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

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Universidad de Alcalá

Introduction

NEW WATER RESOURCES

FAST GROWING
GLOBAL POPULATION

INCREASING
WATER DEMAND

MEMBRANE TECHNOLOGY

ULTRAFILTRATION

WASTEWATER TREATMENT

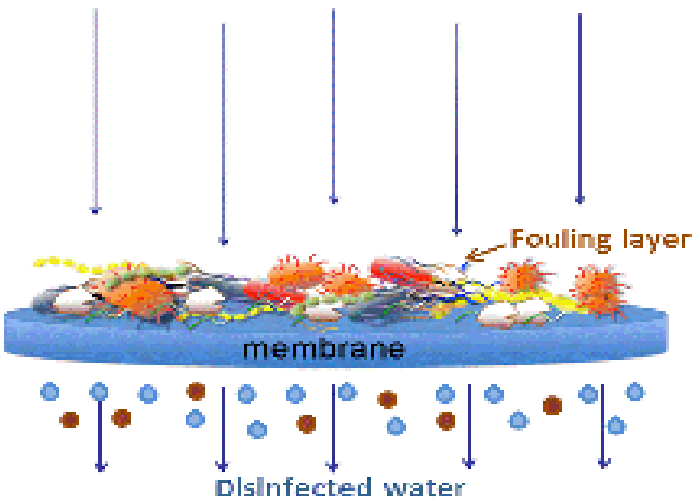
PRETREATMENT OF SEA WATER

INCREASE

WATER RESOURCES

Introduction

POLYSULFONE	
- High **thermal** resistance - Good **chemical** stabilities - High **mechanical** characteristic	**- Hydrophobicity** ⬇ Tendency to suffer the deposition of **fouling** and **biofouling**



EAWAG, aquatic research

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

Biofouling refers to the adhesion and accumulation of microorganism

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

Blending of hydrophilic materials

PVP (PoliVinyl Pyrrolidone)

Increase the porous size and porosity of membrane skin layer

Reduce the tendency of fouling formation

Electrospun nanofibers

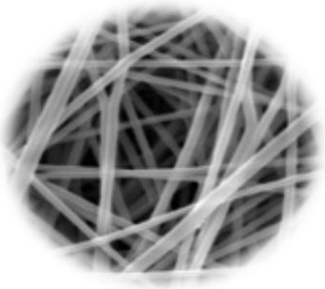
PolyAcrylic Acid (PAA) / PolyVinyl Alcohol (PVA)

Exhibit an important antibacterial activity due to the chelation of divalent cations from prokaryotic cells

Avoid the bacterial attachment of membrane's surface.

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**

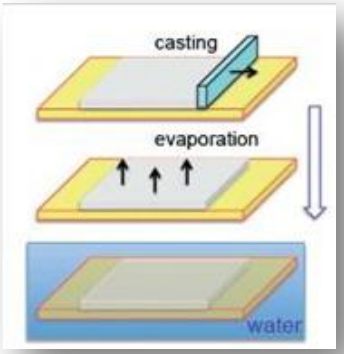
Polymeric solution

PsU (15%)

PvP (5%)

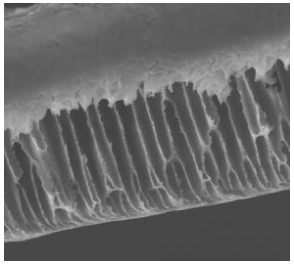
1-Methyl-2-Pyrrolidone

Technique



Soft Matter, 2013, 9, 5557

Ultrafiltration Membrane



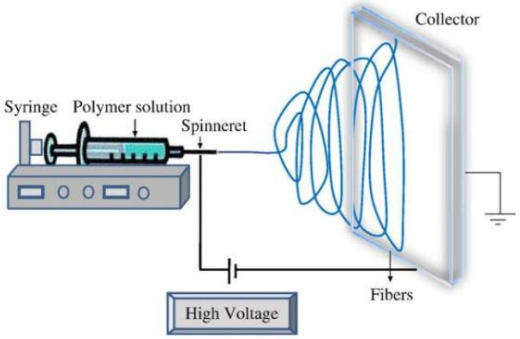
Polymeric solution

PAA (8%)

PVA (15%)

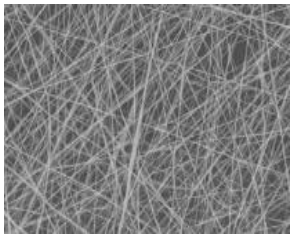
PAA-PVA (80:20)

Technique



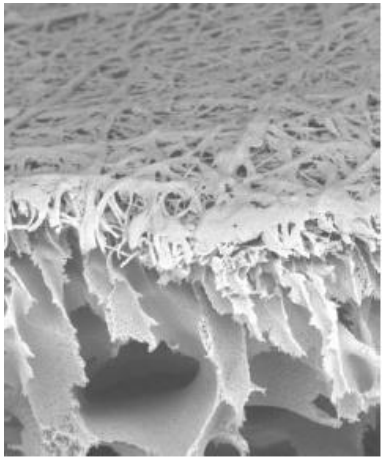
N.Zhu/X.Chen.2013, chapter 12

Nanofibers



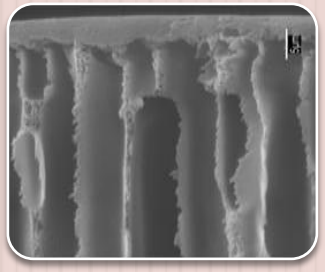
Crosslinking esterification

Composite Membrane



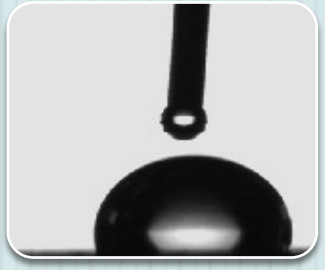
Material and methods.

- **Membrane Characterization**



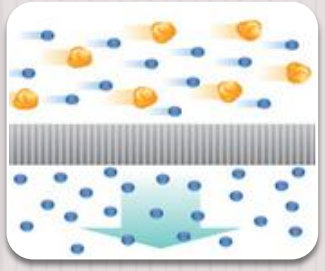
Morphology

SEM (Scanning Electron Microscopy)



Hydrophilicity

Static Water Contact Angle (WCA)



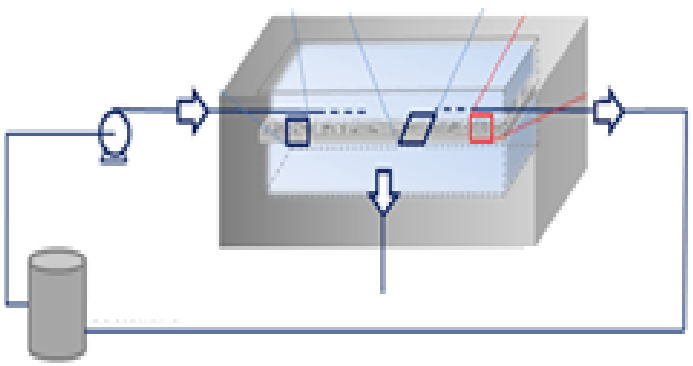
Membrane permeability

Cross/Flow module (1-4 bar range)

Material and methods.

- **Organic Antifouling studies**

Cross-flow module



BSA Solution

(Bovine serum Albumin)

1 g/L in 0.1 M of PBS
(Phosphate physiological saline)
pH:7

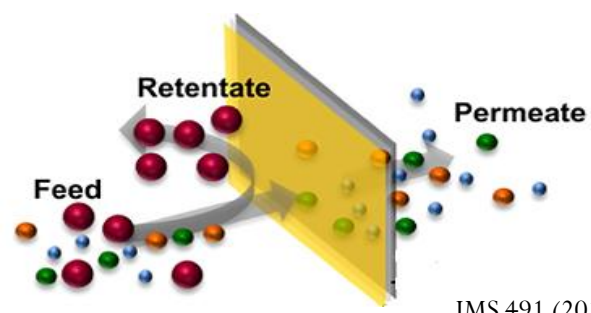
$$Flux\ ratio(\%) = \left(\frac{J_w^f}{J_w^i}\right) \times 100$$

Jw^i : Pure water flux before BSA filtration
$\mathbf{Jw^f}$: Pure water flux after BSA filtration

Water flux clean membranes → 1h BSA filtration → Washed water → Water flux after BSA solution

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

Cp is the solute concentration in the permeate
Cf is the solute concentration in the feed



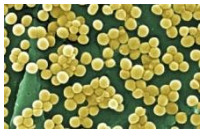
JMS 491 (2015) 132–137

Material and methods.

- **Antibiofouling Behaviour**

Dynamic conditions

Bacterial culture

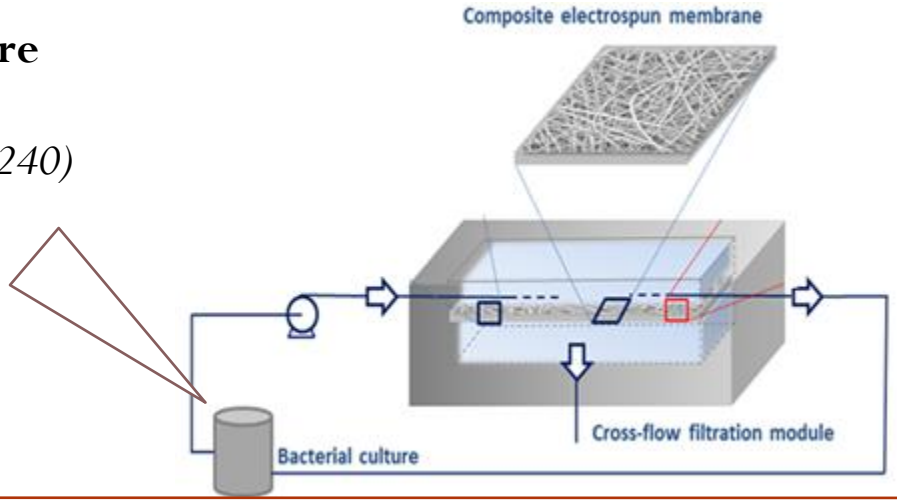


(CECT 240)

S.Aureus

10^6 cells/mL

48 h - 2 bar



Membranes

PAA.PVA(8) / PsU ultrafiltration membrane

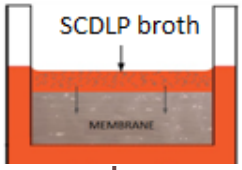
Neat polysulfone membrane

➢ **CFU** (Colonies Forming units)

36 º C - 48 h

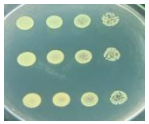
Membrane

36 º C - 20 h



Soybean **C**asein **D**igest **B**roth with **L**ecithin and **P**olysorbate

10 µL



S.aureus

➢ **SEM** micrographs

Membranes

Fixed + Dehydrated

Acetone

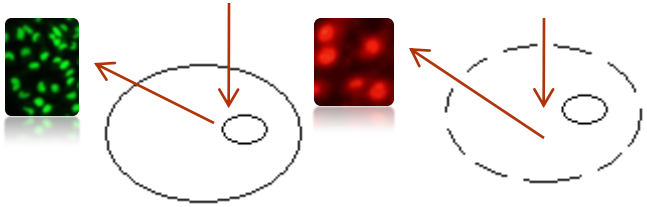
Ethanol

➢ **Confocal** images

Live/Dead dye

SYTO9

PI (PropidiumIodide)

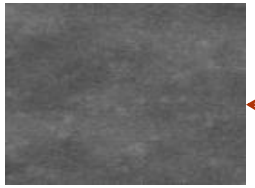


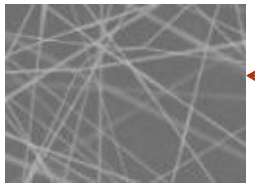
Viable cells

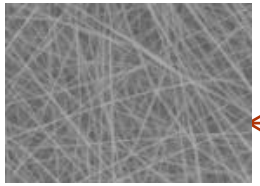
Non-Viable cells

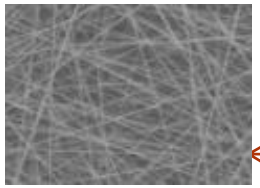
Results and discussion

- **Physicochemical properties**









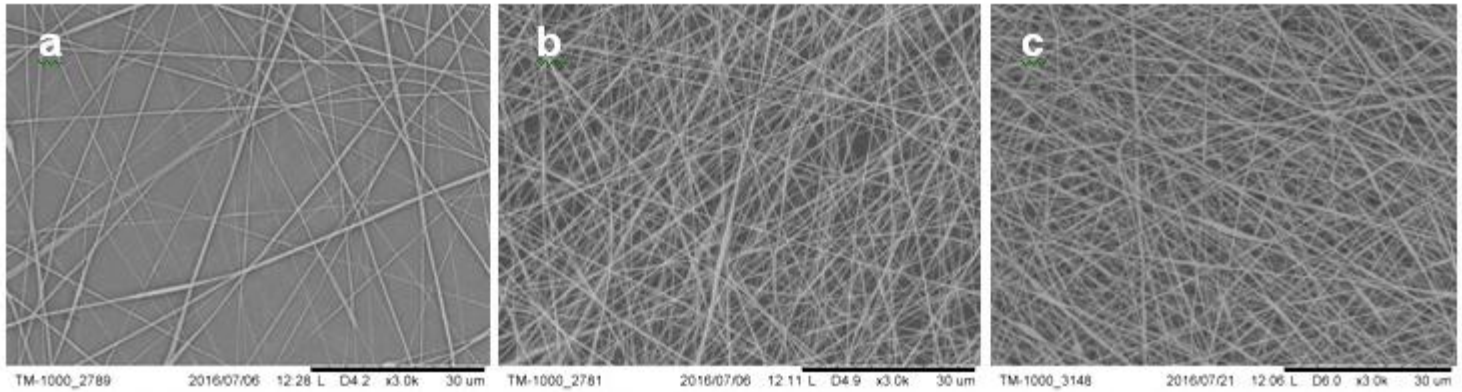
Membrane	Weight density of fibers (mg/cm2)	Water contact angle (WCA)	Permeability (LMH)
PSU	-	65.3 ± 3.1	133.1 ± 3.2
PAA-PVA[1]@PSU	0.03±0.01	65.5 ± 0.9	138.3 ± 1.4
PAA-PVA[2]@PSU	0.04±0.02	62.6 ± 1.3	139.6 ± 2.2
PAA-PVA[3]@PSU	0.05± 0.01	58.8 ± 1.4	140.8 ± 1.9
PAA-PVA[4]@PSU	0.12 ± 0.03	55.6 ± 1.1	142.3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

Results and discussion

- **Membrane morphology**

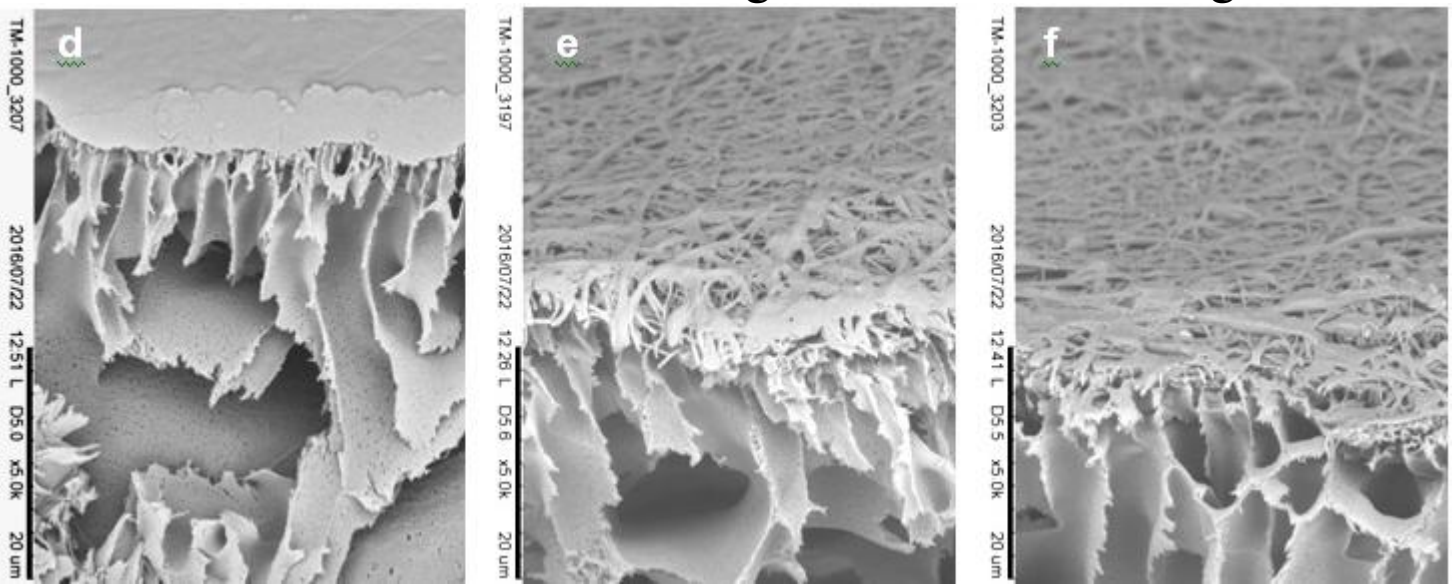
Upper view

0.03 mg/ cm^2 **0.46 mg/ cm^2** **1.85 mg/ cm^2**



Cross-section

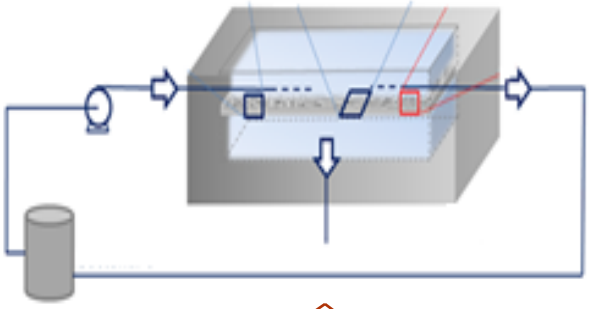
Neat PsU **0.46 mg/ cm^2** **1.85 mg/ cm^2**



Results and discussion

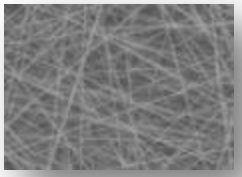
- **Organic - antifouling studies**

BSA Solution
(Bovine serum Albumin)

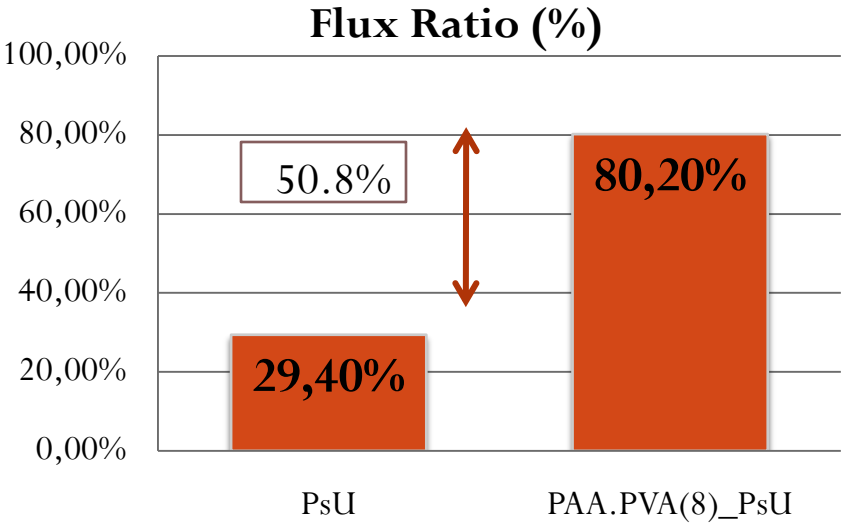


PsU membrane

PAA.PVA(8)_PsU. membrane



Flux recovery ratios



Protein rejection

MEMBRANE	REJECTION (%)
PsU	94 ± 2
PAA.PVA(8)_PsU	91 ± 3

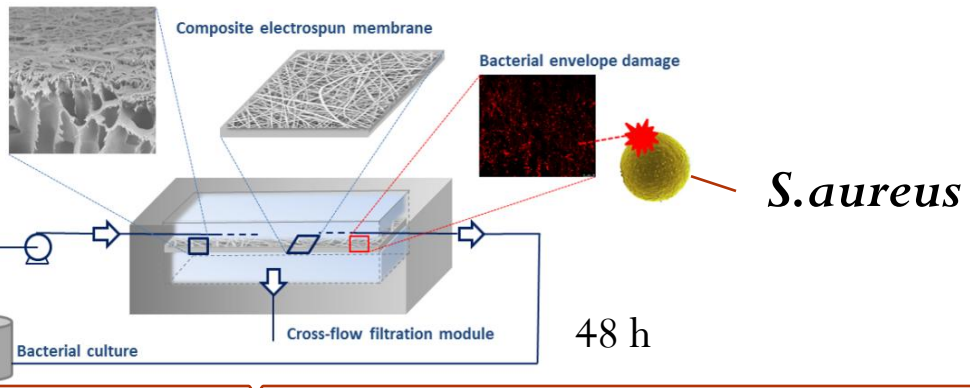
Results and discussion

- **Antibiofouling behaviour**

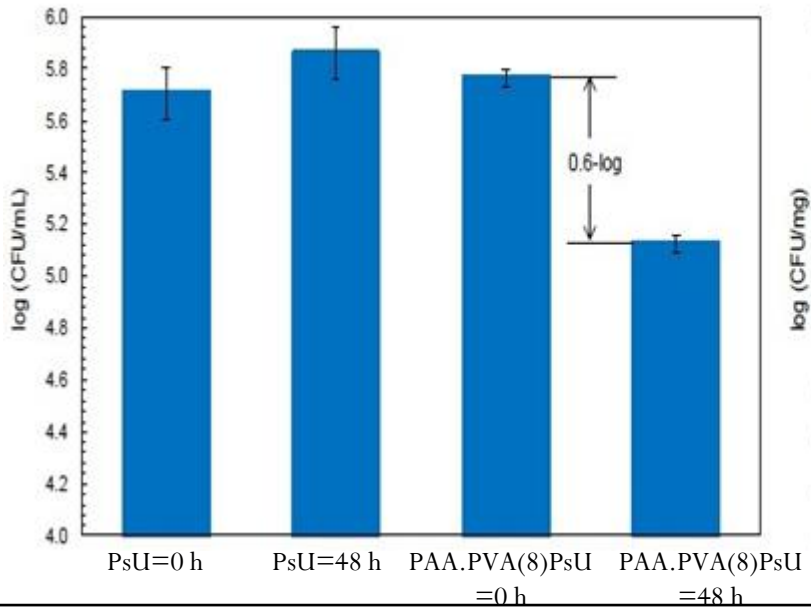
Dynamic test : Colony Forming Units (CFU /mg membrane)

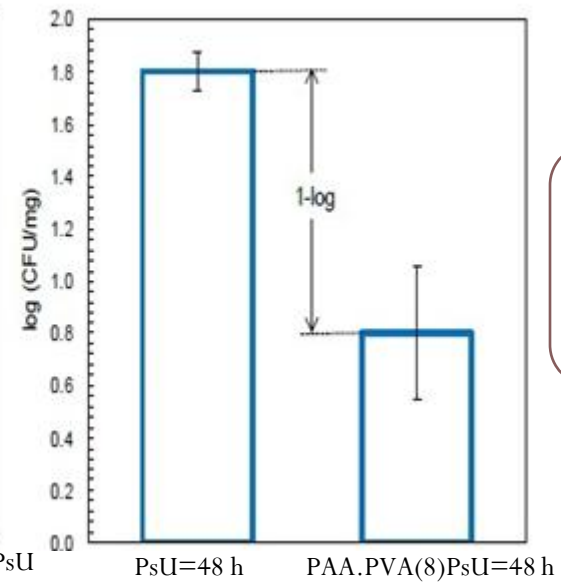
Membranes

- 1.85 mg/ cm^2 PAA.PVA / PsU ultrafiltration membrane
- Neat polysulfone membrane



Viable bacterial in the circulating liquid



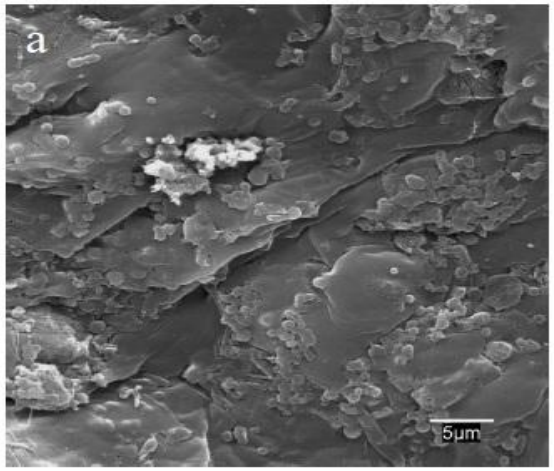
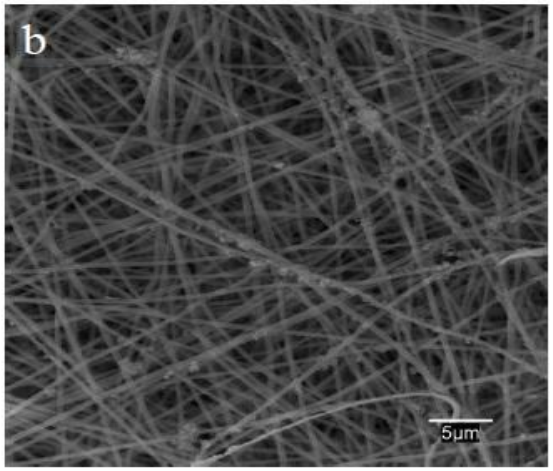
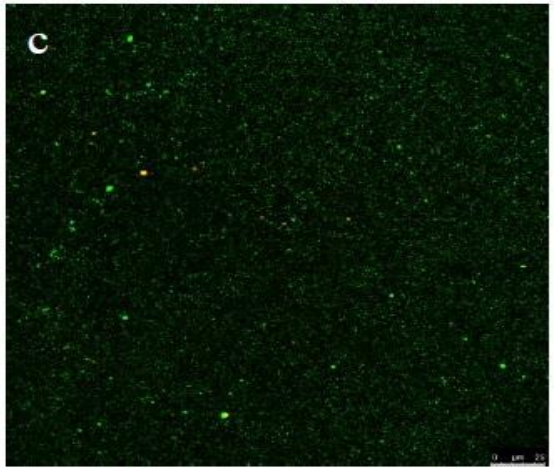
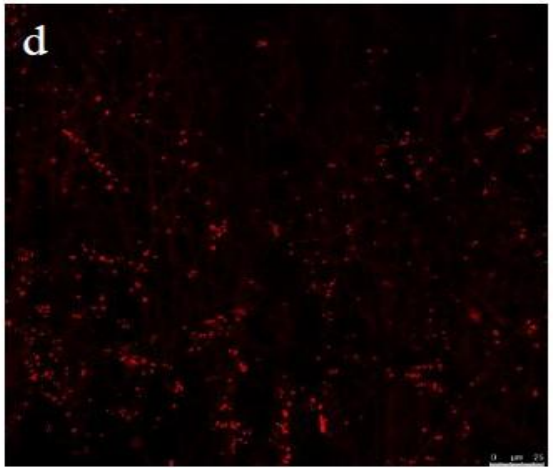


CFU membrane surface

Results and discussion

- **Antibiofouling behaviour**

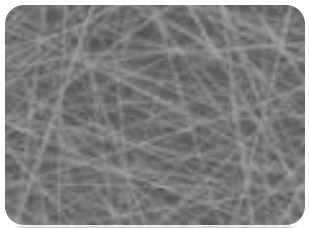
Dynamic test : SEM micrographs and Confocal images

	PsU	PVA.PAA(8)PsU
SEM images		
Live / Dead Confocal images		

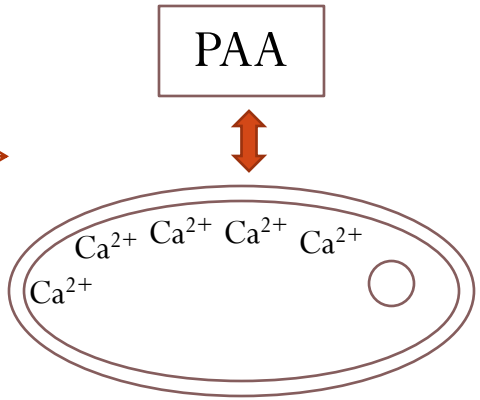
Results and discussion

- **Antibiofouling behaviour**

PAA.PVA Antimicrobial activity

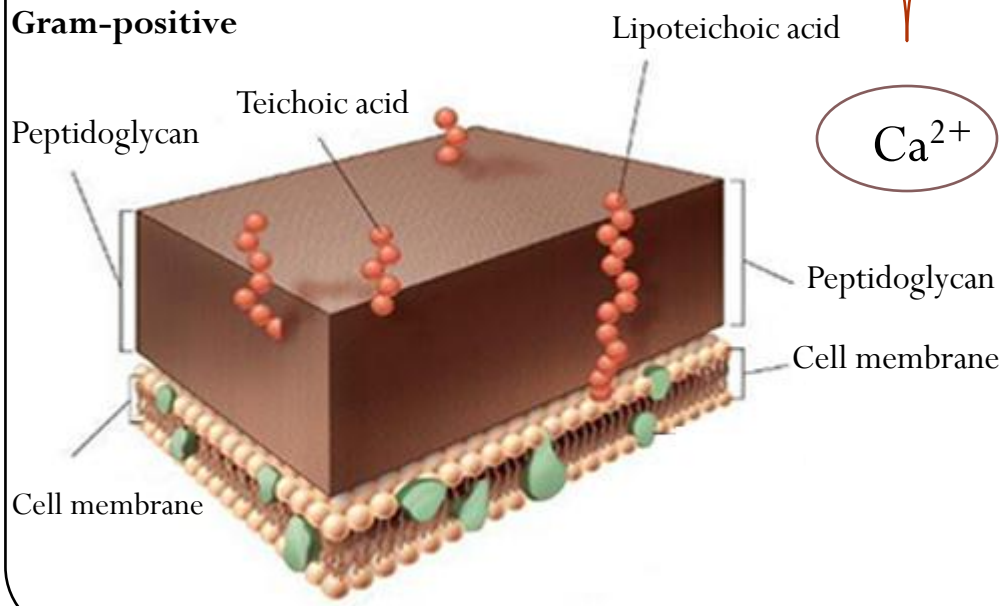


PAA-PVA nanofibres



Ca-PAA
Complexes

Gram-positive



McGram-Hill Companies imagen.

Ca^{2+}

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

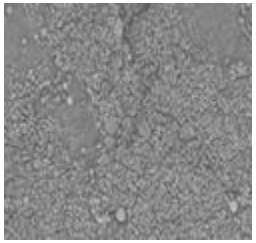
↓

Binding affinity of calcium

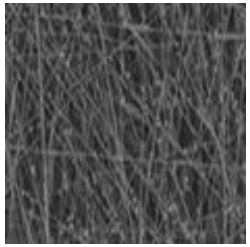
Peptidoglycan Teichoic acid	PAA
LOWER	HIGHER

Conclusion

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**.



PAA.PVA nanofibers →



THANK YOU FOR YOUR ATTENTION

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