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Fabrication of polyamide thin film composite on functionalized supports for backwashing RO

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Riassunto in italiano

Realizzazione di membrane composite a film sottile in poliammide per osmosi inversa su supporti funzionalizzati per il controlavaggio

I. Introduzione e letteratura

L'acqua, chiamata anche oro blu, è un elemento essenziale nel nostro organismo e la sua presenza è necessaria per lo svolgimento di tutti i processi biochimici che avvengono nel corpo. L'oceano rappresenta il 70% della superficie terrestre e rappresenta il 96 percento dell'acqua sul pianeta. Il problema fondamentale è che l'acqua proveniente dagli oceani non può essere consumata a causa della presenza eccessiva del sale. Attualmente, circa 10 milioni di m3/giorno di acqua sono dissalati dall'osmosi inversa, fornendo circa l'1% della fornitura mondiale di acqua potabile. La metà di questa capacità viene prodotta in Medio Oriente e in altre regioni desertiche per produrre acqua municipale dalle acque reflue, dalle acque salmastre o dal mare. Il resto è installato negli Stati Uniti, in Europa e in Giappone, principalmente per produrre acqua industriale ultrapura. Attualmente sono in funzione più di 20 impianti di desalinizzazione dell'acqua di mare con capacità superiori a 100 000 m3/giorno. Questi impianti contengono da 0,2 a 1,0 milioni di m2 di membrane. [1]

Negli ultimi 30 anni, le prestazioni delle membrane e dei moduli a membrana sono costantemente migliorate. I miglioramenti e le migliori progettazioni dei processi hanno ridotto il costo della dissalazione dell'acqua marina a meno di $ 0,50 / m3 di acqua. L'energia utilizzata dal processo è stata ridotta da 6,1 kWh / m3 per l'impianto di Jeddah a ~ 2,0-3,0 kWh / m3 per un nuovo impianto dotato di moduli a membrana e dispositivi di recupero di energia. [1]

In generale, i processi di trattamento delle acque nei quali s'impiegano le membrane semipermeabili utilizzano come forza spingente la differenza di pressione (Trans-Membrane Pressure) applicata a monte e a valle del mezzo filtrante. Il funzionamento delle membrana basate sulla differenza di pressione può essere suddiviso in quattro categorie sovrapposte: osmosi inversa (RO), nanofiltrazione (NF), ultrafiltrazione (UF) e microfiltrazione (MF).

Le membrane di microfiltrazione hanno una dimensione dei pori di 0,1-10 μm, sufficiente a trattenere tutti i tipi di batteri, torbidità, macromolecole e colloidi. Mediante ultrafiltrazione vengono rimosse particelle con una dimensione di 0,001-0,1 μm: i virus, macroproteine e antibiotici. Nei processi di nano-filtrazione sono trattenute le particelle con una dimensione di 0,1 nm-0,001 μm.

Nelle membrane ad osmosi inversa i pori hanno una grandezza compresa tra 3 a 5 ° A di diametro. Il meccanismo di trasporto accettato attraverso le membrane per osmosi inversa è chiamato il modello di diffusione-soluzione.

Il punto di partenza per la descrizione matematica del modello di diffusione-soluzione nelle membrane è basato sulla termodinamica: le forze motrici di pressione, temperatura, concentrazione e potenziale elettrico sono correlate e la forza motrice complessiva che produce il movimento del permeante è il gradiente del suo potenziale chimico. Quindi, il fl ux, Ji (kg / m2 · s), di un componente, i, è descritto dalla semplice equazione:

$$Ji = -Li \frac{d\mu i}{dx}$$

Dove (dμi)/dx è il gradiente di potenziale chimico dei componenti i e Li è un coefficiente di proporzionalità che collega questa potenziale forza motrice al flusso. Nell'osmosi inversa, la variazione delle forze motrici è correlata alla concentrazione e ai gradienti di pressione, quindi il potenziale chimico può essere scritto come:

$$d\mu_i = RTdln(n_i\gamma_i) + v_i dp$$

dove n_i è la frazione molare (mol / mol) del componente i, γ_i è il legame di attività (mol / mol) che collega la frazione molare con l'attività, p è la pressione e υi è il volume molare del componente i.

La prima ipotesi del modello delle soluzione-diffusione è che i fluidi su entrambi i lati della membrana siano in equilibrio con il materiale della membrana all'interfaccia. Questo presupposto implica che il gradiente del potenziale chimico da ogni lato della membrana sia continuo.

La seconda ipotesi riguarda il modo in cui il potenziale chimico è espresso all'interno della membrana: il modello di diffusione-soluzione assume che la pressione all'interno di una membrana sia uniforme e questo equivale ad asumere che la membrana polimerica si comporti come un liquido

In due soluzioni separate da una membrana semipermeabile, si ha un flusso di solvente, detto osmosi, orientato dalla soluzione meno concentrata a quella più concentrata se la differenza tra la pressione della piàù concentrata e la meno concentrata è minore della differenza tra le corrispondenti pressioni osmotiche. Il flusso continuerà finchè la pressione idrostatica nella soluzione concentrata non compenserà la diminuzione del potenziale chimico del solvente dovuta alla sua minore concentrazione.

Per quanto riguarda le membrane semipermeabili utilizzate nel processo di dissalazione, queste devono avere la caratteristica di essere il più sottili possibili al fine di massimizzare il flusso dell'acqua. Pertanto, la membrana è spesso formata da un supporto poroso per fornire resistenza. I supporti devono avere pori sufficientemente grandi in modo da garantire il passaggio dell'acqua (permeato) attraverso il supporto ma non troppo grandi in quanto la membrana sarebbe incapace di trattenere le impurità. Scala et al. Suggeriscono come grandezze ottimale dei pori circa 8 micron (8000 nm). [6]

Si possono distinguere due diversi tipi di membrane utilizzate nel processo di osmosi inversa: membrane asimmetriche e membrane composite. Mentre nelle membrane asimmetriche integrali, sia il toplayer che il substrato sono costituiti dallo stesso materiale, nelle membrane composite il toplayer e il sottostrato sono composti da diversi materiali polimerici. Per realizzare membrane composite una delle tecniche più diffuse è la polimerizzazione interfacciale. Da quando Cadotte ha scoperto che le membrane ad osmosi inversa possono essere prodotte mediante polimerizzazione interfacciale. Le membrane realizzate con questo metodo sono diventate lo standard del settore. [9]

La polimerizzazione interfacciale (IP) è un processo in cui una membrana molto sottile è prodotta facendo reagire due monomeri contenuti in due soluzioni immiscibili tra loro all'interfaccia. Il supporto viene prima immerso in una soluzione acquosa contenente un monomero, frequentemente del tipo amminico, e successivamente viene immerso in un secondo bagno contenente un solvente immiscibile con acqua in cui è disciolto un altro monomero, spesso un cloruro acido. Questi due monomeri reattivi reagiscono l'uno con l'altro per formare un toplayer polimerico denso. Il vantaggio della polimerizzazione interfacciale è che la reazione produce un film di spessore estremamente sottile (50 nm).

In questo studio, è stata implementata la tecnica di polimerizzazione interfacciale su due diversi supporti microporosi (polisulfone e poliacrilonitrile) per formare uno strato di film sottile in poliammide necessario per il processo di osmosi inversa.

Da un punto di vista pratico, si afferma che lo strato selettivo e le strutture di supporto utilizzate possono essere adattati in modo indipendente per ottimizzare le prestazioni della membrana composita a film sottile. Tuttavia, questo non è strettamente vero poiché la struttura e le prestazioni dello strato di poliammide preparato dipendono fortemente dalla natura strutturale e chimica del supporto utilizzato. [3]

Dopo aver confrontato le caratteristiche delle membrane prodotte con due diversi supporti, l'obiettivo di questo lavoro è stato quello di aumentare le prestazioni delle membrane attraverso una pulizia sistematica di queste.

Il *fouling* delle membrane è la causa principale del declino del flusso nel tempo e della diminuzione della qualità del prodotto nei sistemi di osmosi inversa. In generale, le fonti di contaminazione possono essere suddivise in quattro categorie principali: incrostazioni, limo, batteri e organico.

Poiché le membrane composite a film sottile mostrano prestazioni ridotte nel tempo a causa dei fenomeni di sporcamento, possono essere applicati diversi metodi di pulizia. I metodi di pulizia chimica attraverso i quali si utilizzano soluzioni acide, alcaline, tensioattive e detergenti e i metodi di pulizia fisica come il controlavaggio o la pulizia osmotica. Il controlavaggio (*backwashing*) usato nelle membrane si basa sul ritorno del permeato al lato concentrato. Pertanto, le membrane devono avere una resistenza ad alta pressione in entrambe le direzioni.

Ridurre al minimo il tempo di controlavaggio e la quantità di acqua necessaria sono gli obiettivi principali del processo di controlavaggio, poiché consente di risparmiare acqua di permeato e tempo di produzione. Per rendere la membrana idonea a resistere alle operazioni di controlavaggio, è stata eseguita una reazione di aminazione in modo da creare un legame chimico stabile tra lo strato di poliammide e il supporto utilizzato. In seguito alla reazione di aminazione, il supporto è in grado di reagire con l'acilcloruro (TMC). [13]

Il lavoro svolto ha avuto come obbiettivo principiale quello di trovare la migliore combinazione, supporto e layer poliammidico, in grado di resistere a un trattamento sistematico di pulizia fisica (backwashing).

II. *Materiali e metodi*

Per lo studio effettuato, sono stati utilizzati divesi tipi di membrane sia commerciali sia fatte in laboratorio. Per quanto riguarda le membrane commerciali, sono state utilizate le membrane DOW SWRO30 e la membrane Hydracore 70. La membrana DOW SWRO30 è una membrana composita a film sottile di poliammide, mentre che la membrana Hydracore 70 è fatta di polietersulfone.

Per quanto riguarda le membrane di poliammide fatte in laboratorio, sono stati usate Ps20 SEPRO fatto di polisulfone e due diverse tipologie di membrane PAN: Ultura^{TM} brand, Long Beach, MWCO 75 kDa e Synder filtration, 4941 allison Pkwy, Vacaville, CA 95688, USA; MWCO 100 kDa.

Per creare il film poliammidico, è stata effettuata una polimerizzazzione interfacciale. La procedura descritta di seguito è analoga a tutti i tipi di supporti utilizzati per la fabbricazione delle membrane. In primo luogo, si è tagliato un campione di membrana di dimensioni 10x13 cm. Il campione poi è stato incollato ad un vetro temperato con nastro adesivo impermeabile -della Fisher Scientific, di colore verde lime e da 1 pollice di larghezza- tenendo il film attivo sulla superficie (Figure 1). Il vetro con il campione di membrana è stato depositato in un contenitore pyrex con pendenza di circa 20 gradi dentro la quale si ha la soluzione contenenete MPD (3.4 % in peso). Si è mantenuto lo strato attivo a contatto con la soluzione di MPD per 2 minuti (Figura 2).

Dopo aver rimosso il campione della membrana dalla soluzione MPD, è stato usato un asciugacapelli per rimuovere la soluzione in eccesso. L'asciugacapelli è stato passato lentamente sul campione di membrana in una sola direzione. Successivamente il campione è stato immerso in una soluzione idrocarburica con benzenetricarbonile tricloruro (0.15 % in peso) per 1 minuto. Contemporaneamente, si è fatta bollire acqua deionizzata. Dopo aver rimosso il campione dalla soluzione di TMC si è lasciata asciugare per 2 minuti. L'acqua deionizzata calda (95 °C) veine versata sul *cooking pan*. Il campione viene quindi immerso nell'acqua deionizzata calda per 2 minuti. In seguito al trattamento termico, membrana è stato rimossa dal vetro attraverso l'uso di un taglierino. La membrana è stata poi immersa in un beaker contenente una soluzione di NaOCl per 2 minuti e successivamente è stata immersa nella soluzione di metabisolfito di sodio per 30 secondi. L’ultimo step è stato quello di immergere la membrana in acqua deionizzata calda (95 °C) per 2 minuti. Alla fine di tutti I passaggi descritti sopra si è creato il toplayer in poliammidico.

Per fabbricare membrane da utilizzare nelle condizioni di controlavaggio si è eseguita una reazione di aminazione grazie alla quale il layer poliammidico crea dei legami chimici stabili con il supporto utilizzao.

La modificazione chimica dei supporti è stata eseguita prima di eseguire il processo di polimerizzazione interfacciale. Sono stati seguiti due diversi protocolli per ottenere l’amminazione delle membrane PES e PAN.

Per quanto riguarda le membrane PES, le membrane sono state immerse in una soluzione di NaOH (ph 11) per una notte, seguite dal risciacquo con etanolo. Dopo ciò, le membrane sono conservate in acqua deionizzata. Per creare il gruppo carbossilico sulla superficie della membrana, è stata eseguita una reazione REDOX attraverso l’utilizzo di una soluzione di acido metacrilico (1 M) disciolto in acqua deionizzata. Quindi la reazione iniziato immergendo un pezzo della membrana PES nella soluzione dei monomeri agitato su una piattaforma di un agitatore orbitale Unimax 1010 (heidolph, Kelheim, Germania). Dopo 2 minuti sono stati aggiunti gli iniziatori: 0.1 M di sodio persolfato ($Na_2S_2O_8$) e 0.1 M di sodio metabisolfito ($Na_2S_2O_5$), in modo da raggiungere una concentrazione equimolare finale di 0.01 M. Il grafting è stato eseguito per 10 minuti a 25° C con agitazione. Infine, la membrana è stata lavata, dapprima con acqua e successivamente lavata tre volte per 10 minuti in un bagno sonico. Le membrane sono state conservate in acqua deionizzata a 4 ° C.

La membrana modificata è stata immersa in una soluzione tampone (50 mM, pH 7,4), 3 mM di N-idrossisolfosuccinimmide sodica (sulfo-NHS), 3 mM N-(3-dimetilamminopropil)-N'-etilcarbodiimmide cloridrato (EDC) e 10 mM di etandiamina. La soluzione è stata agitata su uno shaker orbitale Unimax 1010 (Heidolph, Kelheim, Germania) a temperatura ambiente per 2 ore. Alla fine, la membrana è stata lavata per 10 minuti con la soluzione tampone diluita 5 volte, poi altri 10 minuti con acqua deionizzata in bagno ultrasonico, 10 minuti in una soluzione acquosa di isopropanolo (50%) e infine lavata tre volte per 10 minuti con acqua deionizzata in bagno ultrasonico. La membrana è stata conservata in acqua deionizzata a 4 ° C.

Per quanto riguarda le membrane PAN, prima di eseguire la reazione di amminazione, sono state immerse in una soluzione al 50% di etanolo in acqua per 6 ore e successivamente si è eseguito un risciacquo con acqua deionizzata. Dopo ciò, le membrane PAN sono state immerse in una miscela di dietilentriammina (157,575 g), carbonato di sodio (catalizzatore, 5 g) e acqua distillata (500 ml) per 2 ore a 60 ° C sotto agitazione (120 rpm). Al termine della reazione, le membrane sono state sciacquate e conservate in acqua deionizzata.

Per misurare la permeabilità delle membrane prodotte, è stato utilizzato un sistema a flusso tangente (*crossflow system*). Nel sistema utilizzato l'alimentazione scorre tangenzialmente alla membrana e attraversa la membrana grazie al gradiente di pressione presente sui due lati della membrana stessa.

Si crea un flusso di permeato ortogonale alla membrana e di retentato tangenziale alla stessa. (Figura 6). Il sale e l'acqua permeano la membrane secondo il meccanismo di trasporto soluzione-diffusione.

I test sono stati condotti in un impianto di filtrazione in scala di laboratorio, che comprende: una cella contenente la membrana, tre collettori (alimentazione, retentato e permeato), un foglio di membrana, con un area di 22,12 cm^2, situata all'interno della cella, un pompa idraulica tipo G03 (figura 6) che consente una pressione massima di 1000 psi (70 bar), un manometro da 0 a 1500 psi (0-100 bar), due valvole di controllo della pressione, un flussimetro per misurare la portata e un refrigeratore (Figura 7) che mantiene costante la temperatura di alimentazione dell'acqua di circa 22 ° C (figura 5).

Il flusso di acqua e la ritenzione di NaCl delle membrane sono stati valutati permeando una soluzione acquosa di NaCl (NaCl a 35 mM nella soluzione di alimentazione). Tutti i test per le membrana sono stati eseguiti alle pressioni di 20,68 bar, 19,30 bar, 17,92 bar e 16,54 bar e una portata di 1 L min^{-1}. I dati sulle prestazioni sono stati raccolti dopo 6 ore di compattamento. Il flusso d'acqua (Jw, Lm^{-2} h^{-1}) è stato determinato dalla quantità del permeato raccolto (ΔV) per un intervallo di tempo fisso (Δt) per la relazione data da $Jw = \Delta V \,/\, am\Delta t$.

Nel controlavaggio, la pressione di transmembrana è stata periodicamente invertita mediante l'uso di una pompa secondaria, in modo da permettere al permeato di ritornare verso la feed, sollevando lo strato di incrostazione sulla superficie della membrana. [16] Per eseguire il controlavaggio sono stati aggiunti al sistema *crossflow* un serbatoio e una cillindro di azoto come mostrato nello schema 2. Prima di eseguire ogni esperimento, si è eseguito un compattamento per 6 ore a 300 psi e 4,5 l/h. Successivamente, il flusso è stato misurato a tre diverse pressioni (280, 260, 240 psi) per 10 minuti. Dopo l'ultima misurazione del flusso, al sistema viene aggiunta una soluzione 1 M di NaCl per ottenere una concentrazione finale di 35 mM. Il permeato è stato raccolto dopo 45 minuti e sono stati prelevati tre campioni per misurare il rigetto salino. Una volta terminata questa fase classica, si è iniziata la seconda parte dell'esperimento, il controlavaggio (*backwashing*). Come riportato di seguito nella figura 8, un serbatoio ausiliario è stato direttamente collegato al permeato da una valvola a tre vie. Questo serbatoio fornisce il permeato per l'esperimento di controlavaggio. L'esperimento di controlavaggio è composto dai seguenti passaggi: dopo aver prelevato l'ultimo campione per la misura della ritenzione salina, si rimuove la pressione di alimentazione e si mantiene la portata sempre a 4.5 l/h. Dopo 1 minuto la pressione viene nuovamente applicata. Dopo 45 minuti in cui vengono misurati il flusso e il ritenzione salina, viene nuovamente diminuita la pressione di alimentazione ma questa volta contemporaneamente il serbatoio ausiliario viene pressurizzato raggiungendo il valore di 6 bar. La pressione del permeato (*backwashing*) viene mantenuta per 1 minuto. Quindi, la pressione sul permeato viene rimossa e applicata nuovamente dal lato di alimentazione. Il processo descritto viene ripetuto tre volte dopo il terzo controlavaggio, l'esperimento termina

III. ***Risultati e discussioni***

L'obiettivo principale di questo lavoro è stato quello di formare un sottile strato di poliammide avente legami chimici abbastanza resistenti con il supporto utilizzato in modo da poter resistere all'operazione di controlavaggio. Per questo motivo, il primo passo è stato quello di caratterizzare le diverse membrane dove è stato formato un sottile strato di poliammide attraverso la tecnica di polimerizzazione interfacciale.

Nella prima parte della tesi, il primo obiettivo è stato quello di eseguire con successo la polimerizzazione interfacciale sul supporto di PES. Nella figura 14 lo spettro ATR della membrana fabbricata (linea blu) è riportato e confrontato con la membrana poliammidica commerciale (DOW SW 30). Si nota chiaramente che i picchi caratteristici della formazione di poliammide sono presenti: i picchi sono attribuiti all'ammide I (stiramento $C=O$, 1668 cm-1), ai gruppi carbonile

(C=O con legami a H, 1610 cm-1) e all'ammide II (NH flessione, 1542 cm-1). Quindi si può concludere che lo strato di poliammide sul supporto della membrana PES è stato creato con successo.

Sebbene la presenza dello strato di poliammide sul supporto PES, lo strato di poliammide formato con polimerizzazione interfacciale classica è solo fisicamente attaccato al supporto, lo scopo è quello di fabbricare una membrana poliammidica che è chimicamente legata sul supporto. Quindi, il passo successivo è stato quello di modificare prima il supporto delle membrane per renderle idonee alla formazione di un forte legame chimico tra i supporti e lo strato di poliammide.

Il supporto PES ha richiesto una modifica della superficie della membrana seguita da una reazione di amminazione. L'idea è stata quella di formare prima un gruppo acido carbossilico mediante una reazione redox utilizzando come monomeri solo MA o una soluzione di MA + MOETMA. I gruppi funzionali formati dopo la reazione redox sono mostrati nelle figure 15 e 16. Come si può vedere dalle figure 17 e 18 all'aumentare del tempo di reazione, aumenta il picco corrispondente al gruppo carbossilico (1700 cm-1)

Il secondo passo è stato quello di funzionalizzare la membrana attraverso una reazione di amminazione descritta in figura 19. Lo spettro di una PES bianca è stato confrontato con quello di una PES in cui è stata eseguita la reazione di aminazione (figura 20)

Per quanto riguarda le membrane PAN, sfortunatamente non è stato possibile eseguire test ATR sufficienti. In figura 22 è stato mostrato un confronto tra una membrana PAN bianca e una in cui è stata eseguita la reazione di aminazione e polimerizzazione interfacciale.

I risultati dell'angolo di contatto le membrane PES confermano i risultati ATR. I valori dell’angolo di contatto delle PES bianche risultano in accordo con quelli trovati in letteratura. Dopo la prima modifica delle membrane PES con MA (o MA + MOTMA) gli angoli di contatto sono diminuiti fino a 30° gradi (tabella 1) e questo conferma che la superficie di PES è stata modificata.

I valori dell'angolo di contatto dopo la fase di aminazione, aumentano e si nota che la membrana diventa piuttosto idrofoba. Ciò dimostra la presenza dei gruppi amminici -NH2 appartenenti all'ammina utilizzata nella reazione. Si nota inoltre che in seguito alla reazione di polimerizzazione interfacciale, i valori diminuiscono fino a ~ 65°, che è un valore tipico per le membrane poliammidiche.

Come si vede dalla tabella 2, le membrane aminate con polimerizzazione interfacciale e le membrane con solo polimerizzazione interfacciale hanno gli stessi valori.

I test di filtrazione eseguiti sia su membrane commerciali e sia su membrane fatte in laboratorio sono stati effettuati per valutare le loro prestazioni prima di sottoporle al controlavaggio. Sono stati riportati i flussi, J, in funzione della pressione P alla quale sono stati misurati. La pendenza della retta è la permeanza (A) della membrana, espressa in LMH / Bar. Insieme alle misurazioni del flusso sono stati valutati e riportati anche i valori di ritenzione salina per ciascuna membrana.

In figura 23 sono stati riportati i risultati dei test di filtrazione eseguiti su due membrane commerciali DOW SWRO30, membrana composita a film sottile in poliammide e Hydracore 70, membrana in polietersulfone solfonato (figura 24).

La Figura 25 e la Figura 26 mostrano il flusso medio di acqua [LMH] rispetto alla pressione media [bar] per tutte le membrane in cui è stata eseguita la polimerizzazione interfacciale. È evidente che il flusso e le permeabilità sono chiaramente i più alti per le membrane con i supporti PES. In particolare, il flusso osservato con le membrane di supporto PAN (UlturaTM, Long Beach) è 4 volte inferiore alle membrane con supporto PES. Una delle possibili ragioni per questo risultato ottenuto è la diversa bagnabilità dei due supporti, la quale influisce sulla formazione dello strato poliammidico.

Una scoperta interessante è che, nonostante la formazione di uno strato di ammina, il flusso non è diminuito.

Per quanto riguarda la ritenzione salina, dalla figura 30 si nota che dopo la reazione di aminazione si ha un aumento significativo del valore della ritenzione salina nelle membrane PAN (marchio UlturaTM, Long Beach) mentre c'è una diminuzione del valore delle membrane PES.

Come si vede dalle figure 31, 32, 33 e 34, i valori di ritenzione salina più elevati sono stati raggiunti dalle membrane PES con la sola polimerizzazione interfacciale mentre si nota una diminuzione notevole della ritenzione salina nelle membrane PES modificate. Non c'è una ragione specifica per avere questa riduzione del rifiuto, tuttavia si è riscontrata una riduzione del rifiuto per supporti PES (appartenenti allo stesso lotto delle prime PES non modificate) nei quali la sola polimerizzazione interfacciale è stata eseguita in un secondo momento. Pertanto, sembra che i risultati ottenuti siano cambiati per un motivo non determinato che potrebbe essere dovuto al degrado del supporto.

Si nota inoltre che non ci sono differenze significative nella variazione della permeabilità tra membrane PES modificate e non modificate.

Per quanto riguarda le membrane PAN (marchio UlturaTM, Long Beach), è interessante notare che dopo il processo di amminazione c'è un aumento significativo del valore di rigetto e anche della permeabilità.

Lo step finale è stato quello di testare le membrane commerciali e quelle prodotte in laboratorio in modalità backwshing seguendo il protocollo descritto nel capitolo 2.

La Figura 34 mostra il codice colore utilizzato per mostrare i diversi passaggi a cui le membrane sono state sottoposta durante i test di controlavaggio.

Come mostrano le figure 35 e 36, le membrane commerciali testate hanno avuto un comportamento completamente diverso: dopo il primo controlavaggio, la membrana DOW SW30 si è rotta presentando un evidente distacco del lato attivo dal supporto PES mentre la membrana Hydra70 durante il controlavaggio è rimasta stabile sia per quanto riguarda il flusso sia per quanto riguarda la rimozione salina.

Per quanto riguarda le membrane PES, i risultati del controlavaggio sono mostrati nelle figure 37 e 38. Sia le membrane PES aminate sia non aminate hanno presentato un comportamento simile durante il controlavaggio, infatti entrambi i tipi di membrane non hanno subito rottura e hanno mostrato una riduzione di rimozione salina probabilmente determinata dallo spaziatore.

Per quanto riguarda le membrane PAN, poiché nell'ultima fase del lavoro, il marchio UlturaTM, Long Beach, MWCO 75 kDa non è più stato disponibile si è utilizzato un nuovo supporto (Synder, 4941 Allison Pkwy), con caratteristiche diverse (permeabilità e dimensione dei pori). In quanto la disponibilità di queste membrane è stata limitata si sono testate solo membrane in cui si è eseguita aminazione e polimerizzazione interfacciale. Durante le operazioni di controlavaggio si è notato un aumento repentino del flusso e la perdita totale di rimozione salina. Questo comportamento si può tradurre con un distacco dello strato poliammidico dal supporto.

Si può concludere che le membrane poliammidiche commerciali hanno un valore di rimozione salina migliore ma una bassa permeabilità e sono soggette a rottura. Inoltre le membrane HYDRA risultano essere le più resistenti alle operazioni di controlavaggio, le membrane PES modificate e non modificate necessitano di ulteriori ricerche anche se sembrano essere più resistenti rispetto alle corrispondenti commerciali e infine le membrane PAN a causa del cambio di supporto hanno mostrato un miglioramento dopo l'aminazione ma non è stato possibile eseguire i test di controlavaggio.

Abstract

Water scarcity is considered a future danger to human activity and a trend to develop alternative water resources such as desalination can be observed. One of the methods used for water treatment is reverse osmosis. The use of reverse osmosis water has grown exponentially since it was introduced as a domestic water purification system. One of the major obstacles to the diffusion of its application is that the filtration performance certainly decreases with the filtration time, due to fouling. Membrane fouling is a process whereby a solution or a particle is deposited on a membrane surface or in membrane pores so that the membrane performance decreases.

This work was focused on developing robust membranes, able to withstand physical cleaning:in particular, a chemical modification of the support layer of thin-film composite membranes was performed, with the aim of fabricating more robust reverse osmosis membranes where the thin polyamide film is covalently bound to the support to minimize delaminatin or destruction of the membrane during cleaning under backwashing conditions. An amination reaction had to be carried out to create strong chemical bonds between the polyamide thin film and two different types of support used, made of polyacrinonitrile (PAN) or polysulfone (PES).

The first step was to characterize the thin-film composite membanes created on two different supports: the performance of the PES membranes was clearly better than that of the PAN membranes, as the flux observed with PAN support membranes was 20/30 times lower than that of membranes cast on PES supports. Furthermore, membranes cast onto PES supports exhibited the highest NaCl rejection (99%).

The transport caharacteristics of the different membranes cast during this study were evaluated and compared with those of commercial membranes and thin-film composite membranes cast in a traditional way. Subsequently, backwashing tests were carried out to understand and identify possible improvements of the membrane fabricated onto the modified supports compared with the traditional procedures.

Aackwashing system was designed and built specifically for this study. Commercial polyamide membranes subjected to backwashing broke during cleaning, while the system worked well with commercial asymmetric membranes not containing a thin film. No significant differences were observed between lab-made membranes fabricated onto modified and unmodified supports. In general, membranes cast onto PAN supports broke during backwashing while membranes cast onto PES layers were more robust.

In the future, it is necessary to study more about the system and identify the most suitable support layer.

Introduction

Water treatment is a very interesting thing to be discussed, because water is something that is always needed in our lives. The ocean makes up 70 percent of the earth's surface and accounts for 96 percent of the water on the planet. The problem is, this water can not be consumed. It is oversaturated with salt. One of the most important ways of purifying water and making it safe for drinking is reverse osmosis. Reverse osmosis systems are widely used throughout the world. Reverse osmosis membrane technology has developed over the past 40 years to a 44% share in world desalting production capacity, and an 80% share in the total number of desalination plants installed worldwide.

Currently, approximately 10 million m3/day of water are desalted by reverse osmosis, providing approximately 1% of the world's drinking water supply. Half of this capacity is installed in the Middle East and other desert regions to produce municipal water from wastewater, brackish groundwater, or the sea. The remainder is installed in the United States, Europe, and Japan, principally to produce ultrapure industrial water. More than 20 seawater desalination plants with capacities of more than 100 000m3/day are now in operation. These plants each contain from 0.2 to 1.0 million m2 of membrane.[1]

Over the past 30 years, the performance of membranes and membrane modules has steadily improved. The improvements and better process designs have cut the cost of seawater desalination to below $0.50/m3 of water. The energy used by the process has also been reduced from 6.1kWh/m3 for the Jeddah plant to ~2.0–3.0kWh/m3 for a new plant fitted with today's membrane modules and energy recovery devices on the high-pressure brine concentrate solution.[1]

Today, reverse osmosis membranes are the leading technology for new desalination installations, and they are applied to a variety of salt water resources using tailored pretreatment and membrane system design. [2]

From a practical perspective, it is claimed that the selective layer and support structures can be independently tailored to optimize thin film composite membrane performance. However, this is not strictly true since the structure and performance of the prepared polyamide layer are dependent strongly on the structural and chemical nature of the support used.[3]

In this study, it was implemented interfacial polymerization technique on two different microporous supports (Polysulfone and Polyacrylonitrile) to form polyamide thin film layer necessary for the reverse osmosis process.

After a comparison of the characteristics of manufactured membranes with two different supports, the objective of this work was to increase the performance of the membranes through a systematic cleaning of these.

Membrane fouling is the main cause of permeant flux decline and loss of product quality in reverse osmosis systems, so fouling control dominates reverse osmosis system design and operation. Find the best polyamide support-layers combination with good filtration characteristics and at the same time find the combination able to withstand a cleansing treatment were the goals on which work was focused

In chapter 1, a literature review is presented to provide an overview of the current knowledge about reverse osmosis membranes prepared by interfacial polymerization and cause of permeant flux decline.

Chapter 2 contains a definition of methods and materials used in the work (preparation of thin film composed membrane and set up of Backwashing system).

In chapter 3, the results of the studies on the different types of membranes in which the interfacial polymerization was performed and the modification to make it suitable for backwashing are presented and discussed.

Finally, chapter 4 provides key conclusions of this overall research.

1. Literature Review

1.1 Membranes

A membrane is a thin film of porous material that allows water molecules to pass through it, but simultaneously prevents the passage of larger and undesirable molecules such as viruses, bacteria, metals, and salts (American Water Works Association 1999). Membrane process are characterized by the fact that the feed stream is divided into two streams, the retentate (or concentrate) and permeate streams.[4]

1.2 Membrane processes

In general, membrane treatment processes use either pressure-driven, therrmally-driven or electrical-driven technologies. Pressure driven membrane operation can be divided into four overlapping categories: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF).[1]

Micro-filtration membranes have a pore size of 0.1-10 µm, enough to restrain all types of bacteria, turbidity, macromolecules and colloidals. By means of ultra-filtration, particles with a size of 0.001-0.1 µm are removed. All viruses, macroproteins, antibiotics, etc, are restrained in these membranes. In nano-filtration procceses, particles with a size of 0.1 nm-0.001 µm are restrained, allowing water separation from most molecules, although low molecular weight particles are partially restrained in the membrane.

The mechanism of separation by reverse osmosis membranes is quite different. In reverse osmosis membranes, the membrane pores are so small, from 3 to 5 ˚A in diameter, that they are within the range of thermal motion of the polymer chains that form the membrane. The accepted mechanism of transport through these membranes is called the solution-diffusion model. [1]

1.3 Membranes transport

Mass transport through the membrane is controlled a difference of driving force, in general a difference of the chemical potential, µ, of the components, from one of the two sides of the membrane, normally in the feed. The difference of chemical potential between the two sides of the membrane is practically a difffernce of pressure or concentration (or activity).[5]

At constant temperature T, the chimica potential of component i in a mixture is given by

$$\mu_i = \mu_i^0 + RTln a_i + V_i P$$

Where μ_i^0 is the chimica potential of 1 mol of pure substance at a pressure P and temperature T. For pure components the activity is unity but for liquid misture the activity is given by the product of mole fraction x_i and activity coefficient γ_i

$$a_i = x_i * \gamma_i$$

For ideal misture the activity coefficient is unity, $\gamma_i = 1$, so that the activity is equal to the mole fraction. However, since many non-acqueous mixtures are non ideal, activities rather than concentrations should be used.

1.3.1 Transport mechanisms

The most important property of membranes is their ability to control the rate of permeation of different species. Nowadays the most exhaustive model to explain the separation mechanism in reverse osmosis membranes is solution-diffusion model.

In solution-diffusion model permeants dissolve into the membrane material and then diffuse through it down a concentration gradient. Permeants are separated because of differences in their solubilities with the membrane and differences in the rates at which they diffuse through the membrane.[1] Figure 1 shows that dense solution-diffusion membranes separate because of differences in the solubility and mobility of permeants dissolved in the membrane material instead of microporous membranes, which separation phenomenon id dependentedn of the pore size and it is achieveed by molecular filtration.

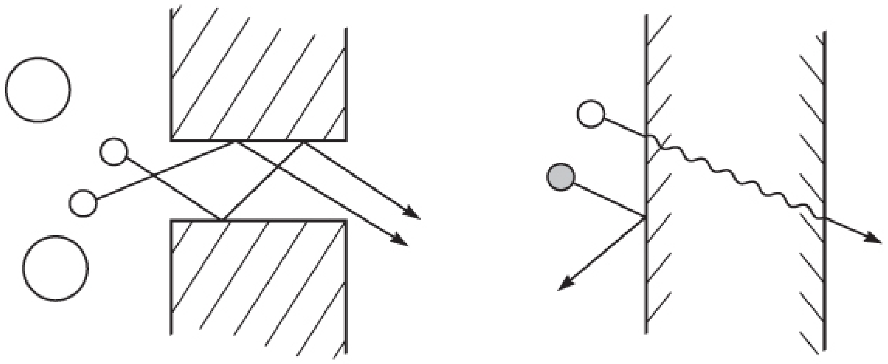


Figure 1. Differences between Pore-flow and Solution-Diffusion Model. [1]

1.3.2 Solution-Diffuson Model

The starting point for the mathematical description of diffusion in membranes is the proposition, solidly based in thermodynamics, that the driving forces of pressure, temperature, concentration, and electrical potential are interrelated and that the overall driving force producing movement of a permeant is a gradient in its chemical potential. Thus, the flux, Ji (kg/m2·s), of a component, i, is described by the simple equation

$$\text{I.} \qquad Ji = -Li \frac{d\mu i}{dx}$$

Where $\frac{d\mu i}{dx}$ is the chemical potential gradient of component i and Li is a coefficient of proportionality linking this chemical potential driving force to flux. In reverse osmosis, the variation of driving forces is related to concentration and pressure gradients, thus the chemical potential can be written as

$$\text{II.} \qquad d\mu_i = RTdln(n_i\gamma_i) + v_i dp$$

where n_i is the mole fraction (mol/mol) of component i, γ_i is the activity coefficient (mol/mol) linking mole fraction with activity, p is the pressure, and vi is the molar volume of component i. In incompressible phases, such as in a liquid or a solid membrane, volume does not change with pressure. In this case, integrating Equation *II* with respect to concentration and pressure gives

$$\text{III.} \qquad \mu_i = \mu_i^0 + RTln(n_i\gamma_i) + v_i(p - p_i^0)$$

where μ_i^0 is the chemical potential of pure i at a reference pressure, p_i^0

The reference pressure p_i^0 is defined as the saturation vapor pressure and can then be rewritten as

$$\text{IV.} \qquad \mu_i = \mu_i^0 + RTln(n_i\gamma_i) + v_i(p - p_{isat})$$

The first assumption governing transport through membranes is that the fluids on either side of the membrane are in equilibrium with the membrane material at the interface. This assumption means that the gradient in chemical potential from one side of the membrane to the other is continuous. Implicit in this assumption is that the rates of absorption and desorption at the membrane interface are much higher than the rate of diffusion through the membrane. This appears to be the case in almost all membrane processes, but may fail in transport processes involving chemical reactions, such as facilitated transport, or in diffusion of gases through metals, where interfacial absorption can be slow.

The second assumption concerns the way this chemical potential across the membrane is expressed within the membrane: The solution-diffusion model assumes that the pressure within a membrane is uniform and that the chemical potential gradient of a permeant across the membrane is represented only as a concentration gradient.

The solution-diffusion model assumes that when a pressure is applied across a dense membrane, the pressure everywhere within the membrane is constant at the high-pressure value. This assumes, in effect, that solution-diffusion membranes transmit pressure in the same way as liquids. Consequently, the chemical potential difference across the membranes is represented as a concentration gradient within the membrane, with Equation IV providing the mathematical link between pressure and concentration.

In the solution-diffusion model, the pressure within the membrane is constant at the high pressure value (p_0), and the gradient in chemical potential across the membrane is expressed as a smooth gradient in solvent activity ($\gamma_i n_i$). The flow that occurs down this gradient because no pressure gradient exists within the membrane, can be rewritten as

V.

$$J_i = -\frac{RTL_i}{n_i}\frac{dn_i}{dx}$$

Using the term concentration (g/cm3) defined as $c_i = m_i \rho n_i$ where m_i is the molecular weight of i (g/mol) and ρ is the molar density (mol/cm3), J can be written as

VI.

$$J_i = -\frac{RTL_i}{C_i}\frac{dC_i}{dx}$$

Equation *VI* has the same form as Fick's law, in which the term RTL_i/c_i can be replaced by the diffusion coefficient D_i. Thus,

VII.

$$J_i = -\frac{\boldsymbol{D}_i dc_i}{dx}$$

Integrating over the thickness of the membrane then gives

VIII.

$$J_i = -\frac{\boldsymbol{D}_i\left(c_{io(m)} - c_{il(m)}\right)}{l}$$

The membrane in contact with the permeate-side solution is in equilibrium with this solution. Thus, Equation *IV* can be used to link the two phases in terms of their chemical potentials:

IX.

$$\mu_{il(m)} = \mu_{il}$$

X.

$$RTln\left(n_{il(m)}\gamma_{il(m)}\right) + v_i p_0 = RTln\left(n_{il}\gamma_{il}\right) + v_i p_l$$

At osmotic equilibrium,

XI.

$$\Delta(\gamma_i n_i) = \gamma_{il} n_{il} - \gamma_{il(m)} n_{il(m)}$$

Since the permeate fluid is pure water, $\gamma_{il} n_{il} \approx 1$, and it follows, on substituting Equation X into XI, that

$$\text{XII.} \qquad RTln[1 - \Delta(\gamma_i n_i)] = -v_i(p_0 - p_l)$$

Since $\Delta(\gamma_i n_i)$ is small, $ln[1 - \Delta(\gamma_i n_i)] \approx \Delta(\gamma_i n_i)$ and equation XII reduces to

$$\text{XIII.} \qquad \Delta(\gamma_i n_i) = \frac{-v_i(p_0 - p_l)}{RT} = \frac{-v_i \Delta\pi}{RT}$$

Thus, the pressure difference, $\Delta\pi$, across the membrane balances the solvent activity difference $\Delta(\gamma_i n_i)$ across the membrane, and the flow is zero. If a pressure higher than the osmotic pressure is applied to the feed side of the membrane, then the solvent activity difference across the membrane increases further, resulting in a flow from left to right. This is the process of reverse osmosis. The fluids on either side of a membrane may be at different pressures and concentrations, within a perfect solution-diffusion membrane, there is no pressure gradient – only a concentration gradient. Flow through this type of membrane is expressed by Fick's law.[1]

1.4 Reverse Osmosis

Reverse osmosis and normal osmosis are directly related processes. If a selective membrane separates a salt solution from pure water, water will pass through the membrane from the pure water side of the membrane into the side less concentrated in water. The solvent has a propencity to move from low to high solute concentrations due to chemical potential equilibration. This process is called normal osmosis. If a hydrostatic pressure is applied to the salt side of the membrane, the flow of water can be retarded and, when the applied pressure is sufficient, the flow ceases. The hydrostatic pressure required to stop the water flow is called the osmotic pressure (π). If pressures greater than the osmotic pressure are applied to the salt side of the membrane, then the flow of water is reversed, and water begins to flow from the salt solution to the pure water side of the membrane. This process is called reverse osmosis, which is an important method of producing pure water from salt solutions.[1]

1.4.1 Membranes and material

The semipermeable membrane used in the desalination process ordinarily will be thin in order to maximize the water flux. Thus the membrane often is formed on a porous support to provide strength, named thin film composite (TFC) membrane. The supports should have pores which are sufficiently large so that the water (permeate) can pass through the support without reducing the flux of the entire composite. Conversely, the pores should not be so large that the thin semipermeable membrane will be unable to bridge the pores or will fill up or penetrate too far into the pores. Scala et al. suggest that with pores above about 8 microns (8000 nm) the rejection of impurities is reduced.[6]

Most reverse osmosis membranes have an asymmetric structure with a thin dense toplayer (≤1µm) supported by a porous sublayer (50-150 µm), the resistance towards transport being determined mainly by the dense toplayer. Two different types of membrane with an asymmetric structure can be distinguished: asymmetric membranes and composite membranes. In integral asymmetric membranes, both toplayer and the sublayer consist of the same material and an important class of this membrane are celulose esters that are suitable for desalination because of high permeability towards water in combination with a low solubility towards the salt. Other materials that have been used frequently for reverse osmosis membranes are aromatic polyamides that show high selectivities towards salts but their water flux is somewhat lower.

Composite membranes constitute the second type of structure frequently used in reverse osmosis and in such membranes toplayer and sublayer are composed of different polymeric materials.[5]

To realize composite membranes one of the most widely used techniques is the interfacial polymerization

1.4.2 Membranes Supports

Most commercially available RO membranes are fabricated predominantly on polysulfone (PSF) microfiltration supports.[3]

In past studies, porous support structures for polyamide composite membranes were prepared from polymers like polysulfone, polyethersulfone, polycarbonate, polyphenylene oxides, poly(styrene-co-acrylonitrile), poly(phthalazinone ether sulfone ketone) (PPESK), polyacrylonitrile, polyetherimide, polypropylene and others by conventional phase inversion techniques. [7] Polymer surface modification offers large possibilities to purposeful alteration of the contact properties of porous materials by alteration of their surface chemistry and morphology. The contact properties are dependent on the type and amount of the presenting on the surface functional groups, the density, structure and thickness of the modified surface layer, the hydro philic/hydrophobic balance, the presence of electric discharges on the surface, etc. Membrane surface modification turned lately in a conventional tool for control over all complex of surface physicalchemical properties and thus to effective control over the fluid membrane surface interaction.[8] Polysulfone appears to be the most popular polymer for fabricating composite RO membranes because it is widely available, relatively cheap, easy to process,and is fairly stable against thermal, mechanical, chemical and bacterial attack. Note that polysulfone is relatively hydrophobic compared to most of the other polymers.[7]

1.4.3 Interfacial Polymerization

Since the discovery by Cadotte and his coworkers that high-flux, high-rejection reverse osmosis membranes can be made by interfacial polymerization membranes made by this method have become the industry standard. [9] Interfacial composite membranes have significantly higher salt rejections and fluxes than cellulose acetate membranes.

Interfacial polymerization (IP) is a process in which a very thin film (or membrane) can be made by reacting two monomers at the interface between two immiscible solutions.[10]

The support layer is immersed in an aqueous solution containing a reactive monomer, frequently of the amine-type. The film is then immersed in a second bath containing a water-immiscible solvent in which another reactive monomer, often an acid chloride, has been dissolved. These two reactive monomers react with each other to form a dense polymeric toplayer. Heat treatment is often applied to complete the interfacial reaction and to crosslink the water-soluble monomer. The advantage of interfacial polymerization is that the reaction is self-inhibiting through passage of limited supply of reactants through the already formed layer, resulting in an extremely thin film of thickness within the 50 nm range. [11]

1.4.4 Separation principle

The solution-diffusion model is used to describe transport in reverse osmosis membranes. According to this model, solutes permeate the membrane by dissolving in the membrane material and diffusing down a concentration gradient. Separation occurs because of the difference in solubilities and mobilities of different solutes in the membrane. The resulting equations, linking the driving forces of pressure and concentration with flow, are then shown to be consistent with experimental observations. The general approach is to use the first assumption of the solution-diffusion model, namely, that the chemical potential of the feed and permeate fluids are in equilibrium with the adjacent membrane surfaces. From this assumption, the chemical potential in the fluid and membrane phases can be equated using the appropriate expressions for chemical potential given below:

XIV. $$\mu_i = \mu_i^0 + RTln(\gamma_i n_i) + v_i(p - p_{isat})$$

Following the general procedure for application of the solution-diffusion model, the chemical potentials at both sides of the membrane are first equated. At the feed interface, the pressures in the feed solution and within the membrane are identical (as shown in Figure 2).

XV. $$c_{i_{0(m)}} = K_I^L c_{i_0}$$

Substituting the appropriate expression for the chemical potential of an incompressible fluid to the liquid and membrane phases yields

XVI. $$ln(\gamma_{i_l}^{L} n_{i_l}) = ln(\gamma_{i_{l(m)}}^{L} n_{i_{l(m)}}) + \frac{v_i(p_0 - p_{isat})}{RT}$$

Rearranging and substituting for the sorption coefficient, K_I^L gives the expression

XVII. $$c_{i_{l(m)}} = K_I^L c_{i_l} * \exp\left[\frac{-v_i(p_0 - p_l)}{RT}\right]$$

The expressions for the concentrations within the membrane at the interface in Equations *III* and *VII.* can now be substituted into the Fick's law expression, Equation *II*, to yield

XVIII. $$J_i = \frac{K_I^L D_I}{l}\left\{c_{i_0} - c_{i_l} * \exp\left[\frac{-v_i(p_0 - p_l)}{RT}\right]\right\}$$

The term $K_I^L D_I$ can also be written as a permeability and so Equation *VIII* becomes

XIX. $$J_i = \frac{P_I^L}{l}\left\{c_{i_0} - c_{i_l} * \exp\left[\frac{-v_i(p_0 - p_l)}{RT}\right]\right\}$$

Equation *XIX* and the equivalent expression for component j give the water flux and the salt flux across the reverse osmosis membrane in terms of the pressure and concentration difference across the membrane.

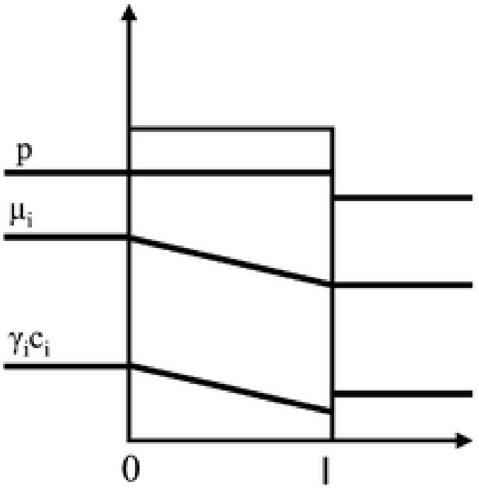


Figure 2. Solution-diffusion model for reverse osmosis.

The pressure in the membrane is uniform and equal to the high-pressure value, so the chemical potential gradient within the membrane is expressed as a concentration gradient

1.5 Drawbacks of thin film composite membranes

Although the best performances of water flux along with salt rejectcions, thin film composite membranes have some drawbacks.

Thin film composite membranes show permanent loss in selectivity that results from exposure to even ppb levels of chlorine or hypochlorite disinfectants. [1]

Membrane fouling is the main cause of permeant flux decline and loss of product quality in reverse osmosis systems, so fouling control dominates reverse osmosis system design and operation. The cause and prevention of fouling depend greatly on the feed water being treated, and appropriate control procedures must be devised for each plant. In general, sources of fouling can be divided into four principal categories: scale, silt, bacteria, and organic. More than one category may occur in the same plant. Fouling control involves pretreatment of the feed water to minimize fouling as well as regular cleaning to handle any fouling that still occurs.[12]

1.5.1 Cleaning methods for RO membranes

Since TFC membranes show reduced perfomances along with time, some remediations are applied to limit or completely avoid the drawbakcs discussed in the previous paragraph. There are different cleaning methods: chemical and physical chemical cleaning methods through the use of acid, alkaline, surfactant and detergent solutions are assigned to weaken cohesion forces between the foulant and the membrane surface. Physical cleaning methods include backwashing, and osmotic cleaning. Among the physical methods, the backwash method has proven to be an efficient physical cleaning method for flux recovery of membranes not severely fouled.[11] The backwash used in membranes is based on permeate back-flow to the concentrate side. Therefore, membranes must have high pressure durability in both directions.

An osmotic cleaning of RO membranes is based on flow induced by osmotic pressure as direct osmosis cleaning (DOC). The cleaning process in DOC is based on negative driving pressure between the operating and the osmotic pressures of the water solution in the feed side of the membrane. This can be done either by reducing operation pressure below the osmotic pressure of the solution or by increasing the permeate pressure to a level that allows backflow. The membrane to be backwashed must have sufficient inherent integrity to withstand the hydraulic stress imparted. The later possibility is carried out without changing parameters of the feed side of the RO process, yet high pressure piping is required at the permeate side. Minimizing the backwash time and the amount of water needed are major purposes of the backwash process, as it saves permeate water and production time.[13]

1.5.2 Amination of thin film composite membranes

To make the membrane suitable for resisting backwashing operations, an amination reaction was carried out to create a chemical bond between the polyamide layer and the support. Following the amination reaction, the support is able to react with the acyl chloride (TMC).[13]

For PES, the support was first modified through the use of a redox reaction through which the formation of a carboxylic bond on the surface is formed and subsequently the amination reaction was carried out. As for PES, the support amination was directly performed.

2. Materials and Method

This chapter contains materials and methods used in the work. In the first part is described the following protocol to fabricate a polyamide layer. Subsequently, the amination protocol used for different supports used in the thesis were described. Finally, there is the description of the crossflow unit and backwashing system used to test the membranes fabricated and the description of the various characterization tecquiniques used.

2.1Membranes

For this study. were used different type of membranes, commercial and labmade. As regards the use of commercial membranes, were used DOW SWRO30 and Hydracore 70. DWO SWRO30 is a polyamide thin-film composite membrane. HYDRACORE made of polyethersulfone.

In the fabrication of polyamide labmade, three different support were used: Ps20 from SEPRO; two differentt PAN membeanes, one from Ultura^{TM} brand, Long Beach, MWCO 75 kDa and the second was Synder filtration, 4941 Allison Pkwy, Vacaville, CA 95688, USA; MWCO 100 kDa.

2.2 Interfacial Polymerization

To create the polyamide layer an interfacial polymerization has been carried out. The followed protocol is analogous for all types of membranes supports used fabrication. First of all, a membrane sample of dimensions 10x13 cm was cutted. The support sample was attached to toughened glass with laboratory adhesive tape waterperoof: green lime colour, fisher scientific brand 1-inch size tape, keeping the active layer on top (Figure 3). The glass with the membrane sample was laied down on the MPD solution (3.4% in weight), spilled in pyrex dish on an approximately 20-degree inclined and was kept only the active layer in contact with the MPD solution for 2 minutes (Figure 4).

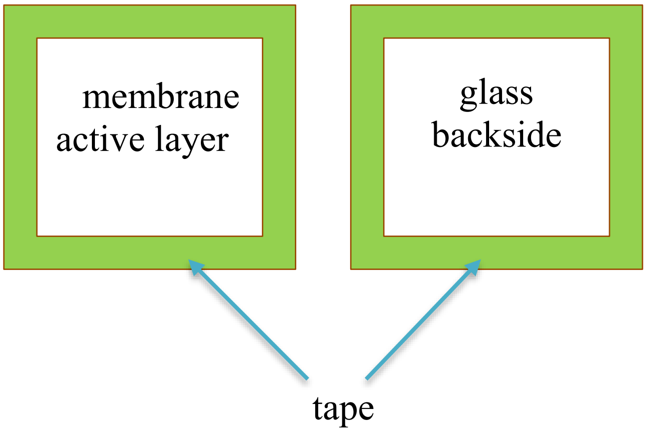


Figure 3. Membrane sample attached to thoughened glass.

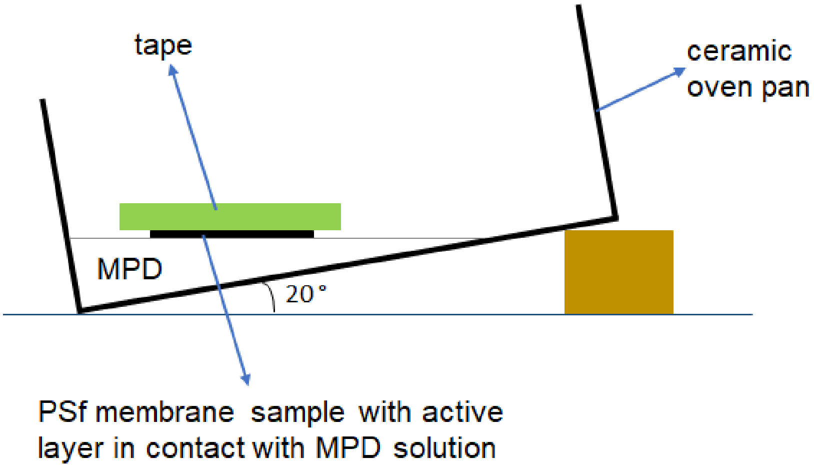


Figure 4. The glass with the membrane sample was laied down on the MPD solution, spilled in pyrex dish on an approximately 20-degree inclined.

The glass with the membrane sample was removed from the oven pan. The active layer of the membrane sample was removed from the MPD solution and it was used a hair dryer to remove excess solution. The hair dryer was moved slowly on the membrane sample in only one direction. The glass with membrane sample was immersed in a parallelepiped filled up with Benzenetricarbonyl trichloride (0.15% in weight) in Hydrocarbon solvent (enough solution to cover the whole membrane sample) for 1 minute. In the meantime, a kettle must be filled up with DI water and was turned on. The glass is removed from the parallelepiped and was kept it outside for 2 minute. In the meantime, the cooking pan must be arranged on the heating plate. The hot DI water is spilled from the kettle to the cooking pan to maintain the water temperature in the heating plate at 95°C. Glass was soaked with the membrane sample in the hot DI water for 2 minutes. The glass was removed and the membrane sample was cutted with skiver. The membrane sample is put in the beaker filled up with the NaOCl solution (13 drops to 500ml of DI water) for 2 minutes. Chlorination of polyamide membranes is known to structurally degrade the membranes. Here the NaOCl is believed to first scavenge unreacted MPD that has not yet escaped the structure.[13]

The DI water was replaced in the cooking pan with the new one boiled just now in the kettle. Keep the heating plate operative, so as to maintain the temperature of the new DI water at 95°C. The membrane sample was moved from the beaker with the NaOCl solution to the one with the sodium metabisulfite solution (1g/l with DI water). The Na2S2O5 is believed to neutralize any of the unreacted NaOCl and prevent it from further attacking the polyamide.[9] The membrane sample must be left there inside for 30 seconds. The membrane sample was removed from the metabisulfite solution and was dunked in the hot DI water for 2 minutes. After that, the polyamide toplayer has been made on the support membrane.

2.3 Amination treatment

The aim of amination reaction is to fabricate “stronger” RO membrane to be used in backwashing conditions.

The chemical modification of the surface supports was performed before to carry out the IP process. Below are the two different protocols that are followed to achieve amination of PES and PAN membranes.

2.3.1 Amination PES membranes

Before performing the amination reaction, the membranes were soaked into a NaOH solution (ph 11) for one night, followed by rinsing with ethanol. After this, membranes are stored in DI water.

To create carboxylic group on membrane surface, a REDOX reaction has been performed on the membrane. After the creation of the group, it is possible to proceed with the amination.

The PES membrane amination protocol consists of two phases: 1) modification and 2) amination.

At the beginning, two solutions were prepared: Methacrylic acid (1 M) dissolved in DI water and [2-(methacryloyloxy)ethyl]-trimethylammonium (1 M) again dissolved in DI water. Afterwards, a third solution was prepared by mixing the two monomers solutions at the concentration of 0.4 M for each monomers (concentration of both monomers was 0.8 M). Then the reaction started soaking a piece of PES membrane in the monomers solution and stirred on a platform of Unimax 1010 orbital shaker (Heidolph, Kelheim, Germany). After 2 minutes the initiators were added: 0.1 M sodium persulfate ($Na_2S_2O_8$) in DI water and 0.1 M sodium metabisulfite ($Na_2S_2O_5$), reaching a final equimolar concentration of 0.01M. The grafting was performed for 10 min at 25 °C with stirring. Finally, the membrane was washed, first with water intensively to remove unreacted monomers and loosely-bound polymers, and then washed three times for 10 min in a sonic bath. The membranes were stored in DI water at 4 °C.

The membrane sample modified, was immersed in a solution made of sodium phosphate buffer solution (50 mM, pH 7.4) containing 3 mM N-hydroxysulfosuccinimide sodium salt (sulfo-NHS), 3 mM N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and 10 mM ethanediamine. The solution was agitated on a Unimax 1010 orbital platform shaker (Heidolph, Kelheim, Germany) at room temperature for 2 hours. At the end, the membrane was washed first for 10 min with sodium phosphate buffer solution diluted 5 times, then other 10 min with DI water under sonication, again for 10 min in an aqueous solution of isopropanol (50%) and finally was washed three times for 10 min with DI water with sonication. The membrane was stored in DI water at 4 °C.

2.3.2 Amination PAN membranes

Before performing the amination reaction, PAN membranes were soaked into a solution at 50% ethanol in water for 6 hours, followed by rinsing with DI water. After this, PAN membranes were immersed in a mixture of diethylenetriamine (157.575 g), sodium carbonate (catalyst; 5 g), and distilled water (500 ml) for 2 hours @60°C under stirring (120 rpm)

When amination is finished, the membranes are been rinsed and stored in DI water.

2.4 Cross flow unit

In order to measure permeability of the manufactured membranes, a crossflow system was used. In this type of system, the fluid on the upstream side of the membrane moves parallel to the membrane surface and the fluid on the downstream side of the membrane moves away from the membrane in the direction normal to the membrane surface (Figures 5, 6 and 7). [14]

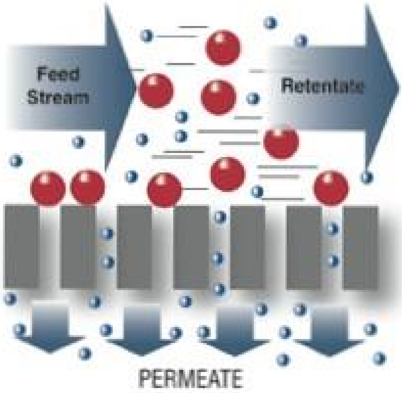


Figure 5. Continuous crossflows used in separations. [15]

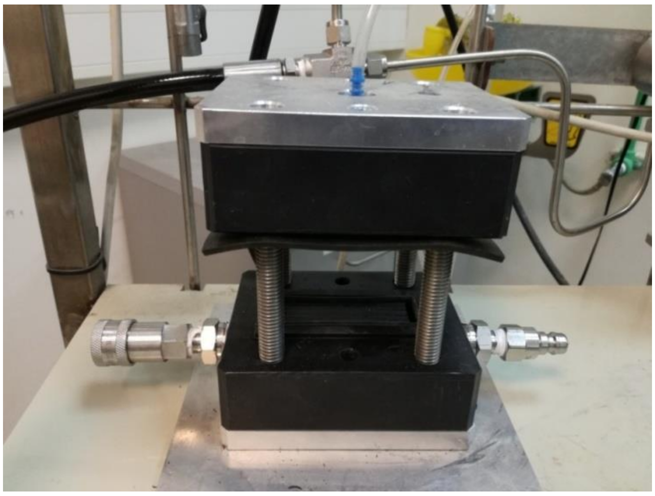
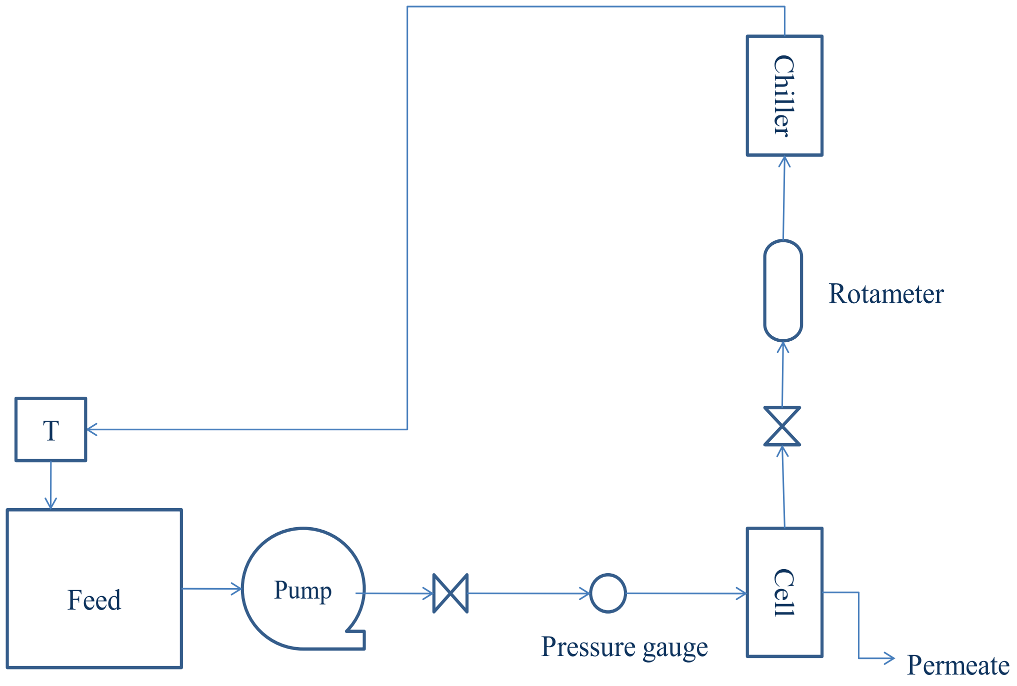


Figure 6. Cell of Crossflow System.

Salt and water permeate reverse osmosis membranes according to the solution-diffusion transport mechanism.

The tests were conducted in a laboratory scale filtration setup, which comprises: a cell containing the membrane, with three collectors (feed, outlet and permeate), a sheet of membrane, 22.12 cm^2 area, located inside the cell, a hydraulic pump type G03 (Figure 8) thatallows a maximum pressure of 1000 psi (70 bar), a pressure gauge measuring 0 to 1500 psi (0-100 bar), two pressure control valves, a flowmeter for measuring flow rate and a chiller (Figure 9) which keeps the water supply temperature constant about 22 °C (scheme 1-2 and Figure 5). The water flux and NaCl rejection of the membranes were evaluated by permeating a NaCl aqueous solution (NaCl at 35 mM in the feed solution.) in a cross-flow filtration system. All of the membrane tests were performed at a pressure of 20.68 bar, 19.30 bar, 17.92 bar and 16.54 bar, a flow rate of 1 L min-1. Performance data were collected after 6 h when the system had reached steady-state. Water flux (Jw, L m-2 h -1) was determined from the amount of the collected permeate (ΔV) for a fixed time interval (Δt) by the given relationship, $Jw = \Delta V/am\Delta t$.



Scheme 1. Crossflow System.

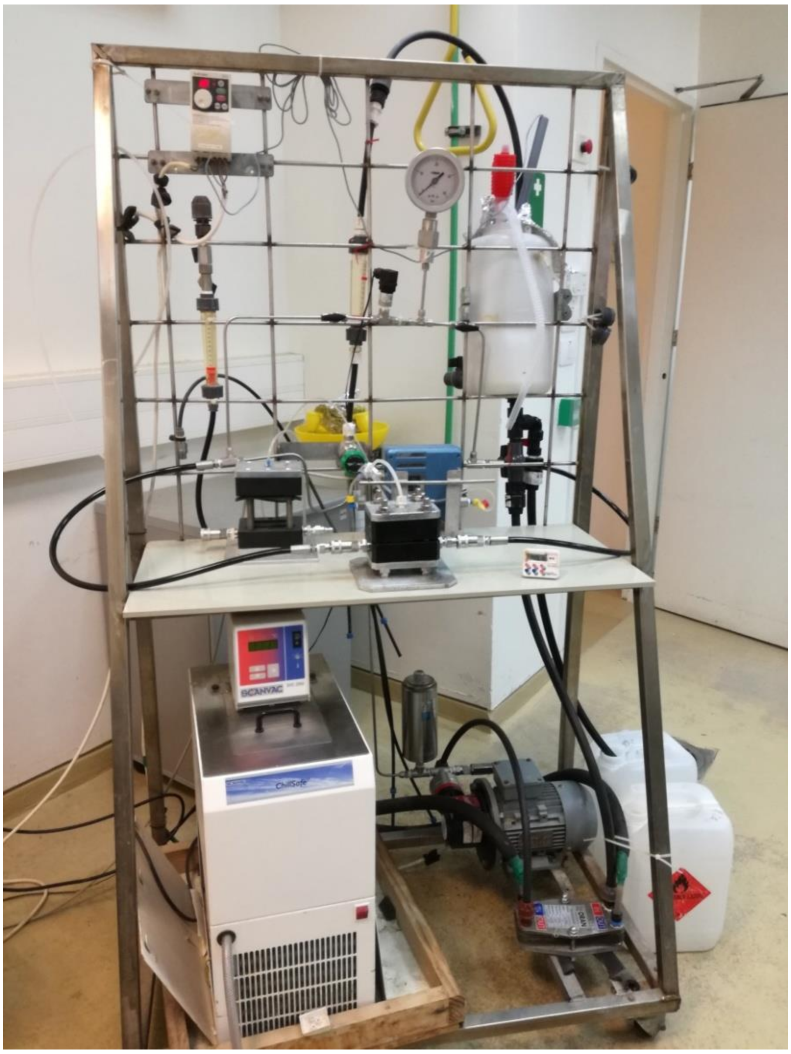


Figure 7. Crossflow used in Zuckerberg Institute for Water Research (Israel).

Figure 8. Hydra-cell pump G03.

Figure 9. Chiller LAUDA.

2.5 Backwashing system

In backwashing system (see Figure 10 and 11) the transmembrane pressure was periodically inverted by the use of a secondary pump, so that permeate flows back into the feed, lifting the fouling layer from the surface of the membrane.[16] To carry out the backwashing, a tank and a vessel were added to the the crossflow system as showed in scheme 2. Each experiment starts compacting the membrane system for 6 hr at 300 psi and 4.5 l/h. Afterwards, membrane fluxes is measured at three different pressure (280, 260, 240 psi) for 10 min each. After the last pressure flux measurement, a solution containing NaCl at 1M is added to the system to have a final concentration of 35 mM. The Permeate is collected after 45 min and three sample are taken to measure salt rejection. Once this classical phase is finished, the second part of the experiment, the backwashing, can start. As reported below in the figure, an auxiliary tank is directly connected by a three ways valve to the permeate. This tank supplies permeate for the backwash experiment. The backwashing experiment is made of the following steps:

After the last sample of salt rejection, the operation halts removing feed pressure and keeping the flowrate always at 4.5 l/h. After 1 min the pressure is applied again.

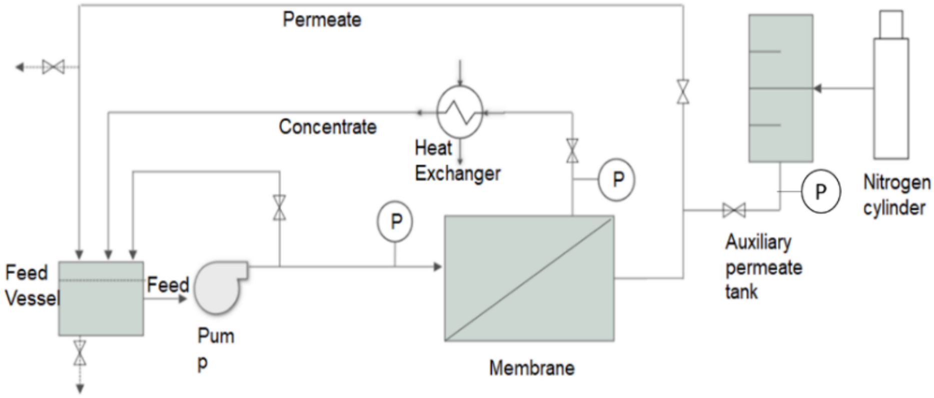
After 45 min in which flux and salt rejection are measured, step 1) is repeated.

This time in the meanwhile of step 1) the auxiliary tank is pressurized reaching the value of 6 bar. The permeate pressure (backwashing) is kept for 1 min.

Then the pressure on the permeate is released and the applied again by the feed side.

Repeat steps 3) to 6) three times.

Once the flux and rejection are measured after the third backwashing, the experiment ends.



Scheme 2. Backwashing set-up.

Figure 10. Backwashing System with Crossflow.

Figure 11. Tank with DI water and Nitrogen Vessel.

2.6 Contact angle

The wettability of the membranes was determined via static contact angle measurements using a Krüss DSA-100 apparatus. The sessile drop method was chosen to measure the contact angle of deionized water in equilibrium mode and in several replicates.[3]

2.7 Infrared spectroscopy (FTIR/ATR)

An attenuated total reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. This evanescent wave protrudes only a few microns (0.5 μ - 5 μ) beyond the crystal surface and into the sample. Consequently, there must be good contact between the sample and the crystal surface. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave. is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum.[17] A Thermo-Nicolet 5700 apparatus was employed for Fourier transform infrared spectroscopy (FTIR) and for attenuated total reflectance (ATR)–FTIR analysis. The instrument is equipped with an ATR accessory containing a diamond crystal internal reflection element. The analysis was carried out with a resolution of 4 cm−1 and samples were scanned 32 times in the wavenumber range between 750 and 3750 cm−1.[3]

2.8 Conductimeter

Selectivity can be measured in a number of ways, but most commonly, it is measured as the salt rejection coefficient R, defined as

$$R = \left[1 - \frac{c_{jl}}{c_{jo}}\right] \times 100\% \tag{XX.}$$

The salt concentration on the permeate side of the membrane can be related to the membrane fluxes by the expression

$$c_{jl} = \frac{J_J}{J_i}\rho_i \tag{XXI.}$$

where ρ_i is the density of water (g/cm^3). By combining Equations *XXIII* to *XXV*, the membrane rejection can be expressed as

$$R = \left[1 - \frac{c_{jl}}{c_{jo}}\right] \times 100\% \tag{XXII.}$$

Conductivity measures the capacity of a solution to convey an electric current and isoportional to ion concentration in the liquid.

In the specific case the tool was used was showed in figure 12.

Figure 12. Conductimeter used.

The conductivity measurement is carried out by inserting the sensor into the sample to be analyzed. For each sample, the test is repeated three times, washing the sonde with DI water between one measurement and the other.

3. Results and discussion

The main objective of this work was to form a polyamide thin layer, above the support, that is strong enough to resist at backwashing operation. For this reason and according to literature reports, the first step was to characterize the different membranes where has been built a thin polyamide layer through interfacial polymerization technique.

3.1 Infrared Spectroscopy (FTIR/ATR)

3.1.1 PES membranes

In the first part of the thesis, the first objective was to successfully carry out interfacial polymerization on the PES support. Figure 13 shows ATR spectrum of the membrane fabricated (blue line) and is reported and compared with commercial polyamide membrane (DOW SW 30). In the figure the characteristic peaks of the formation of polyamide are clearly present: peaks are attributed to amide I ($C=O$ stretching, 1668 cm−1), carbonyl groups (H-bonded $C=O$, 1610 cm−1) and amide II (N-H bending, 1542 cm−1). Thus it can be concluded that on PES membrane support polyamide layer has been successful created.

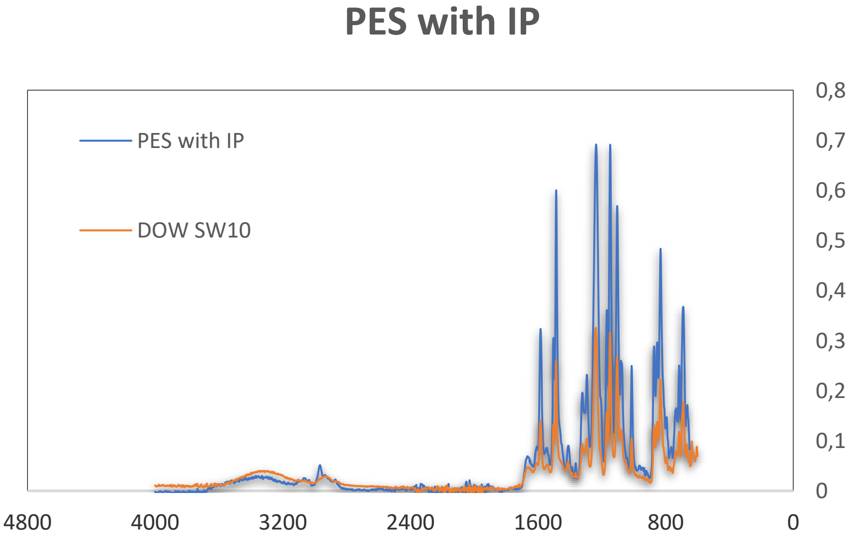


Figure 13. ATR spectrum of the membrane fabricated (blue line) and is reported and compared with commercial polyamide membrane (DOW SW 30).

Although the presence of polyamide layer on PES support, the polyamide layer formed with classical interfacial polymerization is only physically attached on the support, the aim is to fabricate a polyamide membrane that is chemically bond on the support. Then, the next step was to first modify the membranes support to make them suitable for the formation of a strong chemical bond between the supports and the polyamide layer.

The PES support required a modification of the membrane surface followed by an amination reaction. In chapter 2 can be found the description of these reaction steps. In short, the idea is to first form a carboxylic acid group by a redox reaction by using as monomerss only MA or a solution of MA+MOETMA. The functional groups formed after the redox reaction is shown in figures 14, 15.

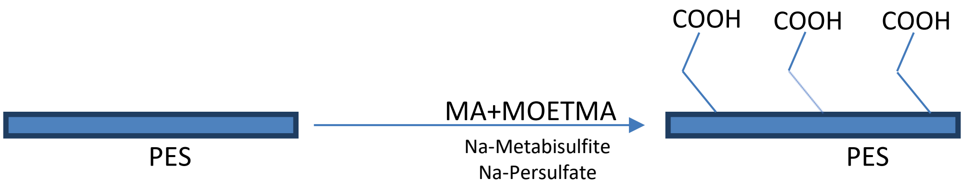


Figure 14. Functional groups formed after the redox reaction with MA+MOETMA.

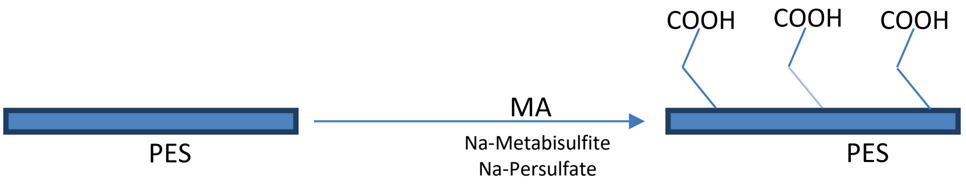


Figure 15. Functional groups formed after the redox reaction with MA

The modification of membranes surfeces was carried out at different time and different percentage of monomers to study the behavior of the membranes at the variation of these parameters. As can be seen from the figures 16 and 17 as the reaction time increases, increases the peak corresponding to carboxylic group (1700 cm-1)

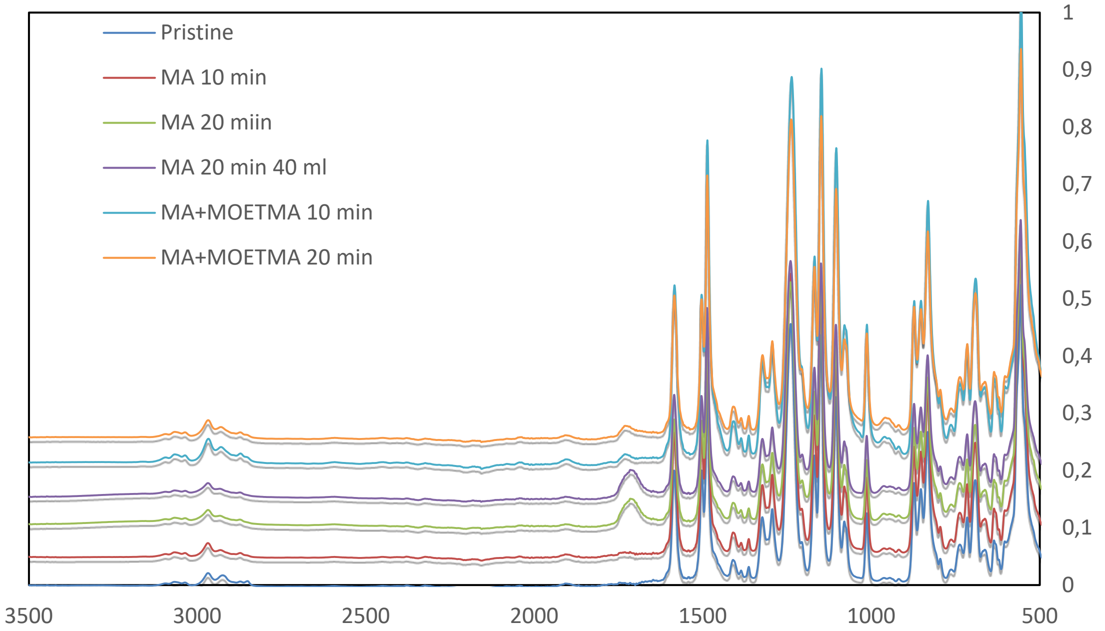


Figure 16. IR spectra of PES membranes after modification.

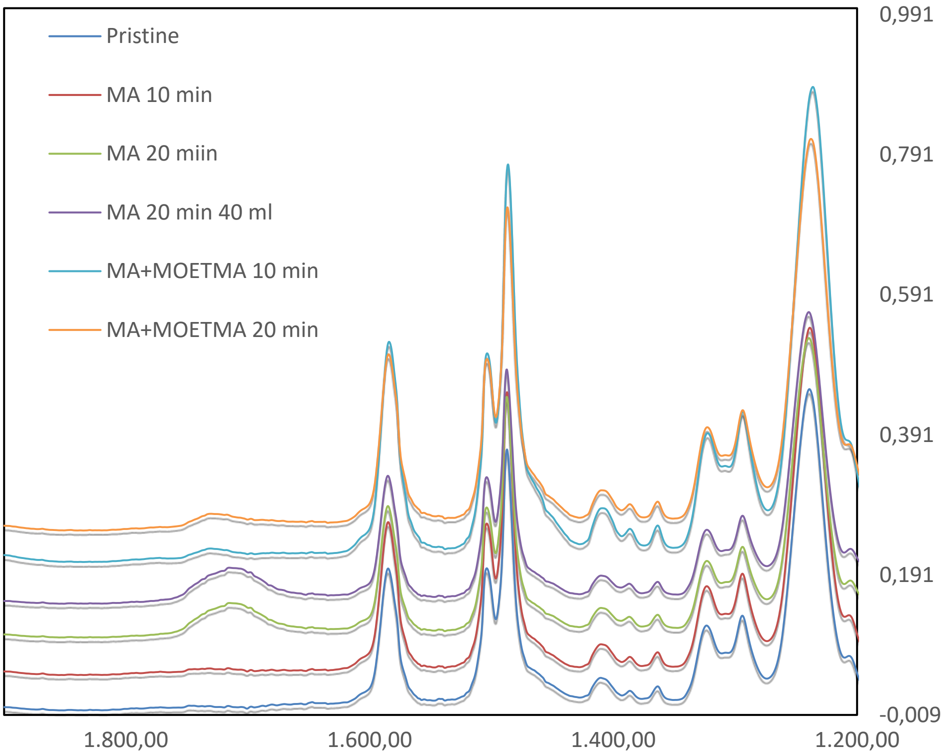


Figure 17. IR spectra of PES membranes after modification showing the main peaks.

In view of the above, it was decided to use the Methacrylic Acid and reaction time of 20 min to modificate the membranes surface.

The second step was to functionalize the membrane through an amination reaction described below (figure 18)

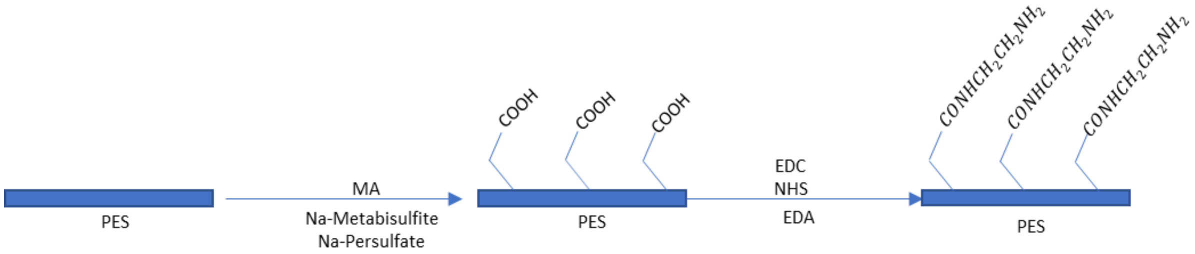


Figure 18. Functionalization of the membrane through an amination reaction.

The spectrum of a pristine PES was compared with that of an aminated PES and as we see there is a peak around the 1700 probably due to the presence of the amine group and a comparison of pristine membrane with grafted membrane and aminated membrane is presented in figure 19.

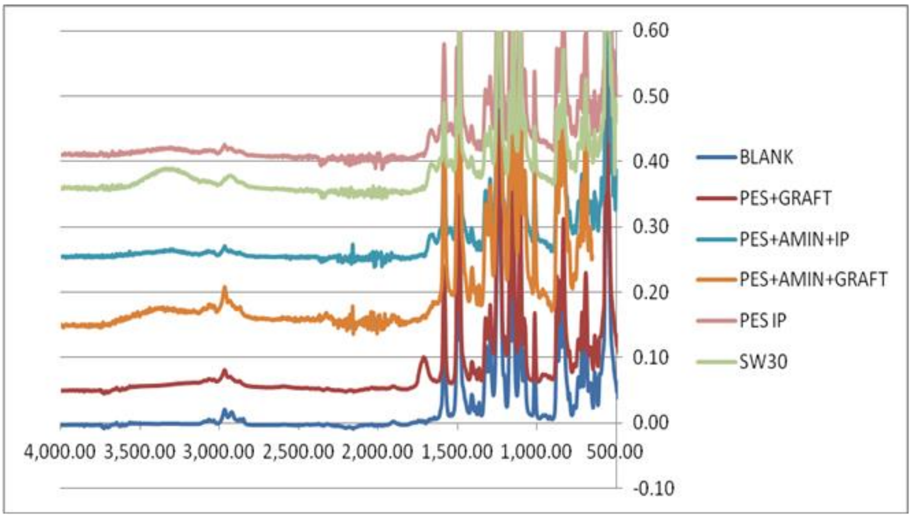


Figure 19. Comparation of different types of PES membranes.

3.1.2 PAN membranes

With regard to the PAN membranes, unfortunately, no sufficient ATR tests could be carried out. The following (figure 20) is a comparison between a pristine PAN and one in which both amination and interfacial polymerization was performed.

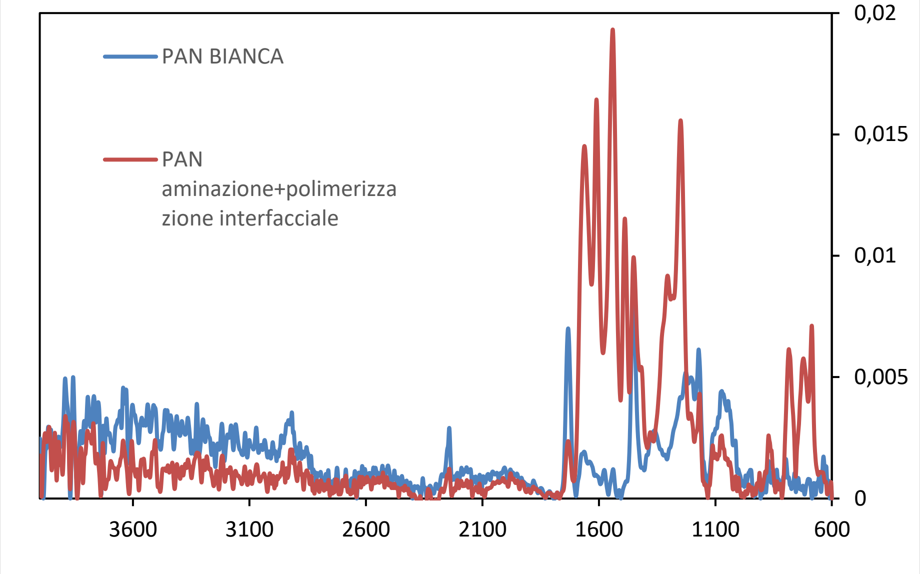


Figure 20. Comparison between a pristine PAN and one in which both amination and interfacial polymerization was performed.

3.2 Contact Angle Results

Water contacte angle results obtained with PES membranes corroborate ATR results by revealing the wettability of the various samples along the fabrication steps pristine values is in accordance with the classical PES found in literature. After the first modification of PES membranes with MA (or MA+MOTMA) it has been assumed the presence of COOH groups on membrane surface, which are rather hydrophilics. Since the contacte angles decreased up to 30 degrees (Table 1), it confirms PES surface was modified. The value of contact angle after the amination step increases and becomes rather hydrophobic. This proves the presence of the amine groups $-NH_2$ belonging to the amine used in the reaction. Finally, after IP, the values decrease to ~ 65, which is a typical value for polyamide membranes. As seen from the underlying results (Table 2), aminated membranes with interfacial polymerization and membranes with only interfacial polymerization have same values.

Table 1. Contact angle of different types of PES membranes.

Membranes	**Contacte angle**
PES blank	80.26 ± 5.4
PES (MA+MOETMA)	68.70 ± 1.22
PES (MA)	50.70 ± 3.8
PES (MA+MOETMA+AMINATION)	81.43 ± 1.44
PES (MA+AMINATION)	81.42 ± 2.21
PES (MA+AMINATION+IP)	67.25 ± 4.57
PES (IP)	68 ± 3.16

Table 2. Contact angle of different types of PAN membranes

Membranes	**Contacte angle**
PAN blank	48 ± 3.23
PAN AMINATION	46 ± 5.03
PAN AMINATION +IP	43.8 ± 4.33
PAN IP	65 ± 5.17

3.3 Filtrations test and membrane rejections

Filtration tests on commercial and labmade membranes have been carried to first evaluete their performances, and after to test their responses under the stress due to the backwashing. In each figure is reported flux, J, in function of the pressure P at which it has been measured. The pendence of the straight line is the permeance of the membrane, A in LMH/Bar. Along with flux measurements, also salt rejection values for each membrane are evaluated and reported.

3.3.1 Commercial membranes

Below are the results from the filtration tests performed on two commercial membranes DOW SWRO30, polyamide thin-film composite membrane (figure 21) and Hydracore 70, sulfonated polyethersulfone membrane (figure 22). In Appendix A are reported the values of of the other membranes tested.

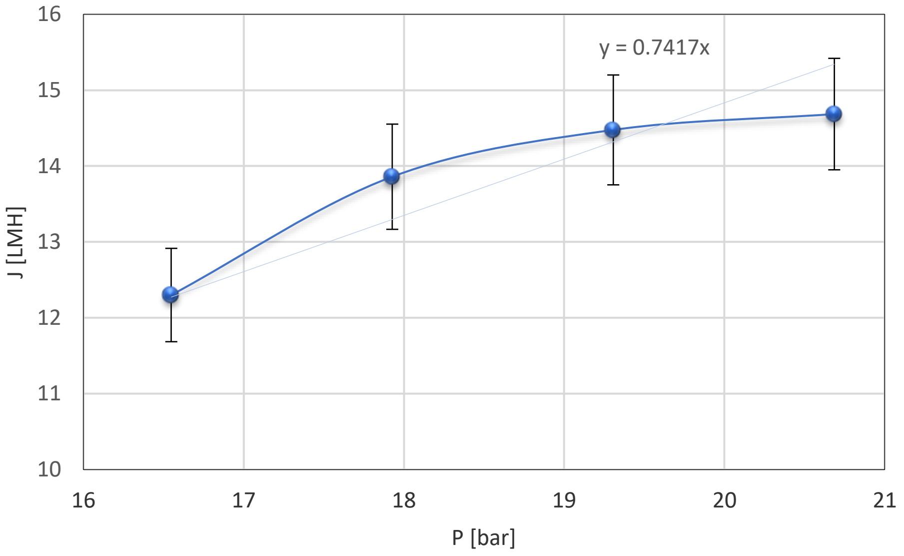


Figure 21. The filtration tests performed on commercial membrane DOW SWRO30, polyamide thin-film composite membrane.

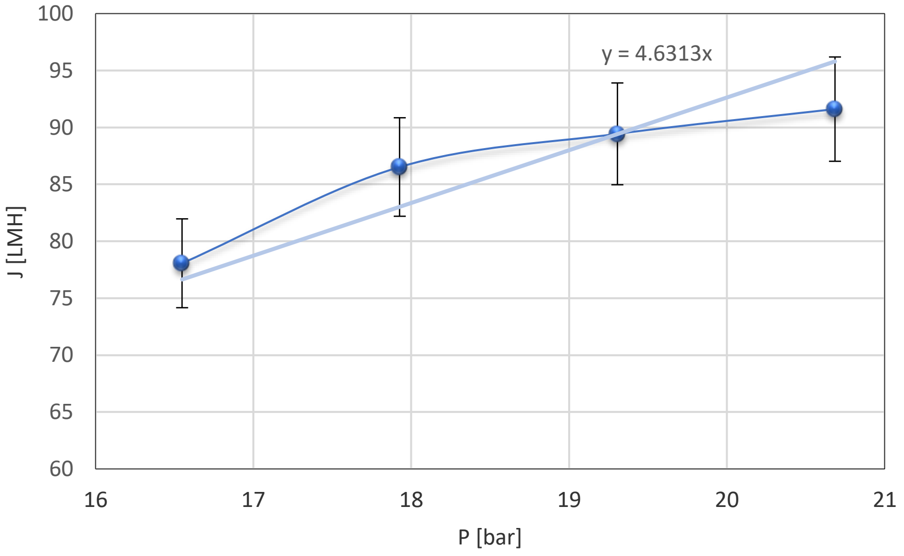


Figure 22. The filtration tests performed on commercial membrane Hydracore 70, sulfonated polyethersulfone.

PA based membrane, SWRO30, has a permeability value almost the same of the one furnished by the producer. HYDREACORE 70 present very high flux, which is expected since this is a nanofiltration membrane.

3.3.2 Unmodified supports of PES and PAN

Figure 23 and figure 24 show average water flux [LMH] versus average pressure [bar] for all the membranes in which interfacial polymerization has been performed.

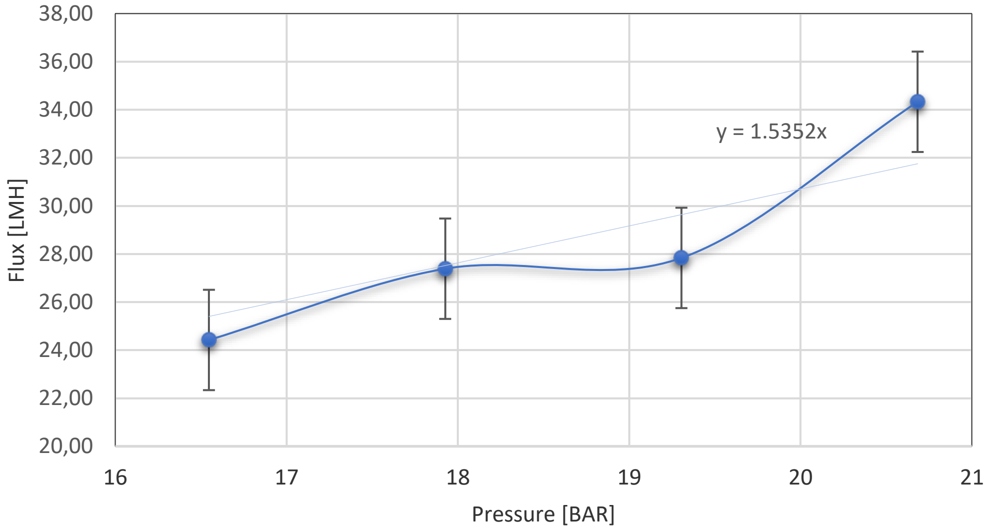


Figure 23. The filtration tests performed on PES with IP.

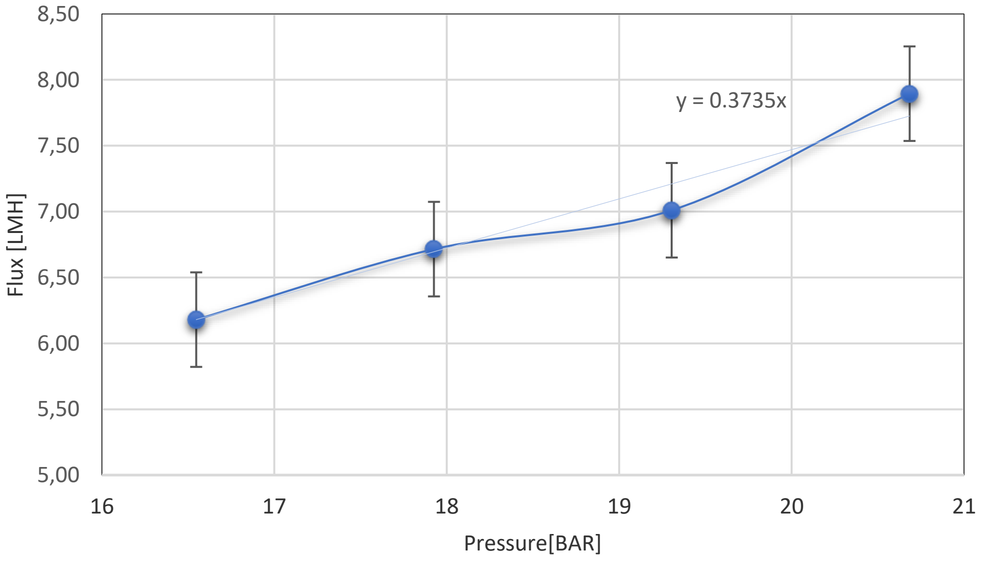


Figure 24. The filtration tests performed on PAN with IP.

It is evident the Flux and permeablity are clearly the highest for the membranes with the PES supports. In particalur, the flux observed with PAN (Ultura^{TM} brand, Long Beach) support membranes is 4 times lower than PES support membranes. This results agree with the literature, since the commercial membrane for RO are on PES support as the one (SWRO 30) used in this work. One of the possible reasons is the different wettability of the two supports, which affects on the layer formation.

In figure 25 is reported the average rejection obtained from different samples. In Appendix A are reported the values of each single membrane.

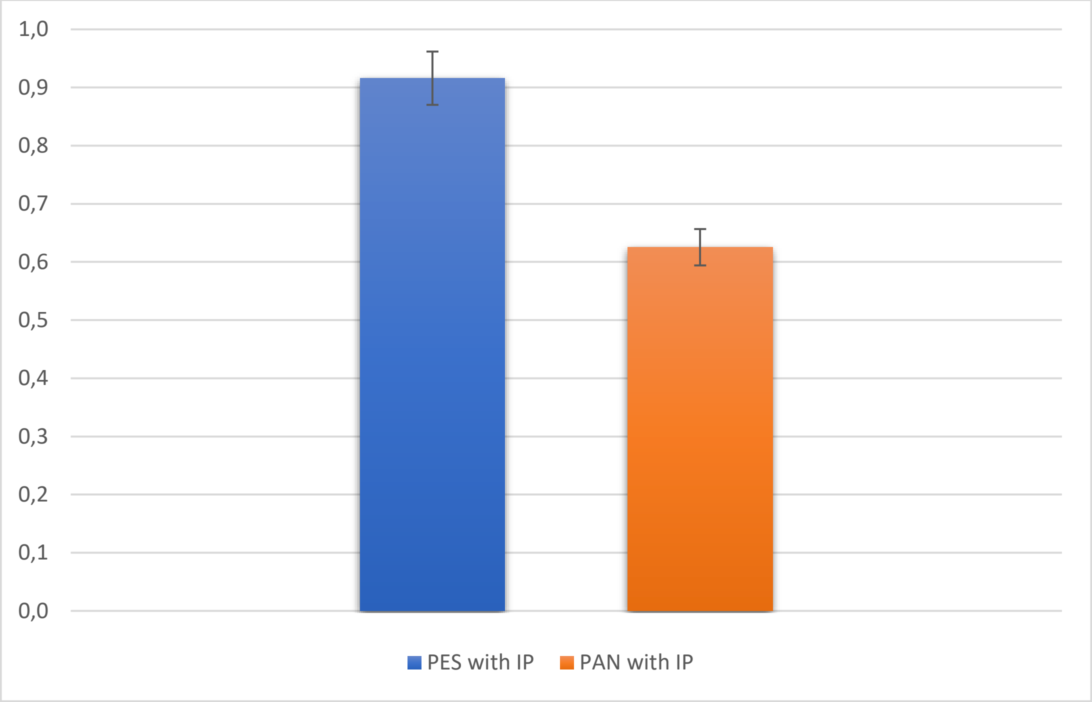


Figure 25. Rejection unmodified membranes for PES and PAN membranes.

Again, the results show that the membrane performance strongly depends on the support type. In fact, PES support exhibited the highest NaCl rejection (99%).

3.3.3 Modified supports of PES and PAN

Afterwards the two different supports were aminated to make the support suitable to withstand a back pressure during a cleaning process. The figure 26 and fugure 27 show average water flux [LMH] versus average pressure [bar] for all the membranes where amination and interfacial polymerization have been performed.

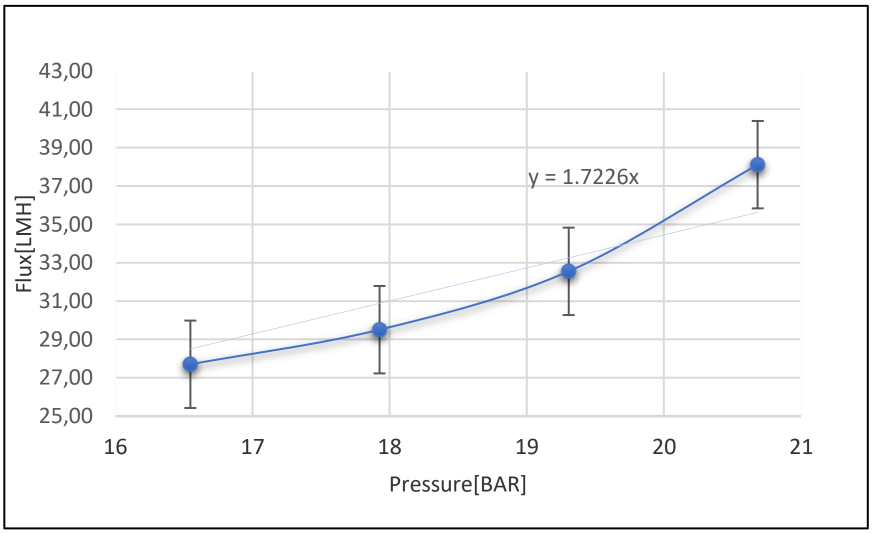


Figure 26. The filtration tests performed on PES with amination and IP.

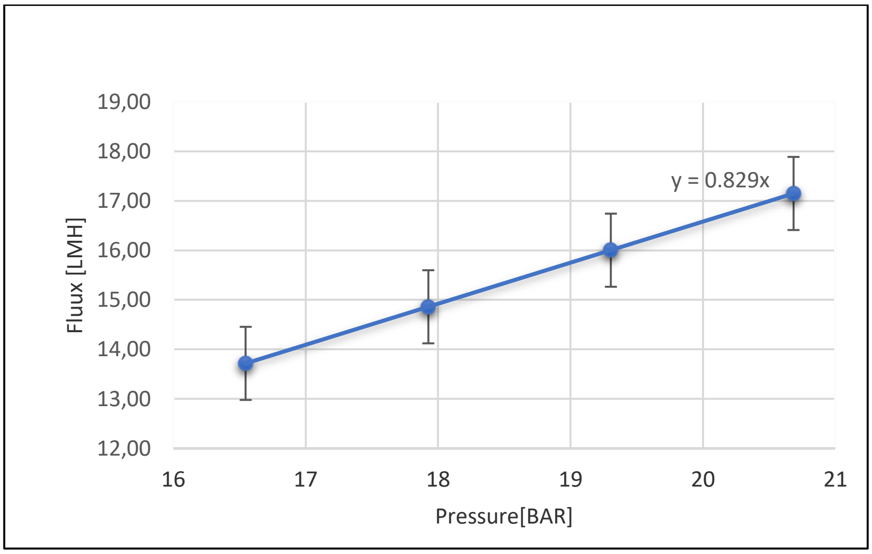


Figure 27. The filtration tests performed on PAN with amination and IP.

As seen above, an interesting finding is that despite the formation of an amine layer, the flux has not diminished. Membranes without modification only interfacial polymerization were tested to verify if the amination reaction would cause changes on permeability and rejection.

As far as rejection is concerned, figure 28 presents the average rejection values obtained from different samples. It is interesting to note that after the amination process there is a significant increase in the value of PAN (Ultura^{TM} brand, Long Beach) membranes rejection while there is a decrease in the value of PES membranes.

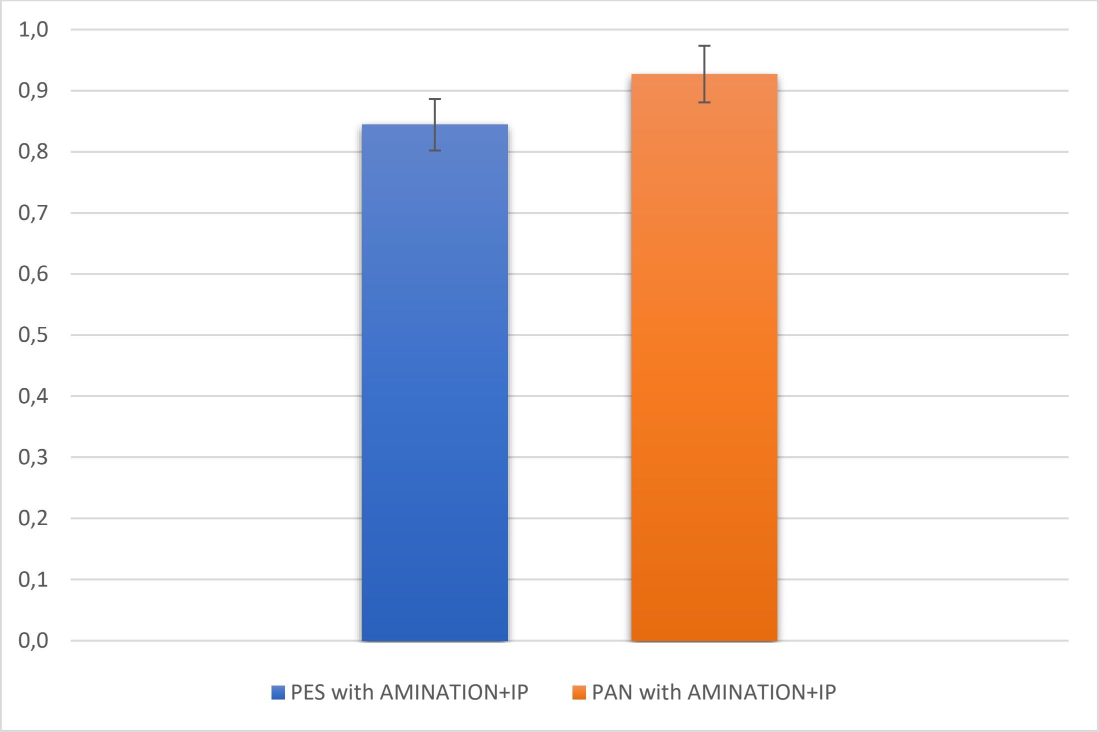


Figure 28. Rejection of modified PES and PAN membranes.

The values used to bring the average values of the permeability values of the PAN and PES membranes modified and unmodified used are shown in appendix A.

3.3.4 Comparison between PES and PAN membranes

Below (figure 29, 30, 31) are rejection and permeability values of various tested membranes. As can be seen, the highest rejection values have been achieved by the PA-PES with the only interfacial polymerization. There is a noticeable decrease in rejection of PA-PES modifid membranes. There is not specific reason to have this rejection reduction. Nevertheless, the rejection reduction was also obtained for unmodified PES-supports of the same batch of the modified PES. Thus, it seems that the results obtained are changed for an unkonwn reason which might be due to the degradation of the support.

were also the same of the unmodified. There are no significant differences in the variation of permeability between modified and unmodified PES membranes.

As far as PAN membranes (Ultura^{TM} brand, Long Beach) are concerned, it is interesting to note that after the amination process there is a significant increase in the rejection value and also the permeability.

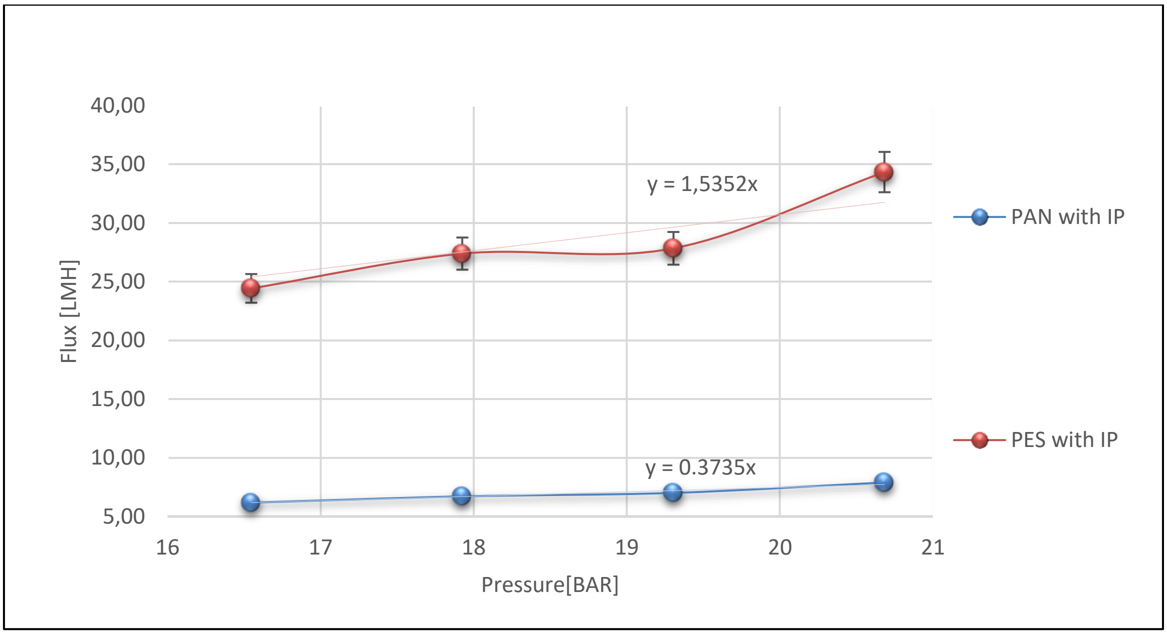


Figure 29. Comparation of filtration tests performed on PAN and PES membranes only with IP.

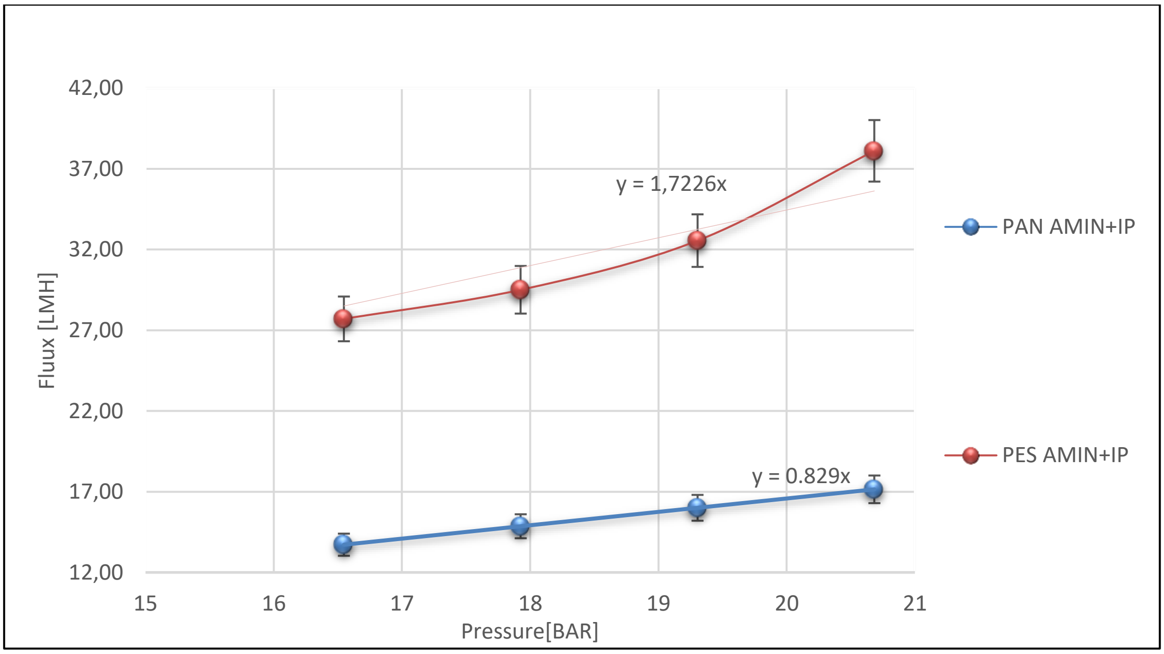


Figure 30. Comparation of filtration tests performed on PAN and PES membranes with amination and IP.

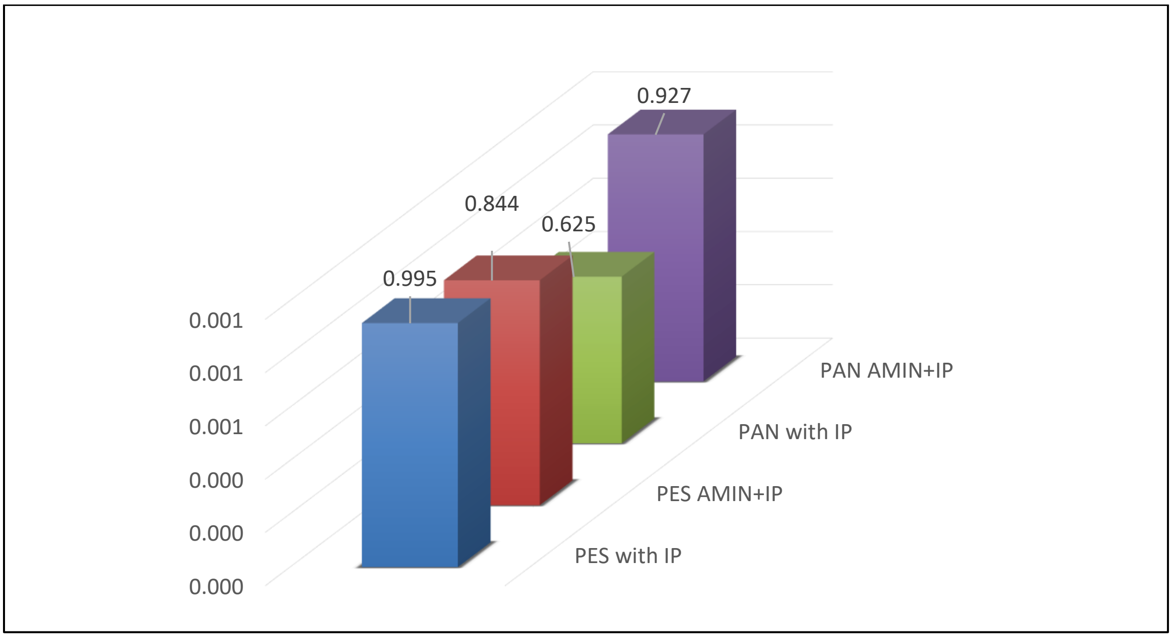


Figure 31. Comparation of rejection values of different PAN and PES membranes.

3.4 Backwashing results

In this section, the commercial and labmade membranes, considered in this work were tested in backwshing mode following the protocol decribed in chapter 2. In Appendix B, the various tests performed on the different membranes were reported, while the results are summarized below.

A spacer was used because the porous stone would damage the membranes.

Figure 32 depicts color code used to show the different steps to which the membrane has been subjected during backwashing tests.

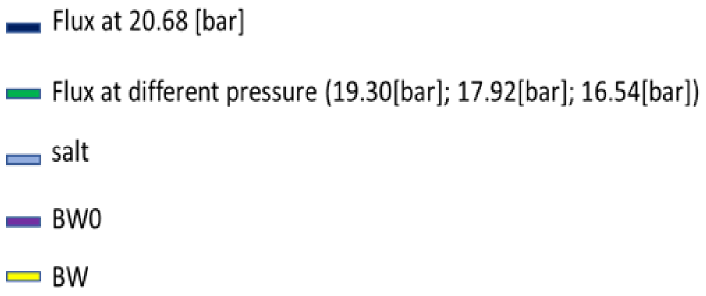


Figure 32. Color code used in backwashing tests.

As shown in the figures 33 and 34, commercial membranes had a completely different behavior. After the first backwashing, DOW SW30 has broken and it was a sudden increase of the flux with no rejection anymore. The membranes were presented an obvious detachment of the the active side along with PES support from the PET support, Hydra70 during backwashing remained rather stable both flux and rejection.

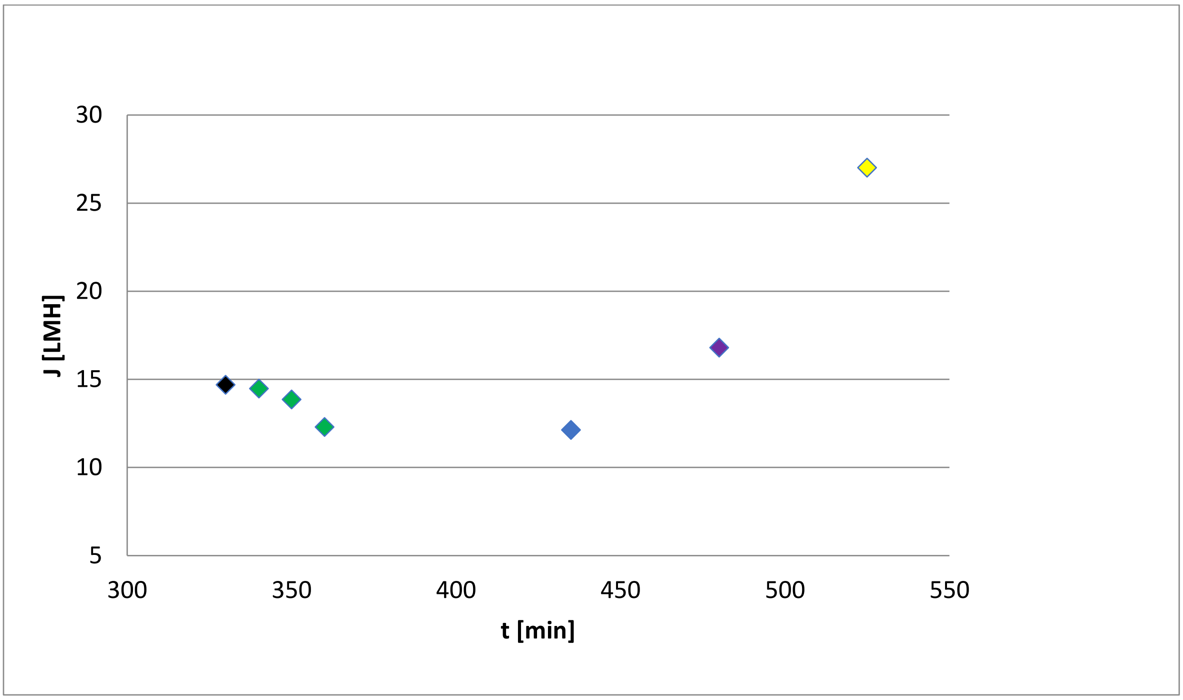


Figure 33. Behaviour of DOW SW30 in backwashing test.

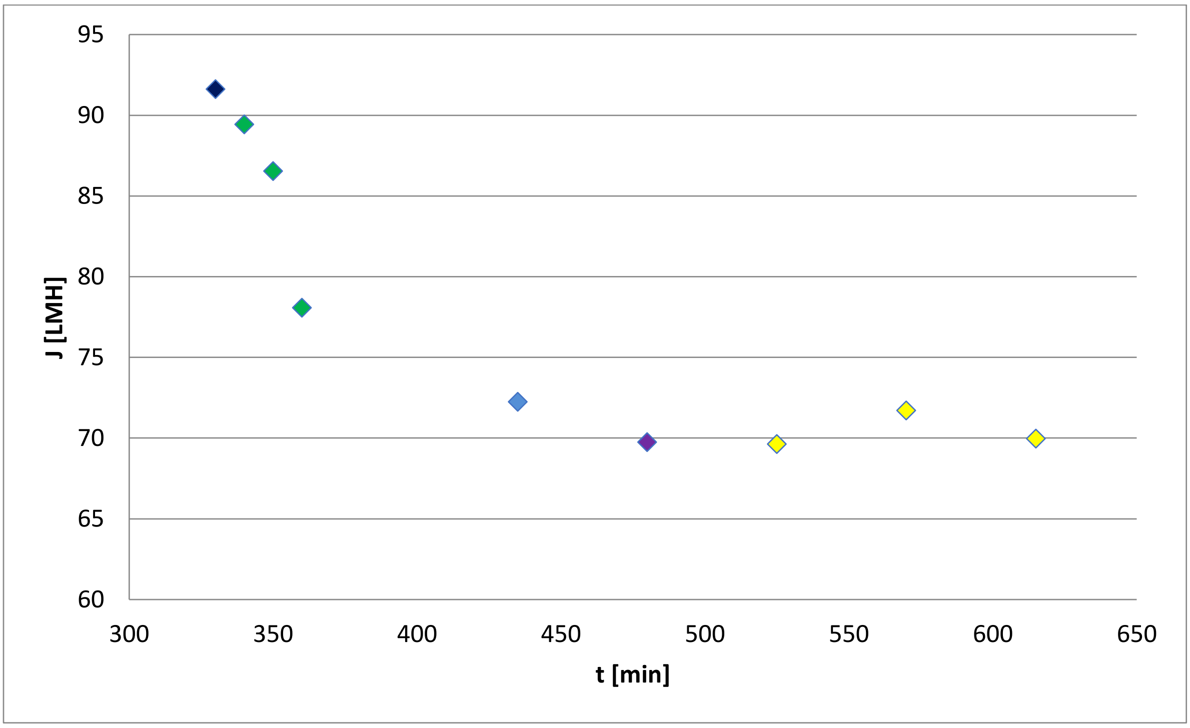


Figure 34. Behaviour of Hydracore 70 in backwashing test

As regards PES membranes, results from backwashing are showed below (figures 35 and 36). As far as PES membranes are concerned, both amineted and no aminated membranes had similar trend during backwashing. Indeed, both the kind of membranes did not break during the counter pressure applied, and showed a reduction in rejection, casued probably by the spacerthat damaged the PA-layer.

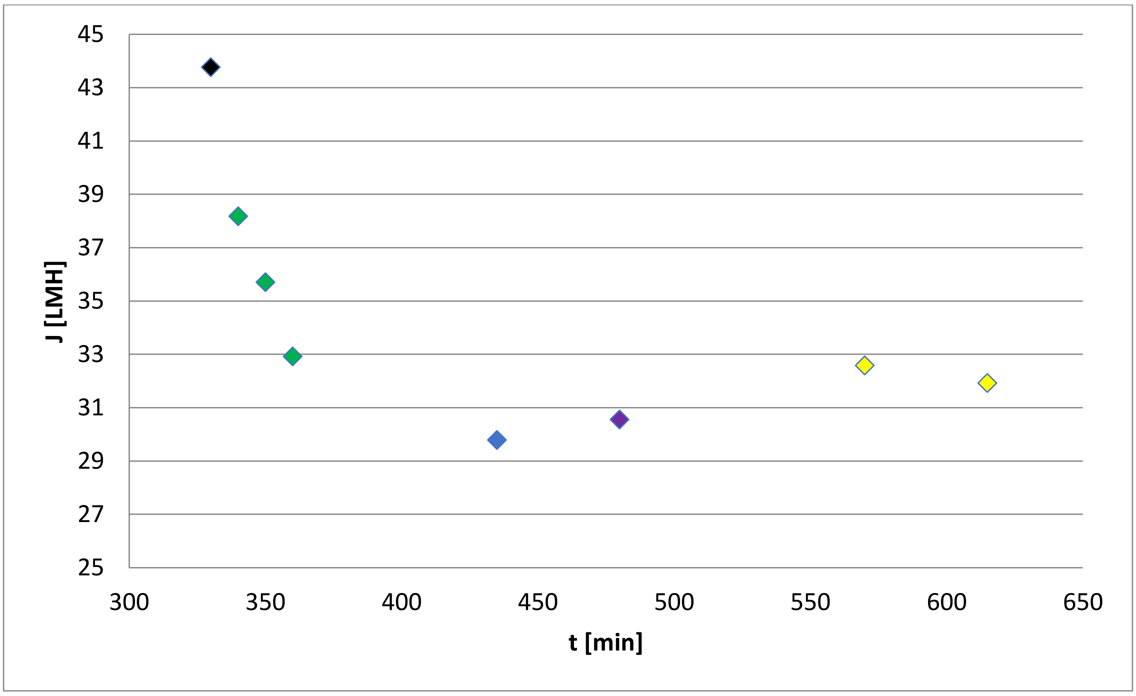


Figure 35. Behaviour of PES with only IP in backwashing test.

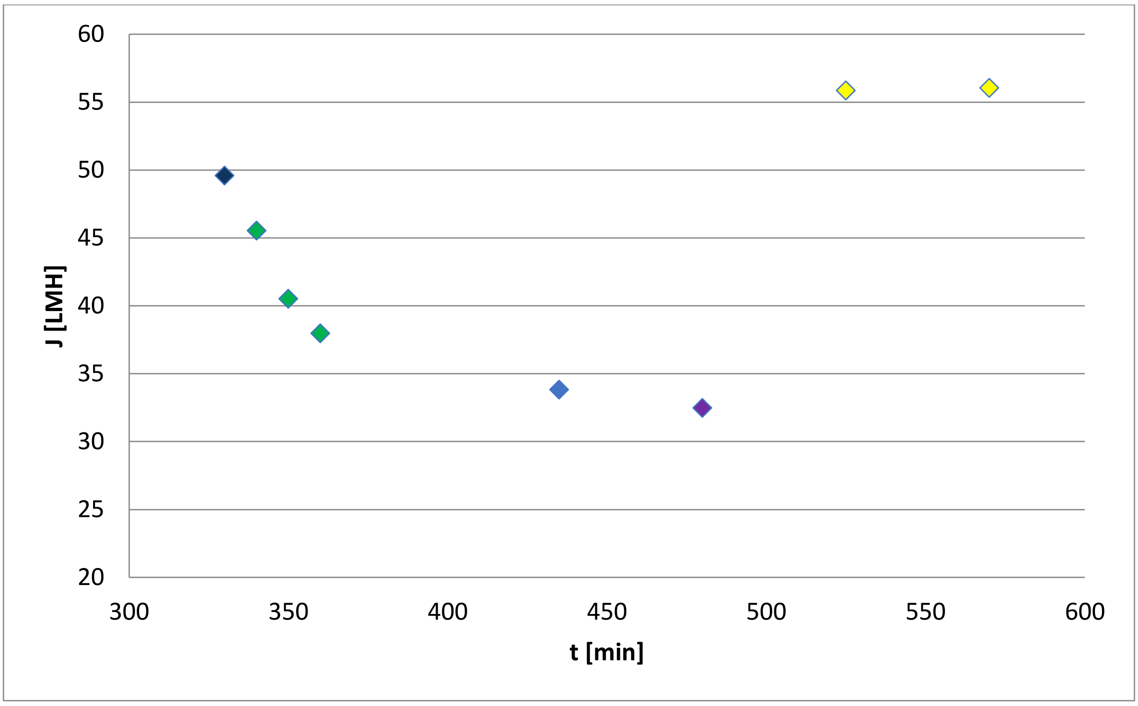


Figure 36. Behaviour of PES with amination and IP in backwashing test.

Concerning PA-PAN membranes, since in the last phase of the work, the Ultura^{TM} brand, Long Beach, MWCO 75 kDa had no longer been available so a new support (Synder filtration, 4941 Allison Pkwy), with different characteristics (permeability and pore size), has been used to backwashing system. These membranes were tested only in the with amination before the IP since thery were few samples. During backwashing test, the flux suddenly increased along with no rejection of salt. This suggests the detachment of the active layer but it was not evident when the membrane was removed frome the cell. It was not possible to notice anything form ATR spectra after the tests, because they were too noisy to notice any missing peak. Their results obtained of backwashing are reporteed in Appendix B, as well.

A finale resume of the all test is reported in table 3.

It can be concluded that commercial polyamide membranes have better rejection but low permeability and are subject to rupture. Moreover, the tests carried out by HYDRA membranes are the most resistant. The modified and unmodified PES need further research even if they were more resistant than the commercial correspondents, the PAN instead due to the change of support showed an improvement after the amination but it was not possible to carry out the backwashing tests.

Table 3. Resume of all backwashing tests.

Membrane	**Permeability (LMH/bar)**	**Rejection [-]**	**Variation Permeability with Backwashing**	**Variation Rejection with Backwashing**	**Break**
PES_IP	1.62 ± 0.42	0.95 ± 0.05	-	-	-
PAN_IP Support 1	0.36 ± 0.20	0.65 ± 0.10	-	-	-
PAN Aminated Support 1	0.67 ±0.26	0.94 ± 0.05	-	-	-
SW30	0.77	0.99	ND	ND	Y
HYDRA	4.63	0.80	N	N	N
PES_IP September	1.32 ±0.64	0.85 ± 0.02	N	Y	N
PES Aminated	1.58 ± 1.07	0.87 ± 0.05	N	Y	N
PAN Aminated Support 2	0.39 ± 0.08	0.83+ 0.03	ND	ND	Y

4. Conclusions

The aim of the study was to find an optimal thin. Film composite membrane capable of resisting backwashing.

The two supports chosen to fabricate the membranes were PS20 from SEPRO and PAN membranes Ultura^{TM} brand, Long Beach, with MWCO of 75 kDa.

The first step was to cast a polyamide separation thin film in a traditional way by performing interfacial polymerization onto the unmodified support layers. Different values of permeance and rejection were obtained for membranes cast onto the two different supports: PES-supported membranes had high NaCl rejection (91%) and permeance (2 LMH/bar), whereas PAN-supported membranes had lower values of both NaCl rejection and permeance (60% and 0,38 LMH/bar, respectively)

The second step was to implement a protocol to make the membranes suitable for backwashing operations. An amination reaction was first carried out to create a strong bond between the support and the polyamide layer during subsequent casting of the thin film. Although the permeance and rejection results obtained by the PAN supports were not optimal and far inferior to those obtained using PES support layers, it was decided to continue the tests on both supports as PAN layers can be modified in a much simpler way. Following amination of the support layer, a polyamide thin film was cast on top of the modified support, thus creating strong covalent bonds between the two layers.

The last step was to test the PES- and PAN-supported membranes under backwashing conditions. No significant differences were observed between lab-made membranes cast onto modified and unmodified PES supports, all being reasonably capable of withstanding backwashing, with minor loss in performance along the cleaning cycles. Membranes cast onto PAN membranes and commercial thin-film composite membranes did not withstand backwashing.

In conclusion, interesting achievements were obtained in this study in terms of the reliability and feasibility of the backwashing system as an optimal engineered process, but no definite conclusions can be draws about the relationship between layer structure and chemical bonding and membrane robustness during backwashing. Nevertheless, the initial information obtained in this study is necessary for further optimization of the chemistry and morphology of thin-film composite membranes to be adopted in RO applications.

Appendix A

Table 1

Membrane	**Permeability [LMH/bar]**	**Rejection% [-]**
Ps20 IP-1	1,5563	0,952
Ps20 IP-2	1,7129	0,95
Ps20 IP-3	0,8212	0,953
Ps20 IP-4	1,8852	0,99
Ps20 IP-5	1,9448	0,88
Ps20 IP-6	1,7632	0,981

Table 2

Membrane	**Permeability [LMH/bar]**	**Rejection% [-]**
PAN IP-1	0,4249	0,76
PAN IP-2	0,3191	0,58

Table 3

Membrane	**Permeability [LMH/bar]**	**Rejection% [-]**
PAN Amin+IP-1	0,3846	0,9814
PAN Amin+IP-2	0,6673	0,9211

PAN Amin+IP-3	1,1003	0,8656
PAN Amin+IP-4	0,5780	0,9660
PAN Amin+IP-5	0,6287	0,9829

Table 4

Membrane	Permeability (LMH/bar)	Rejection (%) [-]
PES Amin+IP-1	2.34	87.2
PES Amin+IP-2	0.8	86.2

Table 5

Membrane	Permeability (LMH/bar)	Rejection%
DOW SW30-1	0,74	98.8; **BW0**: 98.8
DOW SW30-2	0.77	98.5; **BW0**: 98.6
DOW SW30-3	0.79	
HYDRA	4,63	80.2; **BW0**: 82; **BW1-3**: 80.2
Ps20 IP-1	2.02	90; **BW0**: 90.6; **BW1**: 78; **BW2**:75; **BW3**:45.5
Ps20 IP-2	0.645	89.3; **BW0**: 87; **BW1**: 22%
Ps20 IP-3	2.02	90; **BW0**: 90.6; **BW1**: 78; **BW2**:75; **BW3**:45.5
Ps20 IP-4	0.59	81.5; **BW0**: 83.5; **BW1-3**: 57
Ps20 IP-4	0.72	83.5; **BW0**: 82; **BW1**: 52
Ps20 Amin+IP 1	2.34	87.2; **BW0**: 87; **BW1**: 82; **BW2**: 63.4
Ps20 Amin+IP 2	0.8	86.2; **BW0**: 85.3; **BW1-3**: 63.8

Table 6

Membrane	Permeability (LMH/bar)	Rejection (%)
PAN-Amin+IP 1	0.3	86.7; **BW0**: 70
PAN-Amin+IP 2	0.47	81.6; **BW0**: 81.5

Appendix B

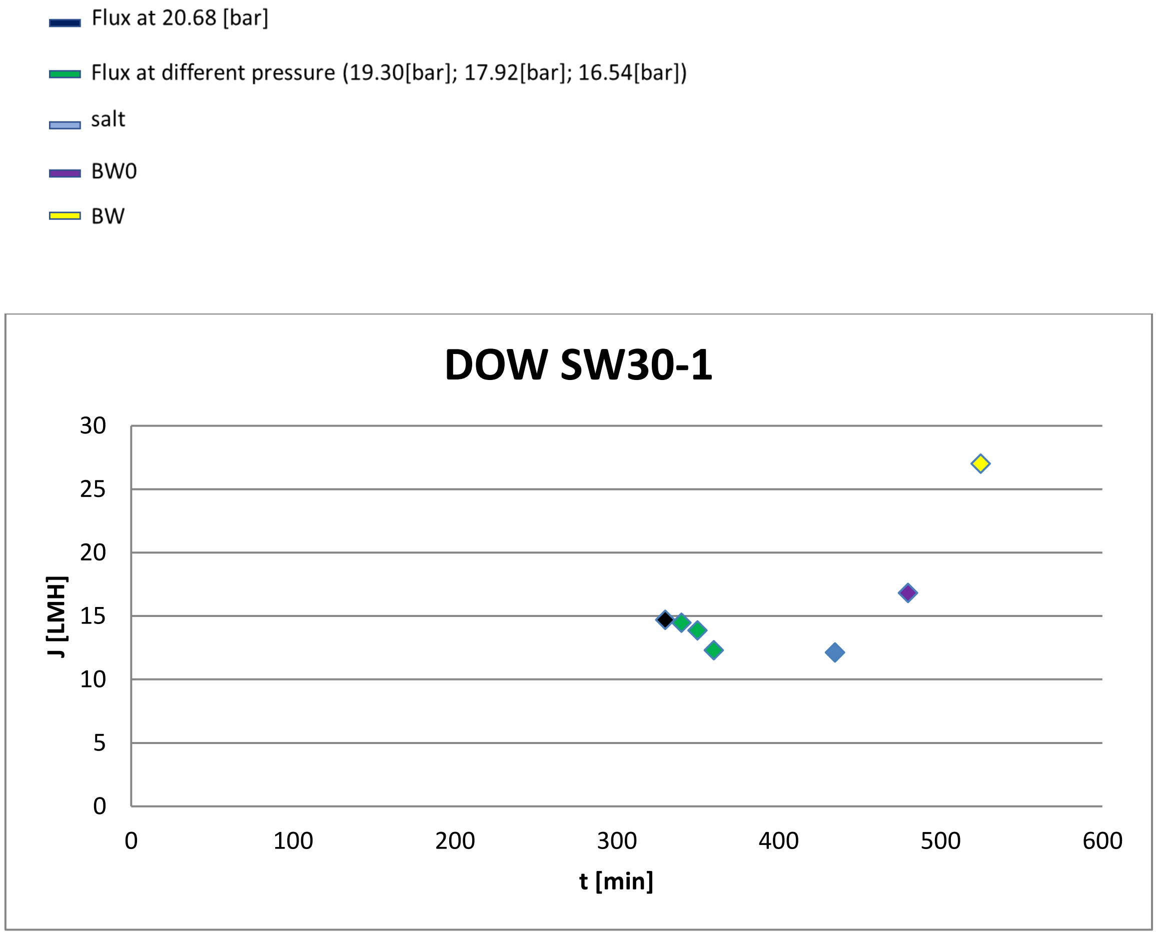


Figure 39

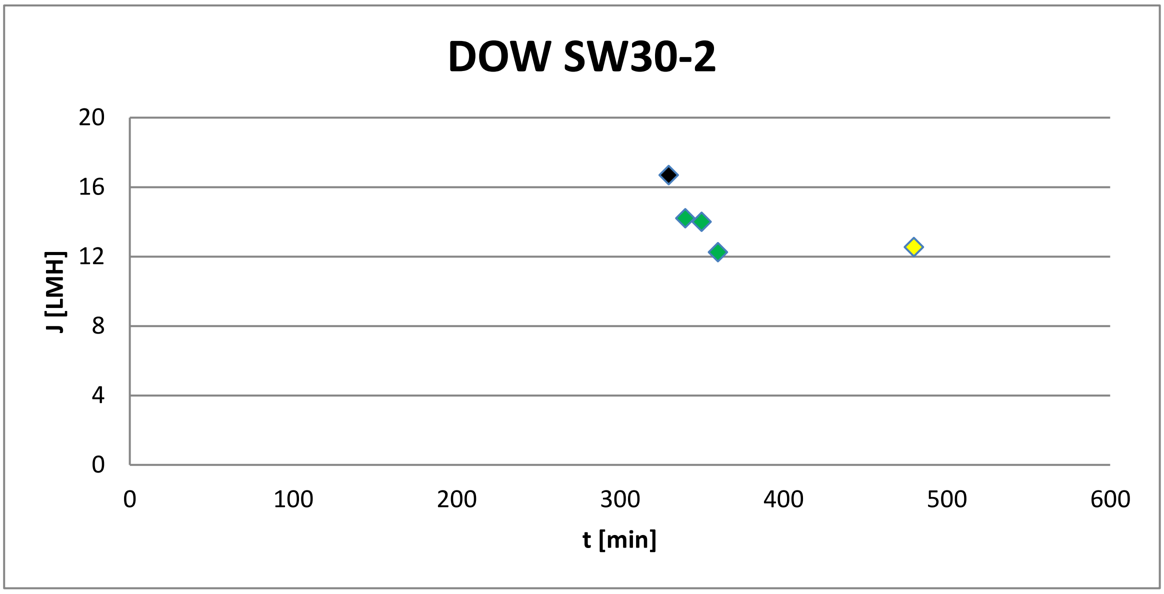


Figure 40

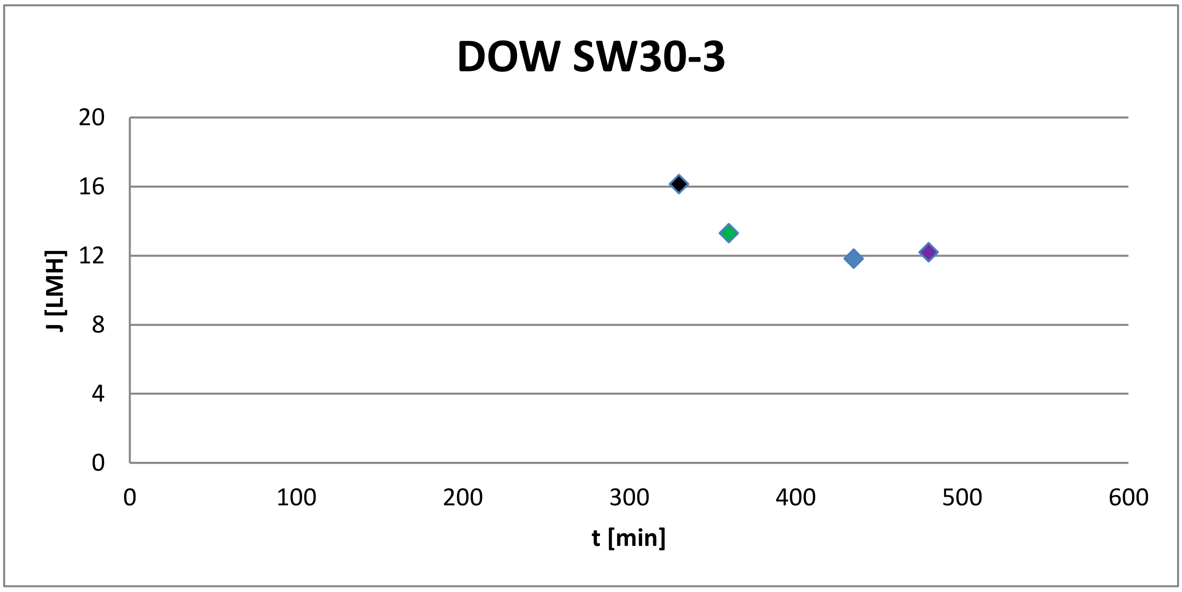
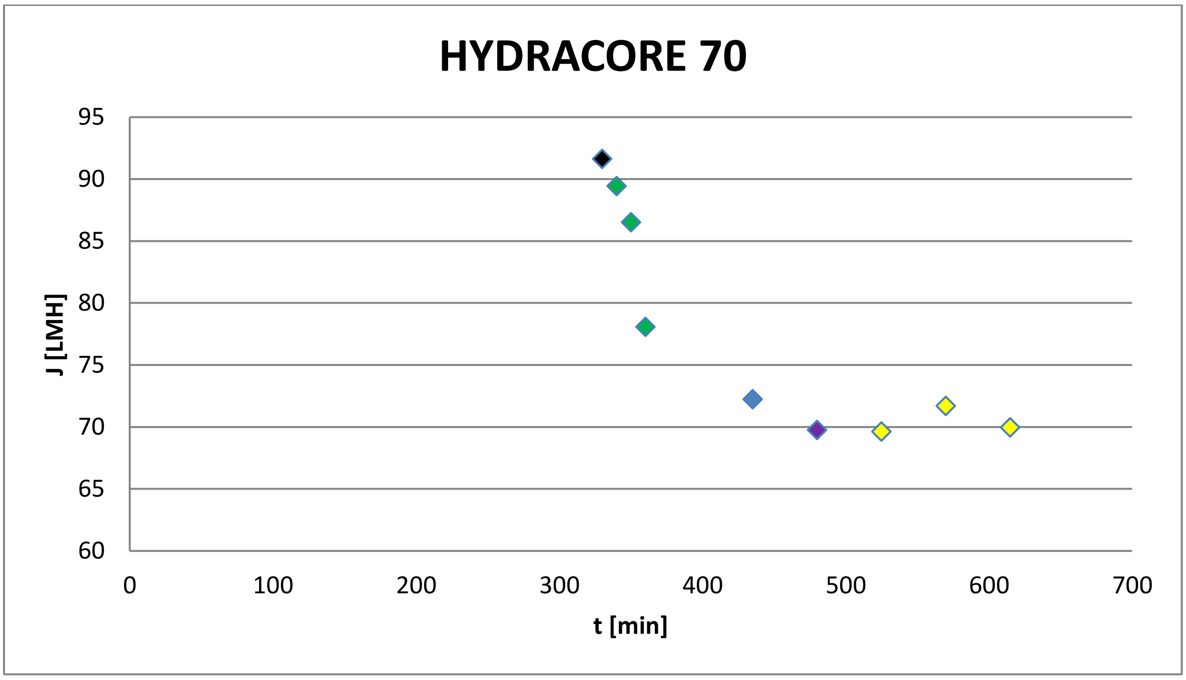


Figure 41



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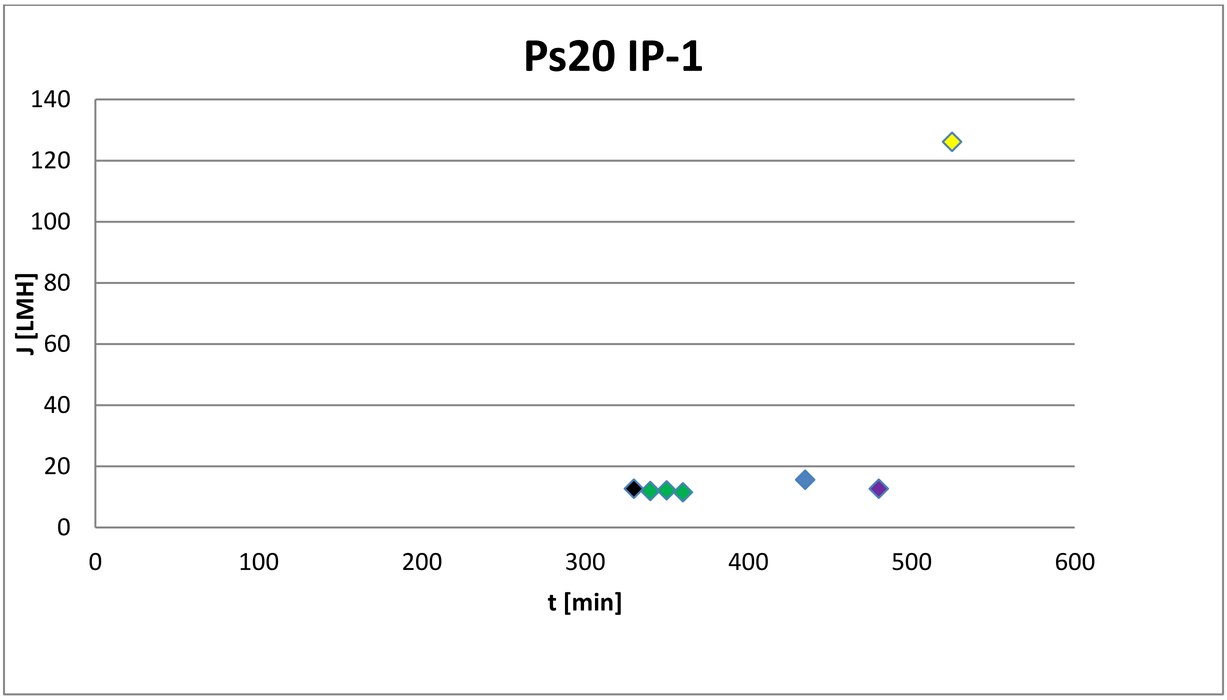


Figure 43

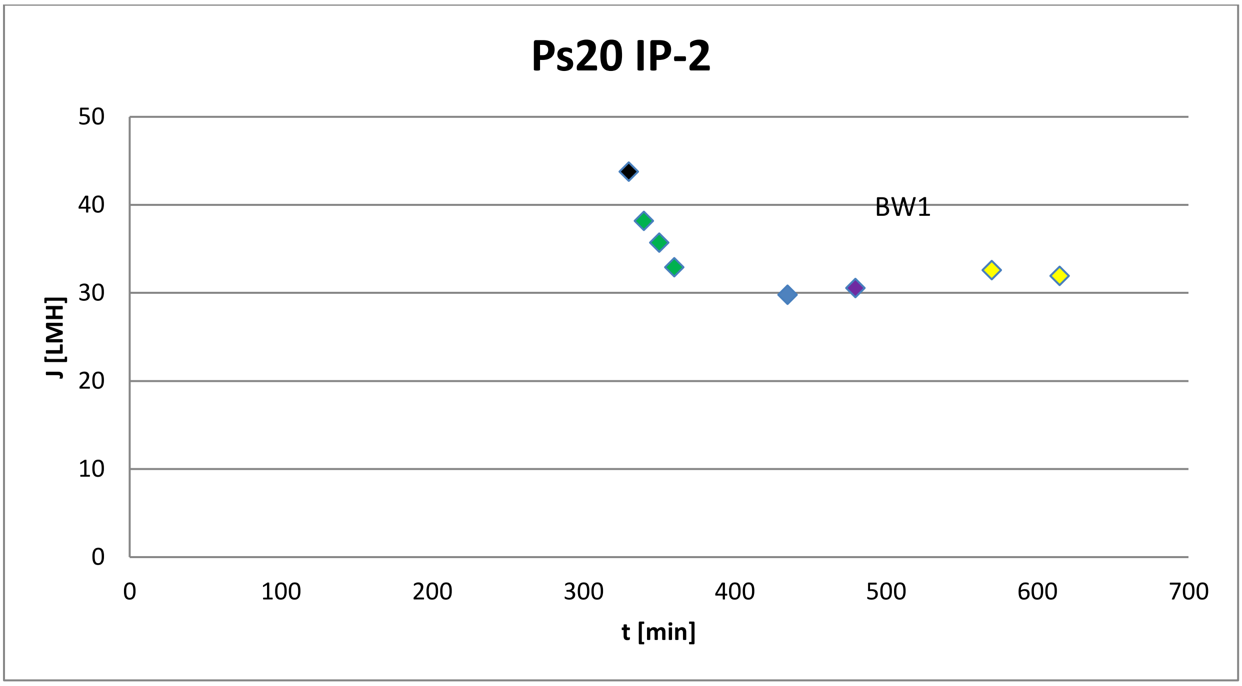
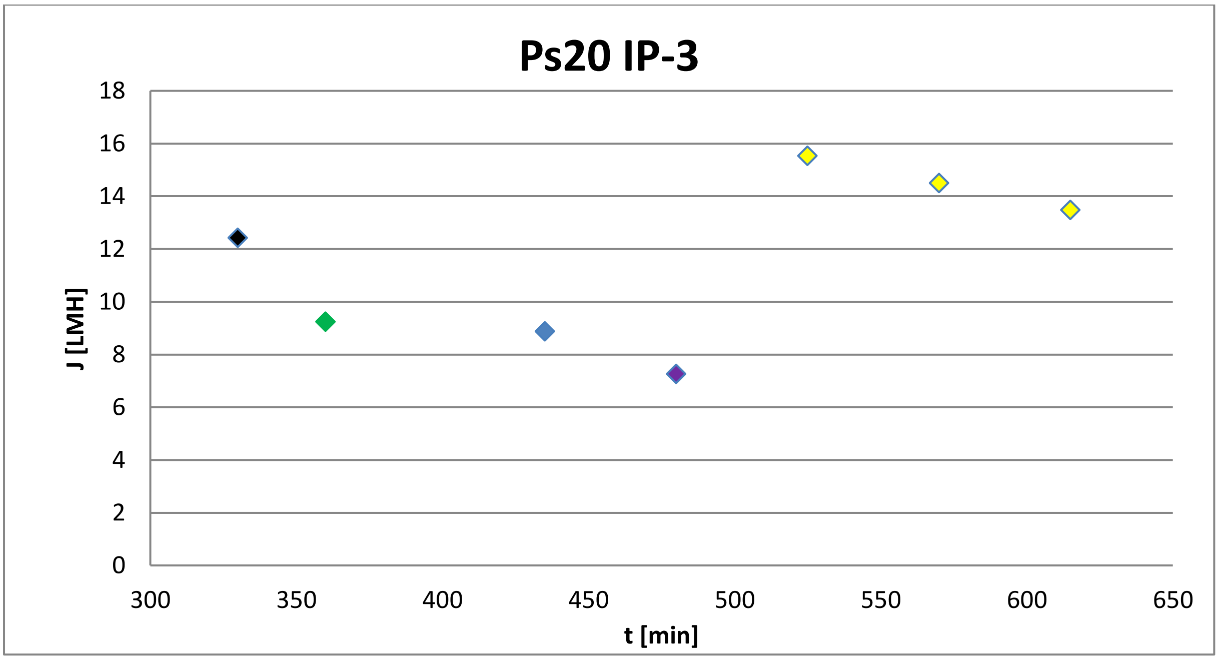


Figure 44



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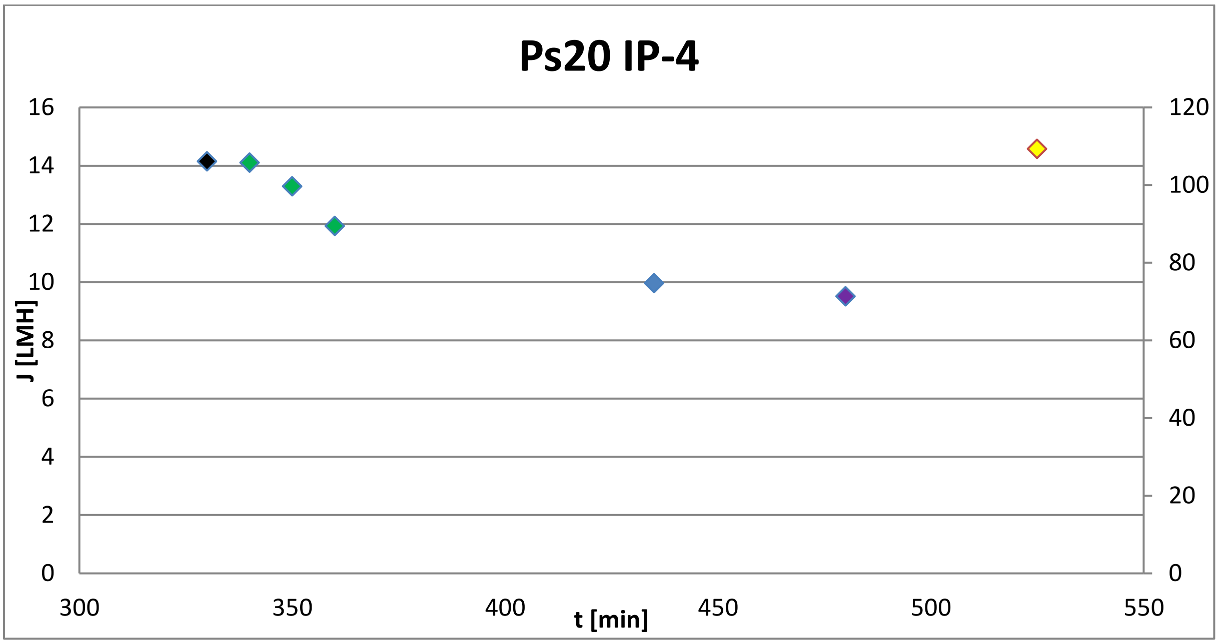
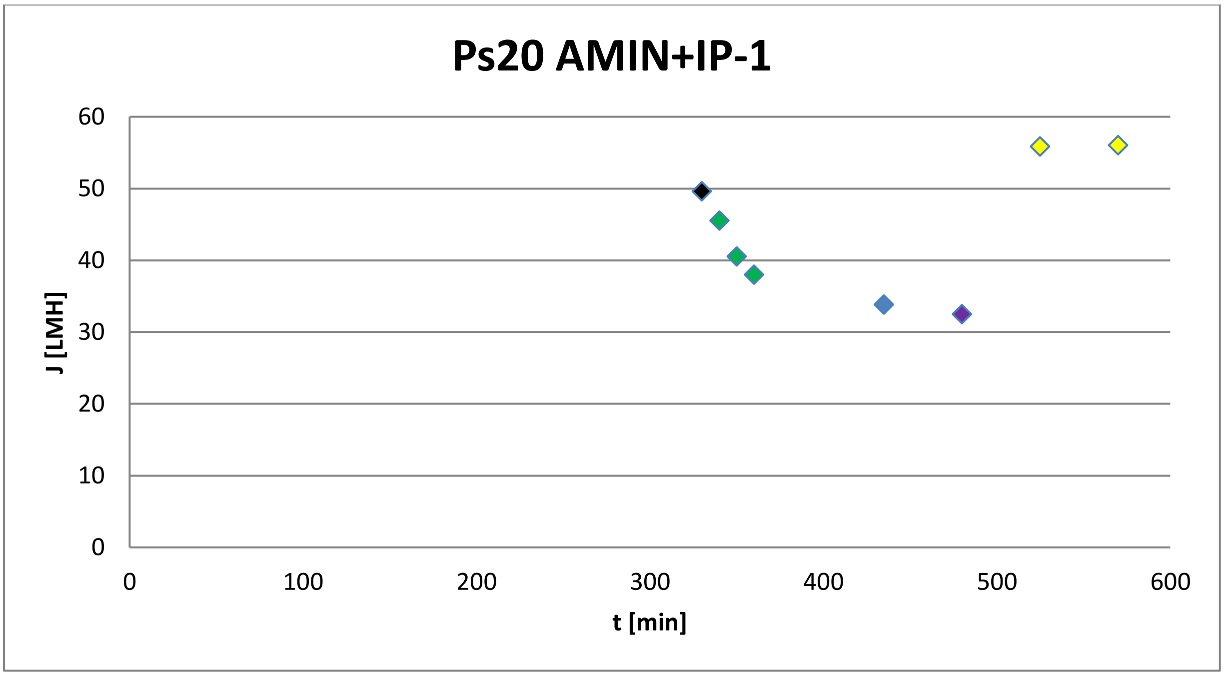


Figure 46



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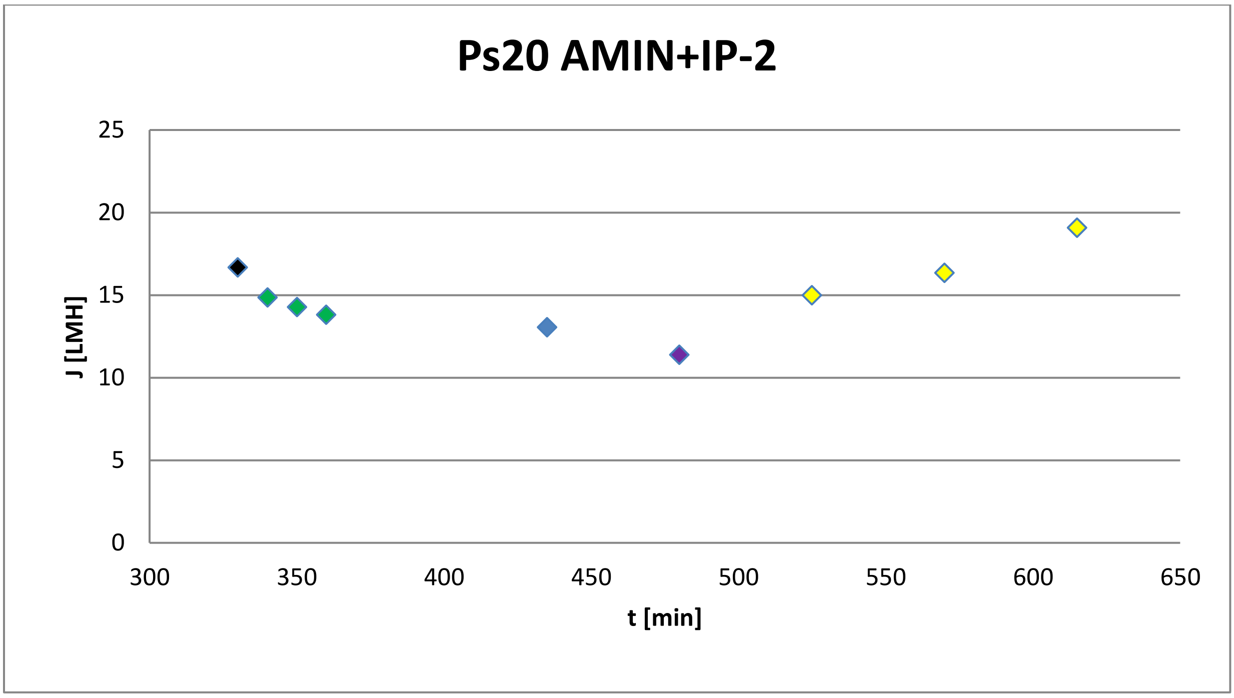

Figure 48

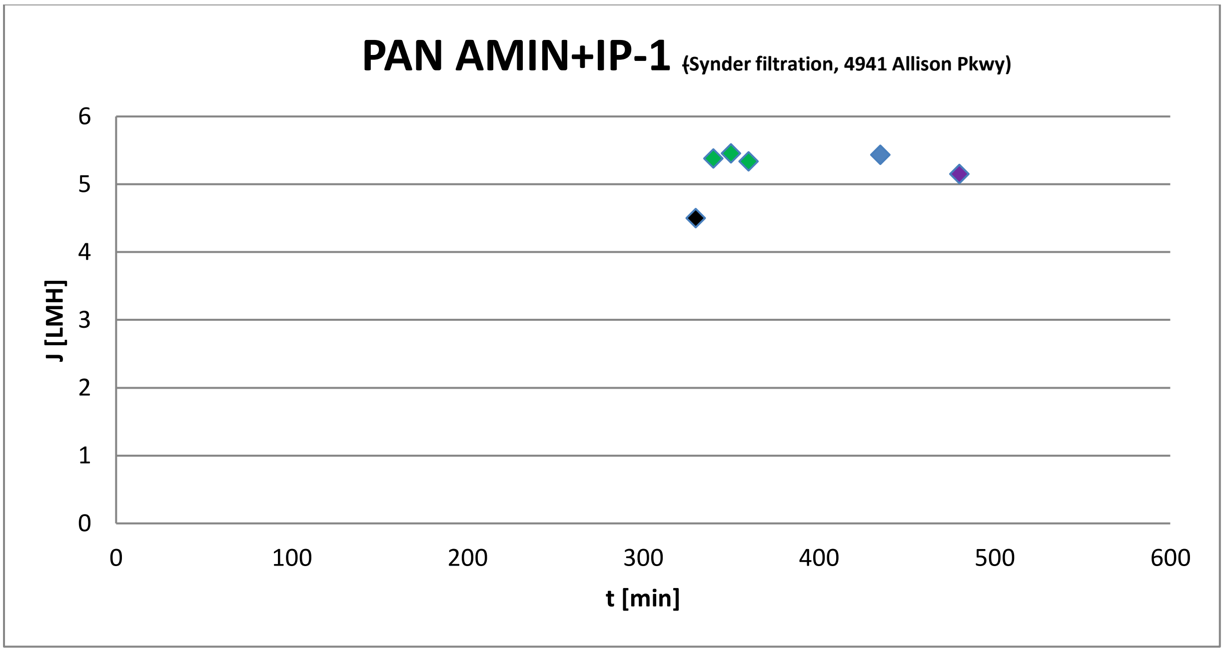

Figure 49

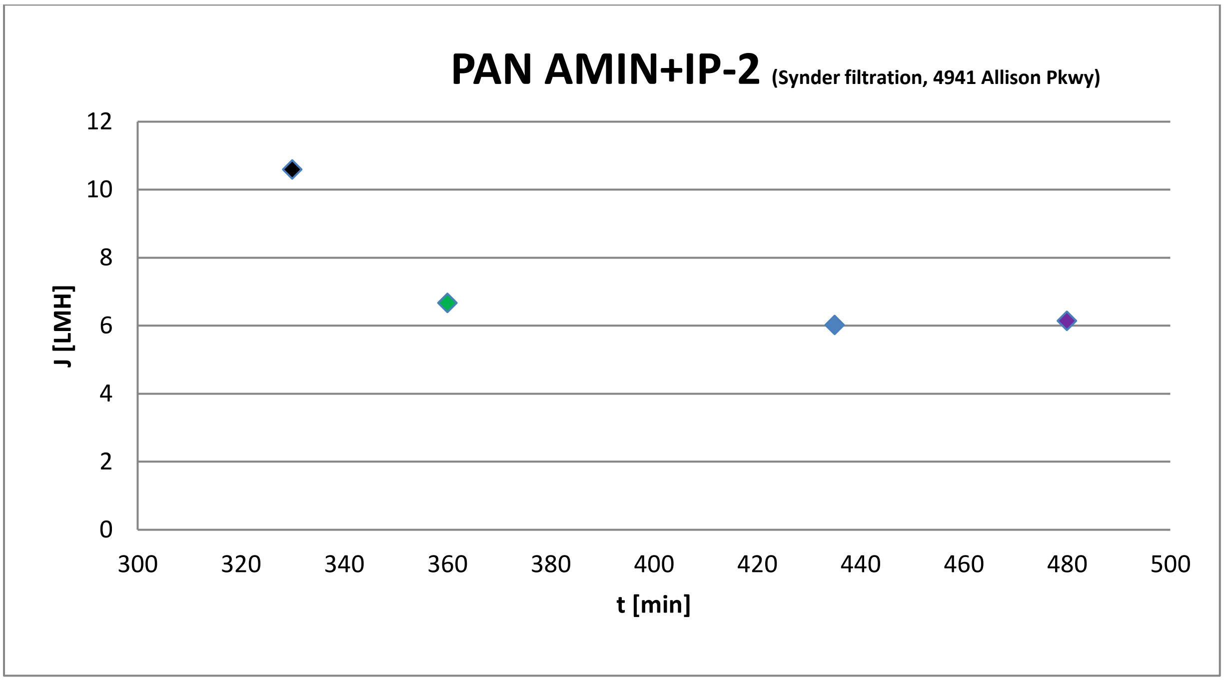
PAN AMIN+IP-2 (Synder filtration, 4941 Allison Pkwy)
J [LMH]
12
10
8
6
4
2
0
300
320
340
360
380
400
420
440
460
480
500
t [min]

Figure 50

5. Bibliography

[1] R. W. Baker, "Membrane Technology and Applications."

[2] "Reverse osmosis desalination: Water sources, technology, and today's challenges," *Water Res.*, vol. 43, no. 9, pp. 2317–2348, May 2009.

[3] "Fabrication of polyamide thin film composite reverse osmosis membranes via support-free interfacial polymerization," *J. Memb. Sci.*, vol. 526, pp. 52–59, Mar. 2017.

[4] T. Younos and K. E. Tulou, "Overview of Techniques Overview of Desalination Techniques."

[5] M. Mulder, "Membrane Technology."

[6] G. G. Chin N- Tran, all O. C. Adrian C. Maldonado, Chula Vista; Ratnasamy Somanathan, San Diego, and _, "US5234598," *United States Pat. USO05234598A [11] Pat. Number 5,234 598 9 [45] Date Pat. Aug. 10, 1993 [54]*.

[7] A. K. Ghosh and E. M. V Hoek, "Impacts of support membrane structure and chemistry on polyamide-polysulfone interfacial composite membranes," *J. Memb. Sci.*, 2009.

[8] S. Petrov, P. Atanasova, P. Dineff, and T. Vladkova, "Surface modification of polymeric ultrafiltration membranes I. Effect of atmospheric pressure barrier discharge in air onto some characteristics of polyacrylonitrile ultrafiltration membranes," *High Energy Chem.*, 2012.

[9] both of O. Harold K. Lonsdale, Bend; Carl C. Wamser, West Linn, "FUNCTIONAL, PHOTOCHEMICALLY ACTIVE AND CHEMICALLY ASYMMETRIC MEMBR'ANES BY INTERFACIAL POLYMERIZATION 0F DERIVATIZED MULTIFUNCTIONAL PREPOLYMERS."

[10] M. L. Lind, D. E. Suk, T. V. Nguyen, and E. M. V Hoek, "Tailoring the structure of thin film nanocomposite membranes to achieve seawater RO membrane performance," *Environ. Sci. Technol.*, 2010.

[11] H. Chang *et al.*, "Hydraulic backwashing for low-pressure membranes in drinking water treatment: A review," *Journal of Membrane Science*. 2017.

[12] A. Sagiv and R. Semiat, "Backwash of RO spiral wound membranes," *Desalination*, 2005.

[13] A. Amelio, M. Sangermano, R. Kasher, R. Bernstein, and A. Tiraferri, "Fabrication of nanofiltration membranes via stepwise assembly of oligoamide on alumina supports: Effect of number of reaction cycles on membrane properties," *J. Memb. Sci.*, 2017.

[14] W. J. Koros ', Y. H. Ma2, T. Shimidzu3, U. H. P. S. A. Hsieh, R. Y. M. Huang, and C. E. Jacobs, "TERMINOLOGY FOR MEMBRANES AND MEMBRANE PROCESSES," *Assoc. Memb. J. R. Lyerla (Boddeker (Germany); A. G. Fane (Australia); W. J. Koros (USA*, vol. 68, no. 7, pp. 1479–1489, 1996.

[15] "tangential cross flow filtration."

[16] "Coulson Richardson's Chemical Engineering Vol.6 Chemical Engineering Design 4th Edition."

[17] *FT-IR Spectroscopy Attenuated Total Reflectance (ATR)*. .

[18] A.S.Sarac, "Redox polymerization," *Prog. Polym. Sci.*, vol. 24, no. 8, pp. 1149–1204, Oct. 1999.