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Treatment of olive mill wastewaters by nanofiltration and reverse osmosis membranes

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ABSTRACT

Treatment of olive mill wastewaters (OMW) by membrane techniques were investigated in this study. For this purpose, OMW was centrifuged, and filtered via UC010 ultrafiltration membrane followed by filtration through NP010, NP030, and NF270 nanofiltration membranes, and XLE and BW30 reverse osmosis membranes. Besides, skipping the ultrafiltration step, the centrifuged OMW was filtered through NP010 and NP030 membranes in order to evaluate the performance of the centrifuging process as a pretreatment option. For the OMW percolated through ultrafiltration membranes, the membrane fluxes reached values of up to 21.2, 5.2, 28.3, 15.5, and 12.6 L $m^{-2}h^{-1}$ for NP010, NP030, NF270, XLE, and BW30 membranes, respectively. The maximum COD removal efficiencies obtained at 10 bars were 60.1%, 59.4% and 79.2% for NP010, NP030, and NF270 nanofiltration membranes, respectively, while they were 96.3% and 96.2% for XLE and BW30 reverse osmosis membranes, respectively. Besides, conductivity removal efficiencies obtained at 25 bars were 93.2% and 94.8% for XLE and BW30 membranes, respectively. Obtained efficiencies are higher than those obtained in the treatment of OMWs with other treatment methods. Thus, it was concluded that membrane processes are a good alternative for the treatment of OMWs. Additionally, the centrifuging process was found to be a promising pretreatment method.

1. Introduction

Olive and olive oil production is an important means of livelihood especially in the Mediterranean coasts. Global olive oil production is 2.88×10^6 tons per year in 2009 [1]. Turkey has one of the most important positions in global olive and olive oil production industry, and has the second and fourth biggest shares in global markets of olive and olive oil production, respectively [2]. Turkey produces olive on an area of 800,000 ha of olive grove with 95 million olive trees.

Olive mill wastewaters (OMWs) are generated in two-phase olive oil production processes along with olive pomace or in three-phase olive oil production processes alone. OMW generation in Mediterranean countries is over 3.0×10^7 m^3 annually [3].

Treatment of OMWs is of great importance and very difficult due to the high organic, phenol, fatty acids, and suspended solids content. It was stated, in previous studies, that biochemical oxygen demand (BOD) of OMWs range from 15,000 to 135,000 mg L^{-1}, while chemical oxygen demand (COD), suspended solids (SS), and pH are between 37,000 and 318,000, 6000 and 69,000 mg L^{-1}, and 4.6 and 5.8, respectively [4–7]. The production process, being batch or continuous, has a great effect on the characteristics of OMWs. Stronger wastewaters are generated in batch processes than in continuous ones due to the lower water consumption.

Due to the above-mentioned properties, OMWs possess great environmental impacts. Besides, olive and olive oil producers suffer from inefficient treatment techniques for OMWs. Anaerobic treatment [8–10], fenton and electrofenton processes [9,11,12], chemical precipitation [12–14], and electrocoagulation process [15–18] were used in previous studies. However, previous research has shown that none of these treatment processes alone offer sufficient treatment efficiencies. Besides, there are no processes for the treatment of OMWs that are accepted and used widely.

Membrane processes have recently become a great topic of research due to their applicability in wastewater treatment. Decreasing costs of installation and operation of membranes favored the use of membrane processes. Of the membrane processes, microfiltration and ultrafiltration are used mainly for primary treatment purposes while nanofiltration and reverse osmosis are used for final treatment. Specifically, reverse osmosis membranes offer so high treatment efficiencies that they are used in a wide range of applications including recovery of materials from industrial wastewaters and treatment of sea water for drinking purposes.

Final treatment of OMWs by membrane processes has not been widely accepted, yet; and limited number of research papers has been published up to date. This study focuses on the investigation of the performance of nanofiltration and reverse osmosis processes in the treatment of OMWs pretreated by centrifuging and ultrafiltration

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Table 1
OMW characteristics.

Parameter	Value
pH	4.6 ± 0.2
Conductivity (mScm^{-1})	5.3 ± 0.2
Turbidity (FAU)	5,111 ± 468
TS (g L^{-1})	24.8 ± 0.5
VS (g L^{-1})	20.2 ± 0.4
TSS (g L^{-1})	6.8 ± 0.7
VSS (g L^{-1})	6.6 ± 0.6
COD (g L^{-1})	40.3 ± 1.0
Soluble COD (g L^{-1})	30.0 ± 0.9
TOC (g L^{-1})	12.9 ± 0.5
TN (g L^{-1})	0.24 ± 0.05
Oil and grease (g L^{-1})	4.2 ± 1.0

processes. Since available literature does not cover the use centrifuging as a primary treatment option, the results from the current study were used to evaluate its performance as a primary treatment step in OMW purification.

2. Materials and methods

2.1. Characterization of the OMW

The wastewater was obtained from a continuous olive-oil producing process (Milas area of Turkey). The characteristics of the raw wastewater are given in Table 1.

Total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), chemical oxygen demand (COD), soluble COD, oil and grease were determined according to the Standard Methods [19]. Total organic carbon (TOC) and total nitrogen (TN) analyses were performed by the Hach Lange IL 550 TOC-TN analyzer.

2.2. Centrifuging process

Centrifuging process was used for primary treatment of the OMW. Beckman Coulter Allegra X-12 centrifuge was used for centrifuging the wastewater for 30 min. at 3750 rpm. COD, TSS, and conductivity of the centrifuged wastewater were measured.

2.3. Membrane processes

The membrane system was supplied from Osmonics® Inc, which was GE SepaTM CF2 membrane cell. The concentrate stream was flowed back to feed vessel while permeate stream was being collected separately as shown in Fig 1. A cartridge filter (10 µm pore size) was used as a prefilter to remove coarse particulates from wastewaters before membrane cell. All membrane experiments were performed at 25 °C with a heat exchanger which is in the feed vessel.

An ultrafiltration membrane (UC010), three distinct types of nanofiltration membranes (NP010, NP030, and NF270), and two distinct types of reverse osmosis membranes (BW30 and XLE) were used in this study. Properties of these membranes are shown in Table 2. The operating pressures were 2 bars for ultrafiltration, 4, 6, 8, and 10 for nanofiltration, and 10, 15, 20, and 25 bars for reverse osmosis.

Prior to application to nanofiltration and reverse osmosis membranes, the OMW was centrifuged and filtered by ultrafiltration membrane. In addition, NP010 and NP030 membranes were used to filter centrifuged wastewater in order to investigate the performance of the centrifuging process alone as a primary treatment option.

After nanofiltration and reverse osmosis processes, COD and conductivity are measured in the treated wastewater. Besides, membrane fluxes in each process were calculated by monitoring permeate flowrates once in a minute.

3. Results and discussion

3.1. Centrifuging and ultrafiltration processes

The change in COD and conductivity of the OMW after centrifuging and ultrafiltration processes is summarized in Table 3.

It is obvious in Table 3 that the primary treatment processes do not affect conductivity values of the wastewater since both of these processes are incapable of removing dissolved solids. However, as a result of particulate separation, COD removal efficiencies of 30.5% and 36.8% were achieved by centrifuging and ultrafiltration processes, respectively. The combined COD removal efficiency of these two

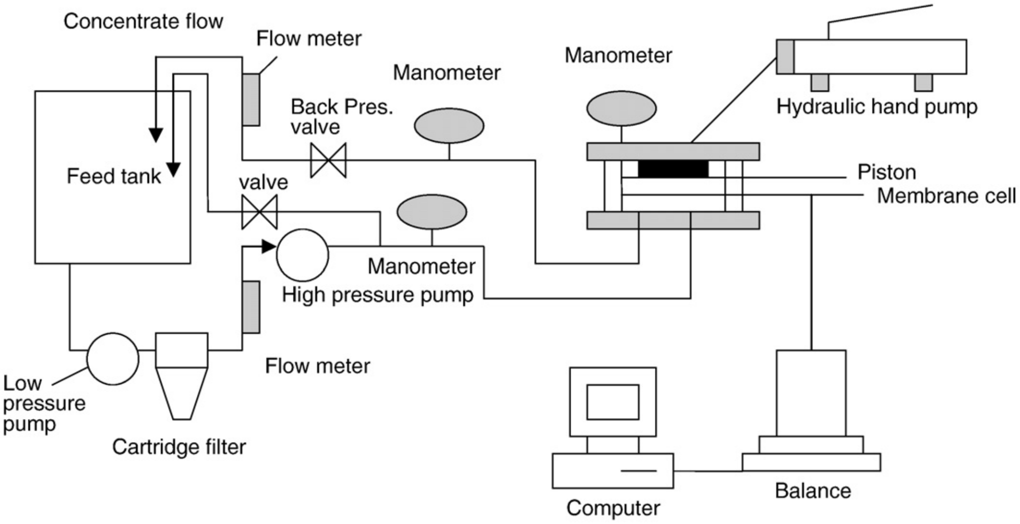

Fig. 1. Schematic diagram of membrane process (adapted from [20]).

Table 2
Characteristics of the ultrafiltration, nanofiltration and reverse osmosis membranes used in experiments.

Membrane type	Manufacturer	Material	Membrane property	MWCO[a], kDa	M.O.P.[b], bar	M.O.T[c], °C
UC 010	Macrodyn® Nadir	Cellulose	NA[d]	10	3	55
NP 010	Macrodyn® Nadir	Polyethersulfone	Hydrophilic	NA[d]	40	95
NP 030	Macrodyn® Nadir	Permanently Polyethersulfone	Hydrophilic	NA[d]	40	95
NF 270	DOW Filmtec™	Polyamide	NA[d]	200–300	41	45
XLE	DOW Filmtec™	Polyamide	NA[d]	NA[d]	41	45
BW 30	DOW Filmtec™	Polyamide	NA[d]	NA[d]	41	45

[a] Molecular weight cut-off.
[b] Maximum operation pressure.
[c] Maximum operation temperature.
[d] Not available.

processes was 56.1% at a membrane flux of 66.9 L m^{-2}h^{-1} in ultrafiltration.

3.2. Nanofiltration processes

Five sets of experimental study were performed using nanofiltration membranes. In the first three, the effluent from centrifuging and ultrafiltration processes was fed to the three types of nanofiltration membranes. The effluent from the centrifuging process was directly applied to NP010 and NP030 membranes in the last two sets. Fig. 2 shows the results from the filtration processes.

As obviously seen in Fig. 2, NF270 provided the highest COD removal efficiency in nanofiltration process while NP010 and NP030, being close to each other, showed lower efficiencies. COD removal efficiencies of all membranes increased with an increase in the operating pressure. The change of COD removal efficiency with respect to the operating pressure showed a linear trend. Highest COD removal efficiencies were observed at 10 bars. At this operating pressure, the COD values of the effluents from NP010 and NP030 (without ultrafiltration) were 11,300 and 11,800 mg L^{-1}, respectively; and COD removal efficiencies were 59.9% and 57.7%, respectively. With ultrafiltration, the effluent COD values from NP010, NP030, and NF270 were 11,200, 11,300, and 5800 mg L^{-1}, respectively. COD removal efficiencies for these sets were 60.1%, 59.4%, and 79.2%.

Membrane fluxes increased linearly with an increase in operating pressure. With ultrafiltration, fluxes of NP010, NP030, and NF270 were 21.2, 5.2, and 28.3 L m^{-2}h^{-1}, respectively, while these values were calculated as 18.6 L m^{-2}h^{-1} for NP010 and 4.0 L m^{-2}h^{-1} for NP030 without ultrafiltration. Performances of membrane processes were also monitored with conductivity measurements. Conductivities of the effluents from membranes are shown in Fig. 3 along with calculated conductivity removal efficiencies.

In Fig. 3, it is obvious that all membranes showed similar degrees of conductivity removal. Conductivity removals in all membranes are lower. Besides, conductivity removal in all membranes showed a linear trend with increasing pressure. Lowest effluent conductivity values under 10 bars when centrifuged wastewater is directly fed to the NP010 and NP030 membranes were obtained as 3.95 and 3.68 mS cm^{-1}, respectively with conductivity removal values of 24.3% and 29.5%, respectively. When ultrafiltration was applied to the centrifuged wastewater, effluent conductivities were 3.90 mS cm^{-1} for NP010, 3.65 mS cm^{-1} for NP030, and 3.61 mS cm^{-1} for NF270 with corresponding conductivity removals of 25.3%, 30.1%, and 30.8%, respectively.

It was proved experimentally that COD and conductivity removals in NP010 an NP030 membranes are not affected by ultrafiltration, that's, the removal rates does not decrease when ultrafiltration was skipped. In contrast, ultrafiltration increased the membrane fluxes. The fluxes increased through NP010 and NP030 membranes increased by 14% and 30%, respectively, when ultrafiltration was applied. Ultrafiltration is considered advantageous because it increases membrane flux in nanofiltration step. However, centrifuging alone is considered adequate as a primary treatment option in the aspect of COD removal.

Since available literature on the treatment of OMWs by nanofiltration membranes is limited, the results of the current study is compared with those obtained in previous research on the use of these membranes for distinct types of wastewaters. COD removal efficiencies in membrane processes depend on the wastewater characteristics and membrane type. For instance, COD removal efficiencies were 98% for dairy wastewaters [21], 96% for alcohol industry wastewaters [22], and 91% for textile wastewaters [23]. Although COD removal efficiencies obtained in this study is lower than these, efficiencies obtained in especially NF270 membranes were comparable with 60% obtained in tomato industry wastewater treatment [24], 78% and 65% obtained in textile wastewater treatment [25,26], and 75% obtained in diluted wastewaters [27]. Besides, compared to those obtained with other two membranes, a higher membrane flux was achieved using this membrane. NF270 membranes were found to be the most successful one in OMW treatment due to their higher flux and higher COD removal efficiency.

3.3. Reverse osmosis

The centrifuged and ultrafiltered wastewaters were filtered through two types of reverse osmosis membranes. Effluent COD values and COD removal efficiencies in these membranes are shown in Fig. 4.

As obvious in Fig. 4, both reverse osmosis membranes showed considerably high COD removal efficiencies in OMW treatment. COD removal efficiencies slightly increased with increasing operating pressure for both membranes. The highest removal efficiencies (with respect to COD values in the effluent of centrifuging process) were 96.3% for XLE membranes and 96.2% for BW30 membranes under 25 bars. Therefore, overall removal efficiencies, regarding the raw wastewater, were 97.5% for both membranes.

Membrane fluxes increased with increasing operating pressure in both membranes. The increases showed linear trends with respect to operating pressure. The membrane fluxes were as high as 15.5 and 12.6 L m^{-2}h^{-1} for XLE and BW30 membranes, respectively.

Table 3
Characteristics of raw and pretreated OMW.

Parameter	Raw OMW	OMW after centrifuging	OMW after ultrafiltration
Conductivity (mS cm^{-1})	5.3 ± 0.2	5.2 ± 0.2	5.2 ± 0.2
COD (g L^{-1})	40.3 ± 1.0	27.9 ± 0.3	17.7 ± 0.4
TSS (g L^{-1})	6.8 ± 0.7	2.1 ± 0.14	0,20 ± 0.01
Turbidity (FAU)	5,111 ± 468	1,060 ± 63	40<

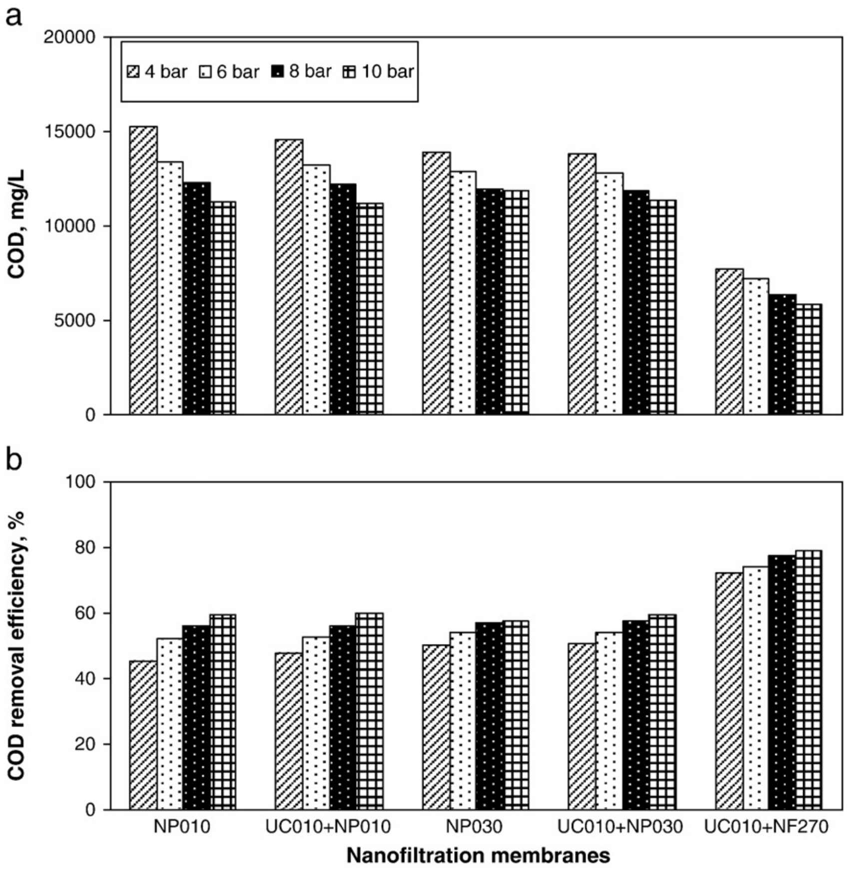

Fig. 2. Permeate parameters from nanofiltration membranes. (a) Permeate COD, and (b) COD removal efficiencies.

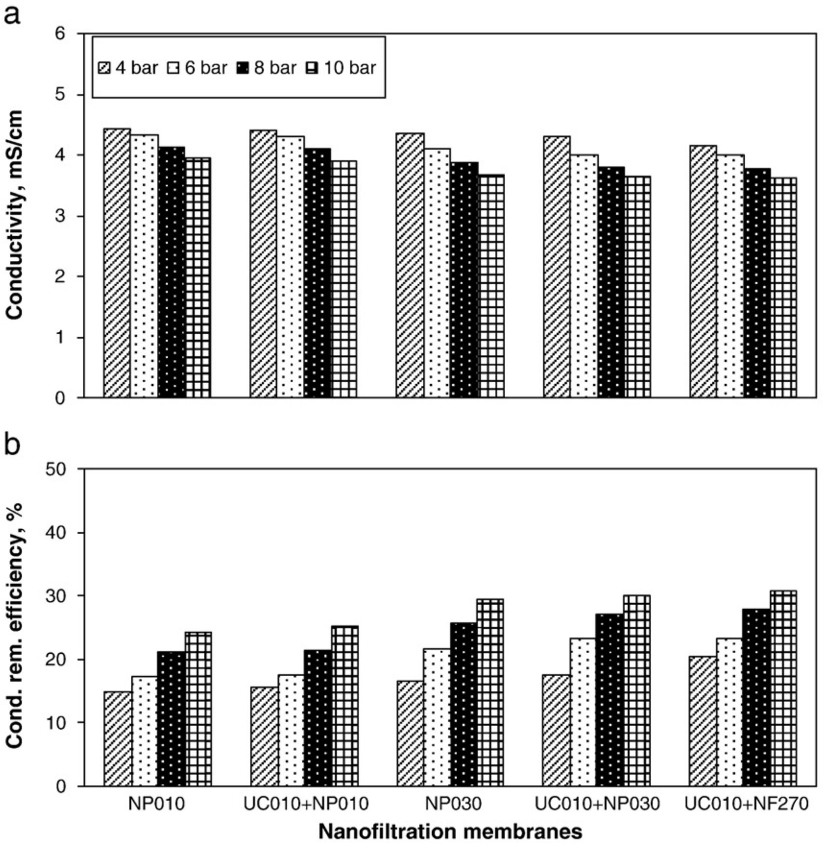

Fig. 3. Permeate parameters from nanofiltration membranes. (a) conductivities, and (b) conductivity removal efficiencies.

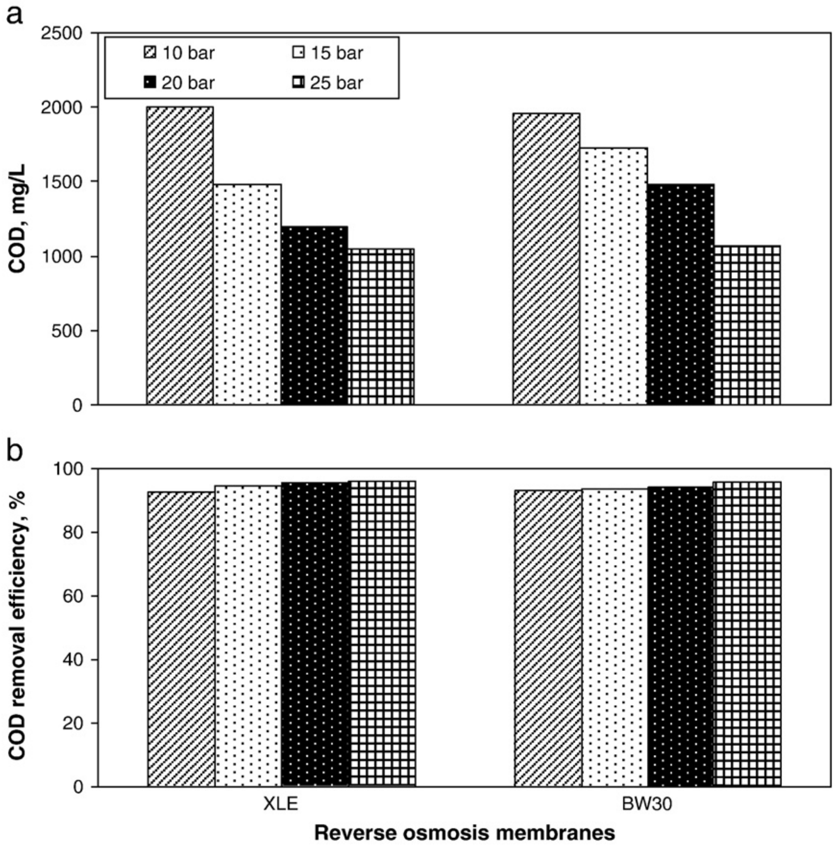

Fig. 4. Permeate parameters from reverse osmosis membranes (a) COD, and (b) COD removal efficiencies.

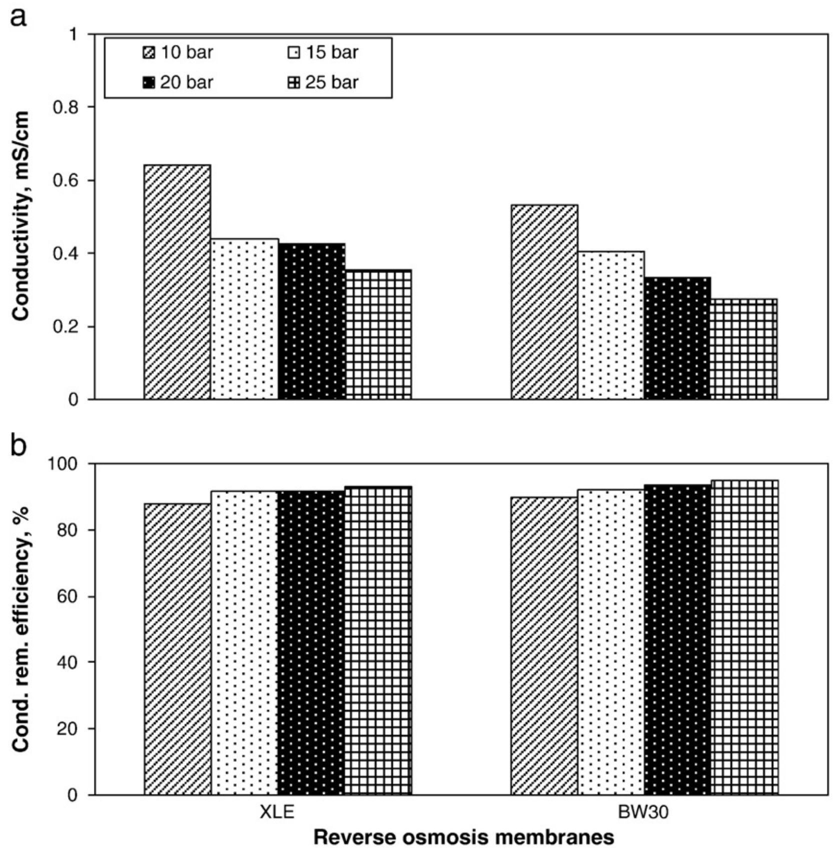

Fig. 5. Permeate parameters from reverse osmosis membranes. (a) conductivities, and (b) conductivity removal efficiencies.

Conductivity measurements were also performed in permeates from reverse osmosis membranes and results are shown in Fig. 5.

Fig. 5 shows that effluent conductivities from reverse osmosis membranes decreased with increasing operating pressure as in the case in COD removal. The lowest conductivity values were obtained as 0.354 and 0.274 mS cm^{-1} for XLE and BW30 membranes, respectively, under 25 bars with corresponding conductivity removal efficiencies of 93.2% and 94.8%, respectively. Even though these values of conductivities were within acceptable ranges for drinking waters, higher effluent COD values were observed, which was considered to be the effect of fermentation products evolved in the storage of the wastewater.

As a consequence, results from the experimental study showed that reverse osmosis membranes can be used as a final treatment option for OMWs. Being free of fatty acids, effluent from the reverse osmosis membranes can be reused in the production process. Although high treatment efficiencies were accomplished with both membranes, XLE membrane showed higher membrane fluxes and COD removal efficiencies than BW30 did.

COD removal efficiencies as high as 97.3% [28] and 97.5% [29] in OMW treatment, 97.7% in tannery wastewater treatment [30], 95.7% in distillery wastewater treatment [31] were obtained in previous studies. COD removal efficiencies with XLE and BW30 membranes were considered satisfactory compared to the results from previous studies.

4. Conclusions

A combination of centrifuging, ultrafiltration and reverse osmosis processes with XLE and BW30 membranes under 25 bars for the treatment of olive mill wastewaters was able to reduce initial COD concentration of 40.000 mg L^{-1} to 1.000 mg L^{-1}. Therefore, overall COD removal efficiencies were 97.5%.

Lower performances were observed in nanofiltration membranes than in reverse osmosis membranes. Among nanofiltration membranes, NF270 membranes were found to be the most applicable one due to their higher fluxes and higher removal efficiencies. Under operating pressure of 10 bars, COD removal efficiencies were 60.1%, 59.4%, and 79.2% for NP010, NP030, and NF270 membranes, respectively. In addition, the effect of centrifuging on the performance of nanofiltration process was also investigated and the results showed that centrifuging alone can be used as a promising option for primary treatment of OMWs.

In conclusion, membrane processes are considered to be more appropriate than others presented in previous research for OMW treatment. Especially, reverse osmosis membranes are capable of producing a high quality effluent from OMW. Further investigation must be done on the reuse of effluents of reverse osmosis membranes.

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