Desalination and Water Treatment
www.deswater.com
1944-3994/1944-3986

11 (2009) 224–228

Cork processing wastewater treatment/valorisation by nanofiltration

J. Oliveira[a], M. Nunes[a], P. Santos[a], P. Cantinho[a], M. Minhalma[a,b,*]

[a]*Department of Chemical Engineering, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro, 1, 1959-007 Lisbon, Portugal*
Tel. +351-21-8317000; Fax. +351-21-8317267; email: jcondelipes@gmail.com, marlene.nunes@gmail.com, paulaalmeidasantos@gmail.com, pcantinho@deq.isel.ipl.pt, mminhalma@deq.isel.ipl.pt
[b]*ICEMS, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1, 1049-001 Lisbon, Portugal*

Received 14 April 2009; Accepted 19 August 2009

ABSTRACT

Nanofiltration process for the treatment/valorisation of cork processing wastewaters was studied. A DS-5 DK 20/40 (GE Water Technologies) nanofiltration membrane/module was used, having 2.09 m^2 of surface area. Hydraulic permeability was determined with pure water and the result was 5.2 $L.h^{-1}.m^{-2}.bar^{-1}$. The membrane presents a rejection of 51% and 99% for NaCl and $MgSO_4$ salts, respectively. Two different types of regimes were used in the wastewaters filtration process, total recycling mode and concentration mode. The first filtration regime showed that the most favourable working transmembrane pressure was 7 bar working at 25ºC. For the concentration mode experiments it was observed a 30% decline of the permeate fluxes when a volumetric concentration factor of 5 was reached. The permeate COD, BOD_5, colour and TOC rejection values remained well above the 90% value, which allows, therefore, the concentration of organic matter (namely the tannin fraction) in the concentrate stream that can be further used by other industries. The permeate characterization showed that it cannot be directly discharged to the environment as it does not fulfil the values of the Portuguese discharge legislation. However, the permeate stream can be recycled to the process (boiling tanks) as it presents no colour and low TOC (<60 ppm) or if wastewater discharge is envisaged we have observed that the permeate biodegradability is higher than 0.5, which renders conventional wastewater treatments feasible.

Keywords: Cork processing wastewater; Nanofiltration; Recycling; Effluent valorisation

1. Introduction

Membrane technology, namely Ultrafiltration (UF) and Nanofiltration (NF), have been playing an important role in the end-of-pipe effluent treatment. However, these technologies have not been used at their full potential for the development of clean production processes. This can be initially approached through the use of UF/NF for the concentration/fractionation of process streams, yielding a permeate water with the required quality to be re-used in the process and concentrate streams that can be purified for raw materials/by-products recovery.

The cork processing industry is an example where membranes can play a crucial role in process optimization and where valuable products can be extracted from the effluents and re-used by other industries, such as the wood agglomerate industry, pharmaceutical industry, wine industry, dye industry and tannery industry. Portugal, with only 30% of the world's cork oak forests, accounts for more than a half of the world's cork production**.**

Previous studies reported that membrane fouling was the main drawback concerning the treatment of cork processing wastewater by UF. The adequate selection of UF/NF membranes and the optimization of the operating conditions may result in fouling minimization with an optimal permeation performance, yielding a feasible treatment for the cork processing wastewater and turning possible the concentration of valuable products (namely tannins) in the concentrate stream.

*Corresponding author.

doi: 10.5004/dwt.2009[illegible]

In the last seven years, the cork processing wastewater treatment has been subject of some research, mainly by Portuguese and Spanish research groups. Most of these works were focussed on chemical treatments, mainly destructive processes like chemical oxidation of the organic matter by ozone, Fenton oxidation, photochemical processes involving UV radiation and hydrogen peroxide, chemical precipitation [1–8]. Some works also focussed on biological treatments [3,9]. The use of membrane technology in this area has been studied by Minhalma *et al*. [10–13], Benítez *et al*. (2005) [14] and Acero *et al*. (2005) [15]. Minhalma *et al*. have been studying the use of UF for the cork processing wastewater treatment since 2000, and have been developing integrated processes envisaging the integration of UF with pre-treatments, namely pre-treatments that allow the removal of the membrane fouling compounds, thus increasing the UF performance in terms of permeate fluxes and solute rejections. These authors concluded that membrane fouling, due to the adsorption of organic materials into the membrane, is the main problem found when applying UF for the cork wastewater treatment and therefore the optimization of a pre-treatment process is a question of major importance.

2. Methods

2.1. Membrane and membrane module

A DS-5 (GE Water Technologies) nanofiltration membrane was used in a DK 20/40 (GE Water Technologies) module having 2.09 m^2 of surface area.

Membranes were characterized in terms of pure water permeability (L_p) and of apparent rejection coefficient to NaCl and $MgSO_4$. The membrane hydraulic permeability was determined by permeating pure water, varying transmembrane pressures from 2.5 to 15 bar, at 25ºC. Salt permeation experiments were carried out at 7 bar, feed flow rate of 530 L/h, 25ºC, with salt/water binary solutions having a salt concentration of 2000 ppm.

2.2. Wastewater, concentrate and permeate characterization

The cork processing wastewater, the concentrate stream and the permeate stream were characterized in terms of pH, conductivity, total organic carbon (TOC), colour, chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5), according to the analytical procedures outlined in *Standard Methods* [16].

2.3. Permeation experiments

The permeation experiments were carried out in a lab-assembled installation having the following components: (a) 60 L feed tank equipped with a cooling system, (b) a microfiltration cartridge and a carbon active cartridge, (c) a Lowara 2HM centrifuge pressure pump and a Hydra-Cell M-03 circulating pump, (d) a NF module, (e) a concentrate flowmeter and a permeate flowmeter, (f) a back-pressure valve (to control the system working pressure).

Two different regimes were used in the cork boiling wastewater permeation process: total recycling mode (where both permeate and concentrate streams are recirculated to the feed tank) and concentration mode (where only the concentrate stream is recirculated to the feed tank, while the permeate is continuously drawn out). The wastewaters were microfiltered prior to the nanofiltration step, in order to remove any large suspended solids.

Total recycling mode was used to determine the optimal operating conditions, namely, the feed circulating velocity (set for the maximum allowed by the installation) and working transmembrane pressure, which was varied from 5 to 15 bar. At this stage, nanofiltration performance was assessed through the measurement of the permeate fluxes as a function of the transmembrane pressure and through the determination of the rejection coefficients to TOC, COD, BOD_5, colour and conductivity.

Concentration mode experiments were used to assess the cork processing wastewater treatability by NF. The NF operating conditions were set to 7 bar, 25ºC and maximal feed circulating flow rate, 530 L/h (in order to minimize concentration polarization phenomena). The initial wastewater volume was 55 L and the concentration experiment was carried out until a volumetric concentration factor (VCF) of 5 was reached. For this permeation experiment, nanofiltration performance was assessed through the measurement of the permeate flux as a function of the VCF and through the determination of the rejection coefficients to TOC, COD, BOD_5, colour and conductivity also in function of the VCF.

3. Results and discussion

Membrane characterization showed that the NF membranes studied have an hydraulic permeability of 5.2 L/(h.m^2.bar) and rejection coefficients of 51% and 99% for NaCl and $MgSO_4$, respectively.

The cork processing wastewater presented very high contents of organic matter and colour. The effluent characterization is presented in Table 1.

Table 1
Cork processing wastewater characterization.

pH	5.21
Conductivity (µS/cm)	1396
COD (mg O_2/L)	2288
BOD_5 (mg O_2/L)	875
TOC (mg C/L)	799.7
Colour (Hazen units)	7000

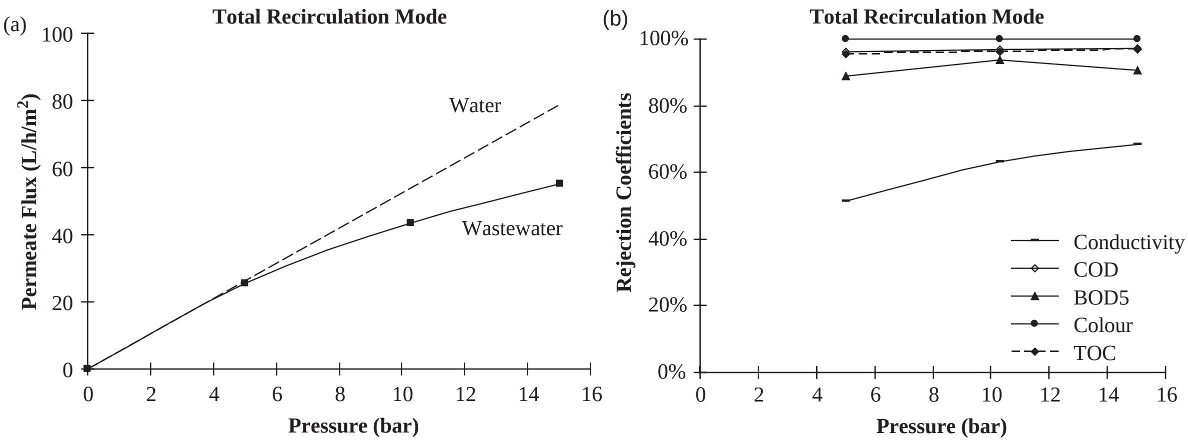

Fig. 1. (a) Water (dashed line) and wastewater permeate fluxes and (b) Rejection coefficients to TOC, COD, BOD_5, colour and conductivity obtained for total recycling mode.

The results of the total recycling mode NF experiments are shown in Fig. 1.

Fig. 1 shows a deviation in terms of permeate fluxes when comparing wastewater and pure water permeation. This deviation increases significantly for transmembrane pressures higher than 7 bar as the effect of concentration polarisation phenomena and adsorption became more and more important, and therefore this transmembrane pressure was selected as the optimal operating pressure. Regarding the rejection coefficients, fig. 1 shows that the values for COD, BOD_5, colour and TOC are all well above 85% and therefore the organic matter concentration can be achieved.

The concentration mode results, presented in Fig. 2 and Table 2, show that the permeate flux decreases linearly with the increase of the volumetric concentration factor (VCF) and that for a VCF of 5 the permeate flux decline is around 30%. Regarding the rejection coefficients to COD, BOD_5, colour and TOC they all remain well above 90%, allowing organic matter concentration.

In Table 3, the cumulative permeate and final concentrate (VCF = 5) characteristics and the Portuguese discharge legislation (VLE) are shown. These results show that the cumulative permeate presents values of pH, COD and BOD_5 slightly above the VLE which renders its release to the environment unviable.

4. Conclusions

The nanofiltration performance was assessed envisaging the treatment/valorisation of cork processing wastewater. In one hand, it was aimed the reduction of wastewater volume discharges by recycling the permeate stream to the process and, on the other hand, organic matter concentration was envisaged in order to reuse

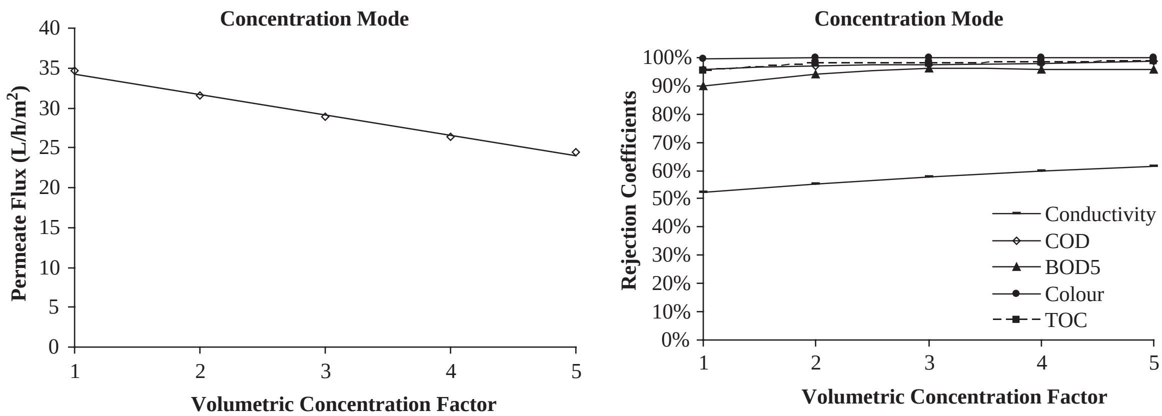

Fig. 2. Permeate flux and rejection coefficients to TOC, COD, BOD_5, colour and conductivity obtained for concentration mode. Transmembrane pressure = 7 bar, Temperature = 25ºC, Feed flow rate = 530 L/h.

Table 2
NF feed, concentrate and permeate characteristics for different volumetric concentration fsactors.

		Volumetric concentration factor				
		1	2	3	4	5
Feed	pH	5.21	4.96	4.92	4.86	4.84
	Conductivity (μS/cm)	1396	2010	2470	2910	3310
	COD (mg O_2/L)	2288.0	4576.0	7040.0	9680.0	14720
	BOD_5 (mg O_2/L)	875.0	2000	3000	3500	4750
	TOC (mg C/L)	799.7	2222.2	3211.7	4254.4	5652.2
	Colour (Hazen unit)	7000	13900	18000	21000	51300
Concentrate	pH	5.07	4.94	4.90	4.84	4.80
	Conductivity (μS/cm)	1486	2100	2580	2990	3390
	COD (mg O_2/L)	2640.0	5280.0	7626.s7	8800.0	12320
	BOD_5 (mg O_2/L)	1100	1500	2667	3000	3500
	TOC (mg C/L)	1276.9	2515.2	3602.2	4724.7	6249.7
	Colour (Hazen unit)	7000	16400	29100	34700	37400
Permeate	pH	5.00	5.00	4.98	4.98	4.97
	Conductivity (μS/cm)	689.0	917.0	1065	1182	1284
	COD (mg O_2/L)	105.6	140.8	176.0	176.0	176.0
	BOD_5 (mg O_2/L)	100	105	113	140	170
	TOC (mg C/L)	47.2	52.4	65.0	72.8	84.9
	Colour (Hazen unit)	34	18	13	11	7.0

Table 3
Characteristics of cumulative permeate and final concentrate (VCF = 5).

	VLE [17]	Global permeate
pH	6.0–9.0	5.1
Conductivity (μS/cm)	–	896
Colour	Not visible	Not visible
TOC (mg C/L)	–	56.5
COD (mg O_2/L)	150	184
BOD_5 (mg O_2/L)	40	125

valuable compounds (namely tannins) in other industries. By doing this, the negative environmental impact of the cork processing industry can be significantly reduced.

Despite the fact that the cumulative permeate presented values of pH, COD and BOD_5 slightly above the VLE (which renders its release to the environment unviable), its characteristics (total lack of colour and low TOC values) would allow the reutilization of this permeate stream in the cork boiling tank, leading to a relevant decrease in fresh water consumption.

The NF concentration experiments also shown that the organic matter concentration (rich in tannins [11]) is easily achievable by nanofiltration, which allows this concentrate stream to be used by other industrial areas, like the tanning and glue/adhesive industries, leading to a significant reduction on the environmental impact of the cork processing industry.

One other important result was the increase obtained for the BOD_5/COD ratio, from 0.38 (initial feed stream) to 0.68 (cumulative permeate). This means that the permeate stream presents a significant higher biodegradability and that it may be possible to remove its organic content by a conventional wastewater treatment, which is not the case for the initial feed wastewater.

Acknowledgments

The authors would like to thank FCT for the funding of the project PTDC/EQU-EQU/68424/2006.

References

[1] J.L. Acero, F.J. Benitez, F.J. Real, A.I. Leal and A. Sordo, Oxidation of esculetin, a model pollutant present in cork processing wastewaters, by chemical methods, Ozone: Sci. Eng., 27(4) (2005) 317–326.

[2] J.L. Acero, F.J. Benitez, J.B. de Heredia and A.I. Leal, Chemical treatment of cork-processing wastewaters for potential reuse, J. Chem. Technol. Biotechnol., 79(10) (2004) 1065–1072.

[3] F.J. Benitez, J.L. Acero, J. Garcia and A.I. Leal, Purification of cork processing wastewaters by ozone, by activated sludge, and by their two sequential applications, Water Res., 37(17) (2003) 4081–4090.

[4] A.M.F.M, Guedes, L.M.P. Madeira, R.A.R. Boaventura and C.A.V. Costa, Fenton oxidation of cork cooking wastewater—Overall kinetic analysis, Water Res., 37(13) (2003) 3061–3069.

[5] J.A. Peres, J.B. de Heredia and J.R. Domínguez, Integrated Fenton's reagent - Coagulation/flocculation process for the treatment of cork processing wastewaters, J. Hazard. Mater., 107(3) (2004) 115–121.
[6] F.J. Benitez, F.J. Real, J.L. Acero, A.I. Leal and C. Garcia, Gallic acid degradation in aqueous solutions by UV/H_2O_2 treatment, Fenton's reagent and the photo-Fenton system, J. Hazard. Mater., 126(1–3) (2005) 31–39.
[7] F.J. Benitez, F.J. Real, J.L. Acero, A.I. Leal and S. Cotilla, Oxidation of acetovanillone by photochemical processes and hydroxyl radicals, J. Environ. Sci. Health A, 40(12) (2005) 2153–2169.
[8] J.R. Domínguez, J.B. de Heredia, T. González and F. Sanchez-Lavado, Evaluation of ferric chloride as a coagulant for cork processing wastewaters. Influence of the operating conditions on the removal of organic matter and settleability parameters, Ind. Eng. Chem. Res., 44(17) (2005) 6539–6548.
[9] E. Mendonça, P. Pereira, A. Martins and A.M. Anselmo, Fungal biodegradation and detoxification of cork boiling wastewaters, Eng. Life Sci., 4(2) (2004), 144–149.
[10] M. Minhalma, C.R. Dias and M.N. Pinho, Adsorptive fouling in ultrafiltration of cork processing wastewaters, Adv. Environ. Res., 3(4) (2000) 539.
[11] M. Minhalma and M.N. Pinho, Tannic-Membrane interactions on ultrafiltration of cork processing wastewaters, Separation Purif. Technol., 22–23 (2001) 479–488.
[12] M. Minhalma and M.N. Pinho, Flocculation/flotation/ultrafiltration integrated process for the treatment of cork processing wastewaters, Environ. Sci. Technol., 35 (2001) 4916–4921.
[13] M. Minhalma, J.R. Domínguez and M.N. Pinho, Cork Processing Wastewaters Treatment by an Ozonization/Ultrafiltration Integrated Process, Desalination, 191 (2006) 148–152.
[14] F.J. Benítez, J.L. Acero, A.I. Leal and F.J. Real, Purification of ellagic acid by UF membranes, Chem. Eng. Technol., 28(9) (2005) 1035–1040.
[15] J.L. Acero, F.J. Benítez, A.I. Leal and F.J Real, Removal of phenolic compounds in water by ultrafiltration membrane treatments, J. Environ. Sci. Health A, 40(8) (2005) 1585–1603.
[16] Standard Methods for the Examination of Water and Wastewater (1989). 17th Ed., APHA, AWWA, WPCF. American Public Health Association, Washington D.C., USA.
[17] Decreto-Lei 236/98 de 1 de Agosto. Diário da República - I Série-A, Nº 176 de 01/08/1998.