Membrane Filtration of Olive Mill Wastewater and Exploitation of Its Fractions

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ABSTRACT: Olive mill wastewater (OMW) produced from small units scattered in rural areas of Southern Europe is a major source of pollution of surface and subsurface water. In the present work, a treatment scheme based on physical separation methods is presented. The investigation was carried out using a pilot-plant unit equipped with ultrafiltration, nanofiltration, and reverse osmosis membranes. Approximately 80% of the total volume of wastewater treated by the membrane units was sufficiently cleaned to meet the standards for irrigation water. The concentrated fractions collected in the treatment concentrates were characterized by high organic load and high content of phenolic compounds. The concentrates were tested in hydroponic systems to examine their toxicity towards undesired herbs. The calculations of the cost of the overall process showed that fixed and operational costs could be recovered from the exploitation of OMW byproducts as water for irrigation and/or as bioherbicides. *Water Environ. Res.,* **79** (2007).

KEYWORDS: olive mill wastewater, hazardous wastes, reuse of olive mill wastewater, toxic effects, bioherbicide, ultrafiltration, reverse osmosis, membrane processes.

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Introduction

Olive tree cultivation is a significant part of land use in Mediterranean countries. The olive tree agriculture and the process of olive oil production have important environmental, social, and economic considerations. Mediterranean countries produce 95% of the total world production of olive oil, which is estimated to reach 2.4 million metric tons per year. The largest producers of olive oil are Spain, Italy, Greece, Portugal, and Turkey. The production of large olive oil quantities in the last few decades is associated with the development of significant environmental problems. The predominant technology of three-phase olive mills results in the production of enormous amounts of residual wastewater (olive mill wastewater [OMW]) practically equal to 1.1 to 1.5 times the weight of milled olives (Borja et al., 1992; Erguder et al., 2000; Fiestas Ros de Ursinos, 1981; Fiestas Ros de Ursinos and Padilla, 1992; Mendia et al., 1986, Tsonis, 1988; Tsonis and Grigoropoulos, 1988). The large volume of wastewater produced from the process is a result of the use of large quantities of water. In the Mediterranean zone alone, the quantity of OMW produced annually is approximately 15 million metric tons and includes a high pollution load. A typical local olive mill is currently producing, on average, 1000 metric tons of toxic liquid wastes per season. The biochemical oxygen demand and chemical oxygen demand (COD) of this wastewater, from only one olive mill, causes environmental damage equivalent to that of the untreated municipal wastes of a town with 30 000 inhabitants. The OMW has a direct effect on the environment, causing pollution of surface and groundwaters, cultivated fields, and aquatic ecosystems, including the sea, mainly because of the high concentration of organic compounds and particularly of polyphenols (Mendia et al., 1986; Tsonis, 1988; Tsonis et al., 1989). Furthermore, because of the high organic load of OMW, it may contribute significantly to eutrophication of recipients in which fluid exchange rates are low (closed gulfs, estuaries, lakes, etc.). Finally, an additional adverse effect of OMW on the environment is the aesthetic degradation caused by its strong odor and dark coloration.

At present, a number of methods for OMW treatment are practiced. A very low-cost method that may be applied is the direct land application of OMW. Depending on soil composition and because of the mineral and organics content of the wastes, it may be beneficial for the soil (Balatsouras, 1997; Di Giovacchino et al., 2002; Papadimitriou et al., 1997; Riffaldi et al., 1993; Tamburino et al. 1999). A method, practiced widely, although illegally, is the disposal of OMW into surface waters, including lakes, rivers, and the sea, with disastrous environmental consequences (Di Giovacchino et al., 2002; Tamburino et al., 1999; Tsonis, 1988; Tsonis et al., 1989). Al-Malah et al. (2000) used a series of treatment steps composed of settling, centrifugation, and filtration to condition OMW followed by post-treatment processes, including adsorption on activated clay. The well-known aerobic and anaerobic processes, proven to be effective methods for municipal or industrial wastewater treatment, may also be applied in OMW treatment (Tsonis, 1988; Tsonis and Grigoropoulos, 1988), provided that substances with antimicrobial action are removed from OMW in a first stage. Composting, instead of direct disposal of OMW to the soil, seems to be a promising method for recycling these pollutant liquid wastes (Chatjipavlidis et al., 1996; Piperidou et al., 2000). Turano et al. (2002) proposed an integrated centrifugation–ultrafiltration (UF) system for the reduction of pollution caused by the wastes and selective separation of useful products, such as fats, sugars, and polyphenols. In the centrifugation step, the suspended solids were removed, and the UF separation process treated the centrifuge supernatant further. The combination of these two processes showed a 90% reduction of COD values. Canepa et al. (1988) proposed a combined system of membrane processes to treat OMW and showed that the cost is affordable for olive mill enterprises. However, because of the complex systems encountered and the fact that new facilities need to be built next to oil mills, no further progress has been made, to date.

Unfortunately, the present situation is approximately the same as in the past; OMW is disposed of in large pits or directly in the sea, lakes, rivers, or soil, with adverse environmental implications. Provided that the fixed cost for the installation of OMW treatment

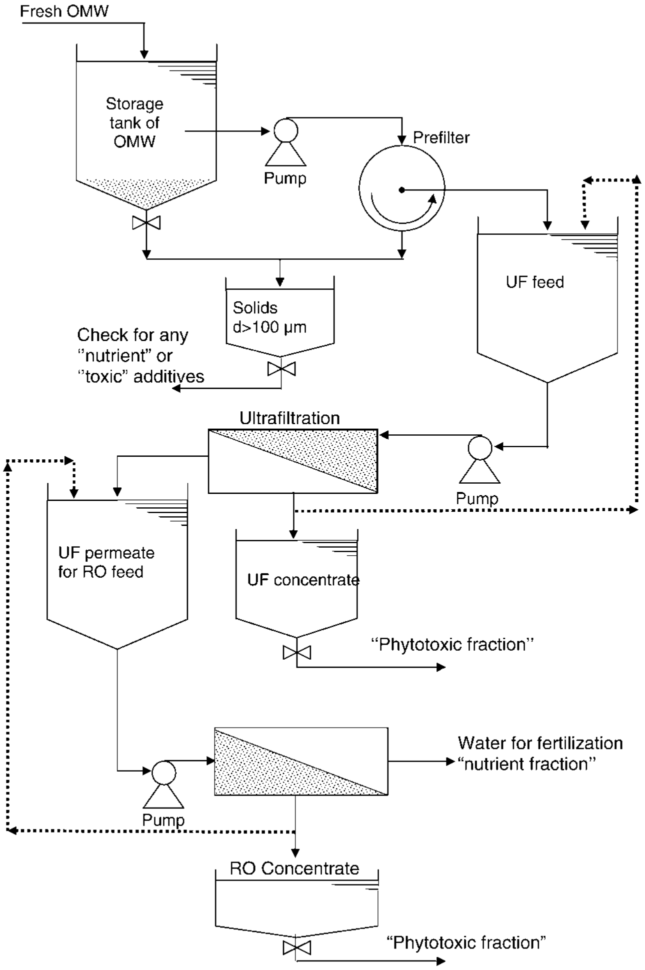

Figure 1—Flowsheet for OMW treatment and fraction isolation. Each process was performed independently, after completion of the previous one.

systems seems to be inelastic, operational cost reduction may be attained through exploitation of the waste byproducts. The present work is a contribution to the solution of OMW treatment, focusing on the use of waste resulting from the treatment process for the production of substances of potential added value. Polyphenols and fats are the most interesting of all OMW components because of their toxicity, which may affect plant growth (Bais et al., 2002; Capasso et al., 1995; Garcia-Garcia et al., 2000). The phenolic components include the various phenolic acids (caffeic, protocatechic, α-hydrocycinnamic, vanillic, flavonoids, anthocyanines, eleoprotein, o-diphenols, mono- and di-glucosides, etc.). In addition to polyphenols, components that may have nutritious value are also present in OMW. Among these nutrients, hydrocarbons, sugars, and inorganic salts are most important, as they may find applications as animal feedstock or as fertilizers for the amelioration of soil productivity. The inorganic components of OMW (ashes, nitrogen, phosphorus, magnesium, potassium, and trace elements) may be used in soil fertilization, either as received or in combination with other inorganic fertilizers. The OMW organic substances, on the other hand, may be mixed with organic fertilizers, such as manure, or with sludge from biological wastewater treatment plants (Fiestas Ros de Ursinos, 1986; Fiestas Ros de Ursinos and Padilas, 1992; Harvey et al., 2002).

The idea of using membrane technology is revisited in the present work, in which a new cost-effective system for complete exploitation of OMW is suggested, offering a viable solution to the problem of OMW disposal. Use of the proposed separation techniques (prefiltration, UF, nanofiltration [NF], and reverse osmosis [RO]) produce byproducts that might include additional benefits. A pilot plant was developed in an olive mill operating in Achaia (Patras, Greece) during an olive harvesting season. Large volumes of OMW produced daily were treated systematically in a semibatch procedure to identify problems relevant to long-term behavior and reliability. Concentrate fractions obtained in membrane systems were examined as growth inhibitors of native plants (bioherbicides) in farming systems. The water—the main constituent of OMW, containing dissolved inorganic nutrients that permeate from the NF or RO system—was tested with respect to potential phytotoxic properties on cultivated plants. In this context, it could be considered for use in irrigation or for reuse in the milling process. Finally, a feasibility-exploitation study was done to estimate if depreciation of the (indeed) expensive investment may occur in a short period of time.

Methodology

Experimental Procedure. A pilot plant was designed (Figure 1), developed, and operated for a full olive harvesting period, in a typical Greek olive mill, in the Achaia region (Patras, Greece), where olive tree cultivation is very common. During olive oil extraction, the host olive mill produced approximately 1 m^3/h of wastewater, a part of which was diverted to the feed storage tank (100 L, Figure 1), for the purpose of the pilot plant study. The treatment operation of OMW was done in a semibatch mode (2 to 3 loads of the storage tank per day). The daily treatment lasted approximately 6 to 8 hours per day, 4 to 5 days per week, depending on the operation of the olive mill, to check for problems related to long-term behavior and reliability. The pilot plant consisted of a rotating screen with 80-µm openings, two membrane units, storage tanks, and pumps. The first membrane unit contained a ceramic tubular membrane and performed the UF process. The second unit was used either as NF or as a RO process using polymeric membranes designed for NF or RO, respectively. The UF, NF, and RO processes included an internal recycle process and proceeded until the attainment of a sufficiently concentrated feed. Therefore, the entire process is a combination of individual batch processes. A schematic representation showing the overall results of these individual batch processes, useful for calculations, is presented in Figure 1. After a prefiltration step (screen, mesh size 80 µm) of the mill effluent to remove the suspended solids and fats was performed, a liquid quantity volume totaling 100 L was collected in the feed storage tank. Next, UF was applied, and OMW collected in storage was recycled, until reaching 90% water recovery. A part of the feed permeated through the UF membrane. At the end of the recycling process, two fractions were collected—the concentrate (approximately 10 L) and the permeate (approximately 90 L). The concentrate was collected for further analyses, while the permeate stream was collected in a separate tank. After treatment of the entire OMW feed quantity by UF, a fresh quantity of prefiltered OMW was introduced to the feed tank. In the next steps, UF permeate (90 L) was used as the feed liquid for the NF or RO processes. The NF and/or RO processes operated as the UF (internal recycle process), and two streams—concentrate (approximately 10 L) and permeate (approximately 80 L)—were obtained. Portions of all fractionation streams were collected for further analyses, including possible phytotoxic activity and nutritive value

(Bais et al., 2002; Capasso et al., 1995; Garcia-Garcia et al., 2000; Ortega et al., 1996; U.S. EPA, 1996). The aqueous permeate obtained from the NF or RO process (''water fraction'') had the physicochemical characteristics required by national and European Union regulations (sanitary provision E1b/221/22-1-65, circular with number YM/5784/1992 and YM4419/1992, and European Directives 91/271/EEC, 76/464/EEC, etc.) for the safe disposal of wastewater.

Characteristics of the Membranes and Operational Parameters. The membrane in the UF process was made of ceramic material (zirconia) with pores of 100 nm, 19 tubes of 1020 mm length and 4 mm diameter, and membrane area of 0.24 m^2. The clean water permeability was approximately 1800 L/hm^2 bar; the flowrates were 3.44 and 4.30 m^3/h for crossflow velocity 4 and 5 m/s, respectively; and the holdup volume was 0.24 L for the feed and concentrate and 0.64 L for the permeate. The concentrate stream of UF contained solids, fats, lipids, sugars, and other high-molecular-weight organic substances. In the permeate stream, low-molecular-weight organic substances, salts, and part of sugars were found in the largest portion of water (approximately 90% of the initial amount of OMW). Transmembrane pressure (TMP) applied across the ceramic membrane of UF was 1.75 bars. The TMP values were selected through a parametric experimental study, and the selection criteria were based on the yield and quality of the products (optimum flowrates, low turbidity values, and organic concentration in permeates [Paraskeva et al., 2006]). The corresponding flowrate of the permeate steam for this TMP value was 40 L/h.

Spiral-wound polymeric membranes with an effective area of 2.5 m^2 were used in NF and RO units. By a simple exchange of the filtering element, the unit may be easily converted for either NF or RO applications. Typical characteristics of the UF membrane used were as follows (data source: Hydro Air Research SpA, Milan, Italy): composite noncellulosic membrane, cutoff = 150 to 300 Daltons, rejection 98% (magnesium sulfate [molecular weight = 120], test conditions 2000 mg/L feed, 25°C, 6.9 bar), recommended operating range 0.5 to 27.5 bar, maximum 41.4 bar. The characteristics of the RO membrane (data source: Hydro Air Research SpA) were as follows: three layers composite noncellulosic membrane, rejection approximately 99% (sodium chloride, [molecular weight = 58.5], test conditions, 32 000 mg/L feed, 25°C, 55.2 bar), typical operating pressure 55.2 bar. The TMP values used in NF were in the range 10 to 20 bars (permeate flowrates 100 and 120 L/h, respectively), whereas for RO, TMP values were in the range 30 to 40 bars (flowrates 30 and 35 L/h, respectively).

Cleaning of Membranes. The duration of the treatment operation of OMW was approximately 6 to 8 hours per day, 4 to 5 days a week, depending on the operation of the olive mill, to check for problems related to long-term behavior and reliability. A gradual decrease of the flowrate was observed during each day's experiments because of membrane fouling. At the end of the day, membranes were washed thoroughly with various solutions. More specifically, the ceramic membrane was washed with dilute acids—1% w/w nitric acid to remove any precipitate salts and 2% w/w sodium hydroxide to clean the ceramic support structure and the permeate side of the module. The polymeric membranes were washed with 0.5% w/w P3-Utrasil 11 (Henkel- Ecolab, Athens, Greece). The membranes were protected from bacterial growth (when the pilot plant was not in operation for more than 3 days, depending on the operation schedule of the olive mill) with the aid of 0.1% w/w sodium bisulfite.

Analysis of Olive Mill Wastewater Fractions. The measurements of pH, conductivity, turbidity, dissolved oxygen, temperature, and salinity were done for both the permeate and the concentrate streams inline (Water Quality Checker, Horiba U-10, Horiba Ltd., Kyoto, Japan). For the rest of the analyses reported, samples were withdrawn, placed in polyethylene bottles, and transferred during the same day to the laboratory. Total organic carbon (TOC) was measured with the appropriate analyzer (Analytik Jena Multi N/C HT1300, Jena, Germany) equipped with an infrared analyzer (method 5310B; APHA et al., 1989). The COD was measured colorimetrically (method 5220D; APHA et al., 1989). Phenols were analyzed by direct colorimetry (method 5530D; APHA et al., 1989). Total solids, total dissolved solids, and fixed and volatile solids were measured gravimetrically (method 2540B-E; APHA et al., 1989). Ammonia content was determined by the phenate method (method 4500D; APHA et al., 1989), and total phosphorus was determined colorimetrically as the vanadomolybdate complex (method 4500 P-C; APHA et al., 1989). The content of chlorine, nitrate, phosphate, and sulfate anions was measured by ion chromatography with a conductivity detector using the appropriate standards and a Dionex DX -120 ion chromatographer (Dionex, Sunnyvale, California). Sugars in the various fractions were measured spectrophotometrically (Josefsson et al., 1972). The concentrations of sodium and potassium were measured by atomic emission spectrometry (Perkin Elmer AAnalyst 300; Perkin Elmer, Wellesley, Massachusetts) and calcium and magnesium by atomic absorption spectrometry (Perkin Elmer AAnalyst 300). Characterization of the concentrate or permeate fractions was performed in a series of samples, each measured in triplicate.

Evaluation of Phytotoxic Activity of Olive Mill Wastewater Byproducts. The possible phytotoxic properties of OMW concentrate fractions were evaluated using the seed germination/root elongation toxicity test suggested by the U.S. Environmental Protection Agency (U.S. EPA, 1996) (Washington, D.C.). The concentrate effect on plant growth was tested in cucumber seedlings. The germination/root elongation toxicity tests were performed using seeds of native plants, including *Avena sterilis* L., *Setaria sp* L., *Sinapis alba* L., and *Sonchus oleraceus* L. The seeds were sterilized with 0.1% sodium hypochlorite solution for 20 minutes and washed with deionized water three times before use. Thirty seeds were positioned in sterilized glass Petri dishes lined with Whatman No. 1 filter paper (Whatman International Ltd., Maidstone, England) at the bottom. The dishes with seeds were incubated in a constant temperature chamber for 2 days (48 hours) at 25°C. The germination rate (Ortega et al., 1996) and corresponding parameters characterizing the dose-response relations were estimated. A sample from the concentrate fraction obtained in UF process was used as a test solution. The sample contained 2760 mg/L phenolic compounds, 25000 mg/L total sugars, up to 85 mg/L total phosphorus, 410 mg/L total nitrogen, and inorganic ions (375 mg/L calcium, 110 mg/L magnesium, 57 mg/L sodium, 2420 mg/L potassium, 965 mg/L chlorine, and 140 mg/L sulfate). The concentrate fraction sample was sterilized by boiling for 30 minutes, because the UF fraction samples are rich in microbes, bacteria, and fungi. The sterilization process may cause oxidation of phenolic compounds, to some extent, but the removal of microorganisms is of prime importance. These microbes may affect the viability of seeds during the experiment. For the needs of the experiments, the concentrated fraction was diluted to 10, 20, 30, 40, 60, 80, and 100 v/v, with tap water.

The experiments, related to the effects of UF concentrate fraction and RO permeate on the cucumber (*Cucumis sativus* L. variety Konto) seedlings growth, were conducted in a growth chamber.

Table 1—Results of physicochemical analyses of raw OMW.

Parameters	Sample 1	Sample 2	Sample 3
Temperature, °C	45	43.4	42
pH	5.24	5.09	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
Potassium, mg/L	2114	1906	2050
Sodium, mg/L	27.7	28	32
Calcium, mg/L	83	48	56
Magnesium, mg/L	88.2	61	76
Copper, mg/L	0.84	0.49	0.56
Manganese, mg/L	0.46	1.17	1.02
Zinc, mg/L	1.7	4.01	2.3
Iron, mg/L	0.45	0.6	0.55
Chlorine, mg/L	377	442	405
Sulfur, mg/L	64.9	76.8	69.4
Nitrogen, mg/L	336	60.5	56
Phosphorus, mg/L	253	261	258

Table 2—Results of physicochemical analyses of sediments collected in prefilter procedure.

Parameter	g/kg[a]
TOC	680
Phenols	3.5
Sugars	23
Fats	640
Magnesium[b]	0.4
Calcium[b]	4
Sodium[b]	0.1
Potassium[b]	8
Phosphorus[b]	8
Nitrogen[b]	20
Sulfur[b]	2
Nondissolved solids[b]	10

[a] Per kilogram of the dried solids collected from the rotating stainless-steel drum.

[b] Following acid digestion of the solids.

Cucumber seeds, obtained from commercial sources, were sown in plastic flats with separate cells. The flat cells were filled with sphagnum moss turf. Seedlings were held in flat pots until the first true leaf emerged. Then, seedlings were transplanted to a hydroponic system, where they remained for 7 to 10 days (before the concentrated fraction was added) for adaptation in the nutrient solution. Approximately 10 to 12 seedlings fixed on flats floated on the nutrient solution. Two nutrient solutions were used—a starter solution and a vegetative one (Bugbee, 2003). The chemical synthesis of starter solution, in macroelements, was 3.0 mM nitrogen, 0.5 mM phosphorus, 1.5 potassium, 1.0 mM calcium, 0.5 mM magnesium, and 0.5 mM sulfur and, in microelements, was 10 µM iron, 25 µM ferric hydroxyethylethylenediaminetriacetic acid (FeHEDTA), 2.0 µM boron, 3.0 µM zinc, 0.3 µM copper, and 0.09 µM molybdenum. The vegetative refill included 6.0 mM nitrogen, 0.5 mM phosphorus, 4.5 mM potassium, 1.0 mM calcium, 0.3 mM magnesium, 2.5 µM iron, 5.0 µM Fe-HeDTA, 1.0 µM boron, 1.0 µM zinc, 0.3 µM copper, and 0.03 µM molybdenum. The pH of the nutrient solution was 4.5 ± 0.5. Seven treatments were tested in this experiment (treatments with increasing concentrations of UF concentrate fraction, with 0% as control [X0], 1% [X1], 2% [X2], 4% [X3], and 6% [X4] solution) by adding the ''toxic'' fraction to the starter nutrient solution and two treatments with RO permeate diluted 1:5 by adding tap water (X5) and the same amount of this fraction to the control nutrient solution (X6). In all cases, both pH and nitrate concentration were corrected during the experiment. The volume and pH of nutrient solution were kept stable during the experiments by adding sulfuric acid solution every 2 days, 5 N after the addition of the vegetative refill solution. The day temperature in growth chamber was in the range 30 to 33°C and, during the night, in the range 22 to 24°C. The light condition was a 14/10 day/night photo period, with irradiance during the day of 750 µE m^{-2} s^{-1}, from four high-pressure sodium lamps (400 W) and two tubular fluorescent lamps. Three to four plant samples were removed per week, and the total plant dry weight was measured.

Results and Discussion

Pilot-plant experiments were performed with untreated OMW obtained directly from the outlet of the olive mill. The results of the physicochemical analyses of three samples of OMW, obtained at different days, are summarized in Table 1. As shown, the values of the physicochemical parameters measured in the three samples were similar. The similarity of the values may be attributed to the fact that all treated olives originated from the same locality and belonged to the same class of olives. Moreover, the operation and treatment methods in the test olive mill were the same for the entire olive-harvesting period.

Prefiltration. Preceding treatment of OMW with membranes, the fluids were filtered using a perforated rotating stainless-steel drum with 80-µm openings. The solids collected were analyzed by physicochemical methods, and the results from a typical sample are summarized in Table 2. The permeate stream was used as feed for the UF unit. The solids and organic material (mainly fats) were retained on the rotating screen. This part was considered with respect to nutritious value that may be exploited as constituents to soil organic fertilizers.

Ultrafiltration. The first stage of membrane filtration and separation into different fractions is the implementation of the UF process, in which condensation of OMW is anticipated. Olive mill wastewater was circulated through membranes until reaching 90% of water recovery and low-molecular-weight organic substances, acids, and some sugars passed through the membranes. The results of the physicochemical analyses obtained for both streams (concentrated and permeated streams) are summarized in Table 3. The initial volume of OMW was fed at room temperature (20°C), and it was gradually heated because of the viscous friction of the solution on the membrane walls and because of the pump that continuously recycles the content of the OMW wastewater tank (feed of UF). Special attention should be paid to the system temperature because of the temperature limit (60°C) set by the manufacturer of the ceramic membranes. Ultrafiltration is an excellent procedure to remove suspended particles from the mixture of OMW, as seen in Table 3, where it is shown that most solids were kept in the

Table 3—Physicochemical characteristics of initial OMW and of concentrate and permeate streams in UF.

Parameters	Feed	Concentrate flowrate: 4500 L/h	Permeate flowrate: 40 L/h
Temperature, °C	25	60	60
pH	5.24	5.6	5.3
Conductivity, mS/cm	4.38	4.46	4.34
TSS, mg/L	4311	32 663	65
Turbidity, NTU	>999	>999	21
Salinity, %	0.22	0.22	0.21
TOC, mg/L	10 990	17 538	6922
COD, mg/L	12 571	22 196	5660
Sugars, mg/L	2300	9628	1350
Fats, mg/L	12 066	9565	317
Phenols, mg/L	604	603	605
Potassium, mg/L	988	1047	938
Sodium, mg/L	80	95	74
Calcium, mg/L	38,4	57	36
Magnesium, mg/L	106	108	98
Copper, mg/L	1.47	1.11	0.6
Manganese, mg/L	0.64	0.58	0.35
Zinc, mg/L	2.4	2.09	1.6
Iron, mg/L	0.87	0.78	0.66
Chlorine, mg/L	392	352	187
Sulfur, mg/L	183	165	147
Nitrogen, mg/L	326	307	288
Phosphorus, mg/L	690	491	482

concentrate stream. Organics responsible for the black color of OMW (mainly tannins; Annesini et al., 1983) remained in the treated sample (permeate). The analytical characterization of the fluids was limited to phenols, because this fraction was of interest for the potential of further applications. The UF helped to remove a large portion of organic material, expressed in terms of fats, COD, and TOC (Table 3). The concentrate stream was rich in biodegradable organic substances and solid particles and may be considered as a fraction with possible nutritive value. However, the high value of phenols that remained constant in both concentrate and permeate streams should not be ignored.

Nanofiltration and/or Reverse Osmosis. The results of the composition of the permeate aqueous phase after treatment with NF membranes at 10 and 20 bars are summarized in Table 4. As shown, TOC was reduced by 95% at 10 bars and by 97% at 20 bars. According to European Union directive 91/271 (1997), the treatment of wastewater should ensure reduction of COD by 75%. Reduction of the phosphorus and nitrogen content is also within the limits set by the same directive. The concentrates, on the other hand, were enriched in total organic content and also with respect to the phenolic content. The aqueous solution after NF was transparent, suggesting that the organic substances responsible for the dark color remained, for the most part, in the concentrated stream. The concentrate was further examined for plant nutrients and toxic components. The pilot-plant experiment using the same feed was repeated at a higher TMP value (20 bars), and the results are presented in the last two columns of Table 4. As shown, higher pressure resulted in better separation of organics from the aqueous phase. At higher pressures, the flux through the membrane increased also (though not always linearly), favoring the passage of low-molecular-weight substances (including water molecules), which passed faster through the membrane tubes. Phenols were concentrated 14 times (from 725 to 9962 mg/L), providing a fraction rich in components with the potential of use as herbicides. On the other hand, the final output (i.e., the final permeate stream) could be used for irrigation. At this point, one of the main tasks of the present

Table 4—Physicochemical characteristics of feed and NF streams (concentrate and permeate streams) for TMP = 10 and 20 bars.

Parameters	Feed (100 L)	Concentrate TMP = 10 bars	Permeate TMP = 10 bars	Concentrate TMP = 20 bars	Permeate TMP = 20 bars
Flowrates, L/h			100		120
Temperature, °C	25	48	45	46	43
pH	5.11	5.41	5.44	5.26	5.24
Conductivity mS/cm	4.6	9.9	1.57	15	0.49
TSS, mg/L	190	408	5,6	1122	2,2
Turbidity, NTU	48	390	16	999	15
Salinity, %	0.23	0.55	0.07	0.88	0.12
TOC, mg/L	9370	19 530	460	24 480	320
COD, mg/L	10 086	19 701	547	55 076	363
Sugars, mg/L	867	3512	31	7148	5.6
Fats, mg/L	320	900	10	920	7
Phenols, mg/L	725	2096	17	9962	10
Potassium, mg/L	1296	4294	25	5320	5
Sodium, mg/L	25	42	15	109	7
Calcium, mg/L	44	202	44	403	2,6
Magnesium, mg/L	55	858	1	1476	1,5
Copper, mg/L	0.35	0.9	0	3.54	0
Manganese, mg/L	0.2	0.57	0	2.13	0
Zinc, mg/L	0.55	1.86	0.02	7.58	0.01
Iron, mg/L	0.22	0.79	0	3.49	0
Chlorine, mg/L	129	173	231	236	39
Sulfur, mg/L	27	98	6.4	348	4.7
Nitrogen, mg/L	343	1061	54	1744	88
Phosphorus, mg/L	234	838	101	1120	74.6

Table 5—Physicochemical characteristics of feed and RO streams (concentrate and permeate streams) for two different TMP values (30 and 40 bars).

Parameters	Feed (100 L)	Concentrate, 30 bars	Permeate, 30 bars	Concentrate, 40 bars	Permeate, 40 bars
Flowrate, L/h			30		35
Temperature, °C	30	33	34	38	36
pH	5.25	5.39	5.71	5.15	5.97
Conductivity, mS/cm	45.07	6.47	0.1	12.6	0.044
TSS, mg/L	245	252	2.1	585	2.3
Turbidity, NTU	40	82	20	117	15
Salinity, %	0.26	0.35	0.0	0.72	0.0
TOC, mg/L	11 240	15 420	220	58 566	117
COD, mg/L	11 537	15 891	311	87 433	206
Sugars, mg/L	1528	2245	5.8	12 548	0
Fats, mg/L	229	1056	0	1145	0
Phenols, mg/L	1018	2335	11.2	6782	2.4
Potassium, mg/L	1804	2255	25	9410	28.2
Sodium, mg/L	25	33	6.5	34.2	14.3
Calcium, mg/L	56	58	2.0	248	4.7
Magnesium, mg/L	62	71	0.8	457	3.4
Copper, mg/L	0.57	0.44	0	2.3	0
Manganese, mg/L	0.73	0.77	0	4.44	0
Zinc, mg/L	1.62	1.59	0.04	10.62	0.02
Iron, mg/L	0.52	0.93	0.09	0.93	0.09
Chlorine, mg/L	349	351	5.6	2257	11
Sulfur, mg/L	12	44	5.8	114	4.3
Nitrogen, mg/L	610	89	33	372	97
Phosphorus, mg/L	314	394	72	719	86

work, to treat large volumes of OMW, was already achieved, avoiding the use of RO, which is an energy-demanding process. For comparison, experiments in an RO pilot plant were done for two different TMP values, and the results are shown in Table 5.

As may be seen in Table 5, the RO process operated at 30 and 40 bars caused reduction of the organic load by 98 and 99%, respectively. The permeate stream was clear, with very low content of phenols. The odor-free water could possibly be used for irrigation purposes. The organic compounds, including phenols, accumulated in the concentrate stream, which may be further examined with respect to the potential of developing ecological herbicides. The best results from the RO pilot plant were obtained at higher TMP values (40 bars).

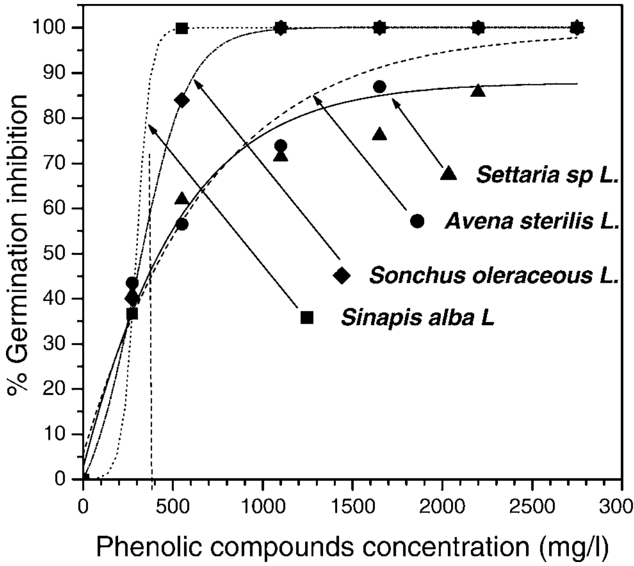

Figure 2—Dose-response curves of percentage germination inhibition for four native species. EC50 = effective concentration for 50% inhibition.

Evaluation of Phytotoxicity of OMW Fractions. The experiment related to the effect of ''toxic'' fractions on seed germination showed that substances contained in the UF concentrate fraction resulted in a strong inhibition of seed germination rates in native species *Avena sterilis* L. *Setaria sp* L. *Sinapis alba* L. and *Sonchus oleraceus* L. (all common weeds). This inhibition showed a dose-response relationship between ''toxic'' fraction concentrations and seed germination rates and was described with classical sigmoid curves (Figure 2). Researchers (Capasso et al., 1995) have demonstrated that the main cause of OMW toxicity was a result of the phenolic compounds present. In Figure 2, the effect of increasing phenolic compounds concentration on the germination inhibition is shown. It should be noted that phenol concentration was adjusted by the addition of UF concentrate fraction in the seed incubation media. The species studied were found to be very sensitive to the toxicity of UF fraction used. The effective concentration for 50% inhibition, EC_{50}, was found in the range 375 to 380 mg/L of phenolic compounds (dashed line in Figure 2).

An additional series of experiments was performed on the cucumber dry biomass production to investigate the effect of UF concentrate and RO permeate fractions. It was found that the presence of a UF ''toxic'' fraction in nutrient solutions in concentrations higher than 2% w/w (Figure 3) caused a decline in dry biomass production per plant and phytotoxic symptoms, both on root and shoot morphology. The UF fraction concentrations below 2% w/w

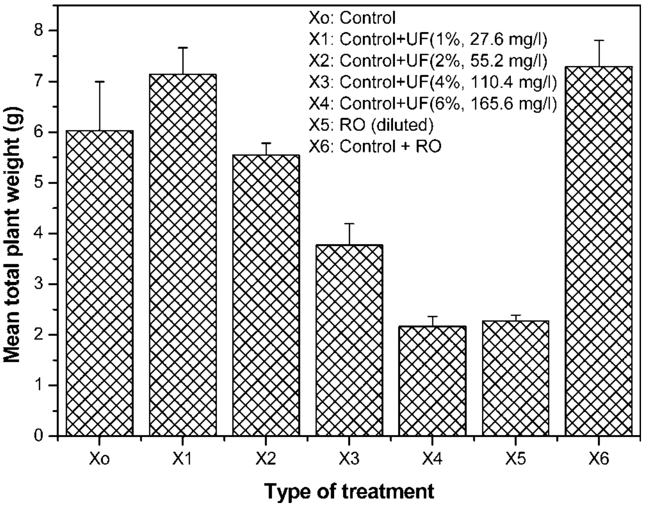

Figure 3—Mean total plant dry weights of cucumber plant for the tested treatment procedures (X0, X1, X2, X3, and X4 UF diluted solutions and X5 and X6 diluted RO solution, respectively). Error bars show the deviation among four plant dry weight values of cucumber plants treated with the same solution.

in nutrient solution showed similar or slightly better results in cucumber plants growth compared with the control (X1 treatment in Figure 3). This finding, confirmed also in a few other experiments not included in the present work, is a rather complicated phenomenon, and additional experiments are needed to further clarify this issue. The addition of RO permeate fraction in the control nutrient solution resulted in the enhancement of the cucumber growth also (X6 treatment in Figure 3). This finding suggested that the RO permeate fraction did not exhibit phytotoxic activity. For treatment X5, in which the same RO dilution in tap water was applied, a delay of the growth of cucumber plants was found. It may be suggested that the delay found was a result of the deficit of the nutrient substances in the growth medium.

As may be seen, the overall task of the efficient OMW treatment was achieved. However, an important factor of interest to the small-scale economies involved is the financial cost involved in the implementation of the treatment procedures suggested. Clearly, a thorough feasibility study is needed, taking into account all parameters affecting the costs involved. A rough estimate of the cost of the entire process and of the profit that may be obtained from the potential exploitation of the treatment byproducts is presented in the following section.

Assessment of Fixed and Operational Costs. *Base Case.* For a typical size olive mill treating 1000 metric tons olives/season (or producing 200 metric tons olive oil/season), and assuming that the working season lasts 4 months/year and the mill operates 25 days/month and 10 hours/day, the treated olive amount is 1 ton/hour, creating, on average, 1000 L/h of OMW. The installation of a UF/NF system, at the above typical olive mill plant, to treat the OMW feed of 1000 L/h (1000 metric tons/season of OMW), has the following approximate cost characteristics.

Fixed Cost. The total purchase and installation cost of the necessary equipment is estimated as \$300,000 (250,000 €) (data source: Hydro Air Research SpA), and it includes the following: UF and NF systems installed on-site, feed tanks, any storage or peripheral tanks, prefilter system, pumps and piping, and hydraulic, electrical, and pneumatic connections. The estimated equipment lifetime is 10 years. It is supposed that the above equipment will be installed at a space in the already existing plant; thus, no special buildings and civil works will be required, otherwise they have to be added to the above amount.

Table 6—Sensitivity analysis results.

Value of the phytotoxic fraction	Pessimistic 0.5 €/t	Basic scenario 0.7 €/t	Optimistic 0.9 €/t
Total fixed cost, C (€)	250,000	250,000	250,000
Operational cost (no tax), OC' (€/y)	32,000	32,000	32,000
Revenues, R (€/y)	100,000	140,000	180,000
Taxes, [T = 0.35 (R − OC')] (€/y)	23,800	37,800	51,800
Net profit, (K = R-OC'-T) (€/y)	44,200	70,200	128,200
Return on investment, i_r (%)	17.68	28.1	51.2
Payout period, τ (years)	5.65	3.56	1.95

Operational Cost. The operational cost includes the following (data Source: Hydro Air Research SpA):

- Raw material: Zero cost (OMW)
- Power: UF installed power, 26 kW
  NF installed power, 9 kW
  Total power consumption = \$3.56/h (2.97 €/h)
- Chemicals: \$17.28/d, equal to \$0.86/h (14.4 €/d, equal to 0.72 €/h)
- Manpower: \$1.82/h (1.52 €/h) (part-time worker—operator from the olive mill plant)
- Maintenance: \$1.99/h (1.66 €/h)
- Total operating cost: approximately \$8.40/h (7 €/h)
- Depreciation: \$300,000/10 y/1000 h/y= \$30/h (250,000 €/10 y/1000 h/y = 25 €/h)
- Total operating cost plus depreciation: approximately 32 €/h.

Economical Potential—Assessment of the Investment. For production of 200 L/h "toxic fraction" and 800 L/h pure water for recycling, taking into account the concentration of the NF concentrate, a modest value of \$0.84/L (0.7 €/L) NF concentrate is estimated, which is approximately \$168/h (140 €/h) (data source: Agrology S.A., Thessaloniki, Greece). Thus, an economical potential of \$168 to 38.40/h (140 to 32 €/h) is expected, or \$129,600/y (108,000 €/y) (1000 h/y) annually. Taking into account that taxes are 35%, a net profit of \$84,240/y (70,200 €/y) is estimated. From the above analysis, a rate of return on investment of 28% (\$84,240/300,000) (70,200 €/250,000) and a mean payout period of approximately 3.56 years (\$300,000/84,240) (250,000 €/70,200) are estimated. This is a very encouraging result, taking into account that a rather low value for the "toxic" fraction was considered (only \$0.84/L [0.7 €/L]). The above result is characterized as positive and indicates that the investment is worth undertaking. Moreover, very reasonable results have been obtained from the sensitivity analysis, regarding the product sale price (see Table 6).

Conclusions

The solids fraction and fats were removed in the prefilter process. The obtained final permeate was a clear transparent wastewater, with a low concentration of organics and salts, which may be disposed in landfills or used for irrigation, without environmental risks. The UF process was found to result in the effective separation of the constituents of high molecular weight and of any suspended solid particles and/or aggregates. The NF and/or RO processes yielded effective separation of the largest part of polyphenols contained in the feed OMW. The ''toxic'' fractions with the potential for use as growth inhibitors of some native plants were accumulated in the concentrate fractions. The final output, permeating the membrane systems, was a non-''toxic'' aqueous medium, which may be used for irrigation. The feasibility study, taking into account the origin, quantity, and composition of the OMW, showed that OMW membrane treatment process produced marketable products, which may contribute to the reduction of the process costs. The rate of return on investment was estimated (approximately 4 years), and the first conclusions for the undertaking of this investment were drawn. The results showed that the application of the proposed method is feasible, assuming the legal acceptance of the marketable byproducts. In general, despite the cost of the present suggested membrane filtration method, it was shown that it is possible to treat OMW effectively with membranes—a process that will contribute decisively in the protection of waters and soil from pollution and the concomitant adverse effects.

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