UNIVERSIDADE FEDERAL DE SANTA CATARINA
CENTRO TECNOLÓGICO
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA DE ALIMENTOS

ESTRATÉGIA ANTI-INCRUSTAÇÃO NA MICROFILTRAÇÃO DE EMULSÕES OLEOSAS BASEADA NA MODIFICAÇÃO DA SUPERFÍCIE DE MEMBRANA DE PVDF COM POLI(DOPAMINA) E POLI(ETILENO IMINA)

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Por

Guilherme Zin

Tese julgada para obtenção do título de **Doutor em Engenharia Alimentos**, área de Concentração de **Desenvolvimento de Processos da Indústria de Alimentos,** e aprovada em sua forma final pelo Programa de Pós-graduação em Engenharia de Alimentos da Universidade Federal de Santa Catarina.

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RESUMO

O tratamento de águas residuais é uma importante etapa na indústria de alimentos devido à grande quantidade de água utilizada nos processos. Dentre as águas residuais geradas pelas indústrias, o tratamento dos efluentes oleosos é um inevitável desafio. Observando este cenário, os processos de separação com membranas (PSM) aparecem como uma tecnologia atraente no tratamento de efluentes oleosos pois apresentam alta seletividade, facilidade de escalonamento, flexibilidade de operação e baixa demanda energética. No entanto, um dos maiores problemas enfrentados por esta tecnologia é a redução da permeabilidade causada pela polarização por concentração e a incrustação da membrana. Dentro deste contexto, o presente trabalho tem como objetivo desenvolver e avaliar melhorias em membranas de microfiltração para aplicação no tratamento de águas residuais oleosas. A melhoria do desempenho do processo de microfiltração foi realizada pela modificação da superfície da membrana (MSM), tornando membranas hidrofóbicas em superhidrofílicas pela utilização do método inspirado em mexilhão, *mussel-inspired* (MI), e da utilização de campos magnéticos (CM) como pré-tratamento da emulsão de óleo. Os ensaios de permeação foram realizados em sistemas de filtração convencional e tangencial pela permeação de emulsões de óleo de canola. As membranas utilizadas nos experimentos foram de microfiltração comerciais confeccionadas de poli(difluoreto de vinilindeno) (PVDF) com diferentes tamanhos de poro (0,1, 0,2 e 0,45 µm), modificadas ou não. As MSM foram realizadas com diferentes abordagens do método MI e diferentes concentrações de dopamina (DA) e polietilenoimina (PEI). Os efeitos das diferentes modificações foram avaliados em relação à hidrofilicidade, molhabilidade, resistência ao pH e no desempenho do processo de permeação das emulsões oleosas. O efeito da aplicação do campo magnético como estratégia anti-incrustação foi estudado pela permeação da emulsão oleosa tratada magneticamente pela circulação por 2 h em dispositivos geradores de campo magnético. Os parâmetros avaliados nas permeações foram a permeabilidade hidráulica inicial, o fluxo da emulsão de óleo de canola, a retenção da membrana e a permeabilidade hidráulica após os procedimentos de limpeza física e química. As membranas foram caracterizadas por diferentes técnicas como microscopia eletrônica e de força atômica, espectroscopia de infravermelho e de fotolelétrons excitados por raio-X e potencial zeta. As modificações da membrana hidrofóbicas pelas diferentes abordagens do método MI provaram ser eficientes para torná-las superhidrofílicas, adequadas para o tratamento de águas residuais oleosas. Por sua vez, o tratamento da emulsão oleosa com CM não alterou o desempenho das microfiltrações realizadas

Palavras-chave: Processo de separação por membranas, polarização por concentração, incrustação, modificação da superfície da membrana, campo magnético, emulsão oleosa.

ABSTRACT

Wastewater treatment is an important step in food industries due to large amount of water used in the processes. Among the effluents generated by industries, the oily wastewater is an inevitable challenge. In this scenario, membrane separation processes appear as an attractive technology in the oily wastewater treatment, due to their high selectivity, easy scale-up, operation flexibility and low energetic demand. However, one of the major drawbacks of this technology is the permeability reduction caused by concentration polarization and membrane fouling. In this context, the present work aimed to develop and evaluate improvements in microfiltration membranes for application in the oil removal of industrial wastewater. The improvement in performance of microfiltration was carried out by the membrane surface modification (MSM), turning hydrophobic membranes into superhydrophilic by a mussel-inspired (MI) method, and by pre-treatment of oil emulsion under a magnetic field (MF). The permeations assays were carried out by the permeation of canola oil emulsion in dead-end and cross-flow filtration systems. Commercial poly(vinylidene difluoride) (PVDF) microfiltration membranes with 0.1, 0.2 and 0.45-µm of pore size, modified or not, were used in the permeations assays. Different approaches of the MI method and different concentrations of dopamine (DA) and polyethyleneimine (PEI) were used in the MSM. The effects of the different modifications were evaluated by the hydrophilicity, wettability, pH resistance and the permeation performance of the oily emulsions. The magnetic field application as an antifouling strategy was studied by the permeation of the oil emulsion previously circulated through a magnetic field device for 2 h. The permeation performance was evaluated by the initial water permeability, flux of canola oil emulsion, membrane retention and the water permeability after the physical and chemical cleaning procedures. Membrane were characterized by atomic force and scanning electron microscopy, infrared spectroscopy, X-ray photoelectron spectroscopy and zeta potential. The MSM by the different approaches proved be efficient to modify hydrophobic membranes into superhydrophilic, suitable for use in the treatment of oily wastewaters. In turn, the treatment of the oily emulsion with MF did not alter the microfiltration performance carried out.

keywords: Membrane separation processes, concentration polarization, fouling, membrane surface modification, magnetic field, oily emulsion.

LISTA DE ABREVIATURAS E SIGLAS

AFM – atomic force microscopy
ATR-FTIR – attenuated total reflectance Fourier transform infrared spectroscopy
BSA – albumina de soro bovino
CM - campo magnético
COT - carbono orgânico total
CTA – celulose tri-acetato
DA – dopamina/dopamine
DW – deionized water
FTIR - espectroscopia de infravermelho com transformada de Fourier
IM - indução magnética
MEV - microscopia eletrônica de varredura
MF - microfiltração
MFA - microscopia de força atômica
MI –mussel-inspired
MI-F – mussel-inspired filtered membrane
MI-T – mussel-inspired temperature membrane
MP – membrane process
MSM - modificação da superfície da membrana
NF - nanofiltração
OEMI – oil emulsion magnetically induced
OI - osmose inversa
PAN – poliacrilonitrila
PDA – polidopamina/polydopamine
PEI – polietilenoimina/polyethyleneimine
PES – polietersulfona
PP – polipropileno
PS – polisulfona
PSM/MSP - processo de separação por membrana/membrane separation process
PVDF – poli(fluoreto de vinilideno)/ poly(vinylidene difluoride)
PVP – poli(N-vinil pirrolidona)
SEM – scanning electron microscopy
TEOS – tetraetossilano
TGA - análise termogravimétrica
TRIS-HCL – tris(hydroximethyl) aminoethane
UF – ultrafiltração

XPS – X-ray photoelectron spectroscopy/espectroscopia de fotoelétrons excitados por raios X

LISTA DE SÍMBOLOS

R_a - resistência da adsorção, m^{-1}
R_b - resistência do bloqueio físico dos poros, m^{-1}
R_g - resistência da camada gel, m^{-1}
R_m - resistência da membrana, m^{-1}
R_{pc} - resistência da polarização por concentração, m^{-1}
W_{up} – water uptake
M_{wet} – weight of the wet membrane, kg
M_{dry} – weight of the dry membrane, kg

LISTA DE FIGURAS

Figura 2.1: Típico sistema de separação com membranas utilizado no tratamento de águas residuais oleosas. 46

Figura 2.2: Representação das resistências ao transporte de massa nos PSM cuja força motriz é a diferença de pressão. 48

Figura 2.3: Esquema do processo da modificação da superfície de uma determinada membrana pela combinação da ativação da superfície via plasma-induzido com posterior processo de polimerização por *graft* (adaptado de LIN et al., 2010). 61

Figura 2.4: Esquema do processo de polimerização da dopamina. 63

Figura 2.5: Estrutura química da polietilenoimina ramificada. 64

Figura 2.6: Esquema ilustrativo da reação de adição de Michael e da base de Schiff 65

Figure 3.1: Schematic diagram of the dead-end permeation system……………………………………………………………91

Figure 3.2: SEM images of the surface for the (a) clean and (b) fouled control membranes; (c) clean DA modified membrane (0.5 mg.mL^{-1}); (d) clean and (e) fouled DA:PEI modified membranes (0.5:1 mg.mL^{-1}). The membrane modifications were carried out with PVDF microfiltration with 0.1-µm pore size and 24 h of deposition time. 93

Figure 3.3: Photographic images of a water droplet (20 µL) deposited on the membrane surface for the (a) control membrane, (b) DA modified membrane (0.5 mg.mL^{-1}) and (c) DA:PEI modified membranes (0.5:1 mg.mL^{-1}). The membrane modifications were carried out with 24 h of deposition time and the images were obtained after 30 sec.. 94

Figure 3.4: ATR-FTIR of the (a) control membrane, (b) DA powder (c) DA modified membrane (0.5 mg.mL^{-1}), (d) DA:PEI polymeric aggregates (0.5:1) and (e) DA:PEI modified membranes (0.5:1 mg.mL^{-1}). The membrane modifications were carried out with 24 h of deposition time and the DA:PEI polymeric aggregates were obtained after 24 h of polymerization. 95

Figure 3.5: XPS of the (a) control membrane, (b) DA modified membrane (0.25 mg.mL^{-1}) and (c) DA:PEI modified membranes (0.25:0.5 mg.mL^{-1}). The membrane modifications were carried out with 24 h of deposition time. 97

Figure 3.6: Water weight gain of 0.1 μm PVDF modified membranes with different DA:PEI concentrations (mg.mL^{-1}) with 24 h of deposition time. 99

Figure 3.7: Water weight gain of the control and modified membranes with selected DA:PEI concentrations (mg.mL^{-1}) at different deposition times (6, 12 and 24 h). 100

Figure 3.8: Weight gain of the dry membranes after modification with 0.5:1 mg.mL^{-1} in different deposition times (6, 12 and 24 h). 100

Figure 3.9: Water weight gain of the control and modified membranes with 0.5:1 mg.mL^{-1} and different deposition times (6, 12 and 24 h) carried out with two treatments. In the first treatment, the membranes were soaked in water overnight (water). In the second, the membranes were soaked in ethanol for 2 h and then in water overnight (ethanol/water). 101

Figure 3.10: AFM images for the (a) dry and (b) wet control membranes and (c) dry and (d) wet DA:PEI modified membranes with 0.5:1 mg/mL^{-1} and 24 h of deposition time. 102

Figure 3.11: Dynamic water contact angle of the selected membranes modified with different DA:PEI concentrations (mg.mL^{-1}) and deposition times (6, 12 and 24 h). 103

Figure 3.12: pH resistance of modified membranes. (a) Images of modified membranes with DA (0.5 mg.mL^{-1}), (b) with DA:PEI (0.5:1 mg.mL^{-1}) and (c) water contact angle of the modified membranes after 24 h immersed into different solutions. The membrane modifications were carried out with 24 h of deposition time.. 105

Figure 3.13: Permeation performance of 0.1 µm PVDF control and membranes modified with 0.5:1 mg.mL^{-1} of DA:PEI at different deposition times (6, 12 and 24 h) in the separation of canola oil emulsions. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures. 107

Figure 3.14: Permeation performance of control and modified 0.1 µm PVDF membranes with different concentrations of DA:PEI and 24 h of deposition time, in the separation of canola oil emulsions. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures. 109

Figure 3.15: Permeation performance of the control and modified membranes with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time applied to three subsequent permeation cycles of canola oil

emulsions. (a) Initial water permeability and membrane retention, (b) three permeations of canola oil emulsion interleaved by physical cleanings and (c) water permeability after a final complete physical (PC) and chemical (CC) cleaning procedures. 111

Figure 3.16: Membrane zeta potential of the control and modified membrane with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time. 113

Figure 3.17: Dynamic underwater oil contact angle of the control and modified 0.1 µm PVDF membrane with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time. 114

Figure 3.18: Dynamic oil contact angle of the control and modified 0.1 µm PVDF membrane with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time. 115

Figure 3.19: Oil emulsion flux recovery of the control and modified 0.1 µm PVDF membranes with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time. 116

Figure 3.20: Membrane retention of the control and modified 0.2 and 0.45 µm PVDF membranes. The modifications were carried out with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time. 117

Figure 3.21: SEM images of the membrane surface for (a) control and (b) modified 0.2-µm PVDF membranes and (c) control and (d) modified 0.45-µm PVDF membranes. 118

Figure 4.1: Surface SEM images of the control, MI-T and MI-F membranes surface at different magnifications (5,000x and 10,000x). (a and d) clean control membranes, (b and e) clean MI-T membranes and (c and f) clean MI-F membranes. (g, h and i) fouled control, MF-T and MF-F membranes, respectively. 132

Figure 4.2: ATR-FTIR of the (a) control, (b) MI-T and (c) MI-F membranes. 133

Figure 4.3: Zeta potential of surfaces of the control, MI-T and MI-F membranes. 134

Figure 4.4: Water weight gain of the control, MI-T and MI-F membranes. 135

Figure 4.5: Dynamic water contact angle of the control, MI-T and MI-F membranes. 135

Figure 4.6: Photographic images of a water droplet (20 µL) deposited on the (a) control, (b) MI-T and (c) MI-F membranes surfaces. The images were taken 1 min after the droplet deposition. 136

Figure 4.7: 2D AFM images of the (a) control, (b) MI-T and (c) MI-F dry membranes; (d) control, (e) MI-T and (f) MI-F wet membranes, and 3D AFM images of the (g) MI-T and (h) MI-F dry membranes, respectively. 138

Figure 4.8: pH resistance of modified membranes. (a) MI-T membranes, (b) MI-F membranes and (c) water contact angle of MI-T and MI-F membranes after 24 h immersed into the different solutions. 139

Figure 4.9: Process performance of control, MI-T and MI-F membranes applied in the separation of canola oil emulsions. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures. 140

Figure 4.10: Dynamic underwater oil contact angle of the control, MI-T and MI-F membranes... 142

Figure 5.1: Schematic diagram of the cross-flow permeation system. 153
Figure 5.2: Schematic diagram of the magnetic induction of the oil emulsion in the (a) Halbach array and in the (b) permanent magnets. 155
Figure 5.3: Permeation performance of control and modified membranes in the separation of oil emulsions in a cross-flow filtration system. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures. 157
Figure 5.4: Permeation performance of control and modified membranes in the separation of oil emulsions in a cross-flow filtration system using the turbulence promoter. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures. 159
Figure 5.5: Water permeability recovery of the control and modified membranes in a cross-flow permeation system with and without the turbulence promoter. 162
Figure 5.6: Permeation performance of control and modified membranes in the separation of oil emulsions and oil emulsions magnetically induced (OEMI). (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures. 164

LISTA DE TABELAS

Tabela 2.1: Fontes de água residuais oleosas. 44
Tabela 2.2: Características dos PSM que utilizam a diferença de pressão como força motriz. 46
Tabela 2.3: Trabalhos anteriores com emprego do campo magnético em diferentes processos.. 52
Tabela 2.4: Trabalhos anteriores que utilizaram o método *mussel-inspired* como estratégia para a modificação da membrana.......... 67
Table 3.1: Different DA and PEI concentrations used in PVDF membrane modification...89
Table 3.2: Elemental composition and atomic ratio of the control membrane, DA modified membrane (0.25 mg.mL^{-1}) and DA:PEI modified membranes (0.25:0.5 mg.mL^{-1}) analyzed by XPS. The membrane modifications were carried out with 24 h of deposition time.. 98
Table 3.3: Water contact angle of membranes modified with different DA:PEI concentrations (mg.mL^{-1}) and deposition times (6, 12 and 24 h)... 103
Table 5.1: Oil droplet sizes of emulsions magnetically induced in flux densities 0.7 and 1.4 T, in different times. 163
Table 5.2: Zeta potentials of emulsions magnetically induced in flux densities 0.7 and 1.4 T, in different times. 163

SUMÁRIO

1 INTRODUÇÃO...33

1.1 Objetivos...35

1.1.1 Objetivo geral...35

1.1.2 Objetivos específicos..36

1.2 Referências..37

2 FUNDAMENTOS TEÓRICOS E REVISÃO BIBLIOGRÁFICA...43

2.1 Água residual oleosa a partir de processos industriais...43

2.2 Aplicação do processo de separação com membranas na recuperação de águas oleosas..45

2.3 Fenômenos que limitam o processo de separação com membranas..48

2.4 Estratégias para a redução da incrustação......................49

2.4.1 Campos magnéticos aplicados em processos industriais..50

2.4.2 Modificação da superfície de membranas.............58

2.5 Referências..69

3 MODIFICAÇÃO DE MEMBRANAS DE MICROFILTRAÇÃO COMERCIAIS HIDROFÓBICAS EM MEMBRANAS SUPERHIDROFÍLICAS ATRAVÉS DO MÉTODO MUSSEL-INSPIRED UTILIZANDO DOPAMINA E POLIETILENOIMINA..85

3.1 Introduction..86

3.2 Material and methods……………………………………..88

3.2.1 Material……………………………………………..88

3.2.2 Methods……………………………………………89

3.3 Results and discussion………………………………...92

3.3.1 Membrane characterization……………………...92

3.3.2 Wettability, hydrophilicity, and pH resistance of the membranes…………………………………………...98

3.3.3 Membrane performance…………………………...106

3.4 Conclusion…………………………………………...118

3.5 References……………………………………………119

4 DIFERENTES ABORDAGENS DO MÉTODO MUSSEL-INSPIRED PARA ACELERAR O PROCESSO DE MODIFICAÇÃO DE MEMBRANAS HIDROFÓBICAS DE MICROFILTRAÇÃO EM MEMBRANAS SUPERHIDROFÍLICAS..125

4.1 Introduction…………………………………………..126

4.2 Material and methods………………………………...128

4.2.1 Material……………………………………………128

4.2.2 Methods…………………………………………...129

4.3 Results and discussion………………………………131

4.3.1 Membrane characterization……………………131

4.3.2 Membrane wettability and pH resistance………134

4.3.3 Separation process performance of the control, MI-T and MI-F membranes...139

4.4 Conclusion…………………………………………...143

4.5 References……………………………………………143

5 EFEITO DO PRÉ-TRATAMENTO DA EMULSÃO OLEOSA COM CAMPO MAGNÉTICO NO PROCESSO DE SEPARAÇÃO COM MEMBRANAS SUPERHIDROFILICAS E AVALAIAÇÃO DO DESEMPENHO DA PERMEAÇÃO EM UM SISTEMA DE FILTRAÇÃO TANGENCIAL..................149

5.1 Introduction…………………………………………..151

5.2 Materials and methods………………………………152

5.2.1 Material……………………………………………152

5.2.2 Methods…………………………………………...153

5.3 Results and discussion………………………………156

5.3.1 Performance of the modified membrane by the Mussel-inspired method in a cross-flow filtration system...156

5.3.2 Performance of the control and modified membrane in the permeation of the oil emulsion pretreated with different magnetic fields……………………………………………163

5.4 Conclusion……………………………………………...165

5.5 Reference………………………………………………166

6 CONCLUSÕES………………………………………..171

6.1 Sugestões para trabalhos futuros.................................172

DIAGRAMA CONCEITUAL DO TRABALHO

ESTRATÉGIAS ANTI-INCRUSTAÇÃO NA MICROFILTRAÇÃO DE EMULSÕES OLEOSAS BASEADAS NA MODIFICAÇÃO DA SUPERFÍCIE DA MEMBRANA E NO USO DE CAMPO MAGNÉTICO

- **Por que?**

– Necessidade de processos cada vez mais limpos;
– Necessidade de processos de separação com membranas mais eficientes no tratamento de efluentes oleosos;
– Aumento da vida útil da membrana e redução de produtos químicos utilizados nos procedimentos de limpeza.

- **Quem já fez?**

– Atualmente, a modificação da superfície de membranas pelo método inspirado no mexilhão, *mussel-inspired* (MI), vem sendo empregada em diversos trabalhos como observado na Tabela 2.4;
– Não há na literatura trabalhos com a aplicação do campo magnético em processos de separação com membranas como estratégia anti-incrustação causada por emulsões oleosas.

- **Hipóteses**

– É possível modificar a superfície de membranas hidrofóbicas em membranas superhidrofílicas pelo método MI; e, quando aplicadas na recuperação de emulsões oleosas obter uma eficiência igual ou superior do que membranas modificadas por outros métodos?
– Utilizando variações do método MI, consegue-se acelerar o processo de modificação da superfície da membrana?
– Com a utilização do campo magnético, seria possível aumentar o desempenho do processo de separação com membranas aplicado na recuperação de emulsões oleosas?
– Com a união das duas técnicas (modificação da superfície de membrana e a utilização do campo magnético) pode-se obter aumento no desempenho do processo de separação

com membranas aplicado na recuperação de emulsões oleosas?

- **Métodos experimentais**
  - Modificação a superfície da membrana pelo método MI;
  - Aplicação de variações do método MI na modificação da superfície da membrana;
  - Indução magnética da emulsão oleosa com a utilização de ímãs permanentes;
  - Caracterização da emulsão oleosa antes e após a indução magnética;
  - Permeação da emulsão oleosa induzida magneticamente ou não através das membranas com e sem modificação, em sistemas de filtração convencional e tangencial;
  - Caracterização das membranas por diferentes análises antes e após a permeação da emulsão.

- **Respostas**
  - Avaliação das membranas em função das caracterizações morfológicas e estruturais e de propriedades como hidrofilicidade e resistência ao pH;
  - Avaliação do desempenho do processo de separação com membranas aplicado na recuperação de emulsões oleosas, para os ensaios realizados com as membranas modificadas e controle, com ou sem a aplicação do campo magnético;
  - Determinação das melhores condições de modificação que minimizam a incrustação
  - Elucidação dos mecanismos que atuam na melhoria do processo de separação com membranas aplicado na recuperação de emulsões oleosas pelas técnicas propostas;

ESTRUTURA DO DOCUMENTO

Este documento está estruturado na forma de capítulos. O Capítulo 1 apresenta a introdução, o Capítulo 2 apresenta a revisão bibliográfica sobre os assuntos abordados, os Capítulos 3 a 5 apresentam a metodologia e os resultados obtidos com a realização de cada etapa do trabalho e o Capítulo 6 apresenta as conclusões gerais do trabalho.

1 INTRODUÇÃO

O tratamento de efluentes é uma importante etapa na indústria de alimentos devido à grande quantidade de água utilizada nos processos. A escassez dos recursos hídricos e as rigorosas regulamentações ambientais têm motivado a busca de processos cada vez mais eficazes para o tratamento e reutilização da água.

Dentre os tipos de águas residuais geradas pelas indústrias, os efluentes oleosos são um inevitável desafio. Processos convencionais de tratamento físicos e químicos como adsorção (carvão ativado, argila, copolímeros e resinas), filtro de areia, ciclones, evaporadores, oxidação fotocatalítica, por ozônio, eletroquímica e Fenton, possuem algumas desvantagens como: custo; a utilização de componentes tóxicos gerando poluentes secundários: e, a necessidade de um grande espaço físico. Observando este cenário, os processos de separação com membranas (PSM) surgem como uma tecnologia atraente para o tratamento de efluentes oleosos (PADAKI et al., 2015).

Os PSM são reconhecidos por suas vantagens como alta seletividade, facilidade de escalonamento, flexibilidade de operação e baixa demanda energética quando comparada a processos envolvendo troca térmica. Por isso, é possível utilizá-los em várias aplicações industriais, principalmente no reúso de águas e no tratamento de efluentes (BAKER, 2004; CHERYAN; RAJAGOPALAN, 1998; MULDER, 2000).

Embora muitos PSM estejam bem desenvolvidos, a recuperação de águas oleosas por esta tecnologia ainda é um desafio para a indústria devido a desvantagens como a polarização por concentração e a incrustação (*fouling*) (CHERYAN; RAJAGOPALAN, 1998; PADAKI et al., 2015). Ambos os fenômenos causam a diminuição do fluxo de permeado podendo atingir tal ponto que tornaria o processo inviável. Assim, estratégias de minimização e controle das incrustações são de grande interesse científico e tecnológico para a área de processos envolvendo membranas.

Alguns métodos químicos e físicos para a redução desses efeitos não desejáveis ao processo podem ser aplicados. A utilização de produtos químicos nos PSM, apesar de ser um método eficiente de limpeza, pode causar danos tanto nas membranas quanto no produto final. Assim, para a escolha correta do agente químico, sua concentração e sequência de limpeza, é necessário um estudo aprofundado das características da membrana, do tipo e da concentração do incrustante que se deseja remover.

Outra forma de abordagem química para a minimização de incrustações envolve a modificação da superfície das membranas (MSM), na qual geralmente, a ideia é obter uma membrana com uma superfície de baixa interação com os solutos (HEGDE et al., 2011; PADAKI et al., 2015). As MSM podem ser realizadas por meio do revestimento da superfície da membrana com um polímero de características especiais (LI; XU; PINNAU, 2007), métodos de enxertia (*grafting*) (MASUELLI et al., 2012; MOGHIMIFAR; RAISI; AROUJALIAN, 2014) e de tratamentos ácido/básico (PADAKI et al., 2011). Um dos métodos de MSM mais investigados atualmente é o método inspirado na capacidade adesiva dos mexilhões em diferentes superfícies, chamado em inglês de "*mussel-inspired*" (MI), o qual envolve a polimerização da dopamina sobre a superfície da membrana. Este polímero é capaz de ligar-se a quase todas as superfícies, e a modificação por este método apresenta, além de alta estabilidade, simplicidade, versatilidade e facilidade no controle do processo, além de menores danos à membrana quando comparados a métodos como modificação por plasma, radiação ultravioleta, feixe de elétrons, etc (DREYER et al., 2013; MILLER; PAUL; FREEMAN, 2014; SI; GUO, 2015; WANG et al., 2015a, 2015b; YANG et al., 2014a, 2014b, 2015).

Técnicas físicas para o controle de incrustações também são atraentes, uma vez que são abordagens limpas e não intrusivas. Dentre as estratégias físicas, destacam-se a utilização de dispositivos geradores de turbulência, ultrassom, centrífugas e a utilização de campos elétricos e magnéticos.

Os efeitos da aplicação do campo magnético (CM) foram largamente estudados na água (CAI et al., 2009; CHO; LEE, 2005; COLIC; MORSE, 1999; PANG; DENG, 2008; SZCZEŚ et al., 2011; TOLEDO; RAMALHO; MAGRIOTIS, 2008), em soluções eletrolíticas (HOŁYSZ; CHIBOWSKI; SZCZEŚ, 2003; HOLYSZ; CHIBOWSKI; CHIBOWSKI, 2002; HOLYSZ; SZCZES; CHIBOWSKI, 2007) e na nucleação, crescimento e deposição dos sais (ALIMI et al., 2007; CHANG; TAI, 2010; COEY; CASS, 2000; FATHI et al., 2006; KNEY; PARSONS, 2006; KNEZ; POHAR, 2005; KOBE et al., 2002, 2003; MADSEN, 1995; MWABA; GU;

GOLRIZ, 2007; TAI; CHANG; YEH, 2011; TAI; WU; CHANG, 2008; TAI et al., 2008, 2014; WANG et al., 2015a).

Nos PSM, a aplicação do CM como método de redução de incrustação, apesar de ter sido discutida por alguns autores, ainda é um desafio. Nesse sentido, já foram realizados estudos para avaliar o controle de formação de incrustações inorgânicas em membranas de osmose inversa no tratamento de águas com altas concentrações de sais (SCHLÜTER, 2014); para avaliar o efeito do tratamento magnético da água na redução de depósitos de carbonatos durante a destilação por membranas (GRYTA, 2011); e, para avaliar a influência do CM na precipitação e na forma de crescimento de sais com a finalidade de aprimorar o desempenho de membranas de nanofiltração e de osmose inversa (BAKER; JUDD; PARSONS, 1997; LI et al., 2007; LONG et al., 2005; OHATA; TOMITA; IKADA, 2004). Observando este cenário, recentes estudos do grupo de pesquisa do Laboratório de Processos de Separação com Membranas – LABSEM vêm sendo desenvolvidos com o intuito de elucidar os efeitos do CM na separação de soluções proteicas e de polissacarídeos e sua influência na estabilidade de emulsões produzidas pela técnica com membranas (CARLESSO et al., 2016; VARDANEGA et al., 2013; ZANATTA et al., 2017; ZIN et al., 2016).

Neste contexto, o presente estudo, realizado em colaboração com a RICE University, Houston, Estados Unidos, investigou estratégias anti-incrustações em membranas, pela abordagem conjunta e separada de técnicas física e química (aplicação do CM e a MSM - através do método MI), no tratamento de emulsões oleosas, visando uma melhoria no desempenho da microfiltração de emulsões oleosas.

1.1 Objetivos

1.1.1 Objetivo geral

O objetivo geral deste estudo é aprimorar a microfiltração de emulsões oleosas pela modificação da superfície da membrana e no uso de campo magnético.

1.1.2 Objetivos específicos

Os objetivos específicos a seguir estão apresentados de acordo com cada capítulo da tese.

Capítulo 3

- Avaliar o efeito da utilização de diferentes concentrações de dopamina e polietilenoimina assim como diferentes tempos de deposição no processo de modificação das membranas;
- Avaliar o desempenho das membranas modificadas aplicadas na permeação de emulsões oleosas;
- Caracterizar, utilizando diferentes técnicas, as membranas modificadas antes e após a permeação da emulsão oleosa.

Capítulo 4

- Acelerar o processo de modificação de membranas hidrofóbicas em membranas superhidrofílicas utilizando variações do método *mussel-inspired*;
- Avaliar o desempenho das membranas modificadas pelas variações do método *mussel-inspired* aplicadas na permeação de emulsões oleosas;
- Caracterizar as membranas modificadas pelas variações do método *mussel-inspired* utilizando diferentes técnicas antes e após a permeação da emulsão oleosa.

Capítulo 5

- Avaliar o desempenho das membranas modificadas aplicadas na permeação de emulsões oleosas em um sistema de filtração tangencial, contrastando com os resultados obtidos em filtração convencional (ou frontal);
- Avaliar o efeito da indução magnética da emulsão oleosa sobre o desempenho da microfiltração.

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2 FUNDAMENTOS TEÓRICOS E REVISÃO BIBLIOGRÁFICA

Esse capítulo apresenta os fundamentos teóricos e uma revisão da literatura com ênfase nos processos de separação com membranas, no efeito da aplicação do campo magnético em diferentes processos e nas técnicas de modificação da superfície de membranas.

2.1 Água residual oleosa a partir de processos industriais

O rápido crescimento industrial, como de indústrias de óleo e gás, petroquímica, farmacêutica, metalúrgica e alimentícia tem levado a um grande aumento na produção de águas residuais (PADAKI et al., 2015). O efluente oleoso é um termo gerado para descrever todos os resíduos industriais que apresentam quantidades variáveis de óleos, graxas e lubrificantes além de uma variedade de outros materiais como sais, metais, detergentes, e inúmeros contaminantes que podem afetar o ambiente aquático e a agricultura. Assim, é de fundamental importância a caracterização do efluente, para que o tratamento mais adequado seja aplicado.

Óleos e graxas geralmente apresentam-se nos efluentes oleosos em duas categorias distintas (CHERYAN, 1998; CHERYAN; RAJAGOPALAN, 1998):

- Óleo livre em solução: apresenta uma fase visivelmente distinta da fase aquosa, isto é, não se mistura com a água, e pela sua densidade aparece flutuando na superfície da água como gotículas ou em suspensão;
- Emulsões óleo/água: apresenta apenas uma fase a olho nu, sendo o óleo, intimamente misturado à água por meio de inúmeras micelas. Este grupo pode ser dividido em emulsões estáveis e instáveis.

A Tabela 2.1 apresenta as diferentes fontes de efluentes oleosos.

Tabela 2.1: Fontes de água residuais oleosas.

Indústria	**Origem do resíduo oleoso**	**Característica**
Acabamentos de metais e lavanderia	Produtos de limpeza alcalinos e ácidos	Altamente emulsionado devido a surfactantes; Difícil de tratar
Fabricação de metais	Fluidos refrigerantes de máquinas	Normalmente emulsionado; Difícil de tratar
Gorduras animais e vegetais, de refino e de acabamento	Produção de óleos e detergentes, processamento de pescado, gelatina, couro, lã	Óleo livre e emulsionado; Dificuldade do tratamento varia
Petróleo bruto	Refino e perfuração de petróleo	Óleo livre e emulsionado; Dificuldade do tratamento varia
Todas	Lavagens de piso industrial	Mistura de vários tipos de óleos; Podem estar presentes na forma livre e emulsionada, podendo estar estabilizadas por diferentes compostos; Dificuldade do tratamento varia

Fonte: adaptado de CHERYAN; RAJAGOPALAN (1998) e PADAKI et al., (2015).

Como visto, são inúmeros os tipos de efluentes oleosos gerados pelos processos industriais, cada indústria produzindo um resíduo com diferentes características e particularidades.

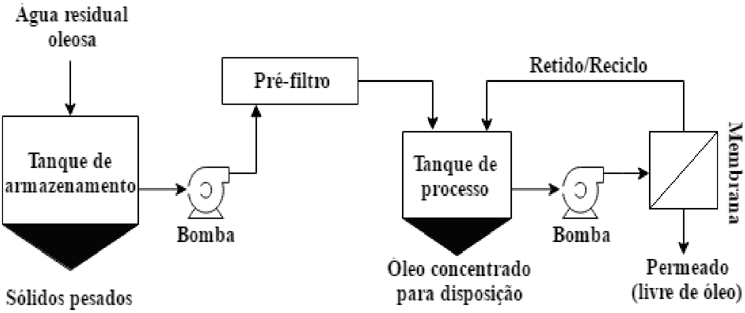
Dentro da indústria de alimentos, os principais produtores de águas residuais oleosas são os frigoríficos, laticínios, sorveterias, padarias e indústrias de processamento de frutos do mar, de cozidos, de óleos comestíveis e ração animal (PADAKI et al., 2015) CHERYAN, 1998). Estes resíduos possuem alta demanda química e biológica de oxigênio, e são convencionalmente tratados por coagulação química seguidos pela flotação de ar dissolvido para a retirada dos sólidos suspensos e de óleos e graxas (CHERYAN; RAJAGOPALAN, 1998; CUI; MURALIDHARA, 2010).

No item 2.2 será abordado o uso dos processos de separação com membranas (PSM) como alternativa aos processos comumente utilizados.

2.2 Aplicação do processo de separação com membranas na recuperação de águas oleosas

O uso de membranas para tratar emulsões oleosas tornou-se uma tecnologia promissora, não somente devido à sua alta eficiência na remoção de óleo, relativa facilidade operacional e a necessidade de atender legislações específicas, mas também quando o valor dos componentes recuperados é alto, por exemplo, na reciclagem de produtos de limpeza e líquidos refrigerantes (CHERYAN; RAJAGOPALAN, 1998; PADAKI et al., 2015). A Figura 2.1 ilustra um típico sistema de separação com membranas utilizado no tratamento de águas residuais oleosas.

Figura 2.1: Típico sistema de separação com membranas utilizado no tratamento de águas residuais oleosas.



Fonte: adaptado de CHERYAN; RAJAGOPALAN (1998) e WESCHENFELDER; BORGES; CAMPOS (2015).

Os tipos PSM aplicados no tratamento de águas residuais oleosas são a MF, UF, NF e OI, todos apresentam como característica a utilização da diferença de pressão como força motriz. Entre eles, a UF é um dos tratamentos mais efetivos na recuperação de resíduos oleosos. Processos como o de NF e OI são comumente utilizado para dar um polimento final ao permeado dos processos de MF e UF (CHERYAN; RAJAGOPALAN, 1998; PADAKI et al., 2015). A Tabela 2.2 apresenta algumas características desses processos.

Tabela 2.2: Características dos PSM que utilizam a diferença de pressão como força motriz.

Processo	**Dimensão dos poros**	**Força motriz (ΔP)**
Microfiltração (MF)	0,1 a 1,0 µm	0,5 - 2 bar
Ultrafiltração (UF)	0,001 a 0,1 µm	1 - 7 bar
Nanofiltração (NF)	5 a 10 Å	5 - 25 bar
Osmose inversa (OI)	Membrana densa	15 - 80 bar

Fonte: adaptada de HABERT; BORGES; NOBREGA (2006)

Como citado no item 2.1, dentre as principais categorias de resíduos oleosos (óleo livre em solução e emulsões óleo/água instáveis e estáveis) os PSM são mais utilizados para recuperação de óleos de emulsões estáveis (MUPPALLA; JEWRAJKA; REDDY, 2015; ZHU et al., 2015; RAJASEKHAR et al., 2015). Os PSM apresentam certas vantagens no tratamento de óleo comparado aos processos tradicionais. Dentre estas vantagens estão (CHERYAN; RAJAGOPALAN, 1998; PADAKI et al., 2015):

- Aplicável em uma ampla gama de indústrias;
- A qualidade da água tratada é mais uniforme devido à membrana ser uma barreira seletiva de componentes;
- Não é necessário adicionar agentes químicos;
- Podem ser usadas com o intuito de selecionar determinados componentes da emulsão;
- Concentrações entre 40-70 % de óleo e sólidos podem ser obtidas a partir de soluções iniciais com concentração de 0,1 ± 1 %;
- Necessidade de pouco espaço para a implantação;
- Custo com energia é menor comparado aos tratamentos térmicos;
- A planta pode ser totalmente automatizada.

Por outro lado, os PSM possuem algumas desvantagens no tratamento de soluções oleosas, como (CHERYAN; RAJAGOPALAN, 1998; PADAKI et al., 2015):

- Necessidade de paradas no processo para a limpeza da membrana (o que pode ser evitado inserindo módulos ao sistema e programando a operação);
- Reposição da membrana devido à degradação durante o uso, o que aumenta consideravelmente os custos de operação.

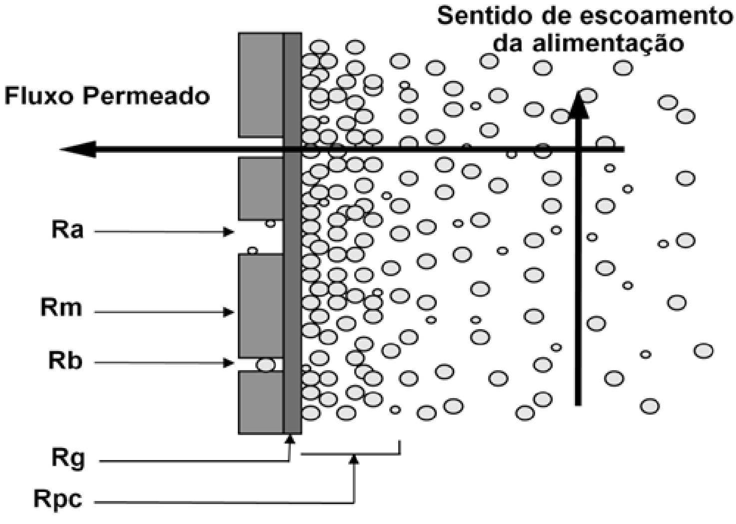
Como resultado desta desvantagem, os PSM de águas residuais oleosas são, às vezes, combinados a outros sistemas de tratamento, com isso formando um processo híbrido o qual eleva a vida útil das membranas, devido em parte, a diminuição na frequência de limpeza (SCHOLZ; FUCHS, 2000; CUI; MURALIDHARA, 2010).

2.3 Fenômenos que limitam o processo de separação com membranas

A diminuição do fluxo de permeado com o passar do tempo de filtração é um comportamento característico nos PSM, tornando-se um dos principais limitantes de seu uso em processos industriais.

O declínio do fluxo de permeado pode ser causado por diversos fatores que conduzem à formação de resistências adicionais ao sistema. Dentro destes fatores destacam-se a polarização por concentração, adsorção, formação de uma camada gel e ligações dos solutos nos poros das membranas (MULDER, 2000). A Figura 2.2 apresenta as principais resistências ao transporte de massa através da membrana.

Figura 2.2: Representação das resistências ao transporte de massa nos PSM cuja força motriz é a diferença de pressão.



Ra: resistência devido à adsorção; Rm: resistência da membrana; Rb: resistência devido ao bloqueio físico de poros; Rg: resistência devido à formação de uma camada gel; Rpc: resistência devido ao fenômeno de polarização de concentração. Fonte: adaptado de HABERT; BORGES; NOBREGA (2006)

O primeiro fenômeno limitante do processo é a camada polarizada, a qual, ocorre após o acúmulo dos componentes com menor capacidade de permeação na interface membrana/solução, formando assim, em virtude da difusão, um contrafluxo em direção ao seio da alimentação. Este fenômeno pode ser amenizado utilizando sistemas de filtração tangencial, uma vez que o escoamento tangencial da solução paralelamente à superfície da membrana atenua a acumulação dos solutos na superfície desta, caracterizando-se então como uma deposição reversível (BAKER, 2004; MULDER, 2000; USHIKUBO, 2006).

Os outros fenômenos citados acima, adsorção, formação de uma camada gel e ligações dos solutos nos poros das membranas são incrustações geralmente irreversíveis, conhecidas como *fouling*, que é definido como uma deposição de partículas retidas, coloides, emulsões, suspensões, macromoléculas, sais, etc. dentro ou fora da membrana, sendo um fenômeno complexo de descrever teoricamente (MULDER, 2000).

Em geral, além da intensidade da interação do soluto com a membrana, a incrustação nos PSM dependerá de parâmetros físicos e químicos como concentração, temperatura, pH, força iônica e interações específicas entre as moléculas da solução como pontes de hidrogênio e dipolo-dipolo. As principais causas desse fenômeno são a deposição de sólidos sobre a superfície da membrana, a precipitação dos compostos solúveis presentes na solução de alimentação e o *biofouling* que é o acúmulo de material orgânico em sua superfície (CUI; MURALIDHARA, 2010; HABERT; BORGES; NOBREGA, 2006; MULDER, 2000).

2.4 Estratégias para a redução da incrustação

Como visto anteriormente, a incrustação no PSM é um fator relevante durante a filtração. Assim, métodos físicos e químicos de redução destas incrustações são fundamentais para o aprimoramento desta tecnologia.

O controle dos parâmetros operacionais como pressão, velocidade de escoamento, tipo de módulo utilizado, pré-tratamento térmico, ajuste do pH, adição de agentes complexantes (EDTA etc.) e a pré-filtração da solução com membranas de menor retenção são estratégias frequentemente utilizadas nos PSM, pois proporcionam ao processo uma considerável economia de tempo e de produtos químicos durante o procedimento de limpeza (BAKER, 2004; CUI; MURALIDHARA, 2010; HARBERT; BORGES; NOBREGA, 2006; MULDER, 2000).

Uma vez que os procedimentos de limpeza dependem da resistência física e química da membrana, a frequência e o melhor procedimento são estimados de acordo com cada processo, analisando o tipo de incrustação, a configuração do módulo e a membrana utilizada (MULDER, 2000).

Métodos físicos como retrolavagem, promotores de turbulência, ultrassom, aplicação de campo magnético e a limpeza mecânica chamam a atenção devido à possibilidade da redução do uso de produtos químicos durante o processo de limpeza química (CUI; MURALIDHARA, 2010; MULDER, 2000; VEDAVYASAN, 2001).

Apesar dos vários métodos de redução de incrustações citados acima, a limpeza química é necessária, devido à inevitável redução de fluxo provocada pela incrustação. Esta pode envolver uma gama de agentes químicos separadamente ou em conjunto, dependendo da membrana e do processo que está sendo realizado. Alguns exemplos são ácidos, bases, detergentes, enzimas, agentes complexantes, desinfetantes e vapor de água (MULDER, 2000).

Outros métodos para o controle de incrustações que podem ser utilizados envolvem a modificação das propriedades da membrana, principalmente em membranas porosas, nas quais a incrustação é mais severa comparado às membranas densas. Estas modificações podem ser na estrutura dos poros, nas propriedades hidrofílicas, nas cargas superficiais e através do recobrimento da superfície da membrana com polímeros que proporcionem alguma característica anti-incrustação como propriedades catalíticas ou de capacidade de resposta (ASATEKIN et al., 2007; KANG et al., 2007; MULDER, 2000; TAMPUBOLON et al., 2013; YU et al., 2010).

Nos itens 2.4.1 e 2.4.2 será dada atenção especial à aplicação do campo magnético (CM) aplicado em PSM e a modificação da superfície da membrana (MSM), ambos assuntos foco desta tese de doutorado.

2.4.1 Campos magnéticos aplicados em processos industriais

Por apresentar vantagens como baixo custo, operação simples, baixo impacto ambiental e nenhum ou baixo consumo de energia (no caso de campos magnéticos permanentes e gerados por corrente elétrica, respectivamente), os processos envolvendo campos magnéticos (CM) são utilizados em uma gama de aplicações industriais (GABRIELLI et al., 2001; NEVEDROV; USHAKOV, 2003; VEDAVYASAN, 2001; WANG et al., 1997).

Dentre as aplicações do CM em processos industriais tem-se a purificação de água e tratamento de águas residuais, através de sua aplicação em conjunta com técnicas como adsorção, processos catalíticos e processos de separação com membranas (AMBASHTA; SILLANPÄÄ, 2010; ZAIDI et al., 2014); e, em processos como a produção de aço e a dessulfurização do carvão, nos quais o CM é usado como um filtro para remover impurezas magnéticas (YAVUZ et al., 2009). Na área biotecnológica destaca-se a utilização do CM na separação celular, na qual as células ligadas aos adsorventes magnéticos são atraídas pelo ímã, separando-se das células não adsorvidas. Processo similar ocorre na purificação de proteínas e peptídeos por meio da sua imobilização em adsorventes magnéticos. Na administração de fármacos é possível, por meio de nanopartículas magnéticas, direcionar o fármaco diretamente ao local desejado. Já para a biocatálise, utilizam-se esferas magnéticas para imobilizar biocatalisadores como a peroxidase, com isso permitindo a dispersão homogênea dos materiais e sua recuperação após o uso (BAŞAR et al., 2007; NITA; CHIRIAC, 2010; SAFARIK; SAFARIKOVA, 2004; YAVUZ et al., 2009).

Também foi investigada a relevância do efeito do CM em diferentes soluções, sua influência na nucleação e crescimento de sais, na deposição de compostos (*scaling*) e durante o PSM. A Tabela 2.3 apresenta estudos anteriores desenvolvidos com a aplicação do CM em diferentes processos.

Tabela 2.3: Trabalhos anteriores com emprego do campo magnético em diferentes processos.

Linha de pesquisa	Autores
Efeito do campo magnético na água e em soluções salinas	(AMBASHTA; SILLANPÄÄ, 2010; AMIRI, 2006; CAI et al., 2009; CHO; LEE, 2005; COLIC; MORSE, 1999; HOŁYSZ; CHIBOWSKI; SZCZEŚ, 2003; HOLYSZ; CHIBOWSKI; CHIBOWSKI, 2002; HOLYSZ; SZCZES; CHIBOWSKI, 2007; KRONENBERG, 1985; PANG; DENG, 2008; SZCZEŚ et al., 2011; TOLEDO; RAMALHO; MAGRIOTIS, 2008)
Influência do campo magnético na nucleação e crescimento de sais em processos de cristalização	(ALIMI et al., 2007; BOTELLO-ZUBIATE, 2004; CHANG; TAI, 2010; CHIBOWSKI; HOŁYSZ; SZCZEŚ, 2003; COEY; CASS, 2000; FATHI et al., 2006; KNEY; PARSONS, 2006; KNEZ; POHAR, 2005; KOBE et al., 2001, 2002, 2003; KOZIC et al., 2010; MADSEN, 1995, 2007; MWABA; GU; GOLRIZ, 2007; TAI; CHANG; YEH, 2011; TAI; WU; CHANG, 2008; TAI et al., 2014; WANG et al., 1997)

Influência do campo magnético na deposição de sais inorgânicos ($CaCO_3$ e sais da água dura) (*scaling*) em diferentes superfícies (PVC, PTFE, Tygon®, cobre, aço inoxidável, alumínio e vidro)	(ALIMI et al., 2009; BUSCH; BUSCH, 1997; CHIBOWSKI; HOŁYSZ; SZCZEŚ, 2003; GILART et al., 2013; KOZIC et al., 2010; KOBE et al., 2001; LIPUS; AČKO; HAMLER, 2011; LIPUS; AČKO; NERAL, 2013; LIPUS; DOBERSEK, 2007; PRISYAZHNIUK, 2009)
Influência da aplicação do campo magnético em processos envolvendo membranas:	
– Tratamento de águas salobras	(BALLESTER; GARRIDO, 2012; LONG et al., 2005; VEDAVYASAN, 2001)
– Soluções salinas	(BAKER; JUDD; PARSONS, 1997; GRYTA, 2011; LI et al., 2007; LONG et al., 2005; OHATA; TOMITA; IKADA, 2004; SCHLÜTER, 2014)
– Solução de carboximetilcelulose (modelo de efluente têxtil)	(CARLESSO et al., 2016)
– Soluções proteicas	(VARDANEGA et al., 2013; ZIN et al., 2016)
– Produção de emulsões óleo/água	(ZANATTA, 2014)

Em relação às referências da Tabela 2.3, os efeitos do CM em água apresentam algumas controvérsias. Segundo a maioria dos autores (CAI et al., 2009; CHO; LEE, 2005; COLIC; MORSE, 1999; PANG; DENG, 2008) a aplicação do CM provoca a diminuição da tensão superficial da água, enquanto outros autores afirmam que esta aumenta (TOLEDO; RAMALHO; MAGRIOTIS, 2008). O mesmo ocorre com a viscosidade e a condutividade, sendo que a maioria afirma que a viscosidade da água aumenta com a aplicação do CM (CAI et al., 2009; TOLEDO; RAMALHO; MAGRIOTIS, 2008), já para a condutividade ocorre uma divisão de opinião entre os autores Szczes et al. (2011) e Pang; Deng (2008), onde um afirma que aumenta e o outro que diminui. Ocorre também o aumento de outras propriedades, como, índice de refração, constante dielétrica e hidrofilicidade (PANG; DENG, 2008).

Em soluções eletrolíticas, ocorre a diminuição da tensão superficial e modificações no potencial zeta, na condutividade e no pH dependendo da natureza dos íons presentes na solução. Por exemplo, para os sais cloreto de cálcio, cloreto de sódio, cloreto de potássio, fosfato trissódico e carbonato de sódio esta modificação é proporcional à espessura da camada de hidratação ao redor dos íons (HOŁYSZ; CHIBOWSKI; SZCZEŚ, 2003; HOLYSZ; CHIBOWSKI; CHIBOWSKI, 2002; HOLYSZ; SZCZES; CHIBOWSKI, 2007).

O CM influencia na maneira como ocorre a nucleação e crescimento dos sais. Madsen (1995) após estudar a influência do CM na precipitação de compostos como carbonato de cálcio e de manganês (II), fosfato de magnésio, cálcio, ferro (II), cobalto (II) e de zinco e oxalato de cálcio e sulfato, observou diferenças somente para os sais carbonatos e fosfatos, os quais possuem íons de metais diamagnéticos. Neste caso, a presença do CM provocou o aumento das taxas de nucleação e crescimento dos cristais devido à rápida transferência de prótons a partir dos carbonatos e fosfatos de hidrogênio para a água.

Inúmeros trabalhos relatam a influência do CM na nucleação e crescimento do carbonato de cálcio. Os principais efeitos do CM nestas soluções é a aceleração e o aumento da quantidade de precipitado (ALIMI et al., 2007; FATHI et al., 2006; KNEY; PARSONS, 2006) WANG et al., 1997) e o aumento da formação cristalina do carbonato de cálcio na forma aragonita, que é menos estável e mais solúvel em água comparados à forma calcita, com isso, diminuindo a ocorrência de deposição (*scaling*) em tubos e trocadores de calor (CHANG; TAI, 2010; COEY; CASS, 2000; KNEZ; POHAR, 2005; KOBE et al., 2001, 2002, 2003; MWABA; GU; GOLRIZ, 2007; TAI; CHANG; YEH, 2011; TAI; WU; CHANG, 2008; TAI et al., 2008, 2014). Um exemplo deste comportamento é descrito por Botello-Zubiate et al. (2004), que relatou a influência do tratamento magnético da água na formação de precipitado do carbonato de cálcio. Os autores observaram que sem a aplicação do CM, a calcita era a forma mais encontrada no precipitado do carbonato de cálcio. Já após o tratamento magnético da solução por aproximadamente 30 horas, a aragonita foi a forma com maior presença no precipitado, passando de 18% em massa de carbonato de cálcio sem o tratamento magnético para 38% após o tratamento.

Em respeito à ação do CM na deposição de compostos, os autores estudaram a deposição de soluções salinas tratadas magneticamente e qual a influência do tipo do material utilizado nas tubulações de circulação da solução. A maioria dos autores relata que o CM reduz a formação de depósitos de sais devido às mudanças que ocorrem no crescimento e nucleação destes compostos, como citado anteriormente (ALIMI et al., 2009; CHIBOWSKI; HOŁYSZ; SZCZEŚ, 2003; GILART et al., 2013; KOBE et al., 2001; LIPUS; AČKO; HAMLER, 2011; LIPUS; AČKO; NERAL, 2013; LIPUS; DOBERSEK, 2007)

Nos PSM, a aplicação do CM como método de redução de incrustação ainda é um desafio. Estudos da aplicação de CM nesta área foram desenvolvidos com o intuito de elucidar questões pouco difundidas sobre o assunto.

Schlüter (2014) avaliou o controle de formação de incrustações inorgânicas em membranas de osmose inversa no tratamento de águas com altas concentrações de sais; Gryta (2011) avaliou o efeito do tratamento magnético da água na redução de depósitos de carbonatos durante a destilação por membranas; e, diversos autores avaliaram a influência do CM na precipitação e na forma de crescimento de sais com a finalidade de aprimorar o desempenho de membranas de nanofiltração e de osmose inversa (BAKER; JUDD; PARSONS, 1997; LI et al., 2007; LONG et al., 2005; OHATA; TOMITA; IKADA, 2004). De maneira geral houve uma melhora na eficiência do processo, seja no aumento no fluxo de permeado, proporcionada pela diminuição da deposição dos precipitados sobre a superfície da membrana (GRYTA, 2011; LI et al., 2007; LONG et al., 2005; OHATA, TOMITA; IKADA, 2004; SCHLÜTER, 2014), ou na retenção de sais (BAKER; JUDD; PARSONS, 1997)

Por sua vez, Vedavyasan (2001) desenvolveu um estudo sobre o potencial uso de CM aplicado em plantas de OI. Com o propósito de diminuir o *biofouling* da água do mar e/ou água salobra, o autor incorporou ao processo dispositivos geradores de turbulência e de CM. Como resultado, os custos de operação e de manutenção da configuração proposta em comparação com processo convencional foi reduzido em 20 % com limpeza e troca de membranas. Houve também redução de 25 % na queda de pressão, o que significa uma economia de energia de 0,6 $kWh.m^{-3}$ por m^3 de água, e o tempo de parada para limpeza das membranas foi reduzido em torno de 30 %, devido à menor incrustação. Para finalizar, o autor assume que devido à economia nos custos citados e o baixo investimento (custo capital da planta com o dispositivo de CM é 13 % maior comparado ao processo convencional) a planta de OI tem uma redução de 8 % no custo total da água (dados de 2001).

Em virtude dos bons resultados apresentados pelos autores citados anteriormente utilizando soluções salinas, o grupo de pesquisa do LABSEM vem aplicando o CM em diferentes processos envolvendo membranas. Dentre os trabalhos desenvolvidos destacam-se a separação de soluções proteicas e de carboidrato e a produção de emulsões óleo/água através da técnica de emulsificação por membranas.

Vardanega et al. (2013), como trabalho pioneiro, avaliou o efeito do campo magnético na permeação da albumina de soro bovino (BSA) através de uma membrana de UF de 60 kDa em um módulo de filtração tangencial. Os testes foram realizados na presença de um par de imãs de intensidade de 0,4 T, colocados paralelamente sobre o módulo da membrana durante a filtração. Também foi realizada uma avaliação preliminar da indução magnética (IM) da solução, que consistia na recirculação da solução através do campo magnético permanente, durante um determinado tempo antes da permeação pela membrana. Os resultados obtidos apresentaram um aumento na recuperação da permeabilidade hidráulica após os procedimentos de limpeza das membranas novas e usadas, tanto na presença do campo magnético quanto nos ensaios de indução magnética da solução.

Zin et al. (2016) e Silva (2015) aprofundaram os estudos sobre a influência do CM em soluções proteicas. Zin et al. (2016) utilizando um CM de intensidade de 0,7 T concentrou soluções de BSA e leite com membranas de UF de poliétersulfona (PES) de 50 kDa, na ausência e presença dos sais cloreto de sódio, em diferentes pH (4,0, 6,5 e 8,0). A presença do CM e o efeito da IM da solução por 2 h mostraram-se eficientes no aumento de fluxo de permeado e na recuperação da permeabilidade hidráulica, chegando a 90 % de aumento no fluxo de permeado e 75 % de aumento na recuperação da permeabilidade hidráulica inicial para as soluções de BSA sem adição de sal em pH 8,0. Por sua vez, Silva (2015) avaliou o efeito de diferentes tempos de indução magnética (IM) (0,5 a 24 h) sobre o desempenho da permeação de soluções de BSA de concentração 2,5 $g.L^{-1}$. Observou-se aumento do fluxo de permeado em relação ao controle e notaram-se diferenças significativas na recuperação da permeabilidade hidráulica entre os ensaios de IM e os ensaios controle. Não foram observadas alterações físico-químicas das propriedades de pH, condutividade, viscosidade e tensão superficial. No entanto, para o potencial zeta da solução houve o aumento da repulsão eletrostática entre as moléculas de proteína. Em resumo, para ambas as pesquisas, a utilização do CM mostrou-se eficaz para o controle de incrustações em membranas de PES quando permeadas por soluções proteicas de BSA e leite.

Carlesso et al. (2015) avaliou a influência de um CM de 0,4 T durante a permeação de soluções compostas de carboximetilcelulose e sulfato de sódio em membranas de UF de polissulfona (PS) de 30 kDa. Os resultados obtidos mostraram que a presença do CM e a IM da solução aumentaram a recuperação da permeabilidade hidráulica somente quando era adicionado sal à solução. Quanto ao aumento do fluxo de permeado da solução, não foi observado mudanças.

Zanatta (2014) avaliou o preparo e a estabilidade de emulsões tipo óleo/água utilizando membranas cerâmicas de tamanho de poro de 0,8 µm com e sem a aplicação do CM. Dados de estabilidade obtidos após 60 dias demonstraram que a emulsão feita sem a presença do CM apresentou instabilidade. Por sua vez, a emulsão obtida com o pré-tratamento magnético (circulação da fase aquosa por 2 h entre dois ímãs permanentes os quais produziram uma densidade de fluxo 0,4 T) permaneceu estável, mantendo o tamanho de gotas e a amplitude de distribuição constante até o último ponto analisado (83 dias).

Como se pode observar, excluindo os estudos realizados pelo grupo de pesquisa do LABSEM, os trabalhos que aplicaram CM em PSM relatados na literatura estudaram apenas processos utilizando soluções salinas. Este fato torna a aplicação do CM em PSM uma linha de pesquisa que ainda tem muito a oferecer.

Assim, a utilização do CM em PSM ainda é um desafio que necessita maiores esforços para se obter respostas e explicações dos mecanismos e dos benefícios que esta aplicação pode trazer.

2.4.2 Modificação da superfície de membranas

Um número considerável de pesquisas com foco em modificação da superfície de membranas (MSM) tem sido desenvolvido a fim de melhorar o desempenho dos PSM. Ganhos no processo como o aumento da propriedades anti-incrustantes, o que aumenta o fluxo de permeado e diminui as paradas para limpeza, têm se tornado um fator chave nesta tecnologia (CHEN; CHIAO; TSENG, 1996; HEGDE et al., 2011; HU et al., 2009; PADAKI et al., 2015; WANICHAPICHART; YU, 2007).

A modificação da superfície de uma membrana compreende a possibilidade da criação de algumas interações adicionais (afinidade, capacidade de resposta ou propriedades catalíticas) em sua superfície, a fim de aumentar o seu desempenho. A MSM difere de outros métodos de modificações com membranas pelo fato de que a barreira natural da membrana permanece inalterada (PADAKI et al., 2015; ULBRICHT, 2006).

Fator importante na MSM é a sinergia entre as propriedades úteis da membrana e o novo polímero funcional (camada da superfície). Estas modificações acontecem principalmente com foco na minimização da incrustação, o qual é proporcionado pela redução da interação entre a membrana e as moléculas da solução de alimentação, pelo aumento da seletividade ou novas funções de separação (ULBRICHT, 2006).

As modificações podem ser físicas e/ou químicas. As físicas são em sua maioria via degradação controlada dos polímeros por meio de radiações de alta energia, aplicação de plasma na membrana e irradiação UV. Radiações de alta energia, por exemplo, feixe de elétrons, apresentam baixa seletividade e geralmente provocam cisões poliméricas no material da membrana (ULBRICHT, 2006). A excitação com plasma possui alta seletividade devido ao plasma ser uma mistura de elementos que tem a capacidade de mudar a biocompatibilidade, adesão e hidrofilicidade dos polímeros. No entanto, modificações em pequenos poros (menores do que 100 nm) são complicadas devido a estas dimensões serem menores do que o caminho livre médio das espécies ativas no plasma (ARNAL et al., 2003; KAI et al., 2005; ULBRICHT; BELFORT, 1996). Por sua vez, a irradiação UV apresenta uma grande vantagem devido ao seu comprimento de onda poder ser ajustado seletivamente para cada reação. Com isso evita-se, ou pelo menos reduz-se a ocorrência de reações paralelas. O uso destas técnicas físicas de MSM comumente se aplica como uma fase inicial de preparação da superfície da membrana para outros tipos de modificação, como a técnica por enxertia (*grafting*) (ULBRICHT, 2006).

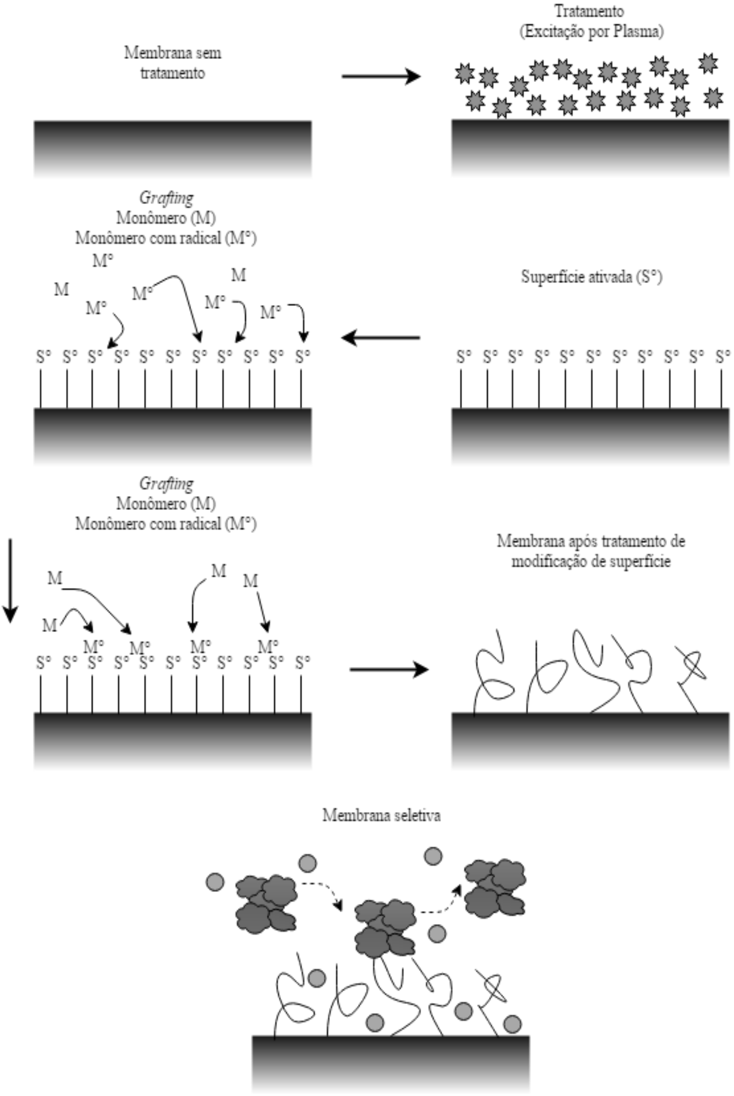
As modificações químicas podem ocorrer por meio de enxertia, revestimento e tratamento ácido/básico. O método de enxertia tem um importante papel no aumento do desempenho da membrana devido a sua abordagem simples, útil e versátil. As principais vantagens deste método são (HEGDE et al., 2011; PADAKI et al., 2015):

- A habilidade de modificar a superfície dos polímeros a fim de proporcionar propriedades específicas por meio da aplicação de diferentes monômeros;
- A possibilidade da introdução controlada de cadeias de enxerto com alta densidade e localização exata na superfície sem afetar as propriedades do meio;
- Fornecimento de superfícies estáveis.

Os métodos de enxertia podem ocorrer por duas abordagens diferentes, *grafting-to* e *grafting-from*, a primeira delas é conduzida pelo acoplamento de polímeros na superfície da membrana, enquanto que na segunda, os monômeros são polimerizados utilizando um iniciador na superfície desta (PADAKI et al., 2015). G*rafting-to* apresenta vantagens em comparação ao *grafting-from*, pois é de fácil caracterização e controle de síntese, em contrapartida alcança densidades de enxerto limitadas e suas reações de ligação requerem maiores esforços. Apesar de apresentar uma maior dificuldade no controle da síntese da estrutura do polímero, o método *grafting-from* possui a vantagem de conseguir uma variação muito grande na densidade dos enxertos e dos comprimentos de cadeias (MINKO, 2008; ULBRICHT, 2006).

A Figura 2.3 ilustra o esquema de uma MSM pela combinação da ativação da superfície da membrana via técnicas físicas como o plasma-induzido com posterior processo de polimerização por *graft*.

Figura 2.3: Esquema do processo da modificação da superfície de uma determinada membrana pela combinação da ativação da superfície via plasma-induzido com posterior processo de polimerização por *graft* (adaptado de LIN et al., 2010).



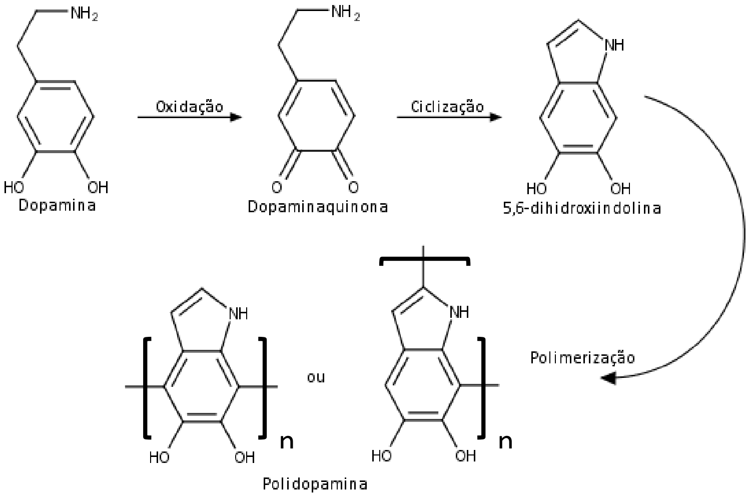
No esquema da Figura 2.3, o tratamento com o plasma-induzido é realizado com intuito de promover a ativação da superfície da membrana para posterior processo de polimerização por enxertia pela utilização de soluções com os monômeros de características desejadas. Este procedimento faz com que se forme uma nova camada na superfície da membrana sem que ocorra grandes alterações das características originais da mesma, com isso tornando-a mais resistente à incrustação e consequentemente melhorando o processo de separação.

Dentro do processo de MSM, um número expressivo de pesquisas tem focado na adição de diferentes compostos na superfície de membranas poliméricas ou inorgânicas (KASEMSET et al., 2013; XIANG; LIU; XUE, 2015; YANG et al., 2012). Os compostos utilizados para este propósito incluem nanopartículas metálicas, orgânicas, nanomateriais fotocatalíticos ou qualquer composto com características benéficas ao processo como propriedades anti-incrustante ou antimicrobiana (QU; ALVAREZ; LI, 2013).

Dentro deste contexto, uma abordagem que vem sendo empregada para a adição destes compostos na superfície das membranas é o método inspirado na capacidade adesiva de mexilhões, conhecido como "*mussel-inspired*" (MI). Envolvendo a polimerização da dopamina (DA), monômero capaz de ligar-se em diversas superfícies, a modificação por este método apresenta, além de alta estabilidade, simplicidade, versatilidade e facilidade no controle do processo, menores danos à membrana quando comparados a métodos como modificação por plasma, UV, feixe de elétrons, etc. (DREYER et al., 2013; MILLER; PAUL; FREEMAN, 2014; SI; GUO, 2015; WANG et al., 2015a, 2015b; YANG et al., 2014a, 2014b, 2015).

A polimerização da DA (Figura 2.4), a qual ocorre por meio da oxidação da DA em condições aeróbias e com pH levemente básico (pH ≈ 8.5), fornece estabilidade estrutural às moléculas através das interações do grupo catecol e da rede de reticulação das cadeias moleculares proveniente do processo de polimerização, promovendo ligações covalentes e não covalentes (pontes de hidrogênio, interações π-*stacking*, etc.) (DELLA VECCHIA et al., 2013; DING et al., 2014; DREYER et al., 2013; HONG et al., 2012; LIEBSCHER et al., 2013; WANG et al., 2015a).

Figura 2.4: Esquema do processo de polimerização da dopamina.



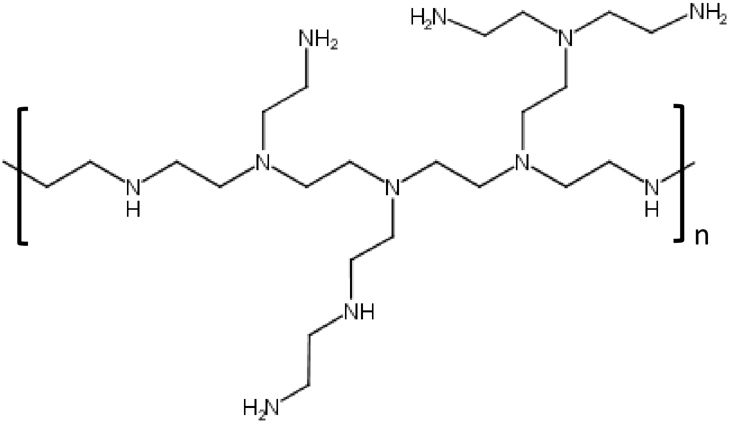
Fonte: adaptado de DREYER et al. (2013) e ZHANG et al. (2013).

Apesar de ser um método de modificação que está sendo largamente estudado, o mecanismo de deposição das moléculas de DA nos mais diferentes substratos ainda não foi estabelecido (DING et al., 2014; JIANG et al., 2011). Uma suposição feita por Bernsmann et al. (2009) propõe que a deposição da DA é iniciada pela adsorção física de monômeros e pequenos oligômeros na superfície do substrato e com o avanço do processo de polimerização leva ao completo recobrimento da superfície deste. Ao final do processo, a superfície modificada com polidopamina apresenta característica hidrofílica e uma grande quantidade de grupos funcionais que podem sofrer uma série de reações criando novas condições para futuras modificações (ZHANG et al., 2013; ZHU et al., 2014).

Uma vez que a modificação com o método MI apresenta a possibilidade da dissolução de outros componentes na solução de DA, a polietilenoimina (PEI) apresenta-se como um composto com grande potencial a ser utilizado, devido ao seu elevado número de grupamentos amina. Além de fornecer grupos hidrofílicos, conferindo à membrana propriedade anti-incrustante contra moléculas hidrofóbicas, a PEI acelera o processo de deposição da

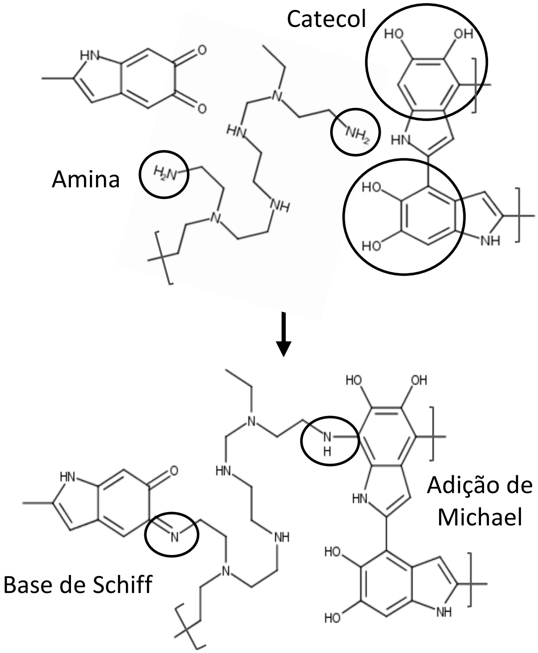
DA/PDA por criar novos sítios de reação, e fornece uma maior estabilidade às membranas, devido às ligações covalentes entre as moléculas de DA/PDA e de PEI. Quando se utiliza somente DA/PDA, a deposição é mais lenta, pois a reação ocorre principalmente pela difusão do oxigênio na solução. Estas ligações podem ocorrer pela adição nucleofílica de aminas primárias presentes na PEI a um composto carbonila *alfa*, *beta*-insaturado presente na DA/PDA (reação de adição de Michael) e/ou pela condensação de aminas primárias da PEI com os compostos carbonila da DA formando a estrutura conhecida como como base de Schiff (TIAN et al., 2013; YANG et al., 2016). A Figura 2.5 ilustra a estrutura química da PEI e a Figura 2.6 o esquema reacional das ligações entre a DA/PDA e a PEI.

Figura 2.5: Estrutura química da polietilenoimina ramificada.



Fonte: adaptado de INTRA; SALEM (2011).

Figura 2.6: Esquema ilustrativo da reação de adição de Michael e da base de Schiff



Como exemplo, o trabalho realizado por YANG et al. (2014a e 2014b) reporta a modificação de membranas de MF de polipropileno (PP) com tamanho de poro de 0,2 µm com uma solução de DA e polietilenoimina (PEI) a fim de separar emulsões oleosas. No primeiro trabalho, a membrana foi modificada pela sua imersão na solução de DA/PEI por um determinado tempo. No segundo trabalho, a solução de DA/PEI foi utilizada como uma camada intermediária a ser recoberta com sílica, servindo assim como uma ferramenta de ligação entre compostos orgânicos e inorgânicos. Em ambos os trabalhos, a membrana modificada apresentou excelente molhabilidade, altos valores de fluxo de água e propriedade anti-incrustante a emulsões oleosas quando a permeação era operada a baixas pressões.

A Tabela 2.4 apresenta outros estudos os quais utilizaram o método inspirado em mexilhão como estratégia para a modificação das membranas.

Tabela 2.4: Trabalhos anteriores que utilizaram o método *mussel-inspired* como estratégia para a modificação da membrana.

Tipo da Membrana	**Material da membrana**	**Aplicação**	**Referência**
MF	PP	antibacteriana e *antifouling* (proteína; emulsão oleosa)	(JIANG et al., 2013)
	PP	*antifouling* (proteína)	(PI et al., 2015)
	PP	Tratamento de soluções com corantes aniônicos	(QIU et al., 2015)
	PVDF	*antifouling* (sais; matéria orgânica)	(HAN et al., 2016)
	PVDF	*antifouling* (emulsão oleosa)	(WANG et al., 2015a)
UF	PAN	Retenção de sais	(DU et al., 2016)
	PAN	*antifouling* (proteína)	(TRIPATHI et al., 2016)
	PAN	Retenção de sais	(LV et al., 2015, 2016)
	PES	Retenção de sais e corantes e *antifouling* (proteína; matéria orgânica)	(MA et al., 2016)
	PES	*antifouling* (emulsão oleosa)	(LI et al., 2015a)
	PS	Retenção de sais e corantes	(LI et al., 2012)
	PS	Separação de CO_2	(LI et al., 2015b)
	PVDF	*antifouling* (proteína)	(SHAO et al., 2014)
OI	PS	Aumento do fluxo de água e retenção de sais	(ARENA et al., 2014)
	PS	Aumento do fluxo de água e retenção de sais	(HUANG et al., 2015)
	CTA	Aumento do fluxo de água e *antibiofouling*	(HEGAB et al., 2016)

MF: microfiltração; UF: ultrafiltração; OI: osmose inversa; PP: polipropileno; PVDF: poli(difluoreto de vinilindeno); PAN: poliacrilonitrila; PES: polietersulfona; PS: polisulfona; CTA: celulose tri-acetato.

Dentre os trabalhos citados na Tabela 2.4 em que o desempenho das membranas modificadas foi avaliado pela permeação de emulsões oleosas, Jiang et al. (2013) modificaram membranas de MF hidrofóbicas de polipropileno (PP) com tamanho de poro médio de 0,064 µm com DA e posterior deposição de poli(N-vinil pirrolidona) (PVP). Após a modificação, a membrana apresentou uma melhora na molhabilidade e hidrofilicidade, passando de um ângulo de contato de água de 117° (membrana controle) para 52° (membrana modificada). Após permeações de emulsões óleo/água e soluções proteicas, observou-se melhora nas propriedades anti-incrustante e no fluxo de permeado. Por fim, apesar das interações entre o PVP e a PDA serem ligações não-covalentes, a imobilização do PVP na superfície da membrana mostrou-se estável e durável em soluções com uma larga variação de pH (1 – 10).

Wang et al. (2015) modificaram membranas de MF não comerciais de poli(fluoreto de vinilideno) (PVDF) utilizando DA e tetraetoxissilano (TEOS) em uma única etapa. A DA foi responsável pela ligação dos compostos com a membrana, a qual teve sua hidrofilicidade ajustada pela concentração de TEOS. As membranas modificadas apresentaram um aumento de 34 vezes o fluxo de água, comparado ao das membranas controle, alta eficiência na separação de emulsões óleo/água em pressão atmosférica e excelente desempenho anti-incrustante.

Já em membranas de UF, Li et al. (2015) sintetizaram PVA funcionalizada com glicina e incorporou a uma membrana de UF modificada com DA a fim de melhorar o desempenho durante a filtração de águas de reúso. A camada incorporada de PVA, estável em condições ácidas e alcalinas, teve como função proteger a camada de DA, instável em condições de extrema alcalinidade. Após testes de permeação de emulsões oleosas, a modificação da membrana com DA e PVA funcionalizada com glicina apresentou uma melhora expressiva nas propriedades anti-incrustantes, uma vez que a permeabilidade hidráulica da membrana após os procedimentos de limpeza foi superior ao obtido com as membranas controle.

Como se pode observar, o método de modificação de membranas MI está sendo largamente estudado uma vez que apresenta bons resultados e é de fácil aplicação. No entanto, este cenário mostra que respostas ainda são necessárias para a correta explicação de alguns mecanismos e fenômenos envolvendo esta técnica. Outro fator observado é que o desenvolvimento de membranas com características anti-incrustações, voltadas aos processos de tratamento de efluentes oleosos ainda necessita de esforços para o seu aperfeiçoamento e posterior consolidação junto aos PSM.

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3 MODIFICAÇÃO DE MEMBRANAS DE MICROFILTRAÇÃO COMERCIAIS HIDROFÓBICAS EM MEMBRANAS SUPERHIDROFÍLICAS ATRAVÉS DO MÉTODO MUSSEL-INSPIRED UTILIZANDO DOPAMINA E POLIETILENOIMINA

Esse capítulo refere-se ao estudo da modificação da superfície de membranas hidrofóbicas em membranas superhidrofílicas através do método inspirado na capacidade adesiva de mexilhão (*mussel-inspired*). O desenvolvimento deste capítulo foi realizado durante o doutorado sanduíche na RICE University (Houston, Estados Unidos). Este estudo atende aos objetivos específicos descritos na seção 1.1.2 (Capítulo 3): estudar o efeito da utilização de diferentes concentrações de dopamina e polietilenoimina assim como diferentes tempos de deposição no processo de modificação das membranas; avaliar o desempenho das membranas modificadas aplicadas na permeação de emulsões oleosas; caracterizar, utilizando diferentes técnicas, as membranas modificadas antes e após a permeação da emulsão oleosa.

Na sequência está apresentado o trabalho completo realizado neste capítulo em formato de artigo.

Modification of hydrophobic commercial microfiltration membranes into superhydrophilic membranes by the Mussel-inspired method with dopamine and polyethyleneimine

Abstract

Polymeric membranes are not widely used to treat oily wastewater due to some drawbacks as concentration polarization and fouling. The aim of the present work is to modify commercial hydrophobic poly(vinylidene difluoride) (PVDF) microfiltration membranes into superhydrophilic membranes in a one-step modification by mussel-inspired (MI) method. PVDF microfiltration membranes with pore size ranging from 0.1-0.45 μm were modified with different concentrations of dopamine (DA) and polyethyleneimine (PEI) in different deposition times (6, 12 and 24 h). The modified membranes where characterized by permeations with canola oil emulsion, wettability tests, hydrophilicity and pH resistance. The membrane modification by MI method with DA and PEI proved to be efficient to produce superhydrophilic membranes, suitable for the treatment of oily wastewaters.

KEYWORDS: membrane modification; superhydrophilic membranes; mussel-inspired method; dopamine; polyethyleneimine.

3.1 Introduction

Water shortages and severe environmental regulations motivate the search for effective processes for water treatment and reuse. Treatment of oily wastewater is often challenging, and many processes are described in literature. Conventional physico-chemical processes, as adsorption, sand filters, cyclones, evaporators, as well as the alternative oxidation processes based on photocatalysis, electrochemical and Fenton reactions offer some disadvantages, as high cost, use of toxic oxidants and need of a large plant footprint. In this context, membrane separation processes (MSP) can be considered an attractive option for oily wastewater treatment (PADAKI et al., 2015).

Although many membrane separation processes are well established and recognized for their advantages as high selectivity, easy scale-up, operation flexibility and low energy demand, the recovery of oily wastewaters by MSP show some complications due to phenomena as concentration polarization and fouling, especially when polymeric membranes are applied. Both phenomena cause flux drop and can then turn the process economically unfeasible (CHERYAN; RAJAGOPALAN, 1998; PADAKI et al., 2015).

Chemical and physical methods for membrane fouling minimization can be applied (CARLESSO et al., 2016; LI et al., 2014; MOGHIMIFAR; RAISI; AROUJALIAN, 2014; RAZMJOU; MANSOURI; CHEN, 2011; VARDANEGA et al., 2013; WU; YU; LI, 2015; YU et al., 2011; ZHANG; MA, 1999; ZIN et al., 2016; ZOU et al., 2011). Among chemical methods, mussel-inspired (MI) modification is an approach that has been increasingly studied due to its simplicity, stability, versatility, easy control and to present low damage to the membrane in comparison to methods as plasma, UV, electron beam, etc (DREYER et al., 2013; MILLER; PAUL; FREEMAN, 2014; SI; GUO, 2015; WANG et al., 2015a, 2015b; YANG et al., 2014a, 2014b, 2015). MI coatings involve the use of dopamine (DA), which is a monomer able to bind to almost all surfaces, yielding polydopamine. The process is based on polymerization of the DA by oxidation in alkaline solutions, yielding structural stability to the molecules by the interactions between the catechol group and the crosslink network of polymer chains, promoting covalent and non-covalent bonding (hydrogen bonds, π-*stacking* interactions, etc) (DREYER et al., 2013; WANG et al., 2015b). At the end of the process, the DA-modified surface turns out to be hydrophilic and with functional groups that can further react, creating conditions for further modifications (ZHANG et al., 2013b; ZHU et al., 2014).

Due to the hydrophilicity of polydopamine membranes, they are suitable for oil and water separations. An approach that is usually reported to increase the process performance is the dissolution of compounds with determined characteristics in the dopamine solution, providing a new functionality to the membranes (KASEMSET et al., 2013; XIANG; LIU; XUE, 2015; YANG et al., 2012).

In this context, polyethyleneimine (PEI), an amino-rich polymer, can be easily immobilized onto membrane and pore surfaces, providing further hydrophilization and improving antifouling properties against non-polar molecules. YANG et al. (2014a, 2014b) reported the preparation of a microfiltration polypropylene 0.2-µm membrane with DA/PEI solution to separate oily emulsions. In the first paper, they describe the modification by the membrane immersion into a DA/PEI solution for a suitable time. In the second paper, the DA/PEI solution was used as an intermediate layer to be doped with silica, proving to be a convenient binding tool between the organic and inorganic compounds. In both modifications, the use of DA/PEI solutions presented high values of water flux and excellent wettability.

Mussel-inspired method using DA and PEI was studied in the present work by modification of PVDF microfiltration membranes with different pore sizes (0.1, 0.2, 0.45 µm). The effect of different DA and PEI concentrations and deposition times on the membrane properties and performance on oil emulsion separation was studied.

3.2 Material and methods

3.2.1 Material

Poly(vinylidene difluoride) (PVDF) microfiltration membranes with different pore sizes (0.1, 0.2 and 0.45 µm) were supplied by Pall Corporation (NY, USA). Before the modification, membranes were cut into small pieces, pre-treated with ethanol (99.5%, Koptec, PA, USA) for 2 h, rinsed with ultrapure water and soaked in ultrapure water overnight.

Dopamine and polythyleneimine solution was prepared with dopamine hydrochloride (DA) and polyethyleneimine (PEI, M_w = 800), purchased from Sigma-Aldrich (USA), and tris(hydroxymethyl)aminomethane (TRIS-HCl, pH = 8.5, 1 mol.L^{-1}) from Teknova (CA, USA).

The oil emulsion was prepared with canola oil purchased from a local market and Tween 80 from Sigma-Aldrich (MO, USA).

3.2.2 Methods

3.2.2.1 Membrane modification

Membrane modification was carried out in one-step. Different DA and PEI concentrations (Table 3.1) were dissolved in a Tris buffer solution (pH = 8.5, 50 mmol.L^{-1}) at 25 °C. DA and PEI concentrations are given in mg.mL^{-1}. Pre-treated PVDF membranes were immersed in the fresh DA/PEI solution and shaken for a definite time (6, 12 and 24 h). After reaction, the membranes were rinsed several times with ultrapure water and dried in a vacuum oven for 2 h at 40 °C.

Table 3.1: Different DA and PEI concentrations used in PVDF membrane modification.

Runs	**DA (mg.mL^{-1})**	**PEI (mg.mL^{-1})**
1-3	0.03	0.03, 0.06, 0.09
4-6	0.06	0.06, 0.12, 0.18
7-10	0.12	0, 0.12, 0.25, 0.36
11-13	0.25	0, 0.25, 0.5
14-16	0.50	0, 0.5, 1.0
17-18	1.0	1.0, 2.0
19-20	2.0	2.0, 4.0
21-22	4.0	4.0, 8.0

3.2.2.2 Membrane characterization

The ability of water absorption of the control and modified membranes were analyzed by soaking the membranes into ultrapure water overnight. The water uptake capacity was calculated by eq. (1):

$$W_{up} = \frac{(M_{wet} - M_{dry})}{M_{dry}} \; x \; 100\% \qquad (1)$$

where, W_{up} is the water uptake (%), while M_{wet} and M_{dry} are the weights of the wet and dry membrane respectively.

The surface morphology of the control and modified PVDF membranes were characterized by scanning electron microscopy (SEM, FEI Quanta 400 FEG SEM, OR, USA).

The element mapping and the changes in the chemical composition were carried out by X-ray photoelectron spectroscopy (XPS, PHI Quantera, MN, USA) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Cary 660, Agilent Technologies, CA, USA). Pure dopamine powder and the resulting polymer aggregate formed by the reaction of dopamine/polyethyleneimine on a Petri dish were also analyzed by ATR-FTIR for better evaluation of membrane modification.

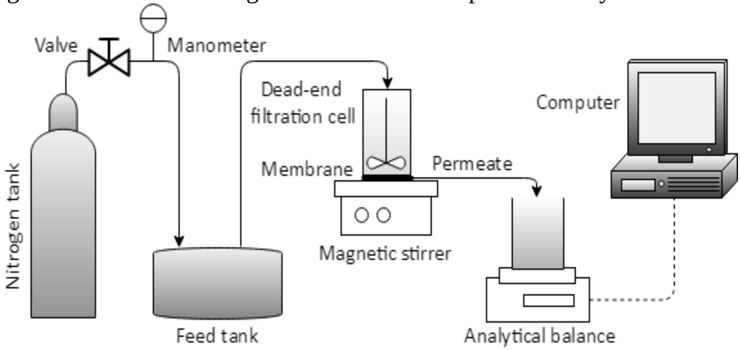
Zeta potential of the membranes was obtained by an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Graz, Austria) and the topographic images were acquired of the dry and wet control and modified membranes in an atomic-force microscope (AFM) (Multimode 8, Bruker Corporation, MA, USA).

Water and oil contact angle and underwater oil contact angle were measured in a drop shape analyzer (CAM 200, KSV instruments, Biolin Scientific, Sweden). Photographic images of water drop on the membrane surface and pH stability were also performed.

3.2.2.3 Membrane performance

Water permeability of the control and modified membranes was carried out in a lab scale commercial dead-end stirred cell (Amicon – Stirred Cell Model 8010, 10 mL) with effective membrane area of 4.9 cm². Figure 3.1 shows a schematic diagram of the dead-end permeation system.

Figure 3.1: Schematic diagram of the dead-end permeation system.



Before water permeation, the modified membranes were soaked in ultrapure water overnight. The pre-treatment of the control membranes was carried out in two different ways: the first one was the same treatment for modified membranes, and in the second one, the membranes were soaked in anhydrous ethanol for 2 h, followed by ultrapure water overnight, to ensure the complete pore wetting. Water permeability was taken after membrane compaction, varying the pressure from 2 to 0.5 bar. The fouling tests were carried out with oil emulsions made with 0.1% (w_{oil}/w_{H2O}) of canola oil and 20 % (w_{T80}/w_{oil}) of Tween 80 as an emulsifier. Firstly, a coarse emulsion was formed under magnetic stirring for 5 min (1,000 rpm), followed by probe sonication at 110 W for 5 min. The average droplet size of the resulting emulsion was 0.159 ± 0.001 µm. The emulsion was permeated under stirring for 2 h at constant pressure of 0.5 bar. Water permeability after physical and chemical cleaning procedures was determined. The cleaning procedures were carried out by manually rinsing the membrane with different solutions, without removing it from the bottom of the permeation module. The physical cleaning procedure was performed by membrane rinsing with ultrapure water; while the chemical cleaning was carried out by rinsing the membrane with ethanol and thereafter with ultrapure water. The long-term fouling experiments were performed by three subsequent cycles of oily emulsion permeation, interleaved by physical cleanings. At the end of these three cycles, a complete cleaning procedure (physical and chemical) was carried out, followed by determination of water permeability.

3.2.2.4 Emulsion analysis

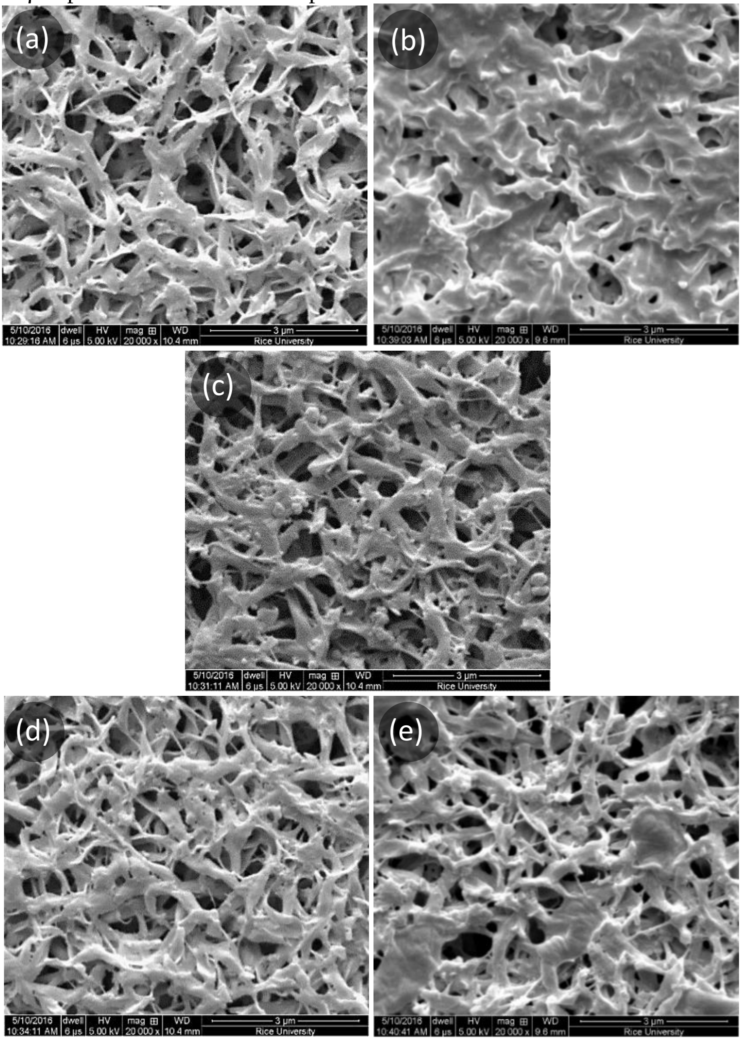
Droplet size and zeta potential measurements of the oil emulsion were determinate by Zetasizer Nano ZS3600 (Malvern Instruments Ltd., UK) and the oil concentration were measured by UV-visible spectrophotometer (UV-2550, Shimadzu, Japan), for membrane retention calculation.

3.3 Results and discussion

3.3.1 Membrane characterization

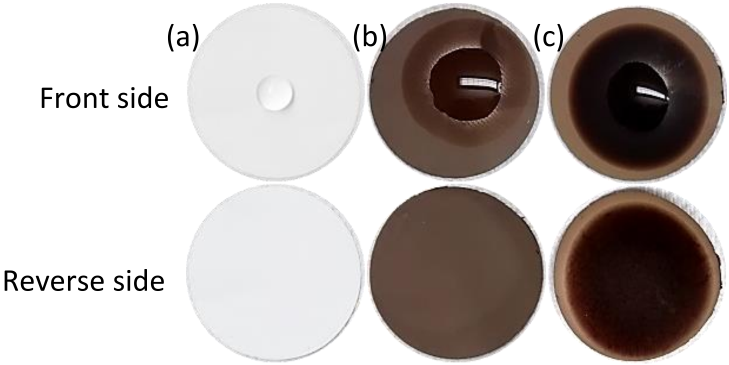
Membrane characterizations were carried out with PVDF microfiltration membranes with 0.1-µm pore size. Figure 3.2 shows the SEM images of surface of the control, DA and DA/PEI modified membranes.

Figure 3.2: SEM images of the surface for the (a) clean and (b) fouled control membranes; (c) clean DA modified membrane (0.5 mg.mL^{-1}); (d) clean and (e) fouled DA:PEI modified membranes (0.5:1 mg.mL^{-1}). The membrane modifications were carried out with PVDF microfiltration with 0.1-µm pore size and 24 h of deposition time.



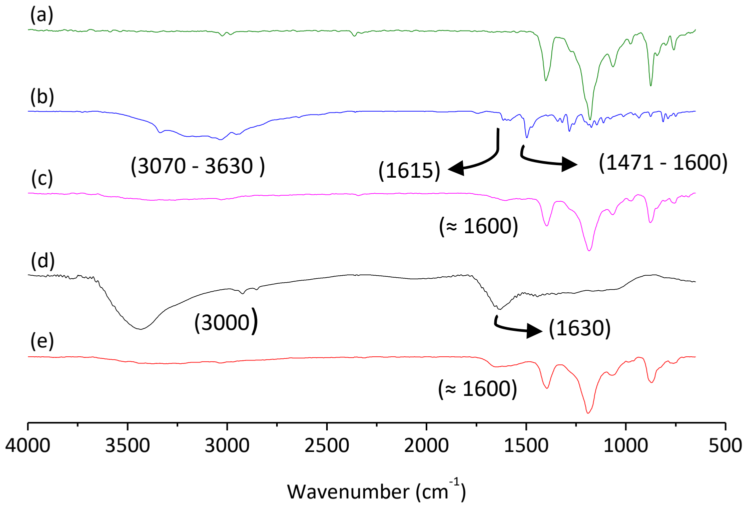
A slight decrease in the pores size can be seen in the modified membranes (Figure 3.2(c and d)) in comparison with the control (Figure 3.2(a)). However, blocked pores were not observed, which is important to maintain the membrane permeability. Figures 3.2(c and d) shows a uniform modification that was also observed by visual inspection of membranes' color after modification (Figures 3.3(b and c)).

Figure 3.3: Photographic images of a water droplet (20 µL) deposited on the membrane surface for the (a) control membrane, (b) DA modified membrane (0.5 mg.mL^{-1}) and (c) DA:PEI modified membranes (0.5:1 mg.mL^{-1}). The membrane modifications were carried out with 24 h of deposition time and the images were obtained after 30 sec.



Changes in the surface chemistry of the modified membranes were verified by ATR-FTIR and XPS analysis (Figure 3.4 and 3.5). To help the investigation, ATR-FTIR of the DA powder and of the DA/PEI polymeric aggregates (formed after 24 h of reaction without the membrane) were also performed.

Figure 3.4: ATR-FTIR of the (a) control membrane, (b) DA powder (c) DA modified membrane (0.5 mg.mL^{-1}), (d) DA:PEI polymeric aggregates (0.5:1) and (e) DA:PEI modified membranes (0.5:1 mg.mL^{-1}). The membrane modifications were carried out with 24 h of deposition time and the DA:PEI polymeric aggregates were obtained after 24 h of polymerization.



The spectrum of the pure DA (Figure 3.4(b)) presented peaks at 1471, 1596, 1580 and 1600 cm^{-1}, which are ascribed to the C=C resonance vibration in the aromatic ring; a peak at 1615 cm^{-1} due to the N-H bending vibrations, and a broad absorbance from 3070 to 3630 cm^{-1} attributed to the N-H/O-H stretching vibrations (GUNASEKARAN; KUMAR; PONNUSAMY, 2007). The DA/PEI aggregates (Figure 3.4(d)) showed an intense peak at 1630 cm^{-1}, assigned to the formation of C=N bonds between DA and PEI and a wide pronounced absorption above 3000 cm^{-1} attributed to the large amount of N-H present in the PEI (YANG et al., 2014a). The peaks around 1600 cm^{-1} observed in the DA and DA/PEI modified membranes (Figures 3.4(c and e)) presented absorption signals similar to the absorption presented by the pure DA (Figure 3.4(b)) and DA/PEI polymeric aggregates (Figure 3.4(d)) that confirms the successful incorporation of the DA and DA/PEI on the PVDF membranes surface after the modification (JIANG et al., 2011; THAKUR et al., 2012; YANG et al., 2014a).

The peak at 1630 cm^{-1}, present in DA/PEI polymeric aggregates spectrum (Figure 3.4(d)), evidences that the reaction between DA and PEI formed the Schiff base structure. This kind of mechanism is possible due to the condensation of primary amine present in the PEI structure with the carbonyl compounds in the DA (TIAN et al., 2013). However, the exact mechanisms of the DA deposition on various substrates are not yet clarified (DING et al., 2014; JIANG et al., 2011). Bernsmann et al. (BERNSMANN et al., 2009) proposed that the DA deposition is initiated by the absorption of monomers and small oligomers on the substrate surface, which, by the polymerization process (DA oxidation) leads to the complete coating of the substrate. During the polymerization reaction, monomers, oligomers, polymers and aggregates can interact with the deposited layer and with each other by covalent bonding, π-stacking and noncovalent interactions (DELLA VECCHIA et al., 2013; DING et al., 2014; HONG et al., 2012; LIEBSCHER et al., 2013). The growth of the polymeric chains reach the steady state when all the DA molecules present in the solution are oxidized or all active polymerization sites were already consumed.

Figure 3.5 shows the chemical composition obtained by XPS. The control membrane (Figure 3.5(a)) shows only F and C peaks, as expected. In the modified membranes (Figure 3.5(b and c)), the F peaks decreased, while the intensity of O and N peaks increased, confirming the deposition of DA and PEI molecules onto the membrane surface. The intensity of the N peak in the DA:PEI modified membrane (Figure 3.5(c)) increased in comparison with the control and DA modified membrane (Figure 3.5(b)).

Figure 3.5: XPS of the (a) control membrane, (b) DA modified membrane (0.25 mg.mL^{-1}) and (c) DA:PEI modified membranes (0.25:0.5 mg.mL^{-1}). The membrane modifications were carried out with 24 h of deposition time.

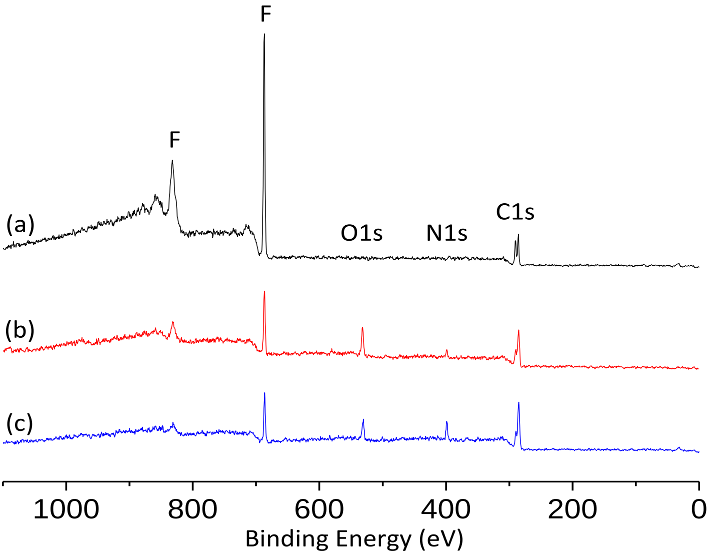


Table 3.2 shows the elemental composition and atomic ratio of the control membrane, DA modified membrane and DA:PEI modified membranes, calculated based on XPS results. The atomic ratio between N and C of the DA membrane was 0.1. Similar ratio was found by Wang et al. (2015). The atomic ratio N/C in the DA:PEI modified membranes increased 2-fold in comparison with the DA membranes, suggesting a higher hydrophilic character in comparison with the two other membranes.

Table 3.2: Elemental composition and atomic ratio of the control membrane, DA modified membrane (0.25 mg.mL^{-1}) and DA:PEI modified membranes (0.25:0.5 mg.mL^{-1}) analyzed by XPS. The membrane modifications were carried out with 24 h of deposition time.

Membrane	**Composition (%)**				**Atomic ratio**		
	C	**F**	**O**	**N**	**N/C**	**O/C**	**N/O**
Control	43.2	56.8	-	-	-	-	-
DA mod.	57.2	20.5	16.3	6	0.1	0.28	0.37
DA:PEI mod.	63.4	12.9	10.7	12.9	0.2	0.17	1.2

3.3.2 Wettability, hydrophilicity, and pH resistance of the membranes

For selection of the potential concentrations of DA and PEI for membrane modification, water weight gain of each modified membrane was determined, and results are shown in Figure 3.6. The concentrations 0.25:0.25 mg.mL^{-1} of DA:PEI were chosen as they were the minimum concentrations that yielded a high water uptake. Then, concentrations below and above this point were chosen for sake of comparison of the effect of DA and PEI concentrations in other important parameters (hydrophilicity and hydrophobicity, resistance to pH, morphology, and permeation performance)

Figure 3.6: Water weight gain of 0.1 µm PVDF modified membranes with different DA:PEI concentrations (mg.mL^{-1}) with 24 h of deposition time.

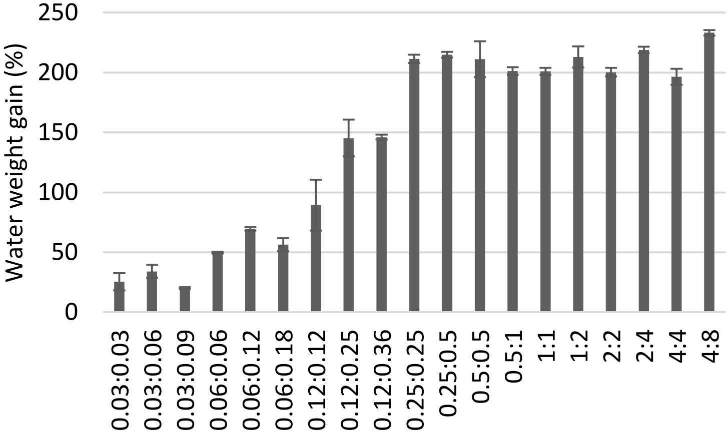
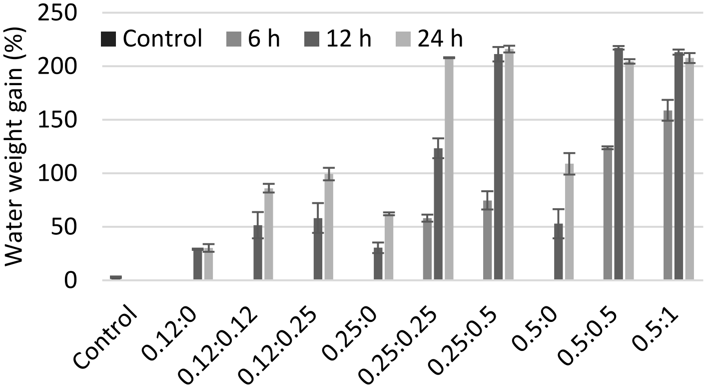


Figure 3.7 shows the water weight gain of the control and modified membranes with the selected DA:PEI concentrations and different deposition times (6, 12 and 24 h). All the modified membranes presented higher water weight gain than the control membrane. The effect of the DA:PEI concentration and the deposition time follows the same behavior. The increase of the time and the DA:PEI concentration induced a higher water weight gain. Photographic images of a water droplet deposited on the control, DA and DA:PEI membrane surface, as shown in Figure 3.3, illustrates the higher wettability of the DA:PEI membrane in comparison with the control and DA membranes. For the control membrane, the water droplet did not permeate due to the high hydrophobicity presented. On the other hand, the modified membranes showed a good wettability, mainly for the membrane modified with DA:PEI, since the water droplet went through the membrane in a few seconds.

Figure 3.7: Water weight gain of the control and modified membranes with selected DA:PEI concentrations (mg.mL^{-1}) at different deposition times (6, 12 and 24 h).



Since the modified membranes presented a high water weight gain (Figure 3.7), and the dry weight of the modified membranes increased around 20% after the modification, as seen in Figure 3.8, experiments to elucidate the reasons for the high percentage of water weight gain presented by the modified membranes (Figure 3.7) were carried out.

Figure 3.8: Weight gain of the dry membranes after modification with 0.5:1 mg.mL^{-1} in different deposition times (6, 12 and 24 h).

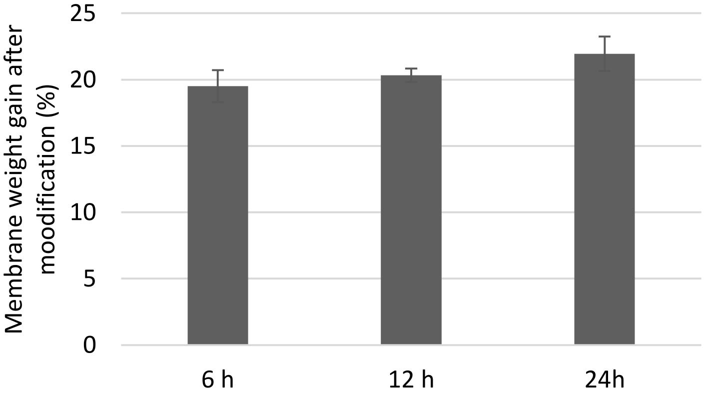
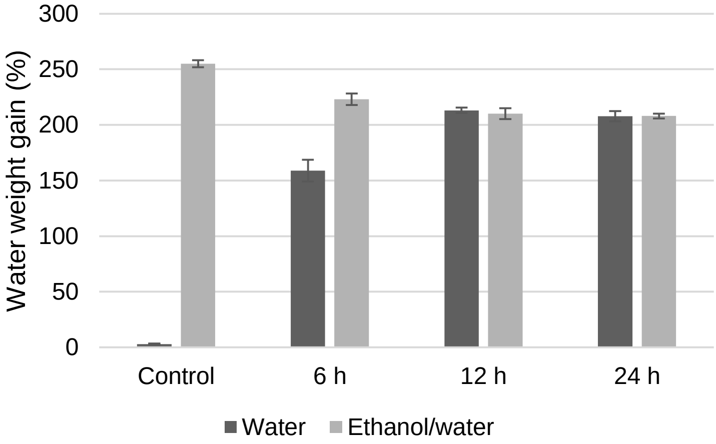


Figure 3.9 shows the water weight gain carried out by two different treatments: in the first one, the membranes were soaked into water overnight. Since the control membrane did not wet using this procedure, a second treatment was tested by soaking the membranes in ethanol for 2 h and then in water overnight, thus ensuring the complete membrane wetting.

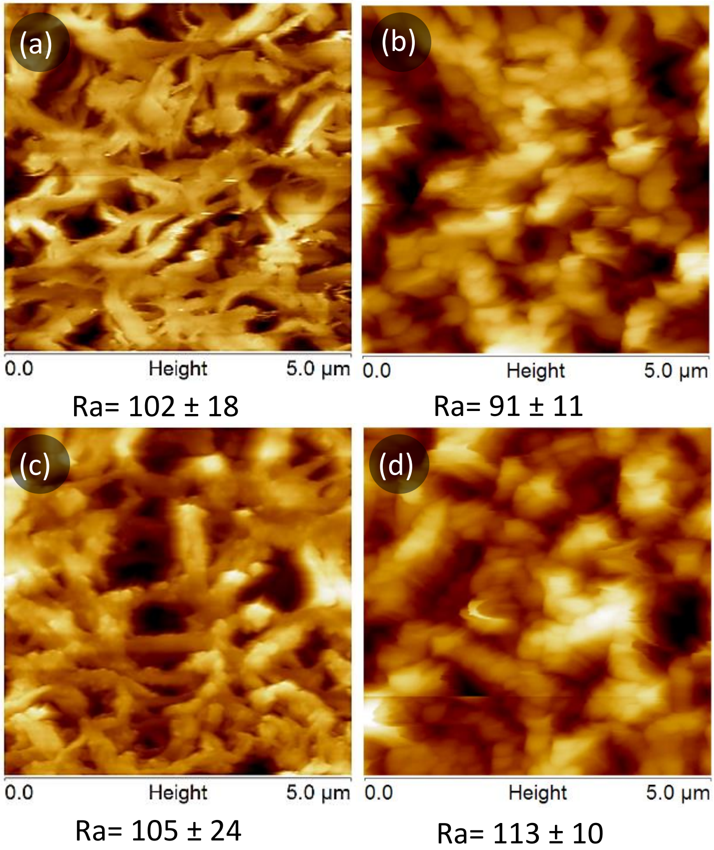
Figure 3.9: Water weight gain of the control and modified membranes with 0.5:1 mg.mL^{-1} and different deposition times (6, 12 and 24 h) carried out with two treatments. In the first treatment, the membranes were soaked in water overnight (water). In the second, the membranes were soaked in ethanol for 2 h and then in water overnight (ethanol/water).



According to Figure 3.9, the water weight gain of the modified membranes with 12 and 24 h of deposition time was similar for both treatments, suggesting that the modification with these deposition times improved membranes wettability without the need of using a lower tension solvent prior to water soaking.

However, the water weight gain of the modified membranes with 12 and 24 h of deposition times after ethanol treatment was lower than the control membrane and that obtained with 6 h of deposition time. These results suggest that the chemical modification may decrease the membrane pore size, thus decreasing the water uptake by the membrane. This hypothesis is supported by the SEM (Figure 3.2) and AFM images for the dry and wet control and DA:PEI modified membranes presented at Figure 3.10.

Figure 3.10: AFM images for the (a) dry and (b) wet control membranes and (c) dry and (d) wet DA:PEI modified membranes with 0.5:1 mg/mL^{-1} and 24 h of deposition time.



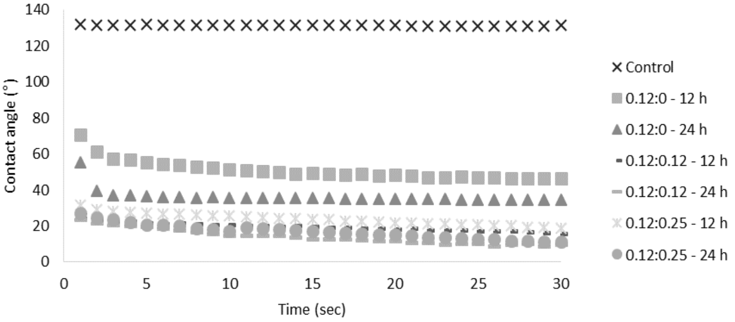
The Ra values did not show any statistically significant difference (Student's t-test, 95% confidence level) between the treatments. The AFM images are quite similar, and no swelling can be detected. The swelling would increase the water weight gain through the water absorption by the new polymeric layer and consequently decrease the membrane pore size when wet.

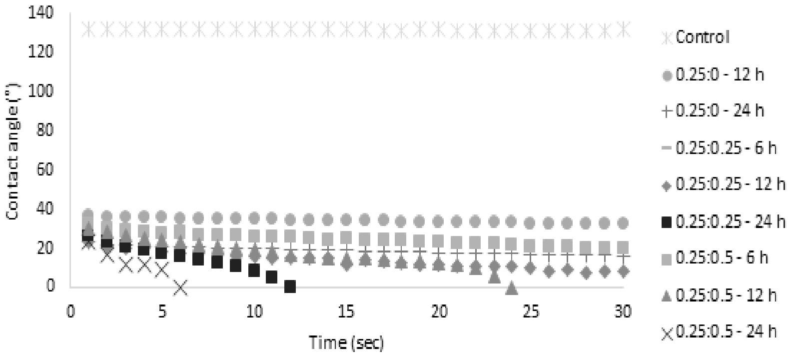
Table 3.3 and Figure 3.11 show water contact angles after 3 sec of the water droplet deposition, and the dynamic water contact angle for 30 sec, respectively.

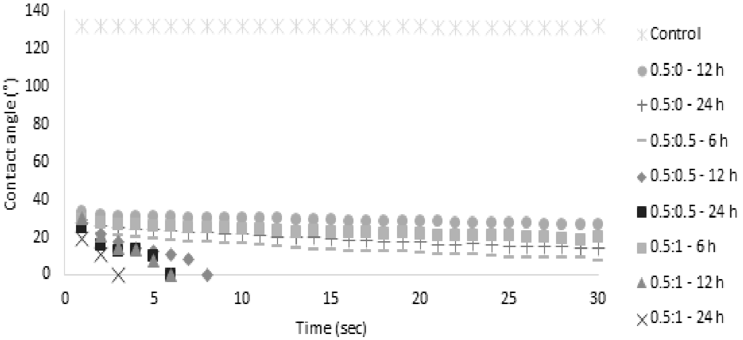
Table 3.3: Water contact angle of membranes modified with different DA:PEI concentrations (mg.mL^{-1}) and deposition times (6, 12 and 24 h).

Concentration (mgDA.mL^{-1}:mgPEI.mL^{-1})	**Contact angle (°)**			
		6 h	**12 h**	**24 h**
Control	132 ± 1	-	-	-
0.12:0	-	-	57 ± 3	37 ± 4
0.12:0.12	-	-	23 ± 3	21 ± 2
0.12:0.25	-	-	28 ± 2	24 ± 1
0.25:0	-	-	31 ± 1	21 ± 1
0.25:0.25	-	26 ± 1	20 ± 1	18 ± 3
0.25:0.5	-	29 ± 1	26 ± 1	12 ± 6
0.5:0	-	-	36 ± 3	25 ± 2
0.5:0.5	-	21 ± 2	17 ± 2	12 ± 7
0.5:1	-	27 ± 7	14 ± 6	0

Figure 3.11: Dynamic water contact angle of the selected membranes modified with different DA:PEI concentrations (mg.mL^{-1}) and deposition times (6, 12 and 24 h).



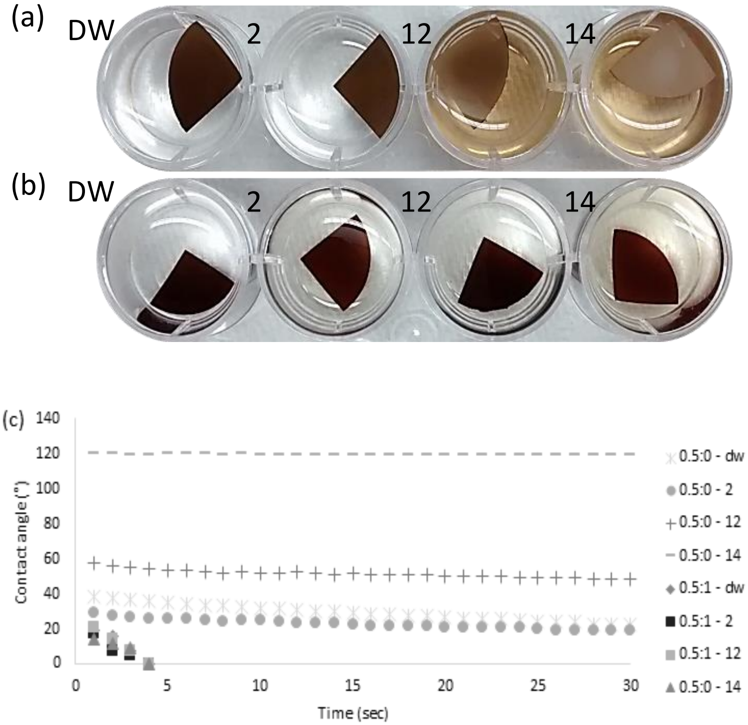




The control membrane presented a water contact angle much higher than the contact angle of the modified membranes, even when the samples modified only with dopamine are considered. The increase in the DA and PEI concentrations and the use of longer deposition times in the membrane modification caused the water contact angle to decrease. Some of the modified membranes reached 0° in just a few seconds. The best result was found with 0.5 mg DA.mL^{-1}:1 mg PEI.mL^{-1} and 24 h of deposition time, yielding a membrane that can be completely wet (contact angle 0°) after 3 sec. These observations conclude that mussel-inspired method using DA and PEI is a time dependent modification and a minimum concentration of DA and PEI is necessary to produce superhydrophilic membranes. The probable mechanism for the high wettability of the modified membranes is related to capillarity, considering the affinity of water with the DA/PEI polymeric layer.

Figure 3.12 evaluates the pH resistance of the DA (0.5 mg.mL^{-1}) and DA:PEI (0.5:1 mg.mL^{-1}) modified membranes with 24 h of deposition time

Figure 3.12: pH resistance of modified membranes. (a) Images of modified membranes with DA (0.5 mg.mL^{-1}), (b) with DA:PEI (0.5:1 mg.mL^{-1}) and (c) water contact angle of the modified membranes after 24 h immersed into different solutions. The membrane modifications were carried out with 24 h of deposition time.



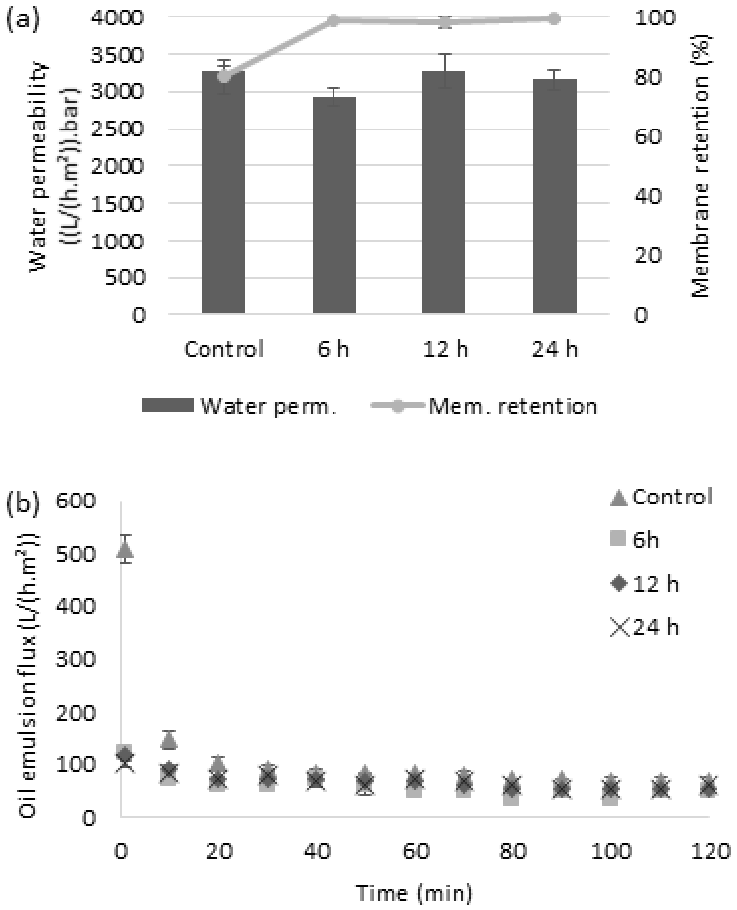
The membranes were soaked into different solutions (deionized water and in solutions with pH=2, 12 and 14) for 24 h. Clearly, the DA modified membranes proved to be instable in alkaline solutions, achieving, in pH=14, values of water contact angle close to the control membranes. On the other hand, for DA:PEI modified membranes, the color of the solutions and the values of the water contact angle were not modified after exposure to different pH, thus proving that the DA:PEI modified membranes are very stable.

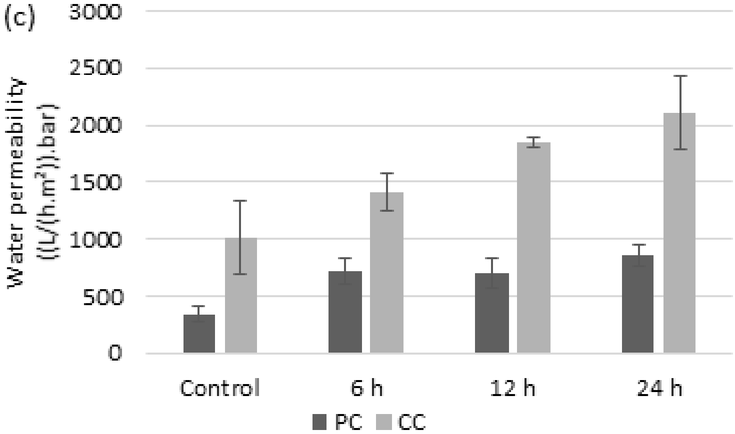
The membrane characterization results showed that mussel-inspired method using DA/PEI proved to be effective to produce superhydrophilic PVDF membranes. Dopamine is a good attachment agent, and allows to bind a hydrophilic polymer to the membrane surface, which otherwise would not bind, as confirmed by adsorption tests of PEI on PVDF films (results not shown). In turn, PEI, an amino-rich polymer, can considerably improve the membrane wettability and hydrophilicity. The covalent crosslinking between DA and PEI guarantee a high stability to the membrane, even when it is submitted to extreme pH.

3.3.3 Membrane performance

The performance of modified membranes, contrasted to control membranes, was evaluated by permeations of canola oil emulsions. Figure 3.13 shows the process performance of the control and modified membranes with 0.5:1 mg.mL^{-1} of DA:PEI and different depositions times (6, 12 and 24 h).

Figure 3.13: Permeation performance of 0.1 µm PVDF control and membranes modified with 0.5:1 mg.mL^{-1} of DA:PEI at different deposition times (6, 12 and 24 h) in the separation of canola oil emulsions. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures.





As mentioned in the Material and Methods (item 3.2.2.3), before permeation, two different pretreatments were applied to the control membranes. When the control membranes were pretreated only in ultrapure water overnight (similar to the modified membranes), no water flux was obtained. This occur because the membrane pores remains unwetted even after 12 h of water soaking. Thus, the pretreatment with ethanol was applied to the control membranes to ensure the complete pore wetting and making possible the evaluation of the permeation performance.

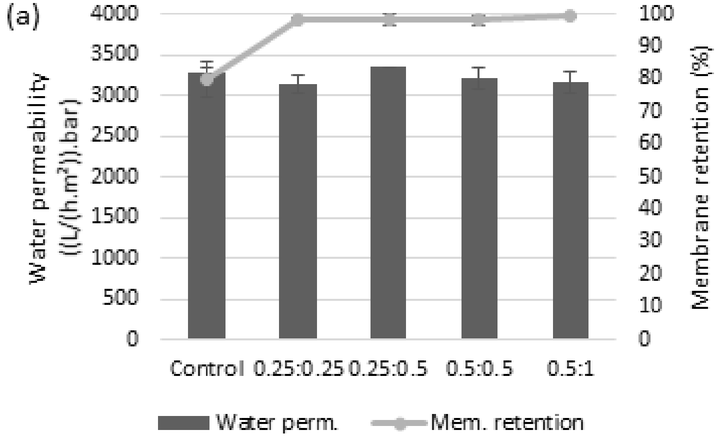
Initial water permeability was similar for both control and modified membranes (Figure 3.13(a)). However, the modified membranes presented oil emulsion retentions around 100%, while the retention of the control membranes was 80%.

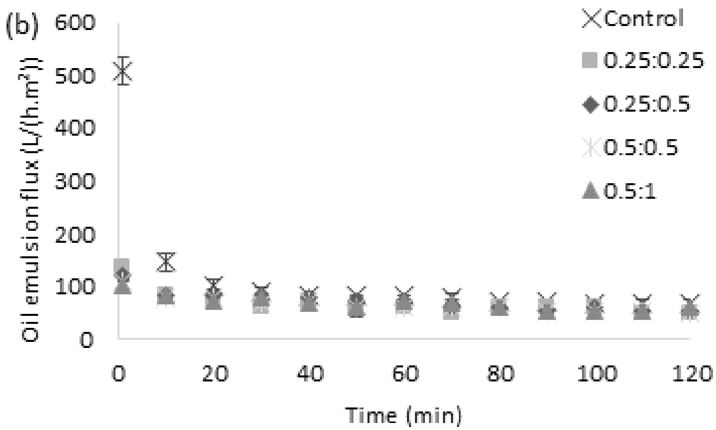
The oil emulsion flux to the control membrane presented a sharp decline in the beginning of the permeation (Figure 3.13(b)). After 20 min, though, the oil emulsion flux for all membranes reached a similar value up to the end of the permeation assay. The higher oil emulsion flux presented by the control membrane in comparison with the modified membranes in the beginning of the permeation was due to the lower retention level presented (around 80 %) and its sharp decline is a consequence of the hydrophobic interaction between the PVDF membranes with the oil emulsion.

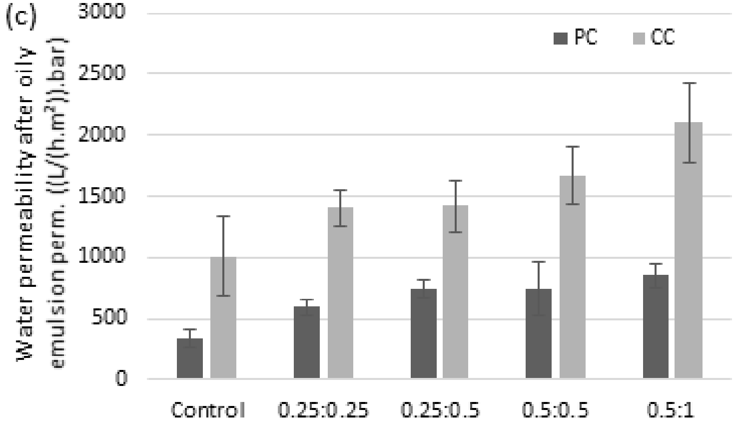
Results depicted in Figure 3.13(c) shows that both physical and chemical, cleaning procedures were more effective in the modified membranes, (mainly for those obtained with 12 and 24 h of deposition time). This suggests that fouling was less severe in modified membranes. These findings are supported by Figure 3.2, which shows the difference among the clean/fouled control and modified membranes. A large difference on surface morphology can be noticed between the control and modified membranes after cleaning procedures.

Figure 3.14 shows the process performance of control and modified membranes with different concentrations of DA:PEI and 24 h of deposition time. The permeation tests were carried out only with the membranes that presented a measurable water flux.

Figure 3.14: Permeation performance of control and modified 0.1 µm PVDF membranes with different concentrations of DA:PEI and 24 h of deposition time, in the separation of canola oil emulsions. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures.



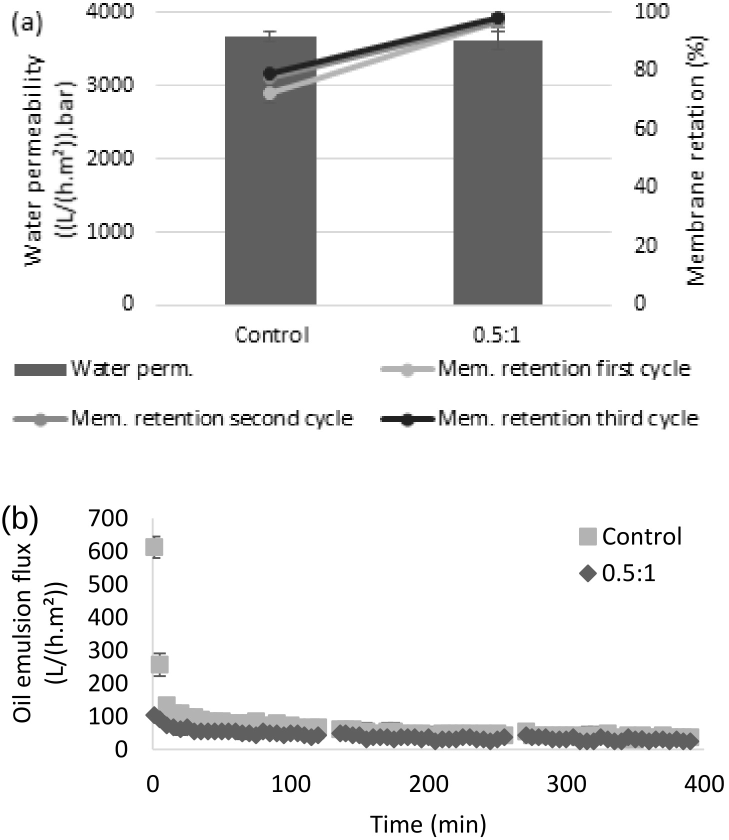


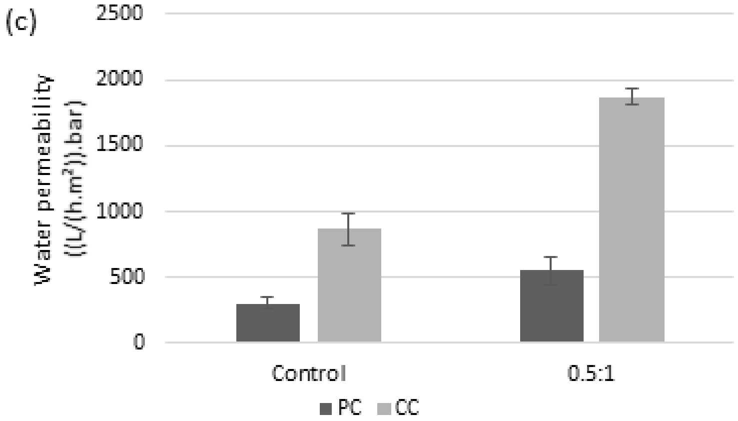


The results shown in Figure 3.14(a and b) follow the same behavior presented in Figure 3.13. The values of water permeability after the oily emulsion permeations (Figure 3.14(c)) decreased when lower concentrations of DA:PEI were used in membrane modification.

Figure 3.15 shows the process performance of control and modified membranes after the three cycles of oily emulsion permeation. The behavior of the membrane in the long-term permeation was evaluated by subsequent cycles of oily emulsions permeation interleaved with physical cleanings, followed by a final complete cleaning procedure as described in item 3.2.2.3.

Figure 3.15: Permeation performance of the control and modified membranes with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time applied to three subsequent permeation cycles of canola oil emulsions. (a) Initial water permeability and membrane retention, (b) three permeations of canola oil emulsion interleaved by physical cleanings and (c) water permeability after a final complete physical (PC) and chemical (CC) cleaning procedures.





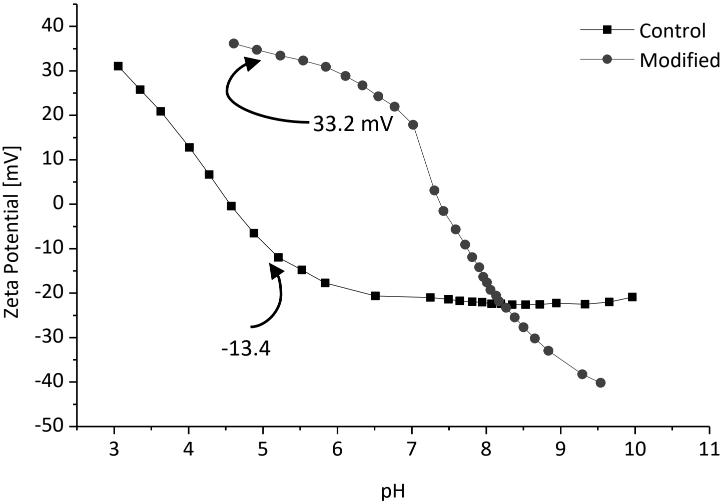
The performance of the membrane in the long-term permeation assay (Figure 3.15) was very stable and consistent with the results of the brand new membrane (Figures 3.13 and 3.14). It is important to highlight that even after three subsequent cycles of oil emulsion permeation, the water permeability of the modified membranes remain in the same level (after physical and chemical cleaning procedure, Figure 3.13(c)) found for the assays carried out with one simple oil emulsion permeation, which is excellent to a possible industrial application.

Some hypotheses, not fully understood in literature, were analyzed to elucidate which factors help to improve the process performance and why the modified membranes by DA and PEI had a better performance in the oil emulsion treatment in comparison with the control membranes.

The first assumptions were the decrease in the membrane pore size after the modification, or the membrane swelling when wet. In both hypotheses, the decrease in the membrane pore size could help to avoid higher amounts of oil droplets into the membrane pores. Both ideas should be discarded after analyzing the results of membrane swelling (already discussed in the previous section – item 3.3.2) and SEM images in Figure 3.2, which only show small differences in the pore size between the control (Figure 3.2(a)) and the modified membranes (Figure 3.2(c and d)).

Determination of zeta potential was carried out to investigate the repulsion between the membranes and the oil emulsion. Figure 3.16 shows the zeta potential of the control and membranes modified with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time.

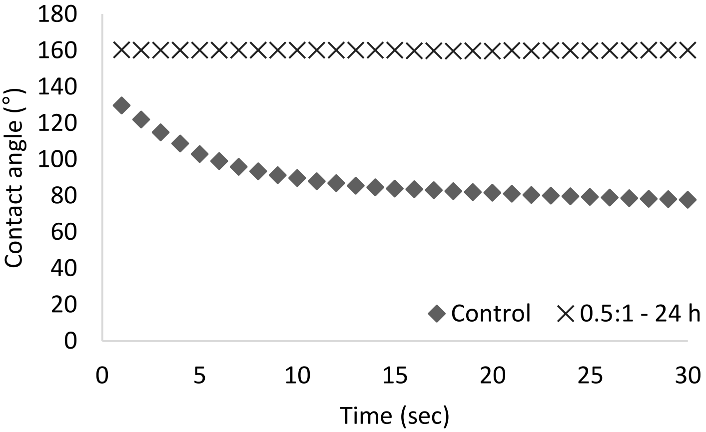
Figure 3.16: Membrane zeta potential of the control and modified membrane with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time.



The emulsion pH used in the permeations was 5.34 ± 0.06. In this pH, the emulsion potential zeta was -22.8 ± 0.3 mV, while the control and DA:PEI modified membranes presented zeta potential equal to -13.4 and 33.2 mV, respectively. The positive charge of the modified membranes was expected, since PEI is a positively charged polyelectrolyte when in solution, due to the amine groups act as a weak base (BELLETTINI et al., 2012; GAO et al., 2014a; ZHANG et al., 2014). Therefore, according to the opposite charges presented by the oil emulsion and the modified membrane, the oil droplets tend to have a higher interaction with the modified membranes in comparison with the control, which would affect negatively the process performance, since this would increase the membrane fouling. Thus, the electrostatic interaction between the membranes and the oil droplets does not seem to be the responsible for the membrane improvement.

The third assumption taken into consideration was the hydrophobic and hydrophilic interactions between the oily emulsion and the modified membranes. The analysis of the repulsion between the modified membrane (hydrophilic character) and the oily emulsion (hydrophobic character) was performed by experiments of underwater oil contact angle (Figure 3.17).

Figure 3.17: Dynamic underwater oil contact angle of the control and modified 0.1 µm PVDF membrane with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time.



The modified membrane presented a constant underwater oil contact angle around 160°, proving that superhydrophilic membranes have superoleophobic characteristics when wetted, agreeing with results found by other authors (GAO et al., 2014b; ZHANG et al., 2013a). The underwater oil contact angle of the control membrane decreased with the time due to the intrusion of the oil into membrane pores, caused by the hydrophobic character of the PVDF membrane. These results suggest that the modified membrane possibly create a hydration layer on the membrane surface, which hinders the contact of the oil droplets present in the emulsion with the hydrophilic membrane surface, improving the process performance. The same assumption was discussed by Dreyer et al. (DREYER et al., 2013).

To prove this hypothesis, Figure 3.18 shows the dynamic oil contact angle of the dry control and modified membranes. The behavior of the dynamic oil contact angle of the dry control membrane was similar to the behavior found in the underwater oil contact angle presented at Figure 3.17. In turn, the results of the dry modified membrane presented at Figure 3.18, differently from the Figure 3.17, showed a decrease of the contact angle with the time, which means that the oil droplet interacts with the dry modified membrane. Another evaluation that can be carried out with the results presented at Figure 3.17 and 3.18 is the intrusion capacity of the oil droplet into the dry and wet control and modified membranes. According to Laplace's law, the intrusion of the oil into the membranes pores (filled with water or air) only occurs when the pressure difference in the boundary layer formed between the oil droplet and the membrane pore is positive. However, to find a positive pressure difference is necessary that the contact angle of the oil droplet on the membrane surface presents values lower than 90° (Laplace pressure’s equation). Contact angles observed for the dry and wet control membranes (Figure 3.17 and 3.18) and for the dry modified membranes (Figure 3.18) were all under 90°. These results support the idea that the modified membranes when wetted possibly create a hydration layer on the membrane surface, providing to the membrane an oleophobic characteristic.

Figure 3.18: Dynamic oil contact angle of the control and modified 0.1 µm PVDF membrane with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time.

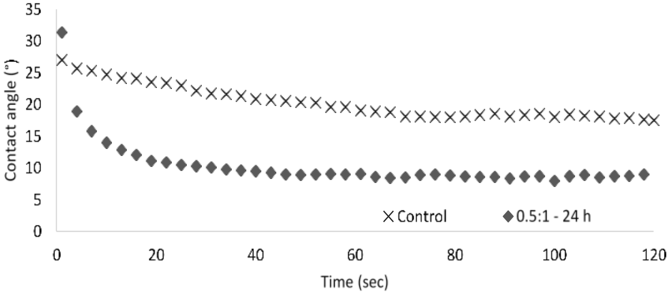
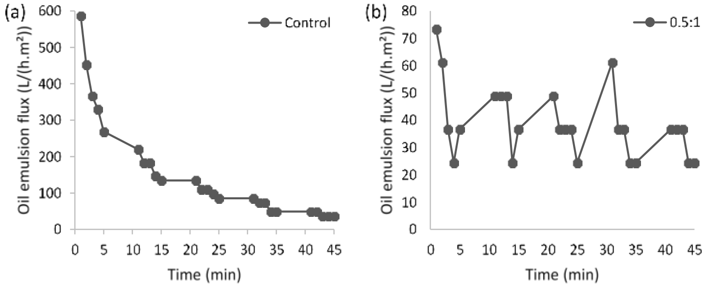


Figure 3.19 shows the oil emulsion flux recovery carried out with the control and modified membranes. The experiments consist in 5 subsequent unstirred oil emulsion permeations in a dead-end cell with constant pressure of 0.5 bar. Between each permeation, the

pressure was removed and the stirring of the dead-end cell was turned on to evaluate the flux recovery in the subsequent oil emulsion permeation.

Figure 3.19: Oil emulsion flux recovery of the control and modified 0.1 µm PVDF membranes with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time.

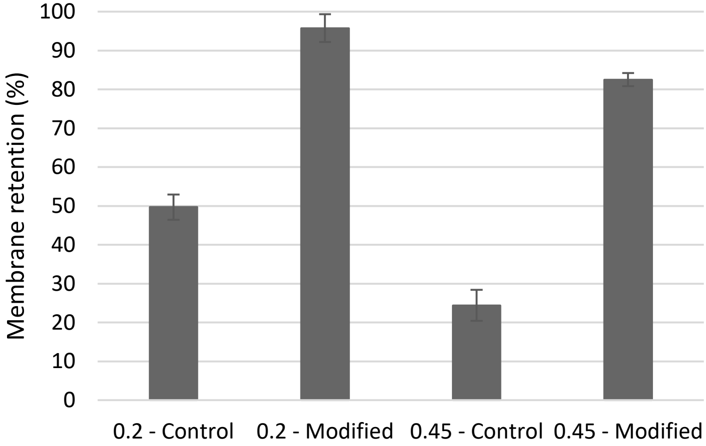


Clearly, for the control membrane (Figure 3.19(a)), the flux continuously decreases due to the hydrophobic interactions between the membrane and the oil emulsion. On the other hand, for the modified membrane (Figure 3.19(b)), there is an increase in the oil emulsion flux after each permeation, proving that just the stirring of the feed emulsion inside the dead-end cell is enough for some flux recovery. The results corroborate the assumption that a hydration layer established on the membrane surface seems to be the mechanism responsible for the better performance presented by the modified membranes in contrast with the control membranes.

It is worth noting the difference in the initial flux of the oil emulsion. As there is no evident membrane swelling, which could block the pores and lead to a decrease of the oil emulsion flux, the repulsive character between the superhydrophilic modified membrane and the hydrophobic molecules contribute to prove the hypothesis of the creation of a hydration layer in the modified membrane when wet. The hydration layer is also the possible reason why the modified membranes presented too higher oil emulsion retentions in comparison with the control.

To evaluate the capacity of retention induced by the hydration layer, Figure 3.20 shows the membrane retention of modified and unmodified PVDF microfiltration membranes with larger pore sizes than the oil droplet sizes present in the oily emulsion.

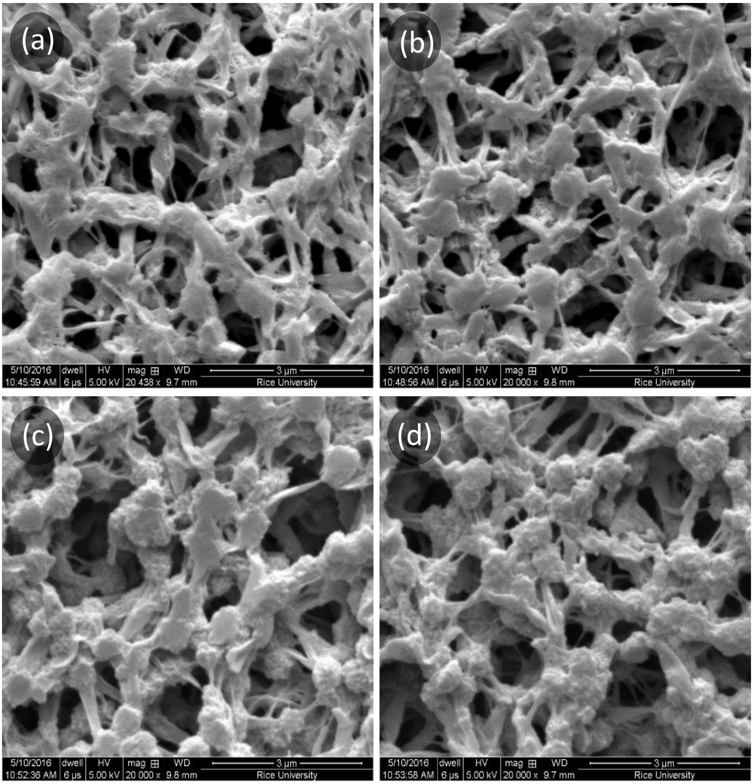
Figure 3.20: Membrane retention of the control and modified 0.2 and 0.45 µm PVDF membranes. The modifications were carried out with 0.5:1 mg.mL^{-1} of DA:PEI and 24 h of deposition time.



As shown in Figure 3.20, the membrane retention of the modified membranes was much higher than the retention of control membranes. The 0.2-µm modified membrane presented an oil retention of 96%. It is interesting to note that the retention of this membrane is almost as high as that obtained for the 0.1-µm modified membrane (>99%, Figures 3.13(a) and 3.14(a)), despite the larger pore size. The modified 0.45-µm membrane showed oil retention of 83 %, in contrast to the 25 % of retention for the control membrane.

SEM images of the control and modified 0.2 and 0.45-µm PVDF membranes (Figure 3.21) showed that the membrane pore size does not seem to be decreased after membrane modification. These results indicate that the hydration layer, when the system operates at low pressures, can be used as a barrier against hydrophobic character molecules.

Figure 3.21: SEM images of the membrane surface for (a) control and (b) modified 0.2-µm PVDF membranes and (c) control and (d) modified 0.45-µm PVDF membranes.



3.4 Conclusion

This work aimed to modify hydrophobic PVDF microfiltration membranes into superhydrophilic membranes in one-step modification by mussel-inspired method with DA and PEI, for application in oily wastewater treatment. The mussel-inspired method proved to be time-dependent and a minimum concentration of the components (DA and PEI) is necessary to produce a membrane with appropriate characteristics. Besides the excellent wettability and notable results for the dynamic water contact angle, the modified membranes with DA and PEI also proved to be resistant to pH from 2 to 14. The results of the permeation performance as initial water permeability, membrane retention, flux of canola oil emulsion and water permeability after oily emulsion permeation, showed that the modified membranes with DA and PEI are a good approach to treat oily emulsions. A probable explanation of the promising results achieved in this work was the creation of a hydration layer in the membrane surface when the modified membranes were wetted, which difficult the contact of the oil droplets with the membrane, consequently decreasing the fouling.

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4 DIFERENTES ABORDAGENS DO MÉTODO MUSSEL-INSPIRED PARA ACELERAR O PROCESSO DE MODIFICAÇÃO DE MEMBRANAS HIDROFÓBICAS DE MICROFILTRAÇÃO EM MEMBRANAS SUPERHIDROFÍLICAS

Esse capítulo refere-se ao estudo de diferentes abordagens do método mussel-inspired para acelerar o processo de modificação de membranas hidrofóbicas de microfiltração em membranas superhidrofílicas. O desenvolvimento deste capítulo foi realizado durante o doutorado sanduíche na RICE University (Houston, Estados Unidos). Este estudo atende aos objetivos específicos descritos na seção 1.1.2 (Capítulo 4): acelerar o processo de modificação de membranas hidrofóbicas em membranas superhidrofílicas utilizando variações do método *mussel-inspired*; avaliar o desempenho das membranas modificadas pelas variações do método *mussel-inspired* aplicadas na permeação de emulsões oleosas; caracterizar as membranas modificadas pelas variações do método *mussel-inspired* utilizando diferentes técnicas antes e após a permeação da emulsão oleosa.

Na sequência está apresentado o trabalho completo realizado neste capítulo em formato de artigo.

Different approaches of the Mussel-inspired method to accelerate the modification process of hydrophobic microfiltration membrane into superhydrophilic membranes

Abstract

Mussel-Inspired (MI) modification is known as a time-dependent modification due the reaction time necessary in the polymerization process of the dopamine monomers. The aim of the present work is to suggest different approaches to accelerate the modification process of PVDF hydrophobic membranes into superhydrophilic membranes for oily emulsion separations using the mussel-Inspired method with dopamine and polyethyleneimine. PVDF microfiltration membranes with 0.1-µm pore size were modified with concentrations of dopamine (DA) and polyethyleneimine (PEI) of 0.5 mg.mL^{-1} and 1 mg.mL^{-1}, respectively. The effect of different modification procedures in the membrane properties and the process performance was studied by membrane characterizations, wettability tests, hydrophilicity, pH resistance and permeations with canola oil emulsion. The different approaches proved to be capable to accelerate the modification process by the MI method, turning hydrophobic membranes into superhydrophilic membranes.

KEYWORDS: membrane modification; superhydrophilic membranes; hydrophobic membranes; mussel-inspired method; dopamine; polyethyleneimine.

4.1 Introduction

The energy crisis, water shortages and severe environmental regulations increased the application of clean technologies to all kind of process. In this scenario, membrane processes (MP) appear increasingly present in the industries. High selectivity, easy scale-up, operational flexibility and low cost minimization are some of the factors that contribute to this fast growing (LUJÁN-FACUNDO et al., 2015; YANG et al., 2015).

A certain delay in the application of this technology is due to phenomena as concentration polarization and fouling. These drawbacks decrease the membrane performance becoming the MP less attractive (CHERYAN; RAJAGOPALAN, 1998; PADAKI et al., 2015; SAXENA et al., 2009).

Chemical and physical approaches have been studied to improve the performance of the MP. As physical strategies, centrifuges, turbulence generating devices and the use of electric and magnetic fields have been applied (AL-QAHTANI, 1996; CARLESSO et al., 2016; LI et al., 2007; LONG et al., 2005; OHATA; TOMITA; IKADA, 2004; VARDANEGA et al., 2013; VEDAVYASAN, 2001; ZIN et al., 2016). Despite the use of chemicals is an effective way to clean membranes, generally these products produce secondary wastewater to be treated and may damage the membranes (ZHANG; MA, 1999). An alternative to chemical approaches, which have been largely applied to improve the performance of the MP, is the membrane surface modification (MSM) focused in the antifouling properties improvement (CHEN; CHIAO; TSENG, 1996; HEGDE et al., 2011; KAI et al., 2005; LI et al., 2014; MASUELLI et al., 2012; MOGHIMIFAR; RAISI; AROUJALIAN, 2014; PADAKI et al., 2015; QU; ALVAREZ; LI, 2013; ULBRICHT; BELFORT, 1996; ULBRICHT, 2006; WANICHAPICHART; YU, 2007).

Among the MSM methods, discussed in the Chapter 3, mussel-inspired method (MI) (modification that involves dopamine (DA) - a monomer able to bind in many surfaces) shows up a promising approach to modify membranes due to its simplicity, stability, easy control and low damage to the membrane. The process is based on the DA solution polymerization (oxidation in alkaline environmental), yielding structural stability due to the catechol group interactions and the crosslink network of polymer chains by covalent and non-covalent bonding (hydrogen bonds, π-*stacking* interactions, etc) (DREYER et al., 2013; MILLER; PAUL; FREEMAN, 2014; SI; GUO, 2015; WANG et al., 2015a, 2015b; YANG et al., 2014a, 2014b, 2015). Another point that should be highlighted in the MI method is the possibility of dissolution of different compounds into the DA solution. This versatility makes the MI method a powerful tool in the development of membranes with desired characteristics and functionalities (KASEMSET et al., 2013; XIANG; LIU; XUE, 2015; YANG et al., 2012; ZHANG et al., 2013; ZHU et al., 2014).

As MI method involves a polymerization *in situ* (membrane immersion in the DA solution), the membrane modification by this method is time dependent. The time necessary to obtain membranes with complete surface coating and desired characteristics varies according with DA concentration and application. In order to accelerate the deposition process large part of the MI studies uses high DA concentrations to decrease the reaction time (generally, 2.0 mg.mL^{-1} of DA). However, to obtain membranes with good performance, high deposition times are necessary, varying from 12 to 90 h (CHENG et al., 2012; KARKHANECHI; TAKAGI; MATSUYAMA, 2014; KIM et al., 2014; LIU; SHAO; YANG, 2013; XI et al., 2009; XIANG; LIU; XUE, 2015).

Thus, this work aims to suggest different approaches to accelerate the membrane modification using the MI method. The modifications methods were carried out using PVDF microfiltration membranes with 0.1-µm of pore size and concentrations of DA and polyethyleneimine (PEI) of 0.5 mg.mL^{-1} and 1 mg.mL^{-1}, respectively. The effect of the different modifications on the membrane properties and in the performance of oil emulsion separation were studied.

4.2 Material and methods

4.2.1 Material

Poly(vinylidene difluoride) (PVDF) microfiltration membrane with 0.1-µm pore size were supplied by Pall Corporation (NY, USA). As a pretreatment, membranes were cut into small pieces and immersed in ethanol (99.5%, Koptec, PA, USA) for 2 h, rinsed with ultrapure water several times and soaked in ultrapure water overnight.

Dopamine hydrochloride (DA) and polyethylenimine (PEI, M_w = 800) were purchased from Sigma-Aldrich (USA) and tris(hydroxymethyl)aminomethane (TRIS-HCl, pH = 8.5, 1 M.L^{-1}) from Teknova (CA, USA).

Canola oil, purchased from a local market, and Tween 80 from Sigma-Aldrich (USA) were used to make the oil emulsions.

4.2.2 Methods

4.2.2.1 Membrane modification

The DA/PEI solution used in the modifications methods were prepared with the same protocol. DA and PEI (0.5 mg.mL^{-1} and 1 mg.mL^{-1}, respectively) were dissolved in a Tris buffer solution (pH = 8.5, 50 mmol.L^{-1}) and pre-polymerized under magnetically stirring for 4 h at 25 °C.

Two different methods were used in the membrane modification:

- Method 1 (mussel-inspired temperature membrane; membrane code – MI-T): the pre-treated PVDF membrane was immersed in the pre-polymerized DA/PEI solution and shaken for 4 h at 50 ± 5 °C.
- Method 2 (mussel-inspired filtered membrane; membrane code – MI-F): the pre-polymerized DA/PEI solution (400 mL) was filtered 4 times through the pre-treated PVDF membrane using a commercial vacuum filtration system (Millipore) pressurized at 500 mmHg at 25 °C.

As a final step, for both methods, the modified membrane was rinsed several times with ultrapure water and dried in a vacuum oven for 2 h at 40 °C.

4.2.2.2 Membrane characterization and emulsion analysis

The capacity of water absorption of the control and modified membranes was analyzed by water uptake assays soaking the membranes in ultrapure water overnight. The water uptake capacity was calculated by eq. (1):

$$W_{up} = \frac{\left(M_{wet} - M_{dry}\right)}{M_{dry}} \; x \; 100\% \qquad (1)$$

where, W_{up} is the water uptake in percentage and M_{wet} and M_{dry} are the weights of the wet and dry membrane respectively.

Scanning electron microscopy (SEM, FEI Quanta 400 FEG SEM, OR, USA) of the control and modified membranes and atomic-force microscopy (AFM, Multimode 8, Bruker Corporation, MA, USA) of the dry and wet control and modified membranes were carried out to observe the surface morphology and membrane differences.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Cary 660, Agilent Technologies, CA, USA) was used to detect changes in the membrane surface chemical composition. Zeta potential of the membranes was obtained by an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Graz, Austria).

Water contact angle and underwater oil contact angle were measured by CAM 200 (KSV instruments LTD). Photographic images of water drop on the membrane surface and analyses of pH stability were also performed.

Zetasizer Nano ZS3600 (Malvern Instruments Ltd., UK) was used to determine the droplet size of the oil emulsion, and UV-visible spectrophotometer (UV-2550 – Shimadzu, Japan) to quantify the membrane retentions.

4.2.2.3 Membrane performance

The membrane performance tests were carried out the same way as in Chapter 3. Water permeability and oil emulsion permeation of the control and modified membranes were carried out with a lab scale commercial dead-end stirred cell with 4.9 cm^2 of effective membrane area (Amicon – Stirred Cell Model 8010, 10 ml) (Figure 3.1). Before permeation, the control and modified membranes were submitted to different pre-treatments. The control membranes (hydrophobic) were soaked in ethanol (99.5 %) for 2 h and thereafter in ultrapure water overnight. In turn, the modified membranes (superhydrophilic) were soaked in ultrapure water overnight. The water permeability was measured after membrane compaction, varying the pressure from 2 to 0.5 bar. The fouling tests were carried out with oil emulsions made with 0.1% (w_{oil}/w_{H2O}) of canola oil and 20% (w_{T80}/w_{oil}) of Tween 80 as emulsifier. Firstly, a coarse emulsion was formed under magnetic stirring for 5 min (1000 rpm) followed by probe sonication at 110 W for 5 min. The average droplet size of the emulsions was 0.159 ± 0.001 µm. The permeations of the canola oil emulsions were carried out under stirring for 2 h at constant pressure of 0.5 bar and the flux was determined each 5 min. As a final step, the water permeability after physical and chemical cleaning was determined. The cleaning procedures were carried out by manually rinsing the membrane with different solutions, without removing it from the bottom of the permeation module. The physical cleaning procedure was performed by membrane rinsing with ultrapure water; while the chemical cleaning was carried out by rinsing the membrane with ethanol and thereafter with ultrapure water.

4.3 Results and discussion

4.3.1 Membrane characterization

SEM images of the control, MI-T and MI-F membranes were obtained to evaluate the membrane surface before and after the oil emulsion permeation (Figure 4.1). Morphology of the clean control (Figure 4.1(a and d)) and MI-T (Figure 4.1(b and e)) membranes were similar. However, the clean MI-F membranes (Figure 4.1(c and f)) presented some polymer clusters on the membrane surface after the modification. This difference between the MI-T and MI-F membranes may be due to the modification method. In MI-T membranes, the modifications were performed by the membrane immersion into the pre-polymerized DA/PEI solutions for 4 h. On the other hand, to modify the MI-F membranes, DA/PEI stirred solutions were filtered perpendicularly through the membranes. Thus, the DA/PEI polymeric aggregates present in the stirred solutions (formed during the DA/PEI solution pre-polymerization step) do not permeate the membrane, creating clusters of polymeric aggregates on the membrane surface.

Figure 4.1: Surface SEM images of the control, MI-T and MI-F membranes surface at different magnifications (5,000x and 10,000x). (a and d) clean control membranes, (b and e) clean MI-T membranes and (c and f) clean MI-F membranes. (g, h and i) fouled control, MF-T and MF-F membranes, respectively.

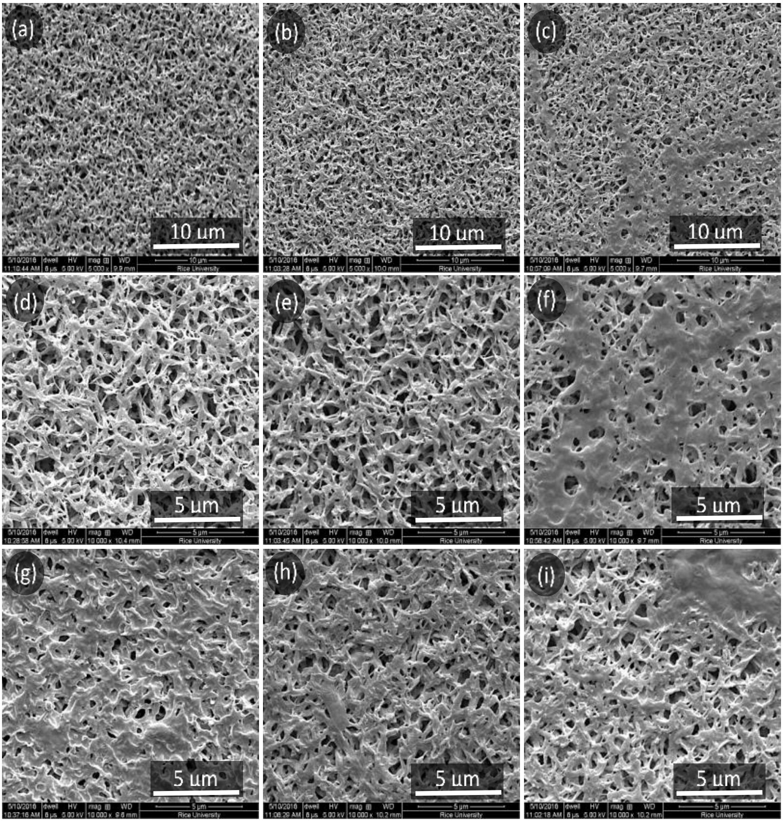


Figure 4.2 shows the ATR-FTIR of the control, MI-T and MI-F membranes. The spectra for both MI-T and MI-F membranes (Figure 4.2(b and c)) presented new peaks at 1208 and 1380 cm^{-1}, which can be assigned to the N-H stretching vibrations of the aliphatic and aromatic amines. A wide absorption band was detected around 1650 cm^{-1}, which can be attributed to the C=C resonance vibration in the aromatic ring, N-H bending vibrations and the CN

bonds between the DA and PEI, due the polymerization process (Schiff base structure) (GUNASEKARAN; KUMAR; PONNUSAMY, 2007; TIAN et al., 2013). In the MI-T membranes, a broadened low intensity band from 3100 to 3500 cm^{-1} was observed, and can be assigned to the N-H/O-H stretching vibrations (YANG et al., 2014a). The ATR-FTIR spectra for both modified membranes show that the peaks presented different intensities. These differences may occur due to the modification method used to produce the membranes. Since the MI-T membranes are immersed in the stirred DA/PEI solution and shaken for 4 h at 50 ± 5 °C, which accelerate the polymerization process, a higher incorporation and growth of the DA/PEI polymeric particles into the membrane pores and on the membrane surface (easy to be detected by the ATR-FTIR) occurs, when compared to the modification method that involves only the permeation of DA/PEI solution. In the MI-F membranes, there is not enough time for growth of DA/PEI polymeric particles on the membrane surface, since the deposition was based on filtration of DA/PEI solution.

Figure 4.2: ATR-FTIR of the (a) control, (b) MI-T and (c) MI-F membranes.

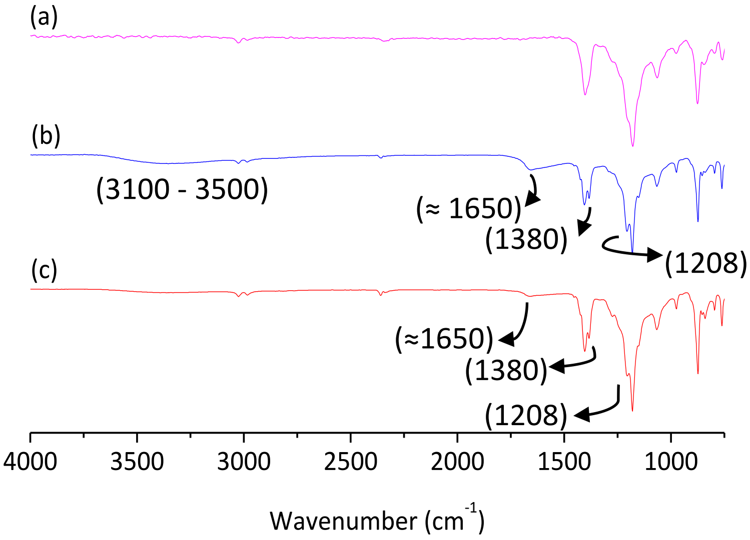
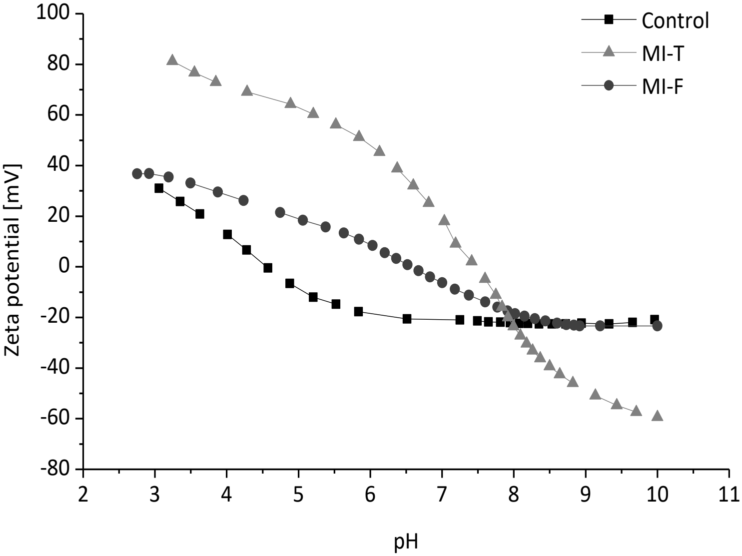


Figure 4.3 shows the surface charges of the control and modified membranes. The control membrane presented a point of

zero charge (PZC) at pH 4.5, and thus is negatively charged above this value. On the other hand, MI-F and MI-T membranes presented PZC at pH 6.5 and 7.5, respectively. The higher difference in the zeta potential of the MI-T membranes when compared with the control membrane also confirms a higher growth of the DA/PEI polymeric chains on the MI-T membrane in comparison with the MI-F membrane.

Figure 4.3: Zeta potential of surfaces of the control, MI-T and MI-F membranes.



4.3.2 Membrane wettability and pH resistance

Membrane wettability of the control, MI-T and MI-F membranes were analyzed by the water weight gain (Figure 4.4) and the dynamic water contact angle (Figure 4.5). As shown in Figure 4.4, the control membranes did not absorb water due to the hydrophobic characteristics of the PVDF membranes. However, after modification, both modified membranes presented more than 200% of water weight gain.

While the control membrane presented a contact angle of 131°, the contact angle of the modified membranes decreased to 0° after some seconds, proving the successful modification of the hydrophobic PVDF membranes into superhydrophilic membranes, and thus agreeing with results presented in the Chapter 3.

Figure 4.4: Water weight gain of the control, MI-T and MI-F membranes.

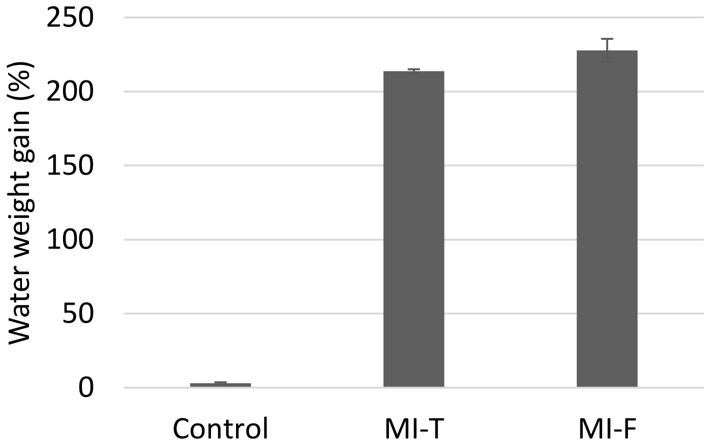
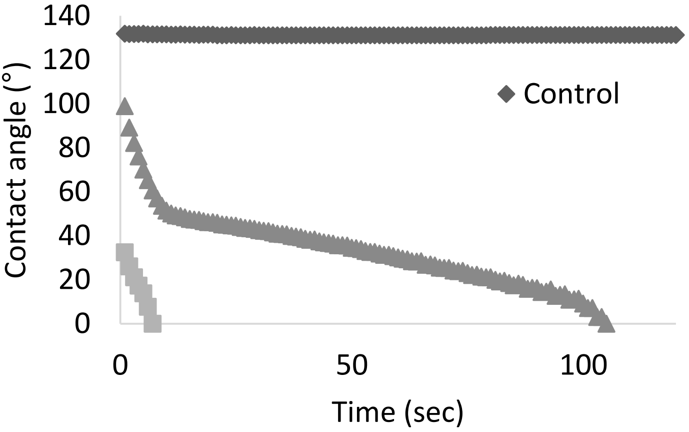
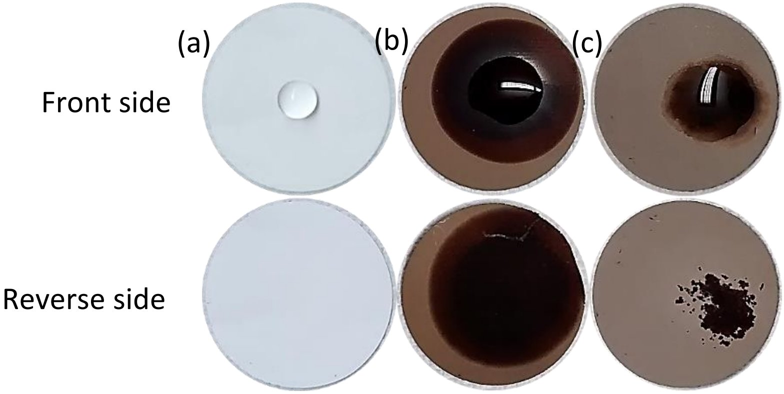


Figure 4.5: Dynamic water contact angle of the control, MI-T and MI-F membranes.



For better visualization of the differences and the behavior of water permeation, Figure 4.6 shows photographic images of a water droplet deposited on the control, MI-T and MI-F membranes surfaces.

Figure 4.6: Photographic images of a water droplet (20 µL) deposited on the (a) control, (b) MI-T and (c) MI-F membranes surfaces. The images were taken 1 min after the droplet deposition.



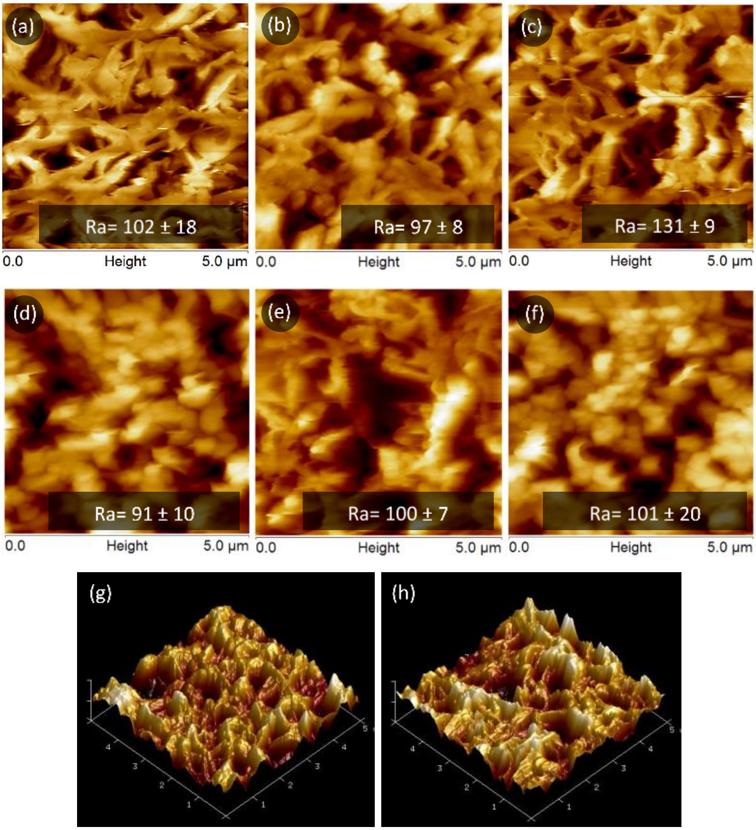
Clearly, there was no water permeation in the control membrane. On the other hand, as shown on the membranes reverse side, the water droplet goes through the modified membranes, especially in the MI-T sample. The different behavior of the water droplet spread on the membrane surface also confirms that dip-coating is more effective for membrane modification by DA/PEI than permeation of solution through the membrane, probably due to higher growth of PDA chain, reaction with PEI and crosslinking of the resulting polymer blend. This could also be the reason for the different behavior found in the contact angle results of the MI-T and MI-F membranes presented in Figure 4.5.

Figure 4.7 shows AFM images of the control, MI-T and MI-F dry and wet membranes. Membrane roughness was not significantly altered (Student's t-Test, 95% confidence level) by DA/PEI coating. However, there is a slight difference in the Ra value between the MI-T and the MI-F dry membranes. In the MI-T membranes the Ra value was close to the value found in the chapter 3 (similar membrane modification method - dip coating), but was a little lower when compared with the MI-F membranes. 3D AFM images of the MI-T and MI-F membranes (4.7(g and h)) were generated for better understanding this issue.

Since the MI-T membranes modification involves the membrane immersion in the DA/PEI solution for a determined time, the polymeric chains present in the DA/PEI stirred solution have enough time to react and create a uniform polymeric network on the membrane surface, decreasing the membrane roughness, as shown in Figure 4.7(g). In the case of MI-F membranes, the higher surface roughness may be due to the non-uniform deposition of the PDA/PEI polymeric chains (Figure 4.7(h)).

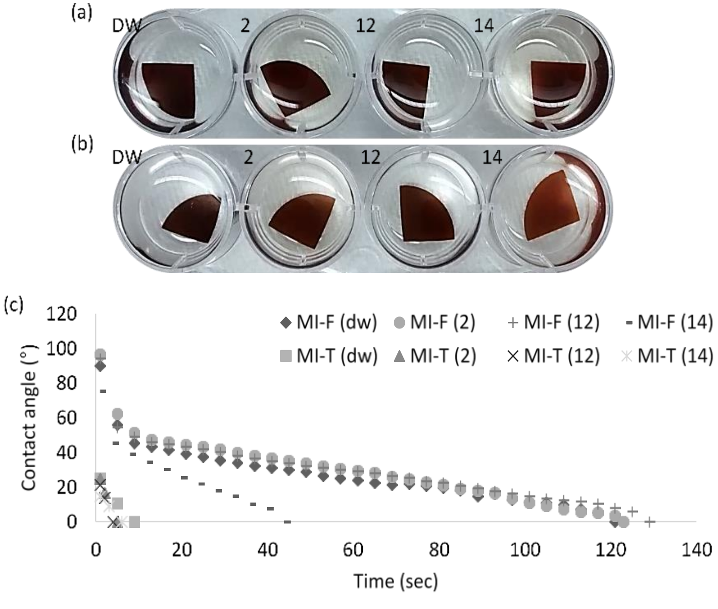
The AFM results with wet membranes (Figure 4.7(d, e and f)) presented similar Ra values. The control membranes did not show statistically significant difference in the roughness when compared with the modified membranes. These results suggest that the high water uptake presented by the MI-T and MI-F membranes was not proportioned by a possible membrane swelling.

Figure 4.7: 2D AFM images of the (a) control, (b) MI-T and (c) MI-F dry membranes; (d) control, (e) MI-T and (f) MI-F wet membranes, and 3D AFM images of the (g) MI-T and (h) MI-F dry membranes, respectively.



The pH resistance of the modified membranes was evaluated by soaking the membranes in deionized water and in solutions with pH 2, 12 and 14 (Figure 4.8). As shown in Figure 4.8(a and b), both modified membranes did not dye the aqueous solution, even in pH 14, suggesting that the modified membranes are very resistant to pH variations. The dynamic water contact angles before and after 24 h of immersion in water at different pH are presented at Figure 4.8(c). No detrimental changes in the membrane wettability were observed, proving that both modified membranes have an excellent pH resistance. The different behavior seen in the Figure 4.8(c) for the MI-F membrane after the treatment with pH 14 is due to the non-uniform deposition of the DA/PEI molecules on the membrane surface, facilitating or not the water permeation.

Figure 4.8: pH resistance of modified membranes. (a) MI-T membranes, (b) MI-F membranes and (c) water contact angle of MI-T and MI-F membranes after 24 h immersed into the different solutions.

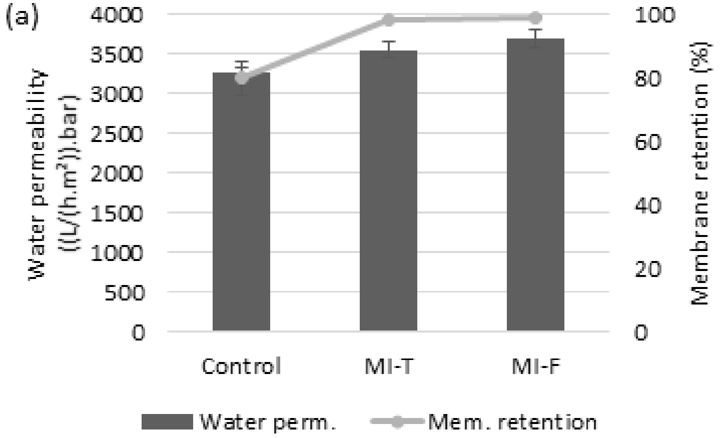


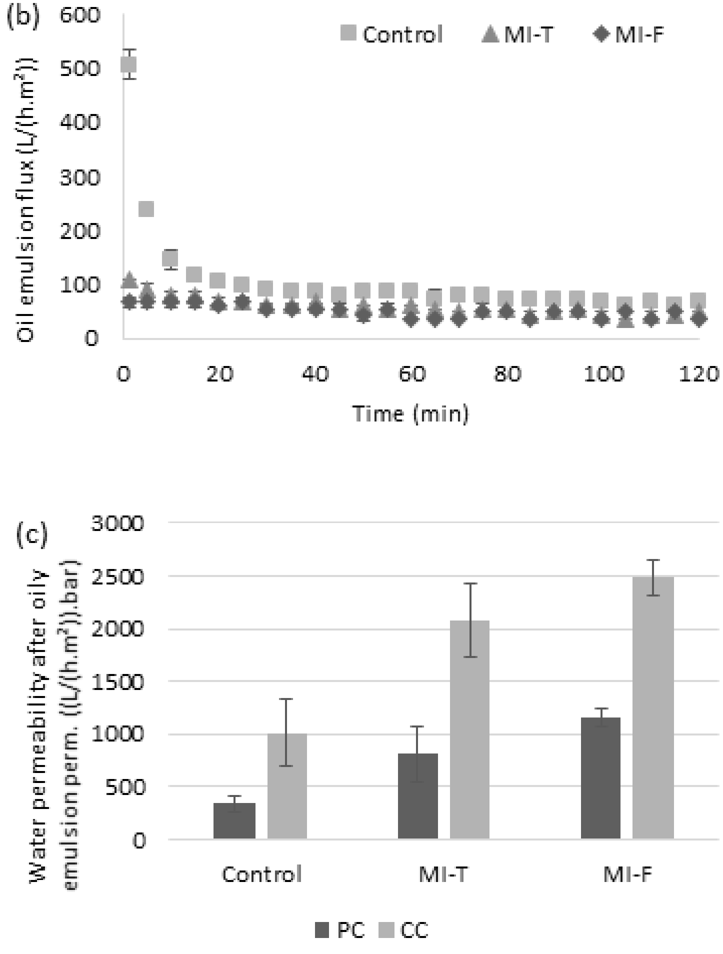
4.3.3 Separation process performance of the control, MI-T and MI-F membranes

Figure 4.9 shows the separation process performance of the control, MI-T and MI-F membranes in the treatment of the canola oil emulsion. The results of the control membrane are the same presented in the previous study (Chapter 3). Figure 4.9(a) shows the initial water permeability and the oil emulsion retention of tested membranes. The modified membranes presented an increase in the initial water permeability when compared with the control membrane. Oil retentions also increased from 80% (control) to 100% (modified membranes).

The oil emulsion flux (Figure 4.9b) varied among the membranes samples. The control membranes presented the highest initial flux, due to the lower retention, with a sharp decline during the first minutes, consequence of the high interaction between the hydrophobic PVDF membranes with the oil emulsion (hydrophobic character). On the other hand, MI-T membranes presented a slight flux decline in the beginning of the permeation, while MI-F membranes presented a constant flux during all microfiltration process.

Figure 4.9: Process performance of control, MI-T and MI-F membranes applied in the separation of canola oil emulsions. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures.



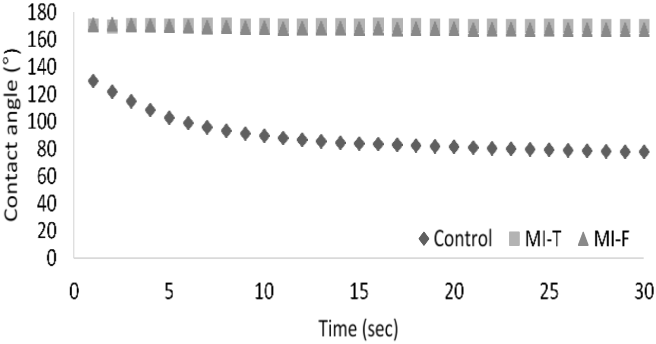


The water permeability after the oil emulsion permeation was carried out after the physical and chemical cleaning procedures (Figure 4.9(c)). Clearly, for both cleaning procedures, the modified membranes presented higher values of water permeability when compared with the control membranes, achieving to the MI-F membranes an increase around 250 %. SEM images of the fouled control, MI-T and MI-F membranes presented in Figure 4.1(g, h and

i) show an evident difference between the control and the modified membranes. After the cleaning procedures, the control membrane appears fully covered by the oil (Figure 4.1(g)). On the other hand, many pores continue unblocked on MI-T and MI-F membranes' surface (Figure 4.1(h and i)), facilitating the water permeation. These results confirm that the modified membranes presented antifouling characteristics to hydrophobic molecules.

To explain the improvement in the separation process of the oil emulsion by the modified membranes, dynamic underwater oil contact angles of the control, MI-T and MI-F membranes were carried out, and results are shown in Figure 4.10. It is evident the difference in the dynamic underwater oil contact angle between the control and the modified membranes. Due to the hydrophobic character of the PVDF, the oil droplet tend to interact with the control membrane resulting in a contact angle lower than 90°. On the other hand, the superhydrophilic membranes presented an underwater oil contact angle around 170°, agreeing with others studies (GAO et al., 2014b; ZHANG et al., 2013). These results, and the membrane retention presented in Figure 4.9a, suggest that when the MI-T and MI-F membranes are wetted by water, a hydration layer is formed and bound onto the surface, decreasing the interaction of the membrane surface with the oil emulsion, thus repelling the oil, and consequently improving the membrane process performance, as discussed in Chapter 3.

Figure 4.10: Dynamic underwater oil contact angle of the control, MI-T and MI-F membranes.



4.4 Conclusion

This study aimed to suggest two different approaches to accelerate the modification of PVDF hydrophobic membranes into superhydrophilic membranes for oily emulsion separations using the mussel-Inspired method with dopamine and polyethyleneimine. The results of FTIR and zeta potential of the modified membranes confirmed that the PVDF microfiltration membranes were successfully modified by both methods. The MI-T and MI-F membranes proved to be resistant to pH from 2 to 14 and presented excellent results of dynamic water contact angle and wettability. The differences in the behavior of the dynamic contact angle, photographic images of a water droplet deposited on the membrane surface and the roughness of dry modified membranes were proportioned by the DA/PEI cluster formation on the MI-F surface membrane and by the crosslink network of the polymer chains on the MI-T membrane surface. The good results of initial water permeability, flux of the canola oil emulsion, membrane retention and water permeability after physical and chemical cleaning procedures proved that the modified membranes can be effectively used to treat oil emulsion at low pressures. Lastly, both approaches of the mussel-inspired method proved to accelerate the modification of hydrophobic membranes into superhydrophilic membranes without losing the efficiency in the treatment of oily emulsions when compared with the usual dip-coating modification (Chapter 3). Both membranes proved to be a good alternative for the treatment of oily emulsions, due to the low interactions between the superhydrophilic membrane and the hydrophobic oil molecules.

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5 EFEITO DO PRÉ-TRATAMENTO DA EMULSÃO OLEOSA COM CAMPO MAGNÉTICO NO PROCESSO DE SEPARAÇÃO COM MEMBRANAS SUPERHIDROFILICAS E AVALAIAÇÃO DO DESEMPENHO DA PERMEAÇÃO EM UM SISTEMA DE FILTRAÇÃO TANGENCIAL

Esse capítulo refere-se à avaliação efeito do pré-tratamento da emulsão de óleo com campo magnético antes do processo de permeação em membranas de PVDF hidrofóbicas e superhidrofílicas e avaliação do desempenho da permeação em um sistema de filtração tangencial. O desenvolvimento deste capítulo foi realizado na Universidade Federal de Santa Catarina, UFSC. Este estudo atende aos objetivos específicos descritos na seção 1.1.2 (Capítulo 5): avaliar o desempenho das membranas modificadas aplicadas na permeação de emulsões oleosas em um sistema de filtração tangencial, contrastando com os resultados obtidos em filtração convencional (ou frontal); avaliar o efeito da indução magnética da emulsão oleosa sobre o desempenho da microfiltração.

Na sequência está apresentado o trabalho completo realizado neste capítulo em formato de artigo.

Effect of the oil emulsion pre-treatment with magnetic field in the separation process with superhydrophilic membranes and evaluation of the permeation performance in a cross-flow filtration system

Abstract

Membrane separation process (MSP) have attracted large attention recently but drawbacks as permeability reduction caused by concentration polarization and fouling continue to be the greater disadvantage in this process. The aim of the present work is to evaluate the effect of the oil emulsion pre-treatment with magnetic field on the MSP and the performance of PVDF hydrophobic and superhydrophilic membranes in a cross-flow filtration system. The magnetic induction of the oil emulsion was performed by the circulation of the oil emulsion through a magnetic field provided by two magnets (magnetic flux density equal to 0.7 and 1.4 T). The process performance in the cross-flow filtration system and in the permeation of the oil emulsion magnetically induced was evaluated by the initial water permeability, canola oil emulsion flux, membrane retention and water permeability after the physical and chemical cleaning procedures varying the turbulence in the permeation module. The results were also compared with results found in permeations carried out in dead-end filtration system. The magnetic induction of the oil emulsion did not alter the results of the permeation process of the membranes and the use of higher turbulence in the permeation module proved to be essential to a good membrane performance.

KEYWORDS: Membrane separation process; magnetic field; oil emulsion permeation; cross-flow filtration system; dead-end filtration system.

5.1 Introduction

Clean sources of water and wastewater treatment are always a challenge to be developed. Due to this and the difficulty of investments to implant new process, many treatments not environmentally friendly continues to be used in several industries. In this scenario membrane separation process (MSP) appears as an alternative to clean technologies (PADAKI et al., 2015).

MSP have attracted large attention due its high separation efficiency, relative low energy consumption, easy scale-up and to present low use of chemicals (LUJÁN-FACUNDO et al., 2015; YANG et al., 2015). However, improvements in the process are necessary once some drawbacks as concentration polarization and fouling makes the MSP infeasible to many kinds of applications (CHERYAN; RAJAGOPALAN, 1998; PADAKI et al., 2015; SAXENA et al., 2009).

In order to minimize this undesirable phenomenon, chemical and physical approaches have been studied and applied to MSP (LI et al., 2014a, 2014b, 2014c; MOGHIMIFAR; RAISI; AROUJALIAN, 2014; RAZMJOU; MANSOURI; CHEN, 2011; RAZMJOU et al., 2012; VARDANEGA et al., 2013; WU; YU; LI, 2015; YU et al., 2011; ZOU et al., 2011). Membrane cleaning with chemicals may be an efficient cleaning procedure, but may damage the membrane and create new wastewater to be treated (ZHANG; MA, 1999). Other chemical approach is the membrane modification as discussed in chapters 3 and 4.

Physical techniques are considered an attractive strategy for fouling control, since they are clean and not intrusive approaches. Among these strategies, some can be highlighted as the use of turbulence generating devices, sonication, centrifuge, backflusing/backpulsing, air sparging and the use of electric and magnetic fields (AL-QAHTANI, 1996; CARLESSO et al., 2016; LI et al., 2007; LONG et al., 2005; OHATA; TOMITA; IKADA, 2004; VARDANEGA et al., 2013; VEDAVYASAN, 2001; ZIN et al., 2016).

The use of magnetic fields have some advantages such as low cost, low power consumption, simple operation and low environmental impact (GABRIELLI et al., 2001; VEDAVYASAN, 2001). In MSP, some studies involving inorganic solutions evidenced that application of a magnetic field to the feed solution can decrease membrane fouling formation on reverse osmosis membranes in the treatment of brackish water (SCHLÜTER, 2014); help in reducing carbonate deposition in membrane distillation processes (GRYTA, 2011); and, improve nanofiltration and reverse osmosis membranes performance by changing the salt growing and its crystalline form (BAKER; JUDD; PARSONS, 1997; LI et al., 2007; LONG et al., 2005; OHATA; TOMITA; IKADA, 2004; VEDAVYASAN, 2001). In ultrafiltration, the magnetic field promoted a greater water permeability recovery after the treatment of carboxymethylcellulose/sodium sulfate solutions (CARLESSO et al., 2016) and when applied to protein solutions increased the permeate flux and the water permeability after physical and chemical cleaning procedure (SILVA, 2015; VARDANEGA et al., 2013; ZIN et al., 2016).

According with the exposed above and the lack of studies in the literature on which the modified membranes by the mussel-inspired method are permeated in a cross-flow filtration system, this work aims to evaluate the performance of the PVDF modified membrane by the mussel-inspired method (presented at chapter 3) in a cross-flow filtration system and the effect of the oil emulsion pre-treatment with magnetic field on the MSP.

5.2 Materials and methods

5.2.1 Material

Poly(vinylidene difluoride) (PVDF) microfiltration membrane with 0.1-µm pore size was supplied by Pall Corporation (NY, USA). As a pretreatment, membranes were cut into small pieces and immersed in ethanol (99.5%, Koptec, PA, USA) for 2 h, rinsed with ultrapure water several times and soaked in ultrapure water overnight.

Dopamine hydrochloride (DA) and polyethylenimine (PEI, Mw = 800) were purchased from Sigma-Aldrich (USA) and tris(hydroxymethyl)aminomethane (TRIS-HCl, pH = 8.5, 1 mol.L^{-1}) from Teknova (CA, USA). Canola oil was purchased from a local market and Tween 80 from Sigma-Aldrich (USA) were used to make the oil emulsions.

5.2.2 Methods

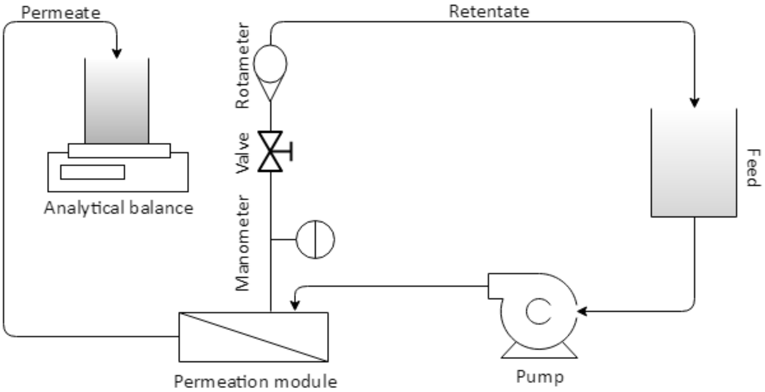
5.2.2.1 Membrane modification

Pre-treated PVDF membranes with 0.1-µm pore size were immersed into a fresh solution of DA and PEI and shaken for 24 h at 25 °C. The DA/PEI solution was prepared by the dissolution of 0.5 mg.mL^{-1} of DA and 1 mg.mL^{-1} of PEI in a Tris buffer solution 50 mmol.L^{-1} at pH = 8.5. As a final step, the membranes were rinsed several times with ultrapure water and dried in a vacuum oven for 2 h at 40 °C.

5.2.2.2 Membrane performance

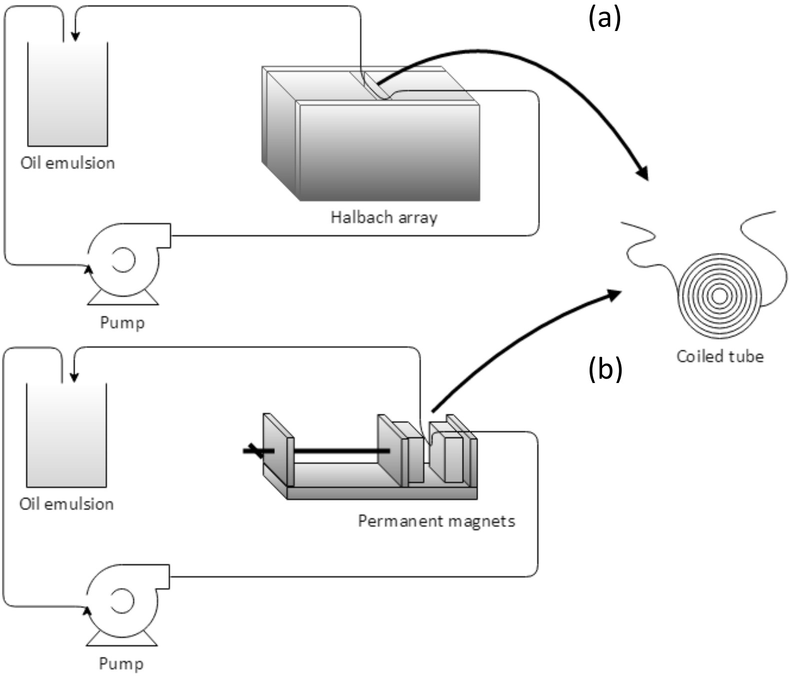
The water permeability and the oil emulsions permeation of the control and modified membranes were carried out with a lab-scale cross-flow permeation system with effective membrane area of 29 cm^2 (Figure 5.1).

Figure 5.1: Schematic diagram of the cross-flow permeation system.



Before permeations, as a membrane pre-treatment, the modified membranes were soaked into ultrapure water overnight and the control membranes were soaked into anhydrous ethanol for 2 h followed by the immersion also in ultrapure water overnight. The experimental procedure was carried out by the following steps: initial water permeability; oil emulsion permeations; and the water permeability after physical and chemical cleaning procedures. All water permeabilities were obtained after membrane compaction at flow rate of 0.3 L.min^{-1} and varying the pressure from 1 to 0.5 bar. The fouling tests were carried out with oil emulsions made with 0.1% (w_{oil}/w_{H2O}) of canola oil and 20 % (w_{T80}/w_{oil}) of Tween 80 as an emulsifier. Firstly, a coarse emulsion was formed with magnetic stirring for 3 min at 2000 rpm, followed by probe sonication at 90 W for 3 min (30 s on and 10 s off) under magnetic stirring at 900 rpm. The average droplet size of the resulting emulsion was 0.154 ± 0.001 µm. The oil emulsion permeation was carried out in two different ways, the standard procedure (control) and the permeation of the oil emulsion magnetically induced (OEMI). The induction consisted in flowing the oil emulsion in a coiled tube positioned inside the gap of a Halbach array (1 cm) or inside the gap of a magnetic field device made with two parallel permanent magnets at flow rate of 0.3 L.min^{-1} for 2 h, before the permeation process. The flux density at the central point of the Halbach array and at the central point of the magnetic field device was 1.4 and 0.7 T, respectively. Figure 5.2 shows the schematic diagram of the magnetic induction of the oil emulsion.

Figure 5.2: Schematic diagram of the magnetic induction of the oil emulsion in the (a) Halbach array and in the (b) permanent magnets.



In order to avoid some wrong evaluation of the permeation carried out with the OEMI, to the control experiments was also performed the oil emulsion circulation in the coiled tube, but without the presence of the magnetic field devices. The oil emulsion permeation was carried out for 120 min at constant pressure of 0.5 bar, feed flow rate of 0.3 L.min^{-1} and pH 5.44 ± 0.07. Permeate flux was determined each 15 min. As a final step, the physical and chemical cleaning procedures were performed at flow rate of 0.3 L.min^{-1} without pressure. In the physical procedure, the system was rinsed with 5 L of ultrapure water and the chemical cleaning procedure was performed by circulating a NaOH solution pH 10 with subsequent circulation of HCl solution pH 4.0, both for 30 min. After each solution change, the system was rinsed with 5 L of ultrapure water.

5.2.2.3 Emulsion analysis

Droplet size and zeta potential measurements of the oil emulsion were determined by Zetasizer Nano ZS3600 (Malvern Instruments Ltd., UK) and the membrane oil emulsion retention were measured by UV-visible spectrophotometer at 240 nm (UV-2550, Shimadzu, Japan).

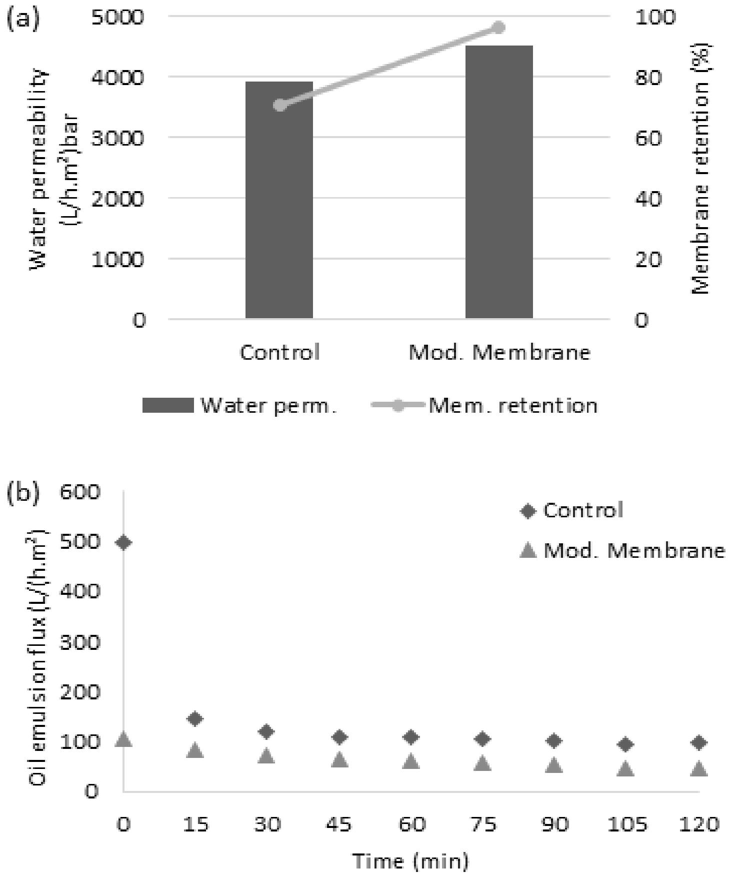
5.3 Results and discussion

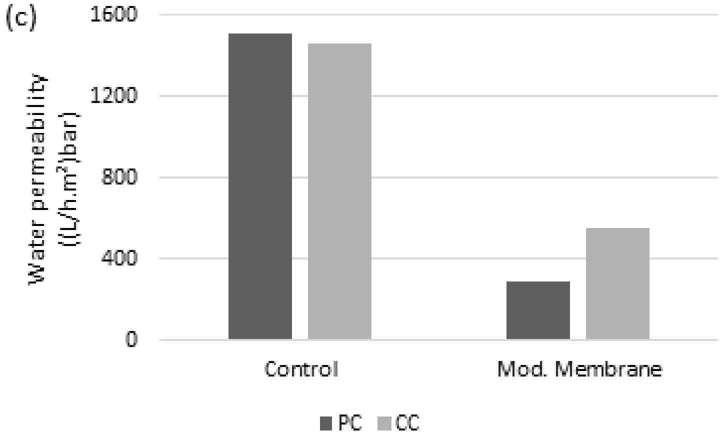
5.3.1 Performance of the modified membrane by the Mussel-inspired method in a cross-flow filtration system

In order to investigate the behavior of the modified membranes in a cross-flow filtration system, Figure 5.3 shows the permeation performance of control and modified membranes in the separation of canola oil emulsion. Figure 5.3(a) shows the water permeability and the membrane retention of the control and modified membranes. The modified membrane presented a higher water permeability in comparison with the control membrane and, as expected, and higher levels of membrane retention.

Comparing the results obtained in the cross flow cell with the results of the permeation assays carried out in the dead-end filtration (chapter 3), both control and modified membranes presented some increase in the water permeability. This increase may be due to the compaction process, since in the dead-end filtration the membrane compaction was carried out in 2 bar and when used the cross-flow system the pressure was 1 bar. Another point that the membrane compaction may have influenced was in the membrane retention of the control membranes. The control membranes in the cross-flow system presented a retention up to 70 %. On the other hand, with the higher compaction pressure used in the dead-end assays, the control membranes presented 80 % of retention.

Figure 5.3: Permeation performance of control and modified membranes in the separation of oil emulsions in a cross-flow filtration system. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures.



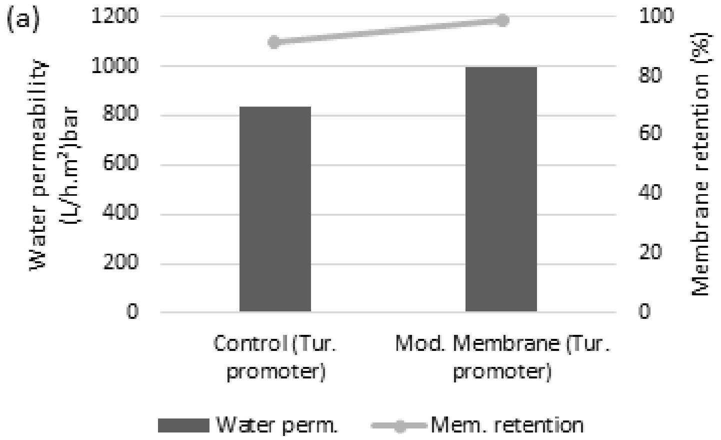


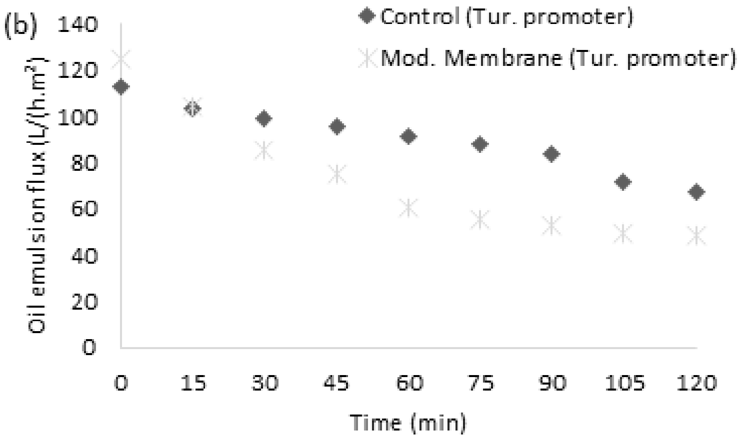
The behavior of the oil emulsion flux of the control and modified membranes (Figure 5.3(b)) was similar to the results presented to the dead-end filtrations. For the control membrane, a sharp decline in the beginning of the permeation was observed, and after 20 min to both membranes, the oil emulsion flux reached similar values up to the end of the permeation assay. A slightly higher oil emulsion flux was observed for the control membranes when compared with the modified ones, and with the control membranes used in the experiments carried out in the dead-end filtration. This higher flux is caused by the lower membrane retention, which makes easier for the oil emulsion goes through the membrane.

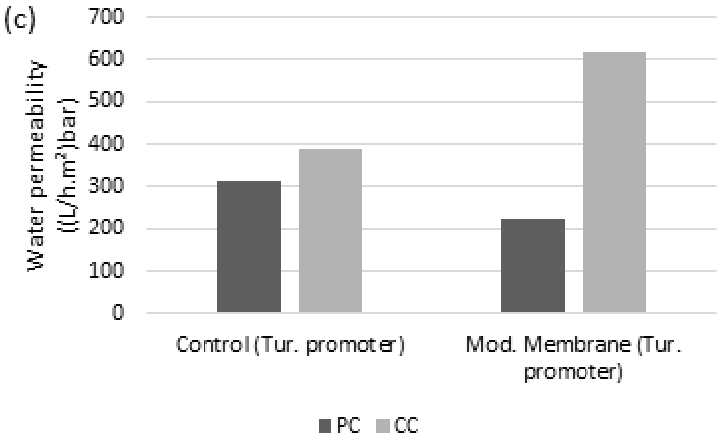
Differently from the results found in the permeations carried out with dead-end filtrations, in the cross-flow permeations assays, the water permeability of the modified membrane after physical and chemical cleaning procedures (Figure 5.3(c)) presented lower values in comparison with the control membranes. These differences may be explained due to the laminar flow presented by the cross-flow permeation module, which had a Reynolds number of 303, calculated based on operation parameters. Since the modified membranes are superhydrophilic, and possibly create a hydration layer on the membrane and pore surfaces when wetted, as discussed in chapter 3, the use of turbulent flow is essential to decrease the membrane fouling. It is important to highlight that the chemical cleaning procedure increased the water permeability recovery of the modified membrane, while the same behavior was not observed for the control membrane.

Figure 5.4 shows the permeation performance of the control and modified membrane in the separation of canola oil emulsion using a turbulence promoter (mesh-shape feed spacer used in nanofiltration membranes) placed on the membrane surface.

Figure 5.4: Permeation performance of control and modified membranes in the separation of oil emulsions in a cross-flow filtration system using the turbulence promoter. (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures.







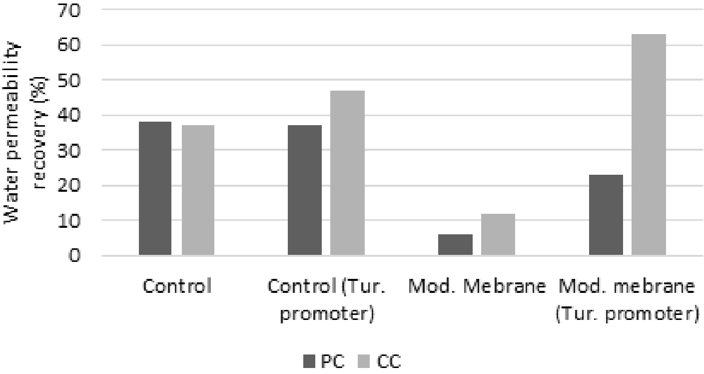
The initial water permeability for the control and modified membranes using the turbulence promoter (Figure 5.4(a)) decreased around 78 % in comparison with the results presented without the turbulence promoter (Figure 5.3(a)). These lower values of initial water permeability were attributed to the decreasing of 50 % in the effective membrane area plus a possible localized head loss in the permeation module when using the turbulence promoter. In turn, higher membrane retentions were found when the turbulence promoter was used.

The characteristic sharp decline in the beginning of the oil emulsion permeation presented by all the control membranes so far, was not observed to the control membrane when was used the turbulence promoter, as shown at Figure 5.4(b). As discussed in the previous paragraph the pressure drop in the permeation module makes the oil emulsion retention of the control membrane increase from 70 % (experiments without the turbulence promoter) to 90 % (experiments with the turbulence promoter) which decreased the high oil emulsion flux observed in the beginning of the permeation when the membrane was clean. Thus, the behavior of the oil emulsion flux from the beginning up to the end of the permeation assays were similar.

Figure 5.4(c) shows the water permeability after the physical and chemical cleaning procedure using the turbulence promoter. In this scenario, differently from the results found to the cross-flow experiments without the turbulence promoter, the modified membrane shows up with a higher water permeability recovery after the chemical cleaning procedure in comparison with the control membrane.

Figure 5.5 shows the water permeability recovery after the physical and chemical cleaning procedures for the experiments carried out with and without the turbulence promoter. The percentages of water permeability recoveries were taken dividing the values of the water permeability after the physical and chemical cleaning procedures by the values of the initial water permeability.

Figure 5.5: Water permeability recovery of the control and modified membranes in a cross-flow permeation system with and without the turbulence promoter.



The water permeability recovery of the control membranes (with or without the turbulence promoter) was the same after the physical cleaning and an increased 10 % after the chemical cleaning using the turbulence promoter. In turn, for the modified membranes there was a large difference in the water permeability recovery when the turbulence promoter was used, as shown in Figure 5.5. After the physical cleaning, the water permeability recovery increased from 6 to 23 %, and after the chemical cleaning from 12 to 63 %. The same evaluation in the experiments carried out in the dead-end filtrations (chapter 3) yielded water permeability recovery after the physical and chemical cleaning procedures of 11 and 31 % for the control, and 27 and 67 % for the modified membranes, respectively.

When the turbulence promoter was used in the cross-flow system, it presented similar water permeability recovery at the end of the cleaning as that obtained in the dead-end system.

The high improvement in the process performance of the modified membrane when the turbulence promoter was used proved that to the superhydrophilic membranes, where the creation of a hydration layer is the mainly responsible for the good membrane performance, the use of turbulence devices plays an important role since it helps the hydration layer work properly, decreasing the contact of the oil droplets with the membrane surface and consequently decreasing the fouling.

5.3.2 Performance of the control and modified membrane in the permeation of the oil emulsion pretreated with different magnetic fields

Size of the oil droplets and zeta potential of the oil emulsion were determined before permeations, with the purpose to choose the time of the oil emulsion circulation through the magnetic field and to investigate the effect of the magnetic induction on the emulsion (Table 5.1 and 5.2).

Table 5.1: Oil droplet sizes of emulsions magnetically induced in flux densities 0.7 and 1.4 T, in different times.

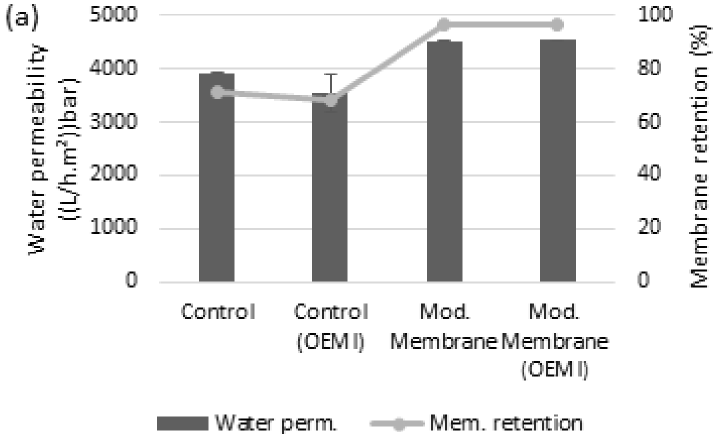
Time (min)	**Size (d.µm)**		
	Without MF	**0.7 T**	**1.4 T**
0	0.153 ± 0.001	0.153 ± 0.001	0.154 ± 0.001
30	0.152 ± 0.002	0.153 ± 0.003	0.153 ± 0.003
60	0.154 ± 0.002	0.154 ± 0.002	0.154 ± 0.002
90	0.155 ± 0.002	0.153 ± 0.002	0.155 ± 0.001
120	0.153 ± 0.001	0.152 ± 0.009	0.154 ± 0.002

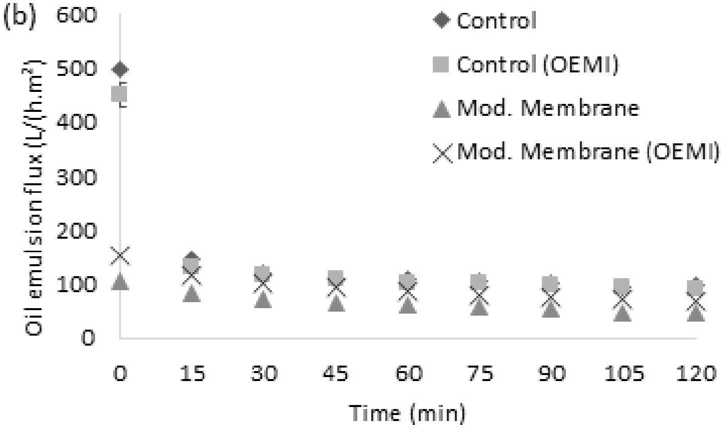
Table 5.2: Zeta potentials of emulsions magnetically induced in flux densities 0.7 and 1.4 T, in different times.

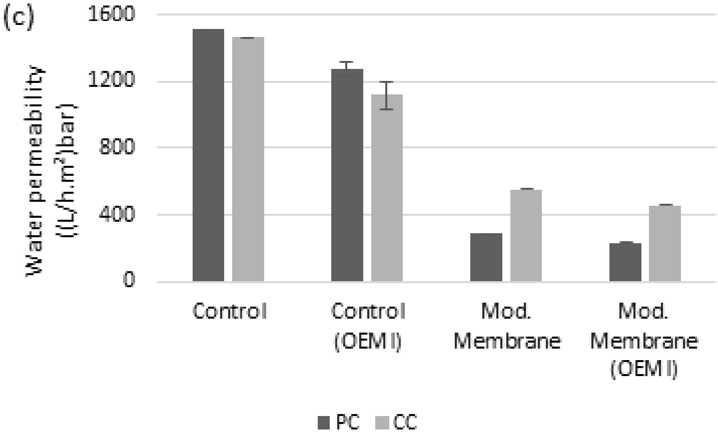
Time (min)	**Zeta potential (mV)**		
	Without MF	**0.7 T**	**1.4 T**
0	-19.5 ± 0.9	-20.9 ± 1.0	-20.2 ± 0.8
30	-28.1 ± 1.2	-30.2 ± 0.8	-31.1 ± 0.9
60	-27.9 ± 0.7	-30.5 ± 1.5	-32.4 ± 2.2
90	-28.4 ± 0.8	-28.0 ± 0.9	-32.3 ± 1.2
120	-28.5 ± 0.2	-28.7 ± 0.1	-31.9 ± 1.8

According to Tables 5.1 and 5.2, the magnetic field did not present any significant effect on oil droplets size and zeta potential of the emulsions. Although no changes in oil droplet size and zeta potential were detected, permeations with canola oil emulsion magnetically induced for 2 h in the Halbach array (1.4 T) were performed to verify if the magnetic field would improve the process. Figure 5.6 shows the permeation performance of control and modified membranes in the separation of canola oil emulsion magnetically induced. The results found to the permeations of the oil emulsion magnetically induced (Figure 5.6) presented similar values and behavior of the experiments carried out without the magnetic induction (already discussed in the previous section 5.3.1 at Figure 5.3). Thus, the use of the magnetic field as a pre-treatment of the oil emulsion did not improve the permeation performance as observed to other solutions (VARDANEGA et al., 2013; ZIN et al., 2016).

Figure 5.6: Permeation performance of control and modified membranes in the separation of oil emulsions and oil emulsions magnetically induced (OEMI). (a) Initial water permeability and membrane retention, (b) flux of canola oil emulsion and (c) water permeability after physical (PC) and chemical (CC) cleaning procedures.







5.4 Conclusion

This work aimed to compare the performance of the superhydrophilic membrane modified by the mussel-inspired method in a cross-flow and dead-end filtration systems, and the effect of the oil emulsion pre-treatment with magnetic field on permeation. The modified membranes in a cross-flow system with laminar flow presented higher initial water permeability and membrane retention, lower oil emulsion flux and lower values of water permeability after the physical and chemical cleaning procedures when compared with the control membranes. Comparing the results of the cross-flow system with laminar flow with the dead-end filtrations (essentially in turbulent condition), the modified membranes presented a much lower water permeability after the physical and chemical cleaning procedures. However, when the turbulence inside of the permeation module was increased, the modified membrane presented similar oil emulsion flux, and a higher water permeability after the chemical cleaning procedure than with the control membrane. The use of a turbulence promoter in the cross-flow system restored the water permeability recovery to the same obtained in the dead-end system. These results support the hypothesis that, for superhydrophilic membranes, the hydration layer created on the membrane surface is the mainly responsible fouling decrease. The permeation of the oil emulsion magnetically induced did not alter the microfiltration performance of the control and modified membranes.

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6 CONCLUSÕES

O presente trabalho desenvolveu e estudou estratégias anti-incrustações na microfiltração de emulsões oleosas baseada na modificação da superfície da membrana (MSM) e no uso de campo magnético (CM).

O método de modificação de membrana *mussel-inspired* (MI) utilizando dopamina (DA) e polietilenoimina (PEI) mostrou ser dependente do tempo de deposição e um mínimo de concentração dos componentes (0,25 $mg.mL^{-1}$ de DA e 0,25 $mg.mL^{-1}$ de PEI) é necessária para a modificação das membranas com as características desejadas. As membranas modificadas com DA e PEI apresentaram excelente molhabilidade, baixo ângulo de contato (0° após 3 segundos da deposição da gota de água - membranas modificadas com 24 h de tempo de deposição e concentração de DA:PEI de 0,5:1 $mg.mL^{-1}$) e resistência a soluções com pH variando de 2 a 14. Comparada à membrana controle (sem modificação), a membrana modificada apresentou excelente desempenho na permeação da emulsão oleosa, apresentando uma maior retenção de óleo e maiores valores de permeabilidade hidráulica após os procedimentos de limpeza física e química. Uma possível explicação para a melhoria do processo foi a criação de uma camada de hidratação na superfície da membrana quando esta encontra-se molhada, dificultando o contato das gotas de óleo com a membrana, diminuindo a incrustação.

As variações do método MI para acelerar o processo de modificação das membranas mostraram-se eficazes uma vez que a hidrofilicidade e o desempenho da permeação da emulsão oleosa apresentaram resultados semelhantes aos da membrana modificada pelo método MI usual. No método realizado pela imersão da membrana na solução de DA/PEI (MI-T) o tempo de deposição passou de 24 h para 4 h, já para a outra variação do método realizada (MI-F), apenas a filtração da solução da DA/PEI foi suficiente para a obtenção das membranas superhidrofílicas.

O desempenho das membranas modificadas utilizando o sistema de filtração tangencial mostrou que para as membranas modificadas, onde a camada de hidratação criada na superfície da membrana é o principal responsável pela diminuição da incrustação, o uso de sistemas com maior turbulência é essencial para o bom desempenho da permeação.

Por sua vez, o pré-tratamento da emulsão oleosa com campo magnético como estratégia anti-incrustação em processos de separação com membranas não alterou o desempenho da permeação para ambas as membranas utilizadas (controle e modificada).

6.1 Sugestões para trabalhos futuros

- Permear soluções/emulsões com solutos de diferentes características (hidrofobicidade e tamanho molecular) e diferentes pH e concentração salina através de membranas de microfiltração modificadas, a fim de estudar o comportamento da camada hidratada sobre o processo de separação com membrana;
- Modificar membranas pelo método *mussel-inspired* com a adição de compostos inorgânicos e/ou novos compostos orgânicos;
- Estudar o mecanismo de ligação da dopamina/polidopamina em diversos substratos.