Processing of black liquors by UF/NF ceramic membranes

Anton Dafinov*, Josep Font, Ricard Garcia-Valls

Departament d'Enginyeria Quimica, Universitat Rovira i Virgili,
Av. Països Catalans 26, 43007 Tarragona, Catalunya, Spain
Tel. +34 (977) 558112; Fax +34 (977) 559667; email: adafinov@etse.urv.es

Received 21 April 2004; accepted 15 July 2004

Abstract

This study deals with the treatment of black liquor from wood pulping by means of membranes. UF/NF membranes with a skin layer of TiO₂ and ZrO₂ have been applied to recover water and to concentrate the residual effluent. Three different membranes with molecular weight cut-off of 1, 5 and 15 kDa have been checked. The membranes have been tested either in single stage operation or in cascade. Total dissolved solids, organic matter, organic to mineral matter ratio and ash have been determined. In addition, chemical oxygen demand (COD) retention was calculated by measuring in the feed solution as well as in the permeate and in the concentrated solution. During the concentration step the steady state was reached after a few minutes running. There was not significant change in the permeate flow until the volume was reduced at half. Only the 15,000 Da membrane showed continuous permeate flow declining. Regardless the membrane used, dry matter, organic matter and COD analyses showed that the retention of organic substances fell in the range of 60–70%, depending on the conditions selected.

Keywords: Ceramic membranes; Ultrafiltration; Nanofiltration; Black liquors; Lignin; Pulping

1. Introduction

In wood pulping, all organic compounds are dissolved in the digesting liquor except cellulose, which remains insoluble. After separation of cellulose fibres, the solution obtained from the above process, called black liquor, is a waste, which must be subsequently treated before disposal. The overall annual world production of black liquor is approximately 500 million tons, where 10% come from the European Community [1]. Total dissolved solids (TDS) in the black liquor usually represents around 15% w/w, which is composed of lignin derivatives, low molecular weight organics, and the rest being remaining chemicals from the digesting liquor. The chemical oxygen demand (COD) and pH varies from 10,000 to 120,000 mgO₂/L and from 10 to 13 respectively, depending on the process applied, usually kraft or antraquinone [2].

The conventional treatment of the black liquor is water evaporation until the dry matter reaches a concentration of 70–80% w/w. Then, the residue
is incinerated and energy is produced, which can be used in the pulping process. From the resulting ash, up to 80% of the digesting chemicals could be also recovered. A small part of the spent liquor is further used as a source of lignin that is isolated either by precipitation or diafiltration. The lignin is a feasible raw material for many valuable substances such as activated carbon, vanillin, vanillic acid, dispersing agents, ion-exchange agents, polymer fillers, binding agents for the production of fibre boards, artificial fertilizers and complexing agents [3–5].

Lignin is a very complex material. Its definition is ambiguous and often depends on the perspective of the author. From the chemical point of view, Meister et al. [6] give an accepted definition stating that “Lignin is the major non-cellulosic constituent of wood. It is a complex, amorphous, highly cross-linked polyphenolic”. Overall, lignin comprises 17–33% of wood [7] and plays a key role in cementing the polysaccharide components in the cell walls, increasing both the mechanical strength of wood as a composite material and the resistance toward micro-organisms. All lignins are made of phenylpropane units, which seem to be randomly joined by ether and carbon–carbon bonds [8].

Any alternative way for black liquor treatment must allow recovering of the reagents (which composition depends on the pulping method, e.g. anthraquinone, sodium hydroxide or sodium sulphide) at low energy consumption, thus substituting part of the evaporation process and minimising the polluting load. A promising way for treating black liquors is the use of membrane processes. Membranes permit to concentrate the organic matter in the retentate as inorganic salts dissolved in the water freely cross the membrane layer. The studies of P.K. Bhattacharya [9–13] deal with black liquors from Kraft process plants of small capacity, total solid content in the liquors was in the order of 5% and the employment of evaporation units was not justified by the energetic reasons.

The chemical and temperature resistance of the ceramic membranes compared to polymeric membranes makes them particularly attractive for the treatment of black liquor effluents. Cortiñas et al. [14] studied the influence of the transmembrane pressure and the cross flow velocity on the elimination of colloidal suspended matter (pitch) in Kraft black liquors using ceramic microfiltration membranes. They concluded that to get satisfactory flux high feed velocities are needed. The influence of the feed temperature and the transmembrane pressure on the performance of 15 kDa ceramic membrane applied in the treatment of Kraft black liquors is studied by Wallberg et al. [15]. At the lowest temperature (60°C) the limiting permeate flux is reached at relatively low pressure. At temperatures close to that of the black liquors in the paper mills (75 and 90°C) no limiting flux is reached in the pressure range studied.

Lui et al. [16] treated Kraft spent liquors with different type of membranes, both polymeric and inorganic, with cut-off in UF and MF range and dead-end and crossflow operation modes, proving the feasibility of membrane treatment.

In this work, multichannel tubular ceramic membranes were used to treat black liquors. This kind of membranes offers both physical and chemical resistance in a wide range of conditions. The membranes were tested in continuous concentration experiments at different transmembrane pressures using a soda-anthraquinone black liquor. The membranes of 5 and 15 kDa were also checked in discontinuous operation regime.

2. Materials and methods

2.1. Materials

Three channel laboratory scale tubular membranes (CéRAM INSIDE 25®) for ultra- or nanofiltration manufactured by TAMI Industries were used in this study. These membranes are composite elements with a support of α-alumina coated with an inner skin layer of either TiO₂ or ZrO₂. The tubular element was 25 cm long, having an outside diameter of 10 mm and 3.6 mm
hydraulic diameter of each channel. Membranes with cut-off values of 1, 5 or 15 kDa were tested. The nominal filtration area of each element, provided by the producer was $9.4 \cdot 10^{-3}$ m$^2$.

The paper mill CELESA (Tortosa, Spain) supplied the black liquors. The pulping process applied by this plant is soda-anthraquinone. Total dissolved solids (TDS) in the liquor was 8.5% w/w comprised of organic matter (3.75%) and mineral salts (4.75%), mostly being reactives used in the digestion process. The original COD of the black liquor was 70 g O$_2$/L with a pH of 12.

2.2. Experimental set-up

The experimental set-up for cross-flow filtration is schematically presented in Fig. 1. The apparatus consists of a positive displacement pump (Hydra-Cell TM) coupled with a pulse dampener (Hidracar, S.A., 0.65 L). All pipes, valves as well as the housing of the membrane module were made of stainless steel. Two valves are used for activating the dampener, V1, and for controlling the outlet pressure in the tubular membrane, V2. Another valve, V3, allows to control the feed flow rate by opening a by-pass. Valves V4 and V5 give the possibility of applying a back flow in order to facilitate membrane cleaning. A 10 L feed tank is coupled with a thermostat that permits to set the temperature in the range of 20–90°C with 2°C accuracy.

The feed flow rate was always set at 3.8 L/min, which corresponds to a flow velocity inside the membrane channels of 2.1 m/s corresponding to a Reynolds number of 8300 calculated for distilled water at 20°C. Before starting a test, the filtration system was always rinsed for 30 min with a 0.5 M NaOH solution at 25°C to wash out any compound that could remain in the system. Subsequently, distilled water was passed through the system to leave it ready for the next run.

The retention characteristics as well as the permeate flow rates of each membrane were examined at 3.0, 5.0 and 7.0 bar of transmembrane pressure. The experiments were conducted for at least one hour from starting or until steady state was established. Previously, the water permeability was determined for each membrane using distilled water at different transmembrane pressures. The water permeability was also used as a

![Fig. 1. Standard membrane testing equipment for cross flow filtration.](image-url)
measure of the cleaning effectiveness. The cleaning was repeated until the initial water permeate flow rate was recaptured.

All tests were performed at 30±2°C. It should be mentioned that at this temperature the effluent viscosity is quite similar to that of distilled water at 20°C. First the effect of the transmembrane pressure on the permeate flux and retention were studied for different membranes in continuous experiments, i.e. total recycle of both retentate and permeate. The membranes with cut-off of 5,000 and 15,000 Da were also tested in discontinuous operation, i.e., the permeate was collected and isolated. The process continued until the initial volume of the liquor was almost halved. In these cases, the transmembrane pressure was maintained at 5 bar. The permeate collected in the above experiments were further filtrated with the membrane of 1 kDa cut-off.

2.3. Analyses

The membrane performance is discussed by employing several parameters. COD was determined by the standard dichromate method [17]. Dry matter was evaluated by heating the sample to dryness (determined as the steady weight) during 24 h at 110°C. Similarly, organic matter and ash content were obtained after heating at 500°C and 600°C, respectively for 24 h. The details of the above analyses have been described elsewhere [18].

3. Results and discussion

3.1. Continuous experiments

Fig. 2 shows the steady state (determined as that when no further flux decline is observed) permeate fluxes for all the membranes tested in function of the transmembrane pressure. For the membranes of 1 and 5 kDa cut-off, the hydraulic permeability behaviour was as expected, so the permeate flow increases with the pressure. In the case of the 15 kDa membrane, the permeate flux trough the membrane seems to be independent of the applied transmembrane pressure, showing a constant value around 52 L m⁻² h⁻¹. In addition, the flux for the 15 kDa membrane is surprisingly lower than that obtained for the 5 kDa membrane even at transmembrane pressures higher than 5 bar. This result could be due to a pore blocking mechanism, in addition to the usual gel layer formation on the membrane surface [19]. The pore blocking could be attributed to the similar sizes of the lignin macromolecules and the pore diameter of the 15 kDa membrane. On the other hand, TiO₂ mainly forms the skin layer of the membranes of 1 and 5 kDa whereas ZrO₂ forms that of the 15 kDa membrane, which could favour some specific adsorption of lignin molecules inside the pores. Further investigation is needed in order to highlight the actual interactions between the ceramic surface and the solutes, which could allow explanation of these different membrane behaviours. Similar results were obtained by Wallberg et al. [15] when a 15 kDa ceramic membrane is applied in the Kraft black liquor treatment in continuous process. When the experiment is performed at 60°C limiting permeate flux is reached at 175 kPa of transmembrane pressure. At higher temperatures no limiting flux is observed in the pressure range studied.

The content of COD, organic matter and dry matter in the permeate samples is depicted in
Figs. 3–5. As it can be seen, the general trends are similar for each parameter discussed. Nevertheless, it must be noted that, while COD retention is in the narrow range 40–60% in the most conditions, there are major differences for the other two parameters, mainly when the 1 kDa membrane is compared to the other two membranes tested (Figs. 4 and 5). Organic matter retention strongly depends on the pore size with a reversing between the cases of 5 and 15 kDa again attributed to the pore blocking appearing in the highest cut-off membrane as can be seen in Fig. 4.

The COD and organic matter retentions obtained for the 1 kDa membrane are quite similar, around 50%, showing a small dependence on the applied transmembrane pressure. Examination of the results for the membranes of 5 and 15 kDa shows that the COD retention is higher than the organic matter retention in both cases. A possible explanation of this fact could be that the gel layer formed on the membrane surface presents some selectivity with respect to the less saturated molecules. The significant dependence of the retention on the applied transmembrane pressure indicates that the formed gel layer plays a dominant role in the separation process. Similar results were obtained by Liu et al. [19]. However, no correlation is observed between the membrane pore diameter and the permeate flux given when polymeric and inorganic membranes with a wide range of cut-off (from 3 kDa to 0.8 μm) are applied in the treatment of Kraft black liquor. As pressure increases the gel layer is progressively compacted resulting in a higher retention of the organic matter and COD and a lower permeate flow. Regarding the dry matter retention (TDS), there is a direct relation between the pore size and the applied transmembrane pressure as demonstrated by Fig. 5.

On the contrary, the ash analyses show no significant differences among the experiments and almost no effect of the applied pressure. The retention in all cases is low, around 10% in the case of 5 and 15 kDa membranes and about 13%
for the 1 kDa membrane, as expected according to the pore size. The retention of the inorganic salts is mainly due to the association of the ions with the lignin macromolecules retained by the membrane and the separation obtained was expected to be very low.

3.2. Discontinuous experiments

The membranes of 5 and 15 kDa were also tested in discontinuous operation. The experiments were performed under a constant applied transmembrane pressure of 5 bar. The permeate flux and the volume concentration factor (VCF) are displayed in Figs. 6 and 7. The VCF is defined as the ratio of the initial feed volume to the retentate volume. The initial and final retention are also presented in Table 1.

The retention in terms of TDS, organic matter and COD for both membranes depends on the lignin concentration, which continuously increases in the feed tank during the operation. On the other hand, the TDS, organic matter and COD levels in the permeates are maintained almost constant for both membranes during the experiments. This fact, once again, proves that the gel layer formed plays a dominant role in the separation process and no reliable relation between the membrane cut-off and the retention could be established.

Considering the permeate flow, different behaviours were observed for the two membranes in the discontinuous concentration experiments. When using the 5 kDa membrane, the permeate flow reached quite rapidly steady state around 35 L m⁻² h⁻¹, which remains almost constant during the 10 h period tested as seen in Fig. 6. In this case, the initial volume of black liquor was reduced 1.6 times. On the contrary, when the 15 kDa membrane was used, the permeation flow rate decreased continuously throughout the experiment.

Table 1
Retention for the 5 and 15 kDa membranes in discontinuous operation

<table>
<thead>
<tr>
<th>Retention, %</th>
<th>5 kDa membrane</th>
<th>15 kDa membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>initial</td>
<td>final</td>
</tr>
<tr>
<td>Dry matter (TDS)</td>
<td>36.3</td>
<td>38.3</td>
</tr>
<tr>
<td>Organic matter</td>
<td>39.0</td>
<td>39.4</td>
</tr>
<tr>
<td>COD</td>
<td>52.5</td>
<td>63.4</td>
</tr>
</tbody>
</table>
as shown in Fig. 7, reaching a final value of 17 L m\(^{-2}\) h\(^{-1}\), which is significantly lower than that obtained with the 5 kDa membrane. For the 15 kDa membrane, a twofold reduction of the initial volume of black liquor was possible with a final permeate flux of 17 L m\(^{-2}\) h\(^{-1}\) as mentioned. The permeate flux for that membrane and the same transmembrane pressure in continuous operation was 52 L m\(^{-2}\) h\(^{-1}\). In comparison, when working in continuous operation, the 1 kDa membrane operating at 5 bar reached a steady state permeate flux value of 27 L m\(^{-2}\) h\(^{-1}\), which is very close to the 35 L m\(^{-2}\) h\(^{-1}\) obtained in the concentration test. The low permeate flux found for the 15 kDa membrane in discontinuous operation is attributed to the progressive pore blockage by some of the compounds present in the treated solution. For smaller pore sizes, the macromolecules cannot penetrate into the pores, and they form only a stable cake layer. It should be mention that for both experiments very fast flux decline is observed in the very beginning of the tests. Similar results were obtained for the continuous experiments, in the most cases the steady state were reached in the first minutes. Probably the increasing of the cross flow velocity will decrease the thickness of the fouling layer. Further study should be considered. Due to the low level of the volume reduction of black liquor it is difficult to notice the typical permeate flux profile as commented by Wallberg et al. [15].

The permeate collected in the experiments using 5 and 15 kDa membranes was subsequently filtrated with 1 kDa membrane at 5 bar of transmembrane pressure. No considerable additional retention was obtained, only about 10% for the permeate of the 15 kDa and about 12% for the permeate of 5 kDa membrane in terms of COD. This result confirms that the separation is mainly governed by the gel layer formed on the membrane surface. This gel layer is not significant when the permeate is fed to be further filtrated, since the large macromolecules have been mostly removed in the first membrane pass.

In comparison with results present in the literature by Bhattacharya et al. [12], applying a membrane of 5 kDa, a transmembrane pressure of 7.5 bar and 2% of total dissolved solids, in the present article a TDS concentration three times greater and a higher permeability was obtained, 72 against 43 L m\(^{-2}\) h\(^{-1}\) for an operating pressure of 7 bar.

4. Conclusions

The cross-flow nano- and ultrafiltration techniques can be employed as an alternative way for the treatment of black liquor from pulping industry. This filtration process can reduce twofold the volume of the spent liquor with no significant changes in the permeate flow across the membranes. The concentrations of TDS, organic matter and COD in the permeate remained constant with values of 2.5%, 1% and 30 g O\(_2\)/L respectively. Because the ceramic membranes have unique properties such as high physical and chemical resistance, they can withstand severe cleaning procedures (e.g. to strong pH conditions or backwashing), which results in the rapid permeate flow recovery without significant damage to the membrane.

In the filtration at the applied conditions, the formation of a gel layer on the membrane surface takes place and that may play an important role in the separation process. Furthermore, in the filtration experiments performed with the 15 kDa membrane, pore blocking may occur. This leads to a continuous decrease in the permeate flux and retention levels, which however are still higher than those obtained for the 1 kDa membrane.

Acknowledgements

The authors would like to thank the Spanish Ministry of Science and Technology (CICYT, QUI98-0464-C03-01) and the Department of Chemical Engineering at the Universitat Rovira i Virgili for its financial support. We also acknowledge the Universitat Rovira i Virgili for providing a doctoral fellowship.
References


