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Nanofiltration of Bleaching Pulp and Paper Effluents in Tubular Polymeric Membranes

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ABSTRACT

A systematic investigation of the nanofiltration (NF) of alkaline bleaching effluent (E_1) from the pulp and paper industry is carried out through a first assessment of NF of model systems, namely, solutions of salts—NaCl and Na_2SO_4—and organic solutes—glucose, saccharose, and raffinose—which develop membrane–solute(s) interactions similar to those developed by the bleaching effluent. The ampholytic polymer of the membrane active layer, under controlled feed conditions, develops a surface charge distribution which determines the membrane performance. The verification of the effects of the anion valence and the feed concentration on the salts rejections, in accordance with the Donnan exclusion principle, is an important feature of this work. For the bleaching effluent, the NF performance is strongly dependent on the pH due to the influence of this parameter on the membrane surface charge. The contribution of this work toward the optimization of the NF operating conditions would allow for future scale-up of this separation process for E_1 effluent purification and water recovery in the pulp and paper industry.

INTRODUCTION

In the bleaching sequence of a kraft mill, the first alkali extraction stage (E_1 stage) produces a dark effluent with a high biological oxygen demand (BOD) due to its high lignin content in the form of strongly colored high-molecular-weight chlorinated compounds. This effluent also contains a high amount of inorganic compounds resulting from the addition of chemicals during the pulping process. With the closure of sulfate mills, bleach plant effluents, specially E_1, constitute the most severe pollution problem in this industry (1).

Several means of concentrating the colored pollutants have been described in the literature, including biological treatment, lime precipitation, adsorption, ion exchange, reverse osmosis (RO), ultrafiltration (UF), and nanofiltration (NF) (2–6). Biological treatment does a poor job regarding the removal of color and high-molecular-weight chlorinated organic compounds from kraft mill bleaching effluents. These two weaknesses of biological treatment are two of the strengths of the RO, UF, and NF membrane processes.

RO is economically prohibitive for the treatment of bleaching effluents due to the low permeate flux, the limited concentration factors attained, and the expensive high-pressure equipment (7, 8).

The treatment of E-stage effluent for color removal by UF is recognised as technically and economically feasible according to the results of three full-scale installations: Sanyo Pulp Mill and Taio Paper Co. in Japan and MoDo Husum Pulp Mill in Sweden (9). Although UF is an efficient process for the removal of color and high-molecular-weight chlorinated compounds, it does not sufficiently reduce the amount of the most toxic low-molecular-weight chlorinated compounds nor does it perform effluent demineralization (7, 10, 11).

In contrast with this, NF removes the high-molecular-weight compounds and a great part of the hazardous low-molecular-weight compounds present in E_1 effluent. The high pH of E_1 effluent induces a negative charge on NF membrane surfaces, enhancing the likelihood of rejection of the chromophotic organics, many of which are negatively charged. Furthermore, at high tangential velocities (2–5 m/s), NF membranes suffer practically no fouling by natural colloids, which are usually also negatively charged, and this fact makes pretreatment practically unnecessary. Besides, NF leads to partial demineralization of the effluent, allowing permeate recycling into the process, concentrate destruction by incineration, and consequently the final closure of bleaching plants (2, 12–16). The present trend of bleaching sequences, in which elemental chlorine is progressively substituted by chlorine dioxide, results in a lower discharge of organochlorinated compounds, but simultaneously there is an increase of the low-molecular-weight compounds fraction. Therefore, the use of tight membranes, such as NF membranes, becomes much more important in order to remove the organochlorinated content of E_1 effluent efficiently (12, 17, 18).

Bindoff et al. (2) tested a NF spiral wrap membrane, FilmTec FT40 1812, and concluded that NF is a suitable method for E_1 effluent color removal. Membrane fouling was reduced through pretreatment of the effluent by crossflow microfiltration (MF).

NF experimental essays were made at our laboratory (19–21) using a P-28 Celfa unit including a flat plate cell. Three commercial membranes, NF 40, ROM 378, and DRA 4020, were tested. The main objective was the removal of chlorinated organic compounds from the E_1 effluent of a kraft pulp mill using eucalyptus wood as a raw material. The total organic halides (TOX) rejections were higher than 92%.

A study was carried out in Canada to evaluate the efficiency of NF for the removal of toxic compounds from a bleach effluent of a kraft mill pulping softwood (9, 22). Two different equipments were tested (a DDS Lab-20 plate-and-frame module and a ABB-Flakt CR-250 unit) and three commercial NF membranes were used. The fluxes measured at 9.7 bar appeared quite promising [117 L/(m^2·h) for the Lab-20 unit and 375 L/(m^2·h) for the CR-250 unit], and the AOX (adsorbable organic halides) and color rejections were in the 93–96% and 99–100% ranges, respectively.

Batch NF experiments of different bleach effluents (C_1, E_1, and total bleaching effluent) from several kraft mills were performed by Ekengren et al. (12). A PCI laboratory plant and two polyamide membranes, a tubular one and a spiral wound, Desal 5, were used. COD (chemical oxygen demand) and AOX removals ranged from 79 to 90% and from 90 to 97%, respectively, and the average fluxes were even more promising, about 120 L/(m^2·h), measured at 1.5 bar for the spiral wound membrane and at 3 bar for the tubular membrane.

NF essays of E_1 effluent were carried out by Zadorecki (23) in a Alfa-Laval PF 26 plate-and-frame pilot unit. Two loose RO membranes, RO-C and RO-PBI, were tested at 40 bar. The initial fluxes were 110 L/(m^2·h), for the RO-PBI membrane and 180 L/(m^2·h) for the RO-C membrane. The COD, color, and aromatic compounds rejections were 73, 99.5, and 92.5%, respectively. As 27% of the organics permeated through the membranes, this means that almost 1/3 of the organics present in the bleach effluent are low-molecular-weight compounds.

Rudie et al. (24) reported the results of a ABB Flakt CR-250 unit with a TLC type B membrane for the removal of lignosulfates from kraft E-stage wastewater streams. They observed high color and COD rejections, 97 and 88%, respectively, and also high permeation fluxes [up to 105 L/(m^2·h)] at a moderate operating pressure (6.9 bar).

The above literature data concerning the NF of bleaching effluents were generally obtained at a single set of operating conditions. However, it is well known that the performance of a NF membrane strongly depends on the operating conditions. This is particularly important when NF membranes revealing an ampholytic behavior are used for the treatment of wastewaters with a complex composition of salts and ionized organic solutes. The synergy membrane/wastewater leads to the development of a surface charge distribution which is highly dependent on the operating conditions, namely, the pH and the hydrodynamic conditions of the feed solution. Moreover, the main problems associated with the membrane processes, i.e., concentration polarization and fouling, are also strongly dependent on the operating conditions.

The objective of this work is an investigation of the interaction effects between NF membranes and the operating conditions in the NF of E_1 wastewaters. This objective has the purposes of NF performance enhancement, minimization of the concentration polarization and fouling phenomena, and also guidance for the development of NF membranes tailored for the processing of effluents similar to E_1 effluent. This research is preceded by the determination of the permeation of model solutions in order to characterize these membrane–solute(s) interactions.

EXPERIMENTAL

Membrane

The NF composite membrane was synthesized by Nederlandse Organisatie voor Toegepast (TNO) by the interfacial polymerization method. The membrane was manufactured in the tubular configuration, with the diameter and the length being 14.4 mm and 20 cm, respectively.

The membrane-forming aqueous phase consists of an amine and an ampholytic polymer containing quaternary amine groups and sulfonic acid groups. The membrane efficiency is mainly determined by the ampholytic polymer since it increases the membrane hydrophilicity, resulting in high permeation fluxes and a low fouling tendency, thus making a tough pretreatment of the E_1 effluent unnecessary.

Experimental Installation

The experimental set-up allows the simultaneous test of two modules (Fig. 1). A rotary pump pressurizes the feed and a centrifugal pump creates partial recirculation of the concentrate allowing the achievement of high circulation velocities tangential to the membrane surface.

Experimental Procedure

Membrane Characterization

The membrane is preserved in a 0.5% sodium bisulfite solution during the transportation and between the essays. Before starting the permeation

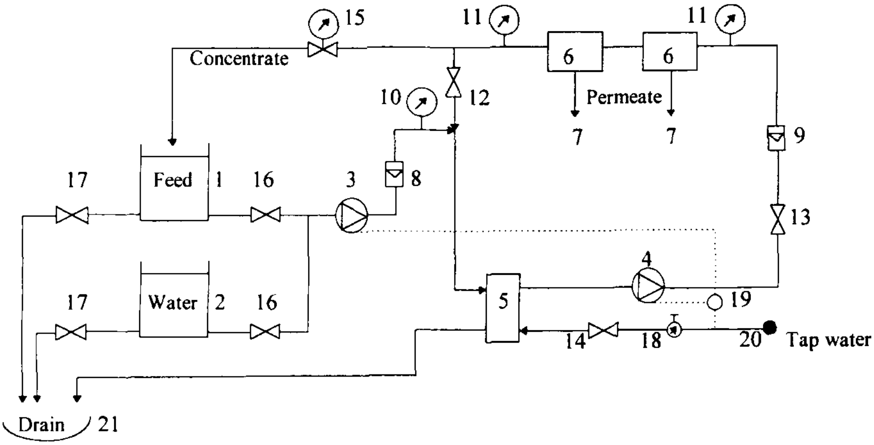

FIG. 1 Scheme of NF experimental installation: (1) Feed tank; (2) washing water tank; (3) rotary pump; (4) centrifugal pump; (5) heat exchanger; (6) tubular modules; (7) permeate; (8, 9) flowmeters; (10, 11) manometers; (12, 13, 14) needle valves; (15) backpressure valve; (16, 17) ball valves; (18) pressure regulator; (19) pressure control; (20) municipal water; (21) drain.

essays, the membrane is conditioned by circulating deionized water at 25 bar for 2 hours.

NF essays are performed in closed circuit, i.e., the concentrate and the permeate are recirculated to the feed tank in order to keep the feed concentration constant. Each essay consists of three steps:

1. Deionized water permeation at pressures of 10, 15, and 20 bar in order to determine the pure water permeation fluxes, PWP, and the membrane hydraulic permeability, l_p.
2. Permeation of solutions of organic and inorganic reference solutes in order to determine the permeation flux, PR, and the solute separation factor, f, defined as

$$f(\%) = \frac{\text{feed concentration} - \text{permeate concentration}}{\text{feed concentration}} \cdot 100$$

3. Membrane washing with deionized water at low pressure and high flow rate to remove the solute from the membrane surface and recover at least 90% of the initial PWP.

Membrane characterization is performed through permeation essays of solutions of two salts with different valences (NaCl and Na_2SO_4) and three organic solutes of molecular masses between 180 and 504 Da (glucose, saccharose, and raffinose).

E_1 Effluent Characterization

Sampling. E_1 effluent samples are collected twice a week during a month and a half from a kraft pulp and paper mill using eucalyptus wood as raw material. The samples are composed of four daily collections in order to attenuate any mill process fluctuations. The samples are acidified and placed on ice in a cooler for transport to the laboratory, where they are maintained below 4°C in order to be preserved and kept stable before being analyzed.

TOX. The TOX method involves adsorption of organic halides from the sample onto granular-activated carbon packed in two microcolumns in series, followed by combustion and microcoulometric detection (25, 26). In bleached chemical pulp effluents the content of halogenated compounds other than organochlorinated compounds is insignificant.

An important characteristic of the TOX method is the possibility of checking the adsorption process efficiency. The adsorption is efficient if the TOX in the 2nd column in series is lower than 10% of the total TOX in both columns. In this work the TOX adsorption operating conditions are optimized for the analysis of E_1 effluent and its NF permeates. For an effluent sample volume of 25 mL, a sample dilution factor of 125, and a nitrogen pressure of 14 psi, the adsorption performance is satisfactory. The dilution factor of NF permeates of E_1 effluent is adjusted to 5, with the other operating conditions kept constant.

E_1 Effluent Permeation

The NF essays of E_1 effluent are performed in the following order:

1. E_1 effluent pretreatment by 3 MF cartridges in series (pore diameters of 45, 25, and 5 μm).
2. NF of microfiltrate E_1 effluent to determine the permeation fluxes, PR, and the conductivity, the total organic carbon (TOC), and the organochlorinated compounds rejections, *f*.
3. Membrane washing with deionized water at low pressure and high feed velocity to assure the solutes removal from the membrane surface and the recovery of 90% of the initial PWP.

The NF essays of E_1 effluent for the study of the effect of operating conditions on the membrane efficiency are performed by recirculating both the concentrate and the permeate. These experiments are performed sequentially by increasing the pressure and then by decreasing the circula-

TABLE 1
Analytical Equipment

pH, 20°C	CRISON micropH 2002
Conductivity, 25°C	CRISON conductimeter 525
TOC	DOHRMANN DC 85-A
TOX	DOHRMANN DX 20-A

tion velocity in order to minimize the cumulative effects of the concentration polarization and membrane fouling. The feed concentration constancy during each experiment is confirmed by collecting two feed samples for analysis, one at the beginning and another at the end of the experiment. After these essays the membrane is washed at 40°C with a 0.1% P3-Ultrasil 11 solution because of the severe fouling at the circulation velocity of 0.44 m/s. After the study of the pH effect the membrane is washed in the same manner because of pronounced fouling at pH values of 9 and 10.

The NF experiments for the study of E_1 effluent concentration are performed in batch mode by recirculating the concentrate stream.

Analytical Methods

Table 1 shows the analytical equipment used. The feed, concentrate, and permeate samples are analyzed by different methods according to the solutes type:

- Salts—conductivity
- Organic compounds—TOC
- E_1 effluent—pH, conductivity, TOC, and TOX

RESULTS AND DISCUSSION

Membrane Characterization

The average value of the membrane hydraulic permeability is 9.5 kg/(m^2·h·bar). Based on this value and the membrane characterization displayed in Table 2, one concludes about the following membrane properties:

- High hydraulic permeability
- Fluxes of the solutions of reference solutes identical to those of pure water

TABLE 2
Permeation Fluxes and Separation Factors of Reference Solutes
(ΔP_{oper} = 20 bar, $\langle u \rangle$ = 5.1 m/s, T = 40°C)

Solute	Concentration (M)	PR [kg/(m^2·h)]	f (%)
NaCl	0.0016	177.8	82.2
	0.0017	168.9	85.3
	0.0203	175.8	68.8
	0.0196	164.6	69.7
Na_2SO_4	0.0009	169.3	100.0
	0.0010	163.6	99.3
	0.0171	164.3	99.4
	0.0176	154.1	99.4
Glucose	0.0018	163.0	95.2
	0.0019	164.7	96.1
	0.0398	152.4	94.1
	0.0404	152.2	93.1
Saccharose	0.0021	164.5	99.2
	0.0020	159.5	98.0
	0.0420	150.2	98.8
	0.0416	147.8	98.1
Raffinose	0.0015	163.2	99.9
	0.0019	159.3	99.0

- High rejections of the organic solutes (>93%) and independent of the feed concentration
- Sodium chloride rejections between 69 and 85%, and dependent on the feed concentration
- Separation factors of sodium sulfate close to 100%

Salts Permeation

The effect of operating conditions on the NaCl and Na_2SO_4 permeation is presented in Figs. 2 and 3. Figure 2 shows that the fluxes vary linearly with the operating pressure and are independent of the feed circulation velocity. This linear behavior is described by a slope close to the membrane hydraulic permeability. As Table 3 displays, the slopes deviate from the value of the membrane hydraulic permeability only for the most concentrated solutions, and this deviation is more pronounced for Na_2SO_4 than for NaCl.

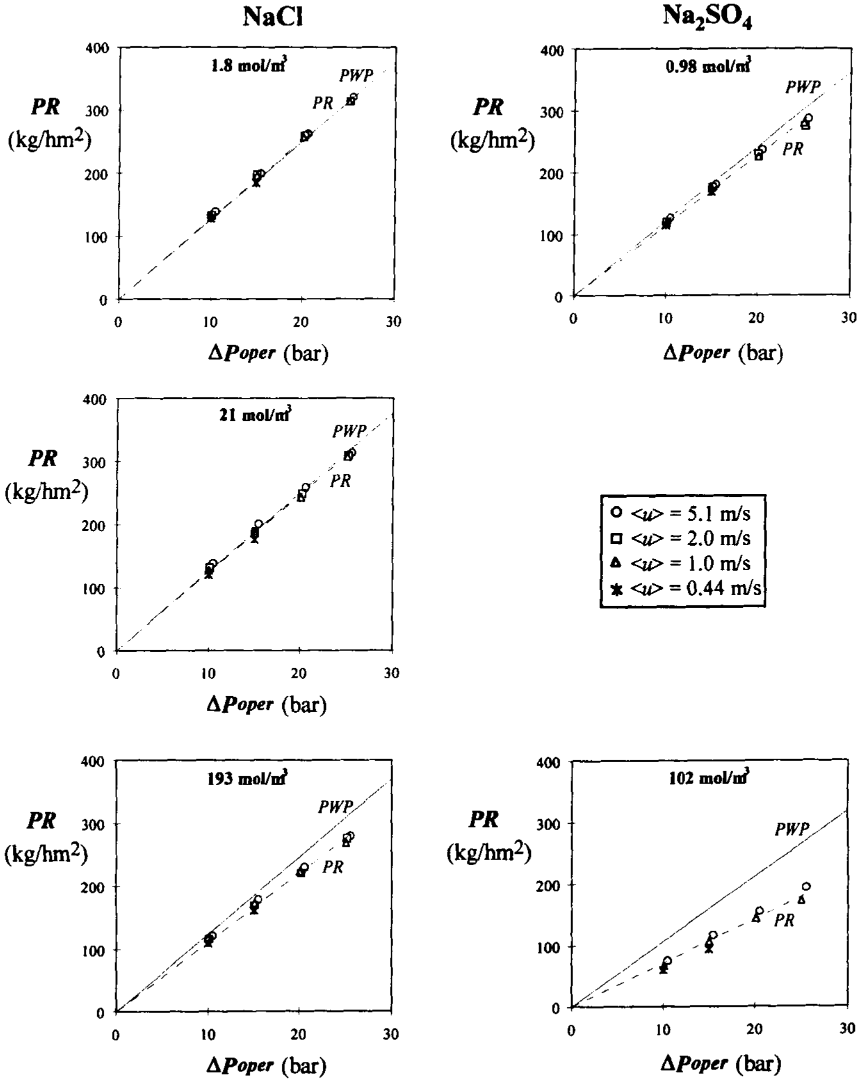

FIG. 2 Permeation fluxes of salt solutions vs operating conditions (T = 40°C).

TABLE 3
Slope of Permeation Flux Variation with Pressure (the slopes relative to pure water permeation are in parenthesis)

Feed concentration (N)	Slope [kg/(m²·h·bar)]	
	NaCl	Na_2SO_4
0.002	12.71	11.33
	(12.54)	(12.06)
0.02	12.37	—
	(12.55)	—
0.2	11.07	7.13
	(12.36)	(10.57)

Figure 3 shows the increase of the salts separation factors with increasing feed circulation velocity and their decrease with increasing feed concentration. For feed circulation velocities of 1 m/s and above, the NaCl separation factor increases with the operating pressure whereas Na_2SO_4 rejection may increase, decrease, or remain constant depending on the feed concentration and the circulation velocity. However, for both salts at the lowest circulation velocity, the separation factors decrease with the operating pressure.

The concentration polarization phenomena partially explains the poor membrane performance at the lowest feed circulation velocity and at the highest feed concentration. The osmotic pressure effect on the permeation flux is not pronounced in the range of operating conditions tested.

Obviously, the most important feature of the experimental data is the effect of the anion valence and the feed concentration on the salts rejections. For a given concentration, NaCl rejections are lower than Na_2SO_4 rejections. On the other hand, for both salts the salt concentration increase results in the rejection decrease. These two facts typically occur in electrically charged membranes and they are qualitatively in accordance with the Donnan exclusion principle (27, 28).

The NF membrane tested should be negatively charged since the anion repulsion mainly determines the solute rejection. In fact, for a given concentration the decrease of the separation factors follows the decreasing order of the anion charge density since the anion repulsion forces become progressively weaker.

The salts rejections decrease for increasing electrolyte concentrations because the cations' shield effect on the membrane negatively charged

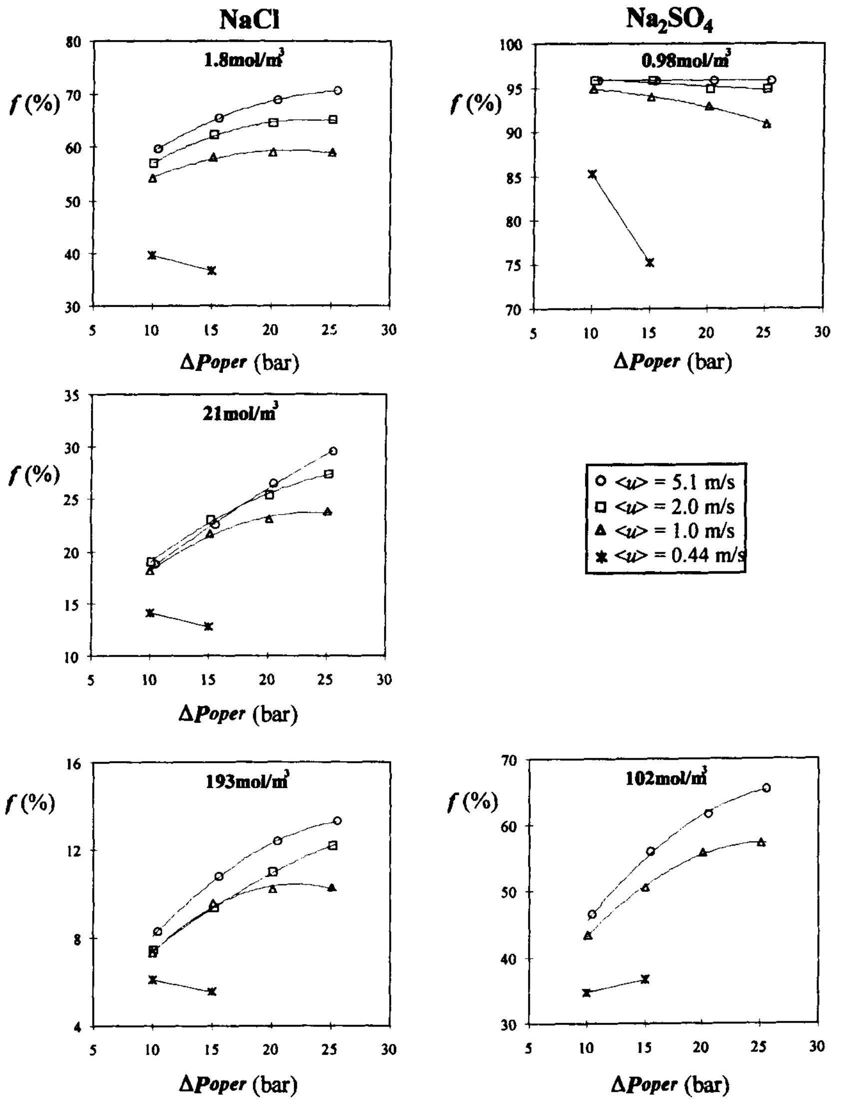

FIG. 3 Salts rejections vs operating conditions (T = 40°C).

groups becomes progressively stronger, causing a decrease of the membrane surface repulsion forces on the anions. This effect is more evident for the chloride ion than for the sulfate ion because the latter has a higher density charge and is rejected by the membrane even for high concentrations.

For high density charge anions the rejections are higher, thus the osmotic pressure difference between the concentrate and the permeate is higher, which in turn causes a higher permeation flux decrease. This fact explains the higher deviations of the fluxes of the most concentrated solution containing divalent anions, with respect to the corresponding pure water permeation fluxes, in comparison to the most concentrated solution containing monovalent anions (Table 3).

E_1 Effluent Permeation

As the permeation experiments are done with a mill effluent subject to process fluctuations, the raw effluent and its microfiltrate are characterized for each set of operating conditions under study, as reported in Table 4.

Figure 4 displays the effect of the operating pressure and the circulation velocity on NF efficiency. The main conclusions are:

- Membrane fouling is not a crucial problem except for the lowest circulation velocity (0.44 m/s), where a limiting flux plateau is reached at approximately 10 bar. At higher circulation velocities there is a linear variation of the permeation flux with pressure.
- The effluent partial desalination, corresponding to values of f_{cond} rang-

TABLE 4
E_1 Effluent Characterization

Operating condition variation	Effluent	pH	Conductivity (mS/cm)	TOC (ppm C)	TOX (ppm Cl^-)
ΔP_{oper}, $\langle u \rangle$, T	E_1	10.1	6.9	750	46
	E_1 microfiltrate	10.0	6.6	736	44
pH	E_1	8.4	7.5	860	76
	E_1 microfiltrate	8.2	7.2	783	75
F_c (up to 2)	E_1	—	7.0	671	54
	E_1 microfiltrate	—	6.8	625	54
F_c (up to 4.5)	E_1	8.0	7.3	931	86
	E_1 microfiltrate	7.9	7.0	874	84

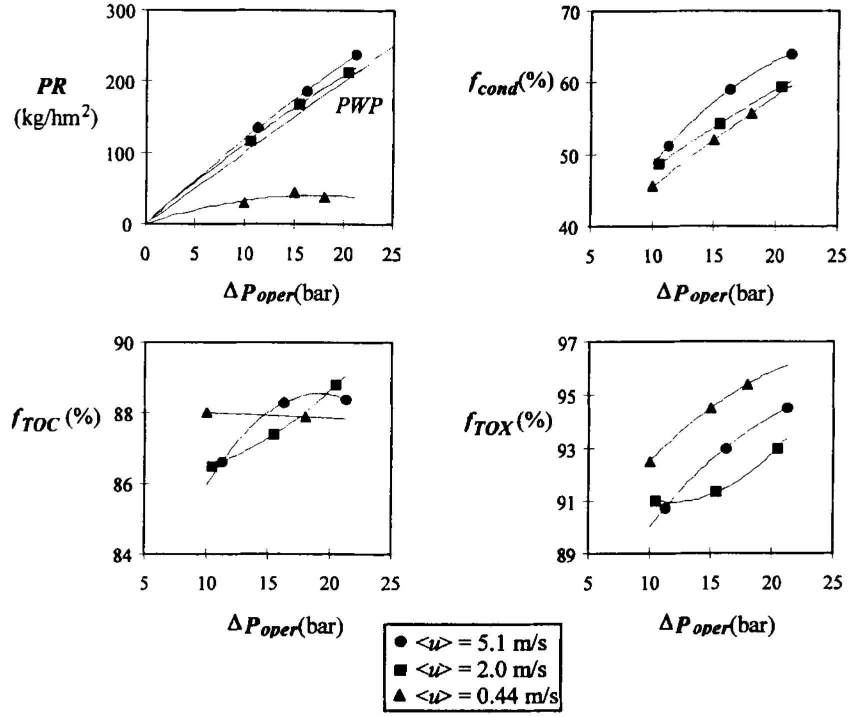

FIG. 4 The effect of the circulation velocity and the operating pressure on E_1 effluent nanofiltration (T = 40°C).

ing from 46 to 64%, is similar to the rejection obtained for the most concentrated solution of Na_2SO_4 tested.

The removal of organic and organochlorinated compounds, expressed by f_{TOC} and f_{TOX}, vary from 87 to 89% and from 91 to 95%, respectively, showing that the representative compounds contributing to the TOC and TOX fractions have average molecular masses slightly lower than the saccharose molecular mass.

An important feature of this work is the investigation of the pH effect on the efficiency of E_1 effluent nanofiltration. According to Fig. 5, the permeation flux ranges from 179 to 62 kg/(m^2·h), f_{cond} from 61 to 75%, f_{TOC} from 92 to 93%, and f_{TOX} from 96 to 98%.

As clearly shown in Fig. 5, the membrane permeation flux presents a maximum at a pH value around 8. On the other hand, the rejections

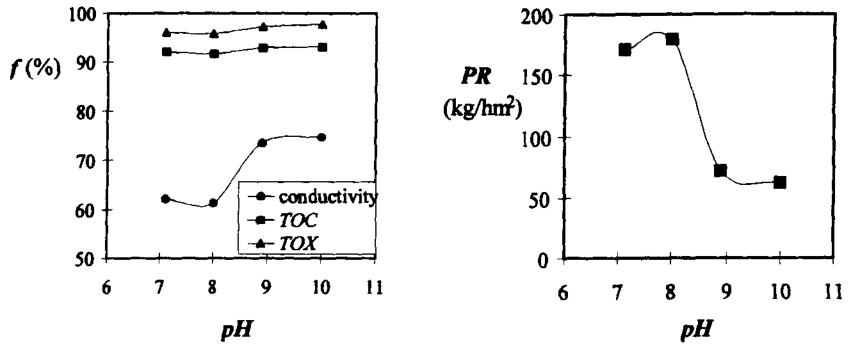

FIG. 5 The pH effect on E_1 effluent nanofiltration (ΔP_{oper} = 20 bar, $\langle u \rangle$ = 5.1 m/s, T = 40°C).

to the conductivity, TOC, and TOX are minimal exactly at this same pH. These two facts allow us to conclude that the membrane tested while processing E_1 effluent presents its isoelectric point at a pH value around 8.

Elmidaoui and Gavach (29), Randon et al. (30), and Vaija et al. (31) studied the variation of the permeation flux of amphoteric membranes with the pH, and they observed that the flux presents a maximum at the membrane isoelectric point. According to Vaija et al. (31), an increase of the surface charge in small pores (D < 20 nm) results in a decrease of the membrane permeability due to the increasing orientation of the water molecules and the increasing viscosity of the solution in the pores.

The rejections are minimal at the membrane isoelectric point because the electrostatic forces established between the membrane and the solutes (salts and negatively charged organic compounds) become weaker.

The severe membrane fouling at pH values of 9 and 10 may be due to the deposition of gallic and ellagic acids on the membrane surface (32).

The optimal operating conditions for processing the E_1 effluent by the NF membrane under investigation are pressure = 20 bar; circulation velocity = 2.0 m/s, and pH 8.

The concentration effect on the efficiency of E_1 effluent nanofiltration is presented in Fig. 6. The membrane fouling during the effluent concentration is minimal. In fact, the flux decreases from 204 to 189 kg/(m^2·h) (8%) for concentration factors up to 2.0 and from 200 to 140 kg/(m^2·h) (30%) for concentration factors up to 4.5. The separation factors range from 67 to 50% for the conductivity, from 86 to 97% for the TOC, and from 95 to 96% for the TOX for concentrations factors up to 4.5.

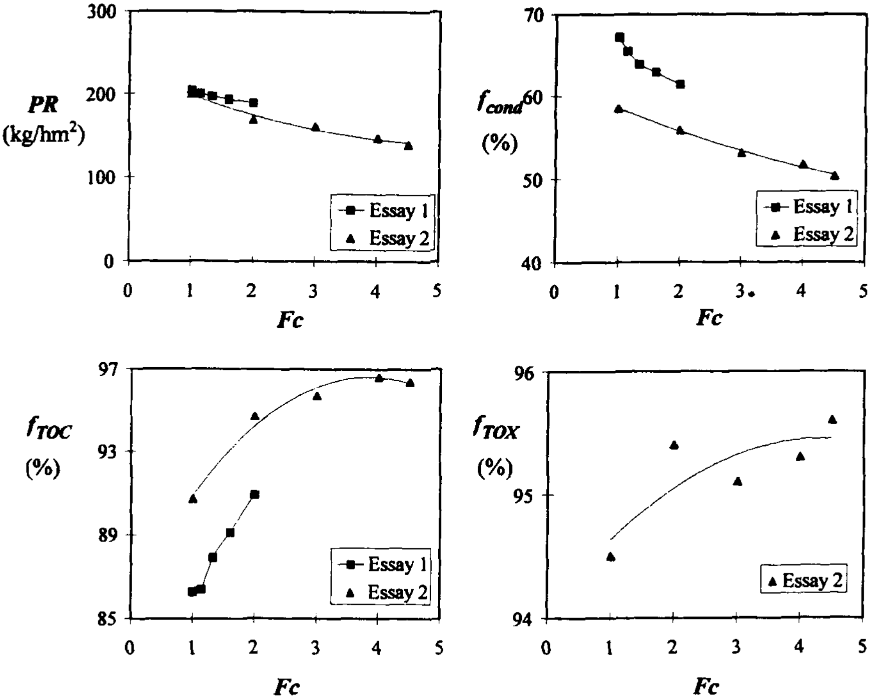

FIG. 6 The concentration effect on E_1 effluent nanofiltration ($\Delta P_{\text{oper}} = 20$ bar, $\langle u \rangle = 5.1$ m/s, $T = 40°C$).

CONCLUSIONS

The study of the operating conditions effect on the efficiency of NF of salt solutions showed that the permeation flux is independent of the circulation velocity and is linearly dependent on the operating pressure. At a given set of operating conditions, $f_{\text{NaCl}} < f_{\text{Na}_2\text{SO}_4}$, i.e., the anion valence mainly determines the solute rejection, which means that the NF membrane tested is negatively charged. Besides, the concentration increase causes the salt's rejections to decrease because the cation's shield effect on the membrane's negatively charged groups becomes progressively stronger. These facts are qualitatively explained by the Donnan exclusion principle.

Obviously, the role played by the anion valence and the feed concentration in these model systems is extremely important. The comprehension of the selective permeation characteristics of these systems is crucial for the prediction and optimization of the NF of an effluent containing inorganic and organic solutes.

Concerning the NF of E_1 effluent, a maximum of the permeation flux and a minimum of the conductivity, TOC, and TOX rejections were observed at a pH of approximately 8, which reveals the membrane amphoteric behavior. This pH value corresponds to the membrane isoelectric point while processing this particular effluent. The concentration essays of E_1 effluent showed that there is a slight decrease of the membrane permeation flux mainly due to the concentration polarization and not to fouling. For the E_1 effluent and the NF membrane under investigation, the optimal operating conditions found are pressure = 20 bar, circulation velocity = 2.0 m/s, pH 8, and concentration factor = 4.5.

In conclusion, NF is an adequate method for E_1 effluent treatment, in particular because the operating conditions can be adjusted in order to get high permeation fluxes and high removal of the organic and organochlorinated compounds. Besides, NF performs the effluent's partial demineralization, allowing permeate recirculation into the process and operation at moderate pressures. Finally, the fouling tendency is low.

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