Life-Transformem: Reuse of recycled membranes (NF-UF) in water treatment

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Membrane technology at the desalination world

Desalination installed capacity distribution by technology. Source: (IDA, 2016)

**Reverse osmosis (RO) membranes**
- **18,426** Desalination plants (IDA, 2016)
- **150** countries (IDA, 2016)
- **56.42 Hm³/d** installed capacity
  - By 2019, RO market is projected to reach **$8.8 billion** (Membr. Technol., 2015)

95% of the existing RO desalination plants have spiral wound aromatic polyamide-based composite membranes (Geise et al.2010)
End-of-life RO membranes: a waste management challenge

RO membrane technology weakness
- High required energy
- Impact and interference of organisms in the inlet of the feed
- Brine effluent discharge
- Membrane fouling - lifespan (5-8 years)

Considering:
- RO membrane modules installed (>5,600,000)
- Annual replacement rate of 15%
- Average of 17 kg (fouled membranes)

Annual waste at World wide scale
> 840,000 RO modules
> 14,000 tonnes of plastics

Environmental and financial concerns

MEMBRANE MANUFACTURING
Developing antifouling membranes

CIRCULAR ECONOMY IN MEMBRANE PROCESSES

MEMBRANE RE-USE
End-of-life membrane regeneration

MEMBRANE RECYCLING
Direct recycling
Indirect recycling

RESIDUAL WASTE
Energy recovery
Landfill disposal

OPTIMISED MEMBRANE USE
Integrated pretreatment
Membrane cleaning

**General aim of this work is...**
To investigate the direct recycling process as an alternative to the current waste management.

**Specific steps to achieve the goal within the life-Transformem project**

1. **Looking for** Spanish desalination plants that want to collaborate by donating end-of-life RO membranes.

2. End-of-life membrane **characterization**. What is the level of degradation? Which is the type of fouling found?

3. **Transformation process**. Scaling up laboratory results and selecting feasible membranes to be used at pilot scale.

   - **2014-2016**

4. **Validation of recycled membranes and lifespan**. Could they compete with commercial models?
   - Sea water as RO pretreatment
   - Brackish water (softening water)
   - Waste water as tertiary treatment

5. **Economical and financial study of the recycling process**

6. **Life cycle assessment**.

   - **2016-2018**

7. **Results dissemination**.

   - **2014-2018**
Among the rest of the presentation we will talk about membranes with diverse origins:

- RO membranes designed to treat seawater (SWM) → Recycled: RSWM
- RO membranes designed to treat brackish water (BWM) → Recycled: RBWM
Membrane autopsy

Fouling identification
Membrane weight.
Visual inspection.
Thermo gravimetric analysis (TGA). Inorganic and organic percentage identification.
Inductively coupled plasma mass spectrometry (ICP). Inorganic elements composition (screening)

Microbiological identification
- *E. coli*
- Other coliforms
- *Clostridium*
- *Pseudomonas*
- Aerobic bacteria
- Molds
- Yeast

Recycled membrane surface characterization
Contact angle
SEM - Feret Diameter
ATR-FTIR
MWCO
Evaluation of membrane performance with BW

- End-of-life RO membranes
- Recycled membranes

**Permeability**

$$\text{Permeability} = \frac{W}{\rho \cdot t \cdot S \cdot \text{TMP}} \text{ or } \frac{Q}{S \cdot \text{TMP}}$$

- $W$ is the permeate weight (g)
- $\rho$ is the solution density, assumed 1,000 g/L
- $t$ is time (h)
- $S$ is the active membrane surface (m$^2$)
- $\text{TMP}$ is the transmembrane pressure (bar)
- $Q$ is the permeate flow (L/h)
- $S$ is the active membrane surface (m$^2$)

**Rejection coefficients**

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100$$

- $C_p$: salt concentration in permeate stream (ppm)
- $C_f$: salt concentration in feed stream (ppm)
Conceptual scheme of the controlled degradation of the polyamide active layer based on the low resistance of polyamide to oxidant reagents
Recycling process

**Passive transformation plant**

LOW COST ALTERNATIVE

- 6 hosting vertically RO membrane structure
- Opaque cylindrical polypropylene container
- Low pressure pumps
- Manually control parameter (pH, redox, conductivity)
- Storage container for chemical solutions

**Transformation by static membrane immersion**
Recycling process

**Active** transformation plant

- 2 hosting horizontally RO membrane pressure vessel
- Low pressure pumps
- Automatically control parameter (pH, redox, conductivity)
- Storage container for chemical solutions

Transformation by circulating solution through the membranes
Case A) Reuse of NF recycled membranes for brackish water treatment

Permeability and rejection of 12 recycled membranes (NF) were evaluated using 2 real pressure vessel tubes within Cuevas del Almanzora desalination plant. Real operation and comparison of recycled performance with OI membranes.

<table>
<thead>
<tr>
<th>Real brackish water</th>
<th>Water quality parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>7.0 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Cl (ppm)</td>
<td>2,074 ± 404</td>
</tr>
<tr>
<td>EC (μS/cm)</td>
<td>10,280 ± 1,226</td>
</tr>
<tr>
<td>TC (ppm)</td>
<td>55 ± 10</td>
</tr>
<tr>
<td>IC (ppm)</td>
<td>53 ± 9</td>
</tr>
<tr>
<td>Na⁺ (ppm)</td>
<td>1,434 ± 43</td>
</tr>
<tr>
<td>SO₄²⁻ (ppm)</td>
<td>2,345 ± 381</td>
</tr>
<tr>
<td>NO₃⁻ (ppm)</td>
<td>147 ± 22</td>
</tr>
<tr>
<td>K⁺ (ppm)</td>
<td>43 ± 8</td>
</tr>
<tr>
<td>Cl⁻ (ppm)</td>
<td>2,345 ± 381</td>
</tr>
<tr>
<td>Ca²⁺ (ppm)</td>
<td>434 ± 62</td>
</tr>
<tr>
<td>Mg²⁺ (ppm)</td>
<td>364 ± 62</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Desalination plant (RO)</th>
<th>TMP (bar)</th>
<th>T(°C)</th>
<th>Conductivity (mS/cm)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube 1: RSWM</td>
<td>14.0 ± 0.6</td>
<td>21.3 ± 0.4</td>
<td>10.9 ± 0.5</td>
<td>50%</td>
</tr>
<tr>
<td>Tube 2: RBWM</td>
<td>6.3 ± 0.9</td>
<td>21.1 ± 0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Reuse of recycled membranes

Case B) Reuse of UF recycled membranes for seawater treatment

- Adaptation of the active transformation plant and installed at Mutxamel /El Campello desalination plant (ACUAMED)

- Use of seawater to simulate RO pretreatment using RBWM

<table>
<thead>
<tr>
<th></th>
<th>TMP (bar)</th>
<th>Conductivity (mS/cm)</th>
<th>Permeate flow (LMH)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBWM (1 module)</td>
<td>0.48-0.55</td>
<td>56.2</td>
<td>30</td>
<td>90-100%</td>
</tr>
</tbody>
</table>

- Filtering and cleaning cycles using UF water
Case C) Reuse of UF recycled membranes for synthetic urban wastewater treatment (laboratory scale)

Synthetic urban wastewater solution (SUWW)

<table>
<thead>
<tr>
<th>Analytical parameter</th>
<th>SUWW</th>
<th>UF validation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.8 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td>1,135 ± 101</td>
<td></td>
</tr>
<tr>
<td>Organic matter (ppm)</td>
<td>1,051 ± 171 (BSA)</td>
<td></td>
</tr>
<tr>
<td>E. Coli (FCU/100 mL)</td>
<td>$[10^5 – 10^7]$</td>
<td></td>
</tr>
</tbody>
</table>

Laboratory scale

Flat sheet membrane coupons (84 cm² active surface area)

- Filtering SUWW solution: 4h
- Filtering Milli-Q water: 1h
- Cleaning step using free chlorine:

Time (h)
PART I: End-of-life membrane characterization

**Membrane stock**
- >100 end-of-life RO membranes
- 14 desalination plants
- Diverse type of fouling

**Management route identification using:**
- Membrane weight
- Membrane performance
- Autopsy information

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<th>Direct reuse</th>
<th>Direct recycling</th>
<th>Other</th>
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<tr>
<td>RO</td>
<td>NF</td>
<td>UF</td>
</tr>
<tr>
<td>NF</td>
<td>UF</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UF</td>
<td>X</td>
</tr>
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</table>
Nanofiltration
Both methodologies require same concentration and exposure time to reach NF performance

Ultrafiltration
In case of SW membranes, fixing the concentration solution, higher exposure time is required using the passive methodology

(>3 –fold in case of seawater membranes)

Permeability (L · m⁻²·h⁻¹·bar⁻¹)
Range obtained from diverse models

<table>
<thead>
<tr>
<th>Performance</th>
<th>Recycled BWM</th>
<th>Recycled SWM</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF:</td>
<td>2 – 6</td>
<td>1 - 2</td>
</tr>
<tr>
<td>UF:</td>
<td>20 - 60</td>
<td>5 – 6</td>
</tr>
</tbody>
</table>
PART IV: reuse of recycled membranes

Case A) Reuse of NF recycled membranes for brackish water treatment

NF commercial rejection coefficients range
10-95% NaCl
50-99 % MgSO₄

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PART IV: reuse of recycled membranes

Case A) Reuse of NF recycled membranes for brackish water treatment

<table>
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<tr>
<th>Membranes</th>
<th>Cl⁻</th>
<th>NO₃</th>
<th>SO₄²⁻</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
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<tr>
<td>NF1 (commercial)</td>
<td>87,9</td>
<td>51,2</td>
<td>99,9</td>
<td>86,7</td>
<td>85,0</td>
<td>99,3</td>
<td>99,8</td>
<td>91,5</td>
<td>93,6</td>
</tr>
<tr>
<td>NF2 (commercial)</td>
<td>23,0</td>
<td>1,9</td>
<td>99,6</td>
<td>28,7</td>
<td>30,9</td>
<td>73,6</td>
<td>88,8</td>
<td>57,5</td>
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<td>97,1</td>
<td>88,2</td>
<td>99,0</td>
<td>96,5</td>
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<td>99,2</td>
<td>99,2</td>
<td>92,2</td>
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<td>Recycled: Tube 1 RSWM</td>
<td>83,3</td>
<td>56,6</td>
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<td>95,9</td>
<td>95,8</td>
<td>80,4</td>
<td>82,6</td>
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<tr>
<td>Recycled: Tube 2 RBWM</td>
<td>39,0</td>
<td>0,5</td>
<td>98,8</td>
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<td>48,6</td>
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![Graphs showing rejection values over time for different membranes and desalination plants.](image-url)
PART IV: reuse of recycled membranes

Case B) Reuse of UF recycled membranes for seawater treatment

**Constant permeate flow: 30 (L/m²·h)**

- 6 days operation filtering seawater
- Cleaning steps with diverse criteria
PART IV: reuse of recycled membranes

Case B) Reuse of UF recycled membranes for seawater treatment

<table>
<thead>
<tr>
<th></th>
<th>FEED</th>
<th>PERMEATE</th>
<th>REJECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS (mg/L)</td>
<td>1,1</td>
<td>0,4</td>
<td>64%</td>
</tr>
<tr>
<td>Turbidez (NTU)</td>
<td>0,71</td>
<td>0,12</td>
<td>83%</td>
</tr>
<tr>
<td>SDI (5 min)</td>
<td>15,43</td>
<td>1,76</td>
<td></td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td></td>
<td></td>
<td></td>
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PART IV: reuse of recycled membranes

Case C) Reuse of UF recycled membranes for synthetic urban waste water treatment (laboratory scale)

All recycled membranes showed similar or better rejection coefficients than UF commercial membrane, e.g.:
- BSA (> 96.7% R)
- *E. coli* bacteria (100% R in most of the cases)

However the recovery flux after applying diverse cleaning procedures was lower than in case of UF commercial membrane.
Does direct recycling processes work using NaClO?

- Membrane recycling is not a standard process
- Membrane recycling roadmap has been created and patented taking into account:
  i) RO membrane design.
  ii) End-of-life membrane rejection coefficients.
  iii) The effect of the combination of free chlorine concentration and exposure time.

Can recycled membranes be reused in water treatment?

a) Nanofiltration recycled membranes
- It was achieved intermediate performance between two NF commercial models
- Recycled membranes are showing stable performance after > 4 months real operation.

Recycled membranes could be reused to treat water for agriculture, for aquifer recharge, in the first steps of RO process, as sacrifices membranes.. etc..

b) Ultrafiltration recycled membranes apparently could potentially be reused in SW and WW treatment
- Good behavior to eliminate suspended solids and E.coli bacteria
- Probably less cleaning efficiency than a commercial UF model
- It has to compete with the commercial UF facilities (not standard and usually do not use pressure vessels).
THANK YOU

Acknowledgments

To IMDEA Water membrane technology group.
Staff from Cuevas de Almanzora desalination plant (Valoriza Agua management) to provide technical help.
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Website: http://www.life-transformem.eu/

