Anti-(bio)fouling composite membranes by Polyacrylic acid/Poly(vinyl alcohol) electrospun layer

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Introduction

NEW WATER RESOURCES

- FAST GROWING GLOBAL POPULATION
- INCREASING WATER DEMAND

MEMBRANE TECHNOLOGY

ULTRAFILTRATION

WASTEWATER TREATMENT

PRETREATMENT OF SEA WATER

INCREASE WATER RESOURCES
**Introduction**

<table>
<thead>
<tr>
<th>POLYSULFONE</th>
</tr>
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<tbody>
<tr>
<td>- High <strong>thermal</strong> resistance</td>
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<tr>
<td>- Good <strong>chemical</strong> stabilities</td>
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<td>- High <strong>mechanical</strong> characteristic</td>
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<td>- <strong>Hydrophobicity</strong></td>
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<td>Tendency to suffer the deposition of <strong>fouling</strong> and <strong>biofouling</strong></td>
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**Fouling** occur due to the adsorption and deposition of hydrophobic non-polar solutes.

**Biofouling** refers to the adhesion and accumulation of microorganism.

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EAWAG, aquatic research
Introduction

POLYSULFONE

- High thermal resistance
- Good chemical stabilities
- High mechanical characteristic

- Hydrophobicity
  Tendency to suffer the deposition of fouling and biofouling

- Non-optimal permeation flux
- Higher energy demand
- Irreversible membrane damage
- Shorter membrane lifetime

Fouling occur due to the adsorption and deposition of hydrophobic non-polar solutes

Biofouling refers to the adhesion and accumulation of microorganism
Introduction

Several strategies

- **PVP (PoliVinyl Pyrrolidone)**
  - Increase the porous size and porosity of membrane skin layer
  - Reduce the tendency of fouling formation

- **PolyAcrylic Acid (PAA) / PolyVinyl Alcohol (PVA)**
  - Exhibit an important antibacterial activity due to the chelation of divalent cations from prokaryotic cells
  - Avoid the bacterial attachment of membrane’s surface.

- **Blending of hydrophilic materials**
  - Electrospun nanofibers
Objetive

This work reports the use of a layer of PAA-PVA electrospun fibers for the surface functionalization of a PSU ultrafiltration membrane with an increased resistant to fouling and biofouling.
Material and methods.

- **Membrane preparation**

  **Polymeric solution**
  - PsU (15%)
  - PvP (5%)
  - 1-Methyl-2-Pyrrolidone

  **Polymeric solution**
  - PAA (8%)
  - PVA (15%)
  - PAA-PVA (80:20)

  **Technique**

  - Ultrafiltration
  - Membrane
  - Nanofibers
  - Composite Membrane

  Soft Matter, 2013, 9, 5557
  N.Zhu/X.Chen.2013, chapter 12
Material and methods.

- Membrane Characterization
  - Morphology
    - SEM (Scanning Electron Microscopy)
  - Hydrophilicity
    - Static Water Contact Angle (WCA)
  - Membrane permeability
    - Cross/Flow module (1-4 bar range)
Material and methods.

- **Organic Antifouling studies**

  \[ Flux\ ratio\ (\%) = \left( \frac{J_w^f}{J_w^i} \right) \times 100 \]

  - \( J_w^i \): Pure water flux before BSA filtration
  - \( J_w^f \): Pure water flux after BSA filtration

  \[ Rejection: \ R(\%) = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \]

  - \( C_p \) is the solute concentration in the permeate
  - \( C_f \) is the solute concentration in the feed

BSA Solution (Bovine serum Albumin)

- 1 g/L in 0.1 M of PBS (Phosphate physiological saline)
  - pH: 7
Material and methods.

- Antibiofouling Behaviour

Dynamic conditions

**Bacterial culture**

- **S. Aureus**
  - 10⁶ cells/mL
  - 48 h - 2 bar

**Membranes**

- PAA.PVA(8) / PsU ultrafiltration membrane
- Neat polysulfone membrane

**Dynamic conditions**

- **CFU** (Colonies Forming units)
  - 36 °C - 48 h

- **SEM micrographs**
  - 36 °C - 20 h
  - Soybean Casein Digest Broth with Lecithin and Polysorbate

- **Confocal images**
  - Live/Dead dye
    - SYTO9 (Propidium Iodide)
    - PI

- **Viable cells**
- **Non-Viable cells**
## Results and discussion

### Physicochemical properties

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Weight density of fibers (mg/cm²)</th>
<th>Water contact angle (WCA)</th>
<th>Permeability (LMH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU</td>
<td>-</td>
<td>65.3 ± 3.1</td>
<td>133.1 ± 3.2</td>
</tr>
<tr>
<td>PAA-PVA[1]@PSU</td>
<td>0.03 ± 0.01</td>
<td>65.5 ± 0.9</td>
<td>138.3 ± 1.4</td>
</tr>
<tr>
<td>PAA-PVA[2]@PSU</td>
<td>0.04 ± 0.02</td>
<td>62.6 ± 1.3</td>
<td>139.6 ± 2.2</td>
</tr>
<tr>
<td>PAA-PVA[3]@PSU</td>
<td>0.05 ± 0.01</td>
<td>58.8 ± 1.4</td>
<td>140.8 ± 1.9</td>
</tr>
<tr>
<td>PAA-PVA[4]@PSU</td>
<td>0.12 ± 0.03</td>
<td>55.6 ± 1.1</td>
<td>142.3 ± 0.8</td>
</tr>
<tr>
<td>PAA-PVA[5]@PSU</td>
<td>0.46 ± 0.07</td>
<td>52.1 ± 4.2</td>
<td>145.9 ± 2.4</td>
</tr>
<tr>
<td>PAA-PVA[6]@PSU</td>
<td>0.83 ± 0.19</td>
<td>48.2 ± 3.3</td>
<td>148.5 ± 1.8</td>
</tr>
<tr>
<td>PAA-PVA[7]@PSU</td>
<td>1.18 ± 0.28</td>
<td>43.8 ± 0.9</td>
<td>151.3 ± 1.4</td>
</tr>
<tr>
<td>PAA-PVA[8]@PSU</td>
<td>1.85 ± 0.32</td>
<td>39.0 ± 1.7</td>
<td>153.7 ± 0.9</td>
</tr>
</tbody>
</table>
Results and discussion

- Membrane morphology

Upper view

<table>
<thead>
<tr>
<th></th>
<th>Neat PsU</th>
<th>0.46 mg/cm²</th>
<th>1.85 mg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03 mg/cm²</td>
<td><img src="TM-1000_2789_L.png" alt="Image" /></td>
<td><img src="TM-1000_2781_L.png" alt="Image" /></td>
<td><img src="TM-1000_3148_L.png" alt="Image" /></td>
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<td><img src="TM-1000_3148_L.png" alt="Image" /></td>
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Cross-section
Results and discussion

- Organic - antifouling studies

BSA Solution (Bovine serum Albumin)

Flux recovery ratios

Protein rejection

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Rejection (%)</th>
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<tr>
<td>PsU</td>
<td>94 ± 2</td>
</tr>
<tr>
<td>PAA.PVA(8)_PsU_MEM</td>
<td>91 ± 3</td>
</tr>
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Flux Ratio (%)

- PsU: 29.40%
- PAA.PVA(8)_PsU: 80.20%
- PsU: 50.8%
Results and discussion

• Antibiofouling behaviour

**Dynamic test**: Colony Forming Units (CFU /mg membrane)

**Membranes**
- 1.85 mg/cm² PAA.PVA / PsU ultrafiltration membrane
- Neat polysulfone membrane

*S.aureus*

Viable bacterial in the circulating liquid

CFU membrane surface
Results and discussion

- **Antibiofouling behaviour**

**Dynamic test**: SEM micrographs and Confocal images

PsU  PVA.PAA(8)PsU

SEM images

Live / Dead Confocal images
Results and discussion

- **Antibiofouling behaviour**

**PAA.PVA Antimicrobial activity**

PAA-PVA nanofibres

Preferred cation for stabilizing the cell wall of gram-positive bacteria

Binding affinity of calcium

Peptidoglycan
Teichoic acid

Ca\(^{2+}\)

PAA

LOWER

HIGHER
The results demonstrated the feasibility of using electrospun layers as top coatings for ultrafiltration membranes in order to improve permeability, fouling behavior and to impart antimicrobial functionality.
THANK YOU FOR YOUR ATTENTION