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Ultrafiltration Based Process for the Recovery of Polysaccharides and Polyphenols from Winery Effluents

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Winery effluents have a high pollution potential, especially those effluents that are obtained from the second racking. However, these effluents are rich in phenolic compounds and polysaccharides and can be potential sources for the recovery of these compounds. Therefore, a process was developed in this study to reduce the pollution potential of the winery effluents from the second racking and to recover the polyphenols and polysaccharides from the effluents by utilizing ultrafiltration (UF) and sedimentation operations. The sedimentation was optimized by varying the pH from 3.8 to 8.0, while the UF experiments were optimized by varying the transmembrane pressure from 0.5 to 4.0 bar and the feed circulation velocity from 0.44 to 0.87 ms^{-1}. This process provided a permeate stream with a reduction in the TOC content by 56.6%, while the polyphenols and the polysaccharides in the concentrate stream were concentrated by 6 times and 5 times, respectively.

Keywords membrane; polyphenols; polysaccharides; ultrafiltration; Winery effluents

INTRODUCTION

The wine industry generates a large volume of effluents. This industry operates seasonally, and the quality of the effluents varies widely according to the type of wine that is being produced, the winemaking technologies used for production, the dimensions of the installed equipment, and the quantity of water consumed. Among these effluents, the effluent from the second racking has a high pollution charge because of its high concentration of organic compounds such as polysaccharides, polyphenols and organic acids. Consequently, the quality parameters in the effluent, such as the chemical oxygen demand (COD) and the total suspended solids (TSS), can be as high as 30 $g\,L^{-1}$ and 20 $g\,L^{-1}$, respectively, as shown in Table 1 (1). Racking is a process that siphons the wine must from one container to the next, to separate the wine from the sediment. The second racking is conducted at the end of fermentation activity, aiding in the clarification of the wine and inhibiting the production of unwanted off-flavors.

The treatment and the disposal of winery effluents are critical issues in wine-producing regions, where wine production is operated at a large scale, producing large volumes of effluents during the grape harvest and racking periods, which span 3–4 months in a year (2).

Therefore, a responsible management of these effluents requires that their potential environmental impacts should be minimized to acceptable levels (3). Several research efforts aiming to develop efficient technologies for the treatment of these effluents have been reported in recent years, based on biological treatments (anaerobic and aerobic), land-based treatments (constructed wetland), and advanced oxidation processes (ozone, Fenton's reagent and several others), as well as various combinations among these technologies (2–11).

The above-mentioned processes are presented only as solutions for the treatment and the discharge of the effluent. However, winery effluents can be considered as an alternative source for the recovery of polyphenols because their concentration in the effluent can be as high as 1350–1450 mg L^{-1} (1,3).

The high commercial value of these polyphenols requires the development of a process that can treat the effluent and recover these polyphenols at the same time. Different membrane technologies such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have already been widely used in the recovery, concentration, and fractionation of value-added

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TABLE 1
Average characteristics of winery effluents (1)

Parameter	Value
COD ($mgO_2\,L^{-1}$)	3000–30000
BOD_5 ($mgO_2\,L^{-1}$)	1000–15000
TS ($mg\,L^{-1}$)	1000–20000
Sugars ($mg\,L^{-1}$)	100–8000
Ethanol ($mg\,L^{-1}$)	1000–9000
Phenolic Compounds ($mg\,L^{-1}$)	280–1450

products in other areas (12–14) and hence can be considered as alternative treatment processes for winery effluents.

Membrane technology, namely ultrafiltration, is best suited for the separation of the macromolecules in the effluent (15,16). Using membrane processes, Meng et al. (17) recovered anthocyanins from vegetable extracts at high recovery rates and Garcia-Castello et al. (18) obtained a concentrated solution enriched in polyphenols from olive mill wastewater.

The objective of this work is to determine the feasibility of using an integrated sedimentation and ultrafiltration process to treat the winery effluent generated in the second racking for the abatement of the pollution charge while recovering the polyphenols and polysaccharides at the same time.

MATERIALS AND METHODS

Winery Effluent

The second racking effluent obtained from the red wine production of the Portuguese cultivar ''Tinta Roriz'', Syrah and ''Alicante Bouchet'' was collected at the ''Escola Agrária de Santarém'' in Santarém, Portugal. The effluent was stored at $-20°C$ after collection until it was used, and it was used at room temperature for the experiments.

The effluent was analyzed for different parameters before and after treatment. These parameters include the pH, the conductivity, the turbidity, the total organic carbon (TOC), the chemical oxygen demand (COD), the total solids (TS), the total suspended solids (TSS), the total dissolved solids (TDS), the total polysaccharides, and the total polyphenols. The characterization of the raw winery effluent is shown in Table 2.

TABLE 2
Raw winery effluent characterization

Parameter	Value
pH	3.6 ± 0.2
Conductivity ($mS\,cm^{-1}$)	5.45 ± 0.02
Turbidity (NTU)	6925 ± 832
TOC ($mg\,C\,L^{-1}$)	7937 ± 570
COD ($mg\,O_2\,L^{-1}$)	27645 ± 2270
TS ($mg\,L^{-1}$)	17767 ± 887
TSS ($mg\,L^{-1}$)	8783 ± 902
TDS ($mg\,L^{-1}$)	8983 ± 1496
Total Polysaccharides ($mg\,L^{-1}$ glucose)	4764 ± 82
Total Polyphenols ($mg\,L^{-1}$ gallic acid)	1171 ± 59

Membrane Characterization

The ultrafiltration membrane selected was the GR95PP membrane, supplied by Alfa Laval, Denmark. The membrane was first compacted through the circulation of deionized water (with a conductivity of less than $1\,\mu S\,cm^{-1}$) that was pressurized at 5 bar for 3 h. This compaction avoids the influence of pressure effects on the membrane structure in subsequent experiments. It was characterized in terms of its hydraulic permeability (L_p) and its molecular weight cut-off (MWCO).

The membrane MWCO was determined using the permeation data obtained by ultrafiltration of $2000\,mg\,L^{-1}$ solutions of neutral polyethylene glycol that had molecular weights of 2000, 4000 and 6000 Da (supplied by Merck).

The solute rejection f, was defined as:

$$f = ((C_{Afeed} - C_{Apermeate})/C_{Afeed}) * 100 \qquad (1)$$

where C_{Afeed} represents the solute concentration in the feed and $C_{Apermeate}$ represents the solute concentration in the permeate. Both concentrations were determined in terms of TOC.

These experiments were conducted at a transmembrane pressure (ΔP) of 0.5 bar, a temperature of 25°C, and a feed flow rate of $9.2\,L\,min^{-1}$. The stabilization time for each experimental run was 20 minutes. Between each run, membranes were washed with Ultrasil® 0.5% at a temperature of 50°C and a pH of 10.5 until the L_p was at least 90% of the initial value measured after the compaction of the membrane.

Process Development

The effluent was highly loaded, hence requiring pretreatment prior to UF. A sedimentation test was conducted at a temperature of $25 \pm 2°C$. The pH was varied from 3.6 to 8.0 and the sediment height was measured after 2 hours to establish the optimal pH for sedimentation. The pH was adjusted by the addition of 1 M NaOH or 1 M HCl solutions. Effluent sedimentation was conducted at natural pH and at the pH that was determined to be optimal for sedimentation for a period of 6.5 h. The clarified solutions were characterized in terms of TOC, TS, TSS, TDS, total polysaccharides, and total polyphenols then concentrated by UF. After the concentration of the effluent by UF, the concentrate was again subjected to a sedimentation step at the optimal pH for sedimentation.

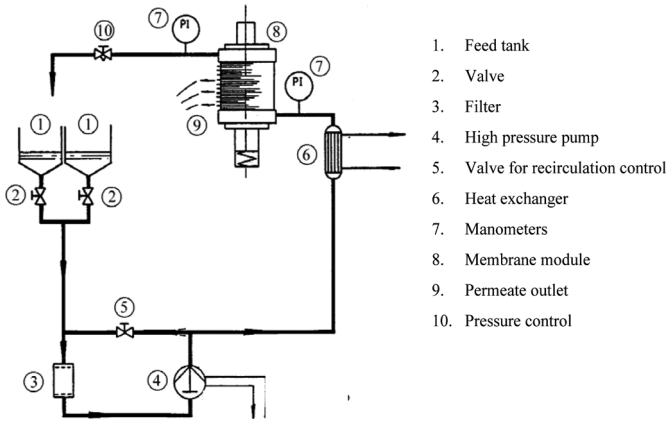

FIG. 1. Schematic illustration of the Lab-Unit M20 UF process.

Ultrafiltration Permeation Experiments

All ultrafiltration experiments were conducted on a Lab-Unit M20 plate and frame filtration unit obtained from Alfa Laval (Denmark) with a membrane surface area of 0.072 m^2, as shown in Fig. 1.

The winery effluent was treated by UF in total recirculation mode, where the permeate and the concentrate streams were recirculated to the feed tank to study the variation in the permeate fluxes and the solute rejection coefficients at two different pH values. The UF setup was operated at a temperature of 25°C, with the ΔP varying from 0.5 to 4.0 bar, and at three different feed circulation velocities, 0.44, 0.60, and 0.87 ms^{-1}. The feed circulation velocities were calculated at 2 bar using deionized water. The initial volume of the feed solution for all experiments was 3 L.

After the optimization of the UF operating parameters, three separate runs were conducted in concentration mode to determine the variation of the permeate flux as a function of the operation time and of the volumetric concentration factor (VCF) and the variation of the solute rejection coefficients. The VCF was defined as:

$$VCF = [Volume_{Feed}/(Volume_{Feed} - Volume_{permeate})] \quad (2)$$

TABLE 3
Feed composition of the three UF experimental runs for concentrating the effluent

Parameter	Run 1	Run 2	Run 3
TOC (mg C L^{-1})	6475	6494	6832
TS (mg L^{-1})	14350	13750	13170
TSS (mg L^{-1})	8650	7600	7390
TDS (mg L^{-1})	5700	6150	5780
Total Polysaccharides (mg L^{-1} glucose)	3141	3458	2625
Total Polyphenols (mg L^{-1} gallic acid)	880	1003	830

Approximately 3.5 L of effluent was first treated by sedimentation and chemically analyzed before each individual UF treatment was run, as shown in Table 3.

Analytical Methods

The different parameters analyzed included the TOC with a Dohrmann DC-85A carbon analyzer, the pH at 20°C using a Crison 2002 pH meter, the conductivity at 25°C using a Crison 525 conductivity meter, the turbidity with an LP 2000 turbidity meter (Hanna Instruments), COD, TS, TDS, and TSS. These analyses were carried out according to the standard methods for the examination of water and wastewater, methods 5310B, 4500-H^+, 2510B, 2130B, 5220C, 2540B, 2540C, and 2540D, respectively (19). The total polyphenols content was determined by a colorimetric method that used a spectrophotometer (UV-1700 Shimadzu) to measure the absorbance at 280 nm (20), while the total polysaccharides content was determined by the phenol-sulfuric acid method (21).

RESULTS AND DISCUSSION

Table 2 reports the characterization of the winery effluents and the very high values of the total suspended solids (TSS) and turbidity stand up as a need for a pre-treatment of sedimentation prior to the ultrafiltration.

Sedimentation Optimization

As can be seen in Fig. 2, displaying the influence of pH on the sedimentation of the suspended solids, the tubes corresponding to pH 4.9 and 5.4 show a better performance with a higher volume of clarified solution. In Table 4 and for the pH of 5.4 the removal rates of suspended solids and turbidity are 84.4% and 86.6%, respectively. This table displays also the removal rates of suspended solids and turbidity for the natural pH of 3.6 and the values are 28.6% and 16.9%,

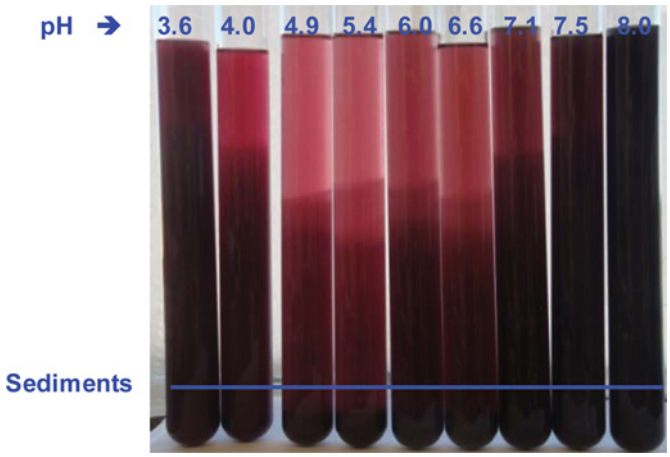

FIG. 2. Sedimentation conducted at pH values ranging from 3.6 to 8.0 at a temperature of 25 ± 2°C. (Color figure available online)

TABLE 4
Effluent sedimentation at a pH of 3.6 (natural pH) and a pH of 5.4 (optimal pH)

	pH 3.6			pH 5.4		
Parameter	Feed	Clarified	Removal (%)	Feed	Clarified	Removal (%)
Conductivity ($mS\,cm^{-1}$)	5.45	5.42	0	6.93	7.00	0
Turbidity (NTU)	7431	6178	16.9	6337	847	86.6
TOC ($mg\,C\,L^{-1}$)	—	—	—	7567	4812	36.4
COD ($mg\,O_2\,L^{-1}$)	29250	25792	11.8	26040	16616	36.2
TS ($mg\,L^{-1}$)	17170	13130	23.5	18590	12430	33.1
TSS ($mg\,L^{-1}$)	10300	7350	28.6	7870	1230	84.4
TDS ($mg\,L^{-1}$)	6870	5780	15.9	10710	11200	0
Total Polysaccharides ($mg\,L^{-1}$ glucose)	4788	4069	15.0	4699	852	81.9
Total Polyphenols ($mg\,L^{-1}$ gallic acid)	1158	1018	12.1	1086	295	72.8

respectively. In association with these results the sedimentation of 3.5 L of effluent yielded 0.10 and 0.25 L of sediments for experiments run at pH of 3.6 and 5.4, respectively.

At natural pH (pH 3.6), the sedimentation showed smaller reductions for all parameters, but the treatment removed the coarser solids allowing the effluent to be subjected to the UF system, without damaging the equipment.

Ultrafiltration

Membrane Characterization

The pure water permeation flux (PWP) was measured at transmembrane pressures ranging from 0.5 to 4.0 bar. The PWP was plotted as a function of ΔP and the membrane hydraulic permeability, L_p, was obtained as the slope of the straight line from that plot. The L_p for the membrane used in this study was determined to be $6.0\,kg\,h^{-1}\,m^{-2}\,bar^{-1}$.

The curve-fitting of plot log (f/(1−f)) as a function of the solute molecular weight was intersected by the 91% rejection line and yielded the molecular weight cut-off of 7600 Da to the GR95PP membrane, as shown in Fig. 3.

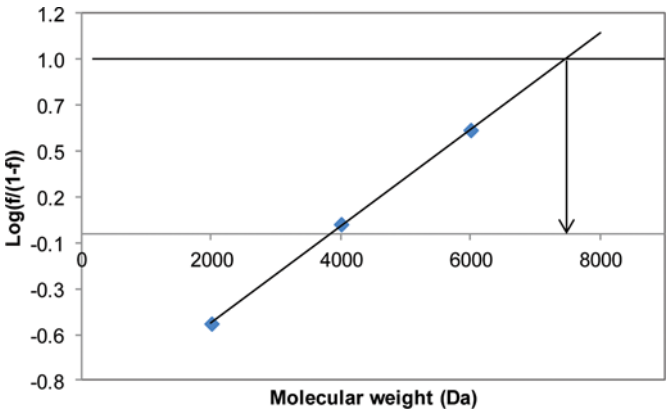

FIG. 3. MWCO determination for the GR95PP membrane. (Color figure available online)

Operating Conditions

Total Recirculation Mode. The ultrafiltration of the effluent after sedimentation at a pH of 5.4 and a pH of 3.6 yielded different permeation patterns, as shown in Figs. 4 and 5, respectively.

Figure 4 displays the UF permeate flux as a function of the transmembrane pressure at feed circulation velocities of 0.60 and $0.87\,ms^{-1}$ after the effluent had been clarified at a pH of 5.4. At the higher tangential velocity of $0.87\,ms^{-1}$, the slope of the variation of the fluxes versus the transmembrane pressure decreases up to 1.5 bar and then remains constant up to 4.0 bar. However, in all pressure range, the limiting flux was never reached. On the other hand, at the tangential velocity of $0.60\,ms^{-1}$, the flux has a linear behavior over the all pressure range but considerably lower than the one relative to the velocity of $0.87\,ms^{-1}$.

Figure 5 displays the UF permeate flux as a function of the transmembrane pressure at three feed circulation velocities after the effluent had been clarified at a pH of 3.6.

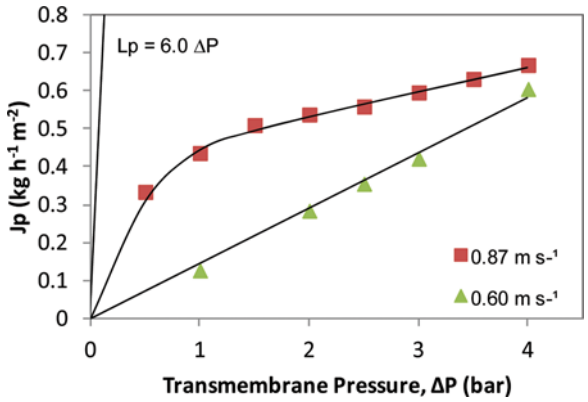

FIG. 4. Permeate flux as a function of ΔP when the clarified effluent was treated with UF after sedimentation at a pH of 5.4 using two different feed circulation velocities, (▲) 0.60 and (·) $0.87\,ms^{-1}$. (Color figure available online)

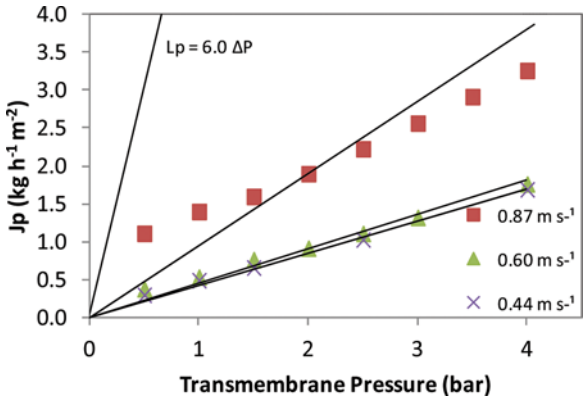

FIG. 5. Permeate flux as a function of ΔP when the clarified effluent was treated with UF after sedimentation at a pH of 3.6 using three different feed circulation velocities, (X) 0.44, (▲) 0.60 and (·) 0.87 m s^{-1}. (Color figure available online)

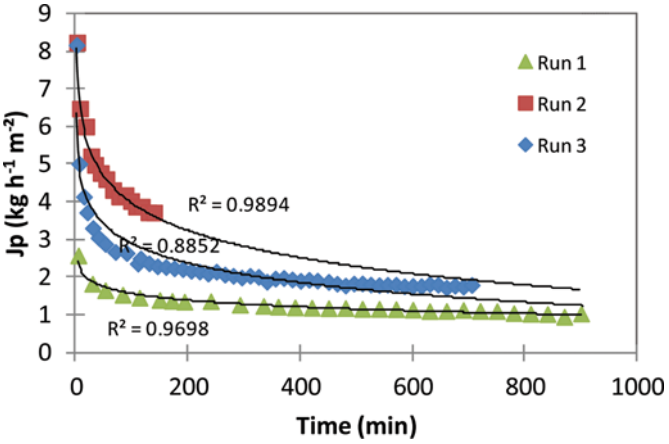

FIG. 6. Permeation flux of the post-sedimentation winery effluent over time. UF was operated at a TMP of 4 bar, a feed circulation velocity of 0.87 m s^{-1} and a temperature of 25 ± 2°C. (Color figure available online)

For all the feed circulation velocities there is a linear variation of the UF permeation fluxes with the transmembrane pressure. The slope of this variation is identical for the low feed circulation velocities of 0.6 and 0.44 m s^{-1} and well below the one corresponding to the velocity of 0.87 m s^{-1}. In all trials, at the pressure range and velocities used, the limiting flux was never reached.

The rejection coefficients to polysaccharides and to polyphenols in the ultrafiltration of the clarified effluents at pH 3.6 and 5.4 are shown in Table 5. The higher values relative to the feed solution resulting from the sedimentation at the natural pH of 3.6 can be attributed to the fact that the suspended solids probably are large colloids formed from the association of these macromolecules and have a cleaning effect of the membrane surface. The rejection coefficients to polysaccharides and to polyphenols are practically independent of the transmembrane pressure.

TABLE 5
Variation of the polysaccharides and polyphenols rejection coefficients with the transmembrane pressure. Ultrafiltration of the clarified effluents at pH 3.6 and 5.4

	Effluent clarified at pH of 3.6		Effluent clarified at pH of 5.4	
Pressure (bar)	Polyphenols rejection (%)	Polysacchar. rejection (%)	Polysacchar. rejection (%)	Polyphenols rejection (%)
0.5	94.7	99.3	95.6	81.3
1.5	93.6	99.2	92.8	66.1
2.5	94.1	99.3	94.0	66.4
4.0	94.6	99.3	97.1	74.9

Concentration Mode. The previous results show that the UF of the effluents clarified at the natural pH of 3.6 yields higher permeation fluxes and these vary linearly with the transmembrane pressure up to 4 bar. Taking that into consideration the ultrafiltration in concentration mode is then run for these effluents clarified at the pH of 3.6 and at a transmembrane pressure of 4 bar. The temperature is kept around 25 ± 2°C. Figure 6 presents the results of three runs corresponding to ultrafiltration operating times of 900, 140, and 700 minutes. The corresponding volumetric concentration factors (VCF) are 2.3, 1.8, and 2.0, respectively. The initial flux decline is associated to a VCF of 1.2 for all three runs.

Cassano et al. (22) have studied the flux decay through three UF fouling models that relate the variation of the permeate flux with the filtration time. Table 6 presents these models and the corresponding mechanisms.

By these results, it is possible to see that the best fitting is achieved for Model II. The resistance of a cake layer covering the entire surface of the membrane is then the best

TABLE 6
Common fouling models used in the analysis of UF fouling

Models	Equations		Fouling mechanisms
Model I	$1/J = (1/J_0) + Kt$	(3)	Cake formation.
Model II	$1/J^2 = (1/J_0^2) + Kt$	(4)	Cake formation/ membrane surface covered by a layer of particles.
Model III	$\ln J = \ln J_0 - Kt$	(5)	Pore blocking.

TABLE 7
Sedimentation of the UF concentrate

Parameter	Feed	Clarified	Sediments
TOC (mg C L^{-1})	9655	5188	26442
Total Polysaccharides (mg L^{-1} glucose)	7214	750	23892
Total Polyphenols (mg L^{-1} gallic acid)	2029	538	7014

explanation for the fouling phenomenon in the treatment of the winery effluent.

In all the three runs, in concentration mode, the polysaccharides and the polyphenols rejection coefficients are practically constant, $99.5 \pm 0.2\%$ and $95.7 \pm 1.2\%$, respectively.

Due to the increase of polyphenols and polysaccharides content in the concentrate and having in view their recovery a new sedimentation operation is investigated.

Sedimentation of the UF Concentrate

One liter of UF concentrate was subjected to sedimentation at a pH of 5.4 for 4 h at room temperature, $25 \pm 2°C$. After sedimentation, 0.9 L of clarified liquid and 0.1 L of sediments were obtained.

Table 7 shows that there was a high concentration of polyphenols and polysaccharides, 7 and 23.9 g L^{-1} remaining in the sediments of the ultrafiltration concentrate, which represent a sixfold and a fivefold increase in their concentrations, respectively, in comparison with their concentrations in the raw effluent (Table 2).

CONCLUSIONS

It can be concluded from the present study that the optimal pH for sedimentation is a pH of 5.4. However, the UF of the effluent that was clarified at a pH of 3.6 yielded higher permeation fluxes than the UF of the effluent that was clarified at a pH of 5.4.

The ultrafiltration data when the UF system was operated in total recirculation mode for the effluent clarified at a pH of 3.6 show the following: the UF permeation fluxes increase linearly with the transmembrane pressure over a pressure range of 0.5–4.0 bar; the slopes of the linear variation J_p versus ΔP increase as the feed circulation velocity increases; the rejection coefficients to polyphenols and polysaccharides are independent of the transmembrane pressure and equal to $94.3 \pm 0.5\%$ and $99.3 \pm 0.1\%$, respectively.

Runs in concentration mode display a strong time dependence of the permeate fluxes, presenting great decline of the initial fluxes. However, when the flux is analyzed as a function of the VCF, it can be observed that the permeate flux declines significantly up to a VCF of 1.2 and remains approximately constant thereafter. The rejection coefficients for the polyphenols and the polysaccharides are independent of VCF, with rejection values remaining consistently at $95.7 \pm 1.2\%$ and $99.5 \pm 0.2\%$, respectively. The TOC rejection coefficients experience a slight increase with an increase in the VCF, ranging from 47 to 65% in this work.

The results obtained in this work show that the sedimentation and ultrafiltration treatment of winery effluent is an alternative for these industries, given that there was a 56.6% reduction in the TOC of the permeate stream and that the polyphenols and the polysaccharides could be concentrated in the sediments by sixfold and fivefold, respectively.

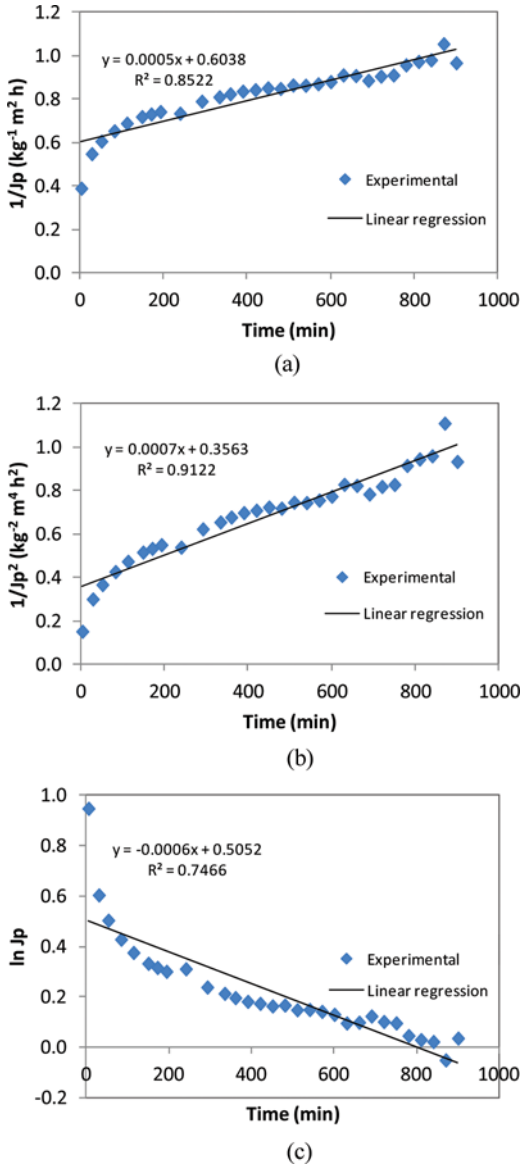

FIG. 7. Fouling models applied to the investigated UF membrane according to Equations (4), (5) and (6). (a) Model I; (b) Model II; (c) Model III. (Color figure available online)

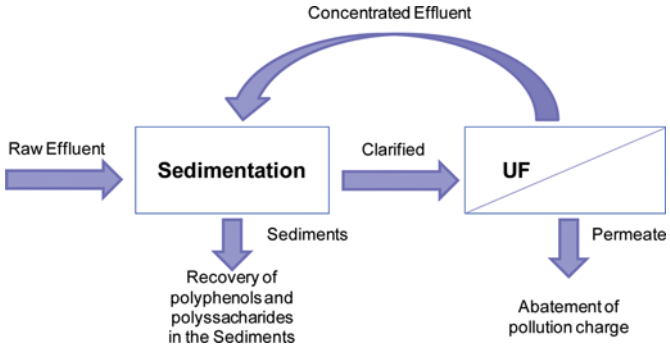

FIG. 8. Development of a process to treat winery effluents and recover polyphenols and polysaccharides. (Color figure available online)

A process was developed to treat winery effluent while recovering polyphenols and polysaccharides at the same time, as shown in Fig. 8.

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REFERENCES

1. Pirra, A.J.D. (2005) Caracterização e tratamento de efluentes vinícolas da Região Demarcada do Douro, PhD Thesis, University of Trás-os-Montes and Alto Douro, Vila Real, Portugal, p. 296.
2. Ormad, M.P.; Mosteo, R.; Ibarz, C.; Ovelleiro, J.L. (2006) Multivariate approach to the photo-Fenton process applied to the degradation of winery wastewaters. *Applied Catalyssis B: Environmental*, 66: 58–63.
3. Braz, R.; Pirra, A.; Lucas, M.S.; Peres, J.A. (2010) Combination of long term aerated storage and chemical coagulation/flocculation to winery wastewater treatment. *Desalination*, 263: 226–232.
4. Agustina, T.E.; Ang, H.M.; Pareek, V.K. (2008) Treatment of winery wastewater using a photocatalytic/photolytic reactor. *Chemical Engineering Journal*, 135: 151–156.
5. Anastasiou, N.; Monou, M.; Mantzavinos, D.; Kassinos, D. (2009) Monitoring of the quality of winery influents/effluents and polishing of partially treated winery flows by homogeneous Fe(II) photo-oxidation. *Desalination*, 248: 836–842.
6. Arfi, V.; Bagoudou, D.; Korboulewsky, N.; Bois, G. (2009) Initial efficiency of a bamboo grove–based treatment system for winery wastewater. *Desalination*, 246: 69–77.
7. Christen, E.W.; Quayle, W.C.; Marcoux, M.A.; Arienzo, M.; Jayawardane, N.S. (2010) Winery wastewater treatment using the land filter technique. *Journal of Environmental Management*, 91: 1665–1673.
8. Kirzhner, F.; Zimmels, Y.; Shraiber, Y. (2008) Combined treatment of highly contaminated winery wastewater. *Separation and Purification Technology*, 63: 38–44.
9. Lucas, M.S.; Peres, J.A.; Li Puma, G. (2010) Treatment of winery wastewater by ozone-based advanced oxidation processes (O3, O3/UV and O3/UV/H2O2) in a pilot-scale bubble column reactor and process economics. *Separation and Purification Technology*, 72: 235–241.
10. Montalvo, S.; Guerrero, L.; Rivera, E.; Borja, R.; Chica, A. (2010) Kinetic evaluation and performance of pilot-scale fed-batch aerated lagoons treating winery wastewater. *Bioresource Technology*, 101: 3452–3456.
11. Serrano, L.; de la Varga, D.; Ruiz, I.; Soto, M. (2011) Winery wastewater treatment in a hybrid constructed wetland. *Ecological Engineering*, 37: 744–753.
12. Santos, F.R.; Catarino, I.; Geraldes, V.; de Pinho, M.N. (2008) Concentration and rectification of grape must by nanofiltration. *American Journal of Viticulture and Enology*, 59: 446–450.
13. Vandanjon, L.; Grignon, M.; Courois, E.; Bourseau, P.; Jaouen, P. (2009) Fractionating white fish fillet hydrolysates by ultrafiltration and nanofiltration. *Journal of Food Engineering*, 95: 36–44.
14. Mello, B.C.B.S.; Petrus, J.C.C.; Hubinger, M.D. (2010) Concentration of flavonoids and phenolic compounds in aqueous and ethanolic propolis extracts through nanofiltration. *Journal of Food Engineering*, 96: 533–539.
15. Catarino, I.; Minhalma, M.; Beal, L.L.; Mateus, M.; de Pinho, M.N. (2008) Assessment of saccharide fractionation by ultrafiltration and nanofiltration. *Journal of Membrane Science*, 212: 34–40.
16. Chabeaud, A.; Vandanjon, L.; Bourseau, P.; Jaouen, P.; Guérard, F. (2009) Fractionation by ultrafiltration of a saithe protein hydrolysate (Pollachius virens): Effect of material and molecular weight cut-off on the membrane performances. *Journal of Food Engineering*, 91: 408–414.
17. Meng, L.; Lozano, Y.; Bombarda, I.; Gaydou, E.; Li, B. (2006) Anthocyanin and flavonoid production from *perilla frutescens*: pilot plant scale processing including cross-flow microfiltration and reverse osmosis. *Journal of Agricultural and Food Chemistry*, 54: 4297–4303.
18. Garcia-Castello, E.; Cassano, A.; Criscuoli, A.; Conidi, C.; Drioli, E. (2010) Recovery and concentration of polyphenols from olive mill wastewaters by integrated membrane system. *Water Research*, 44: 3883–3892.
19. American Public Health Association (1999) *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; APHA: Washington, DC.
20. Curvelo-Garcia, A.S. (1988) *Controlo de qualidade dos vinhos*; Instituto da Vinha e do Vinho: Lisboa.
21. Dubois, M.; Gilles, K.A.; Hamilton, J.K.; Rebers, P.A.; Smith, F. (1956) Colorimetric method for determination of sugars and related substances. *Analytical Chemistry*, 3: 350–356.
22. Cassano, A.; Donato, L.; Conidi, C.; Drioli, E. (2008) Recovery of bioactive compounds in kiwifruit juice by ultrafiltration. *Innovative Food Science and Emerging Technologies*, 9: 556–562.