

POLITECNICO DI TORINO

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**Surface modification of aromatic polyamide
membranes with polyols for improved
antifouling properties**



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RIASSUNTO IN ITALIANO

Modifica della superficie delle membrane in poliammide aromatica attraverso polialcoli per ottenere migliori proprietà anti-sporcamento

Introduzione

Uno dei maggiori problemi mondiali per l'umanità e la società dei nostri giorni è la scarsità d'acqua: infatti, già oltre un terzo della popolazione mondiale soffre la carenza di risorse idriche e, secondo alcune previsioni, dal 2025 questo dato potrebbe crescere e arrivare ai due terzi delle persone sulla Terra. Inoltre, la domanda d'acqua cresce anno dopo anno, a causa della crescita della popolazione, dello sviluppo umano e dell'industrializzazione, in particolare nei paesi con economie in via di sviluppo.

La soluzione potrebbe essere parzialmente trovata nell'acqua di mare, in quanto costituisce il 97.5% dell'acqua totale sul nostro pianeta. Dunque, sarebbe necessario sviluppare una tecnologia che abbia come obiettivo la desalinizzazione dell'acqua in maniera sostenibile. Tra le soluzioni più concrete per affrontare questa sfida, ci sono le membrane artificiali: infatti, sono già disponibili sul mercato una grande varietà di membrane sintetiche. Le membrane più utilizzate nei processi di separazione hanno una struttura polimerica e vengono classificate in base alla composizione chimica della superficie o del resto della membrana, morfologia e metodologia di preparazione. Invece, un processo di separazione a membrana è definito dalle proprietà chimiche e fisiche della membrana sintetica, la natura dei contaminanti rimossi e anche dalla forza spingente, che il più delle volte è un gradiente di pressione. Le ottime performance e il relativo basso costo hanno favorito il mercato delle membrane polimeriche. I polimeri più utilizzati per questo scopo sono:

polietilene, polipropilene, poliammide, polisulfone, acetato di cellulosa, nitrocellulosa e esteri misti di cellulosa.

In questa tesi lavoreremo con le membrane di nanofiltrazione (NF). La nanofiltrazione è definita come “il processo a cavallo tra l’ultrafiltrazione e l’osmosi inversa” ed è una tecnologia che si sta sviluppando velocemente negli ultimi anni. Una membrana NF polimerica ha un diametro nominale dei pori di circa 1 nm (Fig. 1) e un range MWCO tra 200 e 1000 Da. I processi di nanofiltrazione sono ampiamente utilizzati per l’addolcimento dell’acqua e ha trovato le sue maggiori applicazioni nella rimozione di materie organiche naturali, inquinanti e ioni divalenti idratati, per questo il suo mercato sta aumentando vertiginosamente. Tra i materiali disponibili, la poliammide (PA) è il più utilizzato per la fabbricazione di membrane polimeriche per l’addolcimento dell’acqua, per la purificazione dell’acqua da cationi divalenti idratati (per esempio Mg^{2+} , Ca^{2+}) e da metalli pesanti. Le membrane composite a film sottile (TFC), composte da un sottile film in poliammide depositato su una membrana di supporto di ultrafiltrazione, sono regolarmente impiegate per i processi a membrana che necessitano un alto flusso di permeato e buone selettività. I principali vantaggi delle membrane NF sono le basse pressioni operative e l’alta produttività, se confrontata con quelle di osmosi inversa.

Uno dei maggiori problemi delle membrane poliammidiche è l’alta propensione al fouling (o sporcamiento), che è la principale causa del peggioramento della performance ed è dovuto al deposito di sostanze sospese o dissolte sulla superficie attiva o all’interno dei pori. Gli sporcati sono presenti in tutte le acque da trattare e sono il principale ostacolo per la realizzazione di un processo NF performante nel lungo periodo. Il deposito degli sporcati sulla superficie esterna della membrana dipende fortemente dalle sue caratteristiche chimiche e fisiche, dunque uno dei modi

per ridurre il fouling può essere la modifica (chimica o fisica) della superficie. I parametri che più influenzano le proprietà antifouling sono l'idrofilicità, la rugosità e la carica della superficie della membrana. Tra le principali tecniche per modificare questi parametri, è ampiamente riconosciuta la funzionalizzazione attraverso il grafting di altre molecole sulla superficie della membrana. Per mezzo di questa tecnica, in questo studio si sono modificate le proprietà fisico-chimiche della superficie poliammidica della membrana. In particolare, quando il fouling è dovuto a delle sostanze organiche, la soluzione più comune è diminuire la loro deposizione legando delle molecole idrofile alla superficie della membrana.

Più specificatamente, abbiamo funzionalizzato membrane PA NF attraverso il grafting di 3-amino-1,2-propandiolo (APD) o del suo enantiomero (R)-3-amino-1,2-propandiolo sulla loro superficie per aumentare il numero di gruppi ossidrilici e aumentare così l'idrofilicità. Attraverso vari esperimenti si sono valutate le proprietà anti-sporcamento utilizzando alginato di sodio (SA) come modello di sporcante. Dunque, si è anche testato se la chiralità della molecola potesse influenzare i risultati e il tutto è stato confrontato con i risultati ottenuti con la membrana commerciale NF270. Per dimostrare l'esito positivo della funzionalizzazione, le superfici delle membrane sono state caratterizzate attraverso varie analisi suggerite in letteratura: microscopio elettronico a scansione (SEM), microscopio a forza atomica (AFM), spettroscopia IR in trasformata di Fourier (ATR-FTIR), angolo di contatto e l'analisi del potenziale zeta.

Materiali e metodi

Per il lavoro di questa tesi sono state utilizzate sia delle membrane NF commerciali (NF270, FilmTec™ Dow Chem. Company, USA) sia delle membrane NF realizzate in laboratorio, attraverso la polimerizzazione sequenziale interfacciale (SIP), usando

come supporto una membrana di ultrafiltrazione in polisulfone con un MWCO di circa 20000 g/mol, acquistata da Nanostone Water, USA. Su quest'ultima, si è sintetizzata, attraverso una reazione di policondensazione, la poliammide con piperazina (PIP) e cloruro di trimesoile (TMC) (Fig. 2). Le realizzazioni delle membrane sono state condotte a una temperatura di 25 ± 1 °C. Come primo step, il supporto bagnato di polisulfone è stato ricoperto da una soluzione acquosa di PIP 0.25% (w/v) per 120 s. La PIP in eccesso è stata rimossa per mezzo di una corrente d'aria indirizzata parallelamente alla superficie della membrana. Successivamente, la membrana è stata immersa in una soluzione di TMC 0.1% (w/v) in n-esano per 60 s, per poi essere immersa in acqua deionizzata e trattata in forno per 120 s a 80 °C. Infine, le membrane sono state conservate in acqua ultra pura a 4 °C. Si è poi proceduto alla funzionalizzazione. Alcune membrane non sono state poste al processo di funzionalizzazione per avere un mezzo di comparazione e sono state chiamate membrane “control”. Lo step per la funzionalizzazione consisteva nell'immergere la membrana in una soluzione acquosa contenente APD o (R)-APD, a differenti concentrazioni, cosicché i gruppi -COOH della poliammide e i gruppi -NH₂ degli ammino-alcoli si legassero, attraverso una reazione di policondensazione (Fig. 3). Le concentrazioni testate erano 0.4% (w/v) e 0.5% (w/v) per entrambi i casi. APD e (R)-APD sono molecole con differente chiralità dello stesso composto. Poi anch'esse sono state conservate in acqua ultra pura a 4°C.

Per poi valutare la permeabilità e la rejection delle membrane è stato usato un sistema a flusso tangente (cross-flow) (Fig. 4), che comprendeva una cella per la membrana testata con una superficie effettiva attiva di 0.00289 m². Ogni membrana veniva compattata a una pressione di 12 bar per 90 min usando acqua ultra pura come soluzione di alimentazione, fino a che il flusso di permeato non raggiungeva lo stato

stazionario. Successivamente, la pressione veniva abbassata a 10 bar e il flusso d'acqua pura è stato misurato nel tempo. Il permeato iniziale è stato dunque calcolato usando la seguente equazione:

$$J_i = \frac{V}{A \Delta t} \quad (1)$$

Dove J_i ($\text{L m}^{-2} \text{h}^{-1}$) è il flusso di permeato iniziale, V (L) è il volume del permeato, A (m^2) è l'area effettiva della membrana e Δt (h) è l'intervallo di tempo. Per misurare individualmente la rejection di vari sali (NaCl , Na_2SO_4 , MgSO_4 e CaCl_2), sono stati inseriti ogni qualvolta 1000 mg/L nel recipiente di alimentazione (feed tank). Dopo aver raggiunto un flusso stazionario, veniva misurata la concentrazione dei sali nel permeato attraverso un conduttivimetro (pHenomenal VWR MU 6100 H, VWR) utilizzando una correlazione concentrazione-conduttività precedentemente determinata. La rejection osservata è stata determinata attraverso la seguente equazione:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

Dove C_p (mg/L) è la concentrazione nel permeato e C_f (mg/L) è la concentrazione nell'alimentazione. Il protocollo utilizzato per caratterizzare il comportamento della membrana in presenza dello sporcante è il seguente: dopo la misurazione della permeabilità con acqua ultra pura, una soluzione acquosa di alginato di sodio è stato introdotto nel feed tank, per ottenere una concentrazione finale di SA pari a 0.250 g/L. La riduzione del flusso dovuta al deposito dell'alginato è stata misurata per 90 min, a

una pressione di 10 bar e a una temperatura di 25 °C. La perdita relativa di flusso è stata valutata attraverso la seguente equazione:

$$\text{Flux loss} = \frac{J_i - J_f}{J_i} \times 100\% \quad (3)$$

dove J_i ($\text{L m}^{-2} \text{h}^{-1}$) è il permeato iniziale e J_f ($\text{L m}^{-2} \text{h}^{-1}$) è il flusso dopo il fouling.

Risultati e discussione

La morfologia della superficie della membrana control non modificata e delle membrane è stata analizzata tramite SEM (HITACHI S-4800, Japan) e AFM (Nanoman, Bruker Instruments, USA). La morfologia e la rugosità sono parametri importanti per le membrane, che influenzano le interazioni tra la superficie della membrana e gli sporcanti. Fig. 5 e Fig. 6 presentano immagini rappresentative acquisite grazie al SEM e mettono in luce che lo strato sottile poliammidico misura 80 nm e che non ci sono significanti differenze tra la membrana control e le membrane modificate con APD o (R)-APD: ciò suggerisce che il grafting ha cambiato la chimica ma non la struttura fisica dello strato. Questo fenomeno rivela che non c'è stata reticolazione durante il processo di grafting. I valori quadratici medi (RMS) della rugosità sono presentati nella Tab. 1. Essi mostrano che non c'è grande differenza tra i parametri prima e dopo la funzionalizzazione, confermando che la morfologia è rimasta invariata. Le Fig. 7 e Fig. 8 presentano le SEM degli analoghi campioni di membrane dopo il trattamento con l'alginato di sodio. Lo spessore di sporcante formatosi ha raggiunto valori fino a 250 nm (fig. 7), mostrando che il fouling

rappresenta una resistenza aggiuntiva non trascurabile al flusso attraverso ogni membrana studiata. Per quanto riguarda i valori ricavati dall'AFM dopo il trattamento con l'alginato di sodio, l'unico che spicca è quello della membrana funzionalizzata con APD (16.31 ± 10.32 nm) mentre control e (R)-APD, rispettivamente 9.71 ± 3.04 nm e 7.49 ± 1.46 nm, hanno mantenuto livelli simili. Probabilmente, il campione della membrana APD aveva su di essa un sottile strato di sporcante, il quale si deposita in modo eterogeneo e casuale sulla membrana. Invece i campioni della membrana control e dell'(R)-APD facevano parte di una porzione di membrana con una quantità di fouling meno significativa.

La bagnabilità della superficie delle membrane è un parametro chiave di questo studio, infatti verificarne l'incremento significherebbe avere la prova che il grafting è avvenuto con successo e inoltre l'ipotesi di questo lavoro è che una bagnabilità superiore porta a minor sporcamento organico durante le operazioni. Lo strumento utilizzato per verificare ciò è Drop Shape Analyzer DSA100 (KRÜSS GmbH, Germany), che ha permesso di calcolare l'angolo di contatto tra una goccia d'acqua e la superficie della membrana. I risultati (Fig. 9 e Fig. 10) sono consistenti con le ipotesi iniziali: l'angolo di contatto della membrana control era 74° , per poi passare a 58° per le membrane con APD e 57° per le membrane con (R)-APD. Dunque, la bagnabilità è aumentata in modo evidente, fornendo la prova che la funzionalizzazione è avvenuta e ha avuto l'effetto sperato. In questo caso, è poco significante la differenza tra APD e (R)-APD.

I potenziali zeta della superficie delle varie membrane sono stati misurati al variare del pH, attraverso un analizzatore di potenziale (SurPass III, Anton Paar GmbH, Austria) con i campioni immersi in una soluzione 0.001 M KCl e i risultati sono mostrati nella Fig. 11. Questa analisi è utile per verificare se le funzionalizzazioni

possono aver alterato il potenziale della superficie della membrana, il quale è un parametro altamente importante, dato che la rejection dei sali nei processi NF non è dovuto esclusivamente all'effetto setaccio, ma dipende anche dall'effetto elettrostatico repulsivo. I valori dei potenziali delle membrane PA NF, in questo caso, si sono abbassati nei casi delle funzionalizzazioni. Considerando il pH neutro, dato che il pH delle soluzioni d'alimentazione è spesso circa neutro, è interessante notare come le funzionalizzate siano più negative della membrana control. Nello specifico, la più negativa risulta la membrana modificata con l'(R)-APD (-29.2 mV a pH neutro), suggerendo che una geometria molecolare differente potrebbe avere un effetto sulla densità esposta di cariche sulla superficie. Conoscendo già la carica della superficie della membrana e della soluzione d'alimentazione, è possibile prevedere le caratteristiche rettentive della membrana e per questo motivo ci si attende che la membrana funzionalizzata con (R)-APD possa rimuovere meglio gli anioni multivalenti, come ad esempio i solfati.

Sono stati ottenuti gli spettri FTIR delle membrane control, APD e (R)-APD attraverso lo strumento ATR-FTIR Nicolet iS50 FTIR Spectrometer (ThermoFisher, USA) per analizzare la struttura chimica della superficie della membrana, capire le proprietà della funzionalizzazione e esaminare le loro potenzialità anti-sporcamento. I risultati delle membrane prima del fouling sono presentati nella Fig. 12: in ogni campione analizzato sono presenti i tipici picchi delle poliammidi (1625 cm^{-1} e 1567 cm^{-1} , rispettivamente per i legami C=O e -CO-NH-). Non sono presenti i picchi tipici degli alcoli: probabilmente essi non appaiono a causa di una sovrapposizione tra i picchi dei gruppi ossidrilici ($3200 - 3550\text{ cm}^{-1}$) e quelli dell'acqua (umidità) sulla superficie ($3100 - 3700\text{ cm}^{-1}$). Analizzando invece la Fig. 13, che presenta gli spettri delle membrane dopo il trattamento con l'alginato di sodio, l'unica differenza sta in

un picco della membrana control. Questo picco nella membrana control sporcata (Fig. 14) appare a 1417 cm^{-1} e può essere attribuito al legame -COONa, indicando la presenza dell'alginato di sodio. Questo picco, assente o trascurabile nelle membrane funzionalizzate, può suggerire una maggior presenza di sporcante nella superficie della membrana non modificata.

In termini di performance di trasporto, è stato immediatamente evidente il miglioramento del flusso di permeato (calcolato con l'equazione (1)) delle membrane funzionalizzate, in confronto alla membrana control, che ha raggiunto un permeato d'acqua pura pari a $143\text{ L m}^{-2}\text{ h}^{-1}$, mentre le membrane modificate hanno raggiunto valori uguali o superiori a $193\text{ L m}^{-2}\text{ h}^{-1}$. In particolare, il flusso d'acqua più alto è stato misurato per la membrana funzionalizzata con APD (0.5%) con un valore pari a $227\text{ L m}^{-2}\text{ h}^{-1}$. Questo risultato si traduce in un miglioramento della permeanza d'acqua pari approssimativamente al 59% (Fig. 15). Il permeato d'acqua nelle membrane NF è fortemente influenzato dalla bagnabilità della superficie. In questo caso, la bagnabilità è migliorata dalla presenza di gruppi ossidrilici -OH esposti, introdotti dai polioli. Questo risultato avvalora le nostre ipotesi che un aumento della bagnabilità si traduce in una permeanza d'acqua più grande.

Il comportamento delle membrane di questo studio in presenza di sporcanti è stato testato utilizzando alginato di sodio come sporcante. A titolo comparativo, è stata testata con lo stesso protocollo anche una membrana commerciale NF270, membrana ampiamente utilizzata per applicazioni civili e industriali. Considerando il flusso di permeato post fouling, è possibile notare che le membrane funzionalizzate hanno mostrato valori più alti sia della membrana control, sia della membrana commerciale NF270 (Fig. 16). Un indicatore per valutare il declino del flusso di permeato dopo il fouling è stato calcolato attraverso l'equazione (3) così da poter confrontare le varie

membrane. I risultati relativi a questa misura sono riportati nella fig. 17. Una membrana attraversata da un flusso iniziale più grande è più soggetta allo sporcamento, in quanto il trasporto di sporcante attraverso la membrana è proporzionale al flusso di permeato: i risultati in Fig. 17 dimostrano un'apparente assenza di miglioramento tra le membrane funzionalizzate e la control, ma bisogna tenere in conto che il flusso iniziale delle membrane modificate era maggiore, dunque una percentuale di flusso perso simile indica che le proprietà anti-sporcamento delle membrane funzionalizzate con APD e (R)-APD sono migliorate, in confronto alla membrana non funzionalizzata. Non considerando la perdita in percentuale, ma confrontando i valori assoluti dei flussi di permeato dopo lo sporcamento con SA (puntini rossi in Fig. 16), si può affermare che le membrane modificate mantengano valori maggiori e dunque sarebbero più adatte a un'applicazione reale. Confrontando a tali dati anche le performance della membrana commerciale NF270, le membrane funzionalizzate hanno mostrato un flusso di permeato post fouling maggiore: infatti APD (0.5%), (R)-APD (0.4%) e (R)-APD (0.5%) operavano con un flusso dopo sporcamento di circa $180 \text{ L m}^{-2} \text{ h}^{-1}$, mentre la NF270 si fermava a $145 \text{ L m}^{-2} \text{ h}^{-1}$. Tornando al ragionamento descritto precedentemente, la NF270 con un flusso iniziale prima del trattamento con lo sporcante è più incline a un veloce sporcamento. Però le membrane funzionalizzate, mantenendo valori assoluti di permeato dopo il fouling più alti, garantirebbero una produttività più elevata. I risultati migliori sono stati ottenuti con le concentrazioni di polioli più alte, dunque sarebbe interessante realizzare membrane funzionalizzandole con lo stesso protocollo, aumentando però la concentrazione di APD o (R)-APD durante il processo di grafting.

In questo studio sono state valutate le rimozioni di NaCl, Na₂SO₄, MgSO₄ e CaCl₂ delle membrane testate (Tab. 2) e il parametro correlato è stato calcolato attraverso

l'equazione (2). La rejection dei sali nelle membrane di NF dipende dall'impedimento sterico e dalla repulsione elettrostatica. Le membrane funzionalizzate hanno mostrato una rejection dei soluti contenenti ioni divalenti con valori comparabili ai valori della membrana commerciale NF270 e della membrana control non modificata. Sono interessanti i dati ottenuti dalla membrana funzionalizzata (R)-APD (0.5%): la rejection per Na_2SO_4 era pari al 96% e più del 98% per MgSO_4 . Questo risultato è consistente con i risultati dell'analisi del potenziale della superficie (Fig. 11), che mostravano una carica più negativa di questa membrana a pH neutro e si traduce in una rejection più efficiente di anioni divivalenti. Analizzando gli altri risultati, è visibile un leggero peggioramento delle rejection di NaCl e CaCl_2 , probabilmente perché un anione con una carica minore (Cl^-) è meno influenzato dai fenomeni elettrostatici e dunque la sua rimozione è dovuta principalmente all'esclusione dimensionale. Nonostante questo leggero calo, le membrane funzionalizzate sono ancora applicabili ad applicazioni di nanofiltrazione.

Conclusioni

Le membrane realizzate in laboratorio per questo lavoro hanno mostrato capacità di desalinizzazione nel range della nanofiltrazione. Sebbene il flusso di permeato iniziale maggiore è stato della membrana commerciale NF270, le membrane funzionalizzate hanno mantenuto un flusso d'acqua pura dopo il fouling nettamente maggiore ($178 \text{ L m}^{-2} \text{ h}^{-1}$ nel caso del (\pm) 3-amino-1,2-propandiolo, $177 \text{ L m}^{-2} \text{ h}^{-1}$ per (R)-3-amino-1,2-propandiolo contro i $145 \text{ L m}^{-2} \text{ h}^{-1}$ della membrana commerciale NF270). Confrontando i due ammino-alcoli di questo lavoro, si può concludere che l'enantiomero (R) ha mostrato un comportamento anti-sporcamento migliore, tant'è che perde solamente il 17.4% del permeato prima del fouling, mentre (\pm) 3-amino-1,2-propandiolo perde, nel migliore dei due casi, il 21.4%. Il motivo di questo

risultato potrebbe essere dovuto al fatto che la configurazione (R) dell'ammino-alcolo ha meno capacità di formare legami con l'enantiomero (S) dell'alginato di sodio, evitando così l'adesione dello sporcante alla superficie della membrana. Sono state valutate anche diverse concentrazioni di APD e (R)-APD (per entrambi 0.4% e 0.5% in soluzione acquosa): il risultato più interessante è stato anche qua ottenuto dall'enantiomero (R). Infatti, la concentrazione più alta di (R)-APD, oltre a una minore perdita di flusso dopo il trattamento con l'alginato di sodio, ha mostrato anche un'alta rejection dei solfati ($\geq 98\%$).

L'aumento dell'idrofilicità della superficie delle membrane ha fortemente contribuito a raggiungere i risultati di questo lavoro. Infatti, l'interazione con le molecole d'acqua ha un ruolo fondamentale, dimostrato dai flussi nettamente più alti e dalla minore perdita di performance delle membrane funzionalizzate, come conseguenza dei gruppi ossidrilici degli alcoli. In futuro, potrebbero essere testati nuovi polialcoli, differenti concentrazioni o variazioni nel protocollo di fabbricazione delle membrane. Inoltre, si dovrà valutare la resistenza ad altri sporcanti.

1 INTRODUCTION

The scarcity of safe and readily available global water resources has become one of the most sever challenges for humans and societies. More than one third of the worldwide population suffers from water shortage ^[1] and by 2025, two third of the world's population may not have access to clean drinking water ^[2]. With the surge in population growth, urban development and industrialization around the world, the water demand will grow year after year. In addition, the growing demand for environmental protection spurs rightfully to find a way to balance the increasing water demand. The solution may be partly found in the sea: given the fact that the overall water on our planet is 97.5% seawater, without any doubt, a technology is required with the aim of desalinating water sustainably. Another considerable option can be the treatment of the industrial wastewaters: for example, the amount of contaminated water produced by the petroleum industry is extremely large. Directly discharging produced water will not only result in environmental pollution, but also in a waste of water resources, especially for water-deficient areas. Therefore, the reclamation of this industrial wastewater through proper treatments has become the consensus of many researchers and legislators ^[3]. Among the most concrete solutions to face these challenges there are membranes: a wide variety of synthetic membranes is currently available. They can be produced from organic materials, such as polymers, as well as from inorganic materials. The most commercially utilized synthetic membranes in the separation industry are made of polymeric structures and they can be classified based on their surface chemistry, bulk structure, morphology, and production method. The chemical and physical properties of synthetic membranes, the nature of the removed contaminants, as well as a choice of driving force, define a membrane separation process. The most commonly used driving forces of a membrane process in industry

are pressure gradients. Polymeric membranes lead the membrane separation industry market because they are very competitive in performance and economics^[4]. Many polymers are available, but they must have appropriate characteristics for their application. The polymer must be suitable in terms of its chain rigidity, chain interactions, stereoregularity, and polarity of its functional groups. The polymer must also be obtainable and reasonably priced to comply with the low-cost criteria of membrane separation processes. Many membrane polymers are grafted, custom-modified, or produced as copolymers to improve their properties. The most common polymers used to fabricate membranes are cellulose acetate, nitrocellulose and cellulose esters, polysulfone, polyamide, polyethylene and polypropylene, polyethersulfone, and polytetrafluoroethylene. In this work, we will work with nanofiltration (NF) membranes. Nanofiltration is defined by many “as a process between ultrafiltration and reverse osmosis”, and it is a rapidly emerging technology. A polymeric NF membrane has a nominal pore size of about 1 nm (Fig. 1) and a molecular weight cutoff (MWCO) range between 200 and 1000 Da^[5].

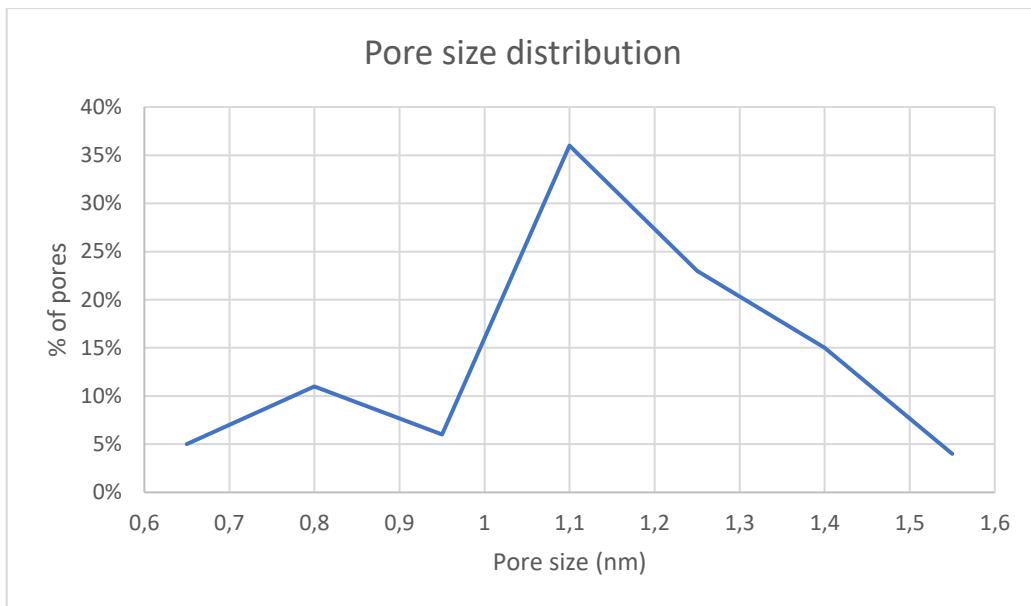


Figure 1. Pore size distribution of a nanofiltration membrane ^[6].

Nanofiltration is now widely used for water softening and has found application in the removal of natural organic matter, emerging pollutants and hydrated divalent ions. Therefore, the market for nanofiltration is growing dramatically. Among the available materials, polyamide (PA) is the most widely used material to fabricate dense polymeric membranes for highly effective desalination and water purification ^{[7] [8]}. PA NF membranes are particularly suitable for water softening ^{[9] [10] [11]}, the water purification from hydrated divalent cations (e.g. Mg^{2+} , Ca^{2+}) and from heavy metals ^{[12] [13] [14]}. Thin-film composite membranes (TFC), consisting of a thin polyamide film as a selective skin deposited on an ultrafiltration membrane support, are regularly used for membrane-based wastewater treatment because of the high permeability and selectivity properties of the polyamide film ^[15]. The main advantages of NF are low operating pressures compared to reverse osmosis and higher productivity ^{[16] [17] [18]} ^{[19] [20] [21]}. However, polyamide membranes have a high propensity to fouling, which leads to loss of performance of a membrane due the deposition of suspended or

dissolved substances on its active surfaces or within its pores [6]. Foulants are present in all the feed waters, thus fouling is one of the major obstacles for reaching the ultimate goal of realizing high fluxes and rejection over a prolonged period of NF operation [22] [23] [24] [25]. Clearly, an improvement of the process is necessary.

Foulant deposition is significantly affected by chemical and physical characteristics of the membrane surface, so one of the main pathways to reduce fouling is the fabrication of fouling-resistant PA membranes by means of cheap and scalable surface modification. Surface hydrophilicity, surface roughness and electrostatic surface charge are the prominent characteristics that influence fouling and the membrane antifouling properties [26] [27]. The main techniques of surface modification to achieve antifouling properties of the membranes are coating, grafting and nanoparticle assembly, plasma treatment/ chemical vapour deposition and surface functionalization/patterning/crosslinking [28].

In this study, we made use of the technique of grafting, which refers to the anchoring of molecules on the membrane surface, changing its physicochemical properties. Surface modifications through grafting techniques to improve antifouling properties have been conducted successfully in previous studies: for instance, Zhang *et al.*^[3] adopted serinol to modify the piperazine-based TFC NF membrane to enhance its hydrophilicity. Yan *et al.*^[29] studied the grafting of triethanolamine on a nascent PA NF membrane and as a result the modified membrane had higher hydrophilicity, water flux and antifouling ability against hydrophobic foulants. Gao *et al.*^{[30] [31]} modified the surface of the NF with the zwitterionic materials, which improved the membrane flux and the resistance to bacteria and protein fouling. Therefore, when fouling is due to a mixture of organic substances, the most common solution is to mitigate the

deposition of organics by modifying the membrane surface with hydrophilic compounds [32] [33] [34].

More specifically, in this study we applied sequential interfacial polymerization (SIP) to bind hydrophilic substances to reach our aim of fabricating antifouling NF membranes for water softening. Particularly, we functionalized PA NF membranes by grafting (\pm)-3-amino-1,2propanediol (APD) or its enantiomer (R)-3-amino-1,2-propanediol ((R)-APD) to the surface to increase the number of hydroxyl groups and enhance the membrane hydrophilicity. Experiments were performed to evaluate the antifouling properties of the modified NF membrane using sodium alginate (SA) as model foulant. We thus tested if the chirality of the molecule could influence the final performance and we compared the results of the functionalized membranes with those obtained with commercial NF270. In order to demonstrate the effectiveness of this modification technique, SEM, AFM, ATR-FTIR, contact angle geometry and surface zeta potential analysis were employed to study the APD grafted and the (R)-APD grafted TFC NF membranes.

2 MATERIALS AND METHODS

2.1 MATERIALS AND MEMBRANES

Flat-sheet polysulfone ultrafiltration membranes with a molecular weight cut-off (MWCO) of around 20000 g/mol were purchased from Nanostone Water, USA, and used as porous support for our TFC membranes. A commercial nanofiltration membrane (NF270, FilmTec™ Dow Chem. Company, USA) was also obtained tested to compare its performance and antifouling properties with those of our lab membranes. Piperazine (99%), trimesoyl chloride (98%), sodium metabisulfite (98,5-100%), sodium alginate, sodium chloride (\geq 99%) were purchased from Sigma Aldrich (USA). Sodium sulfate (\geq 99,5%) was purchased from VWR Chemicals (Leuven, Belgium). 3amino-1,2propanediol (97%), (R)-3-Amino-1,2-propanediol and magnesium sulfate (99,5%) were purchased from Alfa Aesar (Karlsruhe, Germany). Calcium chloride (96%) was purchased from Acros Organics (New Jersey, USA). All solutes and monomers were dissolved in deionized (DI) water or hexane (Sigma Aldrich) prior to utilization. DI water was obtained from a milli-Q purification system. All the reagents and solvents mentioned above were used without any further purification or anhydridization.

2.2 PREPARATION OF THE CONTROL TFC-PA MEMBRANE

For a comparative study, traditional nanofiltration control membranes were synthetized by a polymerization between piperazine (PIP) and trimesoyl chloride (TMC) using a traditional interfacial polycondensation (IP) approach (Fig. 2). All the fabrications were conducted in a clean room with a temperature of 25 ± 1 °C. First,

the wet polysulfone support was coated by a 0.25% (w/v) PIP aqueous solution for 120 s. The excess PIP was then removed from the surface with an air gun. Afterwards, the membrane was immersed in a 0.1% (w/v) TMC solution (n-hexane) for 60 s. Following this step, the membrane was immersed in DI water and cured in an oven for 120 s at 80 °C. Membranes were stored in ultrapure water at 4 °C before testing.

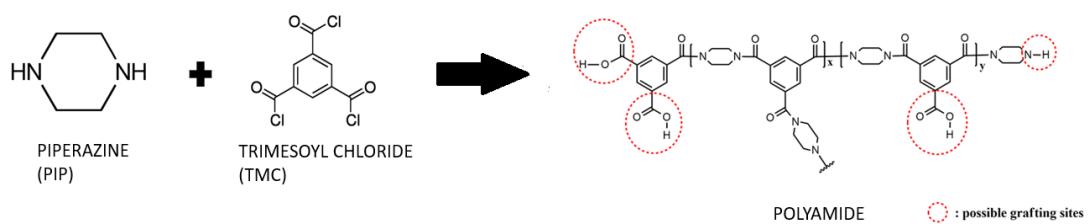


Figure 2. Polycondensation between PIP and TMC.

2.3 FABRICATION OF FUNCTIONALIZED TFC PA MEMBRANES

Functionalized bilayer membranes were fabricated by extending the traditional IP approach described above with an additional reaction step. A sequential interfacial polymerization (SIP) protocol was thus adopted. The polysulfone support was first soaked with a 0.25% (w/v) PIP aqueous solution for 120 s, and an air gun was used to remove the excess solution. The membrane was then immersed in a 0.1% (w/v) TMC solution (n-hexane) solution for 60 s to form the ultra-thin PA layer and, before hydrolysis of the unreacted acyl halides, it was contacted with an aqueous solution containing APD or (R)-APD at different concentrations (Fig. 3). Specifically, the investigated concentrations were 0.4% (w/v) and 0.5% (w/v). APD and (R)-APD are the molecules of different chirality of the same compound. The subsequent curing

steps were identical to those described above and related to the fabrication of the control PA membranes.

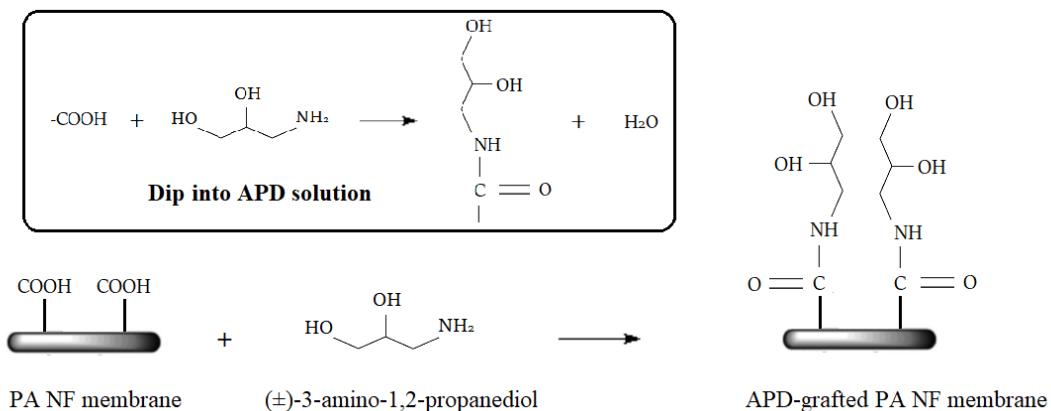


Figure 3. Schematic diagram of the surface modification process with APD.

2.4 CHARACTERIZATION OF THE MEMBRANES

Micrographs of the top layer surface and of the cross-section of each membrane were acquired using a scanning electron microscope (SEM) (HITACHI S-4800, Japan) coupled with an energy-dispersive X-ray (EDX) spectrometer (Aztec System, Oxford Instruments, UK). The membrane samples were sputtered-coated with chromium before SEM analysis. Atomic force microscopy (AFM, Nanoman, Bruker Instruments, USA) was used to analyze the 3D-morphology and surface roughness of the membranes. The root mean square roughness (RMS) values in an area of $5 \times 5 \mu\text{m}^2$ were calculated based on the experimental scans to describe the membrane surface roughness. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR Nicolet iS50 FTIR Spectrometer, ThermoFisher, USA) was used to analyze the chemical structure of different membranes. The wettability of

different membranes was evaluated from contact angle measurements, conducted via a sessile drop method consisting of the measurement of the angle of a water droplet on the solid substrate [35] using a Drop Shape Analyzer DSA100 (KRÜSS GmbH, Germany). Contact angles were calculated using the circle fitting method. Zeta potential analyses were performed with a streaming potential analyzer (SurPass III, Anton Paar GmbH, Austria) and were conducted by varying the pH from 2 to 10 with samples immersed in a solution of 0.001 M KCl. The pH was adjusted using 0.1 M HCl or NaOH.

2.5 EVALUATION OF THE MEMBRANE WATER PERMEABILITY AND SALT REJECTION

The water permeability and the rejections of the membranes were evaluated with a cross-flow NF lab setup (Fig. 4), comprising a cell that accommodated membrane samples with an effective surface active area of 0.00289 m². The temperature of the feed solution and of the surrounding environment was set at 25 °C during all the tests. Each new membrane sample was first compacted at an applied pressure of 12 bar using ultrapure water as a feed solution until steady-state, usually obtained within 90 min. Then, the applied pressure was lowered at 10 bar and the pure water flux was recorded over time. The initial flux through the membrane was thus calculated using the following equation:

$$J_i = \frac{V}{A \Delta t} \quad (1)$$

Where J_i ($\text{L m}^{-2} \text{h}^{-1}$) is the initial permeate flux, V (L) is the permeate volume, A (m^2) is the effective area of the membrane, Δt (h) is the time interval. Membrane rejections were determined for different individual salts, namely: NaCl, Na₂SO₄, MgSO₄ and CaCl₂. Upon measurement of the flux of ultrapure water, a stock solution of one of the salts was introduced into the feed tank to obtain a salt concentration of 1000 mg/L. The permeate flux was recorded under the new steady-state conditions and small samples of the feed and of the permeate streams were collected. The salt concentration in these samples was calculated by measuring the electric conductivity of the samples with a conductivity meter (pHenomenal VWR MU 6100 H, VWR) and then using a previously determined concentration-conductivity correlation. The observed rejection (%) was determined according to the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

Where C_p (mg/L) is the permeate concentration and C_f (mg/L) is the feed concentration.

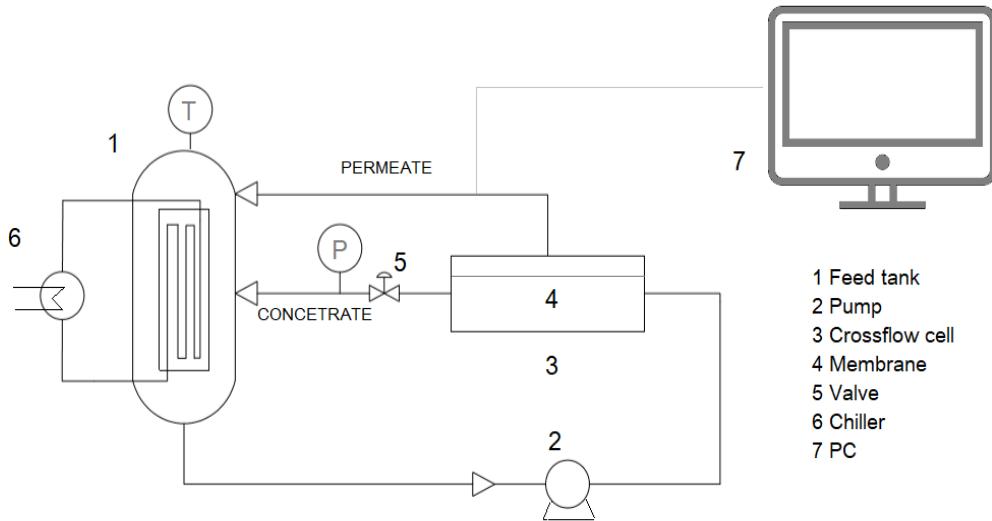


Figure 4. Crossflow lab plant.

2.6 FOULING TEST

The protocol applied to characterize the fouling behaviour was the following: after measurement of the pure water flux of a new membrane sample at steady-state, an aqueous stock solution of sodium alginate (SA) was introduced into the feed tank to obtain a final SA concentration of 0.250 g/L. The flux reduction due to alginate deposition was recorded for 90 min, at an applied pressure of 10 bar and a temperature of 25°C in the feed solutions. The relative loss in flux was evaluated as:

$$\text{Flux loss} = \frac{J_i - J_f}{J_i} \times 100\% \quad (3)$$

Where J_i ($\text{L m}^{-2} \text{ h}^{-1}$) is the initial flux and J_f ($\text{L m}^{-2} \text{ h}^{-1}$) is the flux upon fouling.

After 90 min, the apparatus was completely emptied and the feed solution substituted with pure water. The membrane permeance was thus calculated using the same procedure described above to better evaluate the membrane performance decline.

3 RESULTS AND DISCUSSION

3.1 MORPHOLOGY OF THE ACTIVE LAYER

The surface morphology of the unmodified control membrane and of the functionalized membranes was investigated by SEM and AFM. The morphology and roughness are important parameters of the membranes, which may influence the physical interactions between the membrane surface and foulants [36] [37]. In fact, to reduce foulant deposition, it is important to work with a membrane comprising a smooth and homogeneous surface, as also proven in past studies [38] [39]. Fig. 5 and Fig. 6 present representative micrographs before fouling of three samples of, namely, an unmodified control membrane, an APD-grafted membrane and an (R)-APD-grafted membrane. The thickness of the polyamide layer, observable in Fig. 5, was approximately 80 nm in all cases. No significant differences can be observed in the polyamide structure between the control membranes and the membranes functionalized with APD and (R)-APD (Fig. 6): this result suggests that the modification changed the chemistry but did not alter significantly the physical structure of the active layer. This phenomenon is also related to the fact that there was no cross-linking reaction during the grafting process [3], as there was only one reactive group (the amino group) that could react with the residual unreacted acyl halides on the PA layer of the membrane.

The root mean square (RMS) roughness of the control and (R)-APD grafted membranes was obtained from AFM images and the results are shown in Table 1. We did not observe a significant difference in the roughness parameters between control membranes and the functionalized membranes Therefore, it can be confirmed the

above conclusion: the functionalization left unchanged the morphology and the smoothness of the membrane surface.

Fig. 7 and Fig. 8 present, respectively, SEM cross-sectional and surface micrographs of analogous samples after fouling. The thickness of the fouling layer reached values up to 250 nm (Fig. 7), showing the evident formation of an extra layer with a heterogeneous thickness and distribution (Fig. 8) spread on the membrane surface, likely representing an additional resistance to flux across every membrane investigated in this study. However, the RMS of the fouled membranes did not present significant differences compared to the same membranes before fouling, except for the APD-grafted membrane: the APD-grafted membrane after fouling sample presents the highest RMS value (16.31 ± 10.32 nm) compared to the rest of the samples after fouling (9.71 ± 3.04 nm for the control membrane and 7.49 ± 1.46 nm for (R)-APD-grafted membrane). This slight increment is probably due to a small quantity of foulant on the surface. In fact, the alginate probably had a tendency to deposit in a random and heterogeneous way on the membrane surface, so the values of the RMS after fouling depend strongly to the casualness of the analyzed sample. However, this result showed that the presence of foulants on the membrane surface can increase RMS values of the overall membrane surface. The samples of unmodified control membrane and (R)-APD did not show significant evidences of foulants.

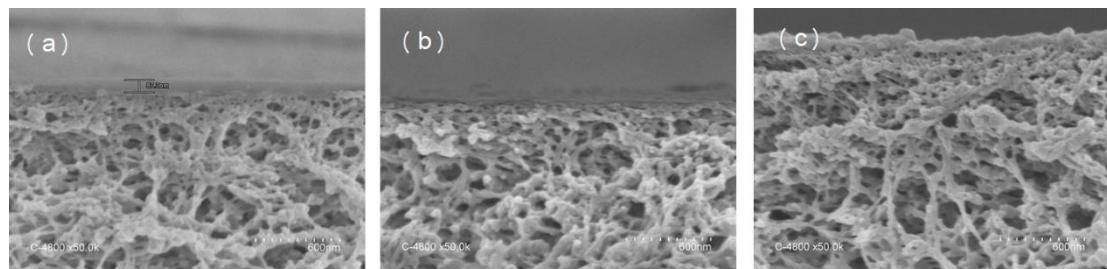


Figure 5. SEM cross-section micrographs of the clean membranes. (a) clean control membrane, (b) clean APD-grafted membrane, (c) clean (R)-APD-grafted membrane.

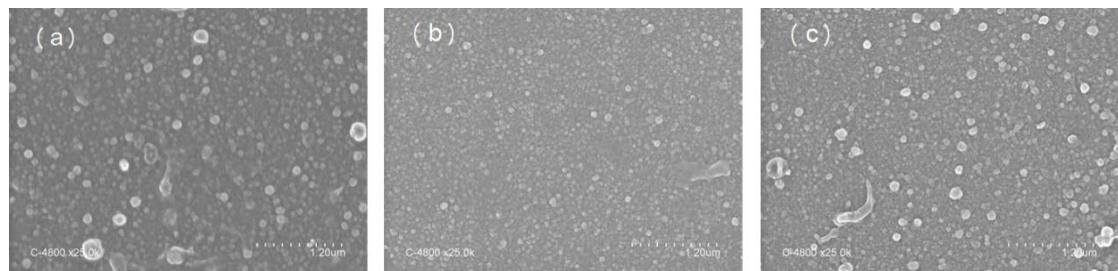


Figure 6. SEM surface micrographs of the clean membranes. (a) clean control membrane, (b) clean APD-grafted membrane, (c) clean (R)-APD-grafted membrane.

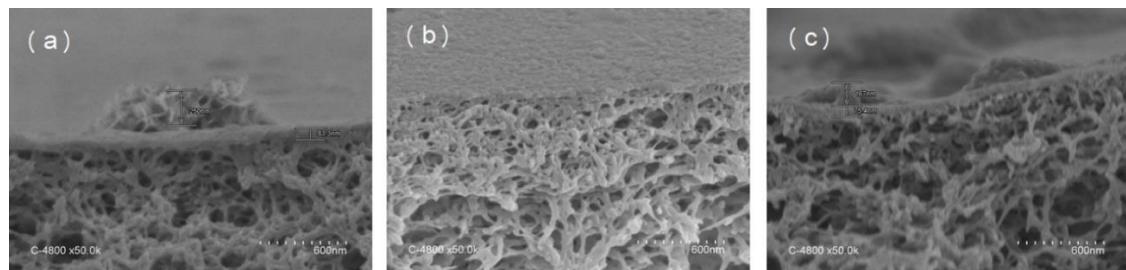


Figure 7. SEM cross-section micrographs of the fouled membranes. (a) fouled control membrane, (b) fouled APD-grafted membrane, (c) fouled (R)-APD-grafted membrane.

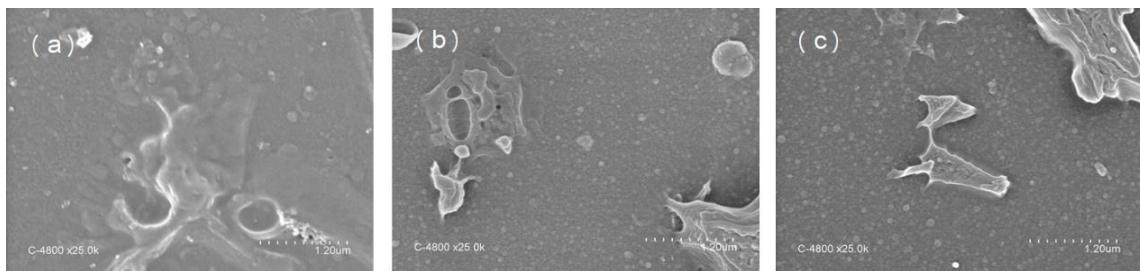


Figure 8. SEM surface micrographs of the fouled membranes. (a) fouled control membrane, (b) fouled APD-grafted membrane, (c) fouled (R)-APD-grafted membrane.

Table 1. AFM results.

Membranes:	RMS (nm)
Clean control	10.26 ± 3.24
Fouled control	9.71 ± 3.04
Clean APD	7.01 ± 1.15
Fouled APD	16.31 ± 10.32
Clean R-APD	9.25 ± 2.08
Fouled R-APD	7.49 ± 1.46

3.2 PHYSICOCHEMICAL MEMBRANE PROPERTIES

The wettability of the membrane surface is one of the key parameters of this study, because its increment would provide us with insight about the success of the grafting and because our hypothesis is that higher wettability leads to reduced organic fouling during operation: in fact, the reduction of deposition of hydrophobic foulants onto the membrane surface can be obtained by the formation of a thin water layer on the hydrophilic surface. Indeed, the modified membranes showed a higher wettability (Fig. 9 and Fig. 10) compared to the unmodified control polyamide membrane, consistently with our initial hypothesis. The improvement of wettability upon

functionalization was significant: the control membrane was characterized by a contact angle of 74°; after grafting, the measured water droplet angle decreased to 58° for the APD-grafted membrane and to 57° for the (R)-APD-grafted membrane. This result suggests that the functionalization was successful and it achieved its main goal, i.e., the wettability was improved. The wettability of the two functionalized membranes was similar as the difference in the water contact angle was negligible.

Surface zeta potentials were measured at different pH (because solution pH strongly impacts surface charge^[40]) and the results are shown in Fig. 11. This analysis was performed to evaluate the change of potential of the membrane surface due to the grafting process of APD and (R)-APD: in fact, membrane charge can have a large effect on the performance of many filtration processes^{[41] [42]}, for example the salt rejection of charged NF membranes is not caused exclusively by the steric hindrance effect, but also largely depends on the electrostatic repulsive effect^[43]. As illustrated in Fig. 11, the grafting process decreased the absolute value of the TFC PA membrane negative potential. The pH of the feed solution during filtration of most natural and industrial water sources is roughly neutral. At neutral pH, all the functionalized membranes showed a larger negative potential compared to the unmodified control membrane. This result is probably due to the ionization of functional groups with very weak acid properties, such as alcohols^[44], as the pH increases. Specifically, the largest negative potential was measured for the (R)-APD-grafted membrane (-29.2 mV at neutral pH), suggesting that the different molecular geometry of the grafting group may possibly have an effect on the exposed density of surface charges at the membrane surface. Knowing the charge of the membrane and the feed solution to be filtered, it is possible to predict the retention characteristics of the membrane. For this reason, the (R)-APD-grafted membrane is expected to reject better multivalent anions,

such as the sulfates, but it could be more inclined to get fouled by positively charged foulants.

The FTIR spectra of the lab-made control membrane, APD-grafted and (R)-APD-grafted membranes were obtained to analyze their surface chemical structure, to understand the properties of the functionalization, and to investigate the antifouling potential. The results before fouling are presented in Fig. 12: the peaks at 1625 cm^{-1} and 1567 cm^{-1} (present in every sample) correspond, respectively, to the C=O stretching band and N-H stretching band of the -CO-NH- group, indicating the formation of the polyamide selective layer by interfacial polymerization [1]. It is evident the similarity between all the spectra, so the presence of the polyols was not highlighted by this analysis: the reason can be found in a possible overlap of the hydroxyl group of the polyols ($3200 - 3550\text{ cm}^{-1}$) and that of water (humidity) on the surface ($3100 - 3700\text{ cm}^{-1}$). In Fig. 13, the FTIR spectra of the samples after fouling are shown: they are similar to the previous ones, except for the fouled control membrane: here, it is possible to observe a small peak, which is not visible in the rest of the spectra (Fig. 14). This peak in the fouled control membrane can be an indicator of the presence of sodium alginate, which appears at 1417 cm^{-1} and it comes from the symmetric stretching mode of carboxylate salt groups (-COONa) [45] [46]. This peak was absent or negligible for the functionalized membranes: this observation may suggest a larger presence of foulants on the surface of the control membrane and, in turn, imply the improvement of the antifouling properties of our membranes in the presence of polyols at their surface.

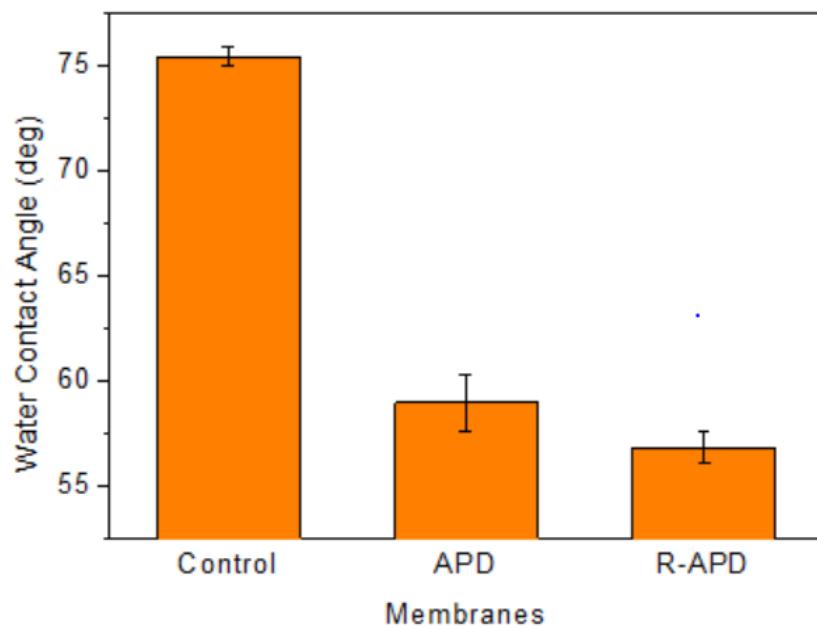


Figure 5. Surface water contact angles of the control membrane and functionalized membranes.

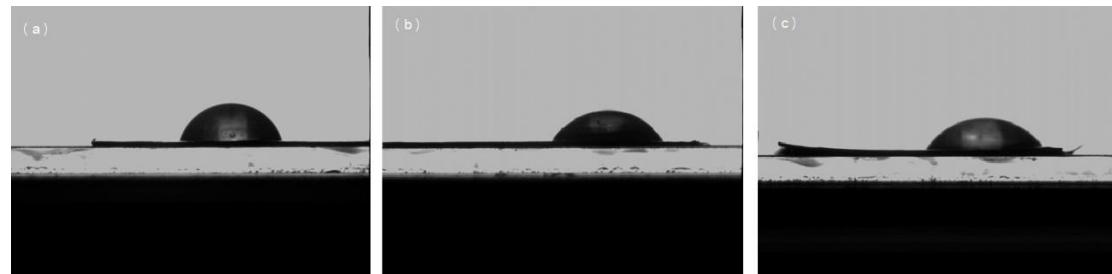


Figure 6. Contact angle images of: (a) control membrane, (b) APD-grafted membrane, (c) (R)-APD membrane.

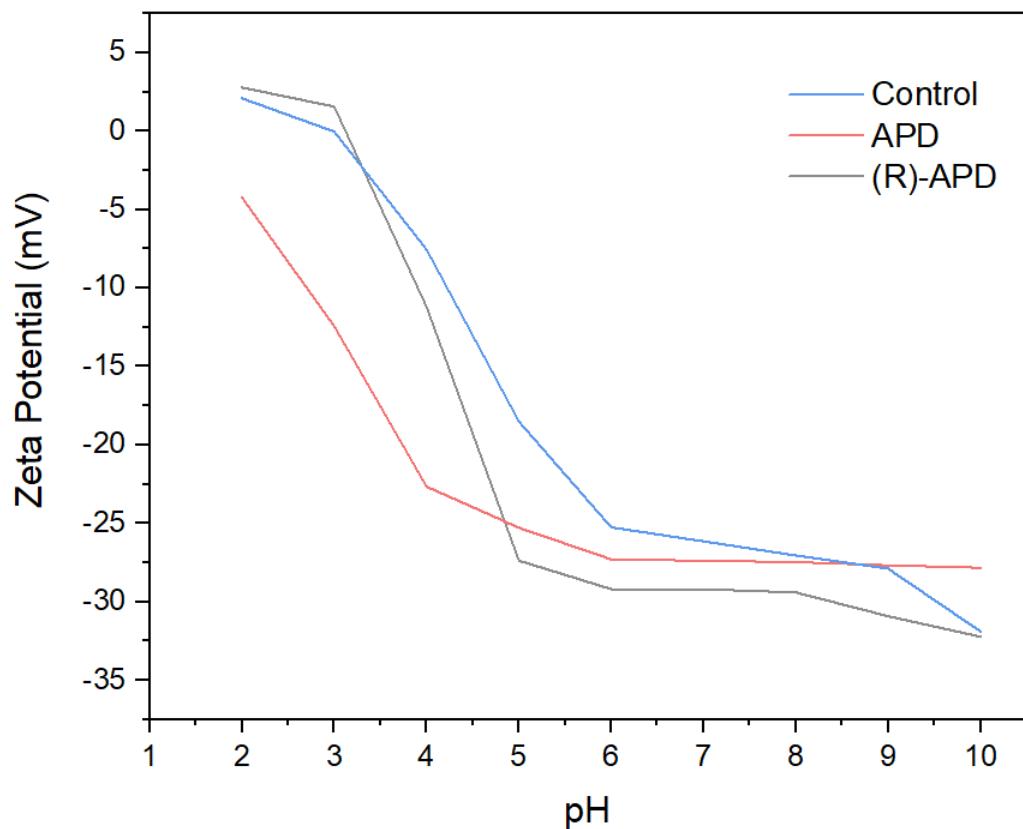


Figure 11. Zeta potential of the Control, APD-grafted and (R)-APD-grafted membranes membrane by varying the pH at 25 °C.

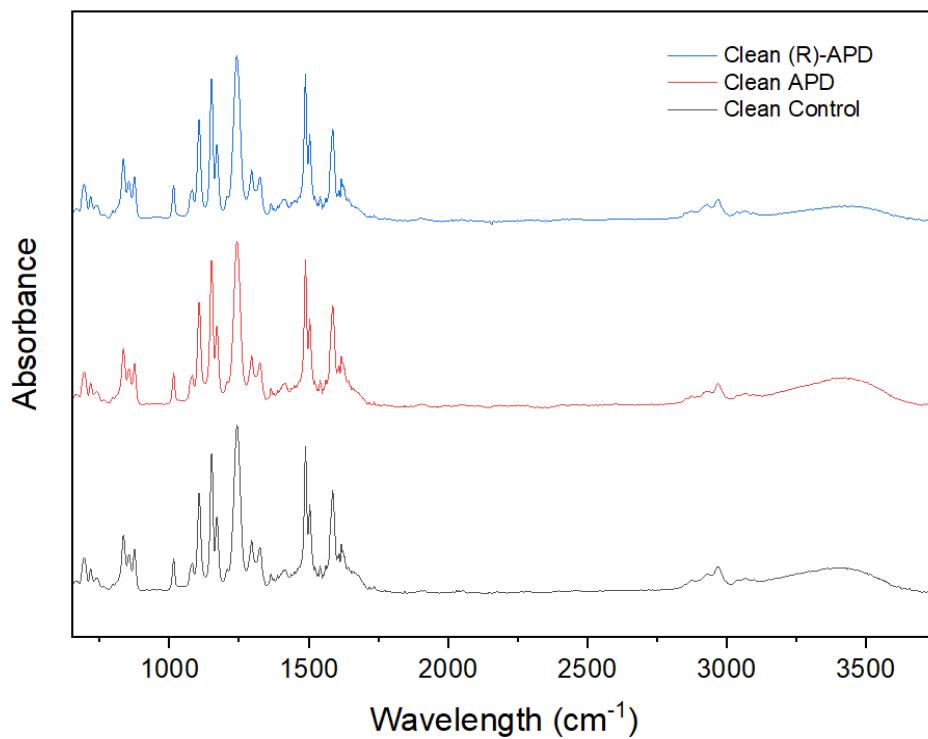


Figure 12. FTIR spectra of the Control, APD-grafted and (R)-APD-grafted membranes before fouling.

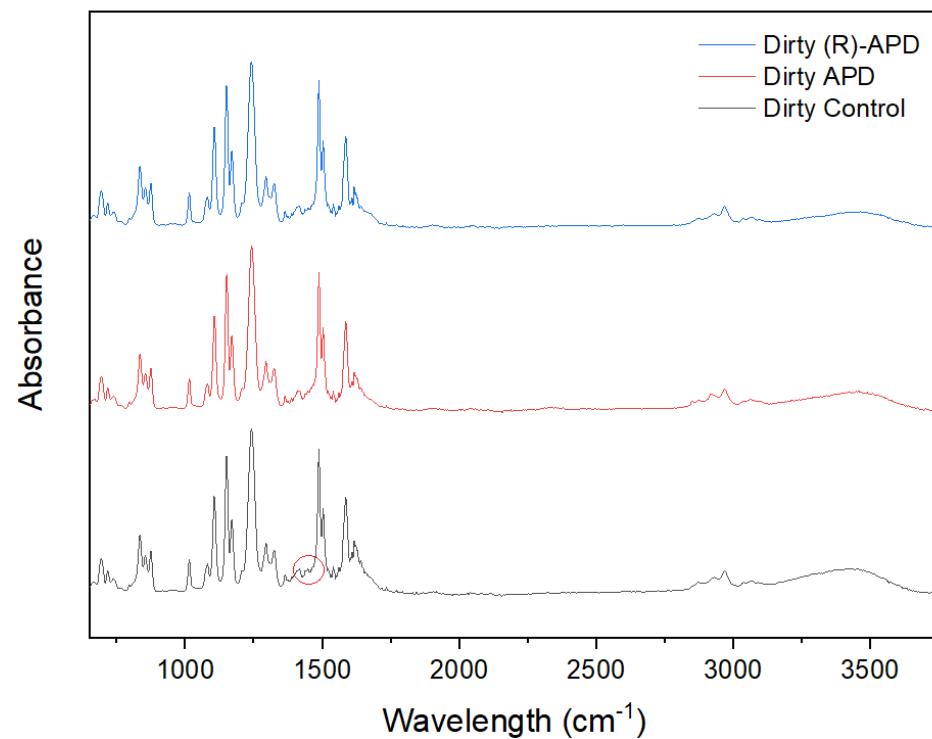


Figure 13. FTIR spectra of the Control, APD-grafted and (R)-APD-grafted membranes after fouling.

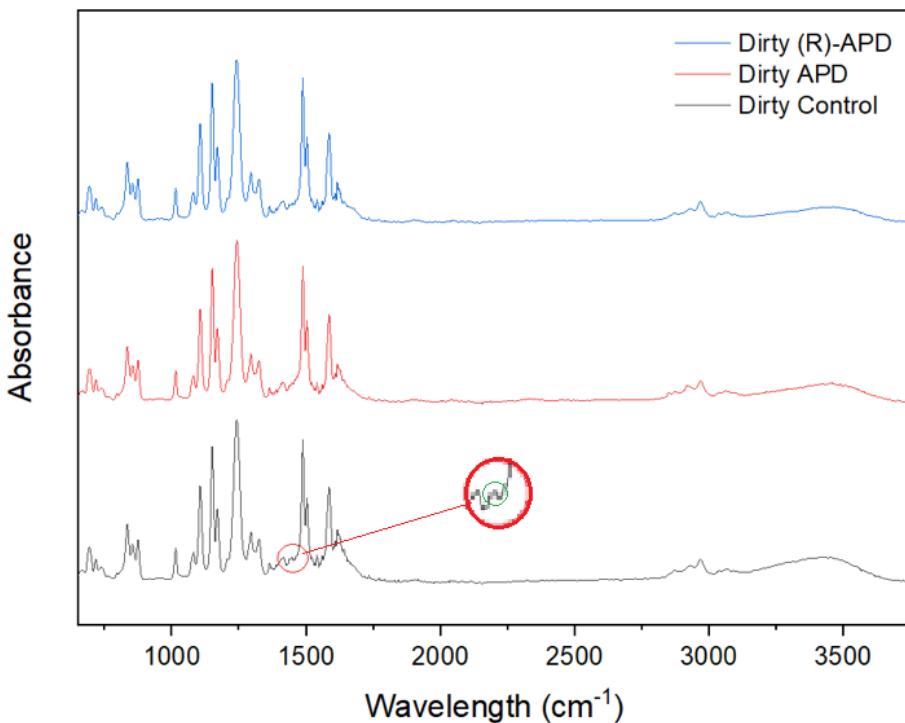


Figure 14. FTIR with zoom on the only different peak among fouled membranes.

3.3 MEMBRANE PURE WATER PERMEABILITY

In terms of transport performance, it was immediately noticeable the improvement of the pure water flux (calculated with equation (1)) of the functionalized membranes compared to the unmodified control membrane: the control membrane was related to a measured water permeate flux of $143 \text{ L m}^{-2} \text{ h}^{-1}$, while all the functionalized membranes reached values equal or larger than $193 \text{ L m}^{-2} \text{ h}^{-1}$. Specifically, the highest water flux was observed for the APD (0.5%) functionalized membrane with a value of $227 \text{ L m}^{-2} \text{ h}^{-1}$. This change represents approximately a 59% improvement in water permeance compared to the unmodified control membrane (Fig. 15), proving to be the most favourable membrane for the mass transfer of water molecules across the layer [47]. The water flux of the NF membrane is strongly affected by surface

wettability of active layer [48]: the interaction between water molecules and pore walls influences significantly water transport [49] (in this case, the wettability is enhanced by the presence of exposed hydroxyl groups -OH introduced by the polyols). This result corroborates our hypothesis that enhancement in the membrane wettability translates into higher water permeance of the membrane.

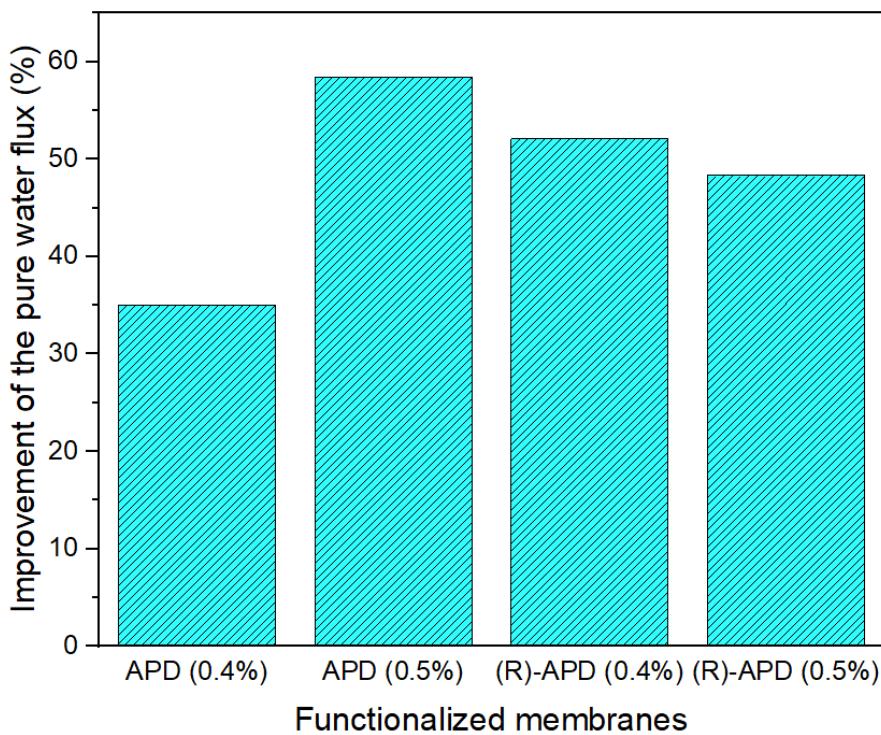


Figure 15. Improvement of the pure water flux of the functionalized membranes compared to the pure water flux of the unmodified control membrane (equal to $143 \text{ L m}^{-2} \text{ h}^{-1}$).

3.4 MEMBRANE FOULING BEHAVIOUR

Sodium alginate was used as model foulants to evaluate the fouling behaviour and the antifouling capabilities of the control and of the functionalized membranes. The NF270 commercial membrane was also tested with the same protocol, as a

comparison with a widely adopted membrane for both civil and industrial applications. Considering the water flux upon fouling, the functionalized membranes showed higher values than the control membrane, and also with respect to the NF270 commercial membranes (Fig. 16). The relative decline rate of the water flux was calculated through equation (3), which provides a useful fouling index for direct and straightforward comparison among the samples. The results associated with this index are presented in Fig. 17. Clearly, a membrane deployed at a higher initial permeate flux is more likely to get fouled rapidly, as the transport of foulants toward the membrane surface is proportional to the permeate flux. The results showed in Fig. 17 demonstrate an apparently absence of improvement between unmodified control membrane and the functionalized membranes, but it must be taken into account that the initial flux of the modified membranes was higher than the control membrane: this similar flux loss percentage indicates that the antifouling properties of the APD-grafted and (R)-APD-grafted membranes improved, compared to the unmodified membrane. Moreover, it follows that the absolute values of the flux upon fouling were higher for the functionalized membranes (red dots in Fig. 16). So, in a real application the flux of the modified membranes would preserve higher values, thanks to the surface modification with polyols. Comparing the flux upon fouling of the NF270 commercial membrane, the modified membranes showed overall higher antifouling performance: in fact, APD (0.5%), (R)-APD (0.4%) and (R)-APD (0.5%) grafted membranes operated at approximately $180 \text{ L m}^{-2} \text{ h}^{-1}$ upon fouling, while the NF270 reached a value of $145 \text{ L m}^{-2} \text{ h}^{-1}$. Clearly, the larger initial permeate flux achieved with NF270 samples acted to accelerate fouling in these tests. However, the final value observed at near steady-state was larger for functionalized membranes, again suggesting the possibility to deploy these membranes with favourable overall

productivity. The best results were achieved with membrane functionalized with the highest polyol concentration. This result suggests that probably it is possible to achieve higher water flux and better antifouling properties following the fabrication protocol described above in this work, but with increased concentration of APD or (R)-APD during modification.

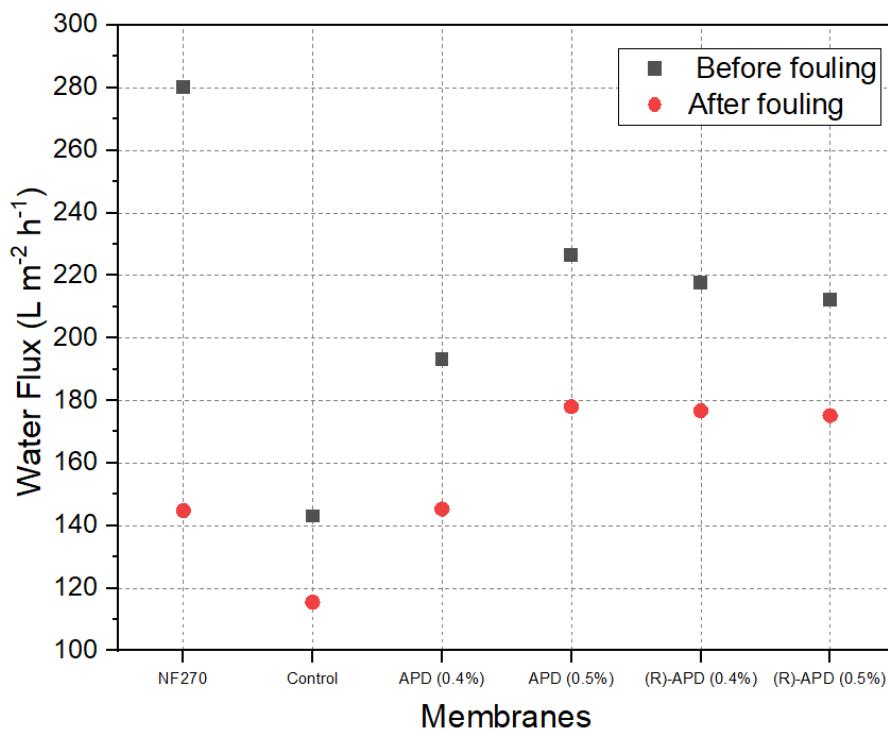


Figure 16. Membrane filtration performance before and after fouling.

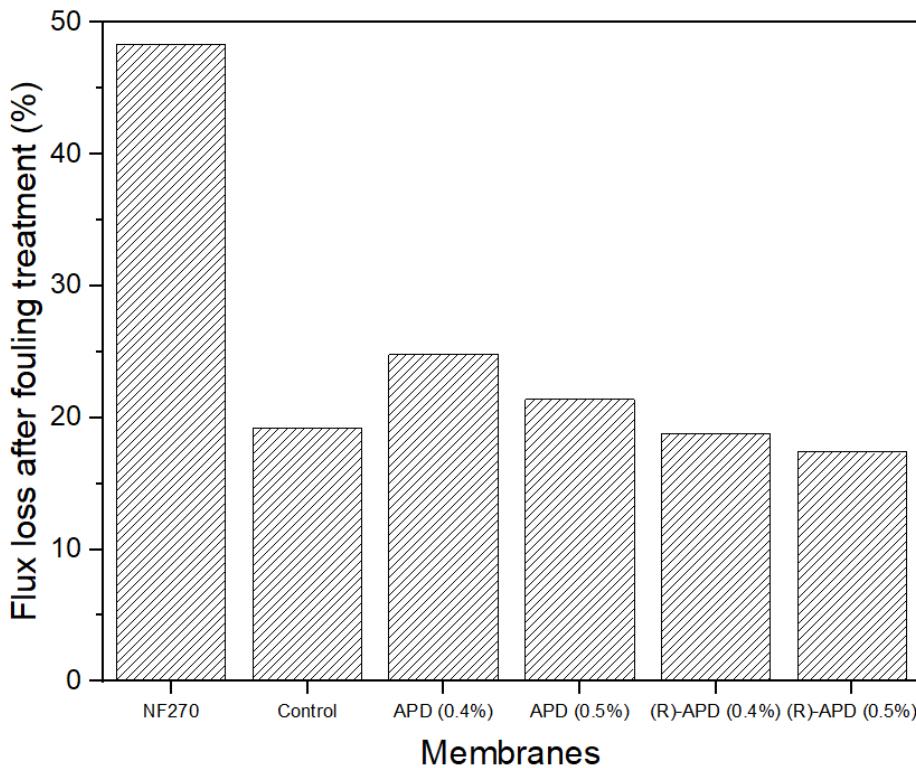


Figure 17. Flux loss after fouling of the NF270, the control membrane and the functionalized membranes.

3.5 SALT REJECTION

The salt rejection of NF membranes mostly depends on the steric hindrance effect and on the electrostatic repulsions. The removal of NaCl, Na₂SO₄, MgSO₄ and CaCl₂ was tested in this study and the related parameters (Table 2) calculated through equation (2). The functionalized membranes showed a comparable rejection of solutes containing divalent sulfates with respect to the commercial and to the control membranes. Specifically, the membrane functionalized with 0.5% (R)-APD showed a rejection of 96% for Na₂SO₄ and more than 98% for MgSO₄. This result is consistent with the data presented in Fig. 11 and related to the surface potential, suggesting that negative charge at near neutral pH resulted in higher divalent anions rejection.

Analyzing the rejection results, the functionalization brought a slight decline of the rejections of NaCl and CaCl₂, probably because an anion with overall lower charge (Cl⁻) is less influenced by electrostatic phenomena and its rejection is more related by size exclusion. Simultaneously, a larger negative charge on the membrane surface may promote the passage of oppositely charged cations, which will bring with them the small chloride ions to maintain electroneutrality. Despite the fact that rejections of chlorides of the functionalized membranes decreased, they may still be applied as treatment membranes for nanofiltration applications. The rest of the functionalized membranes (APD (0.4%), APD (0.5%) and (R)-APD (0.4%) grafted membranes) did not show meaningful differences in salts rejection compared to the unmodified control membrane and this observation suggests that the grafting process did not influence the pore size or the density of the active layer.

Table 2. Different solute rejections of different membranes.

SALTS REJECTION	R NaCl (%)	R Na ₂ SO ₄ (%)	R MgSO ₄ (%)	R CaCl ₂ (%)
NAME				
NF270	56.0	96.3	97.0	48.6
Control	54.5	93.0	93.8	41.5
APD (0.4 %)	55.2	94.0	93.8	44.8
APD (0.5 %)	39.7	93.2	92.9	35.0
(R)-APD (0.4%)	37.2	90.5	90.4	31.8
(R)-APD (0.5%)	46.0	95.9	98.4	37.2

4 CONCLUSION

Thin-film composite nanofiltration membranes were fabricated using interfacial polymerization between piperazine and trimesoyl chloride and they were subsequently modified by surface functionalization with a polyol compound of two different chiral configurations, namely, 3-amino-1,2propanediol and (R)-3-amino-1,2-propanediol, to improve their antifouling properties. The antifouling performance of our hand-cast membranes and of a commercial NF270 membrane was explored using sodium alginate as model foulant and their antifouling properties were evaluated by observing the change permeate flux upon fouling. Water permeability and salts rejection of our fabricated membranes were associated with a desalination performance in the range of nanofiltration. Although our interfacial polymerized membranes exhibited lower pure water permeance with respect to commercial nanofiltration membranes and similar or lower observed salts rejection for monovalent ions, all the polyol-functionalized membranes were less prone to polysaccharides fouling, showing a higher flux after 90 min of filtration comprising fouling. More specifically, commercial NF270 displayed a measured flux of $145 \text{ L m}^{-2} \text{ h}^{-1}$ with up to 48% loss, while our modified membranes were associated with a permeate flux following fouling of $178 \text{ L m}^{-2} \text{ h}^{-1}$ in the case of 3-amino-1,2-propanediol, and $177 \text{ L m}^{-2} \text{ h}^{-1}$ when the absolute configuration (R)-3-amino-1,2-propanediol was adopted. Among the two amino alcohols investigated in this study, the functionalization with the chiral (R)-structure showed the best antifouling behaviour, with only the 17.4% loss in water flux, benchmarking current commercial nanofiltration membrane, while the best APD-grafted membrane lost 21.4% of its initial permeate: this might be due to the fact that the (R)-enantiomer on the surface is not recognized by the (S)-enantiomer of the sodium alginate in the solution, hence avoiding its adhesion to the layer [50]. In addition, two different

concentrations were evaluated for both the polyol moieties, 0.4% and 0.5% respectively. The results suggest that when the highest concentration of (R)-3-amino-1,2-propanediol was applied, an improved sulfate rejection was achieved ($\geq 98\%$), which also demonstrates a non-negligible influence of the enantiomer arrangement in the membrane chemical structure, while maintaining the physical properties intact. The enhanced wettability of the membranes contributed significantly to achieve the results outlined above, in fact the water interaction has a significant function, showing that our modified membranes have both enhanced water flux compared to the control PA membrane, as a consequence of the exposed hydroxyl groups of the polyol on the active surface layer. Future work will aim at testing other possible polyols, different concentrations or experimental conditions during membrane fabrication by interfacial polymerization. Moreover, the resistance to other foulants should be investigated.

5 APPENDIX

5.1 SEM MICROGRAPHS

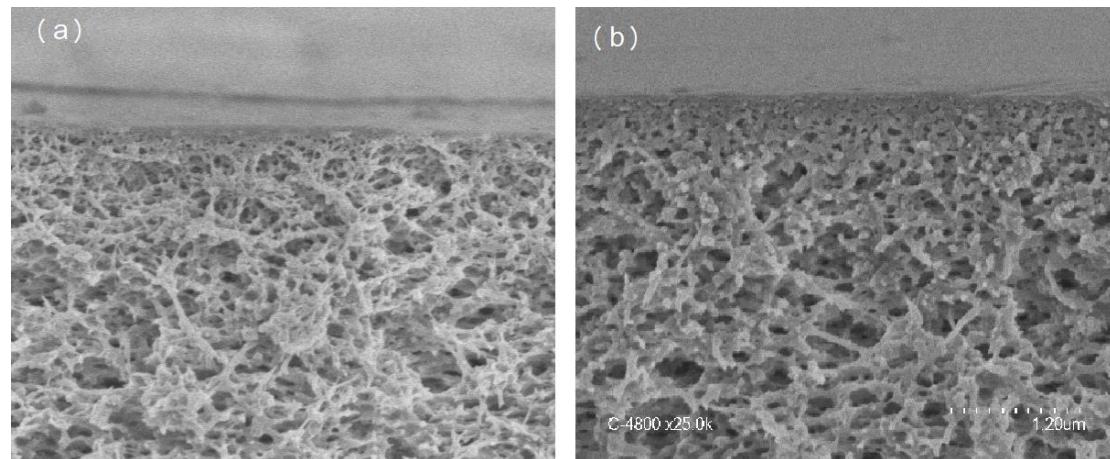


Figure 18. Cross Section images of two clean membranes. Control membrane (a), NF270 commercial membrane (b).

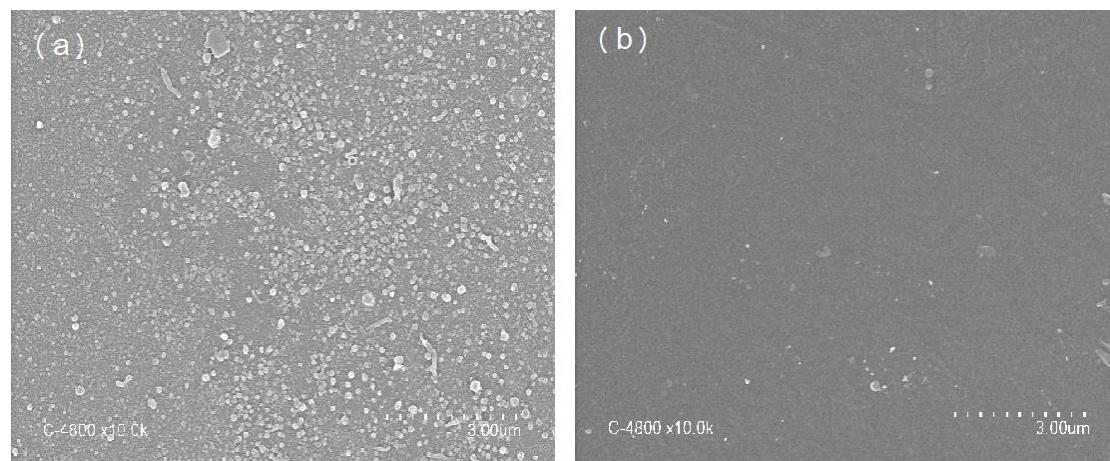


Figure 19. Surface images of two membranes. (a) is the (R)-APD membrane and (b) is the NF270 commercial membrane.

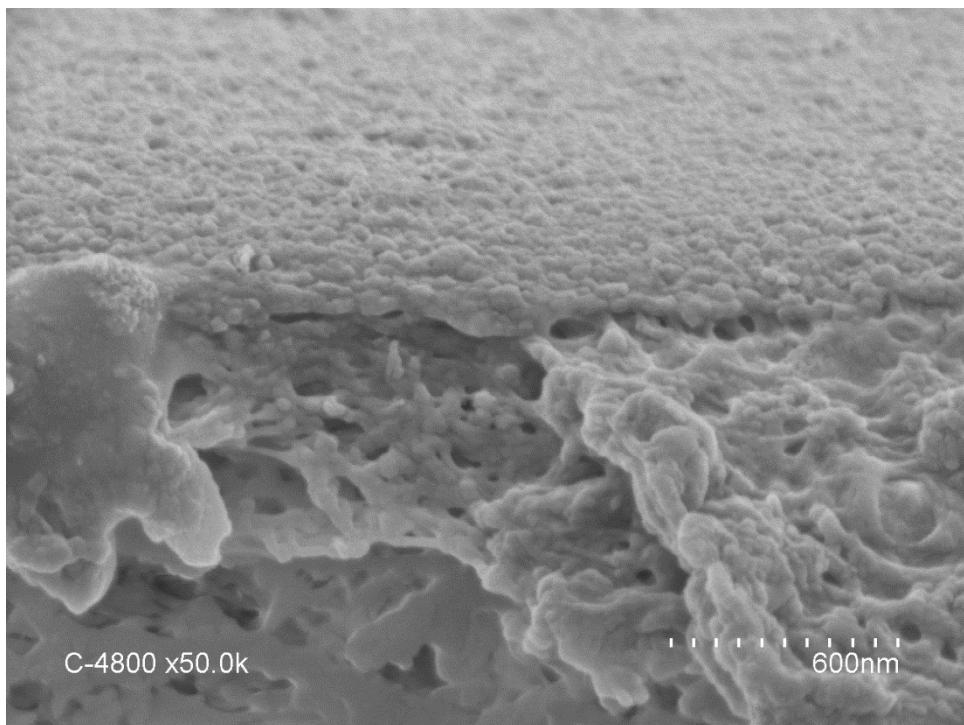


Figure 20. (R)-APD membrane with fouling (cross section)

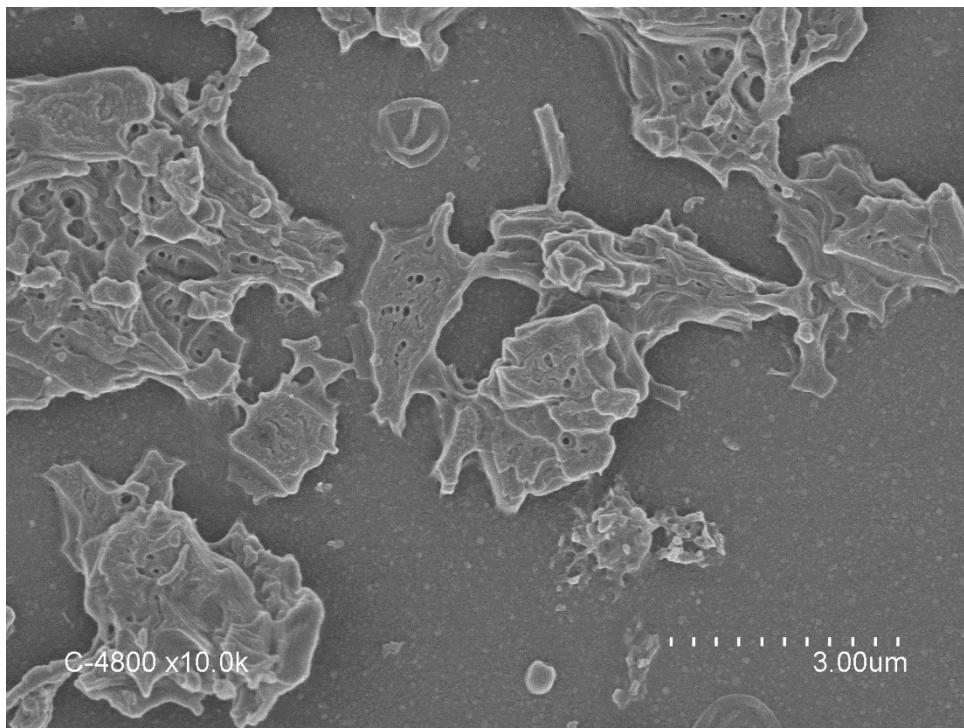


Figure 21. (R)-APD membrane with fouling (surface).

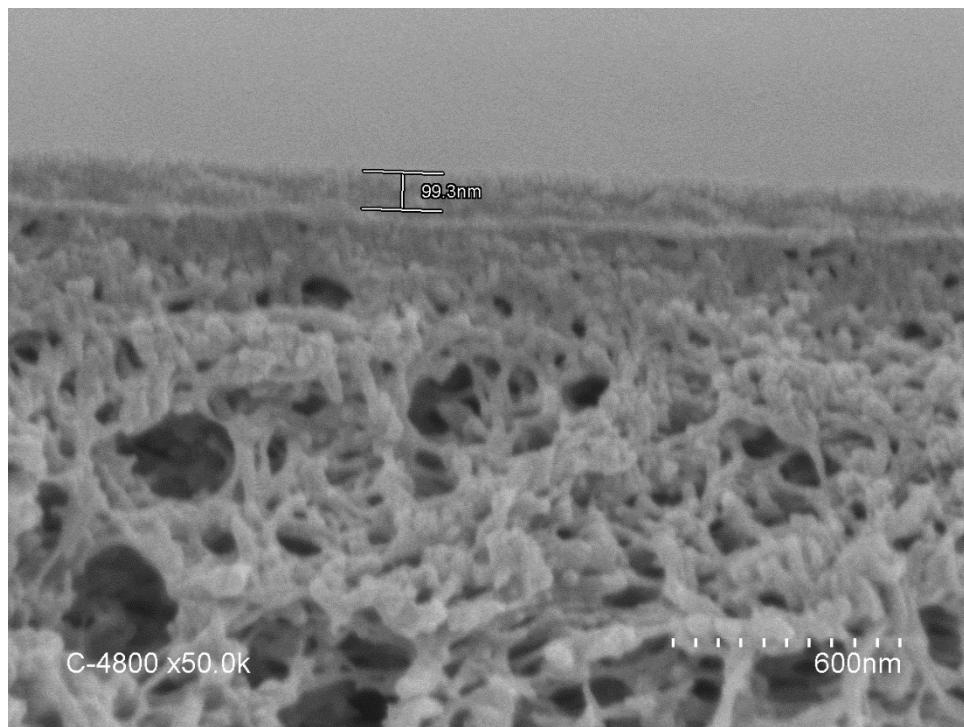


Figure 22. NF270 commercial membrane with a layer of fouling of 99,3 nm.

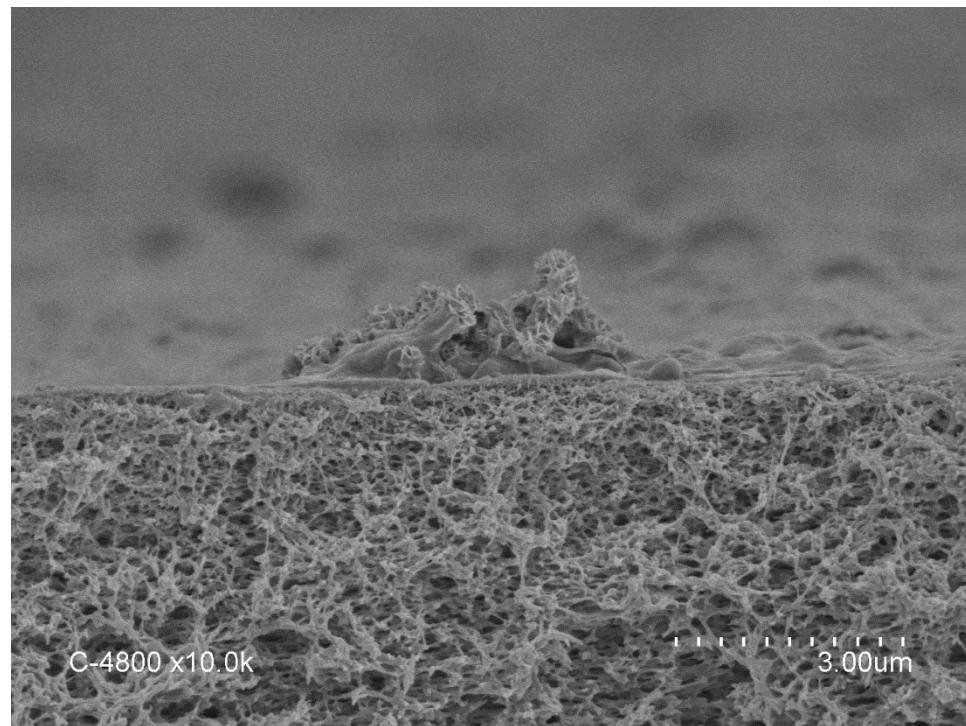


Figure 23. Fouling on the Control membrane.

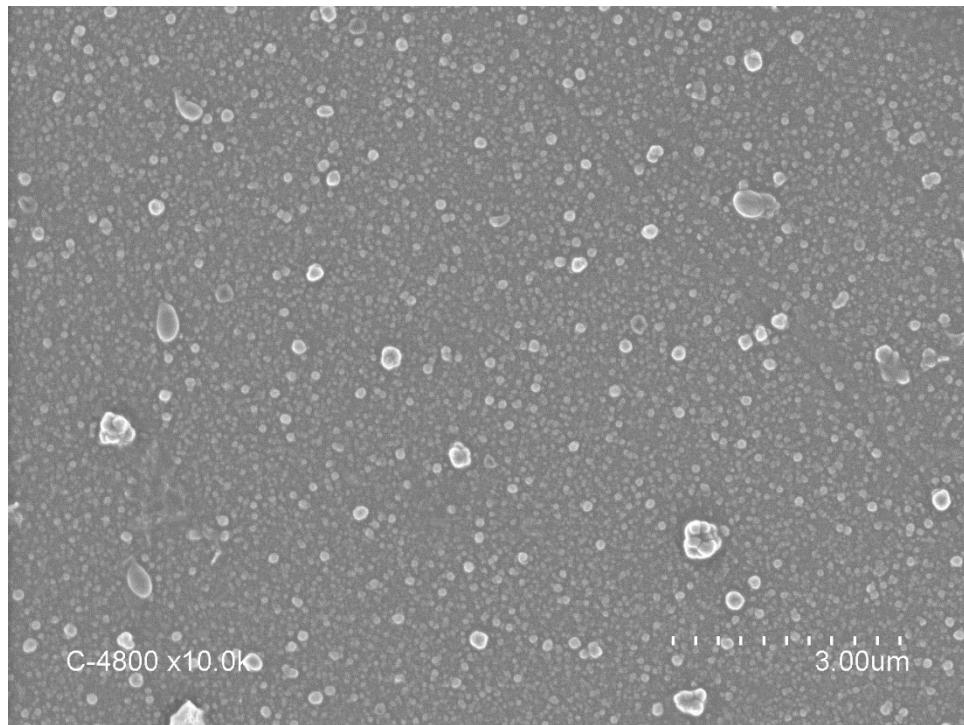


Figure 24. Clean surface of the Control membrane.

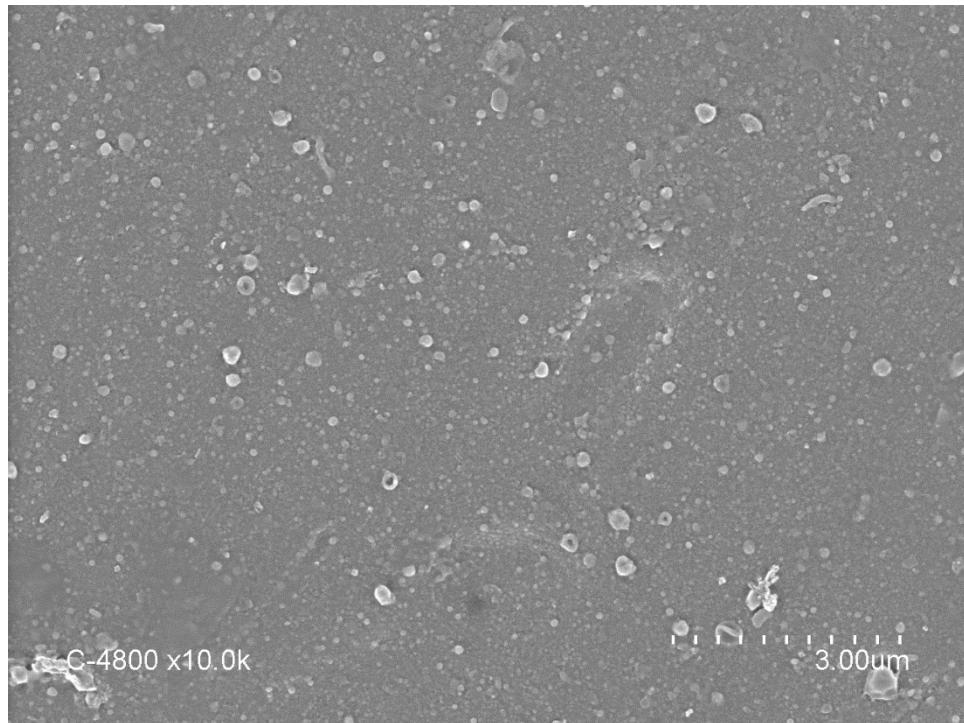


Figure 25. APD membrane with clean surface.

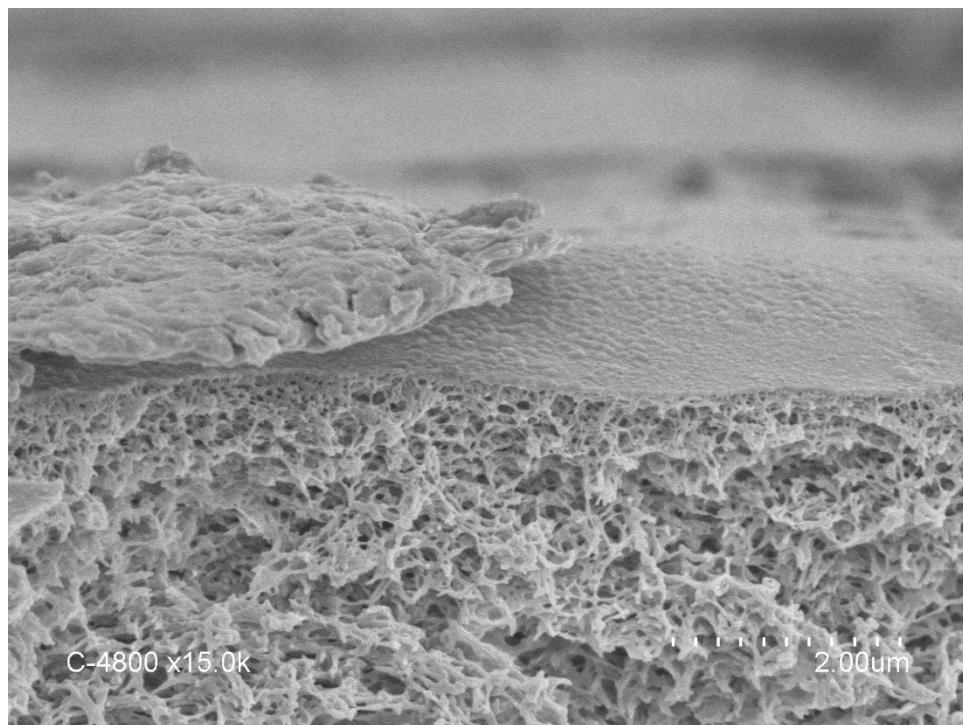


Figure 26. APD-grafted membrane with evident foulant on the surface.

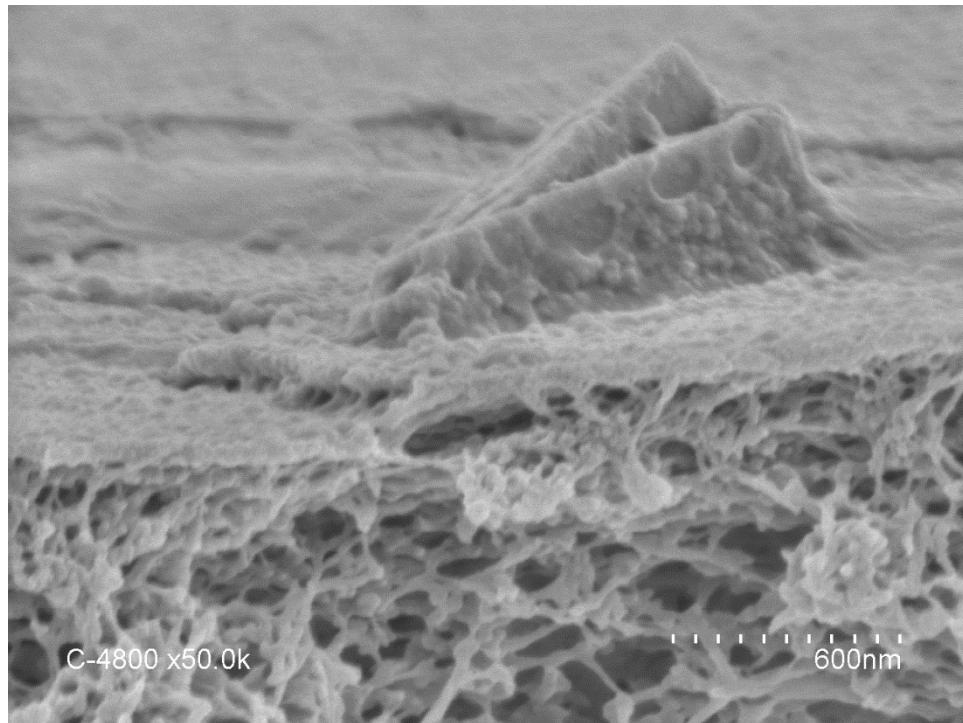


Figure 28. (R)-APD-grafted membrane with evident foulant on the surface.

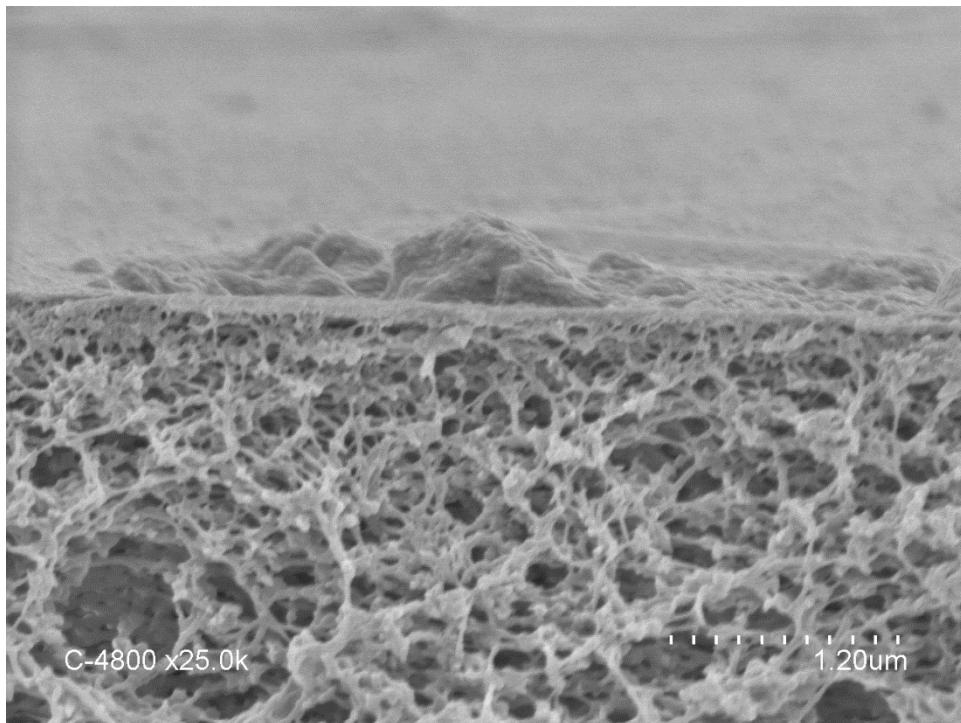


Figure 29. Fouled (R)-APD-grafted membrane.

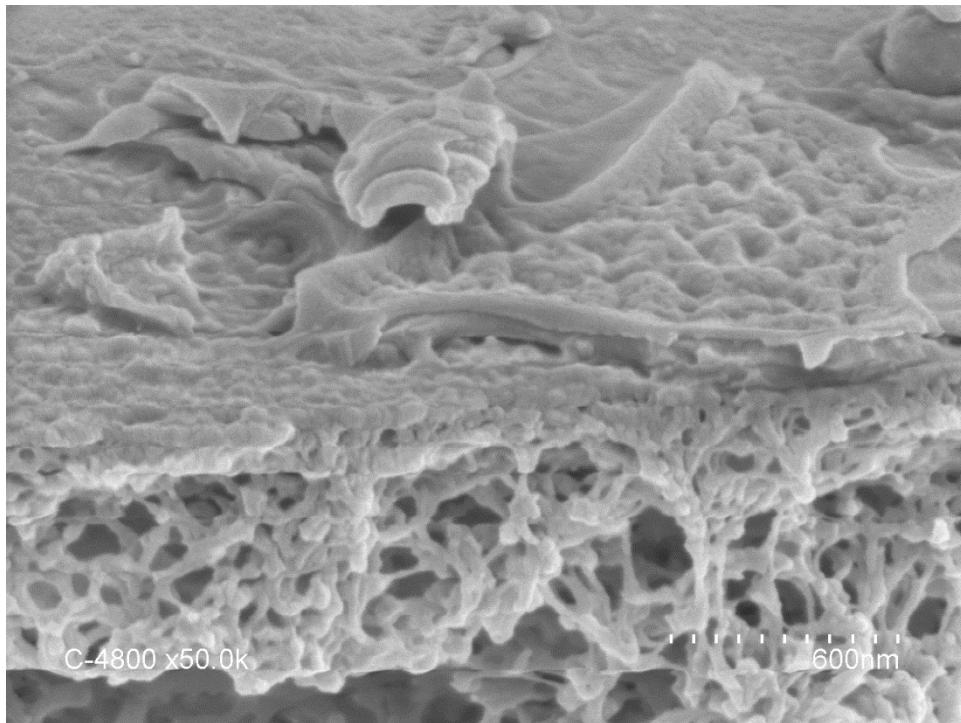


Figure 30. Fouled APD-grafted membrane.

5.2 AFM IMAGES

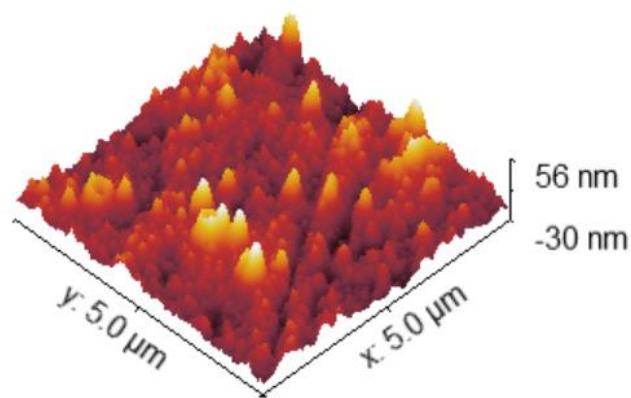


Figure 31. AFM image of the clean Control membrane (5 μm).

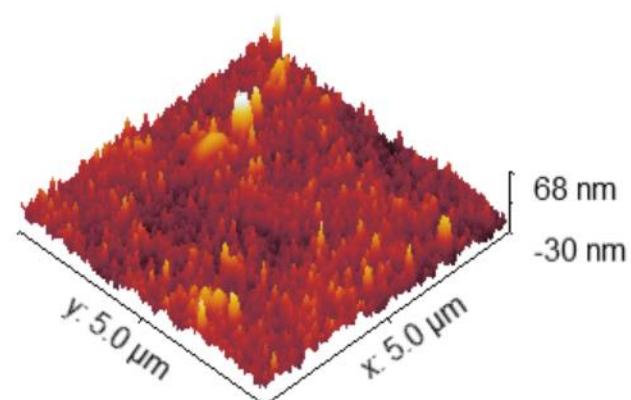


Figure 32. AFM image of the fouled Control membrane (5 μm).

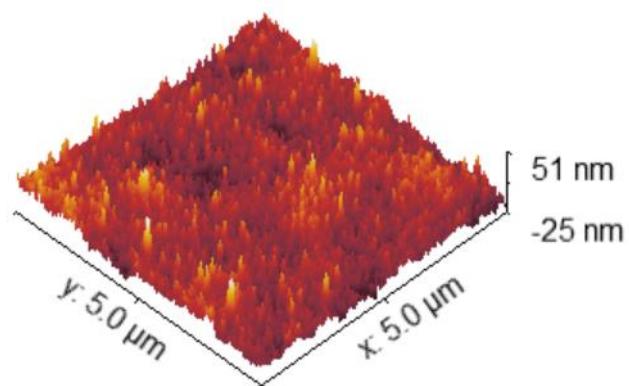


Figure 33. AFM image of the clean APD-grafted membrane (5 μm).

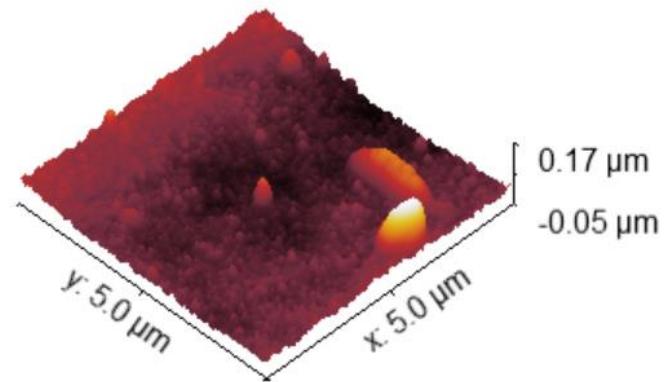


Figure 34. AFM image of the fouled APD-grafted membrane (5 μm).

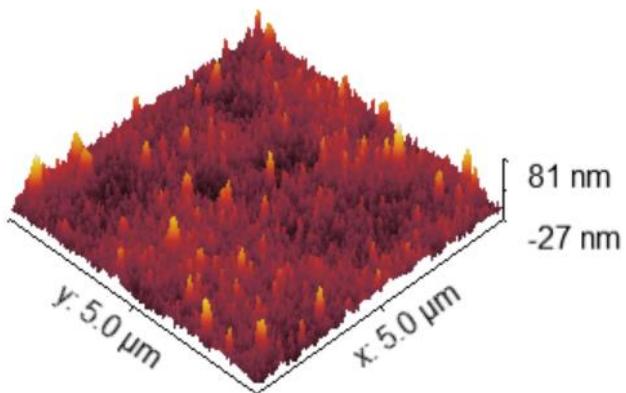


Figure 35. AFM image of the clean (R)-APD membrane (5 μm).

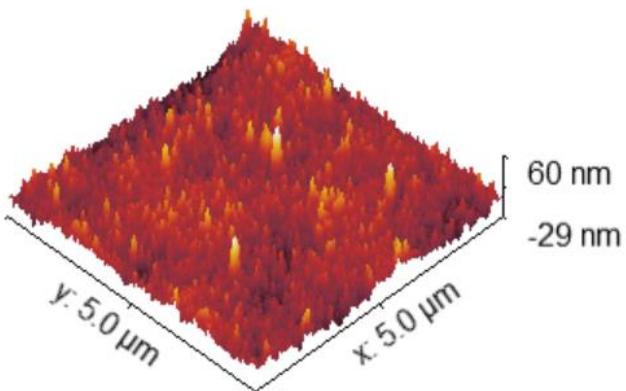


Figure 36. AFM image of the fouled (R)-APD membrane (5 μm).

6 EQUATIONS

$$J_i = \frac{V}{A \Delta t} \quad (1)$$

Where J_i ($\text{L m}^{-2} \text{h}^{-1}$) is the initial permeate, V (L) is the permeate volume, A (m^2) is the effective area of the membrane and Δt (h) is the time interval.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

Where R is salt rejection (%), C_p (mg/L) is the permeate concentration and C_f (mg/L) is the feed concentration.

$$\text{Flux loss} = \frac{J_i - J_f}{J_i} \times 100\% \quad (3)$$

Where Flux loss is the flux decline indicator (%), J_i ($\text{L m}^{-2} \text{h}^{-1}$) is the initial flux and J_f ($\text{L m}^{-2} \text{h}^{-1}$) is the flux upon fouling.

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