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Recovery and concentration of polyphenols from olive mill wastewaters by integrated membrane system

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ABSTRACT

The purpose of this work was to analyse the potentialities of an integrated membrane system for the recovery, purification and concentration of polyphenols from olive mill wastewater (OMW). The proposed system included some well-known membrane operations such as microfiltration (MF) and nanofiltration (NF), as well as others not yet investigated for this specific application, such as osmotic distillation (OD) and vacuum membrane distillation (VMD).

The OMW was directly submitted to a MF operation without preliminary centrifugation. This step allowed to achieve a 91% and 26% reduction of suspended solids and total organic carbon (TOC), respectively. Moreover, 78% of the initial content of polyphenols was recovered in the permeate stream.

The MF permeate was then submitted to a NF treatment. Almost all polyphenols were recovered in the produced permeate solution, while TOC was reduced from 15 g/L to 5.6 g/L.

A concentrated solution enriched in polyphenols was obtained by treating the NF permeate by OD. In particular, a solution containing about 0.5 g/L of free low molecular weight polyphenols, with hydroxytyrosol representing 56% of the total, was produced by using a calcium chloride dihydrate solution as brine. The obtained solution is of interest for preparing formulations to be used in food, cosmetic and pharmaceutical industry. Besides the OD process, VMD was applied as another way for concentrating the NF permeate and the performance of both processes was compared in terms of evaporation fluxes.

Keywords: Olive mill wastewater (OMW); Integrated membrane processes; Polyphenols.

1. INTRODUCTION

The olive tree cultivation is widely extended in the Mediterranean countries (Mantzavinos and Kalogerakis, 2005) and the most important producers are Spain, Italy, Greece and Turkey. As it happens in every industrial process, some residual streams are generated during the olive processing and their pollutant power depends on the specific way the oil is extracted (Martinez Nieto and Garrido Hoyos, 1994; Garrido Hoyos et al. 2002; Garcia Garcia et al., 2000; Fezzani and Cheikh, 2007). The extraction processes are usually grouped into press extraction and centrifugation extraction systems.

The press extraction is the traditional system and, although it is in general falling into disuse, it is still employed in several countries such as Portugal, Italy, Croatia and Malta (Mantzavinos and Kalogerakis, 2005; Roig et al, 2006). The by-products obtained through this system are a solid fraction (cake) and a liquid fraction. Approximately 400 kg of cake per Ton of processed olives (p.o.) are produced and used as combustible to get energy after the extraction of the remaining oil (Azbar et al., 2004). The press extraction system uses small amounts of water (0.1-0.12 m^3Ton/p.o.) that leads to a wastewater liquid stream (olive mill wastewater (OMW)) of about 500-600 kgTon/p.o. (Mantzavinos and Kalogerakis, 2005, Azbar et al., 2004). This OMW is strongly pollutant since the contaminant compounds are highly concentrated.

The centrifugation extraction is a more modern system that was introduced few decades ago. In general, this system shows several advantages with respect to the press system such as the increasing of the quantity and quality of the olive oil produced, the reduction in the working cost since it allows the complete automation and, in addition, less need of space. Compared with the press extraction system, the centrifugation presents some breakdowns such as the huge water and energy consumption what leads

63 to a quite higher wastewater production. The cost of the productive plants is also higher
64 (Roig et al., 2006; Azbar et al., 2004).
65 The centrifugation system can be classified into 2-phase centrifugation or 3-phase
66 centrifugation depending on the number of streams obtained in the process (Roig et al,
67 2006). In the 3-phase centrifugation system are produced: a 500-600 kgTon/p.o. of a
68 solid waste fraction, named olive mill solid wastes (OMSW), that contains around a
69 50% of water and a 4% of remaining oil; a liquid stream of about 200 kgTon/p.o. of oil,
70 and a 1000-1200 kgTon/o.p. of a liquid waste stream (OMW) with a composition of a
71 94% of water and a 1% of oil (Cabrera Capitán, 1995).
72 On the other hand, in the 2-phase centrifugation system are produced an olive oil stream
73 of about 200 kgTon/p.o. and a residual semi-solid fraction (OMSSW) of approximately
74 800-950 kgTon/p.o. that contains pieces of seeds and olive pulp as much as vegetation
75 water. The handling and treatment of this OMSSW is extremely complex mainly due to
76 its high water content (60-70%) that makes difficult its storage. In addition, the presence
77 of polyphenols, sugars and other organic substances make its treatment very
78 problematic under the technical, economic and management points of view. Despite that,
79 the 2-phase system has been defined as “ecologic” (Roig et al., 2006; Azbar et al., 2004)
80 due to the lower water and energy consumption compared with the 3-phase
81 centrifugation system.
82 Different alternatives of valorisation and treatment have been considered for the OMW,
83 OMSW and OMSSW, such as the physical-chemical, the biological (aerobic and
84 anaerobic) and the direct or not placing on soil. The immediate benefits of the treatment
85 of these wastes are the water recycling and the use of the solid fraction as fertilizer
86 directly or after a composting process as well as raw material for the extraction of

87 antioxidant compounds. The treated sludge may be used as fuel after its direct burnt or
88 after the biogas production.
89 The evaporation in open-air lagoons is the most used treatment for the OMW and is
90 favoured by the Mediterranean weather. This treatment needs very low investment cost,
91 requires wide areas and produces several odour, infiltration and insects growth
92 problems. The sludge produced is disposed in landfills although it may be also used in
93 the agriculture, be composted or be employed as a heat source due to its oil content
94 (Roig et al., 2006).
95 Several coagulation-flocculation studies on OMW have also been done. Some
96 coagulants such as ferric chloride, aluminium chloride, ferric sulphate and calcium
97 hydroxide were used as well as their combinations. Also, anionic polyelectrolytes and
98 sulphuric acid were tested. The reduction in suspended solids and COD in OMW
99 reached efficiencies up to 50-90% (Azbar et al., 2004).
100 Some works have been done using membrane technology with the final goal of reducing
101 the organic load of OMWs (Akdemir and Ozer, 2009; Borsani and Ferrando, 1996;
102 Molinari and Drioli, 1988; Stoller, 2008; Stoller and Bravi, 2010). The membrane
103 operations used in these researches were microfiltration (MF), ultrafiltration (UF),
104 nanofiltration (NF) and reverse osmosis (RO).
105 There are several studies on microbiological treatment of the OMW for obtaining
106 biopolymers such as xanthan, pululan and hydroxialcanoates. The aerobic treatment of
107 OMW has also been used for the removal of its pollutant effect, and these studies are
108 nowadays focused on the degradation of the phenolic compounds the main responsible
109 for the OMW phytotoxicity (Roig et al., 2006).
110 The composting is the most used method to recycle and transform OMW into fertilizers
111 but it has to be firstly adsorbed in a solid substrate as for example, lignocellulosic

112 wastes. In this way, the co-composting of the adsorbed OMW with wheat straw has
113 produced fertilzers without phytotoxicity (Roig et al, 2006) and has resulted to be a
114 good alternative to the combustion. The interest of the anaerobic digestion of the OMW
115 relies on the production of biogas, CH_4 and CO_2 but there is a limitation due to the
116 inhibition of the methanogenic bacteria by the phenolic compounds and organic acids
117 existing in OMW (Roig et al, 2006).
118 As it was stated above, the presence of phenolic compounds has a negative effect on the
119 microbiological treatment of the OMW. In contrast with this, phenols are widely used
120 by pharmaceutical, cosmetic an nourishment sectors (De Marco et al., 2007). Their
121 properties, such as anti-inflammatory, antimicrobic and antioxidant activity, the
122 inhibition of oxidative damage and the radicalic elimination, have been largely studied
123 (Ranalli, Lucera and Contento, 2003; Bisignano et al., 1999; Obied at al., 2005).
124 These compounds are usually synthesized by chemical methods that are responsible of
125 their high price. Hence, if phenols could be collected from OMW, this may lead to
126 economic benefits.
127 Some studies focused on the extraction and removal of polyphenols with the treatment
128 of the OMW by fungi such as *Phanerochaete chrysosporium*, *Aspergillus niger*,
129 *Aspergillus terreus* and *Geotrichum candidum* (Garcia Garcia et al., 2000; Bouzid et al.
130 2005). The use of integrated membrane system is becoming another real alternative to
131 recover polyphenols as it is established in some recent works. In particular, Paraskeva et
132 al. (2007) found that the OMW may be treated efficiently by using UF, NF and/or RO
133 to obtain a permeate fraction which can be discharged in aquatic systems according to
134 national or EU regulations or to be used for irrigation. In this case NF was employed for
135 the separation of the most part of phenols present. A membrane process for the selective
136 fractionation and total recovery of polyphenols, water and organic substances from

OMW was also proposed by Russo (2007). It was based on the preliminary MF of the OMW, followed by two UF steps realised with 6 kDa and 1 kDa membranes, respectively, and a final RO treatment. The RO retentate, containing enriched and purified low molecular weight polyphenols, was proposed for food, pharmaceutical or cosmetic industries while MF and UF retentates can be used as fertilizers or in the production of biogas in anaerobic reactors.

The purpose of this work was the recovery and the concentration of polyphenols from the OMW by using an integrated membrane system based on some well-known membrane techniques such as MF and NF)as well as others not yet tested for the treatment of this kind of wastewater like vacuum membrane distillation (VMD) and osmotic distillation (OD). Both VMD and OD are included within the so-called "membrane contactors family". According to Drioli et al. (2006), membrane contactors do not offer any selectivity for a particular species with respect to another but simply act as a barrier between the phases involved. The species are transferred from one phase to the other by only diffusion. Membranes are usually microporous and symmetric and can be both hydrophobic and hydrophilic. Most of the experiences with membrane contactors have been focused on the concentration of fruit juices and other food applications, and for the addition or removing of gas compounds to/from liquid streams.

In this work the vegetation water was first submitted to a MF step; the MF permeate was fed to a NF process and finally the NF permeate was concentrated by OD. The performance of the OD process, in terms of evaporation fluxes, was also compared with that of the VMD.

MATERIALS AND METHODS

2.1. Solutions and reactants

2.1.1. Feed solution

The olive mill wastewater was delivered by the *Istituto Sperimentale per l'Olivicoltura* (Rende, Cosenza, Italy). It was produced according to the press extraction process and its composition is shown in Table 1. OMW was submitted to the microfiltration step without any pre-treatment.

2.2. Equipments

2.2.1. Microfiltration unit and procedure

The microfiltration of OMW was performed by using a laboratory pilot unit supplied by Verind SpA (Milano, Italy). The equipment consists of a 25 L stainless steel feed tank, a feed pressure pump, a pressure control system, a feed flow meter, a thermometer, two manometers for the measure of the inlet and outlet pressures. A tube and shell heat exchanger, placed after the feed pump, was used to maintain constant the feed temperature. A data acquirement system, permitting the continuous monitoring of the transmembrane (TMP) and of the axial feed flow rate, was connected to the MF plant. A digital balance, connected to the system, was used to measure the permeate flux. The plant was equipped with a MF tubular membrane module (membrane material Al_2O_3, mean pore size 200 nm, open porosity 40-55%, membrane surface area 48 cm^2) supplied by Inopor GmbH (Hermsdorf, Germany).

The MF system was operated at a TMP of 0.72 ± 1 bar, at an axial feed flow rate (Q_f) of 760 L/h and at a temperature of 22 ± 0.01 ºC according to the batch concentration mode (recycling the retentate stream and collecting separately the permeate).

184 The MF membrane was cleaned using a concentrated basic solution of 20 g/L NaOH at
185 40 ºC. Each cleaning run lasted 30 minutes. Afterwards, the system was rinsed with tap
186 water for other 30 minutes.
187
188 *2.2.2. Nanofiltration unit and procedure*
189 NF experiments were performed by using a laboratory plant (Matrix Desalination Inc.,
190 USA) equipped with a feed tank, an orbital magnetic drive pump, a vessel for 2.4x40
191 inches spiral wound membrane modules, a cooling coil working with tap water, a
192 manometer and a pressure regulating valve.
193 The NF unit was equipped with a Nadir N30F spiral-wound membrane module
194 (permanently hydrophobic polyethersulphone, 1.6 m^2, NaCl rejection 25-30%, Na_2SO_4
195 rejection 80-95%) supplied by Microdyn-Nadir GmbH (BeNeLux Vertriebsbüro, Venlo,
196 NL). NF experiments were carried out according to the batch concentration
197 configuration at an operating temperature of 20°C and a TMP of about 8 bar.
198 The permeate flux was gravimetrically measured.
199 The NF membrane module was cleaned by following the same procedure described for
200 MF by using a solution of 1 g/L NaOH.
201
202 *2.2.3. Osmotic distillation unit and procedure*
203 Osmotic distillation experiments were carried out by using a compact plant (Celgard
204 LLC, Charlotte, USA; formerly Hoechst Celanese) that allowed the control of the
205 pressure and flow rate of both feed and stripping solutions.
206 The plant was equipped with a Liqui-Cel® Extra-Flow 2.5x8" membrane module
207 supplied by Celgard LLC (effective surface area 1.4 m^2, effective area/volume 29.3
208 cm^2/cm^3, fibre potting material polyethylene, maximum transmembrane differential

209 pressure 4.08 bar, temperature operating range 1-40 °C) containing microporous
210 polypropylene hollow-fibres. These fibres are approximately 0.3 mm in external
211 diameter with a wall thickness of about 0.03 mm; they have a mean pore size of about
212 30 nm and a porosity of about 40%. Feed and stripping solution temperatures were
213 measured by thermometers immersed in their reservoirs. Inlet and outlet pressures for
214 both tube side and shell side streams were registered by pressure gauges in order to
215 control the pressure differentials between the two sides of the membrane. The
216 evaporation flux was determined gravimetrically measuring the weight loss of the feed
217 solution by means of an analytical balance (Gibertini Elettronica, Milano, Italy).
218 The feed solution (NF permeate) was recycled in the shell side of the membrane module
219 at an average flow rate of 153 mL/min, while the stripping solution ($CaCl_2 \cdot 2H_2O$ 60%
220 w/w) was recycled in counter-current into the lumen of the fibres at an average flow rate
221 of 446 mL/min. The temperature of both feed and brine, was 30±2 °C whereas the
222 average TMP was 0.43 bar.
223 The OD system was generally operated working at a slightly higher pressure on the
224 shell side of the membrane module in order to avoid the leakage of the brine strip into
225 the product.
226 After each trial, the pilot plant was cleaned first by rinsing both sides of the module
227 with de-ionised water. The shell side was then cleaned with a 2% KOH solution at 40
228 ºC for 1 hour. To neutralize the remaining basic solution, the module was cleaned with
229 2% citric acid solution at 40 ºC for 30 min. Finally, the shell side was rinsed with
230 distilled water. The tube side was cleaned twice with distilled water at 40 ºC for 1 hour.
231

Vacuum membrane distillation unit and procedure

Vacuum membrane distillation (VMD) runs were performed by using a laboratory set-up equipped with a flat membrane module (membrane area 55 cm^2). Two flat-sheet hydrophobic and microporous membranes made of polypropylene (PP) and polyvinylidenfluoride (PVDF) with a pore size of 0.2 μm and thickness of 90 and 200 μm, respectively, were submitted to swelling measurements, in order to determine the swelling degree of membranes when contacting the solution to be treated. The objective was to select the membrane with the lowest swelling degree for reducing the risk of passage of vegetation water through the membrane-self during the VMD tests. Membranes were cut in small pieces of 1x1 cm and then weighted. Next, they were put separately inside different tubes containing the feed solution and located in a climatic camera for 24 h at a specific temperature (20 – 50°C). Afterwards, the tubes were opened and the membranes were weighted again. The swelling was, then, calculated as:

$$Swelling(\%) = \frac{Weight_{wetted} - Weight_{dry}}{Weight_{dry}} \cdot 100$$

During the VMD experiments the feed stream (the NF permeate) was heated up to the desired temperature (20 - 40°C) and re-circulated at atmospheric pressure and different flow rates (100-180 L/h) to one side of the membrane while a vacuum of about 30 mbar was applied at the other side. Due to the difference of partial pressure established across the membrane, water migrated as vapour through the micropores and condensed in a trap immersed in liquid nitrogen located between the module and the vacuum pump. Feed and vacuum pressures and the feed temperature were controlled by the proper devices. The permeate flux was calculated by weighting the condensed liquid into the trap and then dividing it to the duration of the test and the membrane area. After each test, the set-up was cleaned first with tap water for 10 min and then with distilled water

for 30 min. The membrane was after removed and immersed in hot distilled water at 50°C for 30 min.

2.3. Analytical methods

2.3.1. Analyses of polyphenolic compounds

Polyphenolic compounds were determined by using an HPLC system (Agilent 1100 Series, USA) equipped with an UV detector. Chromatographic separation was performed by using a Luna C18 column (250x4.6mm, 5 μm) (Phenomenex, Torrance, CA). Operating conditions were as follows: flux 1mL/min, temperature 25°C, pressure 100 bar, wave length 280 nm. The mobile phase was a mixture of 100:1 water/acetic acid (v/v) (solvent A) and a mixture of 90:10:1 methanol/acetonitrile/acetic acid (v/v/v) (solvent B). A sixth-step linear gradient analysis for a total run time of 60 min was used as follows: starting from 90% solvent A and 10% solvent B, increase to 30% solvent B over 10 min and then isocratic for 5 min, increase to 40% solvent B over 10 min, to 50% over 15 min and to 100% solvent B over 10 min, and finally isocratic for 10 min. The system was equilibrated between runs for 20 min using the starting mobile phase composition. Prior to HPLC analysis, all samples were filtered using cellulose acetate filters with 0.45 μm pore size and diluted with pure water.

The external standard method was applied. The concentration of phenolic compounds was determined from experimental peak areas by analytical interpolation in a standard calibration curve. Each assay was performed in triplicate. The deviation of each measurement was of 2% from the average value.

Total organic carbon (TOC) determination

Total carbon (TC) and inorganic carbon (IC) were analyzed by a TOC analyzer (TOC-V CSN, Shimadzu, Kyoto, Japan). TOC values were obtained by difference between TC and IC.

2.3.2. Total suspended solids (TSS) determination

TSS were determined by filtering a known volume of the sample through a 0.45 μm cellulose acetate filter. The filter was afterwards dried at 105 ºC and weighted.

2.3.3. Sugar content

The sugar content, in ºBrix, was measured by using an Abbe-60/DR refractometer (Bellingham & Stanley Ltd., London, UK) at 20°C.

3. RESULTS AND DISCUSSION

The general flowchart of the membrane integrated system is shown in Figure 1. The OMW was treated by MF and the permeate obtained was nanofiltered. The permeate of the NF was, then, concentrated by OD. Experiments were also carried out with VMD in order to compare the performance of the two concentration systems in terms of evaporation fluxes.

3.1 Microfiltration

Figure 2 shows the time course of the permeate flux for different experimental runs. At the end of each run the membrane module was cleaned according to the procedure previously described. As expected, the permeate flux decay was quite similar for each run and despite of the membrane cleaning carried out among runs, the initial permeate

flux value was progressively reduced due to an irreversible fouling phenomenon. The normalized flux evolution (J_p/J_o) for each MF run showed a permeate flux decrease ranging between 10 and 30% (Figure 3). Table 2 shows the evaluation of the hydraulic permeability of the membrane after each cleaning procedure made between different runs. Despite to the water permeability decay observed after the run 1 (about 35%), a hydraulic permeability of the MF membrane higher than 106 L/m^{2}hbar was obtained through the cleaning procedure.

3.2 Nanofiltration

The permeate solution coming from the MF process was treated by NF. Figure 4 shows the time evolution of the permeate flux in the selected operating conditions. The initial permeate flux of about 4.68 L/m^{2}h was reduced of 35% when the volume reduction factor (VRF) reached a value of 3. The water permeability of the NF membrane (about 4.1 L/m^{2}hbar at 25°C) was entirely recovered after the membrane cleaning.

3.3 Osmotic distillation

In Figure 5 experimental results concerning the concentration of NF permeate by OD are reported. In this process 3.4 kg of NF permeate were reduced to 0.38 kg through the water removal in an operating time of 200 min. The initial brine concentration of 60 w/w% produced an evaporation flux of about 1.0 kg/m^{2}h (Fig. 5a). The decrease of evaporation flux had a similar behaviour of the dilution of the stripping solution (Fig. 5b); consequently the evaporation flux decay can be attributed to the reduction of the driving force of the process. The evaporation flux reached a value of about 0.35 kg/m^{2}h when the brine solution and the sugar concentrations were around 42% w/w and 8°Brix, respectively.

3.4 Vacuum membrane distillation

Swelling tests were performed at different temperatures (20, 30 and 40°C) on the two commercial flat-sheet PVDF and PP membranes. The swelling results are shown in Table 3. The PVDF membrane showed the lowest swelling degree in the investigated range of temperatures and, therefore, it was chosen for VMD tests on the NF permeate.

Tests on distilled water were previously carried out in order to evaluate the maximum permeate flux achievable at different feed flow rates and temperatures. It was found that the feed flow rate, in the range investigated, did not affect significantly the permeate flux. An increase of temperature led to higher permeate fluxes due to its relationship with the water vapour pressure. In particular, an increase of the operating temperature from 20°C to 40°C increased of about three fold the permeate flux (Figure 6).

Similar tests were performed on the NF permeate in order to optimize the operating parameters for its concentration. Working in the same operating conditions the steady-state evaporation fluxes observed with the NF permeate were 33% lower than those measured with distilled water. Also in this case there was no influence of the feed flow rate in opposition with the clear effect of the temperature. According to these results, VMD tests were carried out at 180 L/h (the maximum feed flow rate) and at 30 ºC. This temperature was chosen, rather than the higher temperatures investigated, for limiting fermentation phenomena naturally occurring in the feed solution containing organic matter while obtaining satisfactory permeate fluxes; in the meantime, working at this temperature, the obtained permeate fluxes are satisfactory.

Figure 7 shows the time course of the evaporation flux in the selected operating conditions. The evaporation flux gradually decreased in the first 200 min and then reached an asymptotic value of about 8 L/m^2h.

354 **3.5 Analytical results**

355 In Table 4 results of physico-chemical analyses performed on samples of OMWs
356 submitted to different membrane operations are reported. Basically, pH was not
357 modified during the overall process. The rejection of the MF membrane towards sugars
358 was of about 37%; this value is quite high considering the nominal molecular weight
359 cut-off of the membrane and could be attributed to fouling phenomena which modifies
360 the rejection characteristics of the membrane-self. Sugars were further reduced in the
361 NF permeate (the NF rejection was of about 55%) and concentrated by the OD process
362 reaching a final value 39% higher than that of the initial feed solution.

363 The MF step permitted to achieve a 91% and 26% reduction of TSS and TOC,
364 respectively. The rejection of the MF membrane towards TC was 25.6%.

365 The NF allowed to reduce the TOC and TC content in the MF permeate of 63%.

366 In Table 5 the analyses of polyphenols detected in permeates and retentates of the
367 different membrane units are reported. In the MF permeate were recovered 78% of
368 polyphenols contained in the initial feed: therefore they were purified from TSS and,
369 partially, from organic compounds. The rejection of the MF membrane towards
370 different analysed low molecular weight polyphenols was between 7.2%
371 (protocatechuic acid) and 27.7% (oleuropein). The HPLC chromatogram concerning the
372 polyphenolic analyses of the MF permeate (Figure 8b) shows that hydroxytyrosol is the
373 main compound being the 54% of the total polyphenols, with a concentration of 88.7
374 ppm. These results are in agreement with what found by Russo (2007). Concentrations
375 ranging from 7 to 39 ppm were found for the others low molecular weight polyphenols.

376 A further purification of polyphenols was obtained by the NF unit as showed in the
377 HPLC chromatograms (Figure 9a vs. Figure 8b). The produced permeate showed TC

and TOC values reduced of about 63% if compared with the MF permeate. The rejection of the NF membrane towards sugars was 55.8% (Table 4).

The rejection of the NF membrane towards low molecular weight polyphenols was about 5%. The lowest rejection, of about 1%, was observed for oleuropein, while a rejection of about 21% was achieved for the protocatechuic acid.

A concentrated solution containing about 0.5 g/l free low molecular weight polyphenols, with hydroxytyrosol representing 56% of the total, was obtained by treating the NF permeate by OD (Table 5). The progressive concentration of polyphenolic compounds can be observed in the HPLC chromatogram of samples collected during the OD process after 60 min, 120 min and 200 min (Figure 10 a, b and c). As also proposed by Russo (2007) this product is suitable for food and pharmaceutical industries.

4. CONCLUSIONS

The proposed integrated membrane system has turned out to be a convenient approach for the separation and concentration of polyphenols contained in olive mill wastewaters.

A preliminary microfiltration treatment permitted to achieve a removal of TOC and suspended solids producing a permeate stream with 78% of the initial polyphenol content.

Nanofiltration led to a nearly pure solution of polyphenols susceptible to be concentrated and used in food, cosmetic or pharmaceutical sectors. A more concentrated solution, enriched in polyphenols (about 0.5 g/l), and particularly in hydroxytyrosol (0.28 g/l), was obtained by osmotic distillation.

Concerning the efficiency of the two concentration processes analysed, even if the VMD has the advantage of higher trans-membrane fluxes, it is remarkable that the energy consumptions should be lower in OD since it does not uses a vacuum pump

neither needs a refrigeration step to condensate the permeate. However, the $CaCl_2$ consumption and the treatment of the stripping solution (e.g., by evaporation) must be taken into account for an overall comparison between the two processes.

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Table 1. Composition of the olive mill wastewater

pH	5.03
TC (g/L)	20.23
TOC (g/L)	20.19
TSS (g/kg)	17.60
Sugar (ºBrix)	5.44
Free low MW polyphenols (mg/L)	211.80

TC: Total carbon; TOC: Total organic carbon; TSS: Total suspended solids

Table 2. Hydraulic permeability of the MF membrane

	J_w (L/m^{2}hbar)
initial	209.76
after run 1 and cleaning	136.19
after run 2 and cleaning	118.15
after run 3 and cleaning	107.10
after run 4 and cleaning	114.18
after run 5 and cleaning	107.81
after run 6 and cleaning	106.33

Table 3. Swelling test results for the hydrophobic membranes

	Membrane material	
	PP	PVDF
Swelling at 20°C (%)	55.6	1.5
Swelling at 30°C (%)	70.8	1.7
Swelling at 40°C (%)	81.5	8.6

Table 4. Physico-chemical analyses in OMWs processed by membrane operations

Sample	TC (g/L)	TOC (g/L)	TSS (g/kg)	Sugars (°Brix)	pH
Feed MF	20.23	20.19	17.6	5.4	5.0
Permeate MF	15.05	15.01	1.6	3.4	5.1
Retentate MF	16.22	16.18	26.1	6.5	5.2
Permeate NF	5.58	5.57	-	1.5	5.5
Retentate NF	-	-	4.9	7.5	5.3
Retentate OD	27.67	27.62	7.4	7.8	5.0

Table 5. Analyses of polyphenols in OMWs processed by membrane operations (data in ppm)

Sample	Free low MW polyphenols	Hydroxytyrosol	Protocatechuic acid	Tyrosol	Caffeic acid	p-cumaric acid	Oleuropein
Feed MF	211.80	108	16.5	15	9.95	8.35	54
Permeate MF	165.54	88.71	15.31	11.28	8.70	7.54	39
Retentate MF	311.87	196.31	19	25.56	9	12	50
Permeate NF	157.32	85	12.13	9.24	8.55	6.70	38.7
Retentate NF	220.10	118	14.8	15	9.95	8.35	54
Retentate OD	493.01	276	29	53.5	49	20.51	65

FIGURE CAPTIONS

Figure 1. Flowchart representing the activities carried out for the recovery, purification and concentration of polyphenols from olive mill wastewaters.

Figure 2. Microfiltration of olive mill wastewaters. Time course of the permeate flux. (Experimental conditions: Temperature, 22 ± 0.01 ºC; TMP, 0.72 ± 1 bar; flow rate, 760 L/h).

Figure 3. Normalized flux evolution in the microfiltration process of olive mill wastewaters.

Jo, initial flux for the run i. (Experimental conditions: Temperature, 22 ± 1 ºC; TMP, 0.72 ± 0.01 bar; flow rate, 760 L/h).

Figure 4. Nanofiltration of microfiltered olive mill wastewaters. Time course of the permeate flux. (Experimental conditions: Temperature, 20 ºC; TMP, 8 bar).

Figure 5. Concentration of NF permeate by OD. Time course of: a) permeate flux and sugar concentration; b) concentration of the extracting solution. (Experimental conditions: Temperature, 30ºC; TMP, 0.43 bar).

Figure 6. Permeate fluxes in VMD as function of the feed flow rate at different operating temperatures. (Experimental conditions: feed, distilled water; permeate pressure, 30 mbar).

Figure 7. Concentration of NF permeate by VMD. Time course of the permeate flux. (Experimental conditions: Temperature, 30ºC; permeate pressure, 30 mbar; flow rate, 180 L/h).

Figure 8. HPLC chromatograms of the polyphenols in a) feed, b) permeate and c) retentate of MF process. **1**: *Hydroxytyrosol*; **2**: *Protocatechin acid*; **3**: *Tyrosol*; **4**: *Caffeic acid*; **5**: *P-Coumaric acid*; **6**: *Oleuropein.*

Figure 9. HPLC chromatograms of the polyphenols in a) permeate and b) retentate of NF process.

1: *Hydroxytyrosol*; **2**: *Protocatechin acid*; **3**: *Tyrosol*; **4**: *Caffeic acid*; **5**: *P-Coumaric acid*; **6**: *Oleuropein.*

Figure 10. HPLC chromatograms of the polyphenols in OD retentate after a) 60 min, b) 120 min and c) 200 min. **1**: *Hydroxytyrosol*; **2**: *Protocatechin acid*; **3**: *Tyrosol*; **4**: *Caffeic acid*; **5**: *P-Coumaric acid*; **6**: *Oleuropein.*

Figure

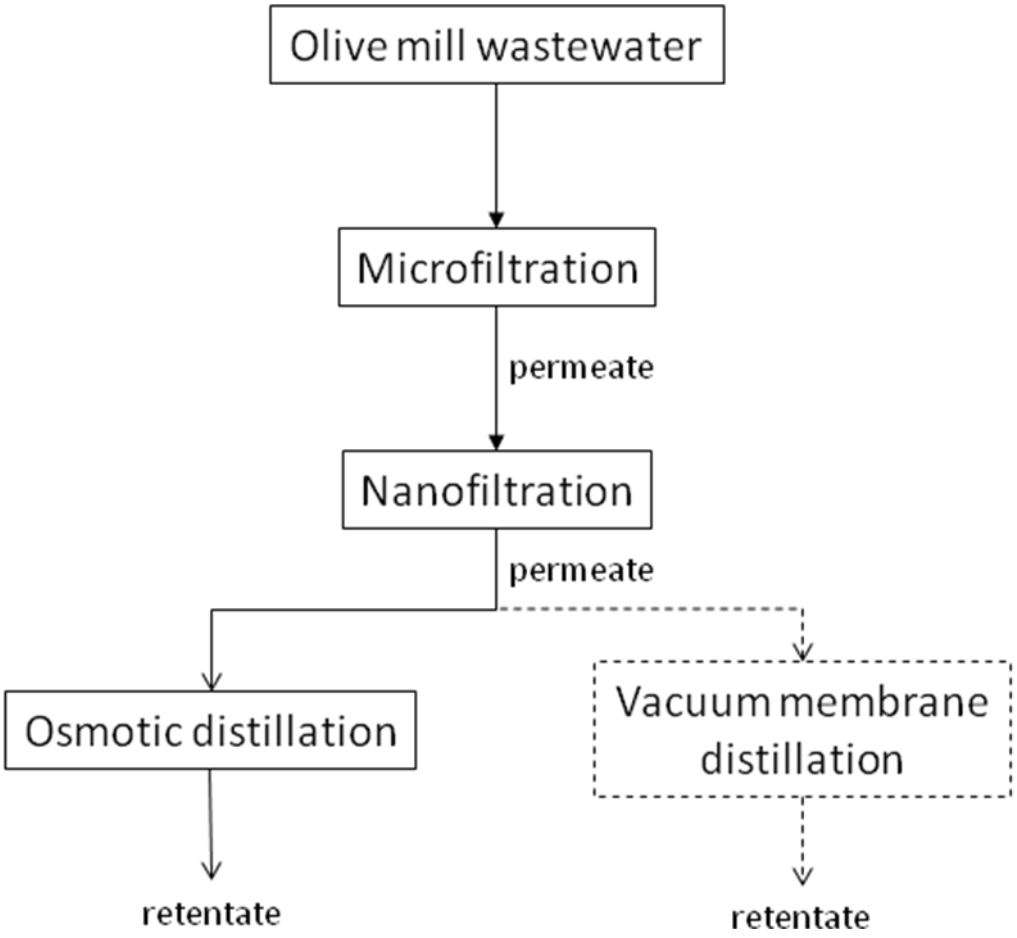


FIGURE 1

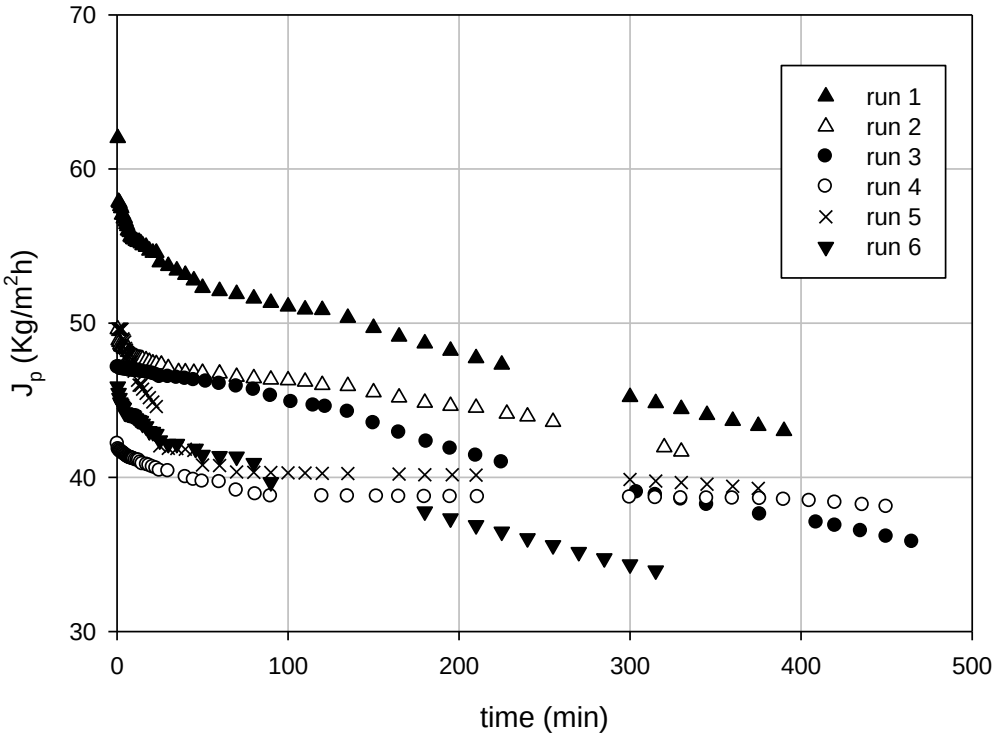

70
60
50
40
30
0
100
200
300
400
500
time (min)
J_p (Kg/m^{2}h)
run 1
run 2
run 3
run 4
run 5
run 6

FIGURE 2

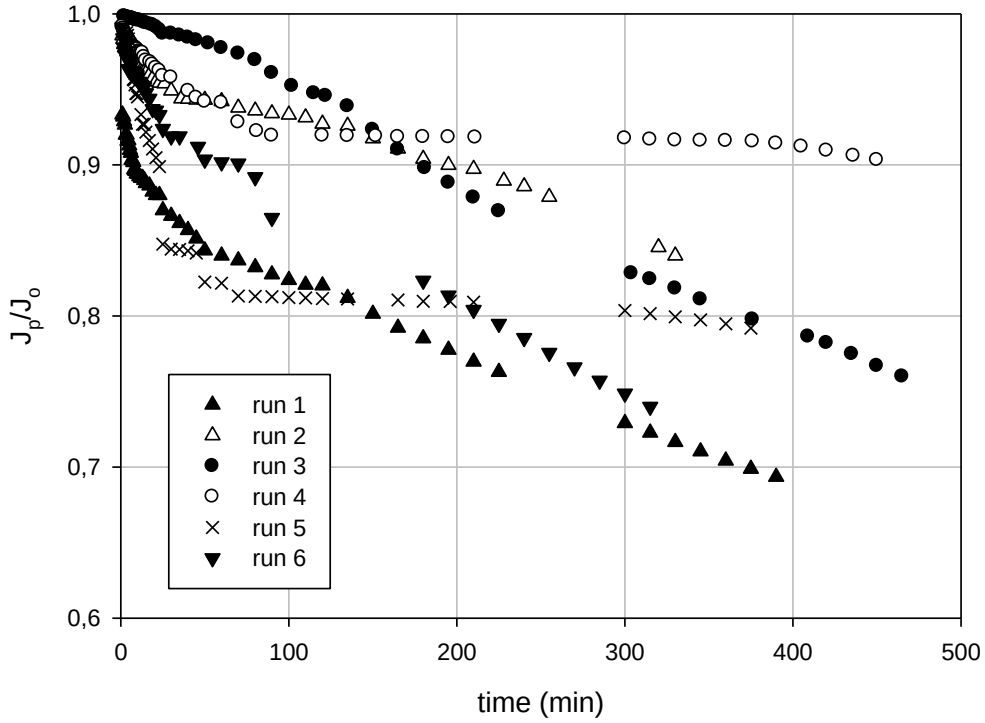

1,0
0,9
0,8
0,7
0,6
J_p/J_o
0
100
200
300
400
500
time (min)
run 1
run 2
run 3
run 4
run 5
run 6

FIGURE 3

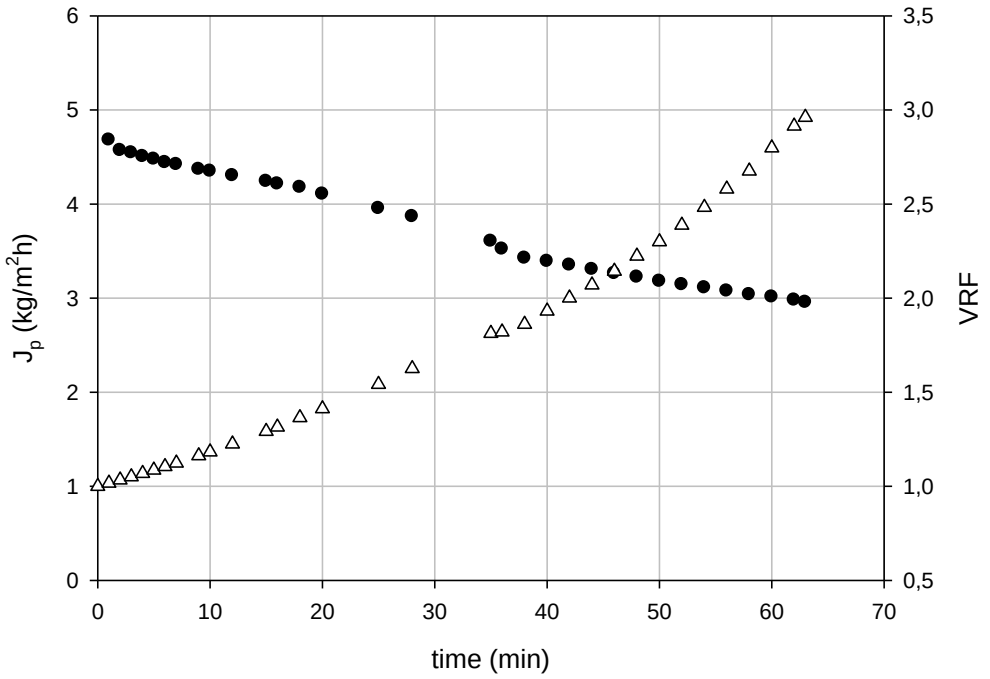

6
5
4
3
2
1
0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0
10
20
30
40
50
60
70
time (min)
J_p (kg/m^{2}h)
VRF

FIGURE 4

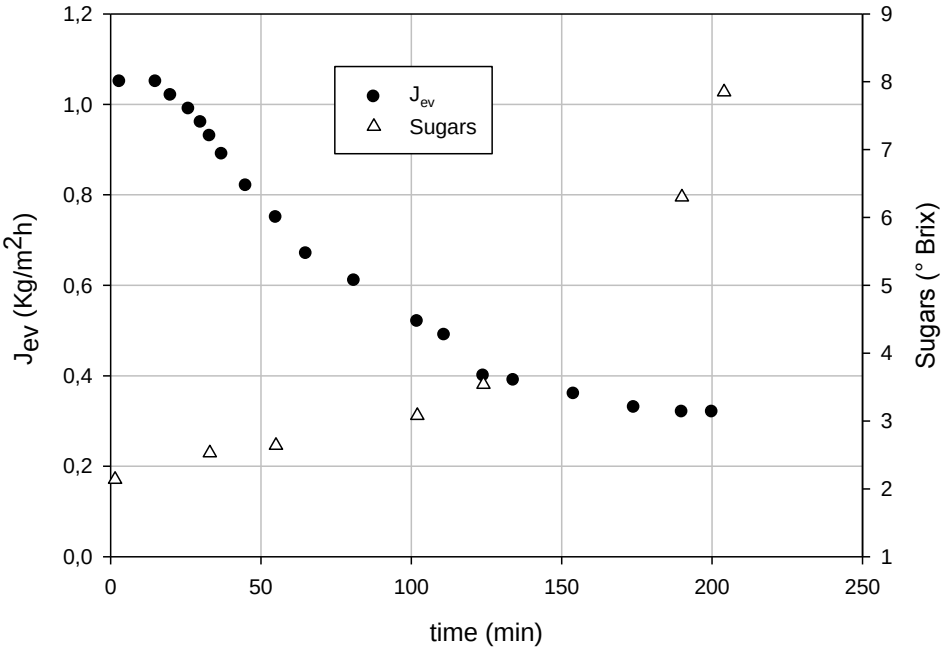


FIGURE 5a

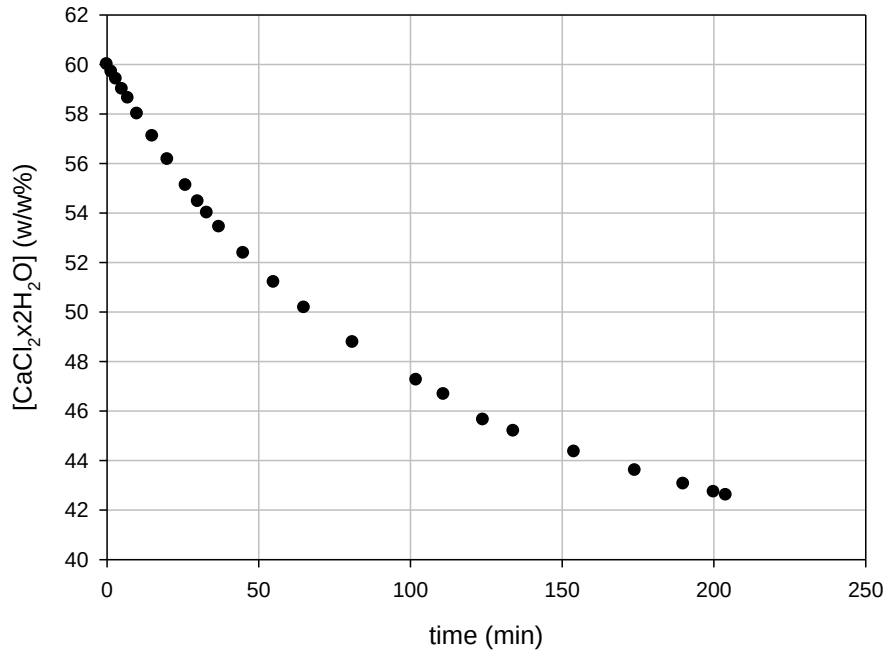


FIGURE 5b

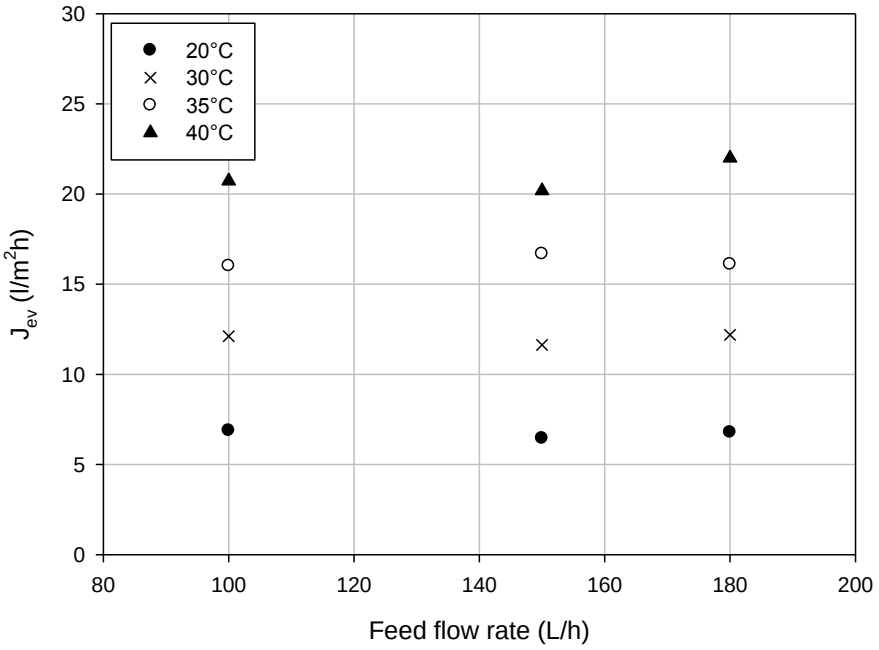

20°C
30°C
35°C
40°C
J_{ev} (l/m^{2}h)
Feed flow rate (L/h)
0
5
10
15
20
25
30
80
100
120
140
160
180
200

FIGURE 6

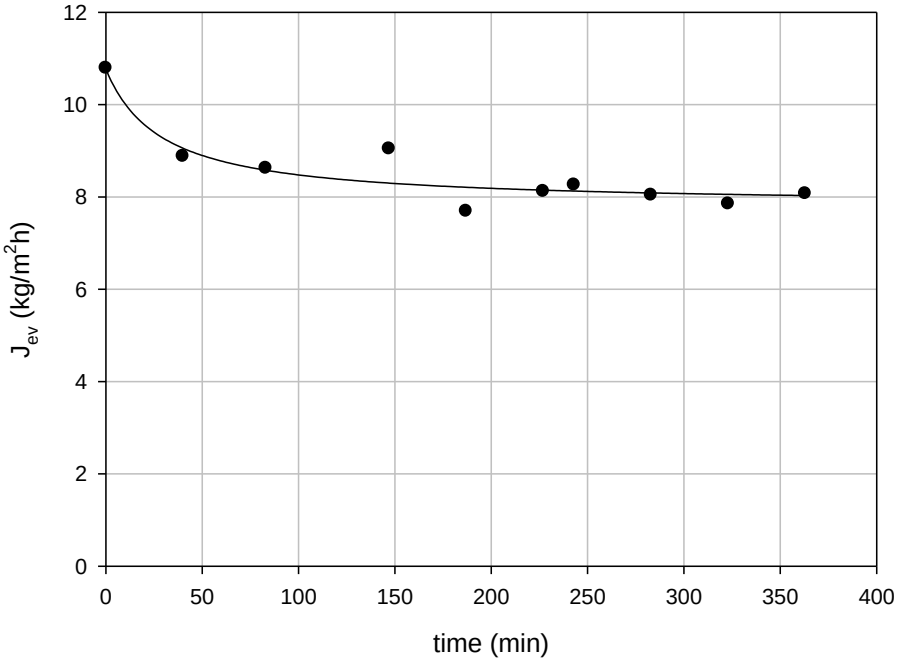
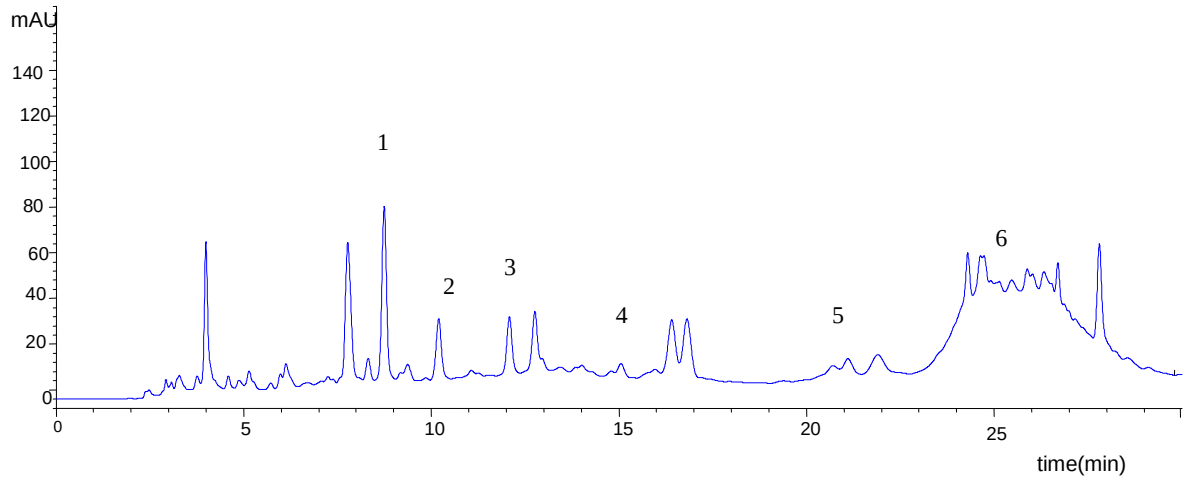
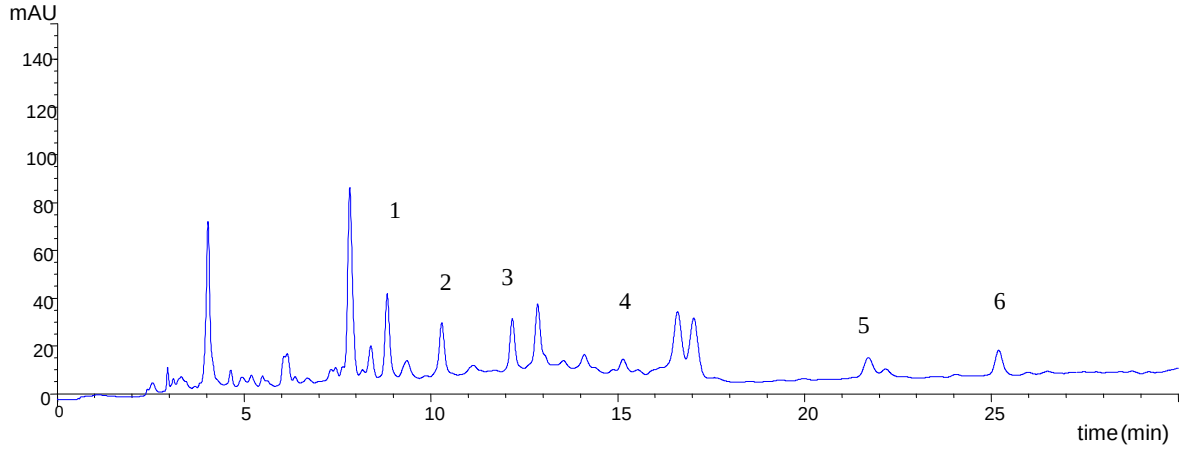


FIGURE 7

a)


mAU
140
120
100
80
60
40
20
0
1
2
3
4
5
6
0
5
10
15
20
25
time(min)

b)


mAU
140
120
100
80
60
40
20
0
1
2
3
4
5
6
0
5
10
15
20
25
time (min)

c)

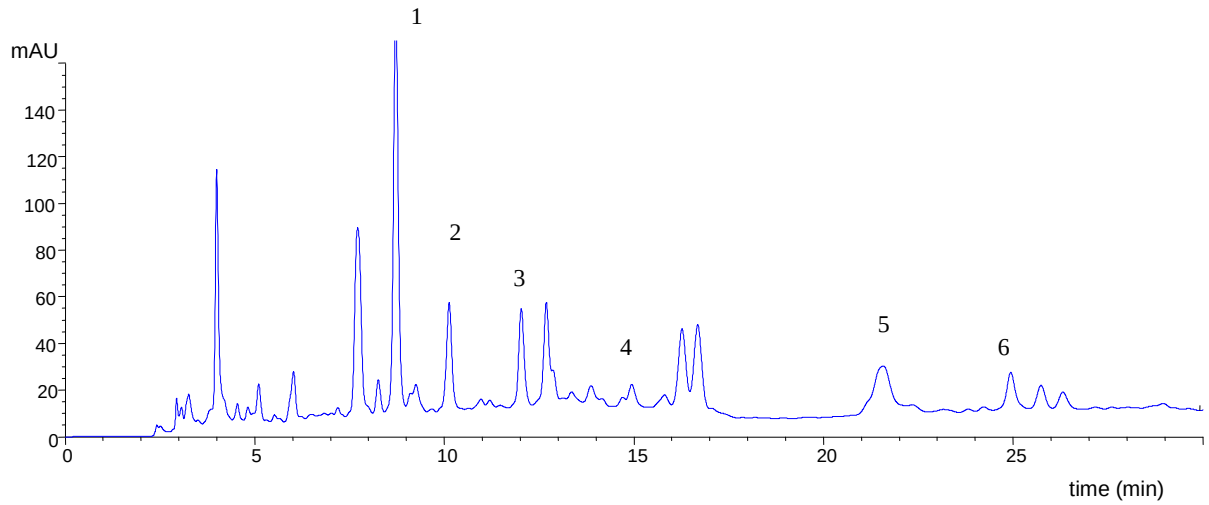
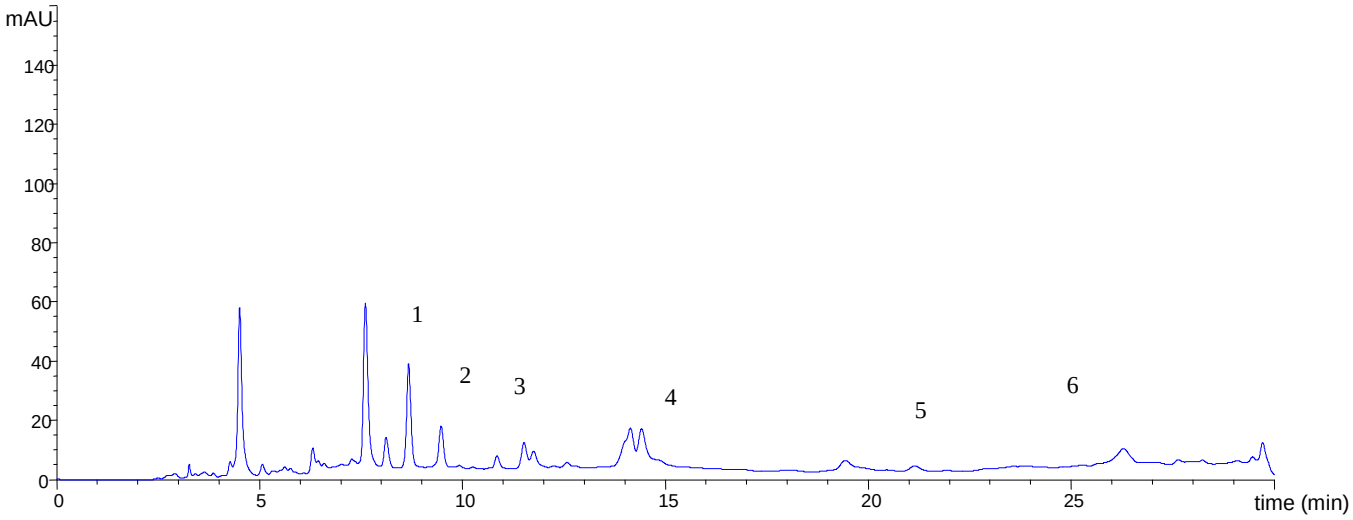

mAU
140
120
100
80
60
40
20
0
1
2
3
4
5
6
0
5
10
15
20
25
time (min)

FIGURE 8

a)


mAU
140
120
100
80
60
40
20
0
0
5
10
15
20
25
time (min)
1
2
3
4
5
6

b)

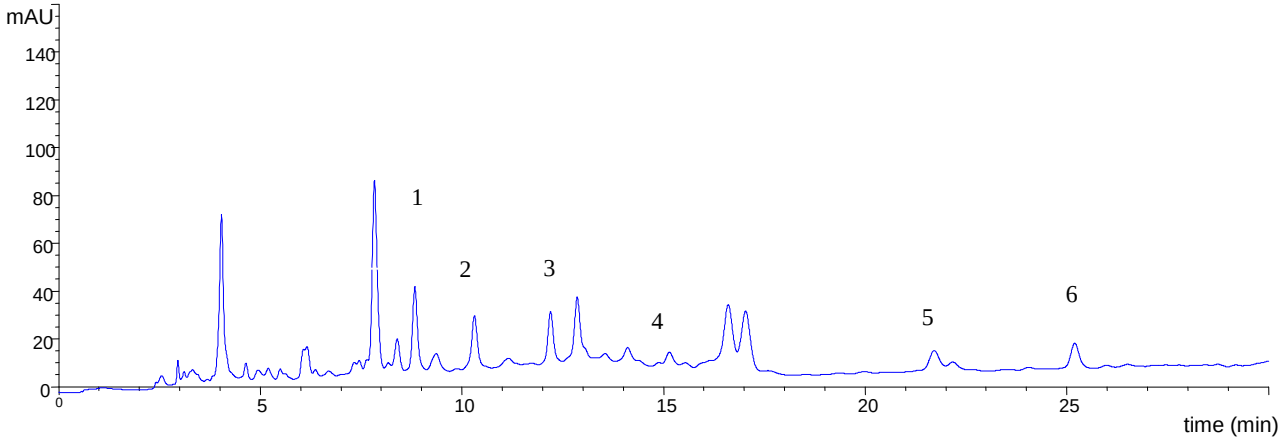
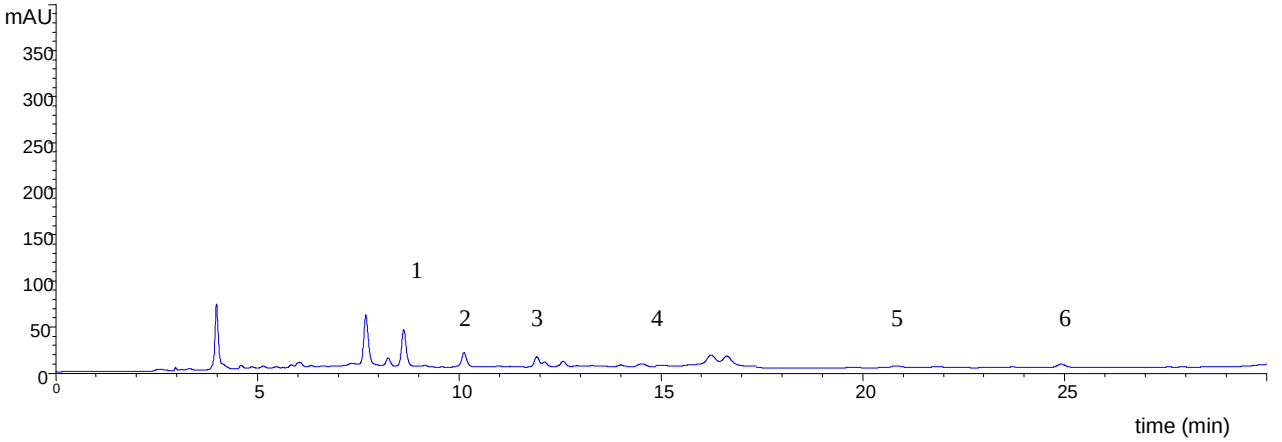
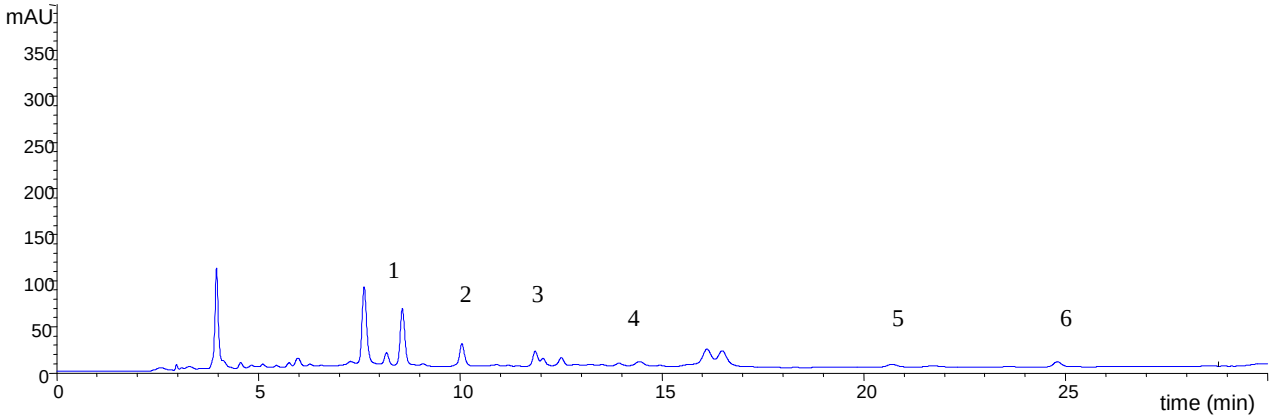

mAU
140
120
100
80
60
40
20
0
0
5
10
15
20
25
time (min)
1
2
3
4
5
6

FIGURE 9

a)



b)



c)

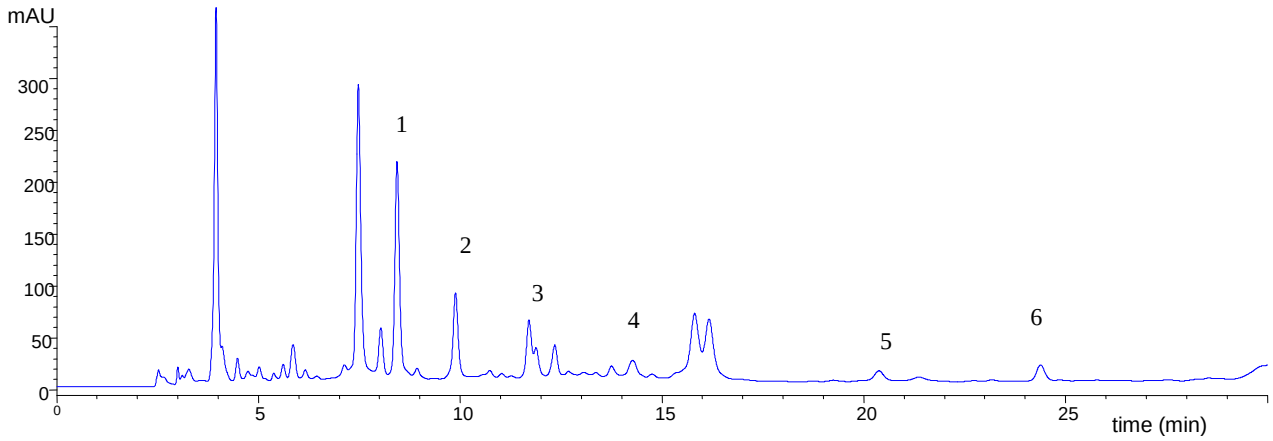


FIGURE 10