

The Performance of a Hybrid Integrated Forward Osmosis (FO) and Contact Membrane Distillation (CMD) Processes to Treat the Olive Mill Effluents and Recovery of Some Polyphenols

Delia Teresa Sponza^{1*}, Yudum Biyink²

¹Dokuz Eylül University, Environmental Engineering Department Buca-İzmir, Kaynaklar Campus, Turkey; ²Dokuz Eylül University, Graduate School of Natural and Applied Sciences, Environmental Engineering Department, İzmir, Turkey

ABSTRACT

This study investigated a Forward Osmosis (FO) and Contact Membrane Distillation (CMD) hybrid system to treat the pollutants and to recovery of polyphenols from the Olive Mill Effluent Wastewaters (OMEW). The aim is to detect a high quality water production and to detect a strong concentration of the polyphenolic compounds to recoveries them. Before FO; a Polyethylene (PE) membrane filter with hollow fiber was used as pretreatment FO worked as a secondary treatment barrier to remove most contaminants in the feed water and CMD was used to recover the draw solutes from FO effluent and simultaneously produce high-quality reusable water. The effects of increasing temperature on water flux and on the rejection was studied in FO >90% removal yields for COD, TSS and total phenols was detected in the permeate of FO while polyphenols namely catechol, 4-methyl catechol, 2-PHE and 3-PHE were concentrated in the retentate of FO. In the effluent of CMD the removals of pollutants were 99.99% while the polyphenols mentioned above were continued to be concentrated. The total cost to treat the OMEW with zero discharge emission was 0,475 € for treat the 10 m³ raw OMEW. The revenue coming from the all polyphenol recoveries was 165.45 €

Keywords: Forward osmosis; Contact membrane distillation; Olive mill; Polyphenols; Retentate; Permeate

INTRODUCTION

The amount of olive mill wastewater generated is about 5 m³ per ton of produced olive oil with a Chemical Oxygen Demand (COD) around 220 g/l [1]. The high variability of feed composition and, in particular, the presence of antibacterial phenolic compounds, makes OMEW difficult to treat coagulation, chemical precipitation, oxidation by UV radiation, aerobic or anaerobic biological treatment, electrolysis, natural or forced evaporation processes suffer from serious inconveniences such as high cost, low efficiency and sludge disposal problems [1]. Besides, there is no specific process for the treatment of OMEW that is accepted and used widely. Recently, integrated membrane operations for combined OMEW reclamation and extraction of bio-phenols have got relevant interest. The motivation for treating and reclaiming OMEW arises from legislation which constrains its illegal discharge to the environment [1,2]. While good quality water reclamation from OMEW is of interest in industrial applications, the biophenolic fractions have antibacterial properties and hold a wide range of antioxidant, and cancer-preventive activities. In Ultrafiltration

(UF) and Microfiltration (MF) membranes, severe fouling affects the investment costs as a result of reduced membrane lifetime and increased chemical cost [1-3]. Nowadays, Forward Osmosis (FO) is emerging as low-energy demanding membrane operation for dehydration of aqueous solution [4,5]. FO is a membrane process that uses an osmotic pressure gradient as a driving force to transport water across an ideally semi-permeable membrane. Low foulant compaction was detected as a result of the negligible hydraulic pressure gradient in FO membranes [4,5]. The advantageous of FO are low energy consumption, simultaneous treatment of two streams in one treatment step, easy removability of fouling layers due to absence of compression and treatment of liquids that are not suitable for other membrane processes. Therefore, FO holds a great potential to treat wastewater including OMEW, which has high fouling propensity. Hybridization of FO with other membrane operations might be a viable strategy toward near-Zero Liquid Discharge goal, thus exploiting the positive synergistic effects of different process units [6,7]. Contact Membrane Distillation (CMD) is a non-isothermal process refers to a thermally driven transport of vapor through the pores of hydrophobic microporous

Correspondence to: Delia Teresa Sponza, Dokuz Eylül University, Engineering Faculty, Environmental Engineering Department Buca-İzmir, Kaynaklar Campus Turkey, E-mail: delya.sponza@deu.edu.tr

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membranes combining simultaneous mass and heat transfer [6,7]. Direct Contact Membrane Distillation (DCMD) is the most used configuration because the condensation step is carried out inside the membrane module leading to more simple MD [8,9].

In this work, the suitability of FO to treat OMEW was researched. The effects of increasing temperature on water flux and on the rejection in FO were studied. The removals of some pollutant parameters in FO permeate were determined while the accumulation of polyphenols in FO retentate was investigated. Moreover, the possibility of integrating of CMD to FO membrane process was investigated for the removal pollutant parameters and for the recovery of polyphenolic compounds. A cost analysis was performed to determine the overall cost of the sequential process treating 10 m³ OMEW.

MATERIAL AND METHODS

Reactor configuration

Before FO; a Polyethylene (PE) membrane filter with Hollow Fiber (HF) with a pore size 0.42 mm was used as pretreatment of OMEW. The inner diameter of membrane was 0.6 mm while the length of membrane was 110 mm. The FO system consists of a custom-built cross-flow membrane module with two channels for feed, draw and permeate, respectively. The two channels (90 mm long, 30 mm wide and 4 mm deep) are built and separated by parallel membrane coupons. For CMD membrane module a flat-sheet membrane with 42 cm² surface area was utilized. The feed temperature for CMD was kept at 60°C and the distillate temperature was held at 20°C. CMD combines membrane separation and evaporation processes water vapor is transported through the pores of a hydrophobic micro-porous membrane via the temperature gradient-induced vapor pressure difference across the membrane. A flat-sheet membrane (TF200) made of Polytetrafluoroethylene (PTFE) polymer and supported by a polypropylene net was used. Its principal characteristics as specified by the manufacturer are 0.4 μm nominal pore size, 200 μm thickness (support included), 80% porosity and 2.76 × 10⁵ Pa liquid entry pressure of water. In order to reduce membrane fouling and enhance process efficiency, large particles present in OMEW were removed prior to FO with PE-HF membrane filter. Figure 1 shows the used sequential treatment processes (PE-HF membrane, FO and CMD) to treat the raw OMEW.

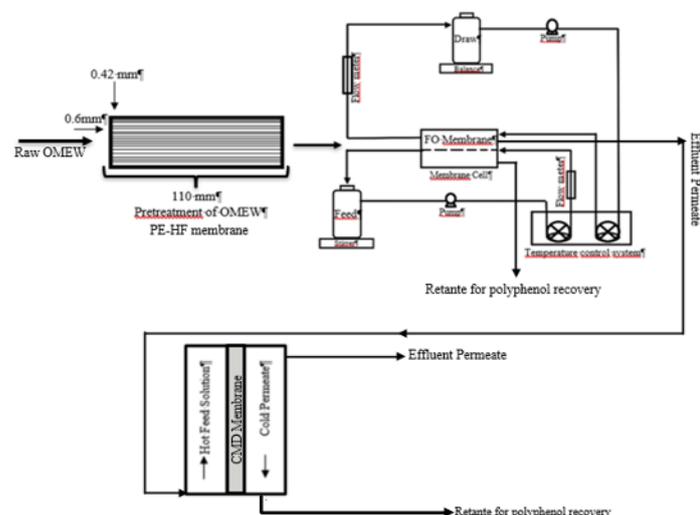


Figure 1: Schematic configuration of sequential treatment processes (PE-HF membrane, FO, CMD).

Analytical procedures

pH, Dissolved Oxygen (DO), Oxidation Reduction Potential (ORP), Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), total nitrogen and NH₄-N were monitored following the Standard Methods [10]. Total polyphenols and individual polyphenols namely Catechol, 4-methyl catechol, 2-PHE and 3-PHE were measured with a high-pressure liquid chromatography (HPLC) (Agilent-1100) with a C-18 reverse-phase HPLC column (25 cm × 4.6 mm × 5 μm, Ace5C-18). The purity of the all individual polyphenols were 99.99% in the effluent of the retentate. The retentate effluent were extracted in soxhlet apparatus with 2 ml hexane and 2 ml Na₂SO₄. Their concentrations were measured in HPLC as before mentioned.

The rejection (α) of a component in the feed solution was calculated by Eq. (1):

$$\alpha(\%) = 1 - \left(\frac{C_{p,t} \times V_{p,t}}{C_{f,0} \times V_{f,0}} \right) \times 100(\%) \quad (1)$$

where $C_{f,0}$ (mg/l) is the initial concentration of any component at the feed reservoir, $C_{p,t}$ (mg/l) is the final concentration at the permeate reservoir after time t , $V_{f,0}$ (L) is the total volume, i.e. the sum of the initial volume and all volumes added to the feed reservoir, and $V_{p,t}$ (L) is the final volume at the permeate reservoir. The conventional pollutant parameters (COD, TSS) and the polyphenols were measured according to Standard Methods [10].

RESULTS AND DISCUSSION

OMEW characterization

The pollutant parameters in the raw OMEW are given in Table 1. As shown in Table 1 the COD and BOD levels are high with high total nitrogen concentrations and elevated polyphenol concentrations. Among the polyphenols the catechol and 4-methyl concentrations were recorded as 16 mg/l and 18 mg/l, respectively.

The effect of pretreatment on OMEW yield

Before FO treatment, the raw OMEW was passed through with Hollow Fiber (HF). This filter reduced the TSS, the COD and the total phenol by 26%, by 25% and by 24%, respectively (Table 2). The COD yields was measured as 27% while no significant losses in Total N and NH₄ concentrations were detected in the effluent of HF. The PE membrane filter improved significantly the flux quality entering to the FO. It provides a channeling effect for liquids by increasing overall flow rate and ensures stability [11].

Table 1: OMEW Characterization.

Parameter	Value	Parameter	Value
pH	4.4	NO ₃ -N (mg/l)	55
DO (mg/l)	0.06	NO ₂ -N (mg/l)	24.2
ORP (mV)	+128.5	Total P (mg/l)	638.7
TSS (mg/l)	57.65	PO ₄ -P (mg/l)	456.1
COD _{total} (mg/l)	112.270	Total polyphenol (mg/l)	60
COD _{dis} (mg/l)	102.275	Individual Polyphenols	
COD _{inert} (mg/l)	57.230	Catechol	16
BOD ₅ (mg/l)	82.030	4-methyl catechol	18
BOD ₅ /COD _{dis}	0.6	2-PHE	5
Total N (mg/l)	259	3-PHE	9
NH ₄ -N (mg/l)	32.9	DOC (mg/l)	67.800

Table 2: The effect of PE membrane pretreatment on OMEW. Effect of transmembrane flux on osmotic pressure

Parameter	Raw OMEW (mg/L)	After PE filter (mg/L)	Removal (%)
TSS	57,65	42.66	26
COD	112.270	84.200	25
COD dis	102.275	80.000	27
DOC	67.800	46.000	31
Total phenol	60	45.6	24
Total N (mg/l)	259	258	0,1
NH ₄ -N (mg/l)	32,9	32	0,02

Effect of transmembrane flux on osmotic pressure

In the beginning of the FO reactor operation, the deionized water containing NaCl as feed and aqueous MgCl₂ as DS were operated. According to Figure 2, trans membrane flux was used as feed. The line between osmotic pressure and membrane flux is linear with a R² value of 0.99. gradient appeared almost linear. Table 3 shows the NaCl diffusion coefficient D and solute transport resistivity K at different DS concentration. Within the concentration range of 1.9 m-3.9 m; D and K showed reduced sensitivity to NaCl concentration (from 2.0 s/m-88 s/m and 1.7 10⁵ s/m) as reported by Gebreyohannes et al. [1] and Alklaibi et al. [6].

Where, the internal polarization is correlated to the draw solute diffusivity resistance (K) into the porous substructure, defined in terms of the membrane structural parameter (S): $S = \delta \times T/\epsilon$, $K = S/D$ (D is the diffusion coefficient).

Effect of crossflow velocity to FO flux

The effect of crossflow velocity on FO was researched by increasing of cross velocity from 1.2 cm/s to 5.2 cm/s. The FO flux increased linearly with a R² value of 0.99 the FO flux was enhanced by 54% (from 3.8 l/m² h up to 15 l/m² h). These results agree with the data performed by Gebreyohannes et al. [1] about OMEW. The overall water and salt permeability coefficients of the membrane, calculated on the basis of water and salt fluxes. They were found to be 0.08 l/m² h atm and 0.011 mol/m² h, respectively. Figure 3 shows that, when crossflow velocity increased from 2 cm/s to 7 cm/s, flux was enhanced by 70% (from 2.2 l/m²h to 7.9 l/m²h) and the osmotic pressure is increased to a certain level and then the osmosis flux increases further. The benefits are progressively reduced at higher crossflow velocity, and a 5,6 cm/s can be identified as optimum for the steady-state conditions of the system. The detected amount of NaCl back-diffusing from draw to feed side after 18 h steady-state lasting during FO reactor operation. This results showed similarities with the data obtained [1,11,12].

Effect of temperature on water fluxes in FO

The high flux (55 l/m²h) was observed at a temperature of 75°C at a flow rate of 16 l/min, while the low flux (37 l/m²h) was detected at the lowest temperature of 25°C at a flow rate of 1 l/min. It was observed that the permeate flux increased linearly as the temperature was increased from 25°C to 75°C (Figure 4). The permeate flux increased with increasing flow rate. The increased flow rate decreased the thickness of the boundary layer by increasing mass and heat transfer [6-9]. This reduced the temperature and the concentration polarization effects and causing increased permeate flux as reported by Alklaibi et al. [6] and El-Bourawi et al. [7]. On the other hand, the difference between vapor pressures of feed and permeate increased due to vapor pressure rises with increasing temperature as reported by Zhang et al. [8] and Rao et al. [9].

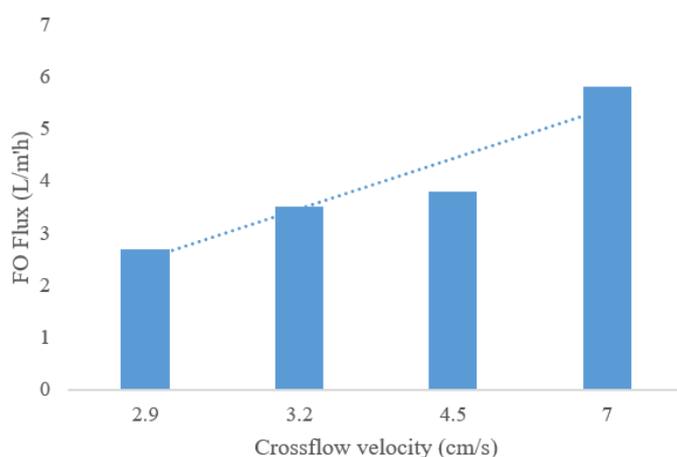


Figure 2: Effect of trans membrane flux on osmotic pressure.

Table 3: Physicochemical properties of NaCl-distilled water draw solute.

Concentration (mol/kg)	μ (10 ³ kg/ms)	D (10 ⁹ m ² /s)	ρ (kg/m ³)	K (10 ⁵ s/m)
0.9	0.8	0.6	591.5	2
1.25	0.9	0.55	614	2.15
1.85	1.05	0.42	653.5	2.85
2.7	1.65	0.19	699.5	6.2
3.7	2.35	0.03	745	43.05

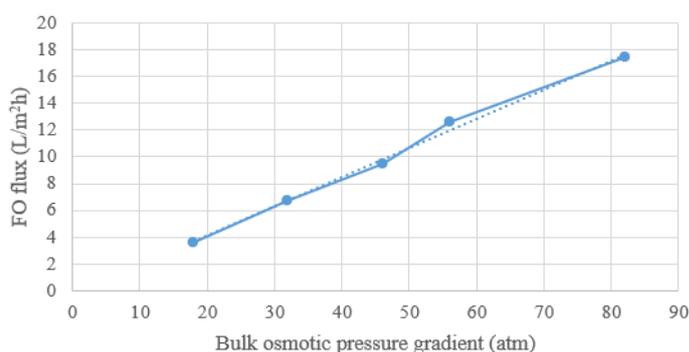


Figure 3: Effect of crossflow velocity to FO flux in the FO reactor.

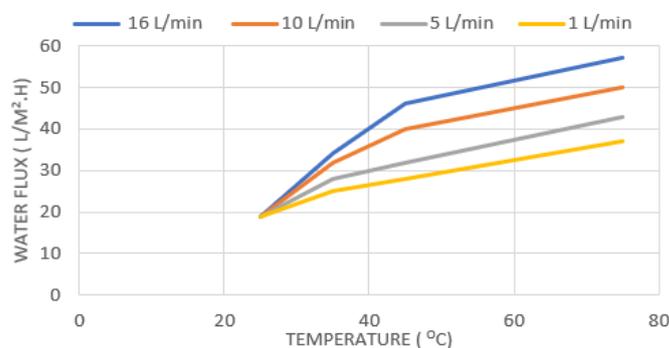


Figure 4: Effect of temperature on water fluxes in FO.

Long term steady-state conditions in FO operation

By taking into consideration the FO flux-recovery analysis and baseline characterization using pure water as feed, 10³ atm and 6 cm/s were selected as optimal conditions to assess the long term operability of FO system. According to Figure 5, cleaning and renewal of DS every 20 h gave the possibility to operate FO system over 112 h. The average recovery was 65.4 ± 0.21% with maximum

recovery of 70% and minimum 35% measured at day 5 and day 8, respectively. VRF is the volumetric reduction factor and can be calculated with Eq (3).

$$1 / (1 - \phi) \tag{3}$$

Where, ϕ is the recovery ratio.

Effect of temperature on phenol rejection in FO

Phenol rejection showed significant changes corresponding to

changes in the trans membrane temperatures and flow rates. The maximum rejection of polyphenolic compounds was 78% in the OMEW. The polyphenol rejection decreased from 77% to 29%-37% when the trans membrane temperature increased from 25°C to 75°C, as shown in Figure 6. This is because a higher trans membrane temperature leads to higher permeation fluxes of both water and phenol and thus a lower phenol rejection as mentioned [13,14].

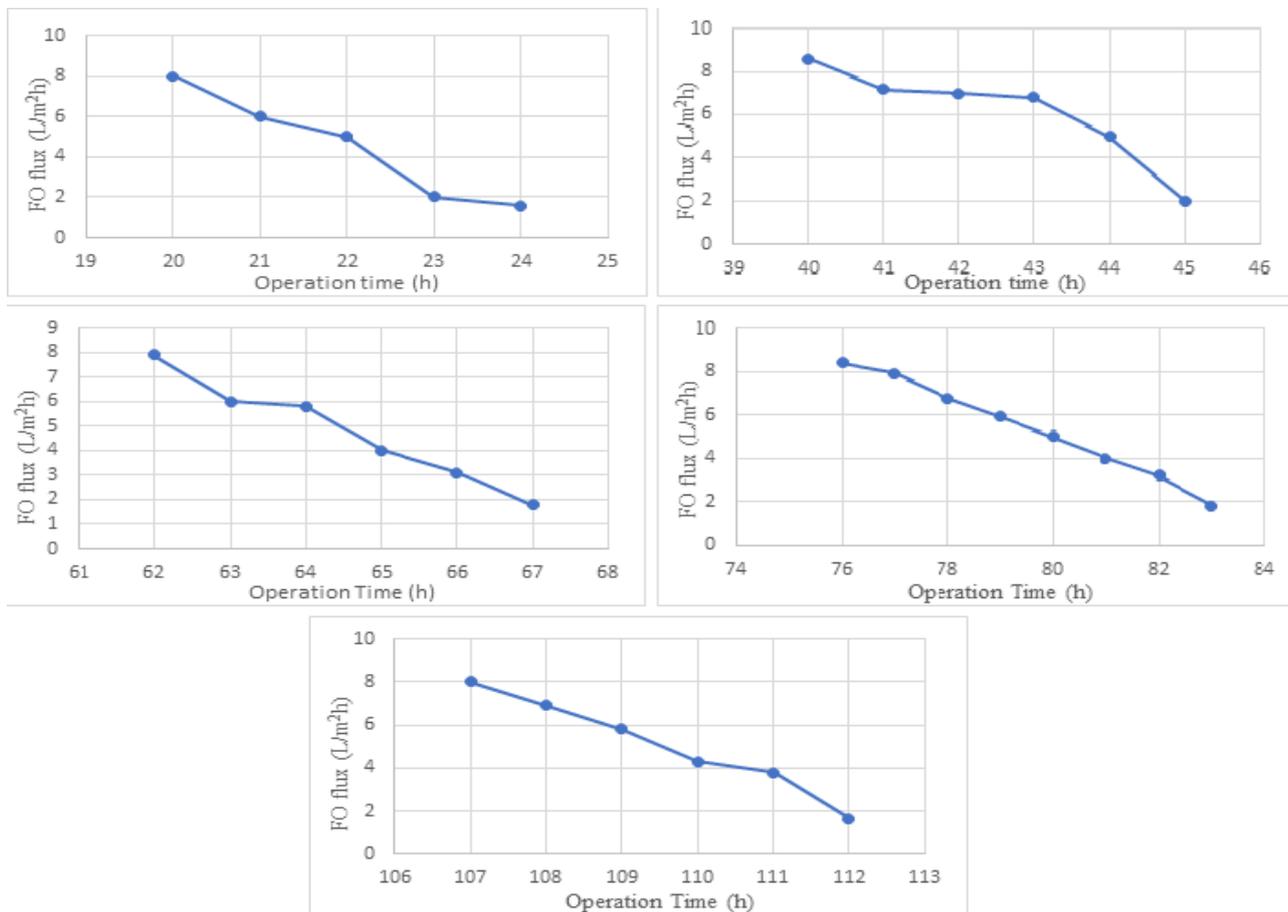


Figure 5: FO-flux recovery analysis during continuous operation period (h).

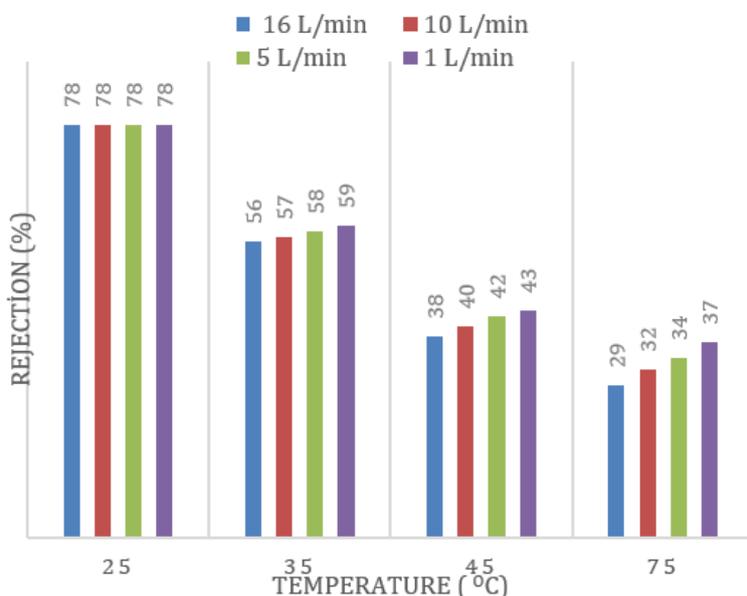


Figure 6: Effect of temperature on phenol rejection in FO versus increasing permeation fluxes.

Influence of draw and feed temperatures on the pollutant removal was researched by some teams. Zhao S et al. [15] reported similar data with our studies indicating that an increase of the temperature led to higher $J_{WP,Exp}$ and reverse salt flux values since at high osmotic pressures the diffusivity of the NaCl increased. Goosen et al. [16] and Phuntsho et al. [17] mentioned that the increase of the $J_{WP,exp}$ at high temperatures can be occurred by the decrease of viscosity, increase of the diffusion coefficient and increase of the number of water molecules. The increase of the flux and the RSF increased the NaCl diffusivity. This can be affect the pore size in the FO membrane throughout active layer based on the difference between osmotic pressure and NaCl diffusivity as reported at high temperatures [16].

Performance of FO

Table 4 shows the pollutant parameters in the permeate and retentate of FO. Based on the optimum FO flux of 37 l/m²h and at a flow rate of 1 l/min at 25°C temperature; the concentrations of individual polyphenolic compounds namely catechol, 4- methyl catechol, 2-PHE and 3-PHE were 3 mg/l, 4 mg/l and 1 mg/l while the levels of these polyphenols concentrated in ret ante of FO. The COD and TSS yields were 99% and 84.38%, respectively, compared their concentrations in raw OMEW. The polyphenol also were rejected from the retentate of FO. In our study, the recovery of polyphenols (45%-59%) were high than the study performed (23%-39%) [11].

Performance of CMD

The efficiency of CMD to treat the concentrate OMEW was evaluated using the phenolic compounds separation factor Eq (4).

$$\alpha = \left(1 - \frac{C_p(t)}{C_{F0}} \times 100\right) \quad (4)$$

Where, $C_{p(t)}$ is the concentration of total phenolic compounds in the permeate versus t (time), and C_{F0} is the initial concentration of phenolic compounds in the raw OMEW. In order to determine the variation of the polyphenol concentrations in the permeate and retentate of CMD factor (β) was defined with Eq. (5).

$$\beta = \frac{C_R(t)}{C_{F0}} \quad (5)$$

Figure 7 shows the concentration factor, β , versus operating time of CMD under two different temperatures (25°C and 38°C). β were calculated as 2.1 and 3.9 at 25°C and 56 °C temperatures, respectively, during 16 h continuous operation. The separation factor (α) was close to 99% during the first 14 h of OMEW treatment by CMD. After 16 h continuous operation, α was 98%. This can be explained probably by the wetting of some membrane pores during pore size distribution and from the temperature

differences at 38 °C and 25°C since the permeate flux at 56°C is higher than the temperature at 25°C. The effluent of the CMD can be used as irrigation purpose since α is high (Table 5). The data is higher than the data obtained [18-20].

First, the FO process removes most pollution parameters in the raw OMEW, thus potentially diminishing the fouling and wetting problem for CMD process. Second, the CMD successfully recovers the draw solution for the FO process, enabling a constant water flux for FO. Third, the synergistic removal capability of FO and CMD enabled the production of extremely high-quality product water. Performance of CMD process is shown in Table 5.

The ret ante yields for polyphenol recoveries and permeate yields found in this study were higher than the studies performed [18-20].

Cost analysis

A cost analysis was performed for all sequential treatment processes used to detect the overall cost spent to treat 10 m³ raw OMEW (Table 6). For PE-HF pretreatment filter the total cost was 0,012 € with a pump and electricity cost of 0,016 € and 0,061 €, respectively. The cost spent for FO reactor system was calculated as 0,265 € while the total cost for CMC membrane reactor system, membrane separation and evaporation processes was 0,198 €. The overall cost to treat 10 m³ raw OMEW was 0,475 €. This cost was extremely low compared to the studies performed [18-20].

Recoveries of catechol, 4-methyl catechol, 2-PHE and 3- PHE

The catechol, 4-methyl catechol, 2-PHE and 3-PHE total

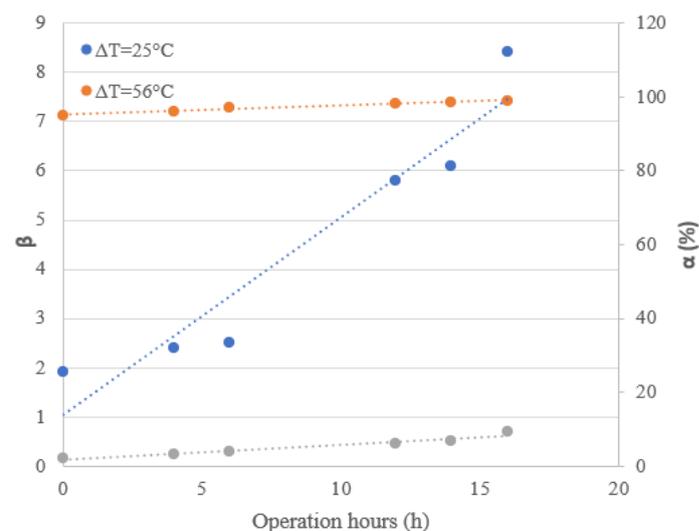


Figure 7: Evolution of the concentration factor, β , of OMEW polyphenols in feed and the polyphenols separation coefficient, α , during CMD at two different temperature conditions.

Table 4: Performance of FO.

Parameter	Raw OMEW (mg/l)	Permeate FO (mg/l)	Ret ante FO (mg/l)
TSS	57.65	9	-
COD	112270	1250	-
COD dis	-	-	-
Total phenol	60	9	86
Catechol	16	3	38
4- methyl catechol	30	4	32
2-PHE	5	1	8
3-PHE	9	1	8

Table 5: Performance of CMD.

Parameter	Raw OMEW (mg/l)	Permeate CMD (mg/l)	Retentate CMD (mg/l)
TSS	57,65	1	-
COD	112270	2	-
COD dis	-	-	-
Total phenol	60	1	98
Catechol	16	0	47
4-methyl catechol	30	1	37
2-PHE	5	0	16
3-PHE	9	0	16

concentrations concentrated from the effluent of CMD ret ante were 47 mg/l, 37 mg/l, 16 mg/l and 16 mg/l respectively. The total support coming from these recovered polyphenols was 165.45 € which this was extremely high than the cost spent to operate the sequential processes. The high phenol recoveries obtained in this study are comparable high than the polyphenol recovery yields calculated [18-20].

CONCLUSION

This study was performed to detect a zero liquid discharge and to valorise the products. The FO process removes most pollution parameters in the raw OMEW, and concentrates the polyphenols. The CMD successfully continue to concentrate the polyphenols and recovers the polyphenols in the concentrate. The synergistic removal capability of FO and CMD enabled the production of extremely high-quality OMEW in the permeate. The maximum COD and TSS yields were 99,99% after sequential FO-CMD treatment while the total phenol yield also was detected as 99,98%. The outlet concentration of each parameter is associated with the amount of water transferred through the membrane. The optimum flux cause increase the pollutant concentration in the permeate while the polyphenols were concentrated in the retentate for recovery.

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