Purification of Olive Mill Wastewater Using Microfiltration Membrane Technology

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Abstract: Olive mill wastewater (OMWW), a by-product of the olive oil extraction process, is a severe polluting waste, but also a source of antioxidants; polyphenols, especially hydroxytyrosol. This study aimed at investigating the potential of microfiltration (MF) for separating the polyphenols from OMWW. OMWW treatment consisted of a preliminary centrifugation step, followed by MF for the separation of fats and polyphenols.Two types of ceramic MF membranes were used. MF flux ranged between 78 and 95 kg m^{-2} h^{-1}, indicating the applicability of the described process on commercial scale. Better results were obtained with MF membrane of 50 nm pore size, due to its higher porosity compared to the membrane of 200 nm pore size. The optimum operative conditions were transmembrane pressure of 3.5 bar, flow rate of 10 m s^{-1}, and temperature of approximately 55 °C. A 3-month storage of OMWW prior to treatment resulted in a 20% decrease in permeate flux, indicating that direct processing of the OMWW is necessary. Membrane pollution was not a problem for MF operation and did not affect membrane permeability significantly. Restoring the permeability of water to baseline levels after each use, confirmed the successful cleaning regime applied. The microfiltrate was an excellent antioxidant, which contained useful polyphenols, including hydroxytyrosol, tyrosol, *p*-coumaric acid, caffeic acid and catechin.

Keywords: Permeate flux, polyphenols, membrane cleaning, OMWW storage, microfiltration.

1. INTRODUCTION

Olive oil production is a key economic activity in the Mediterranean region. Olive mill wastewater (OMWW), a by-product of the olive oil extraction process, is a mixture of vegetation water containing soft tissues of the olive fruit, and the water used in the various stages of the oil extraction process, and is considered to be a significant polluting waste in all Mediterranean countries. OMWW constitutes a serious environmental problem in the area, mainly due to its low pH, high solids and organic compounds, high COD content, phytotoxic properties and resistance to biodegradation caused by its phenolic compounds [1, 2]. In terms of pollution effect, 1 m^3 of OMWW is assumed to be equivalent to 100 - 200 m^3 of domestic sewage.

On the other hand, however, phenolic compounds from olive fruit and its by-products include a wide range of biological activities, such as antioxidant, anti-inflammatory, antibacterial, and antiviral functions [2, 3]. Natural antioxidants are widely used in the pharmaceutical, cosmetic and food industry nowadays, as currently used synthetic antioxidants have been suspected to cause or promote undesirable effects on human health, and also to contribute towards oxidative degradation of food [4-6]. Olive mill wastewater is an excellent source of natural antioxidants. Thus, OMWW treatment that will allow for phenols collection may lead to economic benefits [7].

One of the most promising methods for the treatment of OMWW, considering effectiveness, environmental impact and cost, is membrane filtration [2]. Membrane technology reduces the OMWW organic load and suspended solids content [1, 3, 8]. Microfiltration (MF) and ultrafitration (UF) may be used as a primary treatment step, while nanofiltration (NF) and reverse osmosis (RO) for the final treatment of OMWW [3], or alternatively a pretreatment step could be employed, such as separation with centrifugation, filter-press, vacuum pressure filtering, screening [9-11] and afterwards final treatment using MF or UF. It is reported that OMWW using MF technology, without a pre-treatment step, is possible to reduce oil and grease content by about 94% [1].

Membrane fouling, however, is a common problem related to OMWW purification that severely reduces the permeate flux, resulting in changes in both membrane selectivity and permeability. In general, there are two important parameters for consideration regarding the treatment of olive mill wastewater with membrane technology: a) the extent of separation of the

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polyphenols from the mass of waste, and b) the filtration flux of the membranes used. The degree of separation is important because in the case that polyphenols are efficiently separated from the mass of liquid waste, then olive mill wastewater can be handled as common wastewater and be fed into biological treatment, or used for crop irrigation. Furthermore, the polyphenols separated may be utilized in the pharmaceutical and cosmetic industry.

In this study, two commercial MF membranes with different properties are used to separate the polyphenols from oil substances. The effects of temperature, flow rate, transmembrane pressure, membrane pore size and OMWW storage time on the membrane performance during OMWW treatment process are investigated. Also, the efficiency of the membrane cleaning was studied.

2. MATERIALS AND METHODS

2.1. Olive Mill Wastewater

The olive mill wastewater used in this study was collected from "Tsakiridis" olive mill, in Pournari, Larissa, central Greece. The olive oil extraction process employed was the typical three-phase decanter centrifugation. The raw OMWW produced was centrifuged at 1200 rpm using a rotary finisher bearing a stainless screen with holes of 150 μm diameter.

2.2. Microfiltration (MF)

The pretreated OMWW was microfiltered to separate the polyphenols (permeate) from oil substances. The permeate could then be further treated with polyphenol absorbing resins to extract the polyphenols. A microfiltration rig was constructed to carry out the experiments (Figure **1**). The rig consisted of the following elements: i) two 304 stainless steel MF modules, type CMV3-30 (Jiangsu Sainty Machinery I/E Co., Ltd). Each module was constructed to accommodate three MF membranes of the same pore size, resulting in a total surface area of 0.69 m^2, ii) a pump, with volumetric capacity of 50 m^3 h^{-1} and pressure range between 0 and 6 bar, iii) a 1 m^3 feed tank, equipped with a temperature control system, iv) a pressure control system, installed at the entrance of membrane module, and v) plastic flexible pipes, used to interconnect the rig elements.

The two types of MF membrane used were ceramic and commercially available (Jiangsu Sainty Machinery I/E Co., Ltd). The first MF membrane was of 200 nm pore size (CMF 19033-200nm), whereas the second of 50 nm pore size (CMF 19033-50nm). Both MF membranes had a total length of 1178 mm, surface area of 0.23 m^2, and consisted of 19 channels, with channel internal diameter of 25 mm.

The MF process started with membrane cleaning, as described in section 2.3. Following the cleaning

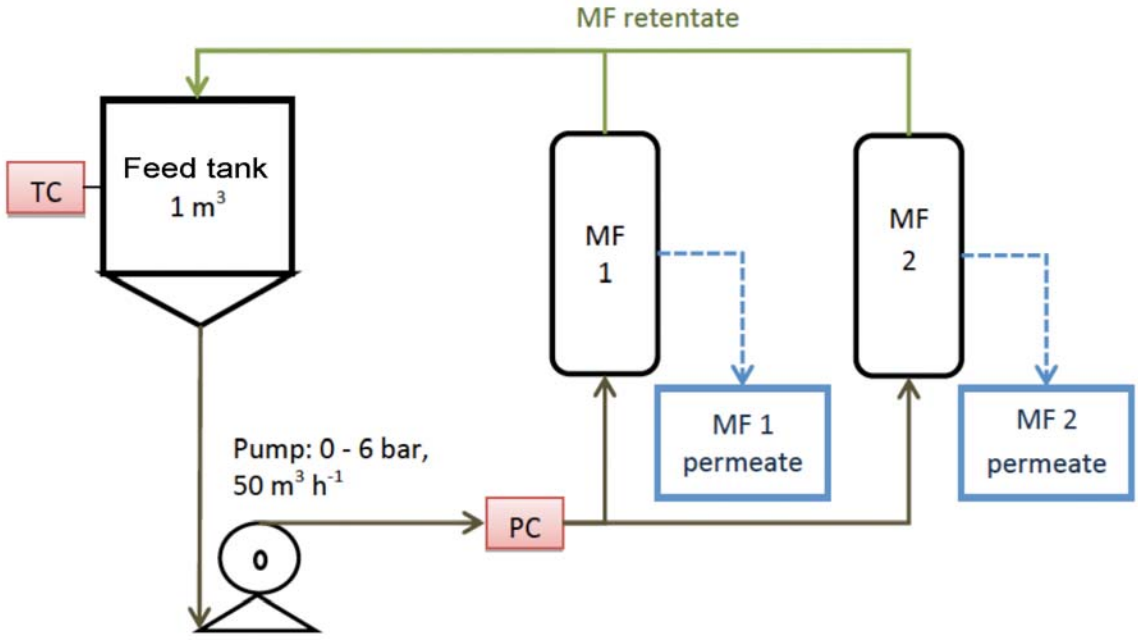

Figure 1: Experimental rig (PC: pressure control, TC: temperature control, MF1: microfiltration module 1, containing three MF membranes of 50 nm pore size, MF 2: microfiltration module 2, containing three MF membranes of 200 nm pore size).

procedure, MF of distilled water took place, aiming at recording a reference flux to be used as "control" for comparison with the flux obtained for OMWW MF at the same experimental conditions, and also to evaluate the effectiveness of the cleaning regime. Following this step, the filtration of OMWW samples commenced. The feed tank was filled up with a quantity of about 1 m^3 of pretreated OMWW. Initially, the temperature was set at 45 °C, OMWW flow rate was 10 m s^{-1} and the membrane flux was measured at transmembrane pressure ranging between 1 and 4.5 bar. Then, at the same temperature (45 °C) and at transmembrane pressure of 2.5 bar, the effect of the following flow rates: 5, 10 and 15 m s^{-1} on permeate flux was studied. Finally, the effect of temperature, within the range of 20 - 80 °C, was investigated at transmembrane pressure of 2.5 bar and flow rate of 10 m s^{-1}.

The performance of the MF membrane was further determined by studying the changes in membrane permeate flux as a function of time, which is also an indication of membrane fouling propensity. MF flux was recorded at 15 s interval by weighing the mass of the permeate produced. MF flux was calculated in kg m^{-2} h^{-1}, using the following equation

$$\text{Flux} = W/(AxB) \quad \text{(Eq. 1)}$$

where W is the weight of the permeate (kg) collected within time B = 1/240 h from a surface area of A = 0.69 m^2.

Measurements were performed at least an hour following the beginning of the experimental rig operation in order to avoid the sharp decrease in the permeability observed due to the initial membrane pollution.

The permeate was collected into a plastic tank, whereas the retentate was returned into the feed tank, where it was mixed with the remaining OMWW sample and then was circulated again for further concentration. The MF process lasted for 20 hours.

The determination of polyphenols in the MF permeate was carried out using high performance liquid chromatography (HPLC) analysis. The equipment utilized was a HITACHI coupled to an autosampler L-2200, pump L-2130, column oven L-2300 and diode array detector L-2455 and controlled by Agilent EZChrom Elite software. The column was a Pinnacle II RP C18, 3 μm, 150x4.6 mm (Restek), protected by a Kromasil 100-5 C18 guard cartridge starter kit for 3.0/4.6 mm id. Column oven was set at 40 °C. Eluent (A) and (B) were 0.02 M sodium acetate adjusted at pH=3.2 with acetic acid and pure acetonitrile, respectively. The flow rate was 1 mL min^{-1} and the injection volume was 20 μL. The elution gradient profile was as follows: started (A) 100%; 3 min, 88%; 10 min, 79%; 12 min, 61%; 18 min, 46%; 25 min, 40%; 28 min, 100%. The elute was monitored at 280 nm for oleuropein, hydroxytyrosol and tyrosol and at 355 nm for flavonols. Total polyphenols was determined according to FolinCiocalteu method.

2.3. Membrane Cleaning

Once the MF process was completed, the membranes were cleaned in order to prevent the reduction of membrane permeability due to particle depositions onto membrane surface, and also to investigate the potential of restoring the membrane permeability to its original condition. The membrane cleaning procedure involved liquid circulation under zero transmembrane pressure and lasted approximately 4 h. Both alkaline cleaning (detergents used were: P3-ultrasil 110, P3-ultrasil 69, P3-ultrasil 67 and P3-ultrasil 02) and acidic cleaning (P3-ultrasil 75) was applied. Similar procedure was applied successfully to MF membrane cleaning following slaughterhouse blood circulation [12].

In detail, the cleaning procedure involved the following steps: 1) membrane rinsing with deionized water under maximum flow rate for complete removal of the residual waste, lasting at least 20 min, 2) circulation of a 150 L aqueous solution containing 1080 g P3-ultrasil 69, 480 g P3-ultrasil 67 and 120 g P3-ultrasil 02 (solution temperature was 48 °C) for 45 min, at zero transmembrane pressure and maximum flow rate, 3) membrane rinsing with deionized water for 15 min, 4) circulation of a 90 L aqueous solution containing 360 g P3-ultrasil 75 (solution temperature was 48 °C) for 30 min, at zero transmembrane pressure and maximum flow rate, 5) membrane rinsing with deionized water for 15 min, 6) circulation of a 90 L aqueous solution containing 720 g P3-ultrasil 110 (solution temperature was 48 °C) for 20 min, at zero transmembrane pressure and maximum flow rate, 7) membrane rinsing with deionized water for 15 min, and 8) final rinsing and membrane preservation using 0.1% potassium metabisoulfite solution.

3. RESULTS AND DISCUSSION

3.1. The Effect of Flow Rate on MF Flux

As shown in Figure **2**, the maximum MF flux was observed at OMWW flow rate of 10 m s^{-1}. Higher flow

rate than 10 m s^{-1} resulted in lower flux. The same result was observed with lower flow rate than 10 m s^{-1}. The decrease in flux after reaching the maximum value of approximately 95 kg m^{-2} h^{-1}, was most likely due to the fact that when OMWW flow rate was higher than 10 m s^{-1}, the oil molecules in the OMWW (oil content was about 1-2%) tended to form emulsion, causing the flux to decrease.

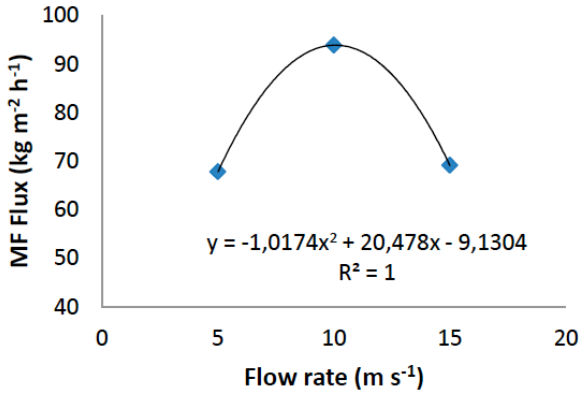

Figure 2: The effect of OMWW flow rate on microfiltration flux (temperature: 45 °C, transmembrane pressure: 2.5 bar, membrane pore size: 200 nm).

3.2. The Effect of Transmembrane pressure on MF flux

OMWW MF flux tripled with increasing transmembrane pressure from 1 to 3.5 bar (see Figure **3**). Further increase in transmembrane pressure to 4.5 bars did not significantly affect the flux. This was mainly attributed to the boundary level which was formed at these pressures due to the existence of macromolecules and fiber in combination with limited oil substances passed through the membranes. Hence, the optimum transmembrane pressure was found to be 3.5 bar.

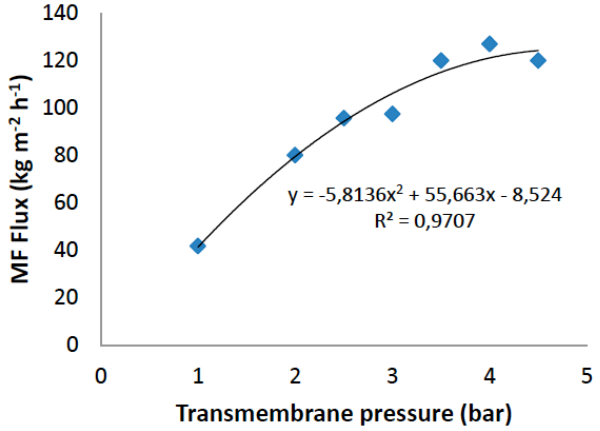

Figure 3: The effect of transmembrane pressure on microfiltration flux (temperature: 45 °C, flow rate: 10 m s^{-1}, membrane pore size: 200 nm).

3.3. The Effect of Temperature on MF Flux

The MF flux increased linearly with the increase in temperature, from 30 to 55 °C, as shown in Figure **4**. As a matter of fact, the value of membrane flux at the temperature of 55 °C was double compared to the flux at the temperature of 30 °C. However, when temperature increased to levels higher than 60 °C, an undesirable polymerization of the material was observed, which resulted in pore blockage. In addition, the presence of polymerized materials could interrupt the flowing pattern of the entire filtration system and because of this, a hot water tank with a spare pump should be placed next to the MF unit for immediate membrane rinsing in the case of flow interruption in order to prevent irreversible membrane damage.

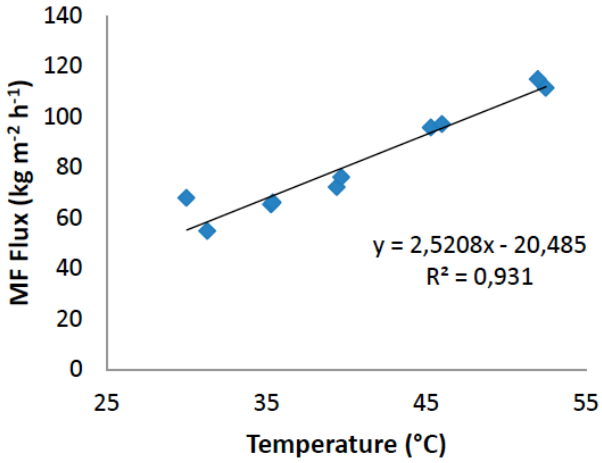

Figure 4: The effect of temperature on microfiltration flux (transmembrane pressure: 2.5 bar, flow rate: 10 m s^{-1}, membrane pore size: 200 nm).

3.4. Membrane Pore Size

During the 20-hour period of continuous operation, the average flux through the MF membrane with the pore size of 50 nm was 95.33 kg m^{-2} h^{-1}, whereas through the MF membrane with the pore size of 200 nm was 78.70 kg m^{-2} h^{-1}. The lower the membrane pore size the higher the flux. This was attributed to the fact that the membrane with the smaller pore size has higher porosity. Similar trends were observed when the membranes were tested with deionized water. It is reported that the average water flux through the MF membrane with the pore size of 50 nm was 626.07 kg m^{-2} h^{-1} (under transmembrane pressure of 1 bar and temperature of 25 °C), compared to 344.35 kg m^{-2} h^{-1} reported in the MF of 200 nm.

With respect to the variation of flux with time during the 20-hour period of continuous operation, the results

for the two membrane types are presented in Figure **5**. There was a mild variation in the flux of the 200 nm pore size membrane, with a slight tendency for decreasing the flux after 15 hours of continuous operation. On the other hand, the flux of the 50 nm pore size membrane showed significant variation through the 20 hour operation period. MF flux increased with time, picked within the third 4-hour period, and then started to decrease. At the end of the 20-hour period, MF flux of the 50 nm pore size membrane was about 22% lower than the initial flux. It is important to note that for both cases, the final value of flux is close to 70 kg m^{-2} h^{-1}, which is significantly higher than that of 15 kg m^{-2} h^{-1}, which is the limit established by the technical and international practice for a membrane process to be considered acceptable, from an economic point of view, for industrial application [13]. It is evident therefore, that there was no problem with membrane fouling during the 20-hour period of continuous operation. The high flow rate (10 m s^{-1}) used acted as a dynamic method of cleaning the membrane surface, thus preventing membrane fouling.

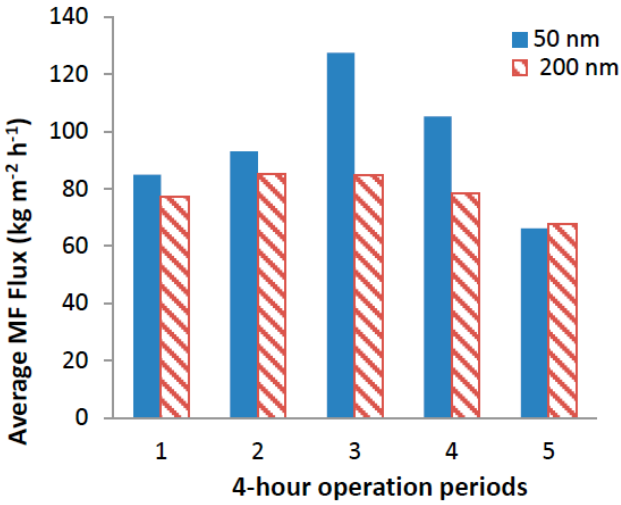

Figure 5: The effect of membrane pore size on OMWW microfiltration flux (transmembrane pressure: 2.6 bar, flow rate: 10 m s^{-1}, temperature: 48 °C).

3.5. Membrane Cleaning

After a continuous 20-hour operation with OMWW, the membranes were cleaned according to the procedure described in section 2.3. Once the cleaning process was completed, the MF flux of deionized water was recorded in order to estimate the effectiveness of the cleaning regime applied. As presented in Figure **6**, water MF flux was varied between 340 and 400 kg m^{-2} h^{-1}, which indicates that the flux remained practically steady. Hence, the membrane cleaning method used was able to restore membrane permeability after its operation with OMWW. Therefore, the suggested cleaning regime could be applied to support the operation of an industrial OMWW purifying unit by MF.

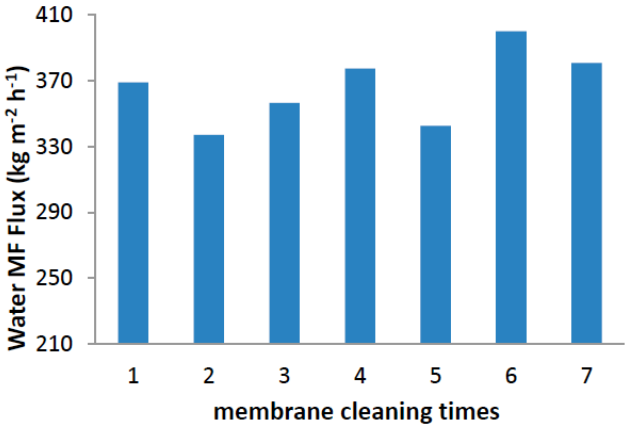

Figure 6: Deionized water microfiltration flux following membrane cleaning (transmembrane pressure: 1 bar, flow rate: 10 m s^{-1}, temperature: 25 °C, membrane pore size: 200 nm).

3.6. Microfiltrate Yield and Quality

Microfiltrate (permeate) yield was found to depend on the storage time of OMWW. In the case of fresh OMWW, the amount of MF permeate produced (microfiltrate yield) was 80% the amount of OMWW processed. In the case that OMWW was processed by MF after a three-month period following its production, microfiltrate yield was 60% the amount of OMWW processed. This was attributed to the lower viscosity of the fresh OMWW compared to the stored one.

The permeate produced was an aqueous solution of low viscosity, dark colour, and the characteristic odour of olive oil. The permeate, with regard to its antioxidant potential, was of good quality, as it contained olive polyphenols, especially hyrdo-tyrosol. Total polyphenols were determined at 38500 ppm on dry matter basis, expressed as gallic acid (Folin-Ciocalteu method). In detail, the microfiltrate consisted of 5000 ppm hydro-tyrosol, 5540 ppm tyrosol, 200 ppm caffeic acid, 420 ppm *p*-coumaric acid (dry matter basis), and also of smaller amounts of anthocyanin, catechin and epicatechin. Permeate total solids content was approximately 10% w/w, and it had 24 °Bx. The pH was 4.5.

4. CONCLUSIONS

From the measured OMWW MF fluxes it is concluded that the described process can be applied to commercial scale, as the average values of flux were

high, in the range of 78 - 95kg m^{-2} h^{-1}. Better results were obtained with the MF membrane of 50 nm pore size, due to its higher porosity compared to the membrane of 200 nm pore size. The optimum operative conditions were transmembrane pressure of 3.5 bar, flow rate of 10 m s^{-1}, and temperature of approximately 55 °C. Higher transmembrane pressure did not cause flux to increase significantly, whilst temperatures higher than 60 °C tended to block membrane pore, and higher flow rates would decrease the flux. MF performance decreased by about 20%, with a shift from using fresh OMWW to 3-months-stored OMWW, which suggested that direct processing of the OMWW is highly recommended. Membrane pollution was not a problem for MF operation, provided that the operative conditions were the appropriate (e.g. the temperature did not exceed 60 °C), and did not affect membrane permeability significantly. Restoring membrane permeability to its baseline levels after each use, confirmed the successful cleaning regime applied. The analysis of the microfiltrate (permeate) showed that it was an excellent antioxidant which contained a number of useful polyphenols, such as hydroxytyrosol, tyrosol, *p*-coumaric acid, caffeic acid and catechin.

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