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RECICLAGEM DE MEMBRANAS DE OSMOSE INVERSA  
POR OXIDAÇÃO QUÍMICA E POSSÍVEIS APLICAÇÕES

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# RECICLAGEM DE MEMBRANAS DE OSMOSE INVERSA POR OXIDAÇÃO QUÍMICA E POSSÍVEIS APLICAÇÕES

Fábio Ivan Seibel

Relatório de Defesa Final apresentado ao Programa de Pós-Graduação em Engenharia Civil e Ambiental, da Faculdade de Engenharia e Arquitetura da Universidade de Passo Fundo, como requisito para obtenção do título de Mestre em Engenharia.

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## RESUMO

A demanda por água potável tem aumentado devido ao crescimento populacional e às necessidades das atividades antrópicas para sustentar essa população. Para atender a essa demanda, um número crescente de usinas de dessalinização por osmose inversa estão sendo instaladas e operadas. Porém, as membranas de osmose inversa tendem a atingir o final do ciclo de vida em torno de dois a cinco anos, quando se tornam resíduos sólidos, necessitando de destinação adequada, gerando custos adicionais. Portanto, estender o ciclo de vida das membranas de osmose inversa é uma necessidade do ponto de vista ambiental e econômico. Estudos indicam que a recuperação de membranas de osmose inversa para a mesma função ainda não é viável, contudo, é possível transformá-las em membranas menos seletivas, sendo uma abordagem para valorizar esse resíduo sólido. Estudos anteriores indicam a possibilidade de transformar membranas de osmose inversa em membranas de nanofiltração e / ou ultrafiltração utilizando agentes oxidantes que removem parcialmente a camada seletiva da membrana. A maioria dos trabalhos publicados nessa linha de pesquisa carecem de estudo de possíveis aplicações para as membranas produzidas. Este trabalho teve como objetivo transformar membranas de osmose inversa através da oxidação da camada seletiva com hipoclorito de sódio em membranas de menor seletividade, bem como buscar possíveis aplicações para as membranas recicladas. Os resultados demonstram que as membranas oxidadas a 10.000 ppm.h tiveram um aumento significativo na permeabilidade, mas diminuíram a rejeição à condutividade elétrica e ao acetaminofeno. As análises por Microscopia Eletrônica de Varredura (SEM) e Microscopia de Força Atômica (AFM) demonstram o impacto do ataque pelo cloro na superfície da membrana, e a análise por Espectroscopia de Refletância por Transformada de Fourier (FTIR) sugere que a oxidação do cloro substituiu o hidrogênio do nitrogênio da amida, mas a camada de poliamida não foi totalmente degradada. Os testes de aplicação sugerem que a membrana reciclada pode ser utilizada para o tratamento de água salobra e superficial. A reciclagem das membranas de osmose inversa pode ser uma alternativa para dar uma segunda vida útil às mesmas, inserindo-as em um maior ciclo de valorização econômica.

Palavras-chave: osmose inversa, oxidação, transformação, valorização.

## ABSTRACT

The demand for drinking water has increased due to population growth and the needs for human activities to support this population. To meet this demand, an increasing number of reverse osmosis desalination plants are being installed and operated. However, reverse osmosis membranes tend to reach the end of the life cycle in around two to five years, when they become a solid waste, requiring proper disposal, generating additional costs. Therefore, extending the life cycle of reverse osmosis membranes is a necessity from an environmental and economic point of view. Studies indicate that the recovery of reverse osmosis membranes for the same function is not yet feasible, but, on the other hand, it is possible to transform them into less selective membranes, being an approach to enhance this solid waste. Previous studies indicate the possibility of transforming reverse osmosis membranes into nanofiltration and / or ultrafiltration membranes using oxidizing agents that partially remove the selective layer of the membrane. Most of the published works lack a study of possible applications. This work aimed to transform reverse osmosis membranes through the oxidation of the selective layer with sodium hypochlorite into less selective membranes, and to search for possible applications for recycled membranes. The results show that membranes oxidized at 10,000 ppm.h had a significant increase in permeability but decreased the rejection of electrical conductivity and acetaminophen. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) demonstrates the impact of chlorine attack on the membrane surface, and analysis by Fourier Transform Reflectance Spectroscopy (FTIR) suggests that chlorine oxidation replaced the hydrogen in the amide nitrogen, but the polyamide layer was not fully degraded. Application tests suggest that the recycled membrane can be used for the treatment of brackish and surface water. The recycling of reverse osmosis membranes can be an alternative to give them a second useful life, inserting them in a greater cycle of economic valuation.

Keywords: reverse osmosis, oxidation, transformation, valuation.

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# Capítulo 1

## Introdução

## 1. INTRODUÇÃO

O sexto objetivo dos Objetivos de Desenvolvimento Sustentável das Nações Unidas é o fornecimento de água potável para a população em crescimento (SØRUP et al., 2020), que é uma necessidade urgente da sociedade (HIBBS et al., 2016). Estima-se que a demanda por água cresça 1% ao ano (AL-NAJAR et al., 2020). Além de estratégias para preservar as fontes de água existentes, é necessário procurar novas fontes e novas técnicas para a produção de água potável para atender à crescente demanda por esse importante recurso (LILANE et al., 2019).

A osmose inversa (OI) surgiu como uma técnica fundamental para o abastecimento de água potável (LILANE et al., 2019), tanto para o tratamento de águas residuais quanto para a dessalinização de água salobra e salina. A taxa de crescimento anual de dessalinização por membranas no mundo é de aproximadamente 55% (OKAMOTO; LIENHARD, 2019), contribuindo para o fornecimento de água potável em todo o mundo.

O uso intensivo destas membranas de OI cria outro problema: as membranas desgastadas. O desgaste intrínseco das membranas e os tratamentos químicos aplicados durante a operação danificam a membrana (BENAVENTE; VÁZQUEZ, 2004). Além disso, a incrustação biológica (NEJATI et al., 2019), inorgânica (RUIZ et al., 2019), e orgânica (GUO; NGO; LI, 2012; SIM et al., 2018) contribuem para os danos e comprometimento da membrana. Mesmo desgastadas, estas membranas podem possuir valor comercial, caso comprovada aplicação viável.

As membranas de OI são feitas de materiais compósitos (LIU et al., 2008; ZAIDI et al., 2015; ZOU et al., 2010), o que dificulta a reciclagem deste material (GOODSHIP, 2007). Como resultado, essas membranas desgastadas estão sendo enviadas como resíduos sólidos para aterros sanitários, gerando passivos ambientais (LAWLER et al., 2012).

A cada ano 14.000 toneladas de membranas são descartadas ao redor do mundo (LANDABURU-AGUIRRE et al., 2016a; LEE; ARNOT; MATTIA, 2011). A reciclagem térmica de membranas desgastadas é a forma mais rápida de recuperar energia, porém, as emissões atmosféricas do processo são altas, principalmente dioxinas e cinzas voláteis. Outra alternativa mais sustentável, como por exemplo a recuperação e o reaproveitamento da membranas desgastadas, pode ser justificada (PONTIÉ et al., 2017). Aplicações como o reaproveitamento se sobrepõem à reciclagem térmica, visto se tratar de material nobre, e ainda assim, após a segunda vida, a membrana pode ser submetida a reciclagem térmica.

Autópsias em membranas de OI desgastadas foram realizadas por Ould Mohamedou et al. (2010) para prever uma possível reutilização. Os autores sugeriram que estas membranas poderiam ser reutilizadas diretamente como nanofiltração (NF) no pré-tratamento da água do mar. Rodríguez et al. (2002) também sugeriram que tratamentos químicos pudessem ser aplicados a membranas de OI desgastadas para viabilizar o reuso dessas membranas. Veza e Rodriguez-Gonzalez (2003) modificaram estas membranas por oxidação superficial usando permanganato de potássio, produzindo uma nova membrana de filtração eficiente para o tratamento terciário de águas residuais municipais. Portanto, o reciclo destas membranas pode ser viabilizado através de tratamentos superficiais ou não, sendo uma forma de oportunizar a redução do envio de membranas para aterro.

De acordo com Lawler et al. (2012), o tratamento superficial das membranas de OI desgastadas viabiliza o seu reuso, o que aumenta a sustentabilidade da tecnologia. Por sua vez, Pontié (2014) sugeriu estratégias para a reciclagem destas membranas, uma delas sendo a transformação de membranas de OI desgastadas em novas membranas de UF, após o tratamento oxidativo usando hipoclorito de sódio.

Pype et al. (2016) expos como as membranas tratadas com hipoclorito de sódio modificaram suas camadas seletivas. De acordo com o autor, ao introduzir cloro na estrutura molecular da camada seletiva, ocorreu o aumento da permeabilidade e a diminuição da rejeição de compostos de interesse. No mesmo sentido, Antony et al. (2016) demonstraram que a rejeição a sais diminuiu de 99% para 40% nas membranas tratadas com hipoclorito, ao passo que a permeabilidade aumentou em 261%. Logo, tratamentos superficiais utilizando hipoclorito de sódio foram capazes de converter estas membranas desgastadas em membranas de menor seletividade e maior permeabilidade.

Por outro lado, Donose et al. (2013) analisaram três tipos de membranas de OI disponíveis comercialmente, que foram expostas à oxidação sem fluxo ou recirculação de oxidante, de forma estática, utilizando soluções de hipoclorito de sódio, alcançando alta rejeição de sal mesmo após a oxidação, enquanto a permeabilidade só aumentou quando a oxidação ocorreu em pH 10. García-Pacheco et al. (2019) relatou que os tratamentos químicos usando hipoclorito de sódio resultaram na transformação de membranas de osmose inversa desgastadas em novas membranas de ultrafiltração e nanofiltração. Assim, a oxidação das membranas pelo hipoclorito de sódio

demonstra ser uma alternativa promissora para convertê-las em membranas NF ou UF, reciclando e prolongando o ciclo de vida delas.

De acordo com Lawler et al. (2013), cada membrana reciclada requer caracterização própria e atribuição individual para aplicação adequada. Como mencionado por Raval et al. (2012), existem inúmeros nichos de aplicações para estas membranas recicladas. Ao passo que vários artigos descrevem e esmiúçam os processos envolvidos na oxidação das membranas e os seus efeitos, poucos artigos de fato utilizam as membranas recicladas em aplicações individuais.

A presença de poluentes emergentes é relatada em todo o mundo, não apenas em fontes de águas superficiais (GEISSEN et al., 2015; MUTIYAR; GUPTA; MITTAL, 2018), mas também em águas subterrâneas (SACHER et al., 2001), lagos (DANESHVAR et al., 2010) e rios (WIEGEL et al., 2004). Os efeitos a longo prazo destes contaminantes emergentes em humanos ainda são incertos (TAHERAN et al., 2018).

O paracetamol, também conhecido como acetaminofeno (MM: 151,2), é um contaminante emergente. Recentemente, sua presença foi percebida em um corpo hídrico fonte de água de abastecimento no norte do Brasil (VERAS et al., 2019). O resultado preocupou a comunidade acadêmica, uma vez que a maioria das estações de tratamento de água e esgoto são incapazes de remover este tipo de contaminantes (VERAS et al., 2019). Dessa forma, o pós tratamento de água tratada se mostra necessário antes do envio para o consumidor final. Nesse sentido, estas membranas recicladas podem ser capazes de remover contaminantes emergentes de água tratada, oferecendo água potável, e estendendo o ciclo de vida das membranas, evitando o seu imediato descarte em aterros sanitários.

No mesmo sentido, existem outras formas de reuso dessas membranas recicladas, como por exemplo a desmineralização de compostos específicos, pré-tratamento de água salobra, pré-tratamento para dessalinização, tratamento de água superficial, pós-tratamento de água potável, clarificação de efluentes, sistemas de reuso de águas cinzas, sistema de reuso de águas pluviais.

A busca por uma alternativa de reciclo de membranas de osmose inversa desgastadas, a proposição de alternativas para uso das membranas recicladas e a necessidade de propor alternativas para a remoção de contaminantes emergentes de água potável fundamentam o escopo deste estudo. Dessa forma, presente trabalho está atrelado à linha de pesquisa de Infraestrutura Sustentável do Programa de Pós-Graduação em Engenharia Civil e Ambiental da Universidade de Passo Fundo.

## **2. OBJETIVOS**

### **2.1. Objetivo geral**

O objetivo deste trabalho é transformar membranas de osmose inversa desgastadas em membranas de menor seletividade, avaliar sua eficiência no tratamento de água salobra e superficial, bem como a remoção de contaminantes emergentes de água tratada.

### **2.2. Objetivos específicos**

Os objetivos específicos serão:

- a) Testar a oxidação de membranas de osmose inversa utilizando hipoclorito de sódio em diferentes concentrações durante imersão estática;
- b) Avaliar os efeitos da oxidação no fluxo, permeabilidade, rejeição de sais e lactose;
- c) Avaliar a eficiência das membranas oxidadas para a remoção de acetaminofeno de água.
- d) Aplicar as membranas recicladas no tratamento de água superficial e salobra.

## Capítulo 2

### Revisão Bibliográfica



### 3. REVISÃO BIBLIOGRÁFICA

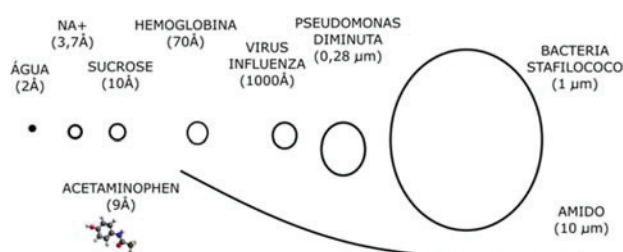
#### 3.1. Processos de Separação por Membranas

As membranas são barreiras físicas entre duas fases, que restringem a passagem de certos componentes presentes em uma delas. A corrente que carrega os contaminantes é chamada de concentrado, enquanto a corrente livre de contaminante é chamada de permeado. O fluxo geralmente ocorre em paralelo às membranas, auxiliando a remoção de incrustações sob a membrana (BAKER, 2012).

Os processos de separação por membranas podem ser classificados em diferentes categorias, sendo que as principais variáveis são: configuração da membrana, tipo de material utilizado, força motriz, mecanismo de separação e faixa de tamanhos dos constituintes removidos. A faixa de tamanhos de constituintes removidos é normalmente resultado do tamanho dos poros da membrana e do mecanismo de separação envolvido (HAMINGEROVA; BORUNSKY; BECKMANN, 2015).

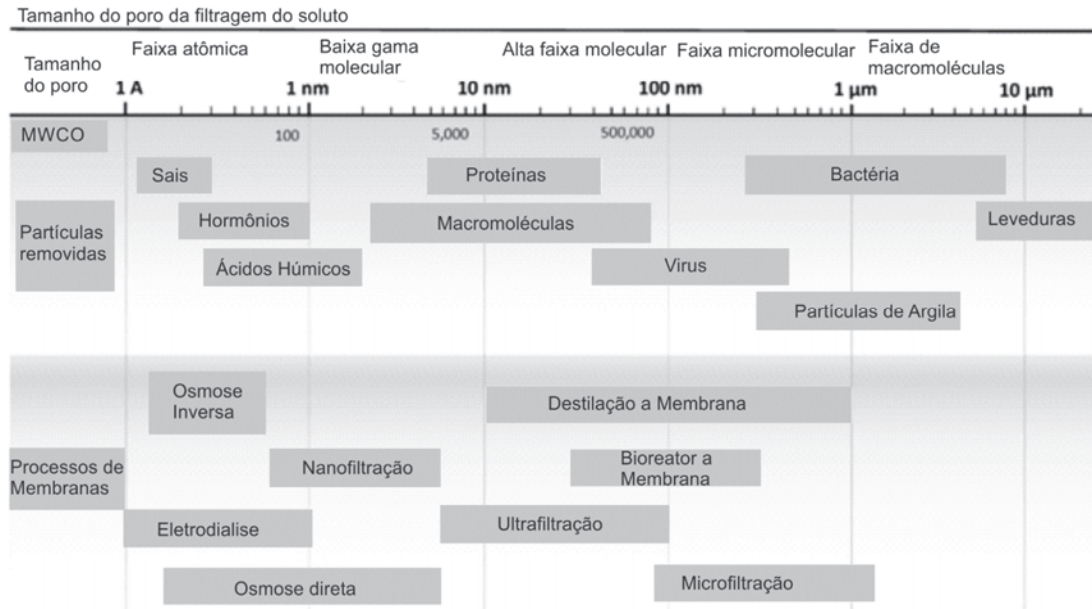
Para as membranas que utilizam pressão como força motriz, à medida que os poros diminuem, o fluxo diminui e a seletividade aumenta, de forma que o processo necessita de mais força motriz para ocorrer (WARSINGER et al., 2018), aumentando também o gasto energético. A Figura 1 ilustra alguns compostos possíveis de serem encontrados em água, junto de suas respectivas dimensões. A Figura 2 resume os tipos de membranas com base nas faixas de tamanho de certos constituintes comuns encontrados na água e no tamanho efetivo dos poros da membrana (VAN DER BRUGGEN; MÄNTTÄRI; NYSTRÖM, 2008).

Figura 1: Diâmetro de certas moléculas/compostos encontrados na água.



Adaptado de Zhang et al. (2019).

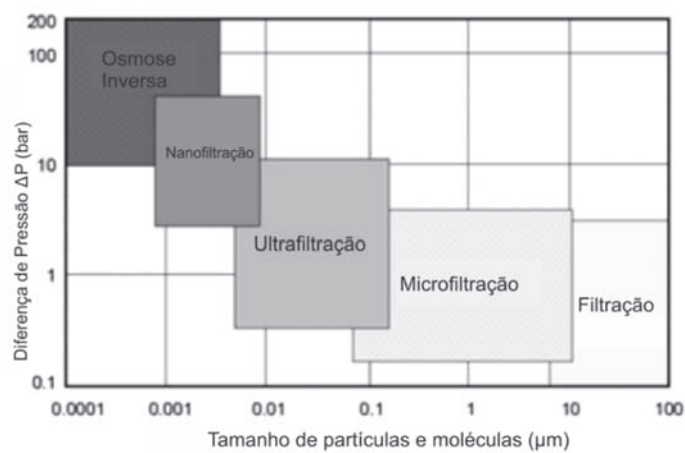
Figura 2: Tipos de membranas, tamanho dos poros e dimensões de compostos encontrados em água.



Adaptado de Warsinger et al. (2018).

As tecnologias são frequentemente classificadas como baixa pressão (Filtração convencional, Microfiltração e Ultrafiltração) e alta pressão (Nanofiltração e Osmose inversa). A Figura 3 resume as faixas de pressão utilizadas para cada categoria.

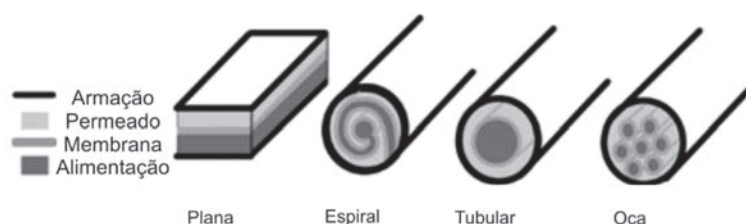
Figura 3: Pressão utilizada e dimensões de partículas removidas por categoria de filtração.



Adaptado de Melin; Rautenbach (2006).

A tecnologia de filtração empregando membranas não desenvolveu apenas o material utilizado nas membranas, mas também a forma com que a membrana é embalada e organizada. Os módulos das membranas são geralmente organizados em configurações diferentes, a Figura 4 apresenta as quatro configurações comumente encontradas no mercado.

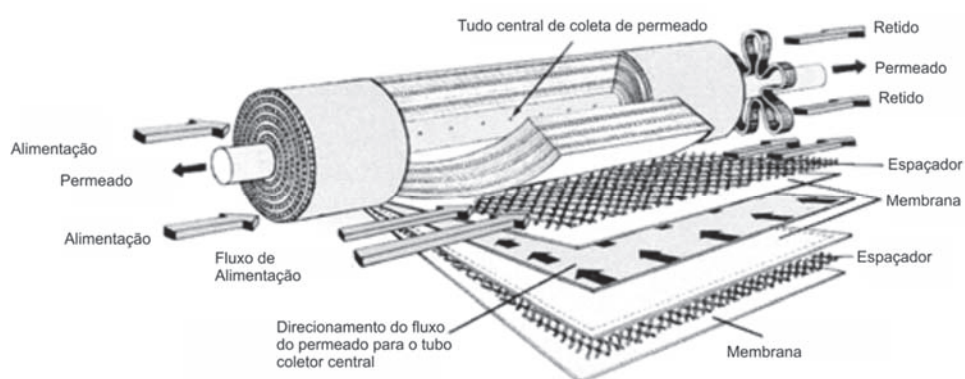
Figura 4: Configurações comuns dos módulos de membranas.



Adaptado de Warsinger et al. (2018).

A membrana espiralada é a mais utilizada, em virtude dos benefícios propostos. A Figura 5 apresenta o detalhamento dos módulos espiralados após a montagem, e o Quadro 1 apresenta as vantagens e desvantagens do uso das membranas espiraladas.

Figura 5: Estrutura de um módulo de membrana inversa.



Adaptado de Fritzmann et al.(2007).

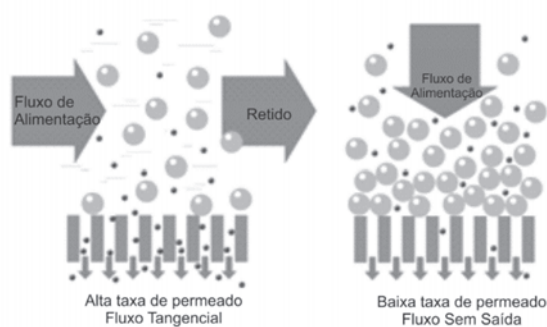
Quadro 1: Vantagens e desvantagens do empacotamento de membranas em formato espiral

Vantagem	Desvantagem
Custos de produção baixo	Alta perda de pressão
Alta densidade de embalagem (<math><1000\text{ m}^2/\text{m}^3</math>)	Suscetível à incrustações
Alta transferência de massa em virtude dos espaçadores.	Difícil limpeza

Adaptado de Fritzmann et al.(2007).

A configuração do fluxo também é outra característica importante, podendo ser tangencial (Cross Flow Filtration) ou perpendicular (Dead End Filtration). A Figura 6 ilustra a diferença entre cada fluxo. No fluxo tangencial, o fluxo do permeado ocorre paralelamente à membrana de filtração, facilitando a remoção de possíveis incrustações da membrana em virtude do fluxo. Enquanto que, na perpendicular, o fluxo ocorre perpendicularmente, favorecendo o acúmulo de incrustações (WARSINGER et al., 2018).

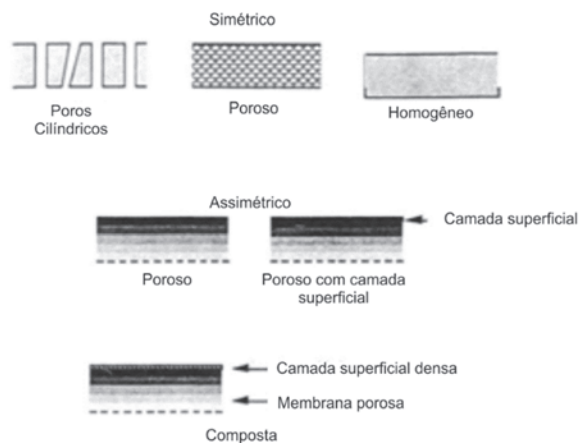
Figura 6: Diferença do fluxo tangencial e perpendicular.



Fonte: Formulatrix (2019).

O material que compõe a membrana também é fator relevante, podendo ser molecularmente homogêneo, ou seja, completamente uniforme em composição e estrutura, bem como, quimicamente ou fisicamente heterogênea, contendo orifícios ou poros, ou também, formado em camadas (BAKER, 2012). A Figura 7 apresenta um resumo esquemático dos principais tipos de membranas sintéticas.

Figura 7: Resumo esquemático dos principais tipos de membranas sintéticas.



Fonte: (SCOTT, 1995).

A camada superficial das membranas compostas é responsável pela seletividade da membrana. A concentração e dimensões dos poros afeta diretamente a permeabilidade e a seletividade das membranas, de forma que o aumento dos poros não aumenta apenas o fluxo de permeado, mas também as dimensões de compostos que permeiam através da membrana.

## 3.2. Osmose Inversa

### 3.2.1. Histórico da tecnologia

A habilidade das membranas de separar solutos de água não é descoberta recente, em 1931 foi gerada a primeira patente acerca da metodologia de membranas empregada na dessalinização de água, denominada de Osmose Inversa (A.G. Horvath, Water Softening, US Patent 1,825,631 (September, 1931)). Reid e Breton (1959) utilizaram membranas de acetato de celulose com espessura de 5 até 20  $\mu\text{m}$ , obtendo fluxos extremamente baixos, porém, a remoção de sais alcançou até 98%.

O avanço que possibilitou o uso das membranas foi o desenvolvimento de membranas anisotrópicas de acetato de celulose, que aumentaram o fluxo em 10 vezes às alcançadas por Reid e Breton, mantendo a rejeição de 98% (LOEB; SOURIRAJAN, 1963). Após alguns anos, foram instaladas as primeiras plantas utilizando as membranas em chapas, que logo foram substituídas

por membranas espiraladas (J.C. Westmoreland, Spirally Wrapped Reverse Osmosis Membrane Cell, US Patent 3,367,504 (February, 1968)).

As membranas anisotrópicas de acetato de celulose eram padrão industrial entre 1960 e 1970, até Cadotte (1985) desenvolver o método de polimerização para a produção de membranas compostas, alcançando altas rejeições e fluxos razoáveis.

A indústria de membranas foi novamente revolucionada por Cadotte, quando foram desenvolvidas membranas compostas baseadas na reação de fenilenodiamina e cloreto de trimesolo (LARSON; CADOTTE; PETERSEN, 1981).

A metodologia de Cadotte ainda é empregada na produção de membranas. No entanto, essas membranas apresentam baixa resistência à oxidação, a presença de cloro livre por exemplo, danifica a camada seletiva da membrana, em virtude da baixa resistência da amida nitrogenada presente na camada seletiva da membrana (GOHIL; SURESH, 2017; LI et al., 2015).

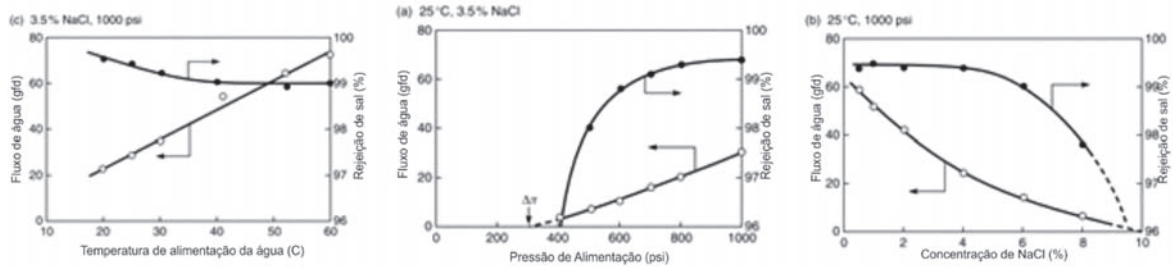
O aumento da elasticidade da membrana, da concentração e dimensões dos poros da membrana são efeitos da oxidação, e consequência disso é o aumento da transferência de compostos pela membrana, que reduz a seletividade e qualidade do produto gerado pela membrana.

### **3.2.2. Situação atual**

As membranas de osmose inversa, normalmente apresentam poros menores que 0,6 nm (LEE; ARNOT; MATTIA, 2011), dessa forma, são capazes de reter a maior parte dos sais. A tecnologia é atualmente a mais difundida na dessalinização, sendo capaz de rejeitar a maior parte da matéria coloidal ou dissolvida de uma solução aquosa, produzindo um fluxo concentrado e um permeado que consiste em água pura (FRITZMANN et al., 2007).

A eficiência da osmose inversa na dessalinização depende de fatores operacionais, como a pressão da alimentação, a concentração de sal, a temperatura da água e as características da membrana utilizada (QASIM et al., 2019). Os parâmetros operacionais estão ilustrados na Figura 8.

Figura 8: Parâmetros operacionais da osmose inversa.



Adaptado de Baker (2012).

### 3.2.3. Bases teóricas

O fluxo ( $J$ ), é definido como a taxa de fluxo volumétrica permeada em uma área específica, proporcional à pressão aplicada no líquido sendo filtrado, apresentado na Equação 1:

$$J = K(\Delta P - \Delta \Pi) \quad (1)$$

Sendo  $K$  a permeabilidade da membrana,  $\Delta P$  a diferença de pressão entre os lados da membrana e  $\Delta \Pi$  a pressão osmótica da membrana.

O tamanho dos poros ( $q$ ) é fator determinante na taxa de fluxo volumétrica da membrana, em virtude disso, o fluxo pode ser estimado utilizando a equação de Poiseuille, apresentado na Equação 2:

$$q = \frac{\pi d^4}{128 \mu l} \times \Delta P \quad (2)$$

Sendo  $d$  o diâmetro do poro  $\mu$  a viscosidade do líquido,  $l$  o comprimento do poro e  $\Delta P$  a diferença de pressão entre os lados da membrana.

A determinação da taxa de fluxo volumétrica ( $J$ ) utilizando a equação de Poiseuille requer a multiplicação da equação pelo número de poros por área, apresentado na Equação 3:

$$J = N \times \frac{\pi d^4}{128 \mu l} \times \Delta P \quad (3)$$

Sendo  $N$  o número de poros por área,  $d$  o diâmetro do poro,  $\mu$  a viscosidade do líquido,  $l$  o comprimento do poro e  $\Delta P$  a diferença de pressão entre os lados da membrana.

O coeficiente de rejeição ( $R$ ) é uma medida da capacidade da membrana de separar o composto da solução de alimentação. A Equação 4 representa a equação do coeficiente de rejeição da membrana:

$$R = \left(1 - \frac{C_{jp}}{C_{ja}}\right) \times 100 \quad (4)$$

Sendo  $C_{jp}$  a concentração de composto no fluxo permeado e  $C_{ja}$  a concentração de composto no fluxo de alimentação.

O diâmetro dos poros de uma membrana desconhecida pode ser estimado usando a Equação 5, onde uma membrana conhecida é usada como referência para determinar o diâmetro dos poros ( $d_p$ ) em nm.

$$d_p = \sqrt{A_p/A_0} \times d_{p0} \quad (5)$$

Sendo que  $A_0$  é a permeabilidade da membrana de referência,  $d_{p0}$  é o diâmetro dos poros da membrana de referência e  $A_p$  é a permeabilidade da membrana semelhante. O Peso Molecular de Corte (MWCO) de uma membrana também pode ser calculado usando a Equação empírica 6 (AIMAR; BACCHIN; MAUREL, 2017).

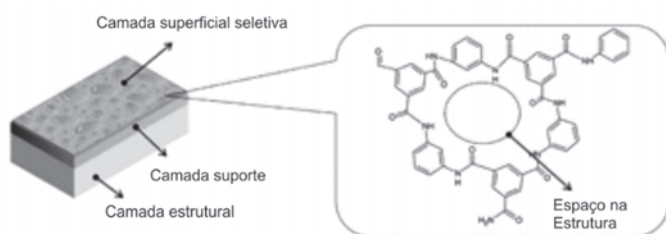
$$MWCO = \sqrt[0,4]{\frac{d_p}{0,076}} \quad (6)$$

### 3.2.4. Composição das membranas

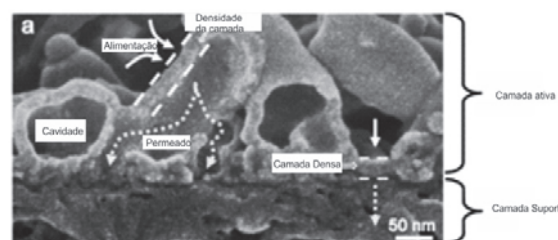
A camada de barreira seletiva das membranas é frequentemente feita de poliamida aromática, formada através da polimerização interfacial de 1,3-fenilenodiamina e o cloreto triácido do benzeno (TARBOUSH et al., 2008). A camada seletiva é assentada em uma camada suporte, formada de polissulfona e polietersulfona (HAMINGEROVA; BORUNSKY; BECKMANN, 2015). A Figura 9 apresenta a estrutura de uma membrana de poliamida.



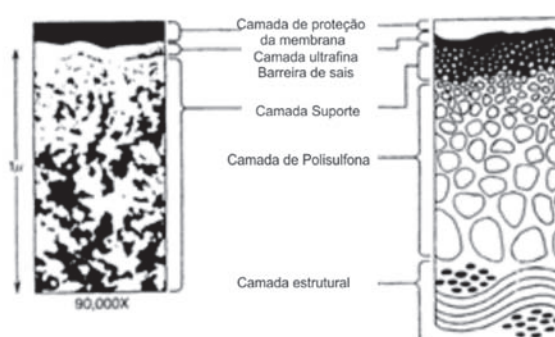
Figura 9: Detalhes da estrutura de membranas de poliamida.



Adaptado de Warsinger et al. (2018).



Adaptado de Warsinger et al. (2018).



Adaptado de Scott (1995).

### 3.2.5. Colmatação temporária, permanente e limpeza

A incrustação de membranas é a principal causa do declínio do fluxo de permeantes e da perda da qualidade do produto nos sistemas de osmose inversa; portanto, o controle da incrustação é ponto crucial da tecnologia (BAKER, 2012).

A incrustação salina é um tipo de incrustação causada pela precipitação de sais dissolvidos na água de alimentação na superfície da membrana em virtude do aumento da concentração do sal. Como a água dessalinizada é removida no permeado, a concentração de íons na alimentação aumenta até que em algum momento o limite de solubilidade seja excedido. O sal então precipita na superfície da membrana em formato de escamas (RAHMAN, 2013).

A incrustação biológica é causada pela deposição, proliferação e metabolismo de microrganismos (bactéria, algas, protozoários e fungos), gerando um biofilme na superfície da membrana (QASIM et al., 2019).

A incrustação da membrana também pode ocorrer em virtude da presença de sólidos suspensos. Colóides orgânicos, resíduos da oxidação de ferro, hidróxido de ferro precipitado, partículas sólidas finas são frequentemente causadoras de incrustação (BAKER, 2012).

A incrustação orgânica é a adesão de matéria orgânica na superfície da membrana, como por exemplo, óleos e gorduras, ácidos húmicos, macromoléculas extra e intracelulares, proteínas, entre outros (QASIM et al., 2019). O material orgânico acumulado na superfície da membrana pode servir de nutrientes em casos de incrustação biológica.

Em virtude das incrustações e dos acúmulos de matéria sobre a superfície da membrana, são necessárias limpezas da membrana para remover os compostos incrustados. As limpezas podem ocorrer utilizando três diferentes métodos: químico, físico e físico-químico (SAGIV; SEMIAT, 2005).

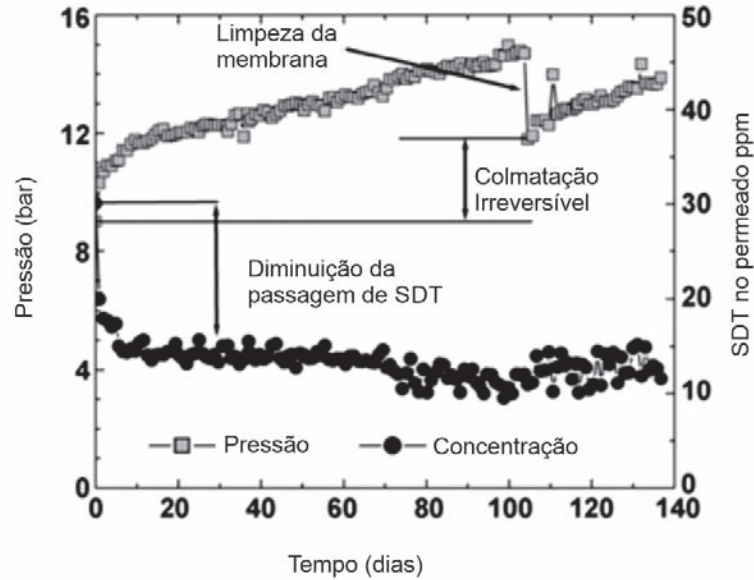
Métodos de limpeza química utilizam a introdução de agentes químicos no fluxo, que são designados para enfraquecer as forças de coesão entre o agente incrustante e a superfície da membrana (SAGIV; SEMIAT, 2005). Os métodos físicos incluem a inversão de sentido do fluxo do permeado, vibração e inserção de ar (SAGIV; SEMIAT, 2005). Os métodos físico-químicos utilizam mais de um processo ocorrendo de forma simultânea.

A limpeza mais comumente utilizada consiste em lavar os módulos de membrana recirculando soluções de limpeza em alta velocidade em ambos os sentidos do fluxo. Os agentes químicos de limpeza geralmente usados são ácidos, álcalis, quelantes, detergentes, produtos formulados e esterilizadores. Na maioria dos casos, as membranas já são acompanhadas de soluções de limpeza, providos pelo fornecedor das membranas.

As frequentes limpezas revertem parcialmente a incrustação de membranas, porém, em virtude de compactações físicas e limpezas incompletas (JIANG et al., 2017), ocorrem incrustações irreversíveis (HOEK et al., 2008). À medida que as membranas se aproximam do final de sua vida útil, o fluxo de água normalmente cai em pelo menos 20%, em virtude das incrustações bem como a rejeição de sal começa a cair (BAKER, 2012), em virtude da sensibilidade das membranas em relação à oxidantes.

A Figura 10 exemplifica os ciclos de operação e de limpeza em relação ao fluxo e a pressão de operação de uma membrana de osmose inversa. Pode ser percebido que mesmo após a limpeza da membrana, as condições de operação não retornam às iniciais, isso se dá em virtude das incrustações permanentes que ocorrem na membrana.

Figura 10: Gráfico dos ciclos de operação e limpeza de uma membrana de osmose inversa.



Fonte: (HOEK et al., 2008).

As sequências de incrustações irreversíveis deterioram o fluxo das membranas até alcançarem o seu fim de vida. Em paralelo, a taxa de rejeição à solutos costuma diminuir, visto que, danos intrínsecos à operação das membranas são passíveis de ocorrência. Neste momento, as limpezas das membranas já não são capazes de retornar as condições adequadas de operação do sistema, quando as membranas são substituídas.

### 3.2.6. Reciclo de membranas

A reciclagem de materiais pode ocorrer de três formas diferentes: Reciclagem mecânica, Reciclagem indireta e Reciclagem direta. A reciclagem mecânica é a principal forma de reciclagem de componentes plásticos (O'FARRELL; ALLAN, 2015). O processo inclui triturar e derreter o material plástico da membrana, produzindo blocos através da extrusão, produzindo matéria prima para novos produtos (PICKIN; RANDELL, 2017). Apenas partes das membranas, como tubos, espaçadores e tampas são adequados para esse método, sendo que o restante deve ser enviado para aterro (HIORNS, 2004, PAULA; AMARAL, 2017).

A reciclagem indireta inclui o desmonte da membrana para reuso em outras funções (LAWLER et al., 2012; PONTIÉ et al., 2017). O Centro Nacional de Excelência em Dessalinização da Austrália (NCEDA) propôs separar as múltiplas camadas da membrana e usá-las criativamente como tecido e decoração de roupas (LANDABURU-AGUIRRE et al., 2016). Entretanto, o mesmo autor indica que não há aplicações industriais para atenderem a demanda.

A reciclagem direta não atua na estrutura do módulo, mas age sobre a camada ativa das membranas de poliamida. As membranas de poliamida apresentam baixa resistência para oxidantes (DO et al., 2012, TERRERO et al., 2015), sendo que a presença destes oxidantes pode modificar a morfologia e o desempenho da membrana. Entretanto, a baixa resistência à oxidantes podem ser benéficas no tratamento das membranas para o reciclo.

O estudo da transformação de membranas de osmose inversa em membranas de ultrafiltração iniciado por Rodríguez et al. (2002) demonstrou que o agente químico mais eficiente na oxidação da camada superficial da membrana foi o  $K_7MnO_4$ . Em contrapartida, pesquisadores descobriram que o melhor agente químico era o hipoclorito de sódio (GARCÍA-PACHECO et al., 2019; LAWLER et al., 2013; MORÓN-LÓPEZ et al., 2019; TERRERO et al., 2015).

### **3.2.7. Oxidantes e condições de oxidação**

A Tabela 1 apresenta algumas condições utilizadas para a oxidação de membranas de poliamida utilizando oxidantes clorados.

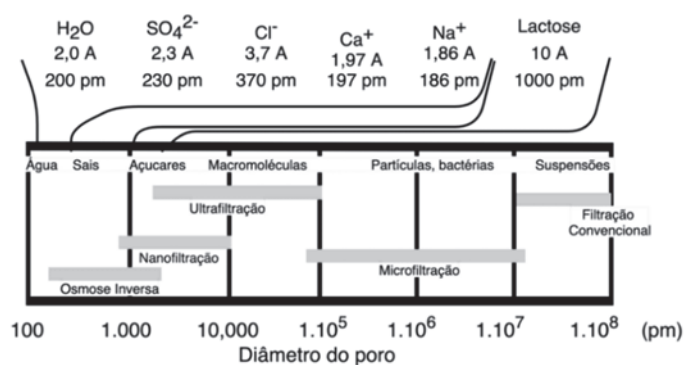
Tabela 1: Condições de oxidação encontradas na literatura.

Autor	Metodologia	Conclusões
Kwon e Leckie (2006)	<p>Membrana: LFC1 – Hydranautics</p> <p>Oxidante: NaOCl</p> <p>Primeira parte: oxidadas com soluções de concentração de cloro livre em 100, 500, 1000 e 2000 ppm por 1 hora em pH 4 e 9.</p> <p>Segunda parte: re-oxidadas em 100 ppm de cloro livre em pH 3, 4, 5, 6, 7, 8 e 9.</p> <p>Reações ocorreram em frascos de vidro Pyrex com tampa.</p>	<p>O cloro em um banho de imersão ligado à superfície da membrana e a porcentagem atômica de cloro ligado à membrana LFC1 aumentaram com o aumento da exposição ao cloro e a diminuição do pH do banho de imersão.</p> <p>Não foi identificada alteração na rugosidade da membrana para o pH 4 e 9.</p> <p>Os resultados demonstraram que a cloração quebra e enfraquece a ligação de hidrogênio, diminuindo o número de locais de ligação de hidrogênio.</p>
Terrero et al. (2015)	<p>Membranas: TM 720 – 400 (Toray), BW30 (Dow Filmtec), TM 820C-400 (Toray), HRLE-440i (Dow Filmtec) e HSWC3 (Hydranautics).</p> <p>Oxidante: NaOCl</p> <p>Oxidadas utilizando 124 ± 8 ppm de cloro livre em: 36, 50, 122, 242 e 410 horas, em pH 10. A reação ocorreu em frasco em condição estática.</p>	<p>As membranas de RO em fim de vida foram eficientemente transformadas em membranas de NF e UF por exposição à solução de NaOCl (imersão passiva). Quando o tempo de exposição aumenta, o fluxo de permeado aumenta. A degradação da camada ativa de poliamida também foi seguida pelo ATR-FTIR (Refletância Total Atenuada - Espectroscopia de Refletância por Transformada de Fourier). A intensidade dos picos de amida I e amida II foi progressivamente reduzida e quase desapareceu quando o tempo de exposição à solução oxidante aumentou para 410 h. A degradação dessa camada ativa leva ao aparecimento da estrutura porosa de polissulfona, como mostrado nas micrografias SEM (Microscopia Eletrônica de Varredura).</p>
García-Pacheco et al. (2019)	<p>Membranas: TM720 – 400 (Toray), SW30 HRLE 440i (Dow Filmtec).</p> <p>Oxidante: NaOCl.</p> <p>Oxidadas utilizando concentrações de 124 até 12,400 ppm de cloro livre durante tempos de 0,5 até 242 horas.</p>	<p>Para transformar membranas de osmose inversa em membranas de ultra ou nanofiltração é preferível menores concentrações de cloro livre durante maiores períodos de reação. Além disso, membranas com incrustações podem afetar o processo de transformação, principalmente quando forem incrustações de argila ou escamas.</p>

### 3.2.8. Indicadores de qualidade da membrana

As membranas são barreiras físicas que restringem a passagem de certos compostos. A figura 11 apresenta o tamanho dos poros de diferentes membranas comerciais, bem como os compostos que são rejeitados por cada membrana. Entretanto, a análise inversa também é possível: de posse dos dados de rejeição de diferentes compostos é possível classificar as membranas de acordo com as características encontradas.

Figura 11: Tamanho de molécula em comparação com o tamanho dos poros.



Fonte: Autoria própria.

De posse dos dados de rejeição, é possível classificar uma membrana desconhecida, ou já desgastada em virtude do tempo de operação. A Tabela 2 apresenta dados de rejeição de compostos para diferentes tipos de membrana.

Tabela 2: Dados de rejeição de compostos para diferentes tipos de membrana.

Composto	Rejeição em Osmose Inversa	Rejeição em Nanofiltração	Rejeição em Ultrafiltração
Dureza	90 – 98 <sup>(1)</sup>	80 – 85 <sup>(1)</sup>	36 - 53 <sup>(6)</sup>
Mg <sup>2+</sup>	99,8 <sup>(4)</sup>	96 – 98 <sup>(5)</sup>	S/R <sup>(7)</sup>
Cl <sup>-</sup>	98,3 <sup>(4)</sup>	>95% <sup>(7)</sup>	< 20% <sup>(7)</sup>
Proteínas	Log 4 – 7 <sup>(1)(a)</sup>	Log 3 – 5 <sup>(1)(a)</sup>	-
Lactose	99,5 – 99,8 <sup>(4)</sup>	95,4 – 98,7 <sup>(2)</sup>	11,67 – 18,25 <sup>(3)</sup>
NaCl	90 – 99 <sup>(1)</sup>	10 – 50 <sup>(1)</sup>	S/R <sup>(7)</sup>

1 (WARSINGER et al., 2018), 2 (CHEN et al., 2018), 3 (BRIÃO et al., 2017), 4 (VOURCH et al., 2008), 5 (IZADPANA; JAVIDNIA, 2012), 6 (ABBASI-GARRAVAND; MULLIGAN; LAFLAMME, 2015), 7 (PARK et al., 2015), S/R = Sem Rejeição. a) Refere-se à remoção de log, onde log 2 é 99%, log 3 é 99,9% etc.

A transformação de membranas de Osmose Inversa em membranas de menor seletividade, como a Nanofiltração ou Ultrafiltração pode ser apurada pelos dados de rejeição dessas membranas, conforme Tabela 2. A possibilidade de caracterizar as membranas com base em suas taxas de rejeição permite caracterizar as membranas após a oxidação induzida.

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## Capítulo 3

Membranas de osmose inversa desgastadas: Procedimento de reciclagem e propostas de aplicação.

## **5. MEMBRANAS DE OSMOSE INVERSA DESGASTADAS: PROCEDIMENTO DE RECICLAGEM E PROPOSTAS DE APLICAÇÃO**

O Capítulo 3 apresenta o artigo científico produzido durante o decorrer do programa. Este artigo será enviado para publicação na revista Desalination (ISSN: 0011-9164).

*Aged Reverse Osmosis Membranes: Recycle procedure and application proposals.*

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### **Abstract**

The demand for drinking water has increased due to population growth and the needs for human activities to support this population. To meet this demand, an increasing number of reverse osmosis desalination plants are being installed and operated. However, reverse osmosis membranes tend to reach the end of the life cycle in around two to five years, when they become solid waste, requiring proper disposal, generating additional costs. Therefore, extending the life cycle of reverse osmosis membranes is a necessity from an environmental and economic point of view. Studies indicate that the recovery of reverse osmosis membranes for the same function is not yet feasible, but, on the other hand, it is possible to transform them into less selective membranes, being an approach to enhance this solid waste. Previous studies indicate the possibility of transforming reverse osmosis membranes into nanofiltration and / or ultrafiltration membranes using oxidizing agents that



partially remove the selective layer of the membrane. Most of the published works lack a study of possible applications. This work aimed to transform reverse osmosis membranes through the static oxidation of the selective layer using sodium hypochlorite into less selective membranes, and to search for possible applications for recycled membranes. The results show that membranes oxidized at 10,000 ppm.h had a significant increase in permeability but decreased the rejection of electrical conductivity and acetaminophen. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) demonstrates the impact of chlorine attack on the membrane surface, and analysis by Fourier Transform Reflectance Spectroscopy (FTIR) suggests that chlorine oxidation replaced the hydrogen in the amide nitrogen, but the polyamide layer was not fully degraded. Application tests suggest that the recycled membrane can be used for the treatment of brackish and surface water. The recycling of reverse osmosis membranes can be an alternative to give them a second lifespan, inserting them in a greater cycle of economic valuation.

Keywords: reverse osmosis, oxidation, transformation, valuation

## 1 - Introduction

The sixth objective of Sustainable Development Goals from the United Nations is the supply of drinking water to the growing population (SØRUP et al., 2020), which is an urgent necessity from society (HIBBS et al., 2016). The demand for water is estimated to grow by 1% per annum (AL-NAJAR et al., 2020). In addition to strategies for preserving existing water sources, it is necessary to look for new sources and new techniques for potable water production to meet the growing demand for this important resource (LILANE et al., 2019).

Reverse Osmosis (RO) has emerged as a key technique for potable water supply (LILANE et al., 2019), either for the treatment of wastewater, or for the desalination of brackish and saline water. The annual growth rate of membrane desalination in the world is approximately 55% (OKAMOTO; LIENHARD, 2019), contributing to the supply of drinking water worldwide.

The intensive use of RO membranes creates another issue: the aged membranes. The intrinsic ageing of the membranes and the chemical treatments applied during the operation damages the membrane (BENAVENTE; VÁZQUEZ, 2004). In addition, biofouling (NEJATI et al., 2019), inorganic fouling (RUIZ et al., 2019) and organic fouling (GUO; NGO; LI, 2012; SIM et al., 2018) contribute to the damages and membrane impairment. Even being aged, these membranes can have commercial value, if proven viable application.

RO membranes are made of composite materials (LIU et al., 2008; ZAIDI et al., 2015; ZOU et al., 2010), and because of that, recycling is difficulted (GOODSHIP, 2007). As a result, these used membranes are still currently being sent as waste to landfills, becoming an environment liability (LAWLER et al., 2012). Each year 14,000 tons of membranes are sent to landfills around the globe (LANDABURU-AGUIRRE et al., 2016; LEE; ARNOT; MATTIA, 2011). Considering the side effects of aged membranes incineration, a more sustainable alternative such as second life to aged membranes could be motivated (PONTIÉ et al., 2017).

Mohamedou et al. (2010) performed autopsies on aged RO membranes to envisage possible reuse. The authors suggested that aged RO membrane could be directly reused as Nanofiltration (NF) for seawater pretreatment. Rodríguez et al. (2002) also suggested that chemical treatments could be applied to aged RO membranes to motivate the recycling of these membranes. Veza e Rodriguez-Gonzalez (2003) modified aged RO membranes by surface oxidation using potassium

permanganate, producing an efficient filtration membrane for tertiary treatment of municipal wastewater, Lawler et al. (2012) confirmed that the surface treatment of aged RO prior to the recycling, could increase the sustainability of this technology. Furthermore, Pontié (2014) suggested strategies for the recycling of aged RO membranes. One purpose was to transform aged RO membranes into ultrafiltration (UF) membranes after hypochlorite oxidation.

Pype et al. (2016) presented how hypochlorite aged membranes had the selective layer modified by introducing chlorine into the molecular structure of the membrane, resulting in the increase of the permeability and decrease of the rejection of interest compounds. Antony et al. (2016) demonstrated that the rejection to salt decreased from 99% to 40% on hypochlorite aged membranes, at the pace that the permeability increased by 261%. On the other hand, Donose et al. (2013) analyzed three types of commercially available RO membranes that were statically exposed to hypochlorite solutions and achieved high salt rejection even after oxidation, when the permeability only increased if the oxidation of the membrane occurred at basic pH. García-Pacheco et al. (2019) reported that these treatments ensued in the transformation of aged RO membranes into NF and UF membranes. Thus, the oxidation of aged RO membranes by hypochlorite is a promising alternative to convert them to NF or UF membranes, prolonging the life cycle of membranes on other applications.

The use of recycled RO membranes must be studied to identify potential applications, such as for the treatment of surface water, tertiary treatment of wastewater, or for the removal of emerging pollutants from water sources. The presence of emerging pollutants is being frequently reported worldwide, not only in superficial water (GEISSEN et al., 2015; MUTIYAR; GUPTA; MITTAL, 2018), but also in groundwater (SACHER et al., 2001), lakes (DANESHVAR et al., 2010) and rivers (WIEGEL et al., 2004). The long-term effects of these emerging contaminants in humans is still uncertain (TAHERAN et al., 2018). Paracetamol, also known as acetaminophen (MM: 151,2) which is one of these emerging contaminants, was found in a river that is source for water supply in northern Brazil (VERAS et al., 2019). As a result, the academic community became concerned, since most water and wastewater treatment plants are unable to remove such compounds (VERAS et al., 2019). Post-treatments may be required to remove these emerging contaminants from treated water, and the recycled RO membranes could be introduced in such

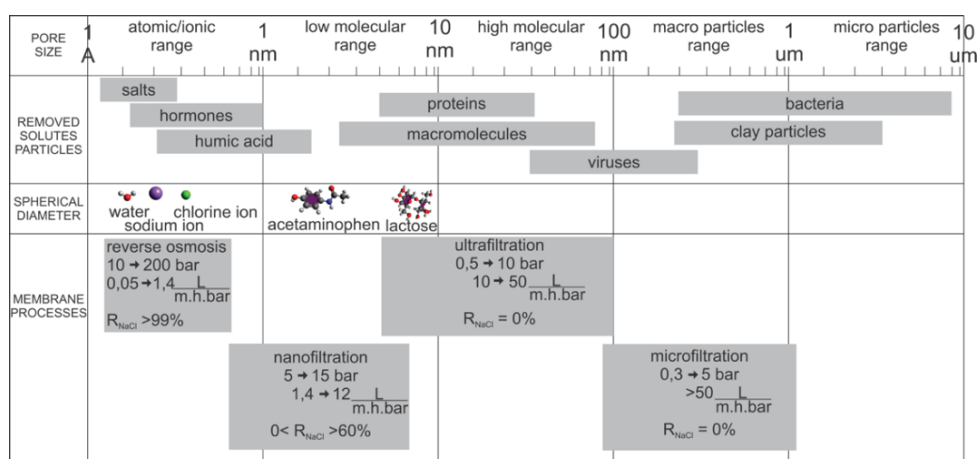
treatment plants. In this study, acetaminophen was chosen as an interest compound, representing medium size molecules, as the spherical diameter is 0.72 nm, details can be found in Figure 1.

In the same sense, there are other ways of reusing these recycled membranes, such as the demineralization of specific compounds, pre-treatment of brackish water, pre-treatment for desalination, surface water treatment, post-treatment of drinking water, clarification of effluents, grey water reuse systems, rainwater reuse system.

According to Lawler et al. (2013), each recycled membrane requires its own characterization and individual attribution for proper application. As mentioned by Raval et al. (2012), there are numerous application niches for these recycled membranes. While several articles describe and break down the processes involved in membrane oxidation and its effects, few articles actually used recycled membranes for individual applications.

The aim of this work is to transform end-of-life RO membrane into a technically viable lower selectiveness membrane as UF or NF by oxidizing the selective layer of the RO membrane and test possible applications for the recycled membrane. To do so, static hypochlorite treatments were applied to the end-of-life RO membranes, the chosen integrity indicators are the rejection to electrical conductivity, acetaminophen, and lactose.

Figure 1: Characteristics of membranes.



Adapted from Warsinger et al.(2018)

## 2 - Materials and Methods

The work followed the steps:

- a) Membrane autopsy and surface cleaning;
- b) Statical oxidation experiments in three different concentration of Sodium Hypochlorite solutions;
- c) Evaluation of the variable responses: Permeate flux, salt (electrical conductivity), lactose and acetaminophen rejection, morphology by Scanning Electronic Microscopy (SEM), Atomic Force Microscopy (AFM) and Fourier Transform Infrared Reflectance (FTIR); additionally, we simulated the permeate flux and salt rejection on ROSA software to obtain references for comparison;
- d) Application of the recycled membrane for the treatment of brackish water and surface water.

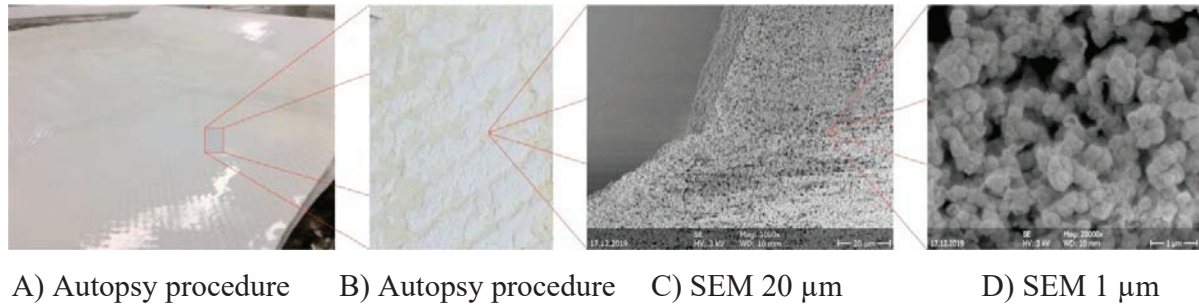
### 2.1 – Membrane autopsy and cleaning

The aged RO membrane was a 4” Ultra Low Pressure 2012 – 100 from Vontron. The aged membrane was gently donated by Purificatta Company (Brazil). During the first life cycle of the membrane, well-water and municipal potable water were applied to the membrane.

The membrane was stored in wet conditions in permeate of RO. An autopsy of the membrane was performed prior to the cleaning procedures and oxidation tests (Figure 2). The membrane was disassembled, and the flat sheets were rinsed using an appropriate protocol. In order to simulate the mechanical effect of the high flux during standard cleaning procedures of membrane systems, the membranes were gently brushed for exact 5 minutes while submerged in a series of different pH solutions, as follows: 7 (water), 11 (NaOH), 7, 4(HNO<sub>3</sub>) and 7. The cleaning procedure inspired upon the protocol of García-Pacheco et al. (2019) with the addition of the extra mechanical procedure.

Coupons of 200 cm<sup>2</sup> (20 cm x 10 cm) were cut from different areas of the membrane and stored in Milli-Q water. Note that even after standard cleaning procedures, the coupons were not scaling free (Figure 2B).

Figure 2: Autopsy procedure of the aged membrane.



## 2.2 – Oxidation of the membrane

The oxidation solution was prepared by diluting NaOCl (12%, Synth) with Milli-Q water without pH correction. Table 1 summarizes the conditions of each treatment as well as the oxidation solution pH. The oxidizer solution was poured into 1 L beakers, and each coupon was submerged in the solution for 1 hour. The oxidation process protocol was inspired from García-Pacheco et al. (2019). Following the exposure time, coupons were soaked in Milli-Q water five times for the complete removal of any residual chemical. The residual chlorine and pH of the rinse water were measured by quick tests (Genco - Brazil) to ensure that the membrane was chlorine free and in neutral pH. Note that “Test 0”, which is also referenced as 0 ppm.h refers to the aged RO membrane, that was not oxidated.

Table 1: Oxidation experiments conditions.

Test name	Exposure dose (ppm.h [Cl <sub>2</sub> ])	Oxidation Solution pH
0	0	-
8,000	8,000	11.32
9,000	9,000	11.56
10,000	10,000	12.08

## 2.3 – Variable responses

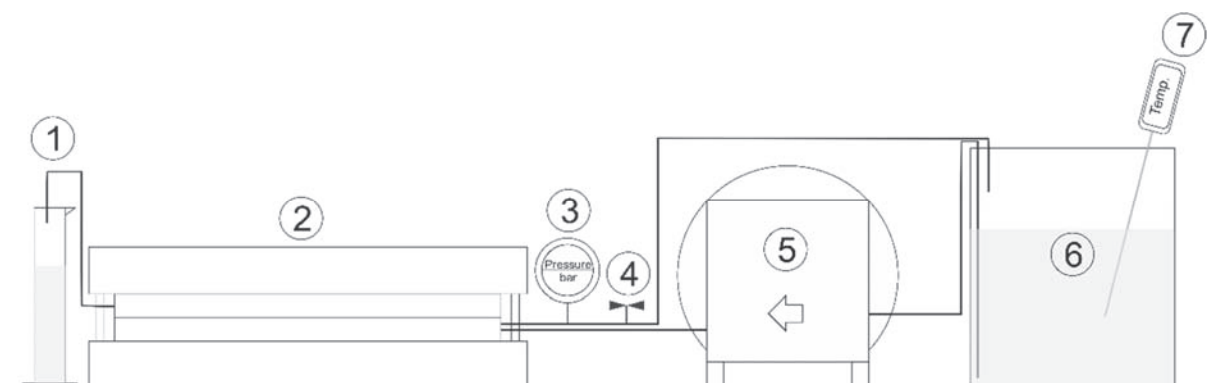
### 2.3.1 Permeate flux and hydraulic permeability

The experiments were conducted using a commercially available bench-scale membrane test cell (Sepa CF, GE Osmonics); Figure 3 illustrates the equipment. The feed solution (6) had the temperature recorded (7) during the process. The pump (5) forced the solution through the test cell (2), the internal pressure was measured using a gauge (3). A valve (4) was used to manage the flow and the pressure. The concentrated was poured back to the feed solution (6) while the permeate was stored (1) for further analysis. To evaluate the flux of the membrane, the operation time was recorded using a regular stopwatch and volume of permeate was measured by a graduated cylinder. During the procedures, the coupons (200 cm<sup>2</sup>) were placed inside the test cell (2).

The hydraulic permeability test utilized Milli-Q water, being the first test of each membrane. Followed by membrane rejection of salt, acetaminophen and lactose (2.3.2) and finally the application test. During the batch of experiments, the membranes were not removed from the test cell, since it would dislocate the membrane, which can cause procedural errors.

The flux and permeability procedure were inspired by methodologies published elsewhere (GARCÍA-PACHECO et al., 2015; GARCÍA-PACHECO et al., 2019; LAWLER et al., 2012; LAWLER et al., 2013; RODRÍGUEZ et al., 2002).

Figure 3: Illustration of the bench-scale membrane test cell, (1) graduated cylinder, (2) test cell, (3) pressure gauge, (4) recirculation valve, (5) pump, (6) feed solution storage beaker, (7) thermometer.



We studied the mechanism of transport through reverse osmosis membranes by the solution-diffusion model ( $q$ ). According to this model, solutes permeate the membrane by dissolving in the membrane material and diffusing down a concentration gradient (BAKER, 2012). A simple model of liquid flow through these membranes is to describe the membranes as a series of cylindrical capillary pores of diameter  $d$ . The liquid flow through a pore ( $q$ ) is given by Poiseuille's law (Equation 1).

$$q = \frac{\pi \times d^4}{128 \times \mu \times l} \times \Delta p \quad (1)$$

Where  $\Delta p$  is the pressure difference across the pore,  $\mu$  is the liquid viscosity and  $l$  is the pore length. The permeate flux ( $J$ ) is the sum of all the flows ( $q$ ) through the individual pores and can be obtained by the Equation 2.

$$J = A(\Delta p - \Delta \pi) \quad (2)$$

Where  $A$  is the hydraulic permeability expressed in  $\text{l.h}^{-1}\text{m}^{-2}\text{.bar}^{-1}$ ,  $\Delta p$  is the difference in pressure across the membrane,  $\Delta \pi$  is the osmotic pressure of the feed solution. The permeate flux ( $J$ ) was determined by volumetrically measuring the permeated at different feed pressures. The permeate was always recirculated back to the feed tank, maintaining the feed solution at constant concentration. The hydraulic permeability can also be obtained from the slope of the linear regression of the permeate flux versus the feed pressure.

The feed temperature rises due to circulating through the membrane module, which has great impact on the permeate flux (SHAMEL; CHUNG, 2006). The rate of change in permeate flux is about 3% per degree Celsius increase in the feed water temperature (AL-MUTAZ; AL-GHUNAIMI, 2001). Therefore, all the measured fluxes were adjusted to the temperature of 20 degrees Celsius using correlation with the viscosity of water at different temperatures.

### 2.3.2 Membrane rejection

To characterize the integrity of membranes, we measured the lactose and acetaminophen rejection. The rejection to salt is a fundamental parameter since most RO membranes are used for desalination. The salt rejection can be easily predicted by measuring the electrical conductivity of



the permeate. A solution of NaCl 0.1 mol/L was used as a model. The electrical conductivity was measured using portable conductivity meter Cond 3151 from WTW (Xylen Analytics - Germany). A solution with 5 % (w/v) of lactose at analytical grade (Synth) and NaCl (0.1 mol/L) was used to evaluate lactose rejection. Lactose was measured by spectroscopy in the near infrared by a Soma Scope MK2 coupled with a Lactoscope FTIR (Delta Instruments).

A solution of 100 mg l<sup>-1</sup> of acetaminophen and 0.1 mol/L of NaCl was utilized as a standard solution for the permeate tests. Acetaminophen was measured according to the procedure of Mbokou et al. (2016). The method is based upon the redox potential of acetaminophen measured by glassy carbon probe, in our study the probe was attached to the equipment PG581 from Uniscan Instruments Further details can be on Mbokou et al. (2016).

The membrane rejection ( $R$ ) for each parameter was calculated using Equation 3.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

Where  $R$  is the membrane rejection in %,  $C_p$  is the concentration in the permeate, and  $C_f$  is the concentration in the feed solution.

### 2.3.3 Morphology of the aged and oxidized membranes

The membranes were analyzed by Scanning Electron Microscopy (SEM) with an acceleration of 3 kV using the equipment JSM JEOL 6301F manufactured by JEOL (USA) and Atomic Force Microscopy (AFM) using the equipment CPII manufactured by Veeco (USA).

### 2.3.4 Simulation of permeation flux and salt rejection

The software from Dow Chemical® ROSA 9.1 was primarily created to simulate and predict the behavior of membranes at standard conditions. Since the software can accurately reproduce the performance of pristine RO (BOULAHFA et al., 2019; SAHINKAYA et al., 2019), it was utilized to generate references in order to compare with the aged and oxidized conditions. All the simulations of rejection on ROSA utilized 5840 mg l<sup>-1</sup> of total dissolved solids (TDS), the equivalent of 0.1 mol/L of NaCl.

### 2.3.5 Prediction of pore diameter and Molecular Weight Cut-Off of the membranes

The pore diameter of an unknown membrane can be estimated using Equation 4. The equation derived from Poiseuille's law, when a well-known membrane can be used as a reference to determine the pore diameter ( $d_p$ ) in nm of similar membranes for specific operation temperatures.

$$d_p = \sqrt{A_p/A_0} \times d_{p0} \quad (4)$$

Where  $A_0$  is the permeability of the reference membrane,  $d_{p0}$  is the pore diameter of the reference membrane, and  $A_p$  is the permeability of the similar membrane. In this case, the reference membrane at the temperature of 20 °C had a permeability of 4.23 L.h<sup>-1</sup>.m<sup>2</sup>.bar<sup>-1</sup>, and the pore diameter of 0.69 nm.

The Molecular Weight Cut-Off (MWCO) is defined as the molecular weight at which 90% of the macromolecular solute is rejected by the membrane (SINGH, 2005). The MWCO of a membrane can be also calculated using the empirical Equation 5 (AIMAR; BACCHIN; MAUREL, 2017).

$$MWCO = \sqrt[0.4]{\frac{d_p}{0.076}} \quad (5)$$

### 2.4 Data Analysis

The statistical analysis of the results was conducted on a statistical software.

### 2.5 – Acetaminophen

The two-electron oxidation of acetaminophen is observed as an anodic (oxidizing) current when the electrode potential is swept in the positive direction (PINE RESEARCH INSTRUMENTATION, 2019). To measure acetaminophen, a glassy carbon probe attached to the equipment PG581 from Uniscan Instruments was utilized to obtain the peak intensity, which is then related to the concentration of acetaminophen using a calibration curve. The potential scan rate of the equipment is 100 V s<sup>-1</sup>. The equation of the calibration curve (R<sup>2</sup>=0,9998) is described in the Equation 6. The rejection was calculated using Equation 3.

$$y = 0,1715 \times x \quad (6)$$

Where  $y$  is the peak intensity ( $\mu A$ ) and  $x$  is the concentration of acetaminophen (in mg/l). According to Mbokou et al. (2016), the peak intensity ( $I_p$ ) of an analyte at a given electrode can be used to determine the calibration of the glassy carbon electrode used on the basis of Randles-Sevcik equation (7).

$$I_p = k \times n^{\frac{3}{2}} \times A \times D^{\frac{1}{2}} \times C \times V^{\frac{1}{2}} \quad (7)$$

Where  $k = 2.69 \times 10^5$ ,  $n$  is the number of moles of electrons transferred per mole of electroactive species,  $A$  ( $\text{cm}^2$ ) is the area of the electrode,  $D$  ( $\text{cm}^2 \cdot \text{s}^{-1}$ ) is the diffusion coefficient of the electroactive species,  $C$  ( $\text{mol L}^{-1}$ ) is the bulk concentration of the electroactive species, and  $v$  ( $\text{V s}^{-1}$ ) is the potential scan rate.

### 3 – Results and Discussion

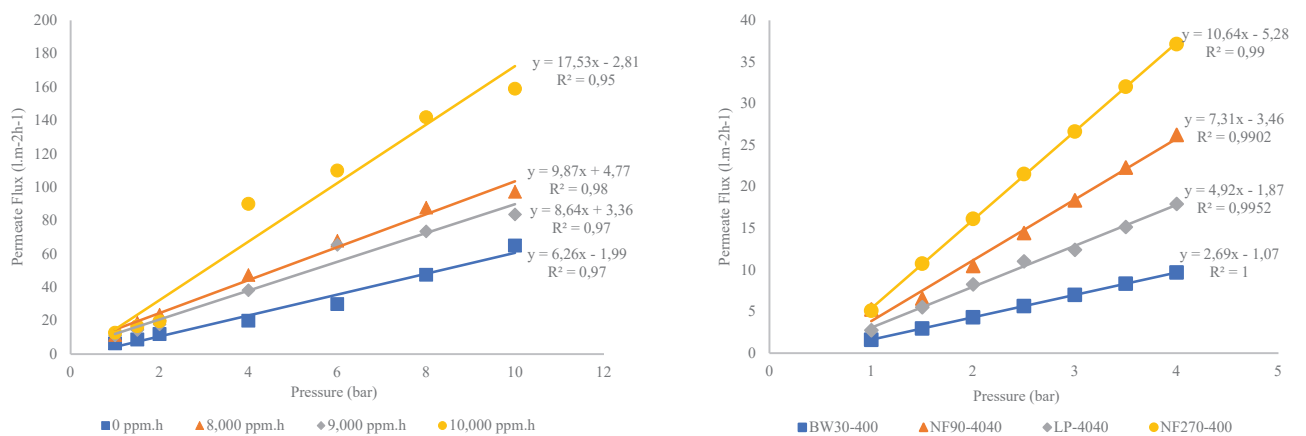
#### 3.1 – Permeate flux and hydraulic permeability

The average permeate flux of the oxidized membranes showed a broad increase when comparing to the reference aged RO membrane (0 ppm.h) as shown in Figure 4a. The surface of polyamide membranes is modified during the chlorinated oxidation, since it breaks and weakens hydrogen bonding and this breakage/weakening can lead to alteration in the permeability and also the membrane rejection (KWON; LECKIE, 2006). Terrero et al. (2015) also demonstrated how chlorinated oxidation impairs the polyamide active layer of the membranes. According to the authors, the intensity of amide I and amide II peaks from the polyamide layer were reduced after the exposure, and nearly vanished when treated at 420 hours of exposure time at 124 ppm.

We simulated the permeated flux of different loose RO (BW30 – Dow Chemical and LP-4040 – Vontron) and tight NF membranes (NF270 and NF90 from Osmonics) in Figure 4b to compare with the permeate flux of the oxidized membranes. The aged membrane (0 ppm.h) showed a higher flux than the references LP-4040 and BW30-4040. The intrinsic deterioration of the membranes during operation was reported to increase the size and the number of pores on the membrane (GARCÍA-PACHECO et al.; 2019); this fact contributes for the permeability increase (LAWLER et al., 2013). Permeate flux of oxidized aged RO membranes can be compared with the

NF membranes. However, the doubt is if the selectivity of the aged RO membrane could be also compared with NF.

Figure 4: Permeate flux at different pressure (a) of the aged RO and oxidized membranes and (b) Simulation of membranes references on ROSA software.



a) Permeate flux at different pressure of the aged RO and oxidized membranes.      b) Permeate flux at different pressure of membranes references on ROSA software.

We normalized the average hydraulic permeability of the oxidized and the reference membranes by the aged RO membrane. The comparison between the effects of the oxidation on the permeability with the literature and the references membranes is summarized in Table 2.

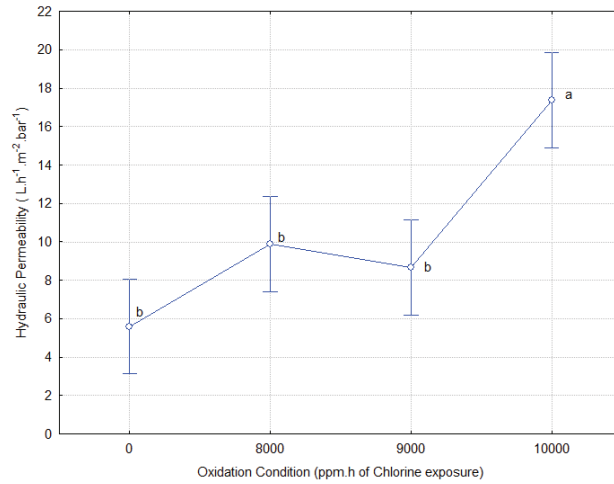
Table 2: Summarized hydraulic permeability of aged, oxidized and reference membranes.

Membrane	Simulated on ROSA				Tested membranes			
	BW30-400	LP-4040	NF90-4040	NF270-400	0 ppm.h	8,000 ppm.h	9,000 ppm.h	10,000 ppm.h
Hydraulic Permeability ( $l \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ )	2.69	4.93	7.31	10.65	5.59	9.87	8.65	17.36
Normalized hydraulic permeability	0.48	0.88	1.31	1.90	1.00	1.76	1.55	3.10

The aged membrane (0 ppm.h) showed almost 15 % higher permeability than the reference LP-4040 - Vontron (generated by ROSA software), as a consequence of the cycles of use/cleaning (LAWLER et al., 2013). Note that the BW-30 membrane is meant for the desalination of brackish water, with a lower permeability than LP-4040. On the other hand, the aged membrane has a lower permeability than the tight NF-90, it means that in terms of permeability, the aged membrane is in a range between NF and RO membranes. Furthermore, the oxidation process drives to permeabilities higher than NF-90 and NF-270 membranes. Additionally, the end-of-life membrane used in this work had the presence of inorganic scaling (Figure 2), which could contribute to the increase of permeability due to mechanical or chemical degradation of the polyamide layer (GARCÍA-PACHECO et al., 2019). Figure 5 shows the permeability of the aged and oxidized membranes.

The permeabilities of the membranes were also statistically analyzed at 95% confidence level. The results confirmed that the 0 ppm.h, 8,000 ppm.h and 9,000 ppm.h are in the same statistical group (b). On the other hand, the membrane oxidized in 10,000 ppm.h showed the higher permeability among all membranes and it is the only member of the second statistical group (a).

Figure 5: Average hydraulic permeability of the aged RO membrane and oxidized membranes.



The permeability of the membrane oxidized in 10,000 ppm.h reached  $17.36 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$  (3.10 times the permeability of the aged membrane). Antony et al. (2016) reached a similar increase on the permeability when oxidized a RO membrane at 10,000 ppm.h of chlorine, and the oxidized membrane has shown a hydraulic permeability of  $7.3 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$  while the reference had  $2.8 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$  (2.6 times the permeability of the aged membrane).

Table 3: Predicted pore diameter and molecular weight cut-off of reference, aged and oxidized membranes.

Membrane	Simulated on ROSA		Oxidized membranes			
	NF90-4040	NF270-400	0 ppm.h	8,000 ppm.h	9,000 ppm.h	10,000 ppm.h
dp (nm)	0.91	1.09	0.79	1.05	0.99	1.40
MWCO (Da)	492.28	787.59	352.17	716.41	607.04	1451.05

The permeability of the membrane 0 ppm.h, 8,000 ppm.h and 9,000 ppm.h presented commercial NF-like range, since most NF membranes have MWCO between 100 Da and 1000 Da.

On the other hand, the most oxidized membrane (10,000 ppm.h) reached commercial UF-like range, since UF membranes MWCO usually ranges between 1,000 Da and 100,000 Da.

A similar fact was described by García-Pacheco et al. (2019), but instead, the authors used the concentration of 300,000 ppm.h to oxidize the aged tight RO membrane SW30 from Osmonics. The permeability achieved in this work by the membrane 10,000 ppm.h was higher than the SW30 RO membrane, since only a fraction of oxidizer was needed to reach UF-like permeability, different from García-Pacheco et al. (2019). Each membrane is designed for specific purposes, the 300,000 ppm.h oxidized by García-Pacheco et al. (2019) could have had a denser polyamide layer, thus requiring more oxidation. Also, as mentioned by Lawler et al. (2013), each membrane must be studied separately and individually, since the ageing of each membrane depend on many factors.

Many researchers have been evaluating the benefits of increasing membrane permeability. Okamoto and Lienhard (2019) described that higher permeability benefits the operation of these membranes for desalination. Reyes-Contreras, Leiva and Vidal (2019) demonstrated that increasing permeability leads to reduction in the water production cost and Cohen-Tanugi et al. (2014) found that the increasing of three times the permeability would result in 63% fewer pressure vessels or 46% less energy for desalinate brackish water by RO. The permeability is indeed a key factor in this subject, during the last few decades, the permeability improvements of membranes is one of the main reasons of water production cost decrease (REYES-CONTRERAS; LEIVA; VIDAL, 2019). On the other hand, Table 3 shows that as the permeability increase as the MWCO also increases. Thus, harm to the selectivity of the membrane could be expected in these extreme oxidization conditions, impairing the selectiveness and rejection to solutes, subject that will be approached in the sequence.

### 3.2 – Membrane Rejection

Figure 7 shows salt rejection of the aged and oxidized membranes (a) in different pressures as well as the reference membranes simulated on ROSA software (b) and the averaged rejection obtained by different pressures of the tested membranes (c). The simulated rejection of references membranes NF 90-4040 and LP-4040 reproduced the theoretical rejection pattern at increasing feed pressure. On contrary, the aged and oxidized membranes did not follow the same behavior

and there was no correlation between the pressure and the rejection. We highlighted the average rejection for each oxidation condition in Figure 7a. ROSA software consider a diffusional flux when predicting the salt rejection on references membranes and maybe the oxidation of the membranes takes to higher salt transmission through the membranes due the convective flow because the pores of the membranes become wider (as predicted in Table 3).

The aged RO membrane (0 ppm.h) achieved the highest salt rejection (64.20%) among the tested conditions. However, this rejection is lower than all the simulated rejections of pristine-reference membranes. Indeed, as extensively reported (DO et al., 2012; ETTORI et al., 2011; KWON; TANG; LECKIE, 2006; SIMON et al., 2009), aged membranes have lower salt rejection than pristine membranes due to the damages during their lifetime. Figure 7a shows that the higher the oxidation conditions the lower the salt rejection. Antony et al. (2016) published the same behavior on pristine membranes that were oxidized at 10,000 ppm.h; the rejection to NaCl decreased from 99% to 40% subsequently the oxidation. As shown in Figure 7a, the oxidation at 10,000 ppm.h decreased the average rejection of the aged membrane by 77%, similar to the 60% reported by Antony et al. (2016).

Figure 6 shows the linearization of the diffusive and convective fluxes, that is used to find the modified Peclet's ( $Pe$ ) number (Table 4). The Peclet's number (Equation 8) express the relationship between the convective and diffusive mass transfer through the membrane (DIAWARA et al.,2003). When  $Pe > 1$  convective mass transfer is dominant, with a  $Pe < 1$  diffusional mass transfer is dominant. For the 0 ppm.h membrane, the flux is mastered by diffusion. On the other hand, as more open the pore size (as predicted on Table 3) as more diffusive mass transfer occurs through the membrane. This implies that the mechanism of mass transfer of salts through the membrane changes as more severe is the oxidation. Still, as more drastic the oxidization, as higher is the predicted MWCO of the recycled membrane (Table 3), reaching the range of NF or even UF. Thus, new applications for these recycled membranes must be tested.

$$Pe = Jv C_{conv} / J_{diff} \quad (8)$$



Figure 6: Linearization of mass transfer by diffusion and convection

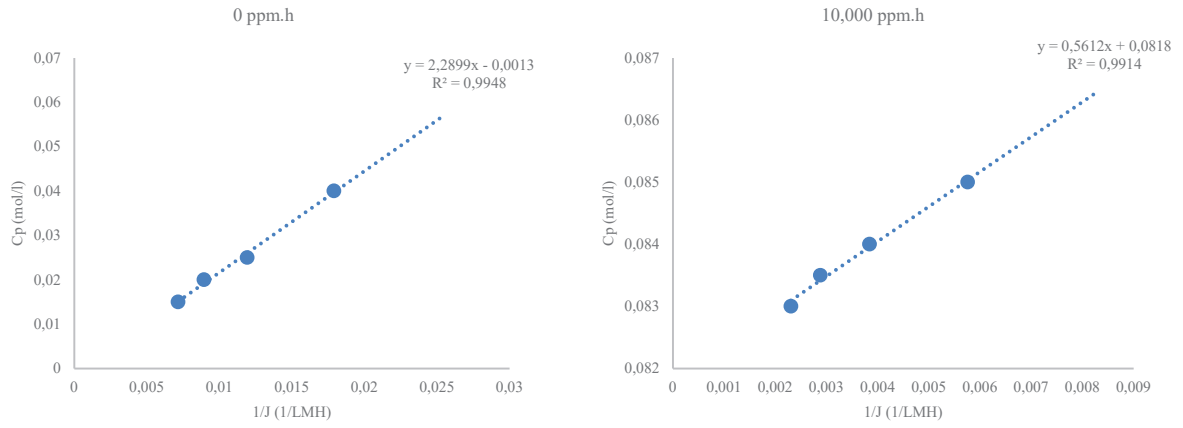
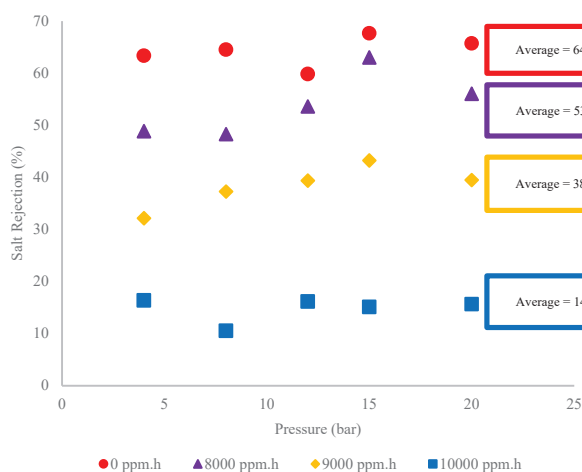


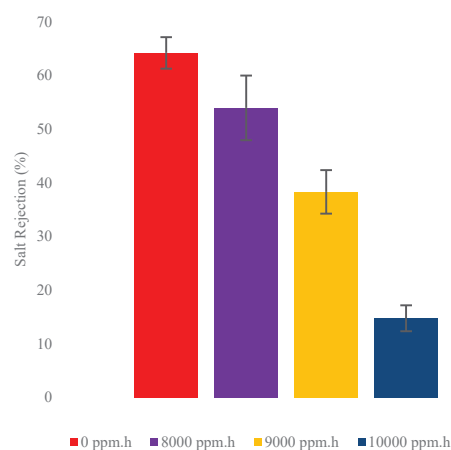
Table 4: Peclet's number for 0 ppm.h and 10,000 ppm.h membrane.

0 ppm.h	10,000 ppm.h
Pe'	Pe'
0.03	25.30
0.04	37.96
0.06	50.61
0.07	63.26
Diffusional membrane	Convective membrane

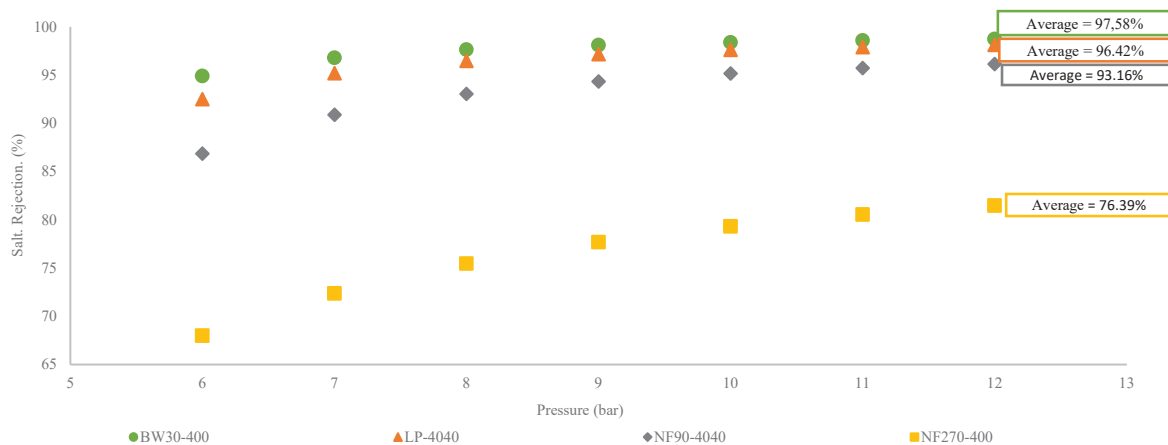
Figure 7: (a) Salt rejection of the aged and oxidized membranes; (b) Salt rejection of references membranes simulated on ROSA (c) Averaged salt rejection of tested membranes.



a) Salt rejection of the aged and oxidized membrane.



c) Averaged salt rejection of tested membranes.

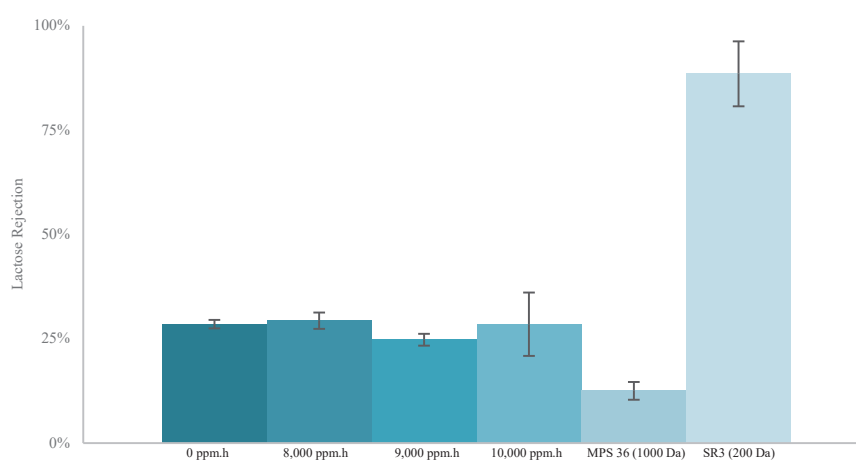


b) Salt rejection of references membranes simulated on ROSA.

Previous data shown that the oxidized membranes are similar to NF membranes in terms of permeability and salt rejection. Additionally, we tested two solutes of average molecular weight to evaluate possible application of the recycled membranes: lactose and acetaminophen. Figure 8 shows lactose rejection of the aged and oxidized membranes. Furthermore, we tested two commercial NF membranes (MPS36 – 1,000 Da of MWCO and SR3 – 200 Da of MWCO, both from Koch Membrane Systems) to compare the recycled membranes with standard NF membranes.

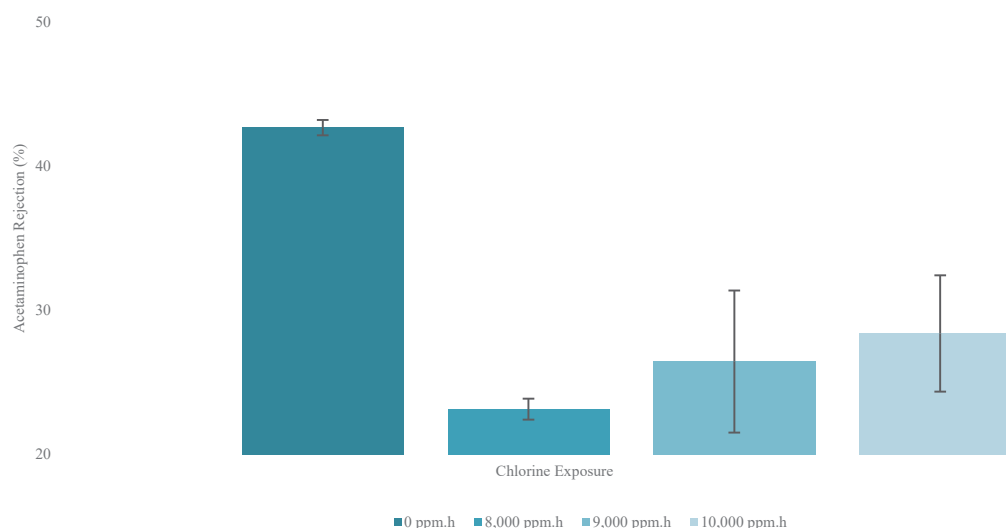
First remark is regarding the effect of different oxidation conditions: there was no difference between lactose rejection on the aged and oxidized membranes and the values ranged in 27 % - 32 % and an average rejection of 30 %. For the 200 Da SR3 NF membrane, 88.5 % of lactose was rejected and the 1,000 Da MPS-36 NF membrane rejected only 13% of lactose. Thus, the expected MWCO of the oxidized membranes seems to be between 200 Da and 1,000 Da.

Figure 8. Lactose rejection of the aged, oxidized and references NF membranes.



The rejection to acetaminophen by the aged and oxidized membranes is shown in Figure 9. The aged membrane has a rejection to acetaminophen of approximately 42%. On the other hand, the statistical analysis at 95% of confidence level has shown that all the oxidized membranes show a lower rejection than the aged membrane, separated in another statistical group (thus, present the same rejection to acetaminophen, between 24 % and 30 %).

Figure 9: Acetaminophen Rejection of the aged and oxidized membranes.



The low rejection to acetaminophen molecule (molecular diameter of 0.285 nm) by NF membranes was reported by Azaïs et al. (2016). The authors suggested that the molecule is smaller than the pores of the membrane NF270 (0.40 nm). The rejection to acetaminophen in pure water on the NF-270 ranged between 5 % and 35%. The authors also reported that the high polarity caused by the substitution of benzene ring by hydroxide and amide groups can contribute to the low rejection of acetaminophen. GE et al. (2017) utilized the same NF-270 membrane model in order to test acetaminophen rejection from ultra-pure water solution. The rejection only reached 16.4 %. Higher rejection was achieved by changing the solution's pH into alkaline condition and results show that electrostatic repulsion has a stronger impact on the rejection rate than steric exclusion. On the other hand, the aged RO membrane (0 ppm.h) had also shown a low acetaminophen rejection as a consequence of its lifetime.

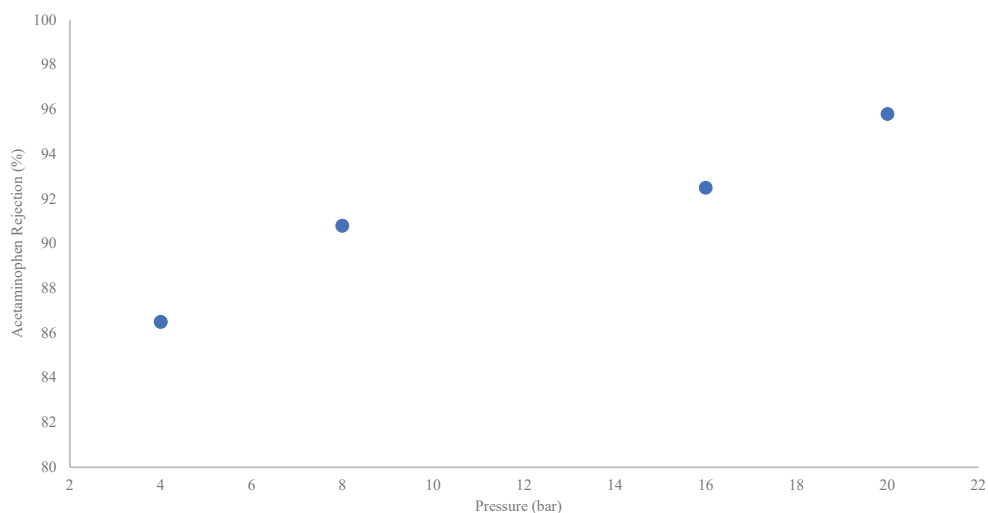
As reported by Kwon (2006), the oxidation of RO membrane increases hydrophilicity and made zeta potential slightly more negative. In this context, the Figure 9 suggest that the rejection of acetaminophen seems to increase at higher concentration of oxidizers. Increasing zeta potential of the membrane during oxidation may have created a coated surface dispelling acetaminophen and increasing the rejection.

The rejection of several pharmaceuticals on NF (NF90) and RO (BW30) membranes were tested by Licona et al. (2018). The study found that acetaminophen as well as caffeine rejection were the lower among all the tested pharmaceuticals, including ibuprofen, dipyron, and diclofenac. Since acetaminophen was in the non-ionic form at the tested pH, there was no electrostatic interaction with the membrane, which is negatively charged, enforcing the idea of the coated oxidized membrane. For this reason, the author suggests that rejection by size (sieving) was the main removal mechanism for the NF90. For the BW30, acetaminophen accumulated on the surface of the membrane due to size exclusion. Radjenović et al. (2008) utilized a full-scale drinking water treatment plant treating groundwater with pharmaceuticals. The acetaminophen rejection (44.8 %-78.3 %) was lower when compared to other pharmaceuticals, possibly due to its small molecular size and low polarity.

The retention of acetaminophen using UF (4.5 %-16.1 %) and NF (13.4 %-39.6 %) was also evaluated by Acero et al. (2010) on water and municipal secondary effluent. According to the author, adsorption is the main retention mechanism for UF membranes, while for NF membranes size exclusion and electrostatic repulsion of negative species at high pH are responsible for micropollutant retention.

The removal of acetaminophen ( $5 \text{ mg.L}^{-1}$ ) was also tested on a nanofiltration NF90 membrane for the sake of comparison and the results are shown in Figure 10. At a feed pressure of 20 bar, the permeate reached  $0.2 \text{ mg.L}^{-1}$ . In comparison to regulations, the phenol index for influent is  $0.3 \text{ mg.L}^{-1}$ . This NF 90 membrane permitted to nearly eliminate acetaminophen.

Figure 10: Acetaminophen removal using pristine NF90 nanofiltration membrane.



### 3.3 – Membrane morphology

Figure 11 (a) shows the micrographs from SEM analysis of the 0 ppm.h and 10,000 ppm.h membranes (Figure 11 - b). The cleaning procedure associated with the oxidation likely removed the inorganic scaling from the membrane surface, since the oxidized membrane 10,000 ppm.h did not show any presence of scaling (Figure 11 - b).

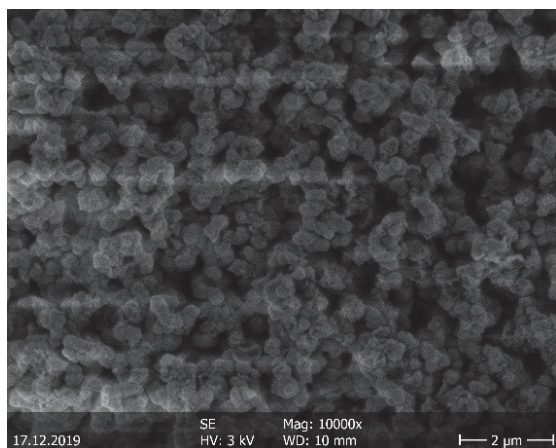
Differences on the morphology of membranes 0 ppm.h and 10,000 ppm.h can be observed in Figure 12. (a) present some impacts on the surface of the membrane, as could be expected for an aged membrane. On the other hand, the Figure 12 (b) shows a much more damaged membrane, which could also be expected for the oxidized membrane. It can be understood that even though the oxidation (10,000 ppm.h) partially damaged the membrane (Figure 12 - b), the characteristics of the polyamide layer is still present on the surface of the membrane (Figure 11 - b).

These differences in oxidized membranes were also identified by García-Pacheco et al. (2019). The authors also confirmed that shorter exposure periods, such as those carried out during this work, are linked to less damage to the polyamide layer.

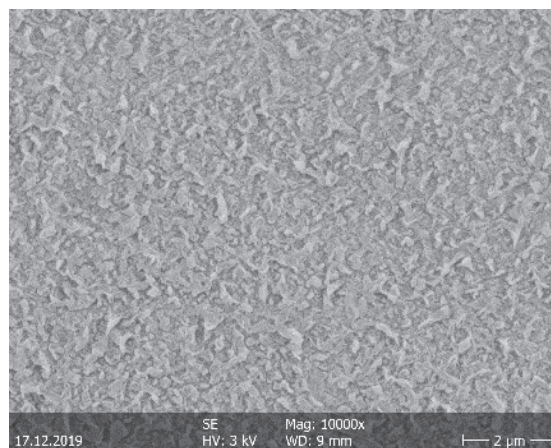
The SEM analysis in Figure 12 confirms a higher Average Roughness (Ra) for the membrane 10,000 ppm.h when compared to the 0 ppm.h. The usual application of RO membranes

can modify the roughness of the membrane, as shown by Mohamedou et al. (2010) when compared new and aged membranes. However, our work suggest that the severity of oxidation can increase the roughness of the membrane. This is of concern for the reuse of the oxidized membranes because higher roughness is linked to fouling. As a reference, the roughness of the pristine NF-270 membrane was reported by Tang (2007) as low as 9.0 nm, and the NF90 presented 129.5 nm. In contrast, our recycled membrane showed a roughness of 276 nm.

Figure 11. (a) SEM image of the 0 ppm.h membrane and b) 10,000 ppm.h.

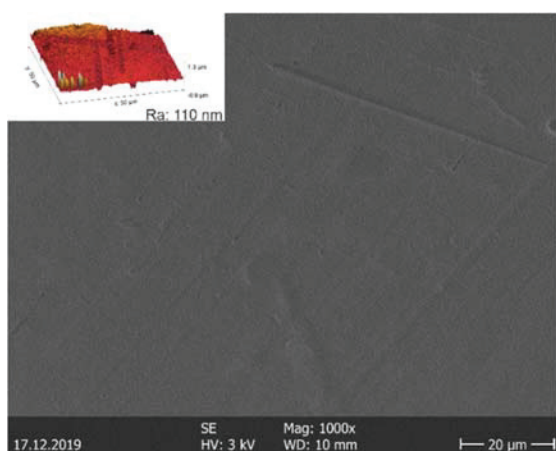


a) 0 ppm.h

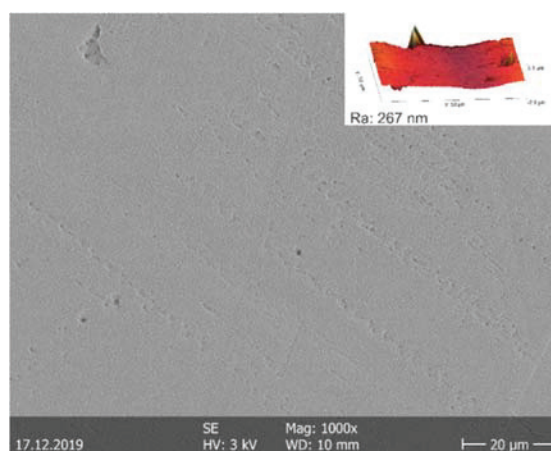


b) 10,000 ppm.h

Figure 12. SEM image and AFM analysis of the a) aged RO membrane and the membrane b) 10,000 ppm.h.



a) 0 ppm.h



b) 10,000 ppm.h



### 3.4 – FTIR analysis

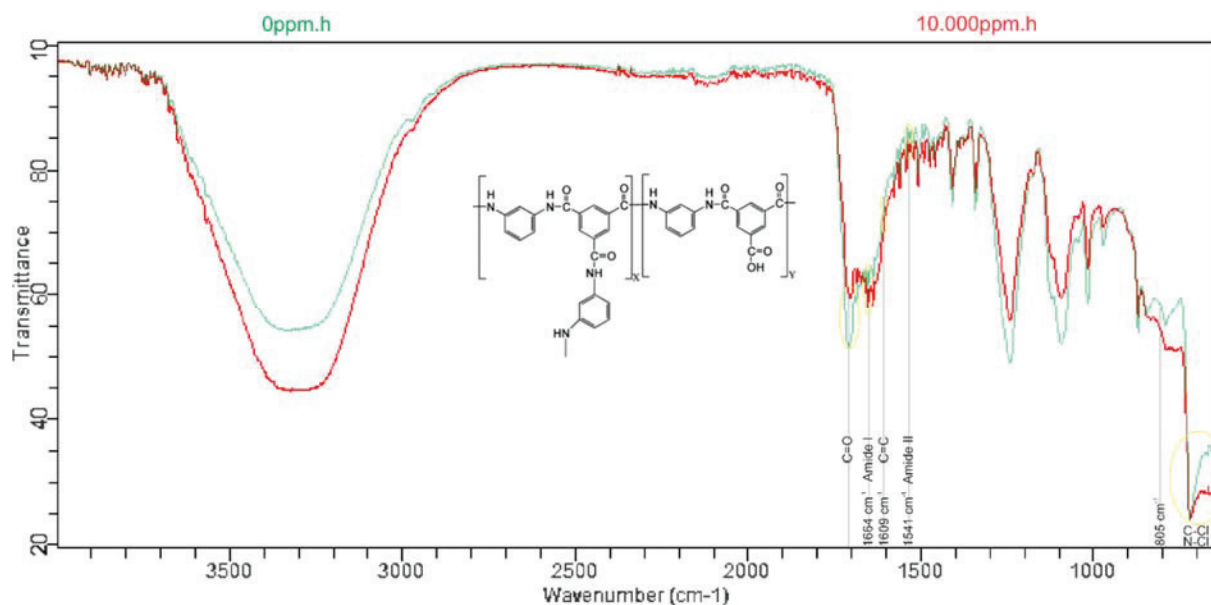
FTIR analysis detects bonds between atoms in a molecule and provides information about functional groups as well as the chemical structure of the analyzed material. The FTIR spectra of the aged (0 ppm.h) and oxidized (10,000 ppm.h) membranes were overlapped and analyzed, as shown on Figure 13.

As reported by Kwon (2006), the chlorinated oxidation modified the peaks at 1541 and 1609  $\text{cm}^{-1}$ , which are mainly contributed by the N-H bending motion of amide (SOCRATES, 1994). The author further explained that the amide nitrogen is the dominant reaction site with chlorine, where the hydrogen attached to the amide nitrogen are replaced by chlorine. The author also demonstrated that the content of chlorine on the surface of the oxidized membrane is linked to the concentration of nitrogen in the membrane. Analysing the FTIR of the 10,000 ppm.h membrane, a subtle difference can also be observed on these bands, meaning that the same phenomenon may have occurred on the oxidized membranes.

Kwon (2006) used exposure time of the membranes as high as 1 hour of contact, finding changes in N-H bending of amide, which is the dominant reaction site with chlorine. On the other hand, Pacheco et al. (2019), submerged the membranes into chlorine solutions for as high as 242 h of exposure time, finding that Amide I, II and band C=C nearly vanished at 124 ppm for 242 hours. The same did not occur when the exposure time was proportionally reduced and free chlorine concentration increased. It can be deduced that the oxidation begins breaking N-H and continues with the degradation of the remaining polyamide molecule if the exposure maintained.

The bands in the range of 805  $\text{cm}^{-1}$  and 690  $\text{cm}^{-1}$ , are assigned to the vibration of N-Cl (PETTERSON, 1960) performed a peak lowering on the oxidized membrane when compared to the aged membrane, also corroborating with the idea that hydrogen from amide nitrogen were replaced by chlorine molecule. As reported by Kwon (2006), the insertion of chlorine in the membrane surface increases hydrophilicity of the membrane, which can then lead to permeability increase.

Figure 13. FTIR of oxidized and aged membrane.



### 3.5 Applications of the recycled membranes

Previous results of our work have shown that the oxidized RO membrane has the characteristics of a loose NF membrane. Thus, we investigated applications for this recycled membrane for desalination of brackish water and treatment of surface water.

#### 3.5.1 Brackish water demineralization

Brackish water ( $2\text{g}\cdot\text{L}^{-1}$  of TDS) was collected. The permeability of the membrane 10,000 ppm.h when treating brackish water is shown in Figure 14. The permeability of the membrane with pure water ( $17.4\text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ ) was approximately 5 times higher than with brackish water ( $3.37\text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ ). In fact, the concentration of salt in the solution reduces the driving force (pressure) due to the osmotic pressure, lowering the permeability of the system.

The rejection of salt from the membrane 10,000 ppm.h is shown in Figure 15. There was a typical behavior of the membrane rejection and, as the pressure is increased, the rejection also heightens. The rejection by NF membranes is a consequence of the sieving effect, electrostatic and

steric interactions (associated with charge shielding), Donnan exclusion, and ion hydration (PAUGAM et al., 2004). Thus, rejection in NF depends on several factors, such as MWCO, pH, ionic strength, water composition, and sieving effects. In 18 bar of pressure, the salt rejection of our oxidized membrane reached 81%; this value is near the 82% of TDS rejection found by Brião et al. (2019) in the desalination of groundwater using SR3 NF membrane from Koch (MWCO 100 Da).

The well-known NF-270 membrane from Dow (MWCO 200-400 Da) has the rejection higher than 97 %, whilst the rejection of NF ESNA1 from Nito-Denko (MWCO 100-300 Da) is 89 % (MOHAMMAD et al., 2015). Thus, the behavior of our recycled membrane is similar of a NF membrane in terms of permeability and salt rejection. The recycled RO membrane has good prospect of use for desalination of brackish water for the production of drinking water in such relation of TDS concentration, which is below 500 mg L<sup>-1</sup>, as suggested by the World Health Organization guidelines for drinking water (WHO, 2011). In addition, to achieve the goal of 500 mg L<sup>-1</sup>, a rejection of 75 % is required to adjust the TDS of the brackish water, and only 8 bar of pressure is required (Figure 15) for the operation of the desalination system using this recycled RO membrane.

Figure 14. Permeate flux of the oxidized RO membrane in 10,000 ppm.h when treating brackish water.

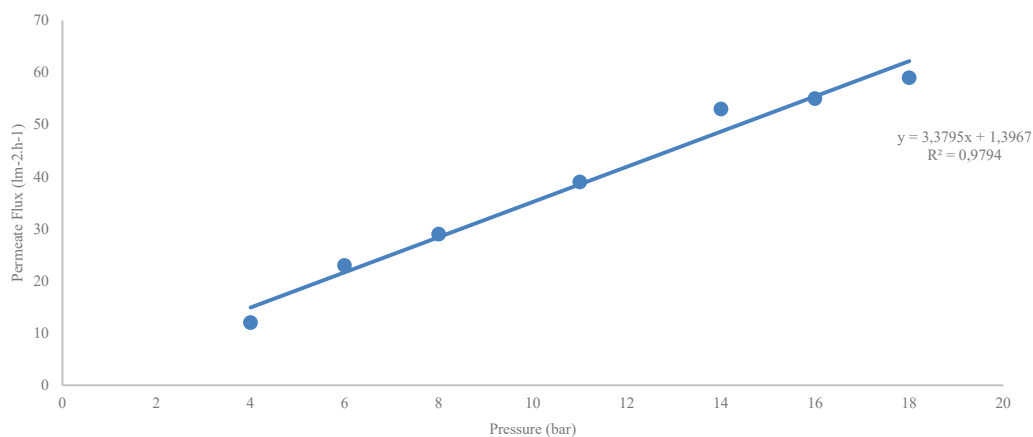
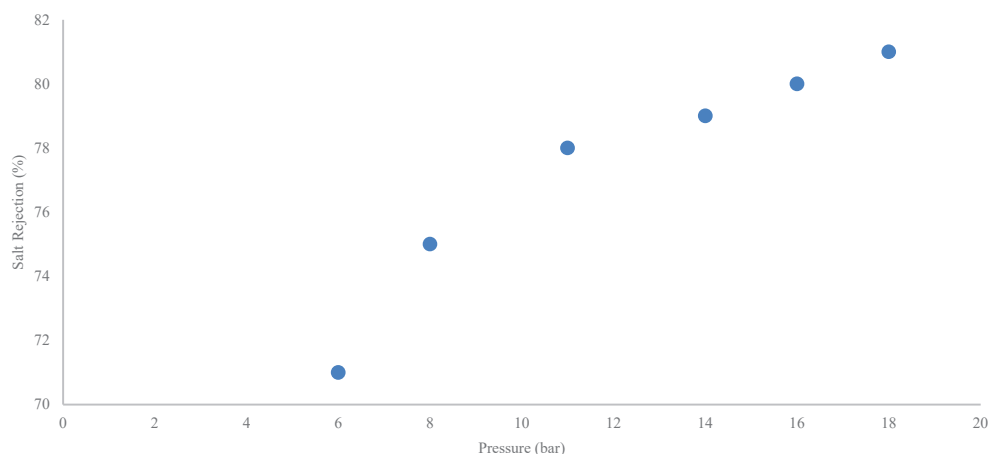


Figure 15. Salt rejection of the oxidized RO membrane in 10,000 ppm.h when treating brackish water.

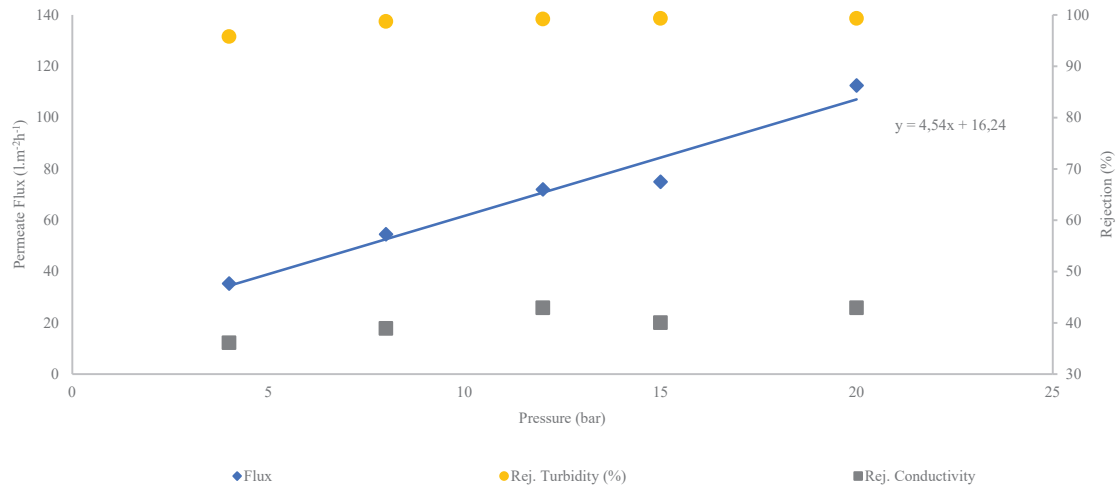


### 3.5.2 Surface water treatment

The permeability of the oxidized membrane in 10,000 ppm.h was approximately a quarter ( $4.54 \text{ L.m}^{-2}.\text{h}^{-1}$ ) of the permeability with pure water ( $17.40 \text{ L.m}^{-2}.\text{h}^{-1}$ ). Figure 16 shows the permeate flux of the recycled membrane in different pressures. Contrary to the application on brackish water, the reduction of permeate flux is attributed to fouling of organic material, such as humid acids. In fact, the presence of humid acids has been preventing the use of these membranes on the treatment of surface water.

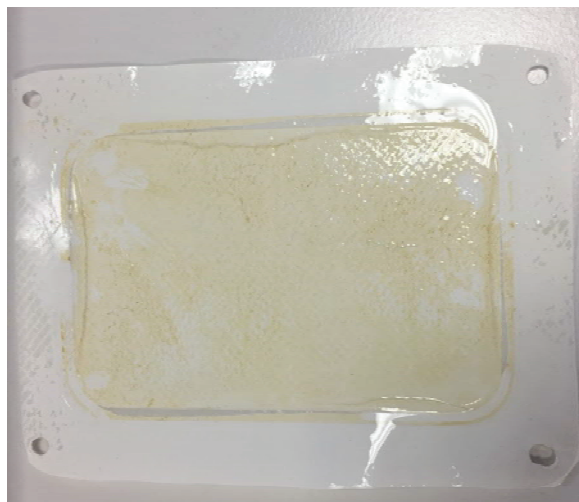
However, the membrane has shown typical permeability of NF applications (MOHAMMAD et al., 2015). This fact, associated with the rejection of turbidity higher than 99.2 % (Figure 16) and 20 % of salts (Figure 16), shows that the recycled membrane could be applied for removal of turbidity as post-treatment of wastewater with low turbidity. Environmental application has been the main focus of NF studies (MOHAMMAD et al., 2015), and there is a great potential for polishing water from water treatment stations.

Figure 16. Permeate flux, salt and turbidity rejection of the oxidized membrane in 10,000 ppm.h treating surface water from Lake Nantes (France).



The Figure 17 shows the membrane after the permeation of surface water. We can see the deposition of material on the membrane surface. As discussed in item 3.3, the high Roughness of the oxidized membrane can be a crucial factor for the operation of these recycled membranes.

Figure 17: Picture of the oxidized membrane in 10,000 ppm.h of chlorine after treating surface water.



#### 4- Conclusion

The permeability of the aged membrane was already higher than the simulated references, probably due to damages through the lifecycle of these membranes. The normalized permeability of the membranes suggests that membranes 0 ppm.h, 8,000 ppm.h and 9,000 ppm.h present NF like permeability, and even higher permeability for 10,000 ppm.h, possibly UF-like, in terms of permeability. Statistical analysis (95% confidence level) confirms higher permeability for the membrane 10,000 ppm.h when compared with all the other oxidized membranes. The MWCO estimation also indicates that the membrane 10,000 ppm.h reached UF characteristics. This increase in permeability can increase competitiveness in terms of cost reduction.

The lack of relation between operation pressure and conductivity rejection efficiency suggests these recycled membranes could be operated in low pressure without negative consequence to the rejection, also leading to cost reduction. The conductivity rejection decreased 77% after the 10,000 ppm.h oxidation, similar results (60%) found by Antony et al. (2016). The linearization of the diffusive and convective fluxes of salt through the membrane implies membrane 0 ppm.h presented a diffusional predominant flux, on the other hand, membrane 10,000 ppm.h reached convective predominant flux, in this case, the presence of pores on the membrane 10,000 ppm.h can be confirmed, as can also be seen on Figure 12.

Application test using lactose suggest that for these oxidized membranes, the MWCO are between 200 Da and 1,000 Da, also suggesting these membranes could be NF-like. Application test with acetaminophen on the aged membrane reached the highest rejection among all tested membranes, for the 8,000 ppm.h, 9,000 ppm.h and 10,000 ppm.h, lower rejection were found. Statistical analysis (95% confidence level) supports these findings. The rejection to acetaminophen on all the oxidated membranes are within the values found for NF by Acero et al. (2010). NF90 nearly removed acetaminophen at higher concentration on the feed, reaching regulations of potable water in European Union, same test could be suggested for further studies using oxidated membranes.

The morphology of the aged membrane from SEM images resembles an inorganic fouled membrane, what could be expected from an aged membrane. The presence of a polyamide layer on the 10,000 ppm.h membrane means that the polyamide was not fully degraded. On the other

hand, the membrane 10,000 ppm.h presents a higher rugosity than the aged membrane, which could be a result of the oxidation of the membrane. FTIR analysis also suggest polyamide layer was not fully degraded, but instead, chlorine was bound to the polyamide. The presence of chlorine on the membrane leads to permeability increase, which indeed was observed for the membrane 10,000 ppm.h.

The membrane 10,000 ppm.h was applied for brackish water treatment; results suggest that the permeability reached in this condition is similar to other NF while treating brackish water. In fact, the membrane 10,000 ppm.h already reached potable water standard at 8 bar of operational pressure. The same membrane was also tested for the treatment of surface water, high rejection of turbidity was achieved, but the membrane fouled during the procedure, as can be seen in the Figure 17.

The objective of this project was fulfilled, a technically viable lower selectiveness UF-like membrane was produced through the 10,000 ppm.h oxidation condition. Application tests suggest membrane 10,000 ppm.h could be used as pre-treatment for brackish water, behaving as a NF membrane in terms of permeability, producing potable water in terms of TDS considering WHO regulations. The membrane 10,000 ppm.h was also effective for the removal of turbidity from surface water, further studies focused on long-operation time could be suggested to evaluate possible fouling problems.

On a large scale, the experience obtained during the execution of this project evidenced that samples of a group of membranes should be oxidized and characterized, followed by a sequence of application tests. The most suitable application result should be considered as a reuse site for the recycled membrane group. It may not be suitable to declare a standard protocol of oxidation for all the aged membranes, since around the world these membranes are witness to great contrasts of usage and post-usage condition. Experience has shown that low pressure applications should be prioritized, considering low mechanical resistance of the membrane, possibly as a result of the oxidation process. The lifespan of these recycled membranes during operation should be considered a factor when choosing an application. As for the application tests, we can suggest specific compound demineralization, brackish water pre-treatment, desalination pre-treatment, superficial water treatment, post-treatment of potable water, wastewater clarification, grey-water reuse systems, rainwater reuse system.

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## **Capítulo 4**

### Considerações Finais

## 6. CONSIDERAÇÕES FINAIS

A permeabilidade da membrana envelhecida já era maior que as referências simuladas, provavelmente devido a danos ao longo do ciclo de vida dessas membranas. A permeabilidade normalizada das membranas sugere que as membranas 0 ppm.h, 8.000 ppm.h e 9.000 ppm.h apresentam permeabilidade semelhante a NF, e permeabilidade ainda mais alta para 10.000 ppm.h, possivelmente semelhante a UF, em termos de permeabilidade. A análise estatística (nível de confiança de 95%) confirma a maior permeabilidade da membrana 10.000 ppm.h quando comparada com todas as outras membranas oxidadas. A estimativa MWCO também indica que a membrana 10.000 ppm.h atingiu as características de UF. Este aumento da permeabilidade aumenta a competitividade em termos de redução de custos.

A falta de relação entre a pressão de operação e a eficiência de rejeição da condutividade sugere que essas membranas poderiam ser operadas em baixa pressão sem consequências negativas para a rejeição, levando à redução de custos. A rejeição da condutividade diminuiu 77% após a oxidação de 10.000 ppm.h, resultados semelhantes (60%) encontrados por Antony et al. (2016). A linearização dos fluxos difuso e convectivo de sal através da membrana implica que a membrana 0 ppm.h apresentou um fluxo predominante difuso, por outro lado, a membrana 10.000 ppm.h atingiu fluxo predominante convectivo, neste caso, a presença de poros na membrana 10.000 ppm.h pode ser confirmada.

O teste de aplicação com lactose sugere que, para essas membranas oxidadas, os MWCO estão entre 200 Da e 1000 Da, sugerindo também que essas membranas podem ser semelhantes ao NF. Teste de aplicação com paracetamol na membrana envelhecida atingiu a maior rejeição entre todas as membranas testadas, para 8.000 ppm.h, 9.000 ppm.h e 10.000 ppm.h, menor rejeição foi encontrada (nível de confiança de 95%). A rejeição ao acetaminofeno em todas as membranas oxidadas está dentro dos valores encontrados para NF por Acero et al. (2010). O NF90 quase removeu o paracetamol em concentrações mais altas, atingindo os regulamentos de água potável na União Européia; o mesmo teste poderia ser sugerido para estudos posteriores usando membranas oxidadas.

A morfologia da membrana envelhecida das imagens de SEM se assemelha a uma membrana inorgânica incrustada, o que poderia ser esperado de uma membrana envelhecida. A presença de uma camada de poliamida na membrana de 10.000 ppm.h significa que a poliamida

não foi totalmente degradada. Por outro lado, a membrana 10.000 ppm.h apresenta uma rugosidade maior do que a membrana envelhecida, o que pode ser decorrente da oxidação da membrana. A análise de FTIR também sugere que a camada de poliamida não foi totalmente degradada, mas em vez disso, o cloro foi ligado à poliamida. A presença de cloro na membrana leva ao aumento da permeabilidade, o que de fato foi observado para a membrana 10.000 ppm.h.

A membrana de 10.000 ppm.h foi aplicada para tratamento de água salobra; os resultados sugerem que a permeabilidade alcançada nesta condição é semelhante a outras NF no tratamento de água salobra. Na verdade, a membrana de 10.000 ppm.h já atingiu o padrão de água potável a 8 bar de pressão operacional. A mesma membrana também foi testada para o tratamento de águas superficiais, alta rejeição de turbidez foi alcançada, mas a membrana foi colmatada durante o teste.

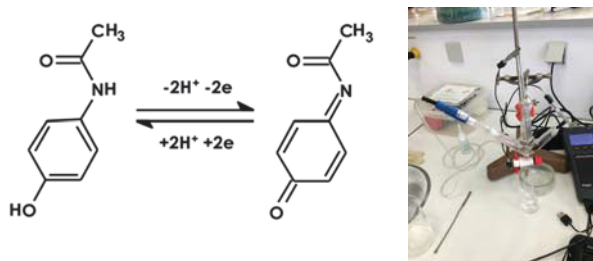
O objetivo deste projeto foi cumprido, uma membrana semelhante a UF de menor seletividade tecnicamente viável foi produzida através da condição de oxidação de 10.000 ppm.h. Os testes de aplicação sugerem que a membrana de 10.000 ppm.h poderia ser utilizada como pré-tratamento para água salobra, comportando-se como uma membrana NF em termos de permeabilidade, produzindo água potável em termos de TDS considerando os regulamentos da OMS. A membrana de 10.000 ppm.h também foi eficaz para a remoção de turbidez da água de superfície, estudos futuros focados em tempos de operação longos podem ser sugeridos para avaliar possíveis problemas de incrustação.

Em larga escala, a experiência obtida durante a execução deste projeto evidenciou que amostras de um grupo de membranas devem ser oxidadas e caracterizadas, seguindo-se uma sequência de testes de aplicação. O resultado de aplicação mais adequado deve ser considerado como uma forma de reutilização para o grupo de membrana reciclada. Pode não ser adequado declarar um protocolo padrão de oxidação para todas as membranas envelhecidas, uma vez que ao redor do mundo essas membranas são testemunhas de grandes contrastes de uso e condição pós-uso. A experiência tem mostrado que as aplicações em baixa pressão deve ser priorizada, considerando a baixa resistência mecânica da membrana, possivelmente em decorrência do processo de oxidação. A vida útil dessas membranas recicladas durante a operação deve ser considerada um fator ao escolher uma aplicação. Quanto aos testes de aplicação, podemos sugerir desmineralização de compostos específicos, pré-tratamento de água salobra, pré-tratamento de dessalinização, tratamento de água superficial, pós-tratamento de água potável, clarificação de efluentes, sistemas de reúso de águas cinzas, sistema de reúso de águas pluviais.

## APÊNDICE A–METODOLOGIA PARA ANÁLISE DE ACETAMINOFENO

O paracetamol tem o nome formal de 4-acetamidofenol, que é uma molécula eletroativa que pode ser oxidada à forma de quinona, também chamada de N-acetil-4-quinoneimina (abreviado como NAPQI) em um processo de transferência de elétrons de dois elétrons e dois prótons. A oxidação de dois elétrons do acetaminofeno (Figura 1) é observada como uma corrente anódica (oxidante) quando o potencial do eletrodo é varrido na direção positiva (PINE RESEARCH INSTRUMENTATION, 2019).

Figura 1: Oxidação eletroquímica do Acetaminofeno



Fonte: (PINE RESEARCH INSTRUMENTATION, 2019)

O reverso de NAPQI para acetaminofeno é obtido com um processo de redução de dois elétrons e dois prótons no eletrodo, varrendo o potencial do eletrodo de volta para potenciais negativos. Para a mensuração do paracetamol, foi utilizada uma sonda de carbono vítreo acoplada ao equipamento PG581 da Uniscan Instruments para obter a intensidade do pico, que é então relacionada à concentração de paracetamol por meio de uma curva de calibração. A taxa de varredura potencial do equipamento é  $100 \text{ V s}^{-1}$ . A equação da curva de calibração ( $R^2 = 0,9998$ ) é descrita na Equação 1. A rejeição foi calculada usando a Equação 3.

$$y = 0,1715 \times x \quad (1)$$

Onde  $y$  é a intensidade do pico ( $\mu\text{A}$ ) e  $x$  é a concentração de acetaminofeno (em  $\text{mg / L}$ ). De acordo com Mbokou et al. (2016), a intensidade de pico ( $I_p$ ) de um analito em um determinado eletrodo pode ser usada para determinar a calibração do eletrodo de carbono vítreo usado com base na equação de Randles-Sevcik (2).

$$I_p = k \times n^{\frac{3}{2}} \times A \times D^{\frac{1}{2}} \times C \times V^{\frac{1}{2}} \quad (2)$$

Onde  $k = 2,69 \times 10^5$ ,  $n$  é o número de moles de elétrons transferidos por mol de espécies eletroativas,  $A$  ( $\text{cm}^2$ ) é a área do eletrodo,  $D$  ( $\text{cm}^2 \cdot \text{s}^{-1}$ ) é o coeficiente de difusão das espécies



eletroativas,  $C$  ( $\text{mol L}^{-1}$ ) é a concentração em massa da espécie eletroativa e  $v$  ( $\text{V s}^{-1}$ ) é a taxa de varredura potencial.

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100 \quad (3)$$

Onde  $R$  é a rejeição da membrana em %,  $C_p$  é a concentração no permeado e  $C_f$  é a concentração na solução de alimentação.

## **APÊNDICE B – TRABALHOS PRODUZIDOS DURANTE O PROGRAMA**

1- Concept, benefits and success factors of product-oriented Product-Service System: A systematic literature review and research agenda

International Journal of Production Research – Sendo revisado por pares.

2- Old RO membranes end-of-life: from autopsy to reuse as NF/UF/MF or IEM in Water and WasteWater Treatments and at the end as an alternative fuel production

FILTECH 2021 Scientific congress international event for filtration and separation technologies

- Cologne, Germany – Congresso cancelado em virtude do Covid-19.

3- Development of a novel proton exchange membrane from an end-of-life reverse osmosis (RO) membrane and its application in a fungal microbial fuel cell (FMFC)

Desalination – Sendo preparado para submissão.

4- Sustainable Processing: Dairy Plant Effluents – Minimization and Treatment

Encyclopedia of Dairy Sciences, 3rd Edition – Sendo revisado por pares.

5- Evolução da Legislação Brasileira sobre efluentes.

Simpósio Mundial de Sustentabilidade – Conferência Internacional BRIDGE 2019 - Publicado

6- Can end-of-life Reverse Osmosis membrane be re-inserted in the circular economy?

Presente artigo sendo revisado.



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