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Research Article

Treatment of Olive Mill Effluent with Sequential Direct Contact Membrane Distillation (DCMD)/Reverse Osmosis (RO) Hybrid Process and Recoveries of Some Economical Merits -

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ABSTRACT

In this study, a sequential Direct Contact Membrane Distillation (DCMD) and a Reverse Osmosis (RO) hybrid membrane system was used to treat the pollutants (Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Total Phosphorous (TP), Total Nitrogene (TN) and total polyphenols) present in the olive mill wastewater. The effects of permeate flux and pressures on the removals of pollutant parameters were studied. Furthermore, the recoveries of the polyhiydroxy acetate, tyrosol, hydroxytyrosol and oleuropeine from the retantate of RO were studied. The DCMD membrane consisting from Polytetrafluoroethylene (PTFE) with a diameter of 199 µm, at a pore size of 0,17 µm in a void volume of 2,45 nm and an effective porosity of 90%. The RO membrane is a flat thin-film composite Brackish water membrane and consists of a polyamide active layer on a polysulfone support with an effective surface area of $9{,}56\times10^{-3}$ m^2 at dimensions of 3,2 cm x 29,2 cm x 13,2 cm. The influence of the main operating parameters (operating pressure, temperature and feed flowrate) on the pollutant parameter removals were studied in RO. The maximum pollutant yields mentioned above varied between 81% and 90% at a permeate flux of 24 L/h m^2 and at a pressure of 12 bar in DCMD. In RO, the maximum removals of pollutants were around 99.00% and 99.99% at a pressure of 20 bar at a temperature of 25°C at a flowrate of 8 L/min. The recoveries of polyhiydroxy acetate tyrosol, hydroxytyrosol and oleuropeine were performed perfectly.

Keywords: Direct Contact Membrane Distillation; (DCMD), Reverse Osmosis (RO); Recovery; Polyhiydroxy Acetate (PHA); Tyrosol; Hydroxytyrosol oleuropeine

INTRODUCTION

OMW effluents exhibits acidity properties, can not be biodegraded readily and contains high organic suspanded solids [1-4]. OMW exhibits huge toxicity to the ecocystem and to the macro and micro biota due to its high polyphenolic ingredients [5,6]. The specifications of OMW were black color, odor, acidic media and huge amount organic ingredients, mainly consisted from polyphenols that may exhibit antimicrobial, ecotoxic and phytotoxic specifications [3,4]. This results with not significant treatment of OMW with conventional treatment processes and the remediation of this wastewater occurs only with advanced treatment technologies. OMW also exhibit significant saline toxicity levels, confirmed by high Electroconductivity (EC) values [7,8]. Inorganic compounds including chloride, sulphate and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper and traces of other elements are common traits of OMW. Moreover, olive oil production is a seasonal activity and a huge amount of OMW are produced in some months, making a storage of the wastewater costly [9,10]. A medium sized olive oil mill produces around 10 m^3/day of OMW, which represents a major threat for the environment and high cost for its disposal, and is associated to an equal amount of potable water consumption. Type of olives, area under cultivation, the use of pesticides and fertilizers, the climate conditions, the harvest time and the harvest year are factors that may change the quality of OMW [11,12]. OMW constitutes an important environmental pollution problem, especially in the Mediterranean area, the main olive oil production region in the world [11]. The detrimental environmental impact of OMW is related to its large organic content and to the phytotoxic and antibacterial action of its relatively high polyphenolic content as aforementioned [11]. It is well known that olives and their derivates are rich in phenolic substances. About 99% of the total phenols present in olives, after oil production, remain in wastewater, whereas only 1% can be found in the extracted [11]. Phenolic compounds from olive mills have some biological activities, such as antioxidant anti-inflammatory and antibacterial fuctions [11-14]. Furtheremore, Polyhiydroxy Acetate (PHA), tyrosol, hydroxytyrosol and oleuropeine have economical merits in industrial activities.

Some treatment processses (settling, chemical precipitation or oxygenated or non oxygenated microbiological treatment processes to remove the organic pollutants, electro-coagulation, photocatalytic treatment with sun and nanocomposite materials) are utilized in the treatment of OMW wastewaters [4,15-17]. The conventional treatment processes are expensive and exhibits low yields and produce high amounts of sludge with high remediation problems. Integrated membrane processes are greatly alternative to treat the OMW wastewater and to recover the phenolic organics [4,18-20]. OMW can be treated with high removal efficiencies using DCMD before RO step to obtain an efficient permeate quality for its utilization as recreational irrigation purpose and reuse of the treated olive mill wastewater [4,19,20]. The previous studies showed that DCMD can be proposed for the removals of pollutants present in the OMW [4,17,18].

Membrane processes can be suggested as efficient treatment processes for the remediation of OMW wastes. Only a small amount of brine was produced, by decreasing the initial volume of OMW pollutants down to 40% [5,8,9,16,18,20]. The permeate quality atteined to limits given by the regulations for discharge in municipality sewer chanels [5]. This cause to a cheap wastewater remediation. Membrane fouling is a big problem in the membrane processes and reduce the the membrane yield [5,8,19-21]. In order to control the fouling process and steady-state operation some pollutants should be treated by pre-treatment processes [5,8,20,21]. Recently, suitable design of membrane process is difficult and it should be taken into consideration to prevent the fouling [5]. The presence of fouling, and consequent reduction of permeate fluxes versus operation time, necessitates the designer to product a over-design the membrane plant to guarantee a sufficient treatment efficiency at optimum operational conditions [5,8,17,20,21].

Membrane Distillation (MD) is used extensively in the municipal and industrial treatment plants in recent years [4,22-24]. This process is operated by a regulated emission of vapor through the pores of hydrophobic membranes via instant mass and heat transportings [4,25,26]. Direct Contact Membrane Distillation (DCMD) is used extensively due to condensation process is occurred in the inner phase of membrane resulting in a direct MD process [4,25-27].

Reverse Osmosis (RO) is an advance technology for the regeneration of the effluents from the OMW [8, 28,29]. These wastewaters are very recalcitrant, contains high organic matter and the salinity of the OMW exhibited toxicity [8]. After DCMD a final separation stage consisting of a thin-film polymeric RO membrane cause the complete removals of effluents of OMW processing by two-phase decanting steps [8,30,31]. By utilisation of optimized

conditions, the RO membrane exhibited stable performance, and the problems originating from the fouling were overcomed [8,32]. Reverse osmosis, involves the application of external pressure to the pollutant in wastewater of a semi-permeable membrane to cause a solvent emission to the pure water side [8,28,29]. The driving force of the RO is applied a pressure. The amount of energy required for the osmotic separation is related to the type pollutant in the wastewater. The RO membrane rejects all suspended substances and 95-99% of dissolved substances [12]. A pre-filtration step is necessary to prevent the fouling problem of RO consisting from the suspended particles [11,12,30,31]. Filtration removes particles of 1-1000 mm. With RO the separation of the fine metal ions were possible. RO permeate water was enough quality for reuse the water while the retentate provides the recovery of merit organic and inorganic compounds [11,12,32].

In this study, the effect of OMW pre-treatment, on the DCMD performance was evaluated. The effects of permeate flux (5-20 L/m^2.h) on the distilled water and OMW water during 4 hs operation at 20˚C temperature, and the effects of increasing temperatures (22, 35 ,45˚C) on the permeate flux variation of the mass transfer coefficient for COD, TSS and phenol were investigated in the DCMD membrane reactor. In RO membrane reactor the effect of increasing pressures (2-15 bar) on the removals of COD, TSS and conductivity was studied.The variation of permeate fluxes (3-25 L/m^2.h) on the RO membrane performance, and the variation of mass-transfer cefficients for COD,TSS and phenol yields were studied.The effects of the temperature difference on the removals of pollutants in the OMW treatment and on the concentration factor of the phenolic compounds were studied.

MATERIALS AND METHODS

Pre-treatment of OMW and used membrane reactors

In this stuy, to prevent the fouling problem and increase the pollutant yields, some suspended solids in the OMW were collected prior to DCMD by using a carthridge filter with a pore size of 0.98 mm.

A TF-200 long membrane originated from polytetrafluoroethylene polymere was used in this study for DCMD membrane reactor. The nominal pore size was 0.17 µm with 199 µm thickness (δ) with 90% effective porosity (ε/Lp) and 1,2 bar liquid entry pressure of water and witha void volume (ε) of 96.6%. A BW30 membrane was used in the RO process after DMCD treatment via utilization of the pocess configuration proposed by Alique, et al. [16]. The thickness of the membrane was 2 µm with a porosiy of 99%, while the membrane area was 9.56×10^{-3} m^2. RO membrane was designed to reject 99.89% of NaCl and it consisted of a non-cellulosic membrane. It can be operated up to 68 bar presurres and up to 60˚C temperature.

The volume of feed tanks of DMCD and RO membrane processes were 120 L. During membrane operation the retentate was recycled in the feed tank and the permeate was collected in a separate tank until the end. At the end of each experiment, the membranes were cleaned using a NaOH (1N) solution for 30 min and finally with deionised water until neutral values of pH 8.0 [16].

Properties of DCMD and RO reactors and operational conditions

The effluent of DCMD was used as the feed of the RO. DCMD and RO processes consist from a central part which is stainless steel cell with two rectangulair tank with a total volume of 2,2 liter. The tanks were connected according to the design of Qtaishata, et al. [21]. One of the tank is connected to a heating system in order to control the temperature of the liquid feed. The other tank is connected to a cooling system to control the permeate temperature. The effective membrane area is 4.98×10^{-3}m^2. The bulk feed and permeate temperatures were measured inside each chamber by electronic heaters. Both the feed and permeate liquids were stirred by using magnetic stirrers to optimize the temperature and concentration polarization as reported by Niaounakis and Halvadakis [21]. The studies were performed using deionized water and OMW wastewater. The reactors were feed at different temperatures (20˚C-55˚C) in order to stabilize the temperature difference constant at 20˚C.

The effects of permeate flux (5- 20 L/m^2.h) on the distilled and OMW water during 4 hs operation at 20˚C temperature was investigated in DCMD. Then, the effect of increasing temperatures (22, 35 ,45˚C) on the permeate flux and the variation of the mass transfer coefficient for COD, TSS and phenol were investigated in the DCMD membrane reactor. The variation of separation factor for phenol was studied in the same reactor. In RO membrane reactor, the effect of increasing pressures (2-15 bar) on the removals of COD, TSS and conductivity was studied. The variation of permeate fluxes (3-25 L/m^2.h) on the RO membrane performance, and the variation of mass-transfer cefficients for COD,TSS and phenol were studied in RO. The removals of the all pollutant parameters in the DCMD and RO were investigated.

Analytical procedures

All the conventonal pollutants (COD, CODdis, DOC, BOD, pH, Fe,TSS, TOC, F, Cl, Br, Na, NO_3, SO_4, K, Ca, HCO_3, conductivity) were measured according to the Standard Methods [33]. In the phenol analysis 9 mL of permeate and feed samples were washed with 10 mL of n-hexane to remove the impurities. Th/e sample was extracted with 10 mL ethyl acetate by mixing and centrifugating in a centrifuge at 6000 rpm for 10 min [4]. The organic sections were evaporated in a vacuum rotary evaporator and the remaining masses was mixed in 10 mL of methanol with a purityof 99% [4]. This extract was analysed in an Agilent HPLC. Separation was performed by a C-18 column (Agilent, 4.6 × 250 mm) washed with acetonitrile/water (70/30) before and after analysis [4]. A mixture of acetonitrile/water (v/v) was used as mobile phase. The Polyhiydroxy Acetate (PHA), tyrosol, hydroxytyrosol and oleuropeine measurement were performed by HPLC analysis of the extract of the permeate samples [34,35]. The analysis was performed using HPLC system (Agilent) equipped by a UV detector.The quantification of Polyhiydroxy Acetate (PHA), tyrosol, hydroxytyrosol and oleuropeine compounds was based on their maximum spectra in comparison with standards of the aforementioned compounds. The polyphenols separation coefficient and the OMW concentration factor were calculated from the equations (1) and (2), respectively [11].

$$(a) = \frac{1-Cp}{Co}$$ **Equation (1)**

$$(\beta) = \frac{Cf(t)}{Co}$$ **Equation (2)**

Where; Cp(t) and Cf(t) are polyphenols concentration in the permeate and feed, respectively, Co is the initial polyphenols concentration in the feed [11].

Wastewater characterisation

OMW wastewaters are known by their seasonality and toxic character due to the presence of polyphenolic compounds and a wide range of other organic pollutants. OMW contains sugars, tannins, polyphenols, polyalcohols, pectins and lipids [8]. More than 30 phenolic compounds have been detected in OMW, which together with long-chain fatty acids present high toxicity to microorganisms, plants and soil [8]. The characterization of raw OMW used in this study was illustrated in table 1.

RESULTS AND DISCUSSIONS

OMW pre-treatment and its effect on DCMD permeate flux

Before entering to DCMD the raw wastewater was passed from a cardrige filter having por diameter of 0,89 micronmeter. This pre-treatment enhanced the quality of the DCMD permeate/treated water. This step provided 18% removal efficiency for total solids, while the polyphenolic content ana COD pollutant yields were 17% 18%,respectively (data not shown).

Variation of permeate fluxes in the distilled water and in the OMW during DCMD operation

The sligth lowering of OMW water permeate flux compared to distilled water is due to the lower water vapor pressure of OMW resulting from the concentrations of the pollutant parameters such as phenol, salt, COD and CODdis [36] (Figure 1). The significant raise of the permeate flux in distilled water was not more significant than that for OMW. The permeate flux raised from 2.0 to 20 L/m^2.h for distilled water and only a raise from 4.6 up to 19.4 L/m^2.h was detected for OMW at a constant permeate temperature of 20°C.

Effect of increasing temperature on the DCMD permeate flux in distilled water and OMW wastewater

When the DCMD was operated with distilled water and OMW wastewater; the permeate flux of OMW is decreased sligtly than that of distilled water. A significant increase in permeate flux was obtained with the increasing of temperature contrarily to the sudies performed in the literatüre [37-39] (Figure 2). This rasing of permeate flux can be defined with Arrhenius eqution (Equation 3) [4].

$$(J) = A\, e^{-BT}$$ **Equation (3)**

Where, A and B were constants in DCMD membrane system; T was the temperature and J was the permeate flux in DCMD.

The variaton of permeate flux versus temperature in the OMW for DMCD

Figure 3 shows the variation of the DCMD permeate flux versus temperature when the DCMD is operated only with OMW. The results show that the permeate flux of OMW was not decrease significantly during the operation time. Since the OMW feed concentration increased due to high pollutant concentrations, the polarization concentration was not increased and as a result a significant membrane fouling phenomenon was not detected [40,41]. The increase of permeate flux can be attibuted to a not significant electrostatic interaction between the membrane surface and the feed solute of the OMW resulting in a non significant fouling on the membrane surface [23,42].

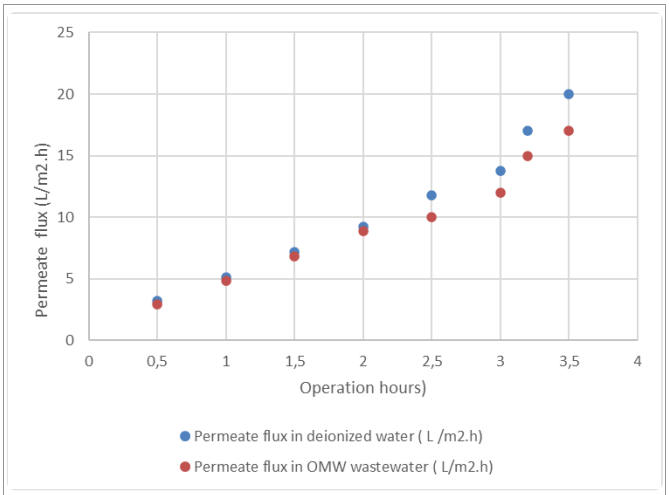

Figure 1: Variation of permeate fluxes in the distilled water and in the OMW during DMCD operation at a constant operation temperature of 20° C.

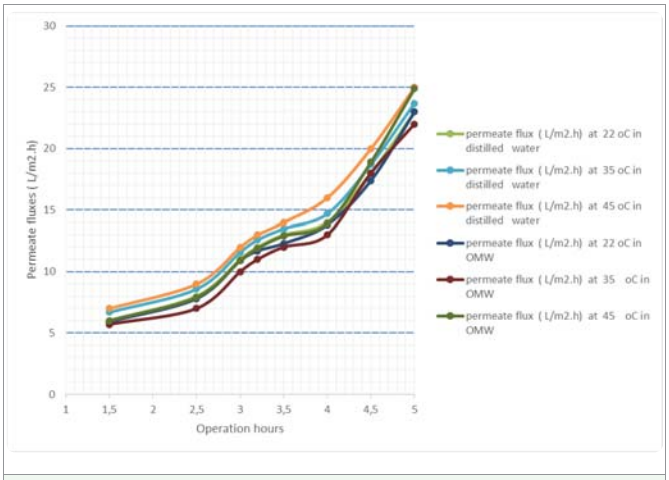

Figure 2: Effect of increasing temperature on permeate flux for distilled water and OMW wastewater in DMCD membrane reactor.

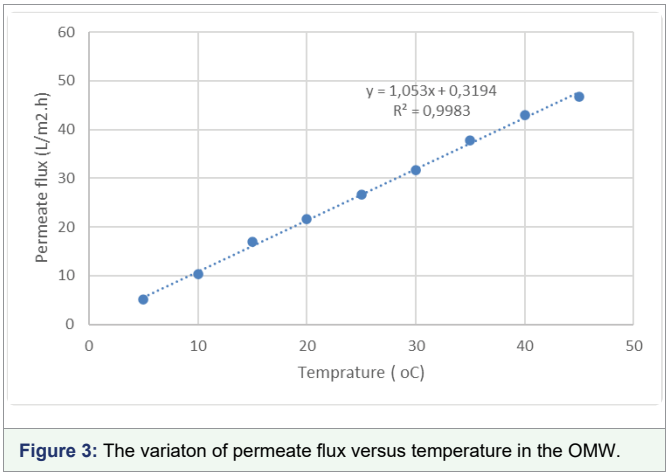

Figure 3: The variaton of permeate flux versus temperature in the OMW.

Variation of Mass transfer coefficients in different OMW pollutants in DCMD

The variation of pollutant concentration; in other words the concentration factor for permeate and retentate (β) was calculated from the Equation (4) [43,44].

$$(\beta) = \frac{Cf(t)}{Ct(o)}$$ **Equation (4)**

Where, CF(t) is the polyphenol concentration in the permeate at the time t. Cto is the polyphenol concentration in the feed.

A linear linearship between membrane permeate flux and removal efficiency of pollutants was proposed. This relationship was defined as the Nernst Planck equation (Equation 5) [45].

$$(R) = \frac{Rs\ x\ Jv)}{Jv + Bs)}$$ **Equation(5)**

Where, Rs is the removal coefficient, while Bs is the mass transfer coefficient.

This equation was linearized as follows: (Equation 6)

$$\frac{1}{R} = \frac{1}{Rs} + \frac{Bs}{Rs}\ x\ \frac{1}{Jv}$$ **Equation(6)**

Equation (6) was utilized to calculate the mass transfer coefficients (Bs) through the membrane permeation flux (Jv) and removal efficiencies (R) of pollutants present in the OMW).

1/R values versus to the 1/J values was plotted for both the COD and conductivity removals. As can be seen from figure 4 and table 2; the Bs values calculated in DCMD were < 1. The Bs coefficients calculated for the COD yields were found to be smaller than those obtained through conductivity and TSS removal efficiencies. Bs values obtained in this study were small. This shows the high pollutant yields of the DCMD membrane (Table 2). The pollutants in the OMW were emitted inside membrane and they were not retained [6]. Low Bs coefficient values indicates that the amount of particles emitted inside the membrane is not high [6,46]. As a result, the Bs values show that pollutant retention was occurred effectively in the DCMD membrane. The mass transfer coefficients calculated from the recent literatures showed ranges between 0.17 (unitless) and 0.46-52.99 (unitless) [6,47,48] for the textile wastewater treated vith advanced photocatalytic processes. In this study, the Bs values showed that that the retention of pollutant particles in the OMW was carried out perfectly in the DCMD membraVariation of concentration and separation factors and effect of feed velocity on permeate flux in DCMD

In this study, the DCMD membrane exhibited high concentration factor (based on total COD) against time due to their relatively high permeate flux (18 L/m².h) at a temperature of 40°C (Figure 5). In this study, it was found that that the separation factor, α, was around 99.99% during the 4 h of OMW operation in the DCMD at ΔT = 30°C (data not shown). This can be explained by sligthly wetting of big pores in the surface of the membrane since DMCD membrane surface contains an effective homogene distribution of pores [4]. As a result, the separation percentage of the DCDM membrane is found to be high.

The temperature of the inlet and permeate effluents were measured as 21 and 22°C, respectively. The permeate flux is enhanced by the feed velocity since it is related to fluid dynamics of the inlet. By increasing of the the feed velocity; the permeate flux increased (Figure 6). By taking into consideration this Figure it can be concluded that the permeate flux raised when the feed velocity was increased. When the feed velocity was raised from 0.2 to 0.6 m/s, the permeate flux raised from 7.32 to 17.40 L/m² h. This can be attributed to the varying of feed velocity which can effectively affect the wastewater dynamics.

Table 1: Characterisation of raw OMW wastewater.

Parameter	Unit	value
pH	-	7.8–8.2
EC	(mS/ cm)	1900-2600
TSS	(mg /L)	3000-4500
Ashes	(mg/ L)	230-550
COD	(mg /L)	4500-6500
COD dis	(mg /L)	2100-3700
DOC	(mg /L)	1100-1300
Total phenols	(mg /L)	670-970
[Fe]Total	(mg /L)	56-78
[F^-]	(mg /L)	24-45
[Cl^-]	(mg /L)	5600-7800
[Br^-]	(mg /L)	34-89
[$NO3^-$]	(mg /L)	450-650
[SO_4^{2-}]	(mg /L)	1280-1393
[PO_4^{3-}]	(mg /L)	34-46
[Na^+]	(mg /L)	2300-4287
[Ca^{2+}]	(mg /L)	450-655
[Mg^{2+}]	(mg /L)	430-456
[K^+]	(mg /L)	450-690
[HCO_3^+]	(mg /L)	1290-1329

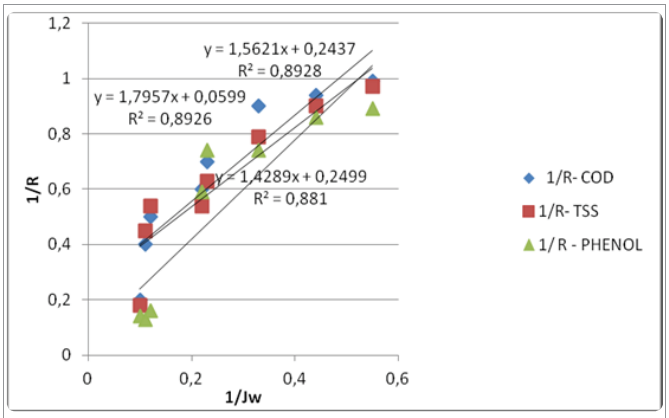

Figure 4: Calculation of concentration factor (β) for COD, TSS and phenol in DCMD.

Table 2: Calculation of concentration factor (β) for COD, TSS and phenolphenol pollutants inthe OMW for DCMD.

Pollutant	Linear Equation	R^2	1/ Rs	Bs/Rs	Bs
COD		0,99	1,021	0,127	0,05
TSS		0,86	1,032	0,136	0,07
Phenol		0,87	1,028	0,141	0,08

Increasing feed velocity will decrease the transferring of mass and heat by increasing the thickness of the pores in the membrane [23,49,50]. Simultaneously, the temperature polarization process was decreased. The vapor and heat was transported effectively inside membrane [23,51]. Therefore, a higher flux was observed. In our research, it was not found an asymptotic relation between feed velocity and permate

flux. The relathionship between fed velocity and permeate flux is linear. This can be explained by the low levels of feed velocity. When the feed velocity and the Reynolds (Re) number were raised, the mass and heat transfer will decrease to a stable level [23]. After this point the mass and heat transfer resistance will not decrease further. However the feed velocity continues to increase [23,52].

Variations of phenol separation factor, phenol coefficient and polyphenol concentrations in the permeate and retentate of DCMD

In this study, to determine the variations of phenol concentration in the permeate, the concentration factor (β) and separaton factor (α) for polyphenol were calculated according to the equation proposed by El Abbasi, et al. [4]. The concentration factor were calculated as 3,2 and 2,8(unitless) at 65˚C and 30˚C, respectively (Figure 7). The polyphenol separation factor was calculated as 99.90% and as 97.6% at 65˚C and 30˚C, respectively in the OMW.

Figure 8 exhibits the phenol levels versus time in permeate and the retentate samples of DMCD. The poyphenol concentration in permeate of the DMCD approached zero (1.9 mg/L) after 8 hs of operation while the polyphenol concentration in the retentate of DMCD was measured as 38 g/l after 10 hours of operation. The reason of this can be explained by the fouling of polyphenols the pores located in the membrane surface [4].

In this study, the permeate flux in the raw wastewater before entering to DCMD was 22.7 L/m².h and after DCMD was 20 L/

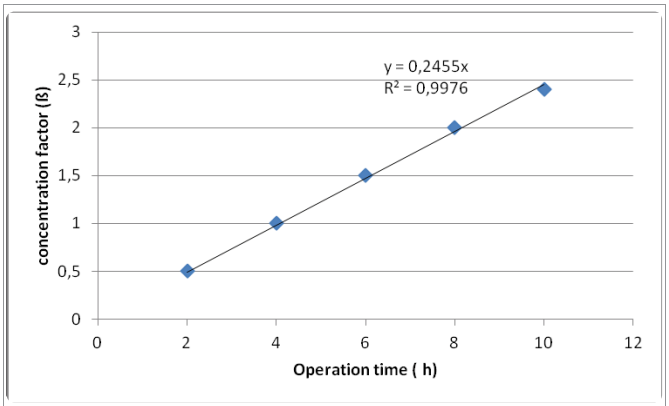

Figure 5: Concentration factor for COD in the DCMD.

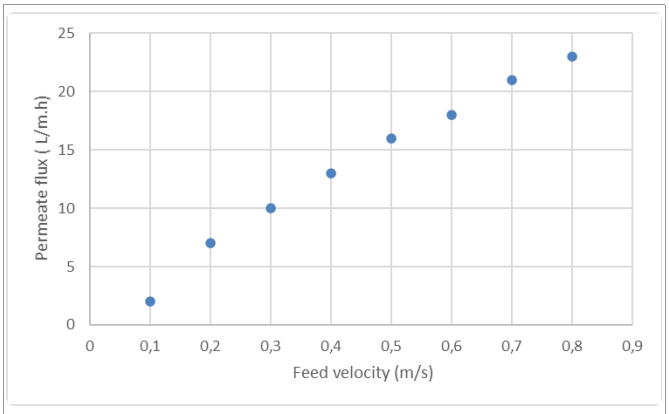

Figure 6: Effect of influent velocity on the variation of permeate flux in DCMD for OMW.

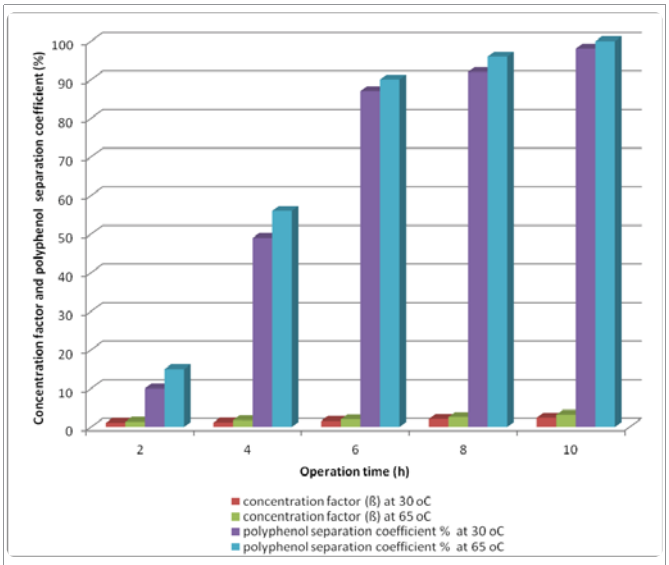

Figure 7: Variation of polyphenol concentration factor, β; polyphenol separation coefficient, α, in OMW during the operation of DCMD at two temperatures (30°C and 65°C).

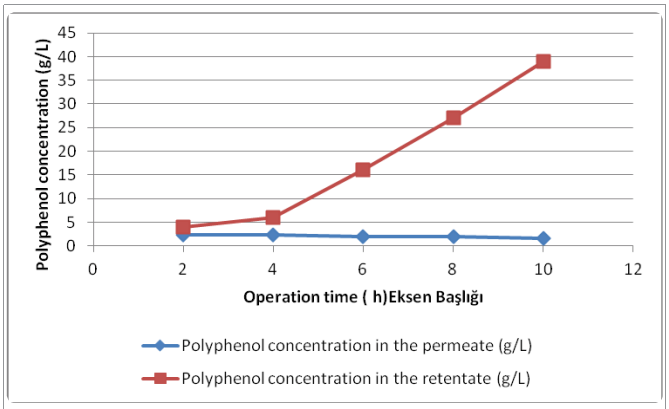

Figure 8: The polyphenol concentrations in the permeate and in the retentate of DCMD.

m²h. The decrease in percentage of wastewater Flux Rate (FR) after 160 h operation in DCMD was about 2.1% (data not shown). During continuous operation of DCMD, the permeate flux of wastewater lowered only 0.21% at the beginning of 40 h operation. The physicochemical properties of the membrane have a big effect on the permeate flux [4]. For example, some big suspanded solids in the olive mill effluent wastewater can be close the pores in some PTFE membranes. This cause to the decrease of permeate fluxes in the membranes [4,52,53].

High removal efficiencies were detected in the permeate of the DCMD for the pollutants namely COD, CODdis, DOC, BOD, pH, Fe,TSS, TOC, F, Cl, Br, Na, NO_3, SO_4, K, Ca, HCO_3 and conductivity. The concentrations in the permeate ana in the retentate of the DCDM was illustrated in table 3.

Effect of membrane pressure on the COD, TSS and conductivity removals versus increasing membrane pressure in the OMW using RO

Reverse osmosis studies were carried out in the samples coming from the permeate of the DCMD in the RO membrane. The results

showed that the COD yields raised as the membrane pressures were increased. It was found a significant linear corelation between COD yields and membrane pressure with a R^2 value of 99.99. When the OMW wastewater passes through the RO membrane, the suspanded solids are remained on the surface of the RO due to have big dimension compared to the pore diameter located on the surface of RO [2,54]. The suspanded solids can be decrease the pore diameter of the membrane in RO by fouling. When the pore dimensions reduced in the RO, the transporting of the dissolved and inorganic solids may decrease [2,55]. Furthermore, the aforementioned solids can be staying on the surface of the RO membrane. As a result, a biofilm layer was carried out. This biofim raise the retention of the particles [56]. However, in this study, the pore size of RO pore was not reduced and a significant cake formation was not detected in RO membrane since in this study a BW-30 membrane was used in the RO process. The retaining dissolved and suspanded particle efficiencies were not decreased since a significant fouling was not detected in the RO. In this membrane the rejection of the pollutants was not decreased significantly. The highest COD, TSS and conductivity removals were 100% in RO at a membrane pressure of 8 bar and this removal efficiency continued to remain as a plateau until 21 bar RO pressure (Figure 9). The recent studies concerning the treatment of OMW with RO were not so extensively. In some recent data, the COD yields were determined to be 97% in the OMW treatment with PTE membranes, while in the other RO membrane types (XLE and PA), the COD yields were around 95% [2]. In this study the removal yields are considered to be very satisfactory compared to the other membrane used in the treatment of OMW.

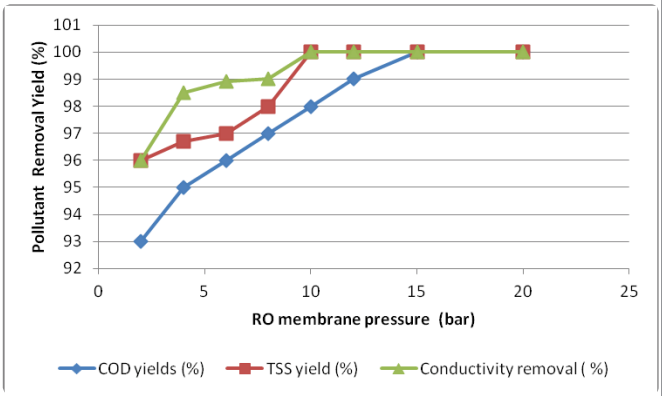

Figure 9: Variation of COD,TSS and conductivity removals versus increasing membrane pressures in RO.

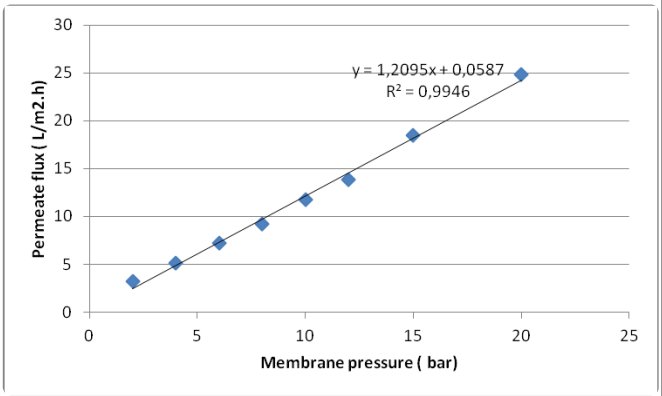

Figure 10: Effect of increasing membrane pressure on the membrane permeate in the RO.

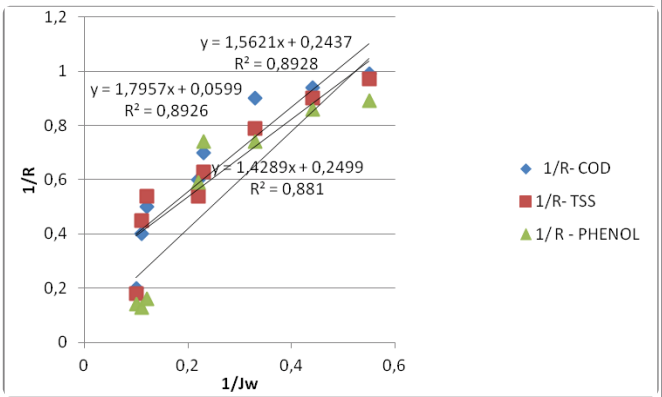

Figure 11: Variaton of mass transfer coefficients in the RO for COD, TSS and phenol in RO.

Variations of membrane permeate fluxes versus membrane pressures and mass transfer coefficients of some pollutants in the RO

The permeat fluxes in the RO increased significantly versus trans-membrane pressure in RO. Fluxes in the BW-30 membrane were significantly bigger. As the RO membrane pressure were increased from 5 bar to 22 bar the permeation flux elevated from 4 L/m².h up to 25 L/m².h (Figure 10).

A linear linearship between membrane permeate flux and removal efficiency of pollutants was proposed . This relationship was defined by the Nernst Planck equation (Equation 5) and it was linearized in Equation 6 [5] as mentioned in earlier pages of paper.

As can be seen from figure 11, and table 4; the Bs values obtained for COD, TSS anD phenol are < 1. The Bs indicates the solids transferring from the RO membrane without accumulating. S mall Bs coefficient shows high removal yields of pollutants in the RO membrane [2]. In other words, small Bs walues exhibits that the solid ionic particles transferring through RO was low [2]. As a result, the Bs values exhibits that suspanded and ion retentions performed significantly with the other pollutant parameters given above [2]. The recent studies showed that data concerning the mass transfer coefficients relevant to RO membranes are not so high [2,56-58]. In these studies the mass transfer coefficients were calculated between 0.79 and 58.89 (unitless) for textile industry treated with RO [58]. In this study, the Bs data calculated illustrated that solid and paollutant retention was performed perferctly in RO membrane.

Pollutant removals in the RO

All the pollutant in the OMW were successely removed with 99.00% and 99.99% removal yields in the permeate samples of RO (Table 5). The phenol, tyrosol, hydroxytyrosol and oleuropeine were accumulated in the retentate of the RO.

Recoveries of Polyhiydroxy acetate (PHA), tyrosol, hydroxytyrosol and oleuropeine from the retentate of the RO

The retentate samples were purified with hexane–ethyl acetate–methanol mixtures. Then chloroform: methanol (8:2, v/v) was used as mobile phase in the Agilent HPLC–UV.The chromatographic

separation was performed on a C18 column (250 mm×4.6 mm, I.D., 5 m,Agilent) at 90°C [3,53]. The mobile phase was 0.2% formic acid in water versus 0.2% formic acid in acetonitrile for a operating time of 70 min. The flow rate was 0.73 ml/min and the injection volume was 50 µl. Mass spectra were acquired using electrospray ionization in the negative ion mode scanning from m/z: 105 to 3050 using the following fragmentation program: from m/z: 0 to 200 (100 V) and from m/z: 200 to 3000 (200 V) (3). Ionization parameters were as follows: drying gas (N_2) at a flow of 10 l/min and ana at a temperature of 350°C. The pressure was 58 psi and the capillary voltage was 4000 V (3). The identification of Polyhiydroxy Acetate (PHA), tyrosol, hydroxytyrosol and oleuropeine compounds in the OMW extract was performed by comparing their UV and MS spectra with those reported in the literature.

From 1 m^3 OMW wastewater treatment 6900 mg/l polyhiydroxy acetate, 7800 mg/l oleuprotein, 8900 mg/l hydroxytyrosol and 4800 mg/l tyrosol were recovered(data not shown).

CONCLUSIONS

This study focused on the removals of the pollutants in the OMW using sequential DCMD and RO process. Furthermore, this study proved that the permeate flux was significantly raised by raising of the transmembrane pressure, and was not lowered by raising the olive mill effluent polutant concentrations in both DCDM and RO. The permeation flux raised with raising of the flow velocity in both memrane reactor systems. The impact of temperature on permeation flux was correlated linearly with transmembrane pressure and flow velocity in both membrane process.

Table 3: Pollutant concentration in the permeate and retentate of DCMD.

Parameter	Unit	Permeate	Retentate
pH	-	7,8- 8,2	8.0-8,2
EC	(mS/ cm)	300-400	2600
TSS	(mg /L)	230-290	3400
Ashes	(mg/ L)	50-55	1200
COD	(mg /L)	600-650	1900
COD dis	(mg /L)	100-370	1700
DOC	(mg /L)	110-130	800
Total phenols	(mg /L)	80-90	6000
[Fe]Total	(mg /L)	18-20	90
[F−]	(mg /L)	8-9	67
[Cl−]	(mg /L)	1000-1100	4500
[Br −]	(mg /L)	9-10	600
[NO_3−]	(mg /L)	45-50	400
[SO_4^{2-}]	(mg /L)	180-193	1900
[PO_4^{3-}]	(mg /L)	7-9	2000
[Na^+]	(mg /L)	600-887	7600
[Ca^{2+}]	(mg /L)	94-98	600
[Mg^{2+}]	(mg /L)	40-42	900
[K^+]	(mg /L)	34-38	340
[HCO_3^+]	(mg /L)	90-99	1200

Table 4: Mass tranfer coefficients of COD, TSS and phenol in RO.

Pollutant	Linear Equation	R2	1/ Rs	Bs/Rs	Bs
COD		0,99	1,021	0,127	0,05
TSS		0,99	1,022	0,129	0,04
Phenol		0,98	1,234	0,138	0,03

Table 5: Pollutant concentration in the permeate ana retentate of RO.

Parameter	Unit	Permeate	Retentate
Ph	-	7,8- 8,2	8.0-8,2
EC	(mS/ cm)	0,01	500
TSS	(mg /L)	0,8	5400
Ashes	(mg/ L)	0,2	1800
COD	(mg /L)	1	3900
COD dis	(mg /L)	0,5	5700
DOC	(mg /L)	0,2	3800
Total phenols	(mg /L)	0,2	9800
[Fe]Total	(mg /L)	0,01	390
[F−]	(mg /L)	0,01	267
[Cl−]	(mg /L)	0,01	4500
[Br −]	(mg /L)	0,01	9500
[NO_3−]	(mg /L)	0,05	1400
[SO_4^{2-}]	(mg /L)	0,02	4900
[PO_4^{3-}]	(mg /L)	0,04	4000
[Na^+]	(mg /L)	0,02	9600
[Ca^{2+}]	(mg /L)	0,05	3600
[Mg^{2+}]	(mg /L)	0,01	1900
[K^+]	(mg /L)	0,01	1400
[HCO_3^+]	(mg /L)	0,01	5800
Tyrosol	(mg /L)	0,01	4800
Hydroxytyrosol	(mg /L)	0,03	8900
Olueprotein	(mg /L)	0,02	7800
Polyhiydroxy acetate	(mg /L)	0,04	6900

The carthridge filtration as peretrearment stage provided % 17-18 COD,TSS ana phenol removals before DCMD. As the temperature was raised from 15 to 35 and 45°C an logaritmic raise in the permeate flux was detected in both distilled and OMW water in DCMD.No significant decreases in permeate flux was detected in the OMW. Mass trasnfer coefficient (Bs) for COD, TSS and phenol pollutants were found to be < 1 in DCMD. As the feed velocity increased from 0.1 m/s up to 0.8 m/s the permeate flux increased from 2.3 L/m^2.h up to 24 L/m^2 .h in DCMD. The polyphenol separation factor was calculated as 99.90% and 97.6% in OMW, at 65°C and 30°C temperatures, respectively, in DCMD. The pollutant yields in the DCMD varied between 81% and 90%. The highest COD, TSS and conductivity removals were 100% at a RO membrane pressure of 8 bar and the removal efficiency continue to remain as a plateau until 21 bar RO pressure. The mass transfer coefficients (Bs) values obtained for COD, TSS and phenol as < 1. Lower Bs coefficients indicates a higher performance of the RO membrane. As the RO membrane pressures were increased from 5 bar to 22 bar the permeation flux elevated from 4 L/m^2.h up to 25 L/m^2.h. Al the pollutants present in OMW were removed with high removal efficiencies varying between 99.00% and 99.999% in the RO. Polyhiydroxy Acetate (PHA), tyrosol,

hydroxytyrosol and oleuropeine from the retentate of the RO were effectively recovered. In steady state operational conditions, the RO membrane exhibited high yield for all pollutant parameters, and no fouling was detected in continous operation of sequential DCMD/RO membrane process.

In conclusion, the performances of both membrane process were found to be satisfactory in terms of the pollutant removals and recoveryof some merit products. Parametric values below the standard limits established for reuse of the RO in olive oil production process again for utilization in the process, washing of machines and as irrigation water.

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