Desalination and Water Treatment

Olive mill waste water (OMWW) treatment by diafiltration

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Received 3 June 2010; accepted 3 February 2011

ABSTRACT

The present work studied the feasibility of diafiltration for processing olive mill waste water (OMWW). An experimental apparatus, consisted of a tubular membrane accommodation module, a controlled temperature raw material stock tank and a positive displacement pump, was developed to investigate the effects of transmembrane pressure, temperature, membrane type and OMWW dilution on diafiltration flux. Three tubular Ultrafiltration membranes were used, with Molecular Weight Cut Off (MWCO) 8,000, 25,000 and 100,000 Da, respectively. The performance of each one of the three membranes, in terms of UF permeation flux, was studied by using four OMWW:water dilutions (1:2, 1:3, 1:5 and 1:10), at three temperature settings (30, 40 and 60°C). For each one of the 12 respective combination of temperature and dilution setting, six flux measurements at transmembrane pressure values adjusted within the range of 1–6 bars were taken. The experimental results showed that the overall OMWW diafiltration flux, especially in the case of the membranes with MWCO (Daltons) 25,000 and 100,000, was of high magnitude. This fact creates optimism for the commercial follow-up of the process itself by its use as the main component of a promising hybridic scheme for total handling the OMWW pollution problem in an environmentally friendly and sustainable way, according to the EU adopted environmental principle of zero discharge.

Keywords: Diafiltration; High pressure reverse osmosis (RO); Polyphenols; Olive oil mill waste water (OMWW); Membrane methods

1. Introduction

For at least 5,000 years now, olive oil extraction and consumption in the Mediterranean area constitutes an important historical, economic, social and cultural element of the area. The majority of olive oil production worldwide takes place in the Mediterranean region. As a matter of fact, more than three quarters of the annual olive oil production in the world is produced by European Union countries around the Mediterranean Sea (Table 1) [1].

The olive mill waste water (OMWW), which is a mixture of vegetation water with soft tissues of the olive fruit, and the water used in the various stages of the oil extraction process, is considered to be a significant polluting waste in all Mediterranean countries. The difficulty in the OMWW management is mainly due to two facts. First of all, the huge volume of OMWW produced; the annual world OMWW production ranges from about 7 to over 30 million m³ produced...
in a short period of about 3–4 months. Secondly, the severe polluting nature of OMWW, which is evident by its basic characteristics: (a) strong offensive odor, (b) extremely high degree of organic pollution (COD values up to 220 g L$^{-1}$) and a COD:BOD$_5$ ratio between 2.5 and 5 (which is hardly degradable), (c) acidic pH between 3 and 5.9, (d) high content of polyphenols (up to 80 g L$^{-1}$), which are not easily biodegradable and toxic to most microorganisms, and (e) high content of solid matter (total solids up to 20 g L$^{-1}$).

In terms of pollution effect, 1 m$^3$ of OMWW is equivalent to 100–200 m$^3$ of domestic sewage [2]. Its uncontrolled disposal in water reservoirs leads to severe problems for the whole ecosystem and especially for the natural water bodies (ground water reservoirs, surface aquatic reservoirs, seashores and the sea). The most visible effect is discoloration, a result of oxidation and subsequent polymerization of tannins. OMWW also has a considerable content of reduced sugars, high phosphorus content and phenolic load that has a toxic action to certain organisms. Some microorganisms that metabolize sugars develop more rapidly on the expense of other living organisms. The high phosphorus content accelerates the growth of algae resulting in eutrophication. Some aquatic organisms (i.e., the river fish Gambusia affinis and some crustaceans) become severely intoxicated even at exposures corresponding to 1 L of unprocessed OMWW into 100,000 L of circulating water [3].

OMWW dispersion onto the ground and its subsequent metabolization (by microorganisms, insects, earthworms, etc.) to humic extracts or acids could also lead to soil enrichment with nutrients (i.e., organic matter, nitrogen, phosphorus and potassium) and a low cost source of water. However, OMWW high concentration of potassium affects the cation exchange capacity of the soil, leading to alteration of the environmental conditions for soil microorganisms and consequently to changes in the fertility of the soil. Soil porosity could also be affected. Other possible negative effects include the immobilization of available nitrogen and decreased available magnesium, perhaps because of the antagonistic effect on potassium. Finally, no land disposal of OMWW should be undertaken, without taking into consideration its severe phytotoxic and antimicrobial properties which may damage the existing crops [4–7].

The phytotoxic and antimicrobial properties of OMWW are mainly attributed to its phenolic content and some organic acids, such as acetic and formic acid, which are accumulated as microbial metabolites during storage.

As far as its antimicrobial activity is concerned, catechol, 4-methyl-catechol and hydroxytyrosol are its most active compounds against a number of bacteria and fungi [8].

These biotoxic properties of phenols in OMWW constitute a significant inhibitor of the biological processes that take place in common wastewater treatment plants. Such plants do not present the desired performance when treating OMWW. Thus, the co-treatment of unprocessed OMWW with domestic sewage is not economically feasible. So, research is oriented towards more complex treatment methods that usually demand higher capital or operational costs.

Several attempts have been recorded in the literature to develop methods for polyphenol removal from OMWW with target either to utilize them or facilitate the biological treatment of OMWW. An Italian group [9] studied an integrated membrane technology scheme including microfiltration with ceramic or polymeric membranes, ultrafiltration and reverse osmosis aiming at the production of clean water, hydrotyrosol and other useful products. Some other methods [10–13] are also using solvent extraction or supercritical extraction with several solvents in order to isolate the most valuable polyphenol of OMWW which is the hydroxytyrosol. This technology was patented by ENEA and Verdiana Company with international publication number WO2005123603. Fenton’s reagent was successfully used for oxidative pretreatment of OMWW [14] to remove phenolics while in other studies catalysis based oxidation with various inorganic catalysts [15] or biological treatment with laccase or peroxidase (POD) producing fungi were used in order to remove polyphenols from OMWW. Furthermore in a recent study crude peroxidase (POD) extract produced by onion solids was used in order to oxidize OMWW phenolics [16].

The problems mentioned above make the technological design of an OMWW treatment plant difficult.
The factors which contravene the economic design of such a plant are related to the intense and seasonal production of the waste (maximum 4 mo each winter), the great variability both of synthesis and quantity, the high regional scattering of the olive mills and also, the small size of the majority of them in the olive oil producing regions.

An interesting approach to the OMWW problem is the involvement of diafiltration membrane process. According to this method, initially, a low membrane fouling process using UF membranes and diluted OMWW is used to collect the major polyphenol quantity originally contained in OMWW in a filtered thin liquid (UF permeate). Then the polyphenolic solution pass through a selective absorbent resin bed and the polyphenols are adsorbed on the resin and consequently eluted in pure form with suitable solvent and dried into powder by using spray drying technique.

According to the above, the main objective of the present work was to investigate the applicability and performance of the low membrane fouling diafiltration process of OMWW in terms of average permeation flux. Furthermore, it aimed at determining the optimum operational conditions for the diafiltration process in order to intercept an economical operation applied for OMWW treatment.

2. Materials and methods

Samples of OMWW raw material were collected from three different olive mills producing olive oil and located in the rural area around the city of Larissa-Central Greece. The crude OMWW was pre-filtered through a 50 μm mesh screen and kept in a cool storage facility at 0–4°C. A 5 kg sample of this filtrate was used for each experiment.

A small scale diafiltration (DF) rig was constructed to carry out the experiments (Fig. 1). The rig consisted of the following elements:

- A 304 stainless steel tubular membrane module, of 1,200 mm length and 50 mm internal diameter, constructed to accommodate two UF membrane tubes.
- A piston positive displacement pump (HP33 model of MARCO PUMPS Co). The volumetric capacity of
the pump was 30 m³ h⁻¹ and its maximum achievable pressure 50 bars. It was equipped with a pressure relief valve to by-pass the liquid in the case of a blockage and thus, to protect the rig from any circumstance developed overpressure.

• A 6 L jacketed stainless steel (St 304) stock tank, equipped with a temperature control system, which consisted of a Pt100 sensor and a digital display, and also an electrical resistance for heating production, immersed in water, hold in an external jacket of the stock tank.

• Two Analog Pressure gauges, within the range of 0—10 bar, installed at the entrance and the exit of membrane module, respectively.

• A pressure control valve, installed at the output of the membrane module.

• ½” OD Plastic reinforced pipes to interconnect the rig elements.

The three types of UF membrane tubes used were commercially available and are described below:

• PU 608 (molecular weight cut off (MWCO) of 8,000 Da) asymmetric type.

• AN 620 (MWCO of 25,000 Da) asymmetric type.

• FP 100 (MWCO of 100,000 Da) asymmetric type.

All the membranes were produced from polysulphone material, and they were supplied in dozens of 1,200 mm tubes in plastic containers along with their rubber gaskets (two for each membrane tube).

In each experiment a new membrane was used in order to avoid cleaning delay and potentially erratic results because of different degree of cleaning. Once a new membrane tube was installed in the module, cleaning with hot water (60°C) was performed at maximum pump speed and zero pressure (completely open back pressure valve). This cleaning was performed by re-circulating de-ionized water through the tube bore in order to clean the membrane surface from preservatives. The cleaning regime lasted for 30 min. The performance of each membrane was tested first by water and then by OMWW dilutions.

Before any measurement cycle, a time period of about 30 min was left to pass since the first contact of the OMWW material with the membrane. The reason for doing this was to get measurements after the first fouling layer was installed on the membrane (asymptotic flux area) and not at the beginning where, due to the initial built up of the fouling layer, a rapid flux reduction versus time is observed.

3. Results and discussion

The initial membrane performance test, using deionized water, indicated that there was a linear relationship between the water transmembrane flux and the transmembrane pressure (Fig. 2). The fact that the UF membrane with MWCO of 8,000 Da had better performance than the one with MWCO of 25,000 Da was attributed to the difference in the membrane construction material, which can implicate differences in the membrane porosity and tortuosity of the pores.

The level of the raw material dilution, starting from 1:3 OMWW:H₂O and heading to pure water, had a prominent effect on the magnitude of the transmembrane flux. Fig. 3 presents indicatively the effect of the OMWW dilution on the diafiltration flux for the “average” experimental case of the MW 25,000 Da membrane at the operating temperature of 40°C. It is obvious from Fig. 3 that on average a fivefold increase of the transmembrane flux was observed by shifting from the 1:3 OMWW:H₂O dilution to pure deionized
water. Moreover, at all tested dilutions the transmembrane flux was high. In particular, at transmembrane pressure of 5 bar, it ranged from 45 to 145 kg m\(^{-2}\) h\(^{-1}\). Such high values indicate that the membrane performance was capable of supporting a potential commercial use of the diafiltration process as an OMWW treatment method [17].

Furthermore, the temperature of the ultrafiltered material had a remarkable effect on the performance of the membrane. As it is indicated in Fig. 4, an increase of approximately 50% in the transmembrane flux was observed by rising the temperature of the ultrafiltered OMWW material from an initial value of 30\(^\circ\)C to a final value of 60\(^\circ\)C. This finding is in line with the well-known Ultrafiltration theory, which demands an Arrhenius dependence of UF flux on temperature, and explains it in terms of mass transfer. This observation is of particular importance, as the OMWW material is not a sensitive material like food and subsequently, it can be handled at high temperatures to facilitate and improve the Diafiltration/UF process performance.

The membrane MWCO had, in general, a significant effect on the Diafiltration/UF transmembrane flux. As the MWCO increased (Fig. 5) the corresponding flux values for a given transmembrane pressure, temperature and OMWW raw material dilution, were found to increase markedly. Considering the transmembrane pressure of 3 bar (middle of the tested transmembrane range), it can be seen that the flux value at 100,000 Da MWCO was approximately double of the corresponding value at 8,000 Da MWCO and this is due to the larger pores of the 100,000 Da membrane compared to the one of 8,000 Da. However, only a slight difference was notable between the flux obtained by the membrane with MWCO of 8,000 Da and the one with MWCO of 25,000 Da probably due to the higher porosity of the 8,000 Da membrane compared to the 25,000 Da that could counteract the advantage of its larger pores.
Concerning the effect of the transmembrane pressure on the Diafiltration/UF flux (Fig. 6), the well known "broken" UF curves with an initial linear section followed by a reduced slope FLUX versus $\Delta P$ profile, was disclosed by graphical representation of FLUX versus $\Delta P$ (transmembrane pressure). Additionally, the graphical representation of the reciprocal flux versus the reciprocal transmembrane pressure confirmed the linear dependence between these two parameters and the validity of the classical UF membrane performance model [18,19]

$$\frac{1}{\text{FLUX}} = K + \frac{Rm}{\Delta P}$$

or equivalently:

$$\text{FLUX} = \frac{\Delta P}{Rm + K \times \Delta P}$$

where $Rm$ is membrane resistance, $K$ is transmembrane pressure coefficient and $\Delta P$ is transmembrane pressure.

The parameters $Rm$ (membrane resistance) and $K$ (transmembrane pressure coefficient) were determined by applying linear regression statistics using the formula of Eq. (1) along with the measured values of Flux versus $\Delta P$. The following conclusions were drawn by graphically representing them versus OMWW dilution and temperature, respectively:

- $Rm$ was decreasing as OMWW dilution was increasing (Fig. 7). This was due to the lower viscosity of the higher dilutions, which facilitates the passage of the diafiltrate/UF filtrate through the used UF membrane. The trend was more notable with tighter membranes, and also when moving towards highly diluted OMWW.
- $Rm$ was decreasing as temperature was increasing (Fig. 8), due to the effect of the higher temperatures to permeate viscosity which tends to be significantly lower as the temperature rises thus facilitating the permeation through the membrane.
- $K$ was decreasing as OMWW dilution was increasing (Fig. 9). This was because of the lower viscosity at the higher dilutions, which facilitates the passage of the diafiltrate/UF filtrate through the used UF membrane. This trend became more obvious with tighter membranes.
- $K$ tends to be higher at higher temperatures (Fig. 10). This is due to the higher fluxes at higher temperatures which lead to the formation of thicker gel layer
on the membrane surface. This affects accordingly the $K$ parameter which is increasing proportionally to the size of this gel layer.

The results presented in Fig. 6 indicate that a transmembrane pressure increase over 4 bar does not give any significant advantage of higher process performance in terms of permeation flux. Additionally, according to the data graphically presented in Fig. 4, the highest possible temperature within the allowable operational limits of the used UF membranes (60°C) yielded the most favorable flux values. For these two reasons the average flux values of Diafiltration of OMWW dilutions were all determined at 4 bar and 60°C.

Fig. 11 graphically represents the obtained average UF flux versus the OMWW/water dilution at UF membrane MWCO of 8,000, 25,000 and 100,000 Da. The conclusion drawn from the shape and the order of the curves are shown in Fig. 11, is that there is a considerable increase in transmembrane flux as the OMWW becomes more diluted. Moreover, the dependence established between the average transmembrane flux and the OMWW dilution is hyperbolic.

On top of this, the membrane performance improved as the MWCO of the used UF membrane became higher. On the other hand, focusing on the magnitude of the determined average transmembrane UF flux (with the exception of the average flux values obtained by using the tighter membrane - MWCO of 8,000 Da) in combination with the only slightly diluted OMWW, this was exceptionally satisfactory, thus giving the potential of using this process at large commercial scale.

The commercial and practical interest in the Diafiltration process is apparent, since this technique results in the isolation and recovery of the polyphenols in a low viscosity liquid, which comes as the UF filtrate (diafiltrate). Simultaneously, the high viscosity UF retentate will contain less than the 1/10 of the polyphenols contained in the processed raw material. The low viscosity permeate will easily pass through columns filled with resins suitable to remove the polyphenols and organic acids without the problem of column blockage and fouling due to fibrous and viscous material. The output material from the resin column, free of polyphenols, can be concentrated by high pressure RO (reverse osmosis) and then used as hydrofertilizer for crops. In parallel, the eluted polyphenolic solution from the resins column can be used as raw material to obtain high added value polyphenol powder by spray drying which in turn can serve as raw material for producing pesticides and insecticides, or alternatively antioxidants for the food or pharmaceutical industry, or even finally as raw material for the pharmaceutical industry to produce certain medicines.
to prevent heart disease. The idea of this processing scheme is graphically presented, in detail, in Fig. 12 and can be used in a central facility to serve several independent olive mills.

A feature to note in Fig. 12, however, is the high amount of retentate produced, which in fact is as high as the initial amount of the unprocessed OMWW. This retentate could be utilized by spreading it to agricultural land. As mentioned earlier, unprocessed OMWW is often applied to agricultural land, aiming at treating/disposing the wastewater, and simultaneously, improving soil fertility. Research undertaken so far has demonstrated that the application of unprocessed OMWW can increase soil fertility [20, 21] but also can endanger both the crop production and the environment [6, 22].

The main problem associated with the land spreading of the OMWW is related to its severe phytotoxic and antimicrobial effect, which is mainly attributed to its polyphenolic content. Rinaldi [7] demonstrated that unprocessed OMWW application to durum wheat at its early growth stage (3–5 leaf stage), using low rates (50 t ha\(^{-1}\) yr\(^{-1}\)), resulted in short-term partial leaf necrosis and slow emission of secondary stems. The crop, however, managed to recover, and eventually OMWW application had no negative effect on the grain or straw yield of the crop at the end of the growing season. Saadi [22] observed lower phytotoxicity on cress with increasing dilution of raw OMWW, which they attributed to lower phenol concentration, lower pH and EC and/or potentially lower content of other compounds, such as fatty acids. By using the Diafiltration process shown in Fig. 12, both the OMWW is diluted and also the majority of polyphenols, and in particular those with the lower molecular weight which are more toxic for microorganisms, permeates the membrane and thus the retentate content of polyphenols is low. Consequently, the land spreading of the retentate is likely to result in considerably limited phytotoxic effect. Potential risk to groundwater may result from both the presence of polyphenols, which constitute toxic contaminants, or from the transport of high BOD organic material, which in turn may cause oxygen depletion to the water bodies [22]. Research has shown that calcareous heavy soils are capable of effectively reducing the organic load of the unprocessed OMWW, even at high application rates [21]. The BOD value of the retentate is still high and therefore care should be taken when applied to sandy or shallow soils. Applying the retentate using the low rates (50 and 80 m\(^3\) ha\(^{-1}\) for

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*Fig. 12. An overview of the proposed new principle of zero discharge OMWW treatment.*
the pressure and centrifuge method, respectively) suggested by the Italian law [6] is likely to be safe for both crop production and the environment. But higher rates of application may also be rational for our retentate. Research is necessary to determine the agronomic and environmental effects of the retentate on different soils and crops, so as to develop a proper application regime for sustainable agricultural use.

An additional advantage of this method (Diafiltration), compared with the original idea of using cross-flow ultrafiltration (UF), is that the membrane itself does not come in contact with highly concentrated, and thus highly polluting, solution, as it happens in the case of UF. This protects the UF membranes from a premature destruction, caused from the organic material which irreversibly blocks the pores, and thus significantly extends the self-life of the membranes, lowering accordingly the operational cost.

4. Conclusions

From the measured OMWW Diafiltration fluxes it is concluded that this process can be applied in commercial scale as the average values of flux were high, in the range of 74–144 kg h⁻¹. The optimum operative conditions were transmembrane pressure of about 4 bar and temperature of approximately 60°C. Higher transmembrane values do not cause significant flux increase while higher UF temperatures will certainly cause problems to the membrane (e.g. compaction). The Diafiltration performance was higher at higher temperatures, higher dilutions and higher membrane MWCO. The well known UF model was found to fit perfectly the experimental data of transmembrane flux versus transmembrane pressure and there was an exponential type dependence of the DF flux on the OMWW dilution for all the tested membranes. The incorporation of the Diafiltration process in a combined OMWW processing scheme (including according to Fig.12, Diafiltration, absorption of polyphenols on special resins, desorption/elution of them and polyphenol powder production by spray drying, and agro-products production) aims at fully extinguishing and converting the OMWW in useful materials of commercial added value, which is the target and the ultimate goal of the present investigation.

Acknowledgements

This work was carried out in partial fulfilment of a MSc Thesis (Dissertation) in the Master’s Degree Course “Production of Quality Plant and Animal Products in Mediterranean Environment”, which was co-organized by the Technological Educational Institute of Larissa, Greece (Dept of Animal Production and Dept. of Bio-systems Engineering) and the School of Agronomy at the University of Bari, Italy. The authors wish to express their gratitude to the organizing committee for their kind financial and moral support.

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