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Membrane processing for olive mill wastewater fractionation

C.A. Paraskeva[a,b]*, V.G. Papadakis[a], E. Tsarouchi[a], D.G. Kanellopoulou[a,b], P.G. Koutsoukos[a,b]

[a]*Institute of Chemical Engineering and High Temperature Chemical Processes, Foundation for Research and Technology, Hellas, P.O. Box 1414, GR-26504 Patras, Greece*
Tel. +30 2610 997-252; Fax +30 2610 990-328; email: takisp@chemeng.upatras.gr
[b]*Department of Chemical Engineering, University of Patras, GR-26500 Patras, Greece*

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Abstract

The possibility of complete fractionation of olive mill wastewater (OMW) was investigated using membrane technology. Combinations of different membrane processes were used for the fractionation of OMW into by-products that may be further developed to achieve reduction of the expenses involved. Ultrafiltration (UF) in combination with nanofiltration (NF) and/or reverse osmosis (RO) were found to be very efficient for the treatment and fractionation OMW. An extended parametric study for the optimum fractionation yield of OMW involved variation of the operational system parameters including temperature, and the trans-membrane pressure. The final effluent obtained was a clean transparent with very low content of organic compounds and dissolved ionic salts. The chemical composition of the post-treatment effluent showed that it was suitable for disposal in aquatic receptors or for use for irrigation purposes. The ultrafiltration process resulted in the separation of high molecular weight constituents including suspended solid particles. Phenols present in the OMW were removed to an extent exceeding 95% of the initial value following the nanofiltration step. The concentrate obtained at this stage was very rich in phenols. Better efficiency of the OMW treatment was achieved applying RO after UF.

Keywords: Olive mill wastewater; Ultrafiltration; Nanofiltration; Reverse osmosis; Membrane processes; Water and soil pollution

1. Introduction

The management of olive mill wastewaters (OMW) is a very important issue in Mediterranean countries where more than 2.4 million tons of olives are produced per year (95% of the total world production) 90% of which is for olive oil production. The olive milling is a water intensive process and the wastewater produced is estimated to 1.1–1.5 times the weight of milled olives (for three-phase olive mills) [1–5]. In Mediterranean countries, the olive producers operate on a

*Corresponding author.

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seasonal basis and the production units are small and as a rule they do not process the liquid effluents from the production process. As a result, severe environmental problems are caused since among other characteristics OMW effluents have low pH and biodegradability and extremely high solids and organic compounds content [2–9]. OMW composition varies and depends on climatic, cultivation parameters, and on the milling method applied for the olive oil production.

Various waste management practices have been reported, applied either alone or in combination with others. Direct disposal to surface waters although still practiced is both dangerous and illegal resulting in severe pollution problems [2,7]. Disposal of OMW to uncultivated and agricultural soils [8,10–14], natural evaporation [15,16] and thermal concentration [15], treatment with lime [17] and clay [18], oxidation [19] have been reported and in several cases practiced. Composting [15,20,21] and biological treatment [5,22–24] are among methods suggested for the management of OMW. It should be noted however that the efficiency of the process, the complexity and the costs involved (installation, operation, energy) may vary significantly. As a rule, high cost is quite often the main reason for not adopting efficient OMW treatment methods. The development of membrane technology resulted in the introduction of filtration techniques for the treatment of wastewater [25–27].

Ultrafiltration (UF) and nanofiltration (NF) are pressure-driven, membrane filtration processes that are used to separate and concentrate macromolecules and colloids from wastewater. A fluid is placed under pressure on one side of a perforated membrane of a measured pore size. All materials smaller than the measured pore size pass through the membrane, leaving large contaminants concentrated on the feed side of the membrane. The RO system uses a semi-permeable membrane to separate pure water from contaminated liquids. Osmotic theory asserts that when a contaminated solution is separated from pure water by a semi-permeable membrane, the higher osmotic pressure of the contaminated solution will cause the water to diffuse into the contaminated solution. Water will continue to permeate into the contaminated solution until the osmotic pressure of the contaminated solution equals that of the pure water. UF is used as a pre-treatment step to NF and/or RO or as a stand-alone process. Control of pass-through constituents can be achieved using a membrane with a limiting pore size, or by installing a series of membranes with successively smaller pores. The UF process cannot separate constituents from water as effectively as NF or RO. However, the technologies can be used in tandem, with UF removing most of the relatively large constituents of a process stream before NF or RO application selectively removes water from the remaining mixture. The UF process is applicable for particles in the molecular range of 0.1–0.01 μm, while the RO process is applicable for particles in the ionic range of less than 0.001 μm.

In the present work we report on the application of membrane filtration technology for the treatment of OMW [28–32]. In the membrane separation process the liquid to be treated circulates with flow parallel to the filtering surface, thus creating sufficient turbulence to avoid fouling. It is for this reason that cross-flow filtration maintains its efficiency for long periods. The driving force for the separation of solution components is the pressure difference between the two sides of the membrane (TMP, trans-membrane pressure). Ultrafiltration, nanofiltration and/or reverse osmosis techniques were applied for our system. In order to study and optimize the fractionation procedure temperature and trans-membrane pressure were varied. Solvent flow (permeate) and solute rejection (concentrate) are indicative of separation performance.

Among the tasks of the present work was compliance with environmental disposal requirements (OMW cleaning and safe disposal) and examination of the possibility to compensate for the high cost by the efficient OMW fractionation into streams rich in by-products of potential value. Both the inorganic part of OMW (N, P, Mg, K, metal traces) and the organic (hydrocarbons, nitrogenous compounds, organic acids, poly-alcohols, may be used as plant nutrients perhaps in combination with other inorganic or organic fertilizers such as manure or sludge from biological treatment of other types of waste [16,33–35]. Polyphenols and fats are most interesting due to their toxic properties that may affect plants [36–39]. In the applied treatment we have shown that it is possible to obtain an effluent stream of acceptable quality for safe disposal to the environment (surface water or soil), for irrigation or even for recycling and use in the olive mill.

2. Materials and methods

2.1. Experimental procedure and setup

A pilot plant (Fig. 1) was operated for a complete olive harvesting period, in a typical Greek olive mill in Achaia region (Peloponnisos). The mill used the three-phase decanter technology and the production of wastewater was approximately 1 m^3/h. It was decided to investigate the effect of system operation parameters keeping constant the composition of the initial feeding wastewater (Table 1). The OMW used for the parametric study of the treatment process was obtained from this source exclusively. The variables during the study included: trans-membrane pressure (TMP) for all filtration processes and temperature for the UF process.

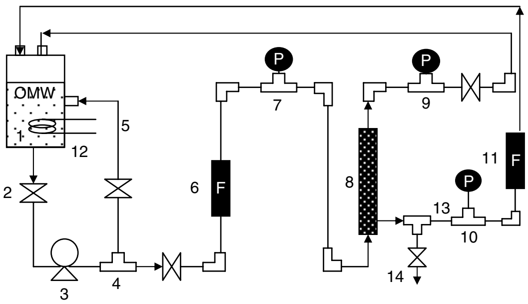

Fig. 1. Flow chart of the membrane units. UF, NF or RO module can be placed in the experimental device (8) thus operating as different membrane process. [feeding tank (1) stainless steel, 100 L; valves (2); pump (3) piston type (SS 316); electric motor 2.2 kW, 220/380 V, 50 Hz, 3 phases; tee (4); tubes (5), (13) SS tube, 3/4 in. and 3/8 in., respectively; F: flow meters (6), (11); P: pressure indicators (7), (9), (10) pressure gauge, up to 60 bar; membrane section (8) material: ceramic of UF, 0.24 m^2, polymeric membrane for NF and RO, 2.5 m^2; electrical heater (12) electrical resistance; (14) valve-permeate].

The main parts of the pilot plant were the membrane unit, storage tanks and the pump. The temperature in the feed tank could be adjusted by

Table 1
Results of physicochemical analysis of OMW samples before treatment

	Sample 1	Sample 2	Sample 3
Temperature (°C)	45	43.4	42
pH	5.24		5.13
Conductivity (mS/cm)	4.38	5.15	5.08
TSS (mg/L)	11,469	11,529	11,700
Turbidity (NTU)	>999	>999	>999
Salinity (%)	0.22	0.26	0.24
TOC (mg/L)	15,980	14,490	15,100
COD (mg/L)	17,343	15,528	16,450
Sugars (mg/L)	1473	1253	1310
Fats (mg/L)	652,000	640,000	650,000
Phenols (mg/L)	701.5	921	850
K (mg/L)	2114	1906	2050
Na (mg/L)	27.7	28	32
Ca (mg/L)	83	48	56
Mg (mg/L)	88.2	61	76
Cu (mg/L)	0.84	0.49	0.56
Mn (mg/L)	0.46	1.17	1.02
Zn (mg/L)	1.7	4.01	2.3
Fe (mg/L)	0.45	0.6	0.55
Cl (mg/L)	377	442	405
S (mg/L)	64.9	76.8	69.4
N (mg/L)	336	60.5	56
P (mg/L)	253	261	258

a temperature controller, an immersed electric heating element and a cooling loop. Proper piping, valves, flow and pressure indicators completed the system. A thick coverage of glass wool and film of aluminium foil was used where possible for the temperature insulation of the tank.

Depending on the membrane used each time, it was possible to operate the membrane unit for ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO). The system was operated in a batch mode. Past a prefiltration step of the mill effluent to remove the suspended solids, 100 L were collected to the feeding storage tank. Next UF was applied as follows: The concentrate was collected for further analysis and study, while the permeate stream was collected in separate tanks. When the initial volume of OMW was consumed in the treatment process, a fresh amount of pre-filtered OMW was introduced in the feeding tank. In the next steps UF membrane was replaced by NF or RO membrane and the collected UF permeate was used as the feed liquid for the respective treatment processes. Portions of all fractionation streams were collected for further analysis. The final permeate was applied to the soil for irrigation. At the end of each day the membranes were washed with chemicals (diluted acids or bases together with compounds with antimicrobial activity). The duration of the treatment tests was between 6–8 h per day although some day's operation was extended to 10 h. The total duration of the operation lasted 2 weeks, 4–6 days a week depending on the operation of the olive mill.

2.2. Prefiltration unit

According to UF membrane manufacturer particles larger than 80 μm should be removed prior to the implementation of ultrafiltration process in order to decrease fouling and enhance the efficiency. Different types of filtration were tested; separation with a filter-press with paper filters of 80 μm, filtration through sand bed filters, vacuum pressure paper filters, polypropylene screens, etc. Screening with an 80 μm polypropylene screen was applied finally since it was the most simple equipment and the pre-filtration procedure was faster than the other methods. Filtered OMW was collected to UF storage feed tank. The solid fraction was kept for analysis (Table 2) and for further study as potential nutrient component.

2.3. UF unit

UF pilot unit can accommodate different types of ceramic membrane varying in size, active area and porosity. The ultrafiltration membrane installed for the OMW treatment had multichannel configuration and was characterized by high resistance towards physico-chemical parameters variation and by excellent reconditioning ability. It was made of ceramic material (zirconia) with pores of 100 nm, 19 channels of 1020 mm length and 4 mm diameter and membrane area 0.24 m^2.

Table 2
Results of chemical analysis of the solid fraction collected and of the permeate from the screen in the pre-filtration step of the OMW treatment process

Parameter	g/kg[a]	mg/L
Solids	10	4311 (TSS)
TOC	680	10,900
Phenols	3.5	506
Sugars	23	2800
Fats	640	10,066
Mg[b]	0.4	94
Ca[b]	4	72
Na[b]	0.1	45
K[b]	8	1560
P[b]	8	276
N[b]	20	60
S[b]	2	–

[a]Per kg of the dried solids collected from the rotating stainless steel drum.
[b]Following acid digestion of the solids.

The clean water permeability was ca. 1800 L/hm^2 bar, the flow rates were 3.44 and 4.30 m^3/h for cross flow velocity 4 and 5 m/s respectively and the hold up volume was 0.24 L for the feed and concentrate and 0.64 L for the permeate. Substances of MW in the range 1000–1,000,000 were retained by the UF membrane while lower molecular weight compounds, salts and water passed through in the filtrate.

The system was operated until the 80–90% of the initial volume of the OMW was treated passing through the membrane. The operating temperature was 15–35°C and TMP applied was between 1.0 and 2.25 bar. At the end, the ceramic membrane was washed with 1% wt/wt HNO_3 to remove any precipitate salts and with 2% wt/wt NaOH to clean the ceramic support structure and the permeate side of the module

2.4. NF/RO unit

Polymeric membranes in spiral wound were used for either NF (200 MWCO) or RO (100 MWCO) tests, with diameter of 2.5 in. and length of 40 in. and active area of 2.5 m^2. Such configuration allows the highest ratio between membrane surface area per occupied volume and fluxes. Maximum allowed operating values for temperature and pressure are 50°C and 60 bar. Typical TMP values used in NF are in the range of 10–30 bar, whereas for RO, TMP values are in the range of 30–40 atm. The permeate from the UF unit was used to feed the NF or RO membranes. Past hundreds of circulation cycles the main part of the OMW volume passed through the polymeric membranes while a small part (concentrate) with high molecule weight organics was retained in the feed vessel. The permeate stream from these units was the water fraction collected. The permeate was analysed further in order to examine the potential for recycling, fertilization-irrigation or discharge. The concentrate was collected and kept separately for further investigation with respect to phytotoxicity, which could show whether it has potential for use as an herbicide.

The polymeric membranes were washed with 0.5% wt/wt Utrasil 11®. The membranes were protected from bacteria growth (when the pilot plant was inactive for more than 3 days, depending on the operation period of the olive mill) with 0.1% sodium bisulfite.

2.5. Methods of analysis

The analysis of the wastewater samples after each treatment step was carried out as follows:

- The solution pH, conductivity, turbidity, dissolved oxygen, temperature and salinity were measured for both the permeate and the concentrate streams in-situ (Water quality checker, Horiba U-10).
- All other parameters were measured in the lab where the samples collected and stored in polyethylene bottles were transported within a few hours.
  - Chemical oxygen demand (COD): closed reflux-colorimetric method 5220 D [40].
  - Total organic carbon (TOC): combustion-infrared method 5310 B. (Analytik Jena Multi N/C HT1300)
  - Phosphorus: vanadomolybdophosphoric acid colorimetric method 4500-P C [40].
  - Total solids, total dissolved solids, total suspended solids, fixed and volatile solids: gravimetric method 2540 B, C, D and E (method numbers according to ASTM Standard Methods, 1989 [40])
  - K, Na: atomic emission spectroscopy (Perkin Elmer Analyst 300)
  - Mg, Ca, Cu, Mn, Zn, Fe: atomic absorption spectroscopy (Perkin Elmer Analyst 300)
  - Cl^-, NO_3^-, PO_4^{-3}, SO_4^{-2}: ion chromatography (DIONEX, DX-120) [41]
  - Sugars: UV–Vis spectrophotometry [42]
  - Phenols: UV–Vis spectrophotometry (Price and Butler method [43]).

3. Results and discussion

Different pretreatment procedures were followed to reduce the amount of suspended solids in OMW. According to UF membrane manufacturer particles larger than 80 μm should be removed prior to ultrafiltration. Thus, separation of the solids with simple screening with an 80 μm polypropylene screen was finally used. The solid fraction was kept for further analysis. The solids separated from the OMW, contained fats, lipids and other organic biodegradable substances and may therefore be considered as components rich in plant nutrients. The results of the physicochemical analyses of the solids collected from the pre-treatment stage are shown in Table 2. As may be seen, organic compounds present are for the most part non-toxic (phenols value is very low in comparison with other organic compounds) which may be mixed with other organic fertilizers such as manure or sludge from biological wastewater treatment plants [33,44]. The presence of the organic substances enhances the microbial activity and hence improves the physical and chemical properties of soil [6,8,10, 12,13]. Salts content expressed in terms of Ca, Mg, Na and K together with phosphorous and nitrogen are expected to further improve the nutritive value of the pre-treatment fraction.

The main separation process was performed in the membrane process apparatus (Fig. 1). Figure caption in Fig. 1 describes the components of the experimental apparatus. A parametric study for the optimisation of the system parameters that resulted in the best fractionation of OMW into water and highly concentrated fractions was performed.

Temperature and trans-membrane pressure (TMP) and consequently the flowrate were the main parameters examined in the present work. All membranes were tested with tap water before the use of OMW. The water permeability (L_{PO}) expressed in L/m^2 h was calculated by Eq. (1):

$$L_{PO} = Q_F/(\text{TMP} \times A) \quad (1)$$

where Q_F is the permeate flowrate, TMP is the trans-membrane pressure and A is the membrane filtration area. Water permeability, L_{PO} according to Eq. (1) depends both on TMP and on the volume flowrate. Unfortunately, the relationship between TMP and the flowrate in membrane units (Fig. 2) in several cases is not linear, necessitating the performance of semi-pilot plant experiments. Water permeability decreased drastically when the OMW was fed into the separation process as may be seen in Fig. 2 in which the variation of L_{PO} with TMP is shown. Similar behaviour was observed for all processes (UF, NF and RO).

3.1. Effect of pressure on UF performance

A parameter important for the optimal operation of UF membranes is the flowrate of the permeate fraction since the function of the ceramic membrane may thus be exploited to the best possible extent. In our parametric investigation TMP values across the ceramic membrane varied in the range of 1–2.5 bar and values for the water permeability were obtained in experiments with tap water and with OMW (initial COD = 12,500 mg/L). According to the results presented in Fig. 2, decrease of permeate flow rate as large

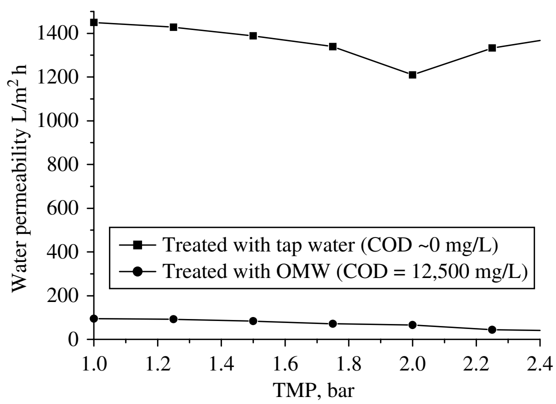

Fig. 2. Water permeability in UF process as a function of the applied TMP values.

as one order of magnitude may be anticipated when OMW is used. Moreover, an additional result demonstrated in Fig. 2 is that the UF process may be operated at TMP values up to 1.75 bar. Above this value, there is no increase of the permeate flowrate (expressed in L_{PO} values). However, deciding on the optimal TMP values for the UF process performance needs examination of the characteristics of the effluents. The results of physicochemical analysis of OMW constituents in permeate and concentrate streams treated with UF over a range TMP values between 1 and 2 bar are summarized in Table 3. It is interesting to note that according to the results shown in Table 3, a dramatic reduction of the turbidity and TSS values of samples collected in permeate stream for all TMP values was found. Initial OMW turbidity values exceeded the limits of the measuring instrument (>999 NTU) while the values of the permeate at all TMP conditions were lower than 100 NTU. The best membrane performance in terms of low turbidity and TSS values were obtained in the range of TMP values of 1.5–1.75 bar. However, the changes for TOC, COD and sugars concentrations (indicative of the organic content of OMW), except for a small increase (10%) in the concentrate streams, as function of TMP between permeate or concentrate streams were not significant. Similar results were obtained for the salt ion concentrations. Generally, UF proved successful in the condensation of solid, fat, lipid components (up to 90%) and of a large part of phenolic compounds (~50%). The permeate streams may be treated further by the NF of RO which shall be fed with relatively "clean" wastewater for the achievement of further isolation of other fractions present in OMW.

3.2. Effect of temperature on UF performance

Provided that the upper temperature limit for the UF membranes was 60°C, the investigation

Table 3
Physicochemical analysis of OMW constituents in the permeate and concentrate streams treated with UF at different TMP values

Parameter/TMP (bar)	Feed	1.25 Conc	1.25 Perm	1.5 Conc	1.5 Perm	1.75 Conc	1.75 Perm	2 Conc	2 Perm
Turbidity (NTU)	>999	>999	94	>999	22	>999	**20**	>999	42
TSS (mg/L)	4311	12,975	196	10,533	201	11,382	**142**	9100	163
TOC (mg/L)	10,900	11,320	9374	10,620	9472	10,210	**9028**	10,850	8816
COD (mg/L)	12,571	13,170	12,444	11,356	10,812	12,444	**9905**	14,984	9900
Phenols (mg/L)	506	506	506	579	408	603	**335**	575	509
Sugars (mg/L)	2800	2630	2851	5400	3457	3457	5330	5165	4283
Fats/lipids (mg/kg)	10,066			6927	229				
Salinity (%)	0.26	0.25	0.24	0.24	0.24	0.23	0.24	0.23	0.23
Conductivity (mS/cm)	5.071	4.75	4.67	4.72	4.64	4.74	4.58	4.56	4.48
K (mg/L)	1560	1684	1296	1778	1526	1530	762	902	762
Na (mg/L)	45	61	43	33	15	34	20.1	37.3	25.73
Ca (mg/L)	72	84.8	68.8	67	43	64	46	50	53
Mg (mg)	94	82	120	93	55.5	87	88	99.6	100
N (mg/L)	60.5	140	142	43	29	29.5	30.7	142	144
P (mg/L)	276	226	230	90	88	78	80.5	229	234

Table 4
Physicochemical analysis of OMW constituents in the permeate and concentrate streams treated with UF at different temperatures

Parameter/temp (°C)	15 Feed	20 Conc	20 Perm	40 Conc	40 Perm	50 Conc	50 Perm
Flowrate	4500	4500	30	4500	39	4500	42
pH	4.81	4.9	4.9	5.09	5.11	5.12	5.14
Turbidity (NTU)	>999	>999	150	>999	58	>999	32
TSS (mg/L)	4675	8180	142	11,382	197	23,653	47
TOC (mg/L)	10,990	10,210	9028	10,630	9282	12,700	5013
COD (mg/L)	12,571	11,719	9179	12,400	9150	16,073	4099
Phenols (mg/L)	725	458	335	579	335	603	116
Conductivity (mS/cm)	5.07	4.74	4.58	4.78	4.60	4.83	4.80
Sugars (mg/L)	2800	3457	5330	5991	5330	9628	978
K (mg/L)	1560	1530	762	1734	762	1338	338
Na (mg/L)	45	34	20	54	12	32	13
Ca (mg/L)	72	64	46	67	52	78	26
Mg (mg)	94	87	88	95	120	108	34
N (mg/L)	60.5	29.5	30.7	69	30	47.4	32
P (mg/L)	276	78	80.5	80.1	97.8	91	82.6

of the temperature dependence of the treatment of OMW was done over the range 15–50°C. The results obtained through this series of parametric study are compiled in Table 4. At 50°C and at constant TMP 1.75 bar higher flow rates were measured, possibly due to the decrease of OMW viscosity. Moreover the permeate stream turbidity at 50°C was lower in comparison with the rest of the temperature values tested. It may therefore be suggested that permeate stream may be more adequately treated better through the subsequent treatment steps (NF and RO). The respective concentrate streams were more concentrated in suspended solids. As may be seen in Table 4, TSS in the concentrate stream (23,653 mg/L) increased significantly at 50°C leaving a relatively "clean" permeate stream (only 47 mg/L). As far as organic content indices are concerned (TOC, COD and sugars) significant changes between permeate and concentrate streams were observed only at 50°C.

The general conclusion from the treatment of OMW with UF process was that better performance of UF unit may be obtained at higher temperatures (50°C) and TMP values between 1.50 and 1.75 bar. It is important to note that the permeate obtained from UF was a "clean" solution appropriate to feed the next treatment processes (NF and RO). Using UF exclusively, it is not possible to isolate individual fractions. However without UF it is not possible to proceed for further purification with the RO and NF.

3.3. Effect of pressure on nanofiltration performance

Nanofiltration (NF) and reverse osmosis (RO) use all permeate stream derived after UF treatment (that is 85–90% of the initial volume of OMW). The temperature was kept constant at 20°C using a cooling system and the measured in situ parameters (pH, conductivity, turbidity and salinity) are summarized in Table 5. The flowrate in permeate stream was between 100 and 120 L/h, which was satisfactory for a

Table 5
Physicochemical analysis of OMW constituents in the permeate and concentrate streams treated with NF at different TMP values

Parameter/TMP (bar)	Feed	10 Conc	10 Perm	20 Conc	20 Perm	30 Conc	30 Perm
Flowrate (L/h)			100		120		100
pH	5.07	5.22	5.20	5.24	5.20	5.26	5.24
Turbidity (NTU)	>151	250	25	390	16	999	15
TSS (mg/L)	190	260	25	408	5.6	1123	2.2
TOC (mg/L)	10,990	14,500	620	17,530	460	24,480	320
COD (mg/L)	12,500	16,500	750	19,701	547	55,076	363
Phenols (mg/L)	725	1369	98	1896	17	9962	11
Salinity (%)	0.24	0.36	0.14	0.39	0.08	0.88	0.12
Conductivity (mS/cm)	4.77	7.07	3.25	7.27	1.71	15.9	2.49
Sugars (mg/L)	867	2512	104	3512	30.7	7148	5.6
K (mg/L)	1296	2890	76	4294	24.4	5320	5
Na (mg/L)	24.5	32	26	41.9	14.6	109.5	6.7
Ca (mg/L)	44.3	120	18	202.1	1.7	403	2.6
Mg (mg)	55	456	12	858.7	0.6	1476	1.5
N (mg/L)	343.4	869	126	1061.7	54	1120.4	74.6
P (mg/L)	233.9	650.7	140.2	838.6	101.3	1744.6	88.2

membrane with a 2.5 m^2 active area. pH values did not vary significantly because the acid components remained both in the concentrate and the permeate streams. Significant changes were however measured in all other “organic” parameter values (TOC, COD and sugars) nitrogen, phosphorous and salts. TOC, COD and sugar concentration measurements showed that the major part of organic compounds remained in the concentrate streams. From the water purification point of view, this result was desirable because the organic compounds responsible for the color (tannins) and toxicity (phenols) remained in the concentrate streams. The permeate streams were colorless, free of salts and with very low concentrations of toxic components (phenolics). The turbidity values in the concentrates increased significantly their values being comparable with the respective initial value of OMW, before the UF treatment. Conductivity values in all concentrate streams increased while in permeate streams decreased drastically. Similar behavior was found in salinity, turbidity, nitrogen and phosphorous values. At all conditions tested concentrate values increased and the corresponding permeate values decreased. The permeate streams with the exception of nitrogen and phosphorous contained very low concentrations of the rest of the components initially present in the OMW. It may therefore be suggested that the final output from the NF treatment may be used for irrigation. Between the three different pressure values tested, the pressure of 20 bar gave better results in terms of conductivity, salinity and turbidity of the permeate. Higher values for TMP were not useful and may be used in other process (e.g. RO unit) where higher-pressure values are needed. Photograph of samples before and of permeate streams after treatment with NF are shown in Fig. 3. As may

Fig. 3. Photograph of samples before (right cylinder-feed) and after nanofiltration process (left cylinder-permeate).

be seen the permeate output was clear enough for irrigation or disposal in aquatic streams. Rejection of NF may be by Eq. (2):

$$NF_{RJ} = \left(1 - \frac{\text{Permeate Conductivity}}{\text{Feed Conductivity}}\right) \times 100 \quad (2)$$

For the optimal operation conditions (TPM = 20 bar) it was calculated that NF_{RJ} was 71%.

3.4. Effect of pressure on RO performance

Treatment of UF permeates streams with nanofiltration membranes (NF) showed that interesting components of the OMW remained in concentrate streams. Further and better separation of the various fractions may be achieved through RO membranes. These membranes have smaller pores and limit the transport of larger molecules. The results obtained following treatment of UF permeate with RO, for three different TMP values are summarized in Table 6. The temperature was kept constant at 35°C. In all cases the permeate streams conductivity, salinity and turbidity decreased significantly. The performance was better at high-pressure values (TMP = 40 bar). On the other hand concentrate

Table 6
Physicochemical analysis of OMW constituents in the permeate and concentrate streams treated with RO at different TMP values

Parameter/TMP (bar)	Feed	20 Conc	20 Perm	30 Conc	30 Perm	40 Conc	40 Perm
Flowrate (L/h)			30		30		32
pH	5.25	5.39	5.44	5.39	5.70	5.39	5.82
Turbidity (NTU)	40	50	28	82	23	115	14
TSS (mg/L)	215	230	12	252	2.1	585	2.3
TOC (mg/L)	11,240	13,345	300	15,420	220	58,566	117
COD (mg/L)	12,500	14,900	526	15,891	311	87,433	206
Phenols (mg/L)	1018	1190	20.2	1336	11.2	6.782	2.4
Fats (mg/L)	230					1145	10
Salinity (%)	0.26	0.30	0.020	0.30	0	0.30	0
Conductivity (mS/cm)	5.07	6.01	0.128	6.7	0.1	20.8	0.053
Sugars (mg/L)	1308	1890	15.7	2245	5.8	2548	2.3
K (mg/L)	1627	1890	48	2255	25.08	9410	38.2
Na (mg/L)	20.9	30.2	7.8	33.1	6.5	24.2	14.3
Ca (mg/L)	51.7	54.3	3.5	57.2	1.9	248	4.7
Mg (mg)	66.6	69	1.9	71.4	0.8	87	3.4
N (mg/L)	60.5	80.1	39	89	33.2	102	47
P (mg/L)	261	87	76	93.6	72	219.4	86.2

streams showed an increase in all the values of all parameters measured. The final sample of permeate stream taken at the end of the treatment at 40 bar showed a drop of salinity to zero, confirmed by a concomitant decrease of the conductivity at 0.053 mS/cm and the turbidity was 14 NTU. This value corresponded to clean water. On the other hand conductivity of concentrate stream increased beyond 20 mS/cm (initial value ~5 mS/cm) and turbidity (that is all components contribute to the change of the color of the sample) increased to 115 NTU. As far as phenols and other organic compounds are concerned they all remained in the concentrate stream. Permeate was almost clear water containing some salt components useful for plant growth. The latter fraction may therefore be safely disposed to aquatic receptors or may be used for irrigation. The rejection obtained through RO treatment was calculated according to Eq. (2) to 98.95%.

4. Conclusions

It is possible to achieve high levels of purification of OMW obtained from a typical olive mill in Western Greece using membrane technology. The parametric study included a number of operational parameter values of primary importance for the operation of UF, NF and RO units. Using the system of ultrafiltration, nanofiltration and/or reverse osmosis the OMW may be treated efficiently to obtain a permeate (water) fraction with quality characteristics that make it possible to be discharged in aquatic systems according to national or EU regulations or to be used for irrigation (~75–80% of the initial volume). The ultrafiltration process may be used to separate high molecular weight components and suspended solid particles. The UF concentrate was found to contain the largest portion of fats, lipids, solids, etc. Further processing with nanofiltration may be employed for the separation of the most part of phenols present. Clearly further research is needed in this direction, related with the sustainability of the treatment process. The NF concentrate and permeate fractions contain other organic compounds including lower molecular weight sugars. Addition of an additional RO step in the treatment sequence, past UF, the performance is equivalent to that corresponding to NF. In this case the economics of the treatment process may be improved.

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