma Aldrich) were used to change the pH value of the raw water.

All reagents needed for quantitative analysis of polyphenols and pectines were purchased from Sigma Aldrich.

3.3 Feed solutions

The OMWW used in this study was a real feed obtained by a three-phase production processes and supplied by Olearea San Giorgio, Fratelli Fazari, snc, San Giorgio Morgeto (RC), Italy. The experiments were performed on many different feed solutions obtained after physical pretreatment or a combination of chemical and physical pretreatments. Starting point of this study was determining the flux reduction (FR) of the different membranes due to fouling caused by adsorption, i.e. by placing each membrane surface in direct contact with a physical pretreated feed (PPf), without applying any driving force that could favor the membrane filtration process. This physical pretreated feed was obtained by filtering the raw wastewater on a metal mesh of 35 μm . The pretreatment does not change significantly the characteristics of the OMWW, it was necessary for removing big pollutants that could damage some systems used during the experiments. In second stage the same tests were performed with a chemical pretreated feed (CPf) obtained adding sulfuric acid 96% to the OMWW to reach 1.6 pH. The chemical pretreatment allows the rapid coagulation and flocculation of the suspended solids by changing the electrokinetic potential of the dispersed particles. After the acid action the feed was filtered with the metal mesh of 35 μm obtaining a solution characterized by only dissolved solids.

In the last part of this study, the chemical pretreated feed was further treated by adding sodium hydroxide to achieve four different pH values between 2.6 and 6 (CPf_{pH}). All membranes were tested at these different feed solutions in order to study the influence of pH during the interaction fouling-membrane.

The characteristics of the all feeds were studied and discussed in the results section.

3.4 Methods

3.4.1 Total and dissolved solids analyses

All feeds used were characterized in terms of total and dissolved solids. Total solids analyses were performed using a thermo-balance (Ohaus S.r.l Milan, Italy) in order to measure the dry solids after water evaporation.

For the dissolved solids analyses the sample was filtered with a syringe filter of 0.45 μm and then analyzed at thermo balance. The filtration step was necessary to remove all the suspended solids.

3.4.2 Analyses of Polyphenols and Pectins amount

The total amount of polyphenols was determined by Folin-Ciocalteu colorimetric method. This method allows the quantification of polyphenols in solution using gallic acid like standard sample. The measurements were performed with a Spectro Lamba. Pectin concentration analyses were performed with another colorimetric test based on the acid galacturonic as standard, using the procedure previously reported. Briefly, a sample of OMWW (0.2 mL) was mixed with 1.2 mL of sulfuric acid. The obtained solution is refrigerated in crushed ice. The mixture was shaken in a vortex mixer and then heated in an oil bath at 100 °C for 5 min. After cooling in a water-ice bath, 20 μL of 0.15% solution of mhydroxydiphenyl in 0.5% NaOH was added. The final solution was shaken, and, within 5 min, the absorbance of a pink complex of galacturonic acid was read at 520 nm in a PerkinElmer spectrophotometer using water as a background. The galacturonic acid is formed from the hydrolysis reaction of pectins with sulfuric acid. A standard solution of galacturonic acid was used for the preparation of the calibration curve (0–1 g/100 mL water). The hydrolyzed OMWW were used to study the microfiltration performance in configuration b). The conversion of the hydrolysis reaction was calculated as the percent ratio of the amount of galaturonic acid produced after hydrolysis over the amount of pectins in the initial reaction mixture.

All chemical reagents and standard analysis were bought from Sigma Aldrich and used without further purification.

3.4.3 Flux Reduction Estimation

For fouling estimations, the initial experimental parameter to measure is the initial clean water flux (J_0) of the virgin membrane. According to the following equation J_0 is defined as:

$$\text{Eq. 3.1} \quad J_0 = \frac{\mu_T}{\mu_{20^\circ\text{C}}} \frac{Q}{A \cdot \Delta P} \text{ (L/m}^2\text{hPa)}$$

Where μ_T and $\mu_{20^\circ\text{C}}$ (Pa·s) are the viscosity of water at room temperature and at 20 °C respectively, Q (L/h) is the clean water flow rate at temperature T , A is the membrane surface area (m^2) and ΔP is the transmembrane pressure (Pa).

At the end of a membrane filtration process, the clean water flux (J_1) can be measured and the new value used for the determination of the flux reduction (FR) according to the Eq. 4.1:

$$\text{Eq. 3.2} \quad FR = \frac{J_0 - J_1}{J_0} \cdot 100 \text{ (\%)} \quad 4.2$$

FR is an important parameter needed for membrane characterization and membrane cleaning efficiencies and it is able to compare different membrane materials performances on the same feed.

Similar factor can be calculated in terms of clean water permeability reduction (CWPR), where permeability can be calculated from the following equation

$$J_0 = L_p \cdot \Delta P \quad 4.3$$

3.4.4 Membranes characterization

All membranes were characterized by measuring the clean water flux (J_{cw}) after membrane compaction corresponding to J_0 . The system used was a metallic housing (1, module) for circular flat sheet membranes, a peristaltic pump (Masterflex 77521-47 Cole-Parmer Instruments) (2), two manometers (Wika) (3 and 4) and a balance (5) connected to a computer (6). The computer permitted to continuously record the water mass variation during the time registered by the balance from which the permeate water flux was calculated (knowing the water density, recording time and membrane area). A scheme of this system is reported below Fig. 3.1

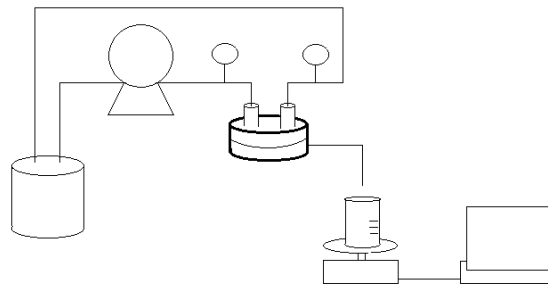


Fig. 3.1: Cross-flow system used for membrane characterization

After the contact with the feed and fouling, discussed in the next paragraph, membranes were washed only with distilled water (DI) and the clean water flux (J_f) was measured again. The flux values J_{cw} and J_f were used to calculate the flux reduction (FR) due to the fouling adhesion.

3.4.5 Systems to investigate fouling

In this study three different systems to investigate the fouling force adhesion were used:

1. A metallic housing for circular flat sheet membrane of 47 mm diameter (Fig 3.1);
2. A bell-shaped glass housing (Fig. 3.2);
3. A beaker glass in which the membranes were immersed in the OMWWs.

Metallic Housing system is the same used for membrane characterization reported in the Fig. 3.1. The different feed solutions were recirculated at very low flow rate into the metallic housing where the membrane was lodged. Feed recirculation was performed at very low flow rate in order to avoid any pressure on the membrane surface (set at 0 bar) while promoting suitable homogeneity of the solution. Tests were carried out for 4h and 8h. During this time every single test was monitored recording transmembrane pressure and temperature variations.

In the Bell-Shaped Glass system, a bell-shaped glass container tightly closable on top was used. On the border of this container there are two openings that make feed recirculation possible. The system can be placed in such a way that a) the membrane is vertically positioned (VP) or b) horizontally positioned (HP) respect to the feed with which it is in contact. In both cases, only the membrane surface was in contact with the OMWW. In the horizontal position, even the pressure due to the column of liquid was avoided, so that to verify that this hydrostatic pressure can be considered negligible for surface adsorption test. A draw of the bell-shaped glass is reported in Fig. 3.2.

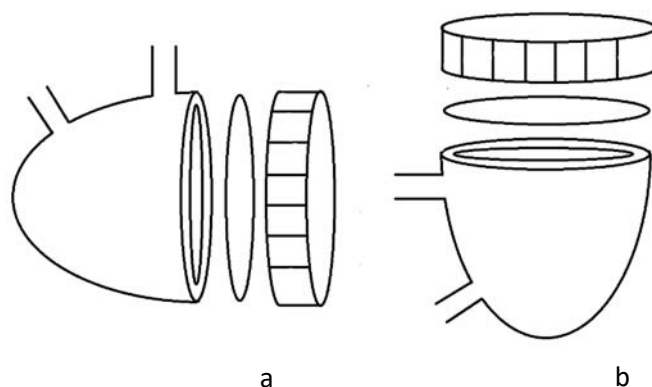


Fig. 3.2: Bell shaped glass systems: (a) membrane in vertical position, (b) membrane in horizontal position.

The other simple method was just to immerse membranes into the OMWW solution contained in a beaker. Here, both membrane surface and support are in contact with the OMWW.

3.4.6 Morphology

Atomic Force Microscopy (AFM), Nanoscope III A (Digital Instruments, VEECO Metrology Group) was used to observe surface morphology and to measure surface roughness both of new and used membranes. Tapping Mode™ AFM operated by scanning a tip attached to the end of an oscillating cantilever across the sample surface. The cantilever was oscillated at or near its resonance frequency with an amplitude ranging typically from 20 nm to 100 nm. Silicon probes were used. These probes can be much stiffer than the silicon nitride ones, resulting in larger force constants and resonance frequencies. Characteristics of the used silicon probes are: resonance frequency 200-400 kHz, Nominal Tip Radius of Curvature 5-10 nm, Cantilever Length 125 μm.

Surface roughness was estimated with respect to the mean absolute value difference, R_a , and the root mean squared difference, R_q , between the actual surface height and

that of the line dividing the surface of the investigated profile into two equal areas. R_a and R_q were calculated from Eq. 3.4 and 3.5, respectively.

Eq. 3.4
$$R_a = \frac{1}{n} \sum_{i=1}^n |y_i|$$

Eq. 3.5
$$R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2}$$

Each of the formulas assumes that the roughness profile has been filtered from the raw profile data and the mean line has been calculated. The roughness profile contains ordered, equally spaced points along the trace, and is the vertical distance from the mean line to the data point. Height is assumed to be positive in the up direction, away from the bulk material.

The reported roughness values are the average of 30 measurements on different membrane samples.

3.5 Results and discussion

Experiments to test the fouling promoted by adhesion of molecules present in OMWW, were carried out with raw OMWW, physical pretreated OMWW feed (PPf) and chemical pretreated OMWW feed (CPf). Here it is recalled that the physical pretreatment means that the OMWW were filtered through mesh of 35 μm , and chemical pretreatment means that the OMWW was acidified to pH 1.6 and then the pH was increased to various values by adding NaOH.

These used streams were characterized in terms of total suspended solids, total dissolved solids, polyphenols and pectines. Results illustrated in Table 3.2, show that the chemical pretreatment reduced the total suspended solids and pectines.

	Raw	PPf	CPf	CPf _{pH}			
				CPf _{2.6}	CPf _{3.6}	CPf _{4.6}	CPf ₆
Wastewater							
Total Solid (%)	14.6	13.8	7.9	7.8	7.8	7.7	7.9
Dissolved Solid (%)	7.8	8.0	7.6	7.7	7.6	7.6	7.8
Polyphenols (g/L)	4.5	4.3	3.7	3.9	3.6	3.7	3.5
Pectins (g/L)	6.3	5.9	4.2	4.3	4.2	4.4	4.2
pH	4,6	4,6	1,6	2,6	3,6	4,6	6

Tab. 3.2: Chemical characteristics of the various feeds used during the experiments

3.5.1 Fouling study using cross-flow cell and bell-shaped glass

Initially, pure water permeability of virgin compacted membranes was measured using a cross-flow system (dedicated exclusively to pure water). Afterwards, membranes were lodged in a metallic housing or in the bell-shaped glass systems containing wastewater. For both systems, contact between membrane and wastewater was monitored during 4 and 8 hours. At the end of each experiment membranes were washed only with clean water and pure water permeability was measured again. Results were also used to define the flux reduction parameter. For each experiment series a new membrane sample from the same membrane sheet type was used.

Results of flux as a function of TMP obtained using the membrane made of PVDF with pore size of 0.5 μm are reported in Fig. 3.4. The permeability values are reported in Table 3.3.

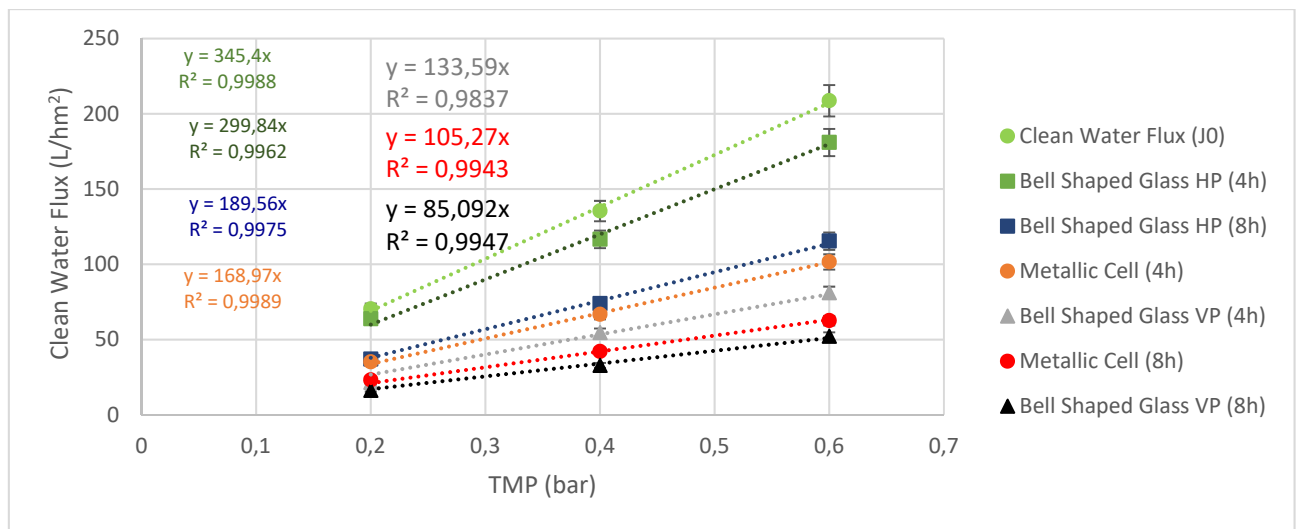


Fig. 3.4: Clean water flux vs transmembrane pressure (TMP) for PVDF 0.5 μm membrane tested in different systems and for different time.

Operating conditions/system	Pure water permeability (L/h·m ² ·bar)	R ²	CWPR (Lp ₀ - Lp _t)/Lp ₀ *100 (%)	
Virgin PVDF 0.5 μm	Lp ₀	345,40	0.99	-
PVDF 0.5 μm after contact with OMWW in bell-shaped glass (HP)	Lp _{t=4h}	299,84	0.99	13.19
PVDF 0.5 μm in contact with OMWW in bell-shaped glass (HP)	Lp _{t=8h}	189,56	0.99	45.12
PVDF 0.5 μm in contact with OMWW in bell-shaped glass (VP)	Lp _{t=4h}	133,59	0.98	61.32
PVDF 0.5 μm in contact with OMWW in bell-shaped glass (VP)	Lp _{t=8h}	85,09	0.99	75.36
PVDF 0.5 μm in contact with OMWW in metallic cross-flow cell	Lp _{t=4h}	168,97	0.99	51.08
PVDF 0.5 μm in contact with OMWW in metallic cross-flow cell	Lp _{t=8h}	105,27	0.99	69.52

Tab. 3.3: Pure water permeability values of PVDF 0.5 μm after being placed in contact with OMWW in various operating conditions.

From Fig. 3.4 it is possible to note that pure water permeability of PVDF is reduced meaning that adsorption of molecules present in the OMWW to this membrane material occurred. The severity of fouling depended on contact time and operation mode with various systems. The experiments carried out with the membrane in horizontal position (HP) in the glass bell system resulted in lowest permeability reduction, which most probably depended on the fact that no pressure was exerted on the membrane surface and penetration of adsorbing molecules in membrane pore was limited.

The same series of experiments were performed with the PS 0.2 μm membrane and the results are shown in Fig. 3.5. Permeability values are summarized in Table 3.4.

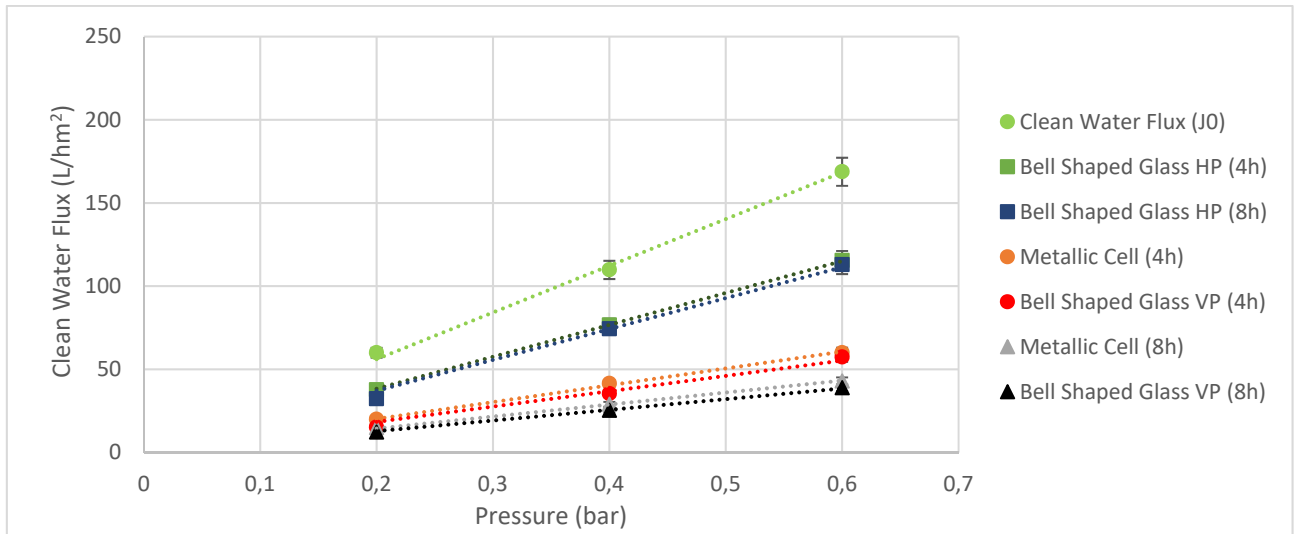


Fig. 3.5: Clean water flux vs transmembrane pressure for PVDF 0.2 μm membrane tested in different systems and for different time.

Operating conditions/system	Pure water permeability (L/h·m²·bar)	R²	CWPR (Lp₀-Lp_t)/Lp₀*100
Virgin PVDF 0.2 μm	Lp ₀ 280,64		-
PVDF 0.2 μm after contact with OMWW in bell-shaped glass (HP)	Lp _{t=4h} 191,81	0.99	31,65
PVDF 0.2 μm in contact with OMWW in bell-shaped glass (HP)	Lp _{t=8h} 185,64	0.99	33,85
PVDF 0.2 μm in contact with OMWW in bell-shaped glass (VP)	Lp _{t=4h} 92,17	0.98	67,16
PVDF 0.2 μm in contact with OMWW in bell-shaped glass (VP)	Lp _{t=8h} 64,21	0.99	77,12
PVDF 0.2 μm in contact with OMWW in metallic cross-flow cell	Lp _{t=4h} 101,10	0.99	63,98
PVDF 0.2 μm in contact with OMWW in metallic cross-flow cell	Lp _{t=8h} 72,14	0.99	74,29

Tab. 3.4: Clean water permeability reduction values of PVDF 0.2 μm after being placed in contact with OMWW in various operating conditions.

The results obtained with the PVDF 0.2 μm show the same trend of fouling exhibited by PVDF 0.5 μm but, no difference between fouling at 4 hours and 8 hours was found. A more pronounced decrease of the PVDF 0.2 μm membrane performance compared to the PVDF 0.5 μm membrane was obtained. This suggests a strong influence of relative foulant molecules and pore size.

3.5.2. Fouling study by immersing membranes in OMWW

3.5.2.1. Fouling behaviour using raw OMWW

All membranes used in this study were tested by simply immersing them in a beaker containing wastewater. Tests were performed using the real waste water without any chemical pretreatment. The feed used has undergone only a physical treatment by filtration on a 35 μm metal mesh so as to remove the coarser materials. Membranes were immersed in the OMWW after membrane characterization and flux reduction (Eq.1) as a function of time was monitored. Fig. 3.6 illustrates the flux reduction for the PVDF 0.5 μm membrane.

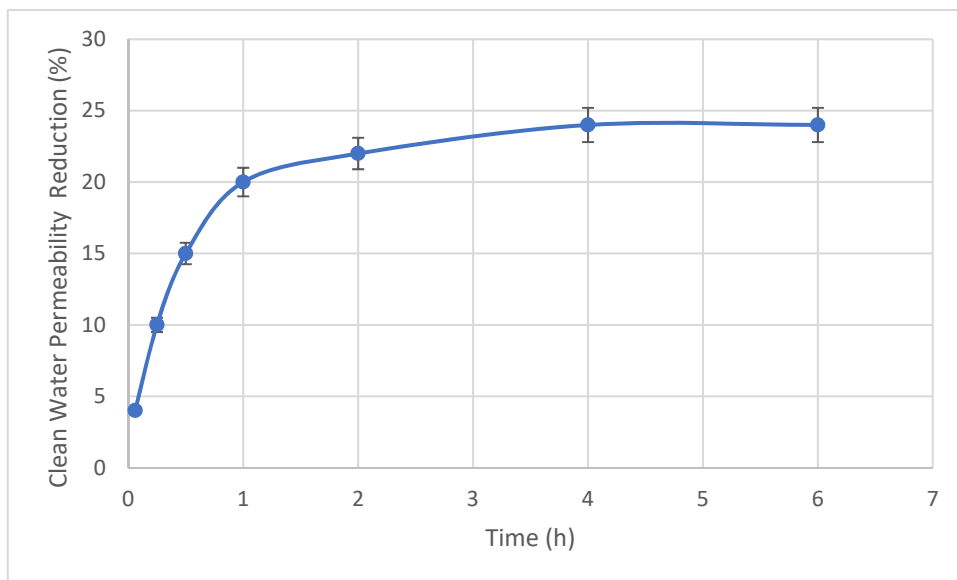


Fig. 3.6: Clean water permeability reduction as a function of time for PVDF 0.5 μm membrane tested by immersing them in OMWW contained in a beaker.

An increase of flux reduction was observed in the first hour then it slowly leveled up and after 4 hours it remained constant.

Fig. 3.7 reports the clean water permeability reduction behaviour for the PVDF 0.5 μm membrane observed as a function of time with the different systems. The study demonstrated that results of fouling due to surface adhesion can be highly affected by

the operation mode. The reason is in the fact that hydrostatic pressure can be exerted on the membrane surface that can cause penetration of molecules within the pores leading to different values of membrane fouling. Even very small pressure values cannot be neglected, especially when pore size in the microfiltration range are used. Both immersing the membrane in OMWW in a beaker and using the bell-shaped container with the membrane positioned in horizontal position (HP) are suitable to avoid interference of hydrostatic pressure.

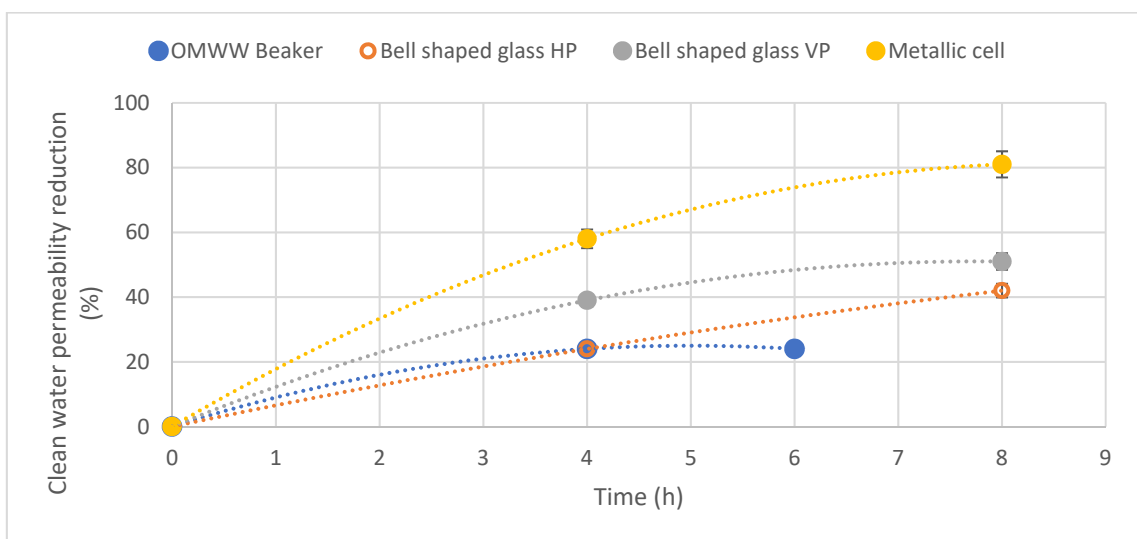


Fig. 3.7: Clean water permeability in time for PVDF 0.5 μm membrane tested in different systems.

For the type of membranes tested in this work, the easiest system to investigate fouling adhesion on membrane surface resulted the simple membrane immersion in OMWW. This system allows to investigate fouling interaction on membrane surface avoiding the filtration through the membrane pore causing other fouling phenomena. Using this system all the other membranes were tested and the results are summarized in the Tab. 3.5.

Membrane	Pore Size (μm)	MWCO (kDa)	CWPR (%)
PVDF	0.5 μm		22
PVDF	0.2 μm		31
PS	0.2 μm		27
PS	0.1 μm		35
PS		100 kDa	100
PSH		100 kDa	44
RC		30 kDa	0

Tab. 3.5: Clean water permeability reduction for various membranes immersed in OMWW.

Results reported in Tab. 3.5 suggest a hydrophobic behavior of the fouling generated by the OMWW, in fact regenerated cellulose, which is highly hydrophilic, showed no clean permeability reduction due to molecules adhesion. Furthermore, comparing the membranes made of polysulfone (PS) and hydrophilized polysulfone (PSH), which have the same molecular weight cut-off of 100 kDa, it is clearly evidenced that hydrophilic character reduced the fouling tendency. For the same membrane material, fouling is more pronounced decreasing the membrane pore size, as it can be seen for PVDF 0.5 and 0.2 μm as well as for PS 0.2, 0.1 μm and 100 kDa. Different membrane materials (such as PVDF and PS) with similar pore size (e.g. 0.2 μm) resulted in higher fouling for the more hydrophobic material.

3.5.2.2. Fouling behaviour using chemical pretreated feed

The raw olive mill wastewater is characterized by a high value of total solids and this represents a serious problem for the membrane process limiting the membrane performances during the time. A chemical pretreatment was performed in order to decrease the total solids percentage. Changing the pH of the water it is possible to alter the Z potential of the particles present in solution (Fig. 3.8). In this way the solution is destabilized and a rapid coagulation and flocculation of the solids takes place [6].

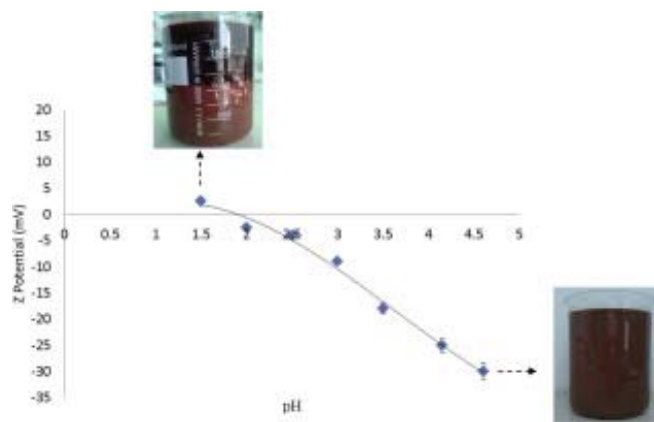


Fig. 3.8: Zeta potential as a function of pH and images of destabilized OMWW at 5 mV [6]

In order to identify the influence of pH on the membrane performance a series of OMWW solution at different pH was obtained and used to investigate the decrease of clean water permeability of the membranes.

In Fig. 3.9 the values of permeability reduction for the PVDF 0.5 μm after 4 hours of immersion in the different feed solutions are reported. The permeability reduction obtained in the same conditions with raw OMWW is also reported.

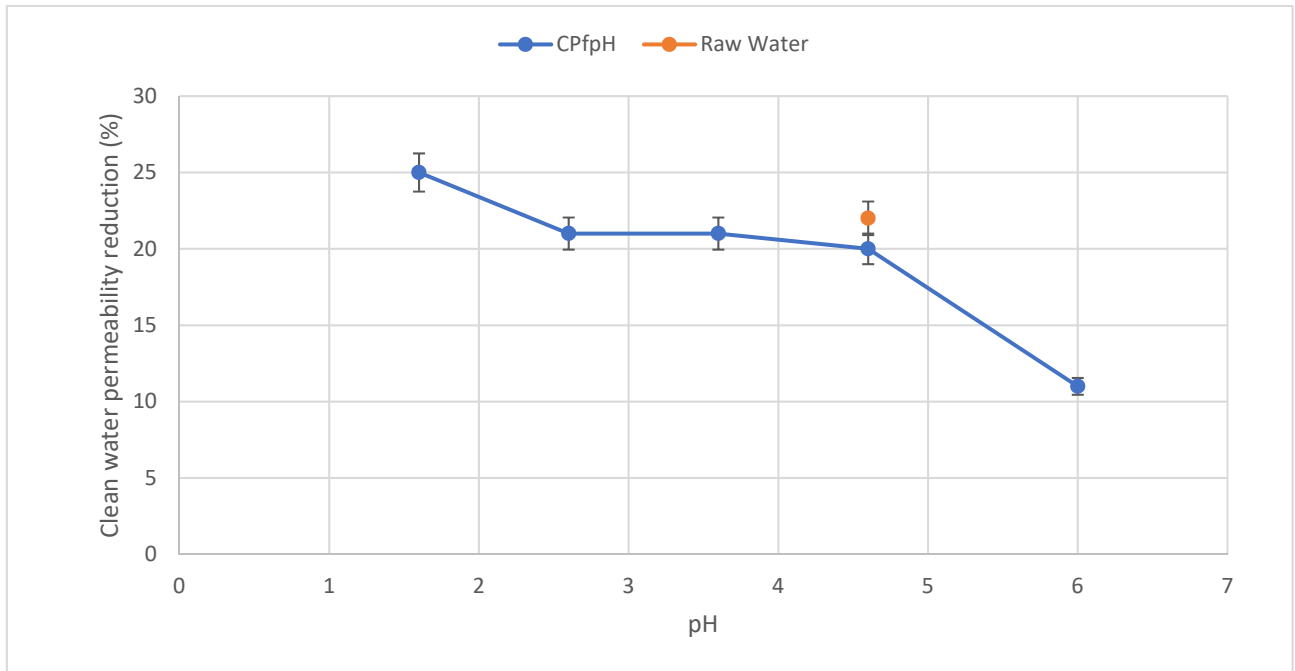


Fig. 3.9: Clean water permeability reduction vs pH for PVDF 0.5 μm membrane tested using OMWW with and without chemical treatment.

Results show that fouling increases with decreasing of pH value. At the same pH value chemical treatment promoted slightly better membrane performance. In Tab. 3.6 clean water permeability reduction for various membranes using OMWW treated with acid and then with base to adjust the pH at 6 is reported. Flux reduction is much less compared to when raw OMWW was used. The general trend is similar to the previous one. Fouling increased with decreasing membrane pore size. Fouling hydrophobic behavior is confirmed, in fact RC resulted in no clean water permeability reduction. Also in this case, for PVDF the clean water permeability reduction resulted slightly higher for PVDF membranes compared to PS membranes having similar pore size (0.2 μm). Overall, the chemical treatment allows to lower fouling, due to decrease of total solids amount.

Membrane	Pore Size (μm)	MWCO (kDa)	CWPR (%)
			CPf _{pH6}
PVDF	0.5 μm		14
PVDF	0.2 μm		23
PS	0.2 μm		21
PS	0.1 μm		28
PS		100 kDa	80
PSH		100 kDa	
RC		30 kDa	0

Tab. 3.6: Different results during the beaker tests using the raw water and the CPf_{pH6}.

3.5.2.3. Analysis of membrane morphology

AFM analysis of membranes was carried out in order to evaluate membrane morphology and its relationship with fouling. In particular, morphological visualization and membrane roughness at different test time was measured. AFM analysis was carried out for PVDF 0.5, PVDF 0.2 and PS 0.2 μm membranes.

All the topographical images are on an area of $5 \times 5 \mu\text{m}^2$. Figs. 3.10a-c show topography of new PVDF 0.5 μm (a), PVDF 0.2 μm (b) and PS 0.2 μm (c) membranes. Images show an increasing roughness trend from PVDF 0.5, passing through PVDF 0.2, up to PS 0.2 μm . Therefore, measurements confirmed the rougher profile of PS membrane and the smoother one of PVDF.

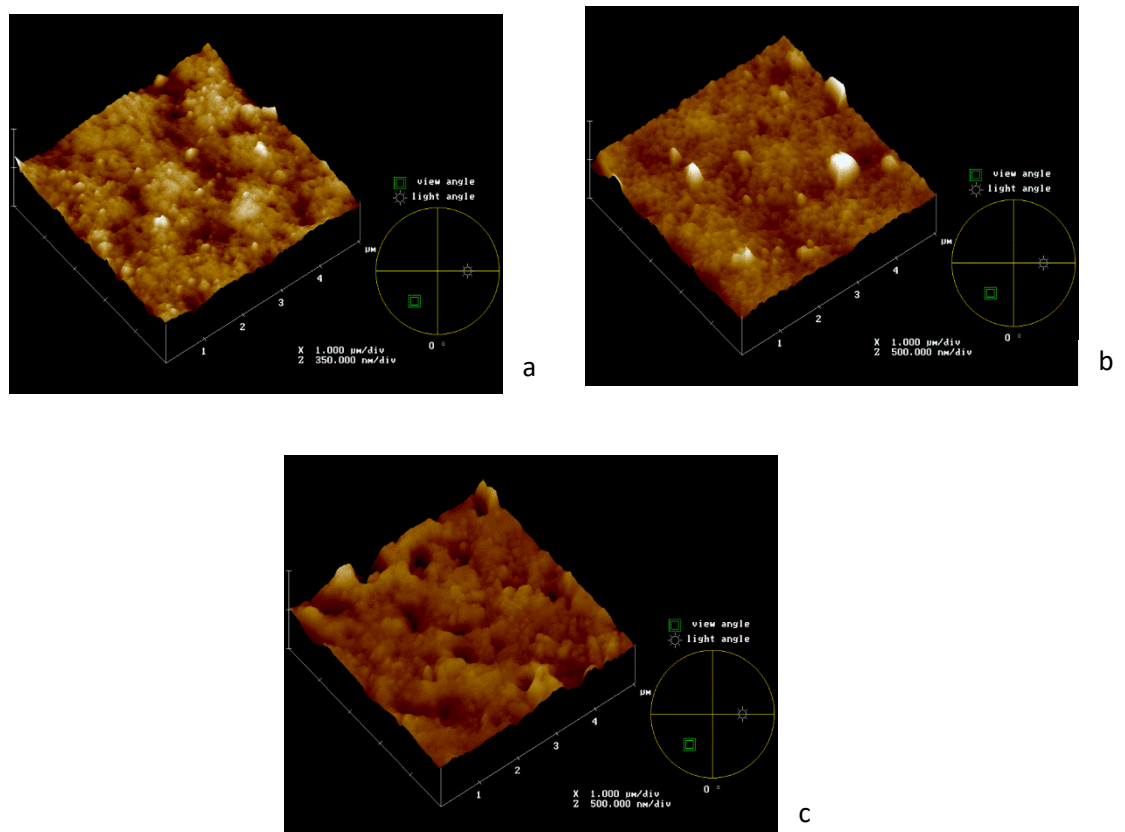
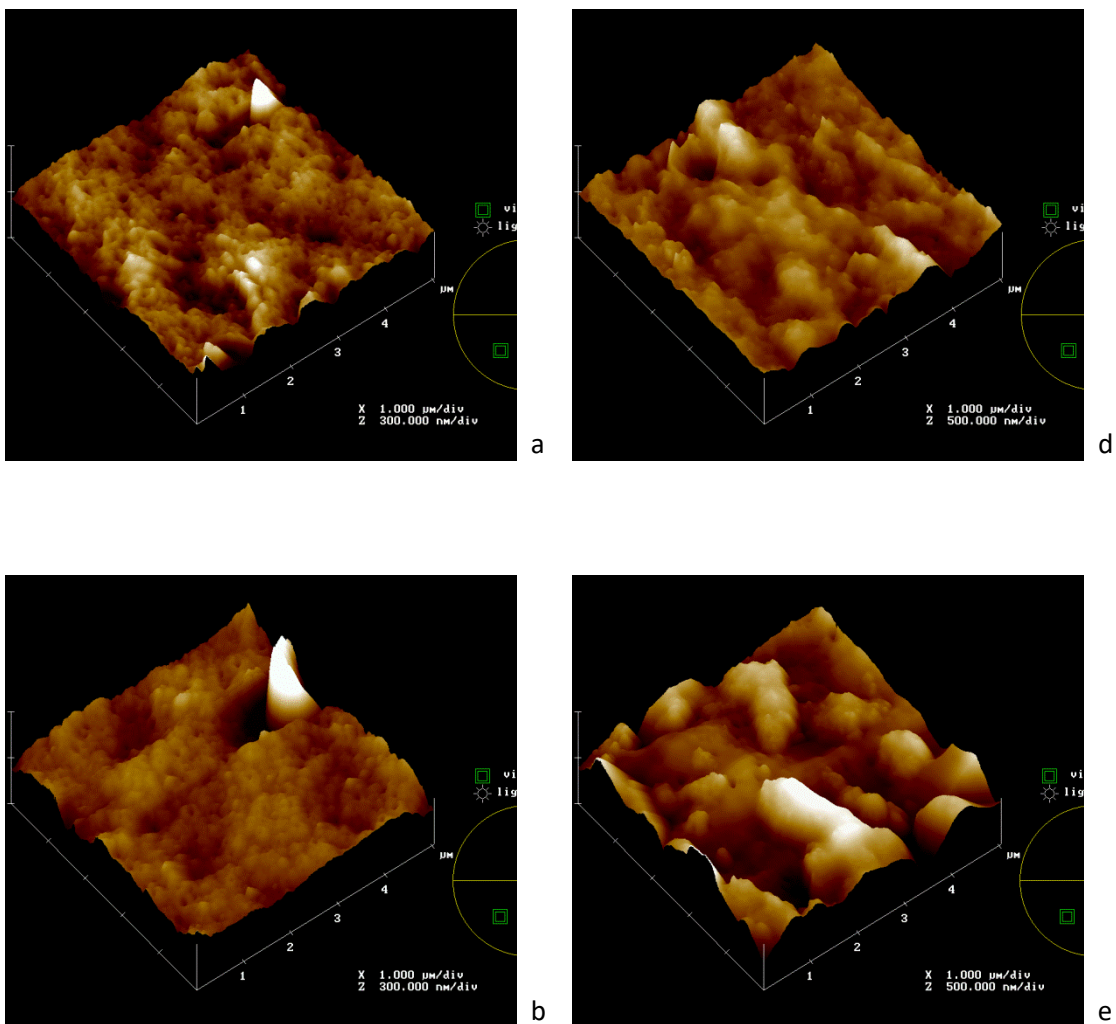


Fig. 3.10: AFM topography of new PVDF 0.5 μm (a), PVDF 0.2 μm (b) and PS 0.2 μm (c) membranes.

Morphology and roughness affect fouling formation. In order to evaluate this aspect, topographical images of PVDF 0.5 μm membrane at different time (5 min, 15 min, 30 min, 60 min, 2h, 4h) of OMWW beaker immersion test are reported in Figs. 10 (a, b, c, d, e, f, respectively). Tests were carried out with the raw OMWW. It's clear from the images that membrane surface is affected by fouling, because of the appearance of some elements higher of the basis surface and this is progressive up to 30 min test. In Fig. 3.11d it seems that something else was rubbed on membranes and morphology changes, up to Fig. 3.11e, in which both of previous foulant aspects are present.



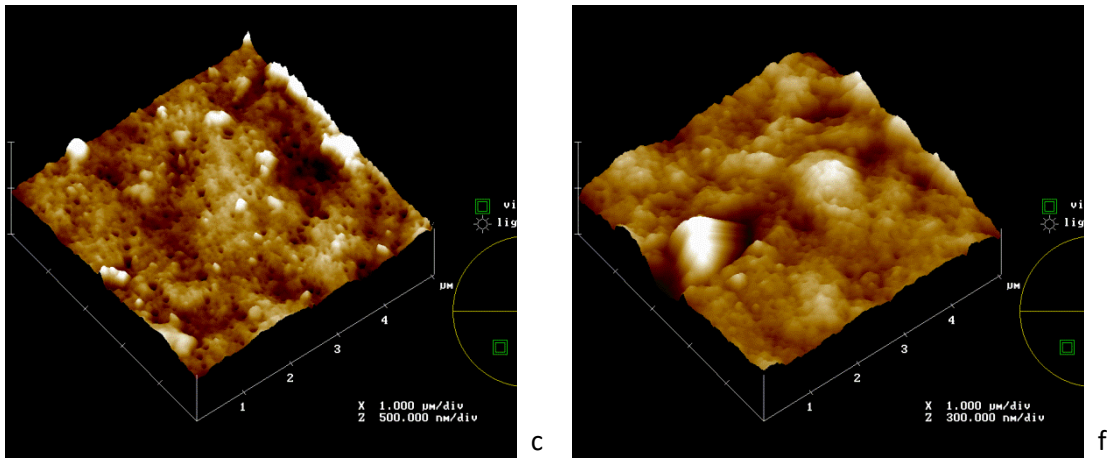
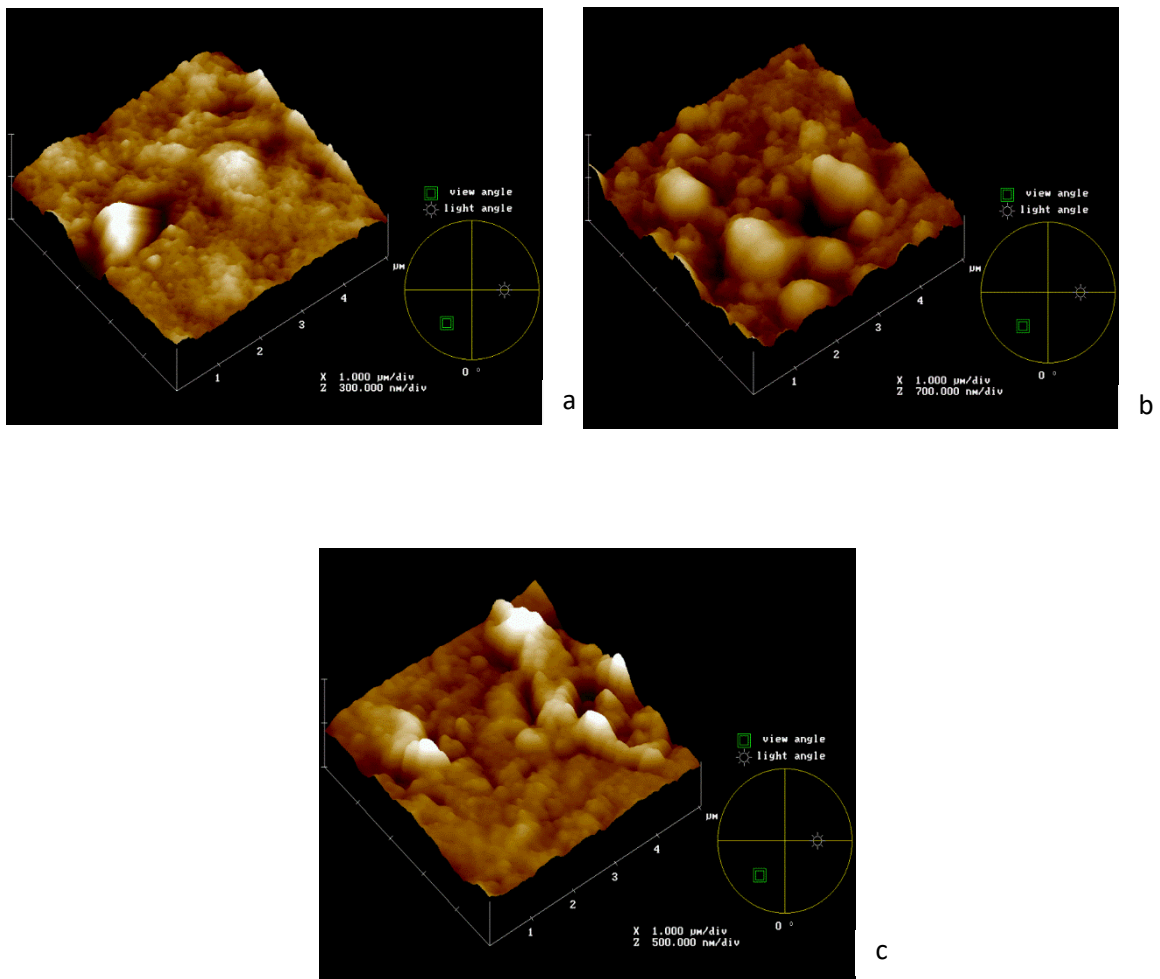


Fig. 3.11: AFM topographical images of PVDF 0.5 μm membrane at different time 5 min (a), 15 min (b), 30 min (c), 60 min (d), 2h (e), 4h (f) of OMWW beaker immersion test.



Figs. 3.12: AFM topography of PVDF 0.5 (a), PVDF 0.2 (b) and PS 0.2 (c) μm membranes after 4h of immersion in OMWW.

Figs. 3.12 (a, b, c) report topography of PVDF 0.5, PVDF 0.2 and PS 0.2 μm membranes after 4h of immersion. Both PVDF 0.2 and PS 0.2 membranes seem to be more affected by fouling phenomena. Roughness measurements for all the analyzed conditions are reported in Tab. 3.7. After 4h immersion test, PVDF 0.2 μm membrane reaches higher roughness value, followed by PS 0.2 and PVDF 0.5 remains the smoother membranes. This is in agreement with the CWPR % values reported in Tab. 3.7.

Membrane	Ra (nm)	Dev. St.	Rq (nm)	Dev. St.	Test Time (min)
PVDF 0.5	12,420	2.71	15,924	3.60	0
PVDF 0.5	15,130	6.60	19,515	9.03	5
PVDF 0.5	15,646	18.41	19,539	23.63	15
PVDF 0.5	16,265	4.49	21,555	5.68	30
PVDF 0.5	25,854	11.29	31,881	12.99	60
PVDF 0.5	33,745	25.97	41,765	30.71	120
PVDF 0.5	14,738	8.07	18,360	9.36	240
PVDF 0.2	16,438	9.32	21,702	11.38	0
PVDF 0.2	48,583	14.21	60,467	17.02	240
PS 0.2	20,498	6.85	26,135	8.40	0
PS 0.2	30,101	19.14	38,295	23.55	240

Tab. 3.7: Roughness measurements of new and used PVDF 0.5 μm , PVDF 0.2 μm and PS 0.2 μm .

Conclusion

PVDF, PS, PSH and RC membranes, with various pore size, were tested in various equipments in order to evaluate fouling mechanism promoted by Olive Mill Wastewater. In order to evaluate only the adhesion or adsorption to membrane surface of foulant molecules, various methods were tested. The simple immersion of the membrane in the OMWW and the bell-shaped container with membrane positioned in horizontal position resulted the best methods to avoid interference with penetration of molecules in the membrane pore due to hydrostatic pressure. Adsorption to the support did not negatively influence the permeability reduction flux. The other used systems have promoted the penetration of fluid through the membrane pores, favoring other fouling mechanisms and not allowing to study with more accuracy the only adhesion mechanism on the membrane. This aspect is important in order to select membranes that are less fouled and can be easily cleaned after cake formation.

Results demonstrated a higher propensity to fouling by molecules present in OMWW of membrane materials having lower hydrophilic character and lower pore size. In particular, this was confirmed by the different behavior of PS and PSH membranes of 100 kDa and the absence of fouling by adhesion in RC membrane. The clean water permeability reduction was strongly affected by pH, it decreased with pH increasing. Best performances were obtained with PVDF 0.5 μm membrane, resulting in a 14% of pure water flux reduction using a chemical pretreated feed at pH 6. The pure water flux reduction obtained with the raw OMWW using the same membrane was 22%.

AFM analysis also confirmed the PVDF 0.5 μm membrane were the less prone to fouling on the basis of their low surface roughness. PVDF 0.2 μm showed a higher CWPR% along with a higher surface roughness, compared to PS 0.2 μm .

It is possible to use hydrophilized hydrophobic commercial membranes to limit the fouling promoted by OMWW. In this way, the membrane surface foulants interaction for materials such as PVDF and PS would be low whilst the mechanical and chemical resistance properties of the membrane would remain. Good results can be obtained

using this type of membrane if the hydrophilized process does not increase significantly membrane surface roughness.

For this reason, it was chosen to use hydrophobic hydrophilized hollow fiber membranes to perform the immersed module performance tests. Complete results of this work are reported in the chapter 4.

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Submerged polyethylene
hollow fibre performance for
the microfiltration of
OMWW

(Submitted Paper)

4

Abstract

Olive mill waste water (OMWW) has a very high organic load that is recalcitrant in nature and possess a high amount of toxicity/phytotoxicity-associated phenolic compounds that, at the same time, may have anti-inflammatory properties. This waste, arising from the production of olive oil in olive mills, is usually disposed on soil and it is used as fertilizer. However, it is known that OMWW is able to destroy the soil structure, then the development of alternative disposal systems becomes of primary importance. The use of an integrated membrane system may represent a very effective solution for water reuse and polyphenols recovery. On the other hand, this strategy is limited by membrane fouling, especially at the initial microfiltration (MF) step. For this purpose, the behaviour of a submerged MF hollow fiber membrane system was evaluated as an alternative to the cross-flow side-stream systems, in order to promote a less prone to fouling process. A systematic characterization of the submerged MF was carried out. Air scouring, back flushing and a combination of them were applied as strategies to control fouling. The system was built with hydrophilized polyethylene hollow fiber membranes having pore diameter of 0.4 μm . These membranes did not suffer of irreversible fouling, i.e. the initial membrane flux was restored with simple water rinsing. Experiments were performed with real waste waters used as raw or as pre-treated by acidifying their pH in order to change the particles electro-kinetic potential and reach a rapid flocculation and coagulation of dissolved solid. By using an air flow rate of 3 L/min (for creating air bubbles at the membrane interface), it was possible to maintain a constant flux of 18 L/hm² for 8 working hours without reaching the limiting-operative pressure of 40 kPa. In addition, more than 95% of polyphenols were recovered in the permeate with a very marginal percentage of polyphenols remained in the concentrated stream, which makes the latter suitable for further biotransformation. The permeate was also processed by an integrated UF/NF system for the recovery of polyphenols.

Introduction

Olive oil production is an important economic resource for many Countries of the Mediterranean basin and it is becoming popular all over the world. At same time the olive oil production generates high quantitative of olive mill waste water (OMWW) that represents a critical problem to be solved. At the moment there is no European legislation regulating olive mill discharges, and standards are left to individual countries. The practices currently applied include land disposal, discharge into nearby rivers, lakes or seas and storage/evaporation in lagoons. Environmental problems such as soil contamination, water body pollution, underground seepage and odor are often encountered.

If the OMWW disposal on soil could appear as a cheap solution to the problem, the continued application destroys the soil structure for the accumulation of salt and the high polyphenols amount represent an antimicrobial and phytotoxic factor [1].

Waste water arising from olive processing is one of the strongest industrial effluents, with chemical oxygen demand (COD) values of up to 220 gL⁻¹ and corresponding biochemical oxygen demand (BOD) values of up to 100 gL⁻¹[2]. Olive oil is produced from olives in olive mills either by the discontinuous press method or by the continuous centrifugation method. The wastewater arising from the milling process amounts to 0.5–1.5 m³ per 1000 kg of olives depending on the process. The discontinuous process produces less but more concentrated wastewater (0.5–1 m³ per 1000 kg) than the centrifugation process (1–1.5 m³ per 1000 kg).

The characteristics of olive mill wastewater are variable, depending on many factors such as method of extraction, type and maturity of olives, region of origin, climatic conditions and associated cultivation/processing methods. Besides its strong organic content (BOD₅ 35–100 gL⁻¹, COD 45–220 gL⁻¹, suspended solids (SS) 1–9 gL⁻¹), OMWW contains high concentrations of recalcitrant compounds such as lignins and tannins which gives it a characteristic dark colour (52,270–180,000 mg L⁻¹ Pt-Co units), but, most importantly, it contains phenolic compounds and long-chain fatty acids which are toxic to microorganisms and plants. The phenolic compounds can be either simple phenols

and flavonoids, or polyphenols which result from polymerisation of the simple phenols. The concentration of phenolic compounds in OMWW varies greatly from 0.5 to 24 gL⁻¹. The high recalcitrant organic load and the associated toxicity make the treatment of OMWW imperative.

A different solution in which OMWW changes its definition from waste to resource could be a very important alternative strategy combining environmental protection and economic exploitation. The biophenolic compounds existing in OMWW though recalcitrant they are also compounds of interest in the food, pharmaceutical, or cosmetic industries due to their high antioxidant and other important bioactivities [3-8]. The prospective of the use of an integrated membrane system for the treatment of the OMWW and the recovery from this waste of molecules of nutraceuticals importance is a green alternative to the disposal on soil. Different papers report the use of an integrated membrane system for this purpose and the main limiting factor for the application of this technology is represented by membrane fouling generated from the OMWW [9-13].

Among the various steps in the integrated membrane operation, microfiltration suffers the most in terms of membrane fouling. As a result, the various works reported in literature employed chemical, physical or biological pre-treatment methods prior to sending the OMWW to the filtration system [14]. Moreover, compared to a submerged system, the microfiltration process was mainly studied in the side stream configuration [15]

In the present study, we used an immersed membrane system as microfiltration step for the treatment of OMWW. We selected the submerged MF system, since lower fouling propensity is a distinguished characteristics of immersed systems. In addition, use of air scouring and back-flushing for fouling control during the MF process are studied. The MF step was characterized in terms of flux, maximum applicable pressure and polyphenol retention. Promising results have been obtained using polyethylene hydrophilized (PEH) hollow-fiber membrane of 0.4 µm supplied by Econity (South Korea).

Initially three different types of membrane material were selected for the immersed system test: PVDF, PS and PE. From previous work on membrane fouling through contact with OMWW we obtained behavior data for PVDF and PS materials. We have also chosen to test PE as it is a material that demonstrates good mechanical and chemical resistance properties. Here only PE hollow fibers are reported, as preliminary test showed that the water flux was completely restored after fouling during OMWW treatment.

In fact, the clean water flux of the PE hollow fibers membranes was restored using only water without chemical agents (as discussed at the end of the chapter).

4.2 Materials and methods

4.2.1 Membranes and Submerged System

Membranes employed in the experiments were a high density Polyethylene (Hydrophilized) hollow fiber microfiltration kindly provided by Econity with a nominal pore size of 0.4 μm , asymmetric structure, 0.65 mm outer diameter (OD), 0.41 inner diameter (ID). Membrane characteristics are reported in Table 4.1.

Table 4.1. Specifications of the hollow fiber membranes used in the microfiltration process.

PE Hollow Fiber			
Manufacturer	Econity		
Membrane Type	Hollow Fiber		
Membrane Chemistry	High	Density	Polyethylene (Hydrophilized)
Membrane Pore Type	Slit Pore and Asymmetric Structure		
Nominal Pore Size	0.4 μm		
Membrane Outer Diameter (OD)	0.65 mm		

Membrane Inner Diameter (ID)	0.41 mm
Allowable pH range	2 – 13
Operating Pressure	5 – 60 kPa
Operating Temperature Range	5 – 40 °C
Initial Membrane Permeability (L/m ² hbar)	1080

All experiments were performed using a 5 L lab-scale submerged hollow fiber membrane system. A schematic diagram of the system is shown in Fig. 4.1.

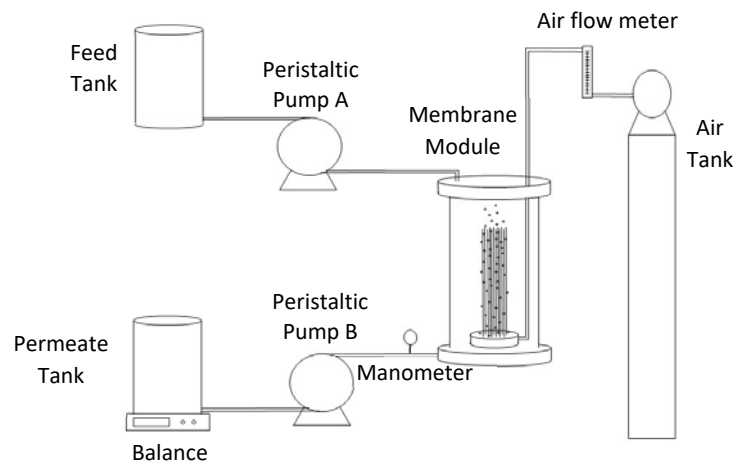


Fig. 4.1: schematic diagram of the submerged membrane system

The membrane module was composed of a membrane bundle of about 50 hollow fibers of 20 cm length, with a total surface area of 0,032 m². An epoxy resin was used both to close the top end of the hollow fiber and to stuck the bottom end of the bundle to the membrane module. In this way, according to the originally developed puron® design, the top end was allowed to float freely in the liquid medium enabling a better fiber motion and fouling control under air scouring conditions [16]. The hollow fibers were oriented

in vertical arrangement in order to ensure better performance during air bubbling [17]. The membrane module was screwed to the permeate channel in the center of a Plexiglas disk with 17 cm diameter and 3 cm height. A cylindrical Plexiglas tank (5 L capacity, 15 cm diameter and 36 cm height) was screwed to the disk (Fig. 1). The peristaltic pump B (Cole-Parmer 7528-10) was used to draw the permeate or (by reversing the rotor pump) for the backwashing step. The total volume of the feed was maintained constant during the overall permeation process by adding equal volume corresponding to the permeated one by means of the peristaltic pump A (ISMATEC Cole-Parmer CP78016-30). The pressure of permeate stream was controlled with a digital pressure transducer (Wika DG-10-S -1..0..2 bar) situated in the permeate line and it was recorded manually. The flow rate of the permeate stream was monitored with a digital precision balance (Gibertini EU-C 1000 PT) connected to a computer. The air was blown into the membrane tank by an air cylinder connected to an air flow meter (Cole-Parmer 1-10 l/min) going through a series of nozzles positioned at the bottom end of the membrane module. The position of the nozzles allows air bubbles to hit the fiber bundle both internally and externally. This allows a better fouling control and thus better system performance.

4.2.2 Feed solutions

The feed used in the experiments was a real olive mill waste water (OMWW) supplied by Olearea San Giorgio, Fratelli Fazari, snc, San Giorgio Morgeto (RC), Italy. The experiments were performed with raw (non pre-treated) and pre-treated OMWW. The pre-treated feed was obtained by adding sulfuric acid (96% v/v) to the OMWW in order to ensure the rapid coagulation and flocculation of the suspended solids as a result of the dispersed particles electro-kinetic potential change [14]. The pH of the solution was adjusted back to the allowable pH value of the membrane by adding NaOH. All the feeds were filtered by a metallic mesh of 35 μm before introducing them in to the submerged system. The feed characteristics before and after acid pre-treatment are reported in Table 5.2.

Table 4.2. Properties of native (Raw feed) and pre-treated with acid (Acid pre-treated feed) OMWW.

	Raw feed	Acid pre-treated feed
Total Solid (%)	6.5 ± 0.1	4.8 ± 0.1
Suspended Solid (%)	3.6 ± 0.1	3.7 ± 0.1
Polyphenols (g/L)	5.2 ± 0.2	4.7 ± 0.2
Pectines (g/L)	2.6 ± 0.2	2.4 ± 0.2
pH	4.6 ± 0.1	1.5 ± 0.1

4.2.3 Chemicals

Gallic acid, Folin-Ciocalteu and calcium carbonate were used for polyphenols analyses. Sulfuric acid was used for feed acid pretreatment and as reagent in pectine analyses. Sodium hydroxide was used for pH adjustment of the feed. Galacturonic acid was used as standard in the analysis for pectines. All chemicals were purchased from Sigma Aldrich (Milano, Italy).

4.2.4 Methods

The total amount of polyphenols was determined by Folin-Ciocalteu method [18]. The total amount of pectins was determined using the procedure previously reported [19]. Briefly, a sample of OMWW (0.2 mL) was mixed with 1.2 mL of sulfuric acid. The obtained solution is refrigerated in crushed ice. The mixture was shaken in a vortex mixer and then heated in an oil bath at 100 °C for 5 min. After cooling in a water-ice bath, 20 µL of 0.15% solution of mhydroxydiphenyl in 0.5% NaOH was added. The final solution was shaken, and, within 5 min, the absorbance of a pink complex of galacturonic acid was read at 520 nm in a PerkinElmer spectrophotometer using water as a background. The galacturonic acid is formed from the hydrolysis reaction of pectins with sulfuric acid. A standard solution of galacturonic acid was used for the preparation of

the calibration curve (0–1 g/100 mL water). The hydrolyzed OMWW were used to study the microfiltration performance in configuration b). The conversion of the hydrolysis reaction was calculated as the percent ratio of the amount of galaturonic acid produced after hydrolysis over the amount of pectins in the initial reaction mixture.

The total solids content of the OMWW was quantified by a thermo-balance: a known volume of sample was weighed and heated up to a temperature of 105°C until a constant weight was reached when all water was evaporated.

Ultrapure water permeability of membranes was determined after membrane compaction. A sequence of increasing and decreasing of pressure was carried out to ensure the membrane was stabilized.

OMWW microfiltration was performed at constant pressure (recording the decrease of permeate flux as a function of time, due to fouling) and at constant permeate flux (recording the increase of pressure as a function of time).

Air bubbling was introduced at three different air flow rates: 1, 2 and 3 L/min.

A pressure value of 40 kPa was not exceeded during the OMWW's filtration to avoid an irreversible fouling of the membrane module. The upper limiting pressure value suggested by the manufacturer was 60 kPa.

All experiments were carried out with the same membrane module, as membranes were easily cleaned without the use of chemical treatment. The initial pure water permeability was restored after each experiment by using only clean water as reported in the 3.6 section.

4.3 Results and Discussion

In this section the results of various microfiltration operation mode using submerged hollow fibers are illustrated and best operating conditions for fouling control are identified.

Initially, membranes were compacted and pure water permeability at steady state was obtained. Then submerged microfiltration experiments using real OMWW were carried out. Raw waste water or pre-treated waste water, aiming at reducing the solid content and attenuating fouling, were used. The combined effect of filtration, aeration and back

flushing on submerged microfiltration performance were studied. The conditions used were: (i) continuous microfiltration without aeration; (ii) continuous microfiltration with continuous aeration; (iii) periodical shut-down of microfiltration at a given frequency with continuous aeration; (iii) continuous microfiltration with periodical aeration and back flushing.

4.3.1 Continuous submerged microfiltration without aeration

Pure water permeability after membrane compaction was $8.3 (\pm 0,5) \text{ L/m}^2\text{h kPa}$. A constant flux value of $330 (\pm 2) \text{ L/m}^2\text{h}$ at 40 kPa was obtained.

OMWW is characterized by a pH of 4.6 and different content of suspended and dissolved solid. In the present case, it has a total solids content of 6.5%. Raw OMWW were obtained by filtering the real waste water through a metallic mesh of 35 μm to remove suspended solids, then they were microfiltered in the submerged system.

The microfiltration of raw waste water was carried out at constant flux operational mode and increase of pressure, accounting for fouling build up, as a function of time was monitored. Experiments at three different constant flux values were carried out. Working at 5, 10 and 18 $\text{L/m}^2\text{h}$, the limiting pressure of 40 kPa was reached after 1 hour, 10 or 4 minutes, respectively. Due to the high dissolved solids content, raw OMWWs are very difficult to treat. In order to standardize the raw OMWW to be treated by submerged microfiltration, it was acidified with H_2SO_4 at pH 1.5, precipitated for 24 h, pre-filtered through a 35 μm metallic filter and then pH was increased again to 2.5 and 4.6. The amount of residual dissolved solid was 2.5%. No higher pH value was induced because of the increase of viscosity.

Fig. 4.2 shows the flux as a function of time of pre-treated OMWW for the two pH values. Experiments were carried out at constant pressure of 5 kPa. After about 40 minutes of microfiltration, a quasi-steady flux of $4.5 \text{ L/m}^2\text{h}$ was reached for both pH values. On the other hand, the initial flux was higher when working with the OMWW at pH 4.6 ($16.5 \text{ L/m}^2\text{h}$) compared to the OMWW at pH 2.5 ($9 \text{ L/m}^2\text{h}$).

Considering the initial higher flux at pH 4.6, this condition was chosen for subsequent investigation on air bubbling and back flushing effect on MF performance.

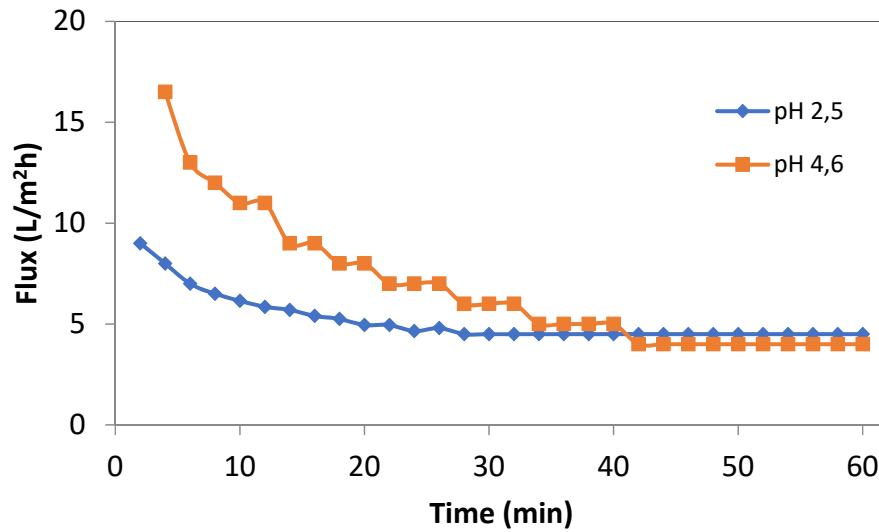


Fig. 4.2. Acidified OMWW flux versus time, at different pH values.

4.3.2 Continuous submerged microfiltration with continuous aeration

In order to achieve a flux for reliable application, it was chosen to work at 10 L/m²h, trying to restore the original flux value by air bubbling. Fig. 4.3 reports the pressure trend of the microfiltration process without and with air scouring, which were introduced at 1, 2, 3 L/min. By introducing course air bubbles, it was possible to remove some impurity and a longer working span before arriving at the set limiting pressure (40 kPa). The best performance was reached with an air flow rate of 3 L/min, which gave the possibility to operate the system for 50 minutes, but it was not enough for having the process in operation for at least a working day (equal to 8 hours).

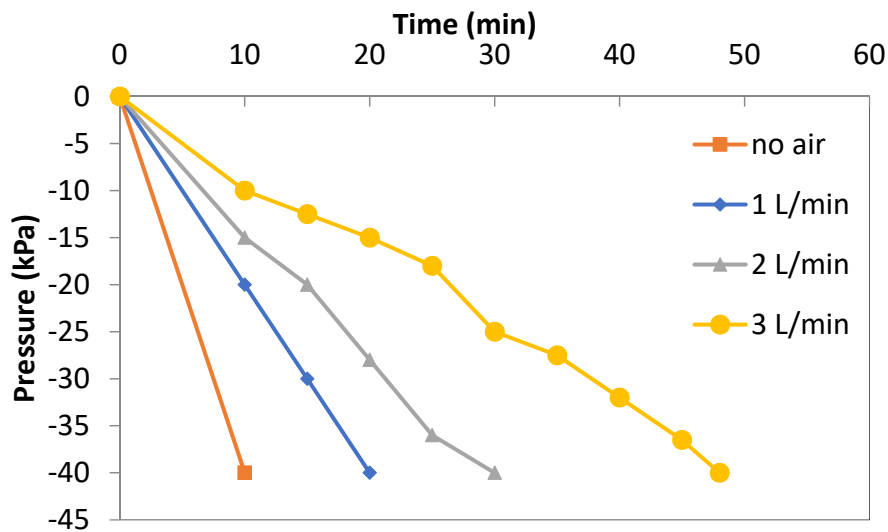


Fig. 4.3. Behavior of pressure as a function of time during submerged microfiltration of raw OMWW at constant flux of 10 L/m²h, without air and with air at different flow rates.

4.3.3 Discontinuous submerged microfiltration with continuous aeration

To improve the control of fouling, microfiltration process was periodically shut-down (by switching off the permeate vacuum pump) while continuous aeration was introduced. The experiments were carried out at constant flux of 10 L/m²h and when the limiting pressure was reached, the system was stopped for 2 minutes. This happened almost every 48-50 minutes (Fig. 4.4). The shut-down of the microfiltration promoted a membrane relaxation while the air flow scoured foulants from the membrane. Consequently it was possible to periodically restore the initial flux. In this way, it was possible to work for 8 hours, without the need for membrane chemical cleaning. It is most interesting to note that a 2 minute relaxation accompanied by coarse air bubble scouring restored the initial performance in most of the cycles.

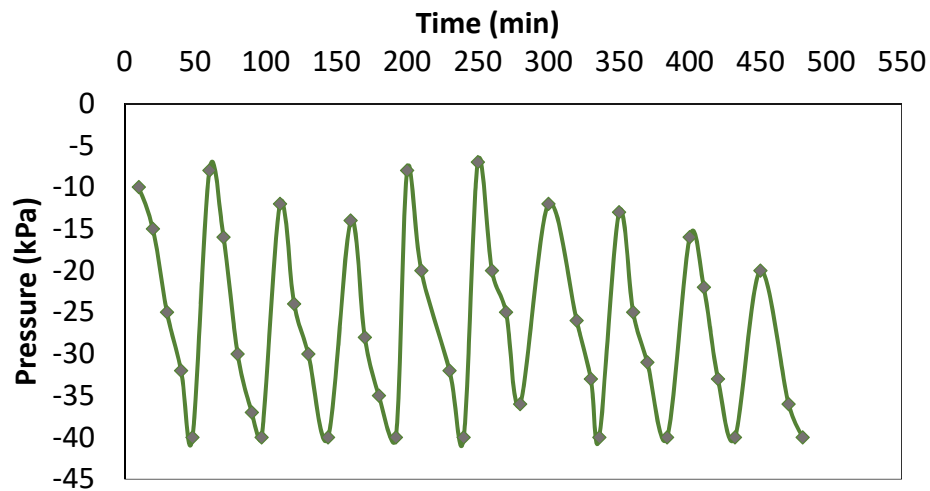


Fig. 4.4. Pressure trend during discontinuous MF of raw OMWW by submerged hollow fibers. The system was operated at constant flux of 10 L/m²h, pump shut down every 48-50 min, for 2 minutes, with simultaneous air bubbling at a flow rate of 3 l/min.

4.3.4 Continuous submerged microfiltration with discontinuous aeration and back flushing

The effect of microfiltration with continuous aeration was evaluated using waste water acidified as described before. Experiments were carried out in such a way that after 10 min of microfiltration, air was introduced at flow rates of 1, 2, or 3 L/min (Fig. 5.5). Flux increased with air bubble flow rate and, in particular, when using a flow rate of 3 L/min, the initial flux of 16.5 L/m²h was restored. Therefore, higher values of air flow rates were not evaluated.

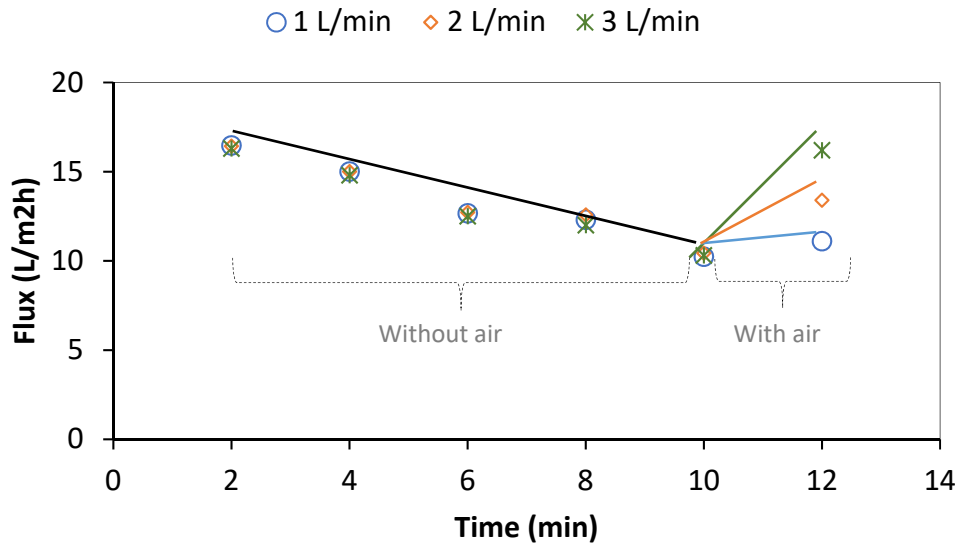


Fig. 4.5. Effect of air bubbling introduction at different air flow rate, during submerged MF of pre-treated OMWW (4.6 pH, 5 kPa TMP).

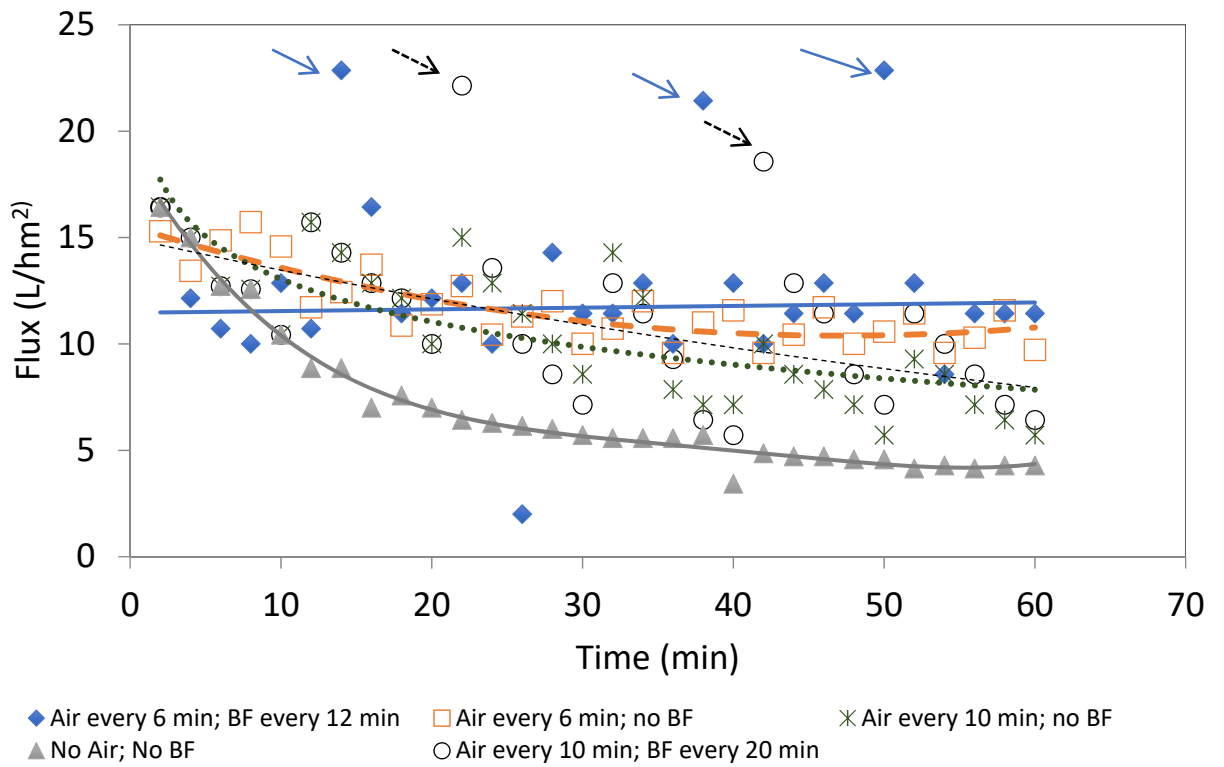


Fig. 4.6. Flux as a function of time during submerged MF of acidified OMWW using various operating conditions: air bubbling every 6 min and BF mode every 12 min; air bubbling every 6 min; air bubbling every 10 min; air bubbling, every 10 min and BF mode every 20 min; MF with no air bubbling nor back-flushing.

Fig. 4.6 illustrates the behavior of flux as a function of time using acidified OMWW during submerged MF in various operating conditions. In particular, the influence of aeration (at a flow rate of 3 L/min) and back-flushing (at 30 kPa) as well as their frequency and duration on MF performance was investigated. Therefore, experiments were carried out introducing i) aeration every 6 min lasting 2 min and back-flushing (BF) every 12 min lasting 2 min; ii) aeration every 6 min lasting 2 min with no back-flushing; iii) aeration every 10 min lasting 2 min with no back-flushing; iv) aeration every 10 min lasting 2 min and back-flushing every 20 min lasting 2 min; v) no aeration nor back-flushing.

As it can be seen, for the 2 min aeration every 6 min, an average flux of $10,4 (\pm 1) \text{ L/m}^2\text{h}$ was reached and when back flushing at 30 kPa every 12 min was introduced an average flux of $11,3 (\pm 2) \text{ L/m}^2\text{h}$ was obtained.

For the 2 min aeration every 10 min, an average state flux of about $8 (\pm 2) \text{ L/m}^2\text{h}$ was obtained, and when back flushing every 20 min was also introduced the steady average flux was nearly the same, i.e. $8,5 (\pm 2) \text{ L/m}^2\text{h}$. When no air nor back-flushing were used a steady-state permeate flux of about $4 \text{ L/m}^2\text{h}$ was obtained.

Introducing air every 6 min maintained the flux to an average constant value. Back flushing allowed to restore the flux to higher values, but mean flux, after 60 min of microfiltration is about the same. On the contrary the amount of permeate decreased, due to reverse flux introduced by back flushing. In fact, when only air bubbling was introduced every 6 min the permeate volume collected after 60 min was $264.4 (\pm 1) \text{ mL}$ while when also back flushing was introduced every 12 min the permeate volume collected after 60 min was $235.3 (\pm 1) \text{ mL}$. When aeration was introduced every 10 min or back flushing was introduced every 20 min, the permeate volumes collected after 60 min were $245.4 (\pm 1) \text{ mL}$ and $223.0 (\pm 1) \text{ mL}$, respectively. It is worth to note that only $145 (\pm 0.1) \text{ mL}$ were recovered in the case of microfiltration alone (without aeration nor back flushing), as in this case fouling was more severe. Based on the high flux restoration using back-flushing (highlighted by arrows in Fig. 6), the type of fouling was basically due to pore-blocking and physical-chemical interaction between foulants and PE membrane surface can be considered negligible. On the basis of quasi-steady state flux value and overall permeate volume collection, aeration at a frequency of 6 min without the need

of back-flushing resulted a suitable condition for microfiltration of acidified OMWW with submerged PE hollow fiber.

4.3.5 Continuous aeration

The influence of continuous aeration was also investigated. 1 L/min flow rate was chosen, allowing to the same air consumption in an hour as for introducing air at 3 L/min for 2 min, every 6 min. Fig 4.7 shows that during 1 hour of microfiltration with continuous aeration the flux value, after initial decline, increased a little and then stabilized at 11.6 L/m²h.

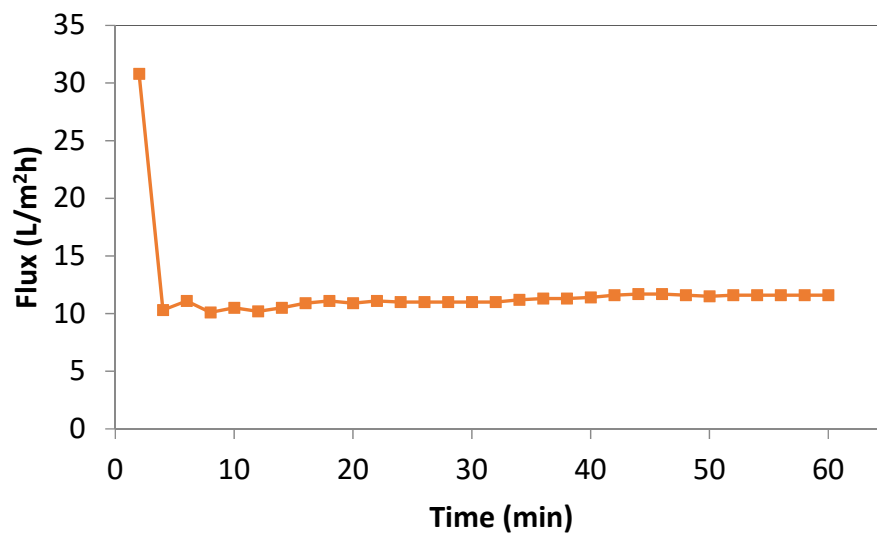
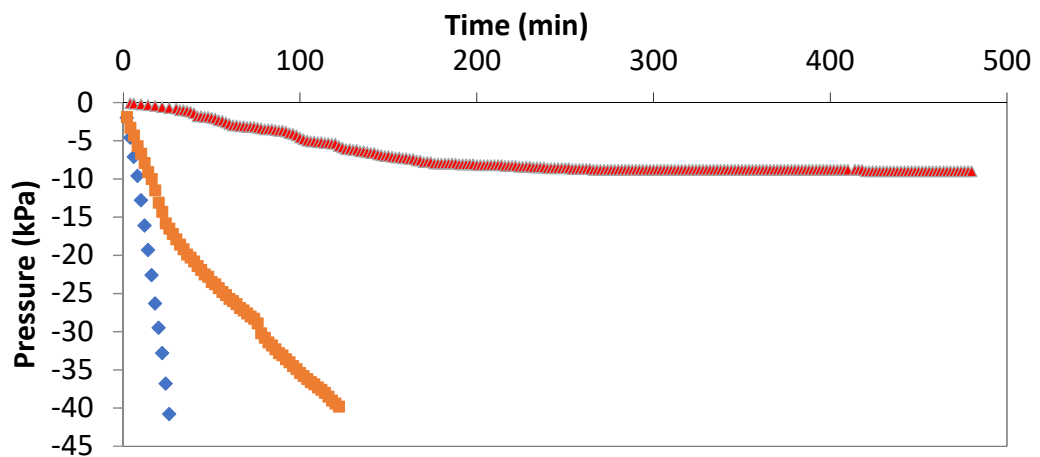


Fig. 4.7. Acidified OMWW microfiltration with continuous aeration at 1 L/min flow rate and 5 kPa TMP.

Experiments with continuous aeration was also carried out in conditions of constant flux (at the value of 18 L/m²h), monitoring the increase of pressure. Fig. 4.8 shows the behavior of pressure as a function of time using air flow rate of 1, 2, 3 L/min. When working at 3 L/min, it was possible to work for 8 hours without reaching the limiting pressure. On the contrary, at 1 and 2 L/min of air bubbling, the limiting pressure was reached after 26 and 124 minutes, respectively.



◆ MF+constant air 1 L/min ■ MF+constant air 2 L/min ▲ MF+constant air 3 L/min

Fig. 4.8. Pressure trends as a function of time during acidified OMWW submerged microfiltration at different air flow rates and constant flux of 18 L/m²h.

4.3.6 Membrane cleaning

Even though the fouling propensity was quite high, the membrane was easily cleaned just with water, without any chemical treatment. In Fig. 4.9, the pure water flux of new and used membranes as a function of time is reported. The used membranes were washed by simply adding pure water in the tank where membranes were immersed, applying a pressure of 10 kPa. In Fig. 4.9, it is possible to see that the initial permeate flux was restored after 40 min. This means that mainly reversible fouling resulting from concentration polarization was built on the membrane and that polyethylene resulted a suitable material to avoid irreversible interactions between foulant molecules present in OMWW and the membrane.

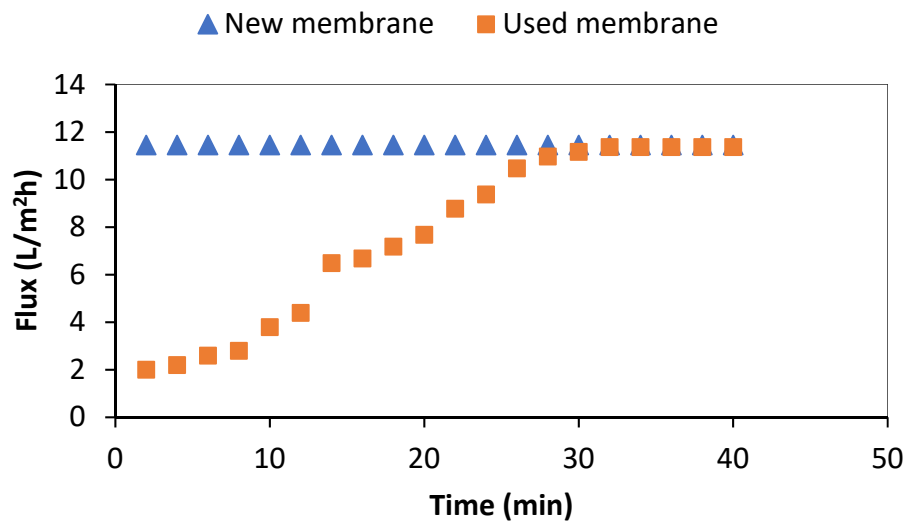


Fig. 4.9. Ultra pure water flux of new membrane and during washing of used membrane.

4.3.7 Integrated membrane process

The permeate recovered from the microfiltration in the submerged hollow fiber membrane system was used for subsequent ultrafiltration and nanofiltration processes in external (or side-stream) configuration, with zirconia ceramic membranes of 20 and 2 nm pore size, respectively. Tests were performed at constant feed volume using membranes of $1.8 \cdot 10^{-3} \text{ m}^2$. Ultrafiltration was carried out at a transmembrane pressure of 100 kPa. A constant flux of about 50 L/m²h for almost one hour was observed, then the flux decreased reaching a value of about 25 L/m²h after 5 hours. Nanofiltration was carried out at a transmembrane pressure of 150 kPa. The NF flux was stable at about 25 L/m²h for 5 hours (Fig. 5.10). Polyphenols rejection was 42% for UF and 64% for NF.

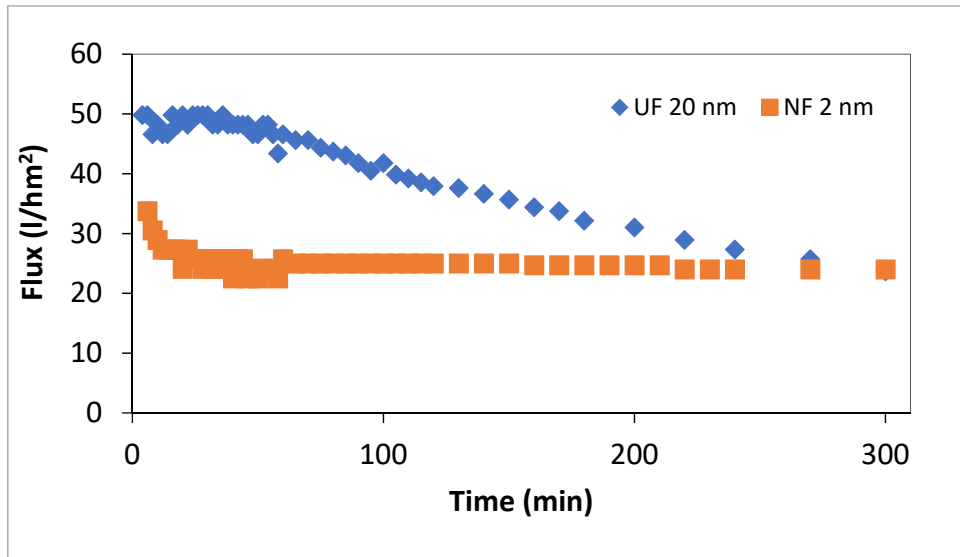


Fig. 4.10. Permeate flux of UF 20 nm and NF 2 nm zirconia ceramic membranes as a function of time.

Conclusions

Submerged hollow fiber microfiltration membrane system was investigated to treat OMWW. To our best knowledge, this is the first example of submerged hollow fiber membrane used for this kind of waste water.

The best process performance was obtained using acidified OMWW with final readjusted value at pH 4.6 and continuous aeration mode. The submerged hollow fiber microfiltration was able to work at steady flux, whose value depended on the air scouring flow rate and the relative absolute pressure, downstream the membrane to draw the permeate. For example, continuous air scouring flow rate of 1 L/min using 5 kPa and 3 L/min using 10 kPa permitted to work at steady-state flux of 12 L/m²h and 18 L/m²h, respectively. The study suggested the great potentiality of submerged systems using hydrophilized hollow fiber membrane for the treatment of OMWW. The low interaction between the foulant present in the OMWW and the polyethylene hollow fibers prevented the need for chemical washing. Cleaning with water was enough to restore the initial water permeability. The subsequent processing of microfiltration permeate with ultrafiltration and nanofiltration showed good steady state flux values confirming the submerged membrane treatment as a suitable step for the treatment of OMWW.

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General conclusions

Conclusions

In this study, a submerged membrane system for the treatment of olive mill wastewater (OMWW) was built and evaluated about performance process and water quality. The work started studying the matrix OMWW in order to find a pretreatment protocol able to decrease the fouling contaminant concentration and thus increase membrane systems performances. OMWW are a variable and heterogeneous solution that need a flexible process for its treatment. OMWW solution was destabilized by an acid treatment. The right pH variation promoted the deposition of about the 50% of solids and the resulting solution affect less membrane performance.

Subsequently it was evaluated the interaction between OMWW and membrane to identify the type of fouling. The various membranes and feeds tested showed a clear hydrophobic behavior of the fouling and the dimensions of the particles in solution negatively affected more rapidly the performance of membranes with pore size in border between MF and UF. From these results, the hollow fiber membrane type, made of hydrophilized polyethylene, having pore size of 0.4 μm , was adopted as candidate for the submerged microfiltration system.

Submerged membrane system tests were performed at different operation conditions, using raw and acidified OMWW as feed. The obtained results confirmed the system flexibility to treat the OMWW. Permeate resulted clarified; membrane fouling could be removed quickly, without any need of chemical detergents nor back-flushing. All tests were performed with the same membrane module using only clean water as washing medium at the end of each test to resume the initial water permeability of the membrane module. Permeate volume recovery was influenced by the used feed. The use OMWW pretreated with acid and then readjusting its pH value at 4.6 permitted to set the most favorable operative conditions and to produce more than the double of the permeate obtained when using raw OMWW as feed. This system permitted to obtain a permeate with 95% of polyphenols initially present in the raw OMWW. This constituted a good feed for the subsequent membrane processes of UF and NF that could be performed for fractionation and concentration of polyphenols.

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