RECOVERY OF POLYPHENOLS FROM OLIVE MILL WASTEWATER BY NANOFILTRATION

MANSOUR JAHANGIRI,[*] AHMAD RAHIMPOUR,[**] SINA NEMATI[*] and MOBINA ALIMOHAMMADY[*]

[*]*Faculty of Chemical, Petroleum and Gas Engineering, Semnan University, Semnan, Iran*
[**]*Faculty of Chemical Engineering, Industrial University of Babol (Nooshirvani), Babol, Iran*
✉ *Corresponding author: Mansour Jahangiri, mjahangiri@semnan.ac.ir*

Received December 19, 2014

In this research, the efficiency of an integrated acid cracking–membrane filtration system in the treatment of olive mill wastewater (OMW) was investigated. OMW was pretreated by acid cracking and subjected to three stages of microfiltration (MF) through membranes with nominal pore sizes of 50, 5 and 0.2 µm. These stages led to reductions of 99%, 23% and 52% in the content of suspended solids, total phenols and chemical oxygen demand (COD), respectively. Then, MF permeates were subjected to ultrafiltration (UF), followed by nanofiltration (NF). The COD and the amount of phenolic compounds obtained as a result of UF were of 50.2% and 60.8%, respectively. NF showed high efficiency in decreasing COD (more than 90%) and in the removal of phenolic compounds (78.3%), as well as moderate desorption of mineral salts (41%). Also, the effect of operating parameters, such as pressure and volume reduction factor (VRF), on the membrane flux was investigated. The results achieved are in good agreement with those reported in the literature.

Keywords: chemical oxygen demand, nanofiltration, olive mill wastewater, phenolic compounds, ultrafiltration

INTRODUCTION

Olive mill wastewater (OMW) is a mixture of solid materials and black liquid. It contains phenolic compounds, fats and organic acids, which have a harmful effect on soil. Thus, the direct dumping of OMW into the environment is prohibited by legislation, which allows discharge only when the effluent meets standard values. Plenty of water is used in conventional olive oil extraction units, which produces a significant volume of wastewater. The olive oil mill wastewater contains water (80-83%), organic components (15-18%) and inorganic components (2%) (mainly, potassium, sodium and phosphate). Furthermore, the effluent is acidic (pH=4-5) and comprises plenty of oil.[2] The maximum chemical oxygen demand (COD) of olive oil wastewater[3] can exceed 200 g/L. It has been reported that the use of biological treatment methods for this type of wastewater is difficult, due to the presence of toxic substances.[4] Thus, the wastewater coming from olive oil mills has a 100-200 times higher pollution load than that of urban wastewater.[5] Uncontrolled release of these effluents into water bodies will lead to serious problems for the entire ecosystem, especially for natural water sources.[6]

On the other hand, some of the constituents of OMW, which make it most toxic and cause serious pollution to the environment, can be exploited both to the benefit of oil mills and of the community. For example, olive oil mill effluents contain a high percentage of organic material, which can be turned into a fertilizer for agricultural activities to bring nutrients to the soil.[1] Also, OMW contains a significant amount of phenolic compounds, which are natural antioxidants and could be valorized in pharmaceutical, health and food industries[7-8] to help prevent heart disease and cancer. Therefore, different techniques were proposed for olive oil wastewater treatment, either individually or in a combination of two or more methods in order to diminish the pollution load and allow the separation of useful constituents.[9-13]

The construction of wastewater treatment units imposes huge costs to companies.

Therefore, particularly owners of small family businesses would be reluctant to embrace such a project. In this context, it is important to choose a method of treatment, which would be both simple and economical. Membrane filtration processes can be considered as an option, as they present a significant number of advantages, such as reduced energy consumption, low space requirement, variation in size and shape, low pressure requirement, high mass transfer, high separation efficiency, low need for additives and solvents, simplicity of design, ease of handling, easy scale-up to an industrial level and environmental friendliness, which makes them highly distinct from other separation methods.[14] A literature review shows that few works using membrane processes, especially an integrated membrane system of MF-UF-NF, have been carried out to achieve the separation of phenolic compounds from wastewater. Therefore, this study investigates the use of an integrated MF-UF-NF system to treat olive oil mill wastewater, the use of nanofiltration being especially important in this process.[15-17] The objective of the present research is to attain the separation of phenolic compounds by this integrated membrane filtration system.

EXPERIMENTAL

Chemicals and reagents

A sample of olive oil mill wastewater was prepared by a company from the industrial town of Bandar Gaz, Golestan, Iran. The wastewater characteristics are given in Table 1. All the chemicals, such as sulfuric acid and sodium hydroxide, as well as cyanide free reagent and 4-Amino-anti-Perrin reagent, were acquired from Merck, Germany.

Equipment

The following equipment was employed in this work: a reactor and a photometer for measuring COD (Model ET-108, Aqualytic, Germany), a digital UV/visible spectrophotometer (Model 6305), an electrical conductivity meter, a performance evaluation system of helical membrane crossflow and a digital scale with an accuracy of 0.01 g (Model EK-300I, Japan).

Method for measuring COD

In order to measure the COD of the samples, a certain volume of wastewater was poured into vials, stirred and then heated in a digester system at 150 °C for two hours. After that, the vials were cooled to room temperature and the COD values were measured by the spectrophotometer.

Method for measuring phenolic compounds

The amount of phenolic compounds in the sample was measured by the spectrophotometer. For this purpose, an ammonium hydroxide solution was added to the sample and its pH was adjusted to 10±1 using a buffer solution. Then, 4-Amino-anti-Perrin was added to the sample under stirring, followed by the addition of ferricyanide solution and by stirring for 2-3 min. After 15 min, the absorption of standard solutions of the samples was measured by the spectrophotometer at a wavelength of 460 nm. Also, the reduction of phenolic compounds was calculated based on the sample feed.

Acidification and sedimentation methods

At the beginning of the treatment process, the wastewater sample was placed in a tank for settling of suspended solids and was kept still for 1 hour. The pH of the wastewater was reduced to 2 by adding sulfuric acid. After 1 hour, the suspended and colloidal solids from the effluent sample in the settling tank were precipitated due to the pH change. Finally, the precipitated materials were separated from the wastewater through the drainage valve at the bottom of the tank.

Microfiltration method

In order to separate micron-size suspended solids, which were not identifiable in the pretreatment step, microfiltration membranes made of polypropylene (PP) with pore sizes of 50, 5 and 0.2 µm were used. In this step, a low pressure pump was used to create the flow in the microfiltration module and on the membrane surface. Operating pressure and temperature in the microfiltration process were of 0.2 bar and 28 °C, respectively.

Table 1
Characteristics of the olive mill wastewater used in this study

Pollution index	Unit	Amount
COD	g/L	58.1±1
Suspended solids	g/L	16.58±2
Phenolic compounds	g/L	5.3±0.2
Conductivity	mS/cm	14.6
pH	-	1.5±0.1

Table 2
Characteristics of membranes used in this study

Membrane	Company	Membrane material	MWCO*
UF(ARS)	Biocon	Polysulfonamide	20 KDa
NF-70	Filmtec	Polyamide	200 Da

*Molecular Weight Cut Off

Purification using ultrafiltration (UF) and nanofiltration (NF)

In this part of purification, UF and NF spiral modules with an active area of 0.5 m^2 were used. The specifications of these membranes are given in Table 2.

Membrane purification performance

Darcy's equation was used to determine membrane flux (J) as follows:[18]

$$J = \frac{1}{A_m}\frac{dV_p}{dt} \quad (1)$$

where A_m, V_p and t are specific area, phase volume through the membrane and time, respectively.

The following equation was used to calculate the percent of pollutant removal (R):

$$R(\%) = (1 - \frac{C_P}{C_F}) \quad (2)$$

where C_P and C_F are pollutant amounts after and before the purification process, respectively. Also, the volume reduction factor (VRF) was determined by the following equation:

$$VRF = \frac{V_F}{V_R} \quad (3)$$

where V_F and V_R stand for the initial feed volume and retentate volume, respectively.

In order to assess membrane fouling, total resistance (R_t), reversible resistance (R_r), irreversible resistance (R_{ir}), flux recovery ratio (FRR) and flux decline (FD) were calculated by the following equations:

a) Total resistance was calculated using the following equation:

$$R_t = 100(1 - J_v/J_{wo}) \quad (4)$$

where J_v is olive oil wastewater flux through the membrane in steady state condition and J_{wo} is water flux through the neat membrane.

b) Reversible fouling resistance on membrane surface (R_r) was calculated as:

$$R_r = 100[(J_{w1} - J_v)/J_{wo}] \quad (5)$$

where J_{w1} is water flux through the membrane after the washing operation.

c) Irreversible clogging resistance of the membrane (R_{ir}) was calculated as follows:

$$R_{ir} = 100[(J_{wo} - J_{w1})/J_{wo}] \quad (6)$$

d) The flux recovery ratio (FRR) was calculated after cleaning operation by the following equation:

$$FRR\ (\%) = 100(J_{w1}/J_{wo}) \quad (7)$$

e) Flux decline (FD) was calculated using the equation:

$$FD = (1 - J_s/J_i) \quad (8)$$

where J_i is the flux through the membrane in the first 15 min and J_s is the flux through the membrane in the last 15 min of the purification process.

RESULTS AND DISCUSSION

Acidification and microfiltration

The results of acidification and microfiltration are presented in Figure 1. The acidification process contributed to the reduction of the amount of suspended solids in the wastewater from 16.58 to 8.62 g/L, with a removal efficiency of 48%. Also, COD value decreased from 58.2 to 46.2, and the removal efficiency was of 20.5%. This removal may be due to the strong oxidation property of sulfuric acid. The total amount of phenols reduced from 5.3 to 4.34 g/L and the removal efficiency was of 18.1%.

Therefore, the acidification stage could remove a significant portion of suspended solids and colloidal material from the wastewater. This can be useful for reducing membrane fouling in the purification process. A polypropylene membrane was used to separate micron-size suspended solids, which were not identifiable in the pretreatment step. This microfiltration process contributed to reducing suspended solids from 8.62 to 0.086 g/L (99%), total phenols from 4.34 to 3.34 (23%) and COD from 46.2 to 22.1 g/L (52%).

Figure 1 shows that the polypropylene membrane retained the suspended solid materials with an efficiency of 99%. However, the results of microfiltration were not satisfactory regarding total phenols and COD. This may be due to the smaller size of phenolic compounds in the wastewater compared to the pore size of the microfiltration membrane.

OMW flux through UF and NF membranes

For appropriate purification, the effluent that was subjected to the microfiltration step was passed through ultrafiltration (UF) and nanofiltration (NF) membranes. The results of these experiments are illustrated in Figure 2. As can be noted in this figure, in the case of the UF membrane, the OMW flux increases with an increase in the applied pressure. The slope of the OMW flux versus pressure rises until it reaches 6 bar and then, it decreases. This may be related to membrane fouling occurring at higher operating pressure.[19] As for the nanofiltration membrane, the slope of the OMW flux versus pressure goes up to 15 bar, and then slowly increases to 20 bar.

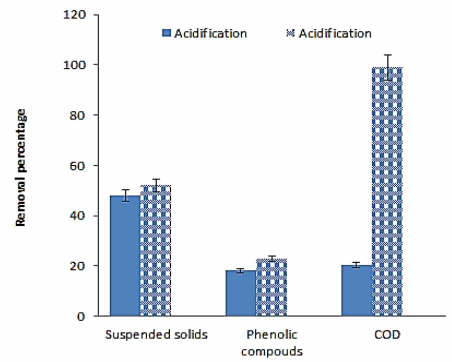

Figure 1: Pollutant removal in acidification and microfiltration stages (error bars with percentage)

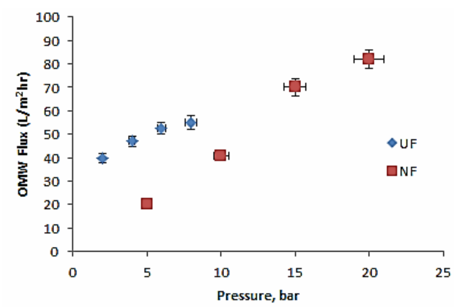

Figure 2: OMW flux through UF and NF membranes versus pressure at T = 28 °C (error bars with percentage)

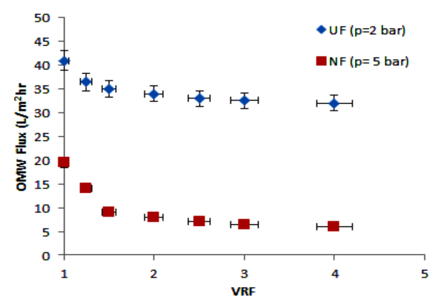

Figure 3: UF and NF membrane flux decline versus VRF at T = 28 °C (error bars with percentage)

OMW flux through UF and NF membranes by VRF experiments

The results of OMW flux through UF and NF membranes obtained as a result of long-term experiments on concentrated olive mill wastewater are shown in Figure 3. In this figure, it can be observed that the olive mill wastewater flux decreased with an increasing volume reduction factor (VRF). Thus, it may be concluded that olive mill waste flux reduction may be influenced by the fouling of the membrane surface.[8]

For a more detailed view, the graph may be divided into two parts. In the first part, the wastewater flow rate through the membrane is reduced sharply to a VRF of 1.5. In the second part, the flux decline is very slow and continues until reaching a steady state condition. Flux decline during the filtration process occurs due to several factors, such as concentration polarization, gel layer formation on the membrane surface and clogging of the membrane pores by compounds in the olive mill wastewater.[8-9] These factors may contribute to a higher resistance on the membrane surface.[9,12] In the first step, polarization may be the cause of flux decline, which occurs rapidly. After that, cake layer formation on the membrane surface may further cause flux decline. The percent of flux decline was calculated using Equation 8 and the results presented in Figure 3 reveal that the UF membrane had a modest flux decline (of 22%), while the NF membrane had a greater flux reduction (of 64.5%).

Resistance and fouling of membranes

In order to analyze the level of fouling and pore clogging in the membranes used in the filtration processes, several parameters, such as R_r, R_{ir}, R_t and FRR, were measured.[10,18] Reversible resistance (R_r), due to polarization and fouling compounds, can be reversed by washing the membrane after the filtration process. In contrast, irreversible resistance (R_{ir}) is related to the fouling of the membrane pores to an extent that the washing method does not help. The resistance values were calculated by Equations 4 to 8. The results obtained for UF and NF membrane fouling and resistance are given in Table 3.

According to Table 3, reversible and irreversible resistance values for UF reached 26.6% and 11.9%, respectively. This is conducive to the desirable anti-fouling property of this membrane. It should be also noted that much of the fouling formed on the surface of the UF membrane was reversible, which may be attributed to its hydrophilic surface and small MWCO. The values of reversible and irreversible resistance for NF equaled 75.4% and 9.8%, respectively. This reveals that the polarization and layer formation make up a larger share of clogging on the membrane surface than the adsorption of compounds onto the surface and inside the pores. The flux recovery ratio of this membrane was of 90%, which led to desirable anti-fouling.

Percent of pollutant reduction of UF and NF

The efficiency of membrane filtration in olive mill wastewater (OMW) treatment was determined by measuring the removal percentage of various compounds present in the OMW effluent. For this purpose, COD, phenolic compounds and conductivity were measured and shown in Figure 4.

Table 3
Clogging of NF and UF membrane modules

	J_{w0}	J_{w1}	J_v	R_r (%)	R_{ir} (%)	R_t (%)	FRR
UF	64	56.4	39.4	6.26	11.9	38.5	88.13
NF	54.3	49	8	75.4	9.8	85.2	90

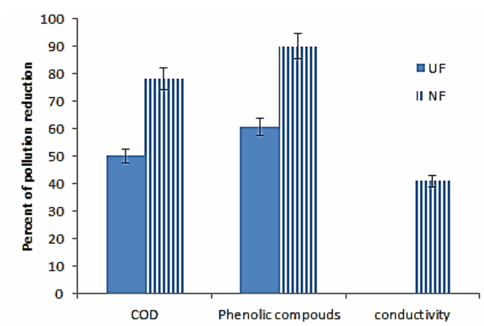

Figure 4: Percentage removal of pollutants by UF and NF membranes (error bars with percentage)

COD value and the amount of phenolic compounds retained by the UF membrane were of 50.2% and 60.8%, respectively. The results indicate that almost half of the compounds have probably passed through the membrane. Further, the UF membrane could not completely expel these compounds. Therefore, the NF membrane was used to better dispose of olive mill pollutants. This membrane showed high removal efficiency for COD (more than 90%), phenolic compounds (78.3%) and moderate desorption of mineral salts (41%). Low desorption of mineral salts by the NF membrane may be attributed to the very small size of these compounds compared to the organic compounds present in the wastewater.[16,19,20]

CONCLUSION

In the present work, the purification efficiency of an integrated MF-UF-NF membrane system was studied on olive mill wastewater. The removal rates of COD, total phenols and electrical conductivity were determined. The effect of pressure on the membrane flux was also investigated. The results obtained have led to the following conclusions:

- The microfiltration process reduced the amount of suspended solids (99%), total phenols (23%) and COD (52%);
- UF allowed obtaining values for COD and phenolic compounds of 50.2% and 60.8%, respectively;

- NF showed good removal efficiency for COD (more than 90%) and phenolic compounds (78.3%);
- The olive mill wastewater flux decreased with an increasing volume reduction factor (VRF). UF and NF purification processes exhibit small changes in the membrane flux after a VRF = 2.5.
- The results of flux decline calculations indicate that the UF membrane had a modest flux decline (22%), while the NF membrane had a greater flux reduction (64.5%);
- Experimental data indicate that most of the resistance exhibited by the filtration membranes in our study was reversible.

Therefore, the study demonstrated that the use of the combined system of acid cracking pretreatment and integrated membrane filtration was quite successful in treating olive mill wastewater to bring it up to the required standards.

ACKNOWLEDGEMENTS: The authors are grateful for the financial support and encouragement provided by the Research Vice Presidency of Semnan University and Faculty of Chemical Engineering of Industrial University of Babol (Nooshirvani).

REFERENCES

[1] A. K. M. Muktadirul Bari Chowdhury, C. S. Akratos, D. V. Vayenas and S. Pavlou, *Int. Biodeter. Biodegrad.*, **85**, 108 (2013).
[2] J. Fiestas Ros de Ursinos and R. Borja-Padilla, *Int. Biodeter. Biodegrad.*, **38**, 145 (1996).
[3] K. Fadil, A. Chahlaoui, A. Ouahbi, A. Zaid and R. Borja, *Int. Biodeter. Biodegrad.*, **51**, 37 (2003).
[4] M. Niaounakis and C. P. Halvadakis, "Olive Processing Waste Management: Literature Review and Patent Survey", 2nd ed., Elsevier, Waste Management Series 5, 2006.
[5] A. Schmidt and M. Knobloch, in *Procs. The First World Conference on Biomass for Energy and Industry*, Seville, Spain, June 5-9, 2000, pp. 452-454.
[6] K. Kestioğlu, T. Yonar and N. Azbar, *Process Biochem.*, **40**, 2409 (2005).
[7] A. El-Abbassi, H. Kiai and A. Hafidi, *Food Chem.*, **132**, 406 (2012).
[8] A. El-Abbassi, H. Kiai, J. Raiti and A. Hafidi, *J. Clean. Prod.*, **65**, 432 (2014).
[9] G. A. Lungotevere and D. R. Thaon, Int. Patent, WO 2005/123603 A1, PCT/IT2005/000327.
[10] N. Azbar, A. Bayram, A. Filibeli, A. Muezzinoglu, F. Sengul *et al.*, *Crit. Rev. Environ. Sci. Technol.*, **34**, 209 (2004).
[11] E. S. Aktas, S. Imre and L. Ersoy, *Water Res.*, **35**, 2336 (2001).
[12] B. Kiril Mert, T. Yonar, M. Yalili Kiliç and K. Kestioğlu, *J. Hazard. Mater.*, **174**, 122 (2010).
[13] F. El-Gohary, M. Badawy, M. El-Khateeb and A. El-Kalliny, *J. Hazard. Mater.*, **162**, 1536 (2009).
[14] E. G. Castello, A. Cassano, A. Criscuoli, C. Conidi and E. Drioli, *Water Res.*, **44**, 3883 (2010).
[15] N. Rahmanian, S. M. Jafari and C. M. Galanakis, *J. Am. Oil Chem. Soc.*, **91**, 1 (2014).
[16] A. Cassano, C. Conidi, L. Giorno and E. Drioli, *J. Hazard. Mater.*, **248**, 185 (2013).
[17] J. Ochando-Pulido, S. Rodriguez-Vives, G. Hodaifa and A. Martinez-Ferez, *Water Res.*, **46**, 4621 (2012).
[18] M. Mulder, "Basic Principles of Membrane Technology", Kluwer Academic Publishers, Dordrecht, the Netherlands, 1996, p. 383.
[19] M. Stoller and A. Chianese, *Desalination*, **191**, 62 (2006).
[20] M. Jahangiri and A. Aminian, *J. Textile Sci. Eng.*, **2**, 5 (2012).