Original Research

Nanofiltration of Cork Wastewaters and Their Possible Use in Leather Industry as Tanning Agents

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Abstract

Cork processing wastewater is a very complex mixture of vegetal extracts and has, among other natural compounds, a very high content of phenolic/tannic colloidal matter that is responsible for severe environmental problems. In the present work, the concentration of this wastewater by nanofiltration was investigated with the aim of producing a cork tannin concentrate to be utilized in tanning. Permeation results showed that the permeate fluxes are controlled by both osmotic pressure and fouling/gel layer phenomena, leading to a rapid decrease of permeate fluxes with the concentration factor. The rejection coefficients to organic matter were higher than 95%, indicating that nanofiltration has a very good ability to concentrate the tannins and produce a permeate stream depleted from organic matter. The cork tannin concentrate obtained by nanofiltration and evaporation had total solids concentration of 34.8 g/l. The skins tanned by this concentrate were effectively converted to leather with a shrinking temperature of 71ºC.

Keywords: nanofiltration, cork wastewater, tannin, tanning, leather

Introduction

The cork planks used in the production of cork wine stoppers must be boiled in water for at least 75 minutes in order to remove any extraneous materials and to render the planks softer and more flexible. This process consumes a large amount of water and generates a highly pollutant wastewater that is rich in tannins, sugars and salts. Tannins are organic compounds containing phenolic groups. These polyphenolic compounds do not decompose easily, and they are powerful toxins and dangerous organic pollutants [1-3]. By discharging waters containing high concentrations of phenolic material to a receiver environment, undesirable changes occur in biological life. For example, it has been detected that physical circulation of N and P is prevented and mineralization of the organic materials in soil is reduced when polyphenol amounts that pass into soil exceed 3% [4]. At the same time, it is known that 6-7 mg/l of phenol concentration in waters has lethal effects on fish [5].

For these reasons, the treatment of cork processing wastewater has been subject of research, mainly by Portuguese and Spanish research groups over the past decade.

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Most of these studies focussed on chemical treatments of the wastewaters that aimed at destructive processes like chemical oxidation of the organic matter using ozone, fenton oxidation, photochemical processes involving UV radiation and hydrogen peroxide, and chemical precipitation [6-13]. Two studies also focussed on biological treatments [8, 14].

Instead of focusing on end-of-pipe treatment, it is more attractive to find efficient uses for these materials in terms of both protecting the environment and preventing loss of resources. In this particular case vegetable tannins, with molecular weights that range from 300 to 20,000 Da, are valuable products that can be found in the cork processing wastewaters and can be used in the leather industry as tanning agents, following a much more sustainable approach to the cork wastewater treatment. The use of cork tannins in the leather industry can lead to the production of high-quality chrome-free leather, as suggested by Ciesla [15]. According to this author, the fine quality of Moroccan leather of the XIX century can be related to the practice of using tannin extracted from the inner bark of the cork oak. The demand for this tree as a tannin source was so high that a large area of Morocco's cork oak forests suffered irreversible damage toward the end of the 19th century and the beginning of the 20th.

The concentration of polyphenolic compounds from cork-processing wastewater using ultrafiltration has been investigated already [16-20]. This process suffers, however, from strong fouling of the membrane, caused by colloidal matter and polyphenolic compounds. Furthermore, with this process the low molecular weight tannins that are valuable for leather tanning are lost in permeate. In the present work, nanofiltration is used instead of ultrafiltration for concentrating the tannins from the cork processing wastewater. A nanofiltration membrane with a molecular weight cut-off of 200 Da was used, which did not exhibit strong fouling.

Materials and Methods

Materials

Cork Processing Wastewater

Samples of the cork processing wastewaters were taken from the boiling tanks at around 100ºC at the Cork Supply Company, Montijo, Portugal. Vessels of 20 l were used to collect the wastewater and were closed completely full to avoid oxidation by contact with head spacer air. The wastewaters were cooled down to room temperature and were processed by nanofiltration one day later.

Membrane Module and Membrane

The Filmtec NF200-2540 spiral-wound module from Dow Chemical Company was used, with a membrane surface area of 2.6 m^2, a diameter of 6.35 cm, a length of 1 m and feed channels 0.71 mm high. The total cross-section open area of the feed channels is 9.2 cm^2. The polyamide thin-film composite nanofiltration membrane, used in this module, has a cut-off of 200 Dalton and a Hydraulic Permeability of 2.3×10^{-11} m.s^{-1}·Pa^{-1} at 25ºC. This membrane withstands a continuous temperature of 45ºC and has a very low tolerance to free chlorine (less than 0.1 ppm).

Nanofiltration Permeation Unit

The NF experiments were performed in a laboratory spiral-wound unit described elsewhere [21]. The feed solution was pumped by a multi-stage centrifugal pump (Tonkaflow, Model SS 1838G-10330-50Hz-GFN) and the operating temperature was controlled by a plate-and-frame heat exchanger. The system could be operated at a maximum trans-membrane pressure of 2.0 MPa and at a maximum recirculation flow-rate of 1 200 L/h. The retention volume of this unit was 9 L and the volume of the feed tank was 50 L.

Methods

Nanofiltration

Approximately 100 L of cork processing wastewater were used in the nanofiltration concentration experiments. Before nanofiltration, wastewater was filtered through a 1-micron cartridge filter, in order to remove harmful particles and therefore prevent the plugging of the membrane module.

The membrane was first compacted through the recirculation of pure water (conductivity < 1 μS/cm) pressurized at 1,000 kPa for 3 hours, to avoid pressure effects on the membrane structure in subsequent experiments.

The nanofiltration tests were performed at around 40ºC in total recirculation mode, with both the concentrate and the permeate streams re-circulated to the feed tank, and in concentration mode, where the permeate stream is continuously removed and the concentrate stream is re-circulated to the feed tank. The feed recirculation flow-rate was set to 1000 l/h in order to minimize concentration polarization effects. The average trans-membrane pressure, ΔP, was varied between 150 kPa and 900 kPa.

Samples of feed concentrate and permeate solutions were collected and preserved at 4ºC until chemical analysis was carried out.

For the concentration mode, the concentration factor, CF, is defined as the ratio between the total initial volume and the remaining volume in the feed tank at any given time.

The NF permeation experiments were performed in the following order:

i) At CF = 1 – Experiments run in total recirculation mode with an initial volume of 50 l: the trans-membrane pressure was varied from 150 to 600 kPa, and the permeate fluxes were measured.
ii) Experiment in Concentration Mode: at this stage the permeate was continuously removed at a constant pressure of 500 kPa until a concentration factor of 2 was reached.

iii) At CF=2 – Experiments run in total recirculation mode: the trans-membrane pressure was varied from 200 to 800 kPa and the permeate fluxes were measured.
iv) Experiment in Concentration Mode: at this stage, 45 l of fresh wastewater was added into the feed tank and permeate was continuously removed at a constant pressure of 625 kPa until a Concentration Factor of 3.5 was reached.
v) At CF=3.5 – Experiments run in total recirculation mode: the trans-membrane pressure was varied from 690 to 900 kPa and the permeate fluxes were measured.
vi) Experiment in Concentration Mode: at this stage, the permeate was continuously removed at a constant pressure of 800 kPa until a Concentration Factor of 5 was reached. The final concentrate volume in the nanofiltration unit was 19 l.

After effluent nanofiltration the membrane module was first flushed with water at room temperature and, after that, washed with a solution of Ultrasil 11 at 1 g/l during 10 min. and at transmembrane pressure of 400 kPa, with a recirculation flowrate of 1,200 l/min at 35ºC. The initial hydraulic permeability of the membrane was completely recovered after this procedure.

Tanning Tests

As the tannin concentration of the nanofiltration concentrate was still low for tanning purposes, this tannin solution was further concentrated by evaporation at 70ºC for 8 hours, in order to obtain a final concentration of total solids of circa 35 g/l. Pickled sheep skins were used after being de-pickled to pH 5.0 with HCOONa and $NaHCO_3$. The cropon of the pelts were cut into four 15×15 cm^2 pieces for subsequent tanning. The skins were tanned individually in a small drum, using a volume of concentrated cork processing wastewater containing an amount of tannins equal to 20% over the skins' weight. Tanning times between 5 and 8 hours were tested. After the tanning period, pH was corrected to 3.5 using HCOOH. The thicknesses of the depickled pelts (T_P) and the tanned leathers (T_L) were determined using a thickness gauge with 100 g pressure on undried leather. The filling coefficient of the tannin was defined as $(T_L-T_P)/T_P$. The shrinkage temperatures of the tanned leathers were determined according to IUP 16 [22].

Analytical Methods

The pH measurements were performed in a Crison micro pH 2002 at 20ºC, and the conductivity measurements were carried out in a Crison conductimeter, model 525, with a cell constant of 1 cm^{-1}. The total organic carbon (TOC) analyses were performed in a Dohrmann Carbon Analyzer DC-85 A. The concentrations of total solids, total dissolved solids, and insoluble solids in the cork processing water were determined according to the methods described in Official Methods of Analysis of the Society of Leather Technologists and Chemists [22]. The non-tannin and tannin constituent concentrations were determined using methods SLC 116 and SLC 117 [22].

Table 1. Physico-chemical characterization of microfiltered effluent and NF concentrate and permeate at FC = 5.

	Microfiltered effluent	NF concentrate (FC = 5)
pH	5.22	5.32
TOC (mg C/L)	1,536	4,340
Conductivity (μS/cm)	1,261	4,420

Results and Discussion

The micro-filtered effluent was characterized in terms of pH, TOC and conductivity, and these results are presented in Table 1. The TOC of effluent is too high for discharging the effluent to the environment without further treatment.

The permeate fluxes versus the trans-membrane pressure for different concentration factors during the nanofiltration of the cork processing wastewaters in total recirculation mode and in concentration mode, are presented in Fig. 1.

The permeate flux obtained in recirculation mode for FC=1 exhibits a linear variation with the trans-membrane pressure. The extrapolation of the trend line to J_v=0 indicates that the osmotic pressure of the wastewater is less than 50 kPa. As the concentration factor increases to FC=2, the permeate flux varies linearly with the trans-membrane pressure until about 600 kPa. After this value, the permeate flux begins to increase more slowly, indicating that a limiting flux is being approached at higher trans-membrane pressures. The data suggests that the limiting flux is circa 65 l m^{-2} h^{-1}. The trend line that fits the permeate fluxes at low trans-membrane pressures crosses the trans-membrane pressure axis at about 100 kPa. This means that the osmotic pressure of the effluent has doubled with the doubling of the concentration factor. At FC=3.5, the permeate flux has reached the limiting flux of 30 l m^{-2} h^{-1} at a trans-membrane

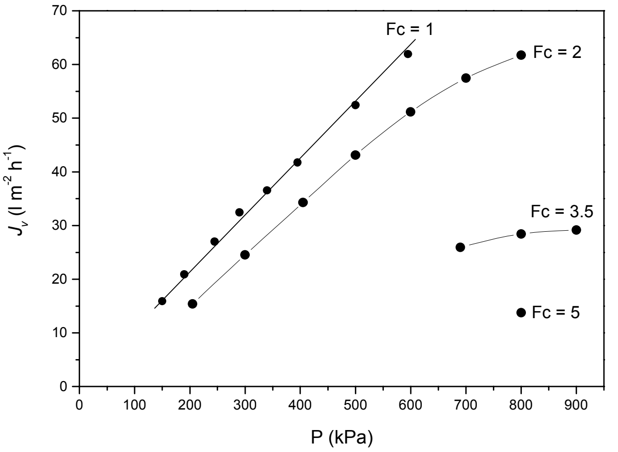

Fig. 1. Permeate fluxes vs. trans-membrane pressure during NF of cork processing wastewaters at different concentration factors.

Table 2. Tannin analysis of concentrated cork wastewater after further evaporation.

Total Solids (TS) (g/l)	Total dissolved solids (%TS)	Insoluble solids (% TS)	Tannins (% TS)	Non-Tannins (% TS)
34.8	94.7	5.3	46.9	47.8

pressure of 900 kPa. Further increasing the concentration factor to FC=5 decreases the limiting flux to a very low value of 14 l m^{-2} h^{-1}. Clearly, at this high concentration factor, the reduction of the trans-membrane pressure cannot be explained only by the increase of the effluent osmotic pressure. Based on the approximate values of the osmotic pressure of the effluent at FC=1 and FC=2, the osmotic pressure at FC=5 should be about 250 kPa, which is relatively low compared with the trans-membrane pressure of 800 kPa. Therefore, the permeate flux is also controlled by a fouling or gel layer of concentrated organic matter that is deposited on the membrane surface. To reduce this additional mass transfer resistance it would be necessary to increase the mass transfer coefficient in the nanofiltration membrane module. This is not possible with the spiral wound module used, because it was operated already at the maximum possible recirculation flow-rate. Therefore, to improve the permeate flux and increase further the concentration factor of the effluent by nanofiltration it would be necessary to use tubular modules that enable the operation at higher recirculation velocities.

The gel or fouling layer was easily removed after cleaning the membrane during 10 min. with a cleaning solution of Ultrasil 11, and this shows that the membrane initial permeation fluxes can be effectively recovered through cleaning.

The rejection coefficients of the TOC and conductivity are displayed in Fig. 2 versus the concentration factor. As shown in this figure, there is no significant change in the conductivity and TOC rejection coefficients with CF during NF of cork processing wastewaters. The TOC rejection coefficient presents an average value of 95% and the conductivity rejection coefficient value is around 60%. The permeation of cork processing wastewaters by membranes, namely ultrafiltration [16-18], has shown that there is a formation of a dynamic layer over the membrane surface that acts as a new surface which is tighter than the original. The effect of this phenomenon is more pronounced when fouling is more severe and expected results like, for example, the decrease of salt rejection with the increase of its concentration, are not observed.

These results show that nanofiltration has the capacity of concentrating the organic matter of the effluent with simultaneous partial demineralization of the final concentrate. The NF permeate has a far lower pollutant charge than the original effluent, and its further treatment or disposal should not pose severe problems, as almost all the compounds that are difficult to treat, namely the tannins, were retained and concentrated by the NF step in the concentrate stream.

As shown in Table 1, the TOC content of the concentrated effluent is almost threefold of the initial TOC value.

Table 3. Mean values of leather tanning results [a].

Thickness (mm)		Filling coefficient	Shrinkage temperature (ºC)	
Skin	Leather		Skin	Leather
1.1	1.79	62.7 %	38	71

[a] based on the tanning of 4 samples of pelts (15×15 cm^2) using concentrated cork processing wastewaters during 8 hours.

Despite that, the concentrated effluent was still too diluted for tanning. For this reason, the concentrated effluent was further evaporated until a total solid content of 34.8 g/l was obtained (Table 2). The concentration factor, based on total solid content, was c.a. 30, after the evaporation step. The composition of the NF concentrate after further concentration by evaporation is given in Table 2. As can be seen in this table, almost half of the concentrated organic matter is tannin. However, the concentrated effluent also contains a considerable amount of insoluble colloidal matter (5.3% of total dissolved solids), which can have adverse effects of the tanning process.

From the results of the tanning with cork wastewater concentrate (Table 3), it is clear that the cork wastewater tannin converted the skins to leathers that have a shrinking temperature of 71ºC, well above the shrinking temperature of the skins (38ºC). The shrinking temperature of produced leather is in the range typical of commercial leathers produced with several types of vegetable tannins, from 70 to 85ºC [23].

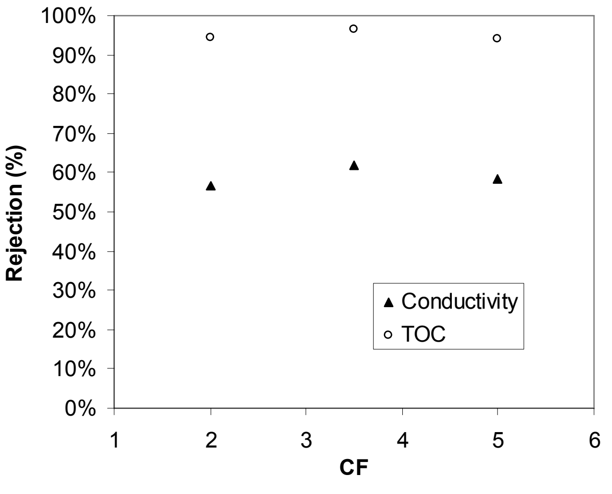

Fig. 2. Variation of conductivity and TOC rejection coefficients with concentration factor (CF) during NF of cork processing wastewaters.

Conclusion

From the results of this study it is seen that cork wastewater contains considerable amounts of tannins that are effective tanning substances that can be used for leather production after concentration by nanofiltration. In fact, tanning experiments have shown a satisfactory conversion of the skins to leather, with 71ºC shrinking temperature – well inside the typical range of shrinking temperatures (70-85ºC).

The nanofiltration experiments show that the permeate fluxes are controlled by both osmotic pressure and fouling/gel layer phenomena. These phenomena are more severe for higher concentration factors, leading to a rapid decrease of permeate fluxes with the concentration factor. This problem could be minimized using tubular membrane modules instead of spiral-wound membrane modules at high concentration factors. The TOC rejection coefficients had an average value of 95%, indicating that nanofiltration has a good ability to concentrate the tannins and produce a permeate with a low content in organic matter. Thus, a contaminating wastewater like the cork processing wastewater could be used in the leather industry as a vegetable tanning material, providing economical and ecological/ environmental profits.

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