Membrane Processes as Best Available Techniques (BAT) in Pulp & Paper Industry

A Technology Collaboration Programme established under the auspices of the International Energy Agency

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Energy Future in Industry

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Case Studies of BAT in Pulp & Paper Industry

• **Case Study 1**
  NANOFILTRATION for WATER RECOVERY in the BLEACH PLANT of a KRAFT PULP MILL

• **Case Study 2**
  ULTRAFILTRATION and NANOFILTRATION for the RECOVERY of LIGNIN and HEMICELLULOSE from the E-stage EFFLUENT of a SULPHITE PULP MILL
CS1: Nanofiltration for Water Recovery in the Bleach Plant of a Kraft Pulp Mill
CS1: Water recovery from E1 effluent

- Production of process water from E1 Effluent requires:
  - Removal of total organic carbon (TOC)
  - Removal of total organochlorinated compounds (TOCl)
  - Partial demineralization

Nanofiltration (NF) Meets these requirements

- Experiments on a NF pilot plant
- NF modeling and design
CS1: Methodology

- Pilot plant data
- NF design equations
- Process simulation
- Sensitivity analysis and scale-up
- Process specifications
CS1: NF Modelling

Spiral wound module:

- Feed tank
- Level 1
- Level 2
- Level 3
- Concentrate

Permeate

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CS1: Required Pilot Plant Data

- Permeate flux

\[ v_p = v_p (F_c, \text{time}) \]

- Organic solutes

\[ f_i = f_i (F_c) \]

- Sodium Chloride

\[ f = f (v_p, F_c) \]
CS1: Essays in Pilot Plant

Recirculation mode (\( F_c = 1 \))

\[
\begin{aligned}
\nu_p &= \nu_p(time) \\
\text{TOC and TOX}: f_i \\
\text{NaCl}: f(\nu_p)
\end{aligned}
\]

Concentration mode

\[
\begin{aligned}
\nu_p &= \nu_p(F_c) \\
\text{TOC and TOX}: f_i = f_i(F_c) \\
\text{NaCl}: f = f(F_c)
\end{aligned}
\]
CS1: NF Pilot Plant

Operation modes:
- Concentration mode
- Recirculation mode
CS1: Effluent pre-treatment

- pH adjustment (pH = 8)
- Coagulation/flocculation
- Sand filtration
- Microfiltration through a battery of three cartridge filters of decreasing porosities: 80, 50 and 5 μm
CS1: Operating conditions

- E1 effluent from PORTUCEL (Setúbal - Portugal)
- Membrane Area = 1.7 m\(^2\)
- \(\Delta P = 1.5\) MPa
- \(T = 50\) °C
- Recirculation flowrate: 1500 l/h \((u_0 = 0.40\) m/s\)
- NF Spiral Wound Module:
  - Thin film composite membrane (CDNF50 from Separem, Italy)
  - Area: 1.7 m\(^2\)
  - Channel thickness: 1.2 mm
  - Open cross-section area: 11 cm\(^2\)
CS1: Pilot Plant Results

Permeate flux: Recirculation mode

\[ v_p = \alpha - \beta t \]

\[ \alpha = 40 \text{ l/m}^2\text{ h}, \quad \beta = 0.23 \text{ l/m}^2\text{ h}^2 \]
CS1: Pilot Plant Results

NaCl rejection: Recirculation mode

\[ f(\%) = \frac{v_p}{v_p + B \exp \left( \frac{v_p}{k_c} \right)} \]

\[ Sh = 0.15 \text{Re}^{0.68} \text{Sc}^{1/3} \]

\[ B = 1.1 \times 10^{-5} \text{ m/s} \]
CS1: Pilot Plant Results

Permeate Flux: Concentration mode

\[ \nu_p = \nu_{p0} F_c^\gamma \]

\[ \gamma = -0.44 \]
CS1: Pilot Plant Results

Apparent rejection coefficients: concentration mode

\[
f_i = f_i^0 \left(1 + \xi F_c\right)
\]

<table>
<thead>
<tr>
<th>Analytical Parameter</th>
<th>(f_i^0) (%)</th>
<th>(\xi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>73</td>
<td>0.0443</td>
</tr>
<tr>
<td>TOCl</td>
<td>72</td>
<td>0.0248</td>
</tr>
<tr>
<td>COD</td>
<td>67</td>
<td>0.0030</td>
</tr>
<tr>
<td>Color</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>
CS1: Average hydraulic permeability at 25 ºC during the cleaning sequence

- Cleaning sequence time: 1 hr
CS1: Design specifications

- Water recovery rate per level: 35%
- Plant capacity: 1000 m³/day
- Cleaning time: 1 hr
- Operation time: 16 hr
- $\Delta P = 1.5$ MPa
- $T = 50^\circ$C
- Spiral wound modules
  - $u_o = 0.4$ m/s
  - $h = 1.2$ mm
Concentration factor ($F_c$) = feed flow rate / concentrate flow rate

Water recovery rate ($W_r$) = permeate flow rate / feed flow rate

Apparent rejection coefficient,

$$f_i = \frac{C_i - C_{Pi}}{C_i}$$

Membrane Area ($A$) = $2 \times w \times l$

$$A = \frac{2Q_0 l}{h u_0}$$
CS1: Design Equations

- Continuity equation: \( \frac{du}{dx} = \frac{2v_p}{h} \)

- Continuity equation for solute \( i \): \( \frac{dC_i}{dx} = \frac{2v_p}{hu} C_i f_i \)

- Boundary conditions:
  \[
  \begin{cases}
    x = 0, & u = u_o, \quad C_i = C_{i0} \\
    x = l, & u = (1 - W_r)u_o
  \end{cases}
  \]
CS1: Design Equations

Required specifications
• Inlet velocity, $u_0$; Slit height, $h$
• Level water recovery rate, $W_r$

Required Experimental Data
• Permeate flux: $v_p = (\alpha - \beta t) F_c^{\gamma}$
• Apparent Rejection coefficients (TOC, TOCl): $f_i = f_i^0 (1 + \xi F_c)$
• Apparent Rejection coefficient (NaCl):
  – Solution-Diffusion model
  – Film theory

Design output
Membrane Area $= \frac{2Q_0 l}{h u_0}$
• Permeate and concentrate composition

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CS1: Water Recovery Rate and Membrane Area

![Water Recovery Rate Graph](#)

![Membrane Area Graph](#)

Technology Collaboration Programme
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CS1: Permeate Productivity

Level Flux (l/m²h)

NF Levels

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CS1: Permeate Quality

- Permeate color (U.C.)
- Permeate TOC (ppm)
- Permeate TOC (ppm O2)

NF Levels: 1, 2, 3, 4
CS1: Permeate Quality
CS1: Economic Analysis

Plant Parameters

- E1 flowrate = 1000 m$^3$/day
- 3 NF stages (Recovery rate = 70%)
- Average Permeate Flux = 23 l/m$^2$h
- Membrane Area = 1300 m$^2$
- Feed Pressure = 1.5 MPa
- Brine Pressure = 1.0 MPa
- Membrane Life = 3 Years

Project Life = 7 Years
CS1: Cost Structure

Investment Costs

- Pressure Vessels: 44%
- Pumps: 13%
- Electric instrumentation: 5%
- Construction costs & costs of tanks: 4%
- Others: 7%
- Membranes: 5%

Operating Costs

- Cartridge filters (changed every 2 years): 22%
- Chemical supplies (cleaning, cartridge filters): 6%
- Maintenance (2% of capital cost): 5%
- Labor: 7%
- Electric power: 6%
- Membrane replacement: 5%
CS2: Ultrafiltration and Nanofiltration for the Recovery of Lignin and Hemicellulose from the E-stage Effluent of a Sulphite Pulp Mill

CAIMA – Indústria de Celulose, S.A., Portugal

Sulphite pulp mill:

Production of 125 kton/year of dissolving pulp from *Eucalyptus globulus*;

Magnesium bisulphite process;

Bleaching process: Total Chlorine Free (TCF)
CS2: Ultrafiltration and Nanofiltration for the Recovery of Lignin and Hemicellulose from the E-stage Effluent of a Sulphite Pulp Mill

Bleaching sequence E-O-P:
Removal of lignin, hemicelluloses and color

- Alkaline extraction with sodium hydroxide (‘E’ stage)
- Oxygen delignification (O)
- Hydrogen peroxide (P)
### CS2: Bleaching Pulp Effluent (BPE) Characterisation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.87</td>
</tr>
<tr>
<td>Specific mass (g/L)</td>
<td>0.44</td>
</tr>
<tr>
<td>Total Suspended Solids (TSS) (mg/g)</td>
<td>28.83</td>
</tr>
<tr>
<td>Total Solids (TS) (mg/g)</td>
<td>14.23</td>
</tr>
<tr>
<td>Ash (mg/g)</td>
<td>2.88</td>
</tr>
<tr>
<td>Total lignin (g/L)</td>
<td>1,31</td>
</tr>
<tr>
<td>Acid soluble lignin (mg/g)</td>
<td>1.31</td>
</tr>
<tr>
<td>Klason lignin (mg/g)</td>
<td>1.05</td>
</tr>
<tr>
<td>Hemicelluloses (mg/g)</td>
<td>0.19</td>
</tr>
<tr>
<td>Arabinose (mg/g)</td>
<td>0.00</td>
</tr>
<tr>
<td>Galactose (mg/g)</td>
<td>0.00</td>
</tr>
<tr>
<td>Glucose (mg/g)</td>
<td>0.03</td>
</tr>
<tr>
<td>Mannose (mg/g)</td>
<td>0.03</td>
</tr>
<tr>
<td>Xylose (mg/g)</td>
<td>0.13</td>
</tr>
<tr>
<td>Others (mg/g)</td>
<td>11.52</td>
</tr>
</tbody>
</table>
CS2: Molecular Weight Distribution of Hemicelluloses and Lignin

Mass average molecular mass: 

\[
\overline{M_w} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}
\]

<table>
<thead>
<tr>
<th></th>
<th>Hemicelluloses by RI</th>
<th>Lignin by UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest peak (kDa)</td>
<td>0.57</td>
<td>0.91</td>
</tr>
<tr>
<td>(\overline{M_w}) (kDa)</td>
<td>0.88</td>
<td>1.32</td>
</tr>
</tbody>
</table>
CS2: Membranes Hydraulic Permeability

\[ J_{wi} = L_p \times TMP \]

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( L_{p, 25^\circ C} ) (Lh(^{-1})m(^{-2})bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETNA01P</td>
<td>23.9</td>
</tr>
<tr>
<td>GR95PP</td>
<td>28.6</td>
</tr>
<tr>
<td>NF99HF</td>
<td>21.5</td>
</tr>
<tr>
<td>NP010</td>
<td>63.2</td>
</tr>
<tr>
<td>NP030</td>
<td>11.7</td>
</tr>
<tr>
<td>MPF36</td>
<td>21.1</td>
</tr>
</tbody>
</table>
## CS2: Optimal Operating Conditions

<table>
<thead>
<tr>
<th>Membrane</th>
<th>GR95PP</th>
<th>NP010</th>
<th>MPF36</th>
<th>ETNA01P</th>
<th>NF99HF</th>
<th>NP030</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>70°C</td>
<td></td>
<td></td>
<td></td>
<td>50°C</td>
<td></td>
</tr>
<tr>
<td>$TMP_{max}$ (bar)</td>
<td>9</td>
<td>9</td>
<td>15</td>
<td>8</td>
<td>13</td>
<td>23</td>
</tr>
<tr>
<td>$J_v$ (L h$^{-1}$m$^{-2}$)</td>
<td>8</td>
<td>39</td>
<td>125</td>
<td>45</td>
<td>166</td>
<td>14</td>
</tr>
<tr>
<td>$R_{total lignin}$</td>
<td>76%</td>
<td>84%</td>
<td>92%</td>
<td>69%</td>
<td>97%</td>
<td>94%</td>
</tr>
</tbody>
</table>
CS2: Molecular mass distribution of lignin and hemiceluloses by size exclusion chromatography (SEC)

<table>
<thead>
<tr>
<th></th>
<th>BPE feed</th>
<th>MPF36 permeate</th>
<th>NF99HF permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemicelluloses $M_w$ (kDa)</td>
<td>0,88</td>
<td>0,52</td>
<td>0,52</td>
</tr>
<tr>
<td>Lignin $M_w$ (kDa)</td>
<td>1,60</td>
<td>1,60</td>
<td>0,88</td>
</tr>
</tbody>
</table>
CS2: SEC of fractionated streams
CS2: Techno-Economical Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flow, $Q_{feed}$ (m³/h¹)</td>
<td>70</td>
</tr>
<tr>
<td>VR (%)</td>
<td>68%</td>
</tr>
<tr>
<td>CFV (ms⁻¹)</td>
<td>0.8</td>
</tr>
<tr>
<td>TMP (bar)</td>
<td>13</td>
</tr>
<tr>
<td>Average flux, $J_{av}$ (Lh⁻¹m⁻²)</td>
<td>24.2</td>
</tr>
<tr>
<td>ΔP in each module (bar)</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Investment cost**

Membrane area = $\frac{Q_{feed} \times VR}{J_{av}} \times 1.2$

Total investment cost = (Cost feed section + Cost membrane section) × factor automation

Cost feed section = $5000€ \times Q_{feed} (m³h⁻¹)$

Cost membrane section = $1000€ \times$ Membrane area (m²) × factor module

**Operating costs**

- Electricity
- Replacement of membranes
- Cleaning
- Maintenance and labor costs
## CS2: Techno-Economical Analysis

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost (€/m² membrane)</td>
<td>2000a</td>
</tr>
<tr>
<td>Electricity price (€/kWh)</td>
<td>0,10c</td>
</tr>
<tr>
<td>Membrane replacement cost (€/m²)</td>
<td>95a</td>
</tr>
<tr>
<td>Membrane lifetime (year)</td>
<td>1,5b</td>
</tr>
<tr>
<td>Cleaning cost (€m⁻²year⁻¹)</td>
<td>50b</td>
</tr>
<tr>
<td>Operating time (h/year)</td>
<td>8000b</td>
</tr>
<tr>
<td>Pump efficiency (η)</td>
<td>0,8</td>
</tr>
<tr>
<td>Maintenance and labor (% of investment cost/year)</td>
<td>5%a</td>
</tr>
<tr>
<td>Annuity factor (%)</td>
<td>10%a</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane area (m²)</td>
<td>2360</td>
</tr>
<tr>
<td>Membrane modules</td>
<td>40</td>
</tr>
<tr>
<td>Investment cost (M€)</td>
<td>4,72</td>
</tr>
<tr>
<td><strong>Capital cost (k€/year)</strong></td>
<td><strong>472</strong></td>
</tr>
<tr>
<td>Electricity required (kWh m⁻³ of permeate)</td>
<td>0,88</td>
</tr>
<tr>
<td>Electricity cost (k€/year)</td>
<td>34</td>
</tr>
<tr>
<td>Membrane replacement cost (k€/year)</td>
<td>150</td>
</tr>
<tr>
<td>Cleaning cost (k€/year)</td>
<td>118</td>
</tr>
<tr>
<td>Maintenance and labor costs (k€/year)</td>
<td>24</td>
</tr>
<tr>
<td><strong>Operating costs (k€/year)</strong></td>
<td><strong>326</strong></td>
</tr>
<tr>
<td><strong>Total cost (k€/year)</strong></td>
<td><strong>798</strong></td>
</tr>
</tbody>
</table>

> **2,14€/m³** of permeate

a (Jönsson, et al., 2008), b (Arkell, et al., 2013), c (YLCE, s.d.)
CS2: Conclusions

Concentration of BPE with a NF99HF membrane and a VR of 68%:
- T=50°C; CFV=0,8 m/s; TMP=15 bar
- Average permeate flux of 24,2 Lh⁻¹m⁻²
- Retention of lignin and hemicelluloses of 94-97%
- Total solids increase from 3 to 7% (w/w)
- VCF of 3.1

High regeneration levels with Ultrasil 10 at 0,5%(w/w)

To treat 70m³/h of BPE with plate-and-frame configuration:
- 2360 m² of membrane area
- Investment cost of 4,72 M€
- Operation costs: 326 k€/year
- 2,14€ per m³ of permeate
Acknowledgments

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