Water recovery from bleached pulp effluents

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ABSTRACT

Nanofiltration processing the alkaline bleaching stream in a kraft pulp mill removed organo and organochlorinated compounds of low molecular weight using three types of membranes especially developed for this work. Pilot scale tests with organic membranes gave total removal of color and 80–90% rejection of organo and organochlorinated compounds. Further development of ceramic membranes is necessary for the same results. Partial demineralization using nanofiltration requires the processing of nanofiltration permeates by electrodialysis. This combination brings the NaCl content to 60 ppm and makes possible the production of process water for recycling to the mill.

Application:

A combination of nanofiltration and electrodialysis for effluent treatment reduces water consumption in kraft pulp mills.

A KRAFT MILL WITH AN AVERAGE production of a thousand tons of pulp per day faces the disposal of approximately 6000 m^3/day of alkaline bleaching streams—E1 effluent. The bleaching process involves the addition of inorganic chemicals for the solubilization of lignins and chlorolignins covering a wide range of molecular weights. The composition of the resultant E1 effluent has a very complex nature *(1, 2)*. The conventional biological and physicochemical treatments are very often therefore not technically or economically feasible.

Since the 1980s, there have also been increasing pressures to minimize the water consumption in pulp mills. This has led to intense research activity on the development of membrane technology for water recovery from the E1 effluent *(3–5)*. One review *(6)* concluded that the removal of organic and inorganic solutes of low molecular weight by reverse osmosis (RO) remains a very costly solution compared to the very efficient color removal using ultrafiltration (UF). Another article *(7)* presented nanofiltration (NF) as a feasible solution for removing organo and organochlorinated solutes of low molecular weight with a partial demineralization.

Although various NF systems are commercially available, the processing of complex wastewaters like the E1 effluent still requires membrane and module developments and NF process optimization for each specific type of wastewater. In this work, we investigated polymeric and inorganic membranes in tubular and spiral-wound configurations and the NF process optimization to remove 95% color, 90% COD, total organic carbon (TOC), and total organic halides (TOX) of the E1 effluent.

Processing the NF permeate water with electrodialysis (ED) provides final adjustment of the water salt content *(8, 9)*. We studied the sequence NF/ED to produce water with a sodium chloride content of 60 ppm. A low salt content at this level allows recycling of the purified water to the pulp plant.

EXPERIMENTAL

Effluent sampling and characterization

At the pulp mill, we sampled the E1 effluent daily for 40 days. The samples are a mixture of four samples taken directly from the E1 effluent pipeline over a 24-h period of mill operation. This sampling procedure made possible representative daily average compositions. The procedure also characterized mill process fluctuations over the 40-day period. We transported the samples from the mill to the laboratory in a cooler with ice. They were always below 4°C to avoid degradation. We used 2.5-L amber glass bottles and eliminated headspace to avoid escape of volatile compounds.

Standard methods tested the following parameters: total solids (TS), total suspended solids (TSS), total volatile solids (TVS), biological oxygen demand (BOD_5), COD (total and soluble), total carbon (TC), phenols, and various ion contents *(10)*. Other references describe the analytical methods used to determine pH, conductivity, color, TOC, and TOX *(1, 2, 7, 9)*.

Membrane development

We developed three types of NF membranes. There were two types of polymeric membranes synthesized by interfacial polymerization and a ceramic membrane produced by the sol-gel process *(11)*.

Membrane development had the following targets:

- A rejection less than 50% for single valent salts
- A rejection over 90% for neutral organic components with mole-

cular weight greater than 300 g/mole
- A hydraulic permeability greater than 5 L/h·m²·bar.

The following equation gives the definition of a rejection coefficient:

$$\text{Rejection coefficient} = (\text{Feed concentration} - \text{Permeate concentration})/\text{Feed concentration} \quad (1)$$

Multiplying the rejection coefficient by 100 then gives the percentage of rejection. Hydraulic permeability is the slope of the straight line of the pure water permeate flux vs. the operating pressure.

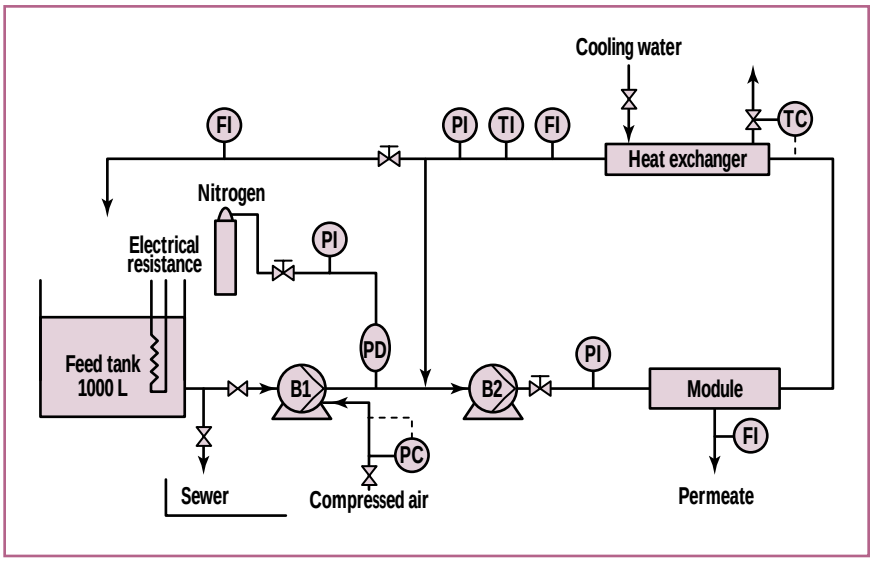
Polymeric membranes. The following is a description of the thin film composite (TFC) membranes:

- Type A consisted of tubes of an active layer formed by interfacial polycondensation on commercial polysulphone tubes. The active layer was an ampholytic polymer containing ammonium and sulfonic acid groups. A prime effort in the membrane development was the synthesis and development of this polymer that is completely fixed into the membrane network by entanglement.
- Type B consisted of flat sheets of a thin film of poly (trans-2,5 dimethyl) piperazinthiofurazanamide (TFZ) formed by interfacial polymerization on polyethersulphone (PES) membrane. We prepared the PES membranes by phase inversion and casting on a nonwoven support.

Membrane type	Module type
A	Tubular Membrane area: 0.86 m² Tube diameter: 14.4 mm Number of tubes: 19[1] Tube length: 1 m Maximum pressure: 4.0 MPa
B	Spiral wound Membrane area: 1.7 m² Spacer thickness: 1.2 mm Cross flow area: 10.9 cm² Maximum flowrate: 1500 L/h Maximum pressure: 4.0 MPa
C	Tubular Membrane area: 0.54 m² Channel diameter: 4 mm Number of tubes: 7[2] Tube length: 0.885 m Maximum pressure: 1.0 MPa

[1]7 tubes were closed to increase the recirculating velocity
[2]2 tubes were closed to increase the recirculating velocity

I. Modules



1. NF pilot plant showing air driven pump (B1), centrifugal pump (B2), flow indicator (FI), pressure dampener (PD), pressure indicator (PI), pressure controller (PC), temperature controller (TC), and temperature indicator (TI)

Ceramic membrane. Type C consisted of an active layer of zirconia coating a macroporous ceramic support—multichannel support Kerasep (TM)—exhibiting an integral layer of 0.2 µm pore diameter. To obtain a defect free NF membrane, we used an intermediate layer between the NF active layer and the support. The intermediate layer made of partially stabilized zirconia provided a good surface allowing an NF final coating not exceeding 1 µm thickness. In addition, this zirconia intermediate layer provides good

Parameters	Units	Mean value	Standard deviation	Number of samples analyzed
pH	-	9.4	0.8	19
Color	U.C.*	2300	840	7
BOD_5	ppm O_2	589	280	9
COD total	ppm O_2	2180	530	19
COD soluble	ppm O_2	2100	690	19
TOC	ppm	526	157	10
TC	ppm	578	171	10
TOX	ppm Cl^-	66	11	15
TS	ppm	5900	1150	19
TSS	ppm	93	27	40
TVS	ppm	1800	396	19
Phenols	ppb	67	24	6
Na^+	ppm	2295	1150	7
Cl^-	ppm	1380	312	7
K^+	ppm	645	579	7
Ca^{+2}	ppm	143	79	7
Mg^{+2}	ppm	25	16	7
Iron	ppm	5.9	2.1	7
Silica	ppm	137	47	7

*Unit of color

II. E1 effluent characterization for samples from March 3, 1991, to April 15, 1991

Selected polymer	611 BC from Stockhausen
Polymer type	Weakly cationic
Concentration, ppm	30
Optimum pH	8
Turbidity removal, %	>90

III. Best coagulation and flocculation conditions for PT I

Membrane type	Pure water flux, L/meters^2 · h	Solute rejection coefficient, %	
		NaCl	Sucrose
A[1]	197	89.0	96.3
B[2]	167	55.9	98.7
C[3]	381	14.8	38.8

[1]5 m/s, NaCl: 200 ppm, sucrose: 200 ppm
[2]1 m/s, NaCl: 2000 ppm, sucrose: 2000 ppm
[3]4.7 m/s, NaCl: 1000 ppm, sucrose: 200 ppm

IV. Membrane characterization on a laboratory scale using 2 MPa at 40°C

compatibility with the NF layer made of zirconia.

Table I describes the different modules supporting each membrane in the pilot plant. In the laboratory scale, we tested membrane B as a flat sheet in a plate-and-frame unit. We tested membranes A and C as single tubes with the same diameter as the membranes used for the pilot scale—20-cm length.

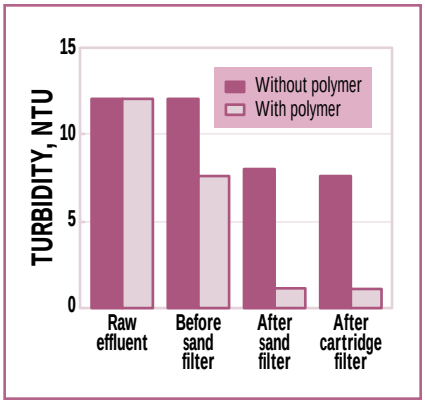
Effluent pretreatment

As Table I describes, the feed stream circulates in tubular modules through a tube with either 14.4-mm or 4-mm diameter, respectively, for membranes A and C. In the spiral-wound modules, the feed stream flows through a very thin channel 1.2-mm thick. Spiral-wound module (membrane B) therefore requires pretreatment I. This is more severe than pretreatment II used for the tubular modules (membranes A and C). The pretreatments were as follows:

- Pretreatment I (PT I) had this physicochemical sequence: (1) pH adjustment with HCl dosing, (2) rapid mixing of polyelectrolyte followed by slow mixing with coagulation and flocculation, (3) sand filtration, and (4) microfiltration through a battery of three cartridge filters of decreasing porosities (45, 25, and 5 µm for laboratory scale and 80, 50, and 5 µm for pilot scale).
- Pretreatment II (PT II) had a similar sequence to PT I except the exclusion of the polyelectrolyte coagulation and flocculation step.

The cartridge filters retain large particles escaping from the sand filter and protect the membrane modules and the pumps.

To determine the type and concentration of polyelectrolyte and the necessary pH, we studied the coagulation and flocculation treatment at both the laboratory and the pilot options. We measured the pretreatment efficiency by the degree of turbidity removal. This method is faster than the silt density index (SDI). Although membrane manufacturers recommend SDI for its potential to predict membrane fouling, there is no reliable proof of this ability. NF pilot plant tests remain the only reli-

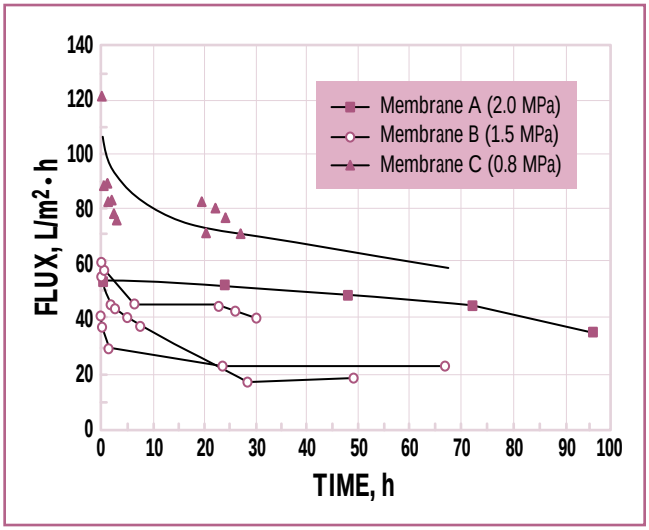


2. Effluent turbidity characterization on different steps of pretreatment

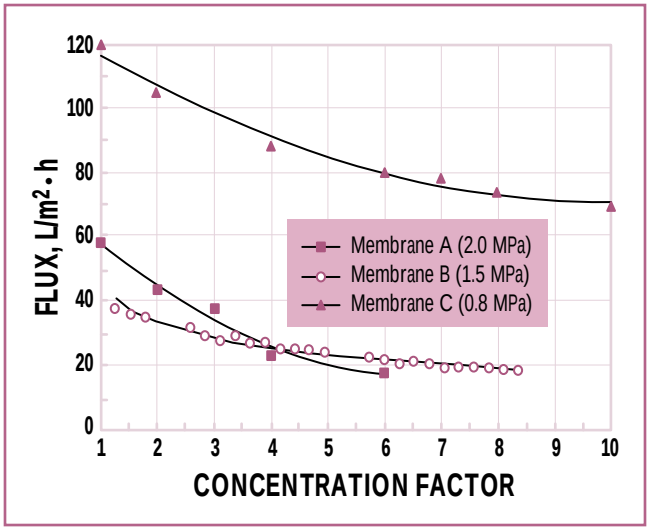
Membrane type	Permeation flux, L/m²·h	Solute rejection coefficient, %		
		Conductivity	TOC	TOX
A[1]	208	64	88	92
B[2]	131	53	90	95
C[3]	96	25	77	82

[1]PT II, 5.0 m/s
[2]PT I, 1.0 m/s
[3]PT II, 4.7 m/s

V. Membrane performance with E1 effluent on a laboratory scale using 2 MPa at 40°C



3. Variation of permeate flux with time for membrane A at 4.2 m/s, PT II; membrane B at 0.3 m/s, PT I; and membrane C at 2.0 m/s, PT II



4. Variation of permeate flux with concentration factor at 40°C using same operating conditions as in Fig. 3

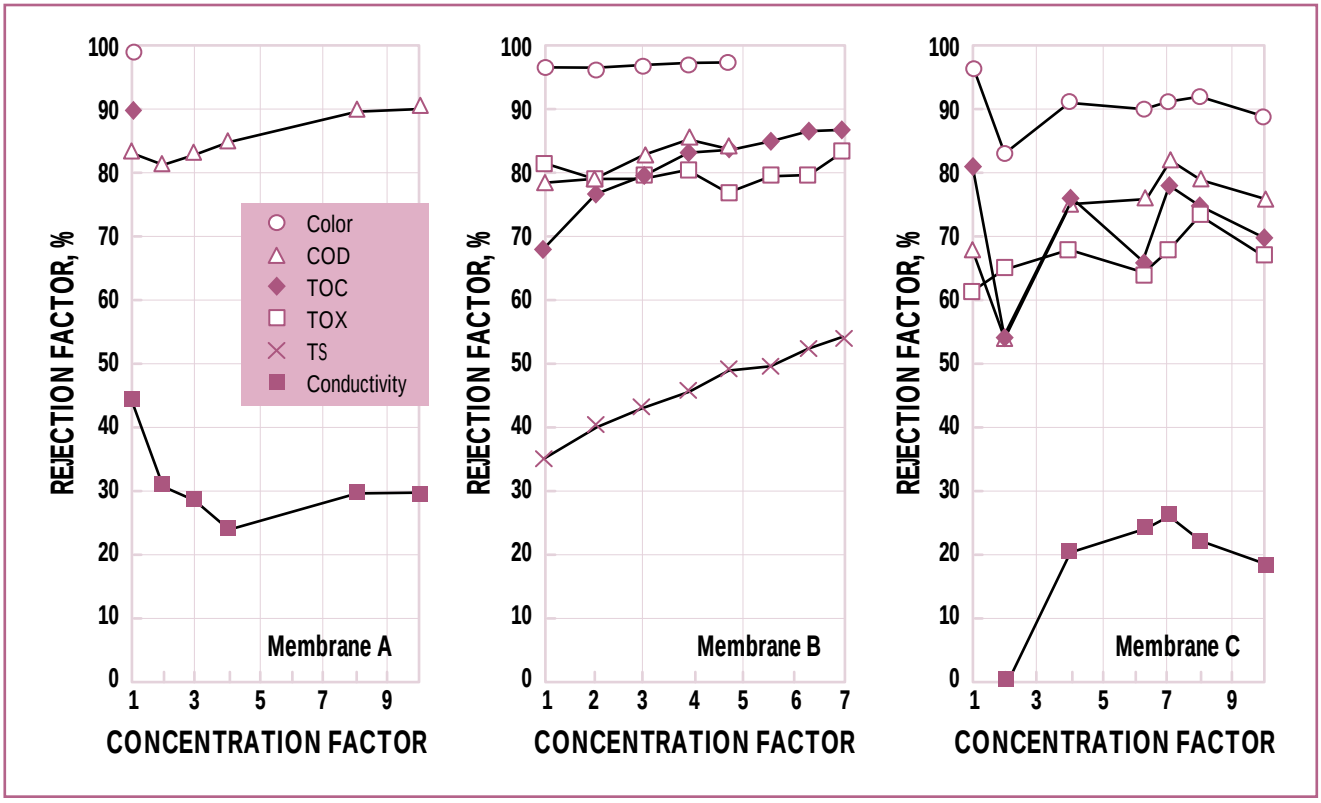
able procedure to predict membrane fouling *(12)*.

Nanofiltration

At the laboratory level, we characterized the membranes by permeation of pure water and reference solutions of sucrose and sodium chloride. We determined the fluxes of pure water and reference solutions and the solute rejection coefficients. Our work encompassed NF of the E1 effluent for the tubular membranes after PT II and for the flat-sheet membrane after PT I. We ran the tests in the batch mode with recirculation of the concentrate stream to the feed tank.

We tested membrane B in a commercial plate and frame unit (Lab-Unit, type 20 from DDS Filtration, Denmark) at 2.0 MPa, 40 °C, and maximum recirculating velocity of 1 meter/s. We tested tubular membranes in a laboratory unit holding two membrane tubes of 20-cm length placed in series. The basic design of this unit was the same as that of the pilot plant. Membrane A testing was at 2.0 MPa, 40 °C, and 5 meters/s recirculating velocity. Membrane C testing used 2.0 MPa, 40 °C, and 4.7 meters/s recirculating velocity.

Installation of the pilot plant was at the Portucel mill in Setúbal, Portugal. A pipeline of E1 effluent ran from the plant to the pretreatment section of the pilot plant. Figure 1 is a schematic of the NF pilot unit. There are two separate pumps. One is for pressurization (air-operated piston pump), and another is for recirculation (centrifugal pump). This apparatus allows the independent variation of the concentration



5. Rejection factor for the three membranes at 40°C using same operating conditions as in Fig. 3

factor and the feed recirculation velocity. For each module, we conducted batch test runs in two different modes:

- Long-term runs with total recirculation of permeate and concentrate to evaluate the fouling process
- Concentration runs with concentrate recirculation to define the best operating concentration factor—the ratio of the feed to the concentrate volume.

In the pilot plant, we set the operating conditions using the module manufacturer specifications:

- Membrane A, PT II: 2.0 MPa, 40°C, and 4.2 m/s recirculating velocity
- Membrane B, PT I: 1.5 MPa, 40°C, and 0.3 m/s recirculating velocity
- Membrane C, PT II: 0.8 MPa, 40°C, and 2.0 m/s recirculating velocity.

The fittings of the last module restricted the operating pressure to 0.8 MPa.

The cleaning cycles to recover the initial pure water flux were the following:

- Membrane A had daily cleaning with industrial water at 1.0 MPa and room temperature for 1–2 hours. After long runs of 4–5 days, we performed cleaning with industrial water for 6–7 hours using approximately 200 L of water.
- Membrane B had daily cleaning with water rinsing, 0.25% nitric acid, water rinsing, 0.1% Ultrasil 11, and water rinsing. This cycle took 1 h, and the operating pressure was 0.1 MPa. It used a total of approximately 200 L of cleaning solutions.
- Membrane C had daily cleaning with water rinsing, 1.0% sodium hydroxide, 0.2% Ultrasil 11, water rinsing, 1.0% nitric acid, and water rinsing. It used a total of approximately 200 L of cleaning solutions.

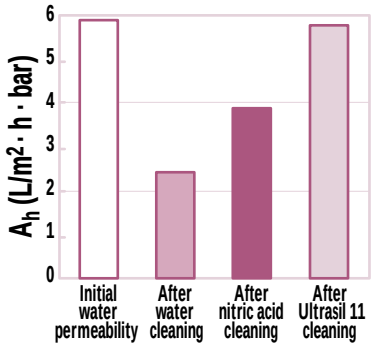
Electrodialysis

We conducted ED studies with model solutions representative of the NF permeate collected at the pilot scale with membrane A *(11)*. We used a preindustrial electrodialyzer in which the hydrodynamic conditions of the stack were the same as those of industrial equipment. The pilot plant was an Aqualyser, model P20, from SRTI, France, with 33 cell pairs and 0.76 m^2 total membrane area. The membranes were Selemion AMV and CMV. The amount of model solutions used in

Parameters	NF permeate*	Industrial mill water
pH	7.0	7.9
Conductivity, millis/cm	3.42	0.31
Na^+, ppm	765	26
$CaCO_3$, ppm	21	115
Cl^-, ppm	945	32
NO_3^-, ppm	21	-
NO_2^-, ppm	5	-
Turbidity, NTU	0.5	-

*E1 effluent with PT II nanofiltered through membrane A at pilot plant operating at 2.0 MPa, 40°C and 4.2 m/s, concentration factor approximately 1

VI. Compositions of the NF permeate and industrial mill water



6. Average hydraulic permeability for membrane B at 25°C during the cleaning sequence

all the tests was 40 L and the flow rate was 560 L/h. The tests were at room temperature using the following sequence:

1. Check the electrodialyzer performance under standard conditions using 5 g/L NaCl.
2. Determine the limiting current by plotting current or voltage vs. the inverse of the current.
3. Perform a feasibility study to determine if it was possible to achieve the conductivity of the required industrial water. We followed the decrease of conductivity in the diluate compartment of an ED cell that started running with the model solution both in the diluate and in the concentrate compartments.
4. Determine the reconcentration level to be obtained in the concentrate. At the beginning, the diluate contains the model solution and the concentrate contains 10 L of solutions that were 20, 50, 100, and 150 times more concentrated than the model solution. The applied electrical potential was always 0.9 volts per cell. This is 90% of the electrical potential corresponding to the limiting current. This mode of ED operation at constant voltage acts as a current regulator and always keeps its value below the corresponding limiting value. The experimental sequence described above incorporates step 2 for measurement of the limiting current. This is 150 A/m^2 for the initial model solution. We checked the evolution of the stack performance by the standard test in step 1 of this sequence.

RESULTS AND DISCUSSION

Effluent characterization

Table II shows the E1 effluent characterization and the statistical treatment of the data. The large values of the standard deviation of some parameters reflect the pulp mill process fluctuations. As already reported *(7)*, the variability of E1 effluent composition does not influence the rejection coefficients.

Pretreatment at laboratory scale

Table III shows the best operating conditions found for the coagulation and flocculation in PT I. Under these operating conditions, the removal of 90% of the effluent turbidity led to an effluent quality that was adequate for processing through spiral-wound modules. One should note that the polyelectrolyte concentration of 30 ppm to achieve this objective was very high. It was very difficult to obtain good pretreatment efficiencies with other tested polyelectrolytes at moderate concentrations.

Membrane performance at laboratory scale

In the membrane characterization shown in Table IV, the pure water flux of membranes A, B, and C far exceeds the target value of 100 L/m^2·h at 2.0 MPa. Membranes A and B fulfill the target rejection coefficients for single valent salts and organics of molecular weight higher than 300 g/mole. The performance of the ceramic membrane is very poor, however, and does not comply with the target value for the organic solute rejection.

Table V shows the membrane performance of NF on E1 effluent and provides a first assessment of the problem of concentration and membrane fouling. In contrast with the very high permeate fluxes of the polymeric membranes, the ceramic membrane presents a permeate flux much lower than the pure water flux at the same pressure. This indicates a potential problem of membrane fouling. The same membrane C does not sufficiently purify the effluent despite presenting rejection coefficients for conductivity, TOC, and TOX greater than expected from the tests with NaCl and sucrose.

Parameters	Concentration, ppm
Na^+	621
$CaCO_3$	21
Cl^-	945
NO_3^-	21

VII. Composition of the model solutions for ED study

Test	Initial concentration, ratio of concentrate/ diluate	Final conductivity of the diluate, millis/cm	Elapsed time, min
1	10	0.15	45
2	20	0.16	45
3	50	0.19	50
4	100	0.20	70
5	150	0.29	90

VIII. ED concentration tests with initial diluate conductivity of 3.42 millis/cm

Although the rejection coefficients of membranes A and B are similar, the first one has a permeate flux that is 60% higher. The high permeate flux of membrane A relates to the tubular geometry of the module and is primarily due to the high feed velocity of 5 m/s causing turbulent flow. The comparison of rejection coefficients for TOC of E1 effluent and reference solute sucrose indicates that approximately 10% of the organics have a molecular weight lower than 342 g/mole. The performance of membranes A and B globally is very promising for this application.

Pilot plant results

Pretreatment. Figure 2 shows the pretreatment effectiveness with and without polymer addition at the pilot scale. One can conclude that the coagulation and flocculation with the weak cationic polyelectrolyte strongly reduces effluent turbidity. The turbidity after cartridge filtration remained the same. This shows that the cartridge filters did not retain colloidal particles.

Nanofiltration. The comparison between the results obtained at laboratory scale shown in Table V with those obtained at pilot scale in Figs. 3 and 4 shows the severe fouling characteristics of the E1 effluent.

Figure 3 shows the results of the fouling tests. The flux decline in the first minutes of operation is particularly pronounced for the ceramic membrane. Although it starts with a high value, the permeate flux of membrane C drops rapidly and approaches the values of the polymeric membranes. The scattering of the permeation results for the three different runs with membrane B is a consequence of the fluctuations of effluent composition. We expected this result, since the effluent comes directly from a pipeline of the industrial plant.

Figure 4 presents the results of the concentration tests and shows the flux decline with the increase of the concentration factor. The flux declines until a concentration factor of 4 and then remains approximately constant. The fact that the concentration test runs have a duration of a few hours means that membrane fouling is also contributing to flux decline. Figure 5 shows the rejection coefficients of TOX, TOC, COD, color, TS, and conductivity for the three modules. The high values of color rejection show that the major source of color relates to high molecular weight compounds. The polymeric membranes achieve a color removal well above 95%. Color removal is approximately 90% for the inorganic membranes. The removal of organic compounds is 80–90% for the polymeric membranes and 60–80% for the ceramic membranes. Salt removal is 25–45% for the polymeric membranes and remains below 25% for the ceramic ones. A comparison of Table II with the first column of Table VI shows the complete removal of multivalent ions.

We optimized the cleaning sequences at pilot scale to guarantee the complete recovery of the initial pure water fluxes. The complete recovery of the water fluxes shows that the irreversible fouling was minimum. Figure 6 shows the hydraulic permeability throughout the cleaning sequence for membrane B. As described in the experimental section, the cleaning cycle of membrane A does not include intermediate steps of chemical cleaning. This contrasts with the intense chemical cleaning required for membranes B and C. One should note that the flow regime for module A is more turbulent than for the other two modules. This allows membrane cleaning using only water.

In all NF pilot tests, the cleaning sequences restored the membrane pure water fluxes. This shows that the irreversible fouling was minimum as Fig. 6 illustrates for membrane B.

Electrodialysis. Table VI gives the ion composition of the NF permeate and the industrial mill water. To produce this industrial mill water, the sodium chloride content should decrease from 945 ppm Cl^- to 32 ppm Cl^-—approximately 60 ppm NaCl. To achieve this reduction and make the water recycling possible, it is necessary to process the NF permeate by ED. The target value of 60 ppm of NaCl content is much smaller than the value of 300 ppm that is usually the lower limit for salt

KEYWORDS
Alkaline pulps, bleaching effluents, chemical pulps, chlorine compounds, dialysis, effluents, electrodialysis, filtration, halogen compounds, kraft pulps, membranes, reuse, separation, spent liquors, ultrafiltration, water reuse.

removal by ED. Because of this fact, the hydrodynamic conditions play a very important role in the feasibility of this process. This was the reason the experimental study used a preindustrial pilot electrodialyzer in which the hydrodynamic conditions of the stack matched those of the industrial equipment. For this study, we used model solutions. Table VII gives the respective composition.

Table VIII shows that the best value of the initial concentrate to diluate ratio is 50. This corresponds to an ED water recovery in continuous operation of 98%. Higher recovery rates correspond to a sharp increase of the operating times and therefore to inefficient ED processing.

CONCLUSIONS

The purification of the E1 effluent—95% color removal, 90% organic compounds removal, and 30% salt removal—occurs well using NF with polymeric membranes. In addition, this operation is efficient at laboratory and pilot scale for tubular and spiral-wound modules with membrane fouling controlled to a water recovery rate of 70%—concentration factor of 3.3.

The purification standards specified above do not result with NF ceramic membranes. Further work is therefore necessary with these membranes.

The quality of water necessary for recycling requires the coupling of NF with other separation techniques. For salt content, one should note that NF removes practically all the multivalent ions. The processing of NF permeates by ED was sufficient to decrease the NaCl content to 60 ppm. It is also possible to decrease the residual organic content of NF permeates by another stage of NF with lower molecular weight cut-off or through coupling of NF with a destructive process like oxidation.

The optimization of the NF/ED sequence for E1 effluent treatment makes possible the production of water where the multivalent ions are practically absent and the NaCl content is as low as 60 ppm. The color is also practically removed, and the residual organic compounds are not major problems for the water recycling. The NF/ED sequence therefore represents a major contribution to the reduction of water consumption in kraft pulp mills. TJ

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