

**COMB-SHAPED AMPHIPHILIC POLYMERS FOR
MEMBRANE FOULING TREATMENT**

BY

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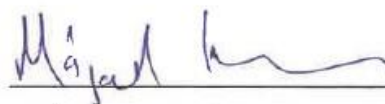


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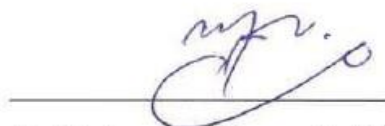


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To my lovely parents and siblings

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LIST OF ABBREVIATIONS

RO	:	Reverse Osmosis
SWRO	:	Seawater Reverse Osmosis
PIMA	:	Poly(isobutylene-alt-maleic anhydride)
PIMA-PEHA	:	Poly(isobutylene-alt-maleic acid-graft-pentaethylenhexamine)
PIMA-TEPA	:	Poly(isobutylene-alt-maleic acid-graft-tetraethylenepentaamine)
PIMA-TETA	:	Poly(isobutylene-alt-maleic acid-graft-triethylenetetraamine)
TFC	:	Thin Film Composite
EDTA	:	Ethylenediaminetetraacetic acid
SDS	:	Sodium Dodecyl Sulfate
MF	:	Microfiltration
UF	:	Ultrafiltration
NF	:	Nanofiltration
FRR	:	Flux Recovery Rate
FTIR	:	Fourier Transform Infrared
NMR	:	Nuclear Magnetic Resonance
SEM	:	Scanning Electron Microscope
EDX	:	Energy Dispersive X-ray
AFM	:	Atomic Force Microscope
DI	:	Deionized
CVD	:	Chemical Vapor Deposition
TDS	:	Total Dissolved Solids
MWCO	:	Molecular Weight Cutoff

ABSTRACT

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Desalination is vital for combating global water scarcity, with RO membranes playing a central role. However, membrane fouling remains a major challenge, necessitating efficient cleaning strategies. Current methods involve sequential use of various chemicals, but they often damage membranes and pose environmental risks. This study focuses on the synthesis and application of environmentally friendly copolymers for cleaning organic-fouled SWRO membranes. Comb-shaped amphiphilic copolymers were synthesized and tested, with PIMA-PEHA showing exceptional performance. FTIR and NMR analysis confirmed copolymer synthesis. Alginate fouling significantly reduced flux within 6 hours. Cleaning with PIMA-PEHA at 2.5 g/L, pH 11, and 40°C achieved over 90% flux recovery, surpassing other copolymer agents tested. SEM, EDX, and AFM surface analyses evaluated cleaning efficacies. SEM and EDX confirmed fouling layer removal and surface restoration, with notable C:O ratio increases (up to 4-6:1) and calcium content decreases. Optimal conditions were identified at pH 9.4 and 40°C, where PIMA-PEHA acted as a surfactant and chelating agent, solubilizing foulants and sequestering Ca^{2+} ions. In conclusion, this study presents an effective, eco-friendly method for cleaning fouled RO membranes.

ملخص الرسالة

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تحتل المياه ضرورية لمكافحة ندرة المياه العالمية، حيث تلعب أغشية التناضح العكسي (RO) دورًا محوريًا. ومع ذلك، تظل مشكلة تلوث الأغشية تحديًا كبيرًا، مما يتطلب استراتيجيات تنظيف فعالة. تشمل الأساليب الحالية الاستخدام المتتابع لمواد كيميائية مختلفة، لكنها غالبًا ما تتسبب في تلف الأغشية وتشكل مخاطر بيئية. تركز هذه الدراسة على تخليق وتطبيق البوليمرات المشتركة الصديقة للبيئة لتنظيف أغشية التناضح العكسي لمياه البحر الملوثة بالمواد العضوية. تم تخليق واختبار بوليمرات مشتركة أمفيبيلية ذات شكل مشط، حيث أظهرت PIMA-PEHA أداءً استثنائيًا. أكدت تحاليل FTIR و NMR تخليق البوليمر المشترك. قلل التلوث بالألجينات بشكل كبير من التدفق خلال 6 ساعات. أدى التنظيف بـ PIMA-PEHA بتركيز 2.5 جم/لتر، ودرجة حموضة 11، ودرجة حرارة 40 °C إلى استعادة أكثر من 90% من التدفق، متفوقًا على عوامل البوليمر المشتركة الأخرى التي تم اختبارها. قامت تحليلات السطح باستخدام SEM و EDX و AFM بتقييم كفاءة التنظيف. أكدت SEM و EDX إزالة طبقة التلوث واستعادة السطح، مع زيادات ملحوظة في نسبة الكربون إلى الأكسجين (حتى 4-1:6) وانخفاض محتوى الكالسيوم. تم تحديد الظروف المثلى عند درجة حموضة 9.4 ودرجة حرارة 40 °C، حيث عمل PIMA-PEHA كعامل فعال سطحي ووكيل تخليبي، مما أدى إلى إذابة الملوثات وعزل أيونات Ca^{+2} . في الختام، تقدم هذه الدراسة طريقة فعالة وصديقة للبيئة لتنظيف أغشية التناضح العكسي الملوثة.

CHAPTER 1

INTRODUCTION

1.1 Background

Water, covering over 70% of the Earth's surface, is essential for various sectors, including agriculture, health, industry, tourism, and domestic use [1]. However, with more than 97% being saline, only a fraction, less than 0.007%, is available for domestic consumption [2]. Rapid population growth and industrialization have quadrupled water usage in the last 40 years, exacerbating the imbalance between supply and demand [2], [3]. Agriculture and industry consume 93% of global water, leaving only 7% for domestic needs [2], [3], [4]. By 2025, it is anticipated that two-thirds of the global population will be living in water-stressed areas, with over 1.8 billion people facing scarcity of clean water [5].

In response, researchers seek sustainable and cost-effective water sources (Adel et al., 2021; M. Ahmed et al., 2023; Chen et al., 2018), acknowledging the untapped potential of the oceans, which hold over 97% of Earth's water [9]. Challenges include population growth, industrialization, and water pollution, impacting around one-third of the global population in water-stressed regions and affecting over 1.2 billion people with clean water scarcity [9], [10].

Recognizing water scarcity as a critical challenge for this century [6], Strategies like water reuse and seawater desalination have been implemented to address the rising demand for fresh water [11]. In this context, membrane technology emerges as one of the most promising approaches for producing high-quality water. Common membrane technologies

include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), each offering specific advantages in various applications [12], [13], [14]. Notably, RO membrane technology is widely used in seawater desalination, drinking water production, brackish water treatment, and wastewater treatment, presenting energy efficiency and adherence to rigorous rules for public health and environmental protection [14], [15]. Over the decades, RO desalination has ascended, commanding over 65.5% of global capacity with remarkable energy efficiency advancements, reducing consumption from over 15 kW h/m³ in the 1970s to under 3 kW h/m³ post-2000. The use of energy-saving/recovery equipment, enhancing the separation efficiency of RO polyamide thin film composite (PA-TFC) membranes, and optimizing desalination plant design—for example, by implementing staged desalination—are some of the strategies that have been developed to lower the energy consumption of RO plants [16], [17]. RO serves a dual purpose, ensuring both high water productivity and remarkably high rejection rates for almost all pathogenic species, inorganic, and organic pollutants, aligning with environmental protection and public health regulations [18]. Commonly, thin-film membrane composites in RO plants are arranged in compact spiral-wound systems [19]. Typically, the RO membrane comprises a 0.2 µm thick active polyamide layer, along with layers of polysulfone and polyester fabrics.

Yet, despite the remarkable progress in membrane technology, fouling remains an impediment to its widespread application [20]. This complex challenge adversely affects RO systems, leading to decreased production, water quality deterioration, and reduced membrane lifespan [20]. Biofouling, a prevalent issue in the desalination industry, alone incurs an estimated annual global cost of approximately US\$15 billion [21]. Fouling

manifests in various forms—colloidal matter accumulation, organic fouling, mineral deposition, and the formation of biofilms comprising microorganisms and organic matter—depending on feed water characteristics and membrane properties [22], [23], [24], [25], [26]. A deep understanding of fouling causes, development mechanisms, and nature is pivotal for implementing effective corrective measures and mitigating the economic burdens on desalination operations [18].

The development of innovative RO membranes, efficient membrane cleaning and surface modifications, and improved pretreatment techniques are some of the strategies used to mitigate fouling issues [26], [27], [28], [29], [30]. While membrane fouling can be evidently mitigated by process optimization, membrane surface modification, and feed pretreatment, membrane cleaning remains the most efficient method of preventing fouling escalation and promptly restoring membrane permeability [31].

1.2 Membrane Cleaning

Physical and chemical cleaning are the two categories of membrane cleaning. Foulants cannot be entirely removed from the membranes by physical cleaning. Chemical cleaning tends to be the most practical method to regenerate membrane performance because forward flushing fails to remove interior fouling and backflushing operations have the potential to cause the thin film composite (TFC) membrane to detach [32]. Chemical cleaning involves the use of chemical agents to remove the foulants. Scaling, inorganic deposits, biofilms, and organic foulants can all be successfully removed from the membrane surface by chemical cleaning [32]. Cleaning is often used to improve the efficiency of a unit when there is a reduction of approximately 10% in normalized permeate data, an increase of about 15% in differential pressure, or a rise of roughly 10% in product

salinity [33]. Chemicals commonly used for cleaning membranes can generally be classified into five classes: acids (such as citric acid and nitric acid), bases (such as NaOH), chelating agents (such as EDTA), oxidants and disinfectants (such as NaOCl, H₂O₂, and peroxyacetic acid), and surfactants (such as detergents) [34]. The choice of cleaning is influenced by various factors such as membrane type, operating time, foulant layer composition, and RO system structure and configuration. The hydrophilicity and smoothness of a membrane's surface can have an impact on fouling [18]. The cleaning materials that are chosen should possess certain qualities like chemical stability, safety, affordability, and water-washability or removal ability. The majority of the precipitated materials must be dissolved by the cleaning agents and removed from the membrane's surface without causing any surface damage. Cleaning agents tend to modify the morphology of foulants (e.g., compaction, swelling), remove foulants from a membrane surface, and/or change the surface chemistry of the deposit. The cohesion forces between the foulants and adhesion between the foulants and the membrane surface may be weakened by the cleaning agents' reaction with the foulant. Foulant may react with cleaning agent via hydrolysis, solubilization, saponification, peptization, dispersion (suspension), and chelation [35].

Different chemical agents apply differently in cleaning or treating distinct kinds of fouling. Acid cleaning agents are effective in dissolving inorganic salts and metal oxides, while composite alkaline cleaning agents can remove salts that are insoluble in acid. Additionally, alkaline cleaning solutions can remove proteins and other organic foulants by electrostatically repelling charged solutes, hydrolyzing proteins, and dissolving organic macromolecules. Disinfectants that break down organic materials and inactivate bacteria,

such as oxidants, nonoxidizing biocides, and copper/silver ions, can eliminate biofilms and lessen biofouling. Metal chelating agents and surfactants reduce the interaction and membrane adhesion of foulants, dissolving the foulants and breaking down the cake layer. Furthermore, in mild conditions, certain biological macromolecules like protein, lipids, and polysaccharides can be specifically broken down by enzymes like protease, lipase, pectinase, and dextranase [31].

The process of cleaning RO membranes with current chemical agents is unappealing due to issues like membrane damage and environmental impact [36]. Membrane hydrophobicity and water permeability are affected by chemical cleaning, and membrane separation efficiency is significantly influenced by pH. The ineffectiveness of commercial cleaning solutions in eliminating adsorbed hydrophobic compounds suggests that present cleaning procedures are inadequate. Through their ability to adsorb onto amide bond segments and shield them from damage, urea and biuret derivatives have demonstrated promise in stopping a decrease in RO membrane rejection rates during cleaning [37]. The demerits associated with the contemporary cleaning materials, especially with relation to eco-friendliness, drive this research towards finding an environmentally benign chemical agent that can effectively treat fouling and restore membrane performance.

1.3 Objective

For this research work, the following are the main objectives we set to achieve:

- 1 Develop comb-shaped amphoteric polymers by grafting ethylene amine compounds onto poly[isobutylene-alt-(maleic anhydride)].

- 2 Confirm the comb-shaped amphoteric polymers synthesis employing FT-IR and NMR spectroscopy.
- 3 Evaluate the effectiveness of synthesized polymers in cleaning fouled membranes by assessing membrane permeability and flux recovery rate (FRR).
- 4 Investigate the impact of polymer cleaning agents on membrane surface .properties using contact angle measurements, SEM and AFM.

1.4 Thesis Outline

The core outline of this thesis includes:

- **Chapter 1 (Introduction):**

This chapter introduced the research topic by discussing the use of reverse osmosis (RO) membranes in desalination to tackle water scarcity. It highlighted the importance of RO membranes, addressed challenges like membrane fouling, and emphasized the need for effective cleaning methods to sustain membrane performance. Additionally, it outlined the study's objectives.

- **Chapter 2 (Literature Review):**

In this chapter, a comprehensive review of existing literature related to RO membrane fouling and cleaning methods was presented. It covered the various types of fouling encountered by RO membranes, the mechanisms involved, and the strategies proposed in previous studies to mitigate fouling. Additionally, it highlighted the synthesis of amphiphilic polymers and their potential role in membrane cleaning.

- **Chapter 3 (Research Materials and Methodology):**

This chapter outlined the materials utilized in the research, including commercial SWRO membranes and various reagents and chemicals. It described the synthesis process of comb-shaped amphiphilic polymers and the characterization techniques employed, such as FTIR and NMR spectroscopy. Furthermore, it detailed the setup and procedures for membrane fouling experiments and cleaning tests.

- **Chapter 4 (Results and Discussions):**

This chapter presented and analyzed the results obtained from the study's experiments. It included the characterization of synthesized polymers, the performance of fouled membranes, and the effectiveness of different cleaning agents and protocols. Discussions revolved around interpreting the findings within the context of existing literature, identifying trends, and addressing research questions.

- **Chapter 5 (Conclusions and Recommendation):**

This concluding chapter draws conclusions based on the research outcomes and objectives outlined in earlier chapters. Recommendations for further investigation or improvements in membrane cleaning methods are also provided.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Technology in Water Treatment

Membrane technology serves as a crucial tool in water treatment, offering efficient separation of colloids, molecules, and salts through engineered barriers. These barriers, based on size exclusion mechanisms, allow for the selective passage of particles depending on their size, shape, and physical or chemical properties [38], [39].

2.1.1 Micro-Filtration Membrane Technology

Micro-filtration membranes, known for their highly porous structure enabling low-pressure separation processes, are crafted from a variety of materials including ceramics, stainless steel, and predominantly polymer-based compounds [40]. Originating in the 1920s and 1930s, the commercialization of nitrocellulose membranes marked the inception of micro-filtration, although its widespread adoption was limited until the mid-1960s, largely confined to laboratory settings and small-scale ventures. During this period, dead-end or in-line filtration prevailed, favored for its straightforward methodology. However, a pivotal transition occurred in the 1970s with the rise of cross-flow filtration as a viable alternative, coinciding with the growing feasibility of membrane deployment in larger industrial contexts. The introduction of ceramic tubular cross-flow filters in the mid-1980s further broadened the spectrum of filtration options, followed by the emergence of semi-dead-end filtration as a significant paradigm in subsequent years [41].

Across diverse industries such as pharmaceuticals, semiconductor manufacturing, and food and beverage production, micro-filtration membranes play a pivotal role in the physical

separation of minute particles, bacteria, pathogens, and yeast cells from various solutions. Particularly in industrial scenarios requiring the retention of particles larger than 0.1 μm , micro-filtration remains the method of choice, well-established and preferred [42].

Strides in micro-filtration technology extend to wastewater treatment, notably in sewage and heavily polluted industrial wastewater treatment such as in semiconductor fabrication. Additionally, in the production of drinking water, micro-filtration has proven effective in reducing chlorine demand by effectively removing contaminants from lake water [43]. Despite its numerous advantages including pH and temperature stability and the ability to operate without chemical additives, challenges such as membrane fouling persist, necessitating solutions to enhance productivity and prolong filter service life for broader applicability [44].

2.1.2 Ultra-Filtration Membrane Technology

Ultra-filtration employs finely porous membranes to separate water and micro-solutes from larger molecules and colloids, with pore sizes typically ranging from 10 to 1000 angstroms. Pioneers like Bechhold, Elford and Ferry, and Zsigmondy and Bachmann laid the groundwork for ultra-filtration, initially utilized in laboratory settings by the mid-20th century but not industrially until the 1960s. Loeb and Sourirajan's development of anisotropic cellulose acetate membranes in 1963 marked a significant breakthrough in membrane technology, which can be crafted from both organic and inorganic materials, requiring precise selection based on various characteristics like molecular weight and chain flexibility [44].

The structure of ultra-filtration membranes can be symmetric or asymmetric, with symmetric membranes ranging in thickness from 10 to 200 μm and asymmetric ones comprising a dense outer layer supported by a porous sub-layer [45], [46]. The operation of ultra-filtration membranes encompasses two modes: dead-end flow, similar to a cartridge filter, and cross-flow, which introduces an additional flow alongside filtrate and feed flows. While dead-end flow maximizes feed water recovery, typically achieving 95 to 98 percent, cross-flow mode yields slightly lower recoveries in the range of 90 to 95 percent [47], [48], [49].

Considered a competitive wastewater treatment technology, ultra-filtration membrane processes require meticulous management for optimal performance. They offer efficient removal of particle pollutants, including viruses and bacteria, making them indispensable in modern water treatment plants for clarity and disinfection. Furthermore, ultra-filtration membranes have proven effective in single-operation drinking water supply without pre-treatment, as well as in wastewater treatment with moderate organic content. Their ability to eliminate waterborne pathogens surpasses traditional methods, achieving removal rates of 90-100% for viruses and bacteria, thus enhancing water safety and quality [50], [51], [52].

2.1.3 Nano-Filtration Membrane Technology

Recent years have seen a rapid advancement in the technology of nano-filtration membranes, which are now widely used in various industries [53], [54]. These membranes, characterized by their small pore sizes (1-5 nm) and operating pressures (7-20 bar), effectively separate low molecular weight solutes and reject contaminants such as heavy metals and dyes [55], [56]. Nano-filtration is particularly promising for wastewater

treatment due to its low energy consumption, high rejection rates, and versatility in selectively separating specific solutes from complex process streams [57].

Nano-filtration membranes find diverse applications in pharmaceuticals, wastewater treatment, biotechnology, and water purification [58], [59]. In industries ranging from textiles to petroleum, they are used for tasks like color separation, metal recovery, and treating various types of industrial wastewater. Additionally, nano-filtration plays a crucial role in domestic wastewater treatment and food processing, offering solutions for removing contaminants from effluents and enhancing product quality [60], [61].

2.1.4 Reverse Osmosis Process Membrane Technology

Reverse osmosis (RO) technology stands as a cornerstone in water purification, offering an effective means to desalinate water across diverse applications. An RO desalination plant typically comprises four primary systems: a pre-treatment system, high-pressure pumps, membrane modules, and a post-treatment system [44]. The pre-treatment system plays a critical role in the removal of suspended materials, prevention of salt precipitation, and inhibition of microbiological growth on the membranes. This is achieved through a series of processes including chemical feed, coagulation, flocculation, sedimentation, and filtration, employing methods such as micro-filtration and ultra-filtration.

High-pressure pumps are utilized to apply pressure to wastewater or saline solutions, surpassing the natural osmotic pressure to initiate the reverse osmosis process. This enables the separation of solutes and the elimination of contaminants such as salt, colloids, microorganisms, organic debris, and heat sources. Essentially, RO desalination operates by exerting higher pressure than natural osmosis pressure on salted water, prompting water

molecules to permeate through the membrane, effectively removing salt from the water [44]. The RO mechanism is shown in **Figure 1** below.

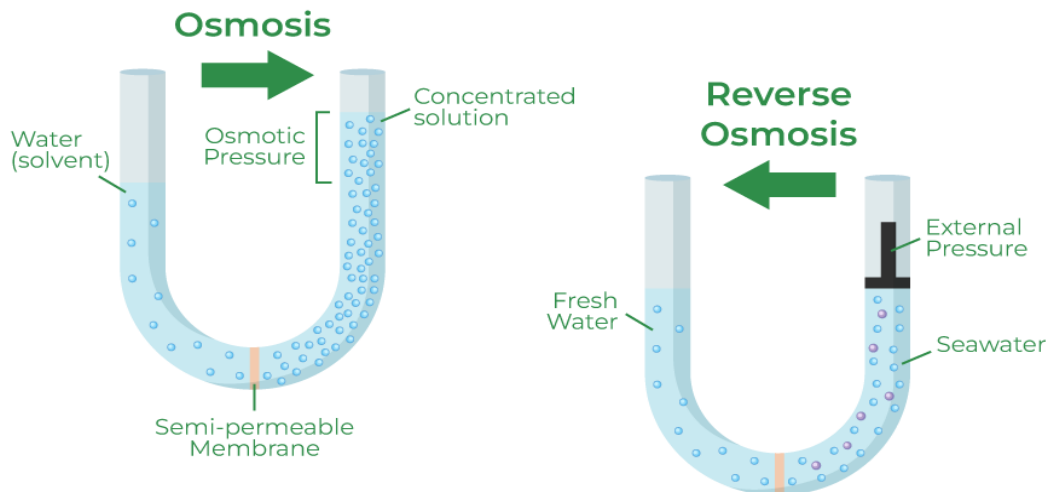


Figure 1. Schematic diagram illustrating the processes of osmosis and reverse osmosis. Adapted from [62]

The versatility and efficacy of RO technology extends beyond desalination alone. In semiconductor manufacturing, RO facilitates the production of ultra-pure water essential for critical processes. Similarly, in food processing, RO ensures the removal of impurities, enhancing product quality and safety. In pharmaceutical production, RO plays a vital role in producing purified water necessary for drug formulation and manufacturing. Additionally, RO technology is integral to municipal water treatment, enabling the provision of clean and potable water to urban populations [63], [64], [65], [66]. This advanced membrane separation technique is at the forefront of wastewater treatment globally, promising to address the growing challenges of water scarcity and pollution. Through continuous innovation and refinement, RO technology continues to evolve, promising even greater efficiency and reliability in the future.

RO desalination processes have evolved significantly, emerging as the predominant technology in addressing global water scarcity. Presently, RO desalination plants constitute over 65.5% of the global desalination capacity [67], as illustrated in **Figure 2a**. This widespread adoption highlights the pivotal role of RO technology in meeting water demand worldwide. **Figure 2b** further provides insights into the feed-water types utilized in desalination operations globally.

RO-based desalination plants have significantly improved energy efficiency over the years, with energy consumption plummeting from over 15 kWh/m³ in the 1970s to less than 3 kWh/m³ by the 2000s (**Figure 2c**). This impressive reduction is attributed to innovative approaches including the implementation of energy-saving and recovery equipment, advancements in membrane separation efficiency, and optimized plant designs like staged desalination, aligning with global efforts to address water scarcity challenges [16], [17]. These advancements not only contribute to lower operational costs but also foster environmental sustainability efforts.

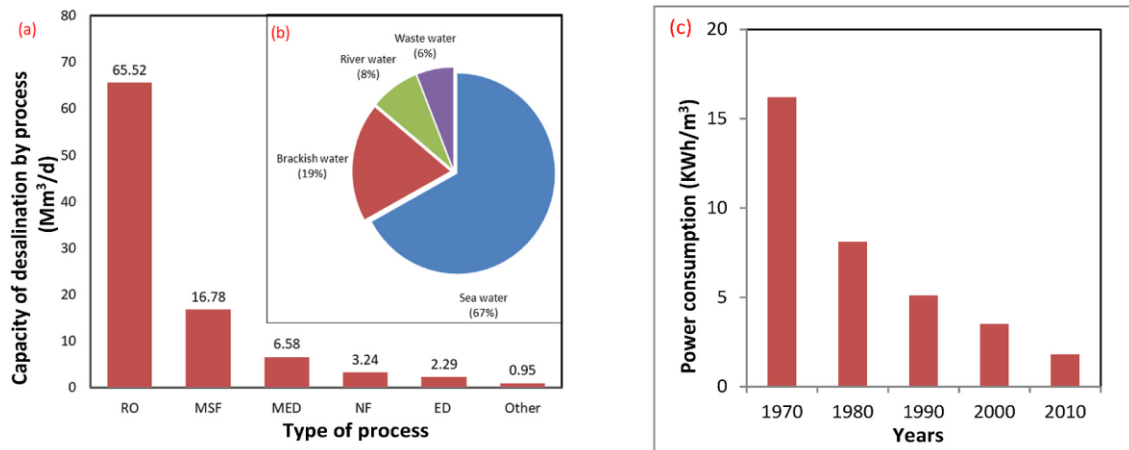


Figure 2. Global desalination capacity categorized by (a) technology employed, and (b) feed water source (Al-Karaghoul et al., 2011). (c) Power consumption improvement in seawater reverse osmosis desalination over decades [69].

The composition and structure of RO membranes significantly influence their properties and performance in desalination processes. Typically, an RO membrane comprises three layers: an active polyamide layer, a polysulfone interlayer, and a polyester backing layer. The polyamide layer facilitates membrane selectivity, while the polysulfone interlayer ensures mechanical strength under high pressures [70].

Despite significant advances in membrane technology, membrane fouling remains a pervasive challenge in RO operations, impacting plant performance and longevity [71], [72], [73]. Addressing membrane fouling through innovative solutions is imperative for maximizing the efficiency and sustainability of RO desalination processes while ensuring consistent water quality.

2.2 Reverse Osmosis Fouling

Membrane fouling is a significant challenge in RO applications, affecting permeate flux, water quality, and overall system performance. This fouling occurs due to the accumulation of particles, colloids, macromolecules, salts, and other undesired materials on the membrane surface and within its pores [74], [75]. Various mechanisms contribute to membrane fouling, including pore blocking, concentration polarization, cake formation, and biofouling, which can occur individually or in combination [76].

Organic foulants, such as proteins, lipids, and carbohydrates, are hydrophobic and tend to adsorb onto the membrane surface, causing severe fouling [77]. Inorganic foulants like calcium carbonate and silica form scales or precipitates, reducing pore size and limiting water flow. Biological foulants, including bacteria and fungi, form biofilms on the membrane surface, further reducing permeate flux and risking membrane damage.

Colloidal foulants, such as clays and nanoparticles, accumulate on the membrane surface, forming cake layers or causing concentration polarization.

The extent of membrane fouling is influenced by factors like feed water quality, membrane characteristics, and operational parameters (Tchobanoglous et al., 1991). Understanding water behavior and ion transport through membranes is crucial for elucidating fouling mechanisms, as water permeation may occur via flush, jump-diffusion, or Brownian diffusion [79]. Surface fouling is more prevalent than internal pore fouling, allowing for more manageable cleaning strategies [80].

2.3 Strategies for Controlling Membrane Fouling

Membrane fouling significantly impacts RO system performance, necessitating effective fouling mitigation strategies to maintain operational efficiency and reduce economic costs [80]. Implementing methods to control or prevent fouling, such as appropriate pre-treatment, cleaning procedures, and membrane selection, is essential for optimizing the performance and longevity of RO desalination plants. Identifying the type of foulant is crucial for devising targeted fouling mitigation strategies [36].

2.3.1 Feed Pre-treatment

Pre-treatment stages are pivotal in reverse osmosis (RO) desalination plants, serving to optimize water quality and membrane performance while minimizing operational costs [81]. An in-depth understanding of feed water characteristics and intended usage is essential for selecting the appropriate pre-treatment methods. These methods aim to adjust feed water to be compatible with RO membranes by reducing concentrations of constituents like bacteria, inorganic colloids, organic compounds, and total dissolved solids

(TDS) [82]. Pre-treatment techniques include conventional methods like disinfection, coagulation, and softening, as well as non-conventional processes such as membrane-based filtration (e.g., nanofiltration, microfiltration, ultrafiltration) [83], [84], [85]. Effective pre-treatment is crucial for mitigating membrane fouling, ensuring optimal water flow, and preserving water quality over time, thus contributing to the economic efficiency of the RO process [83].

2.3.2 Membrane Surface Modification

In recent decades, surface modification of membranes has gained attention as a potentially effective strategy for fouling prevention and control [86]. The primary aim is to modify the membrane surface to discourage the attachment and activity of foulants. For instance, altering the surface to be more hydrophilic can deter the adhesion of bacterial species, which typically favor hydrophobic surfaces [87]. However, it's important to note that increased hydrophilicity may render the surface more susceptible to fouling by hydrophilic organic matter commonly found in feed waters [88]. Effective surface modification techniques often involve adjusting surface properties such as wettability, roughness, and electric charge, as these factors influence the adhesion of various foulants [89], [90], [91]. Researchers have explored diverse approaches to modify the surfaces of commercial reverse osmosis (RO) membranes. For example, Gleason and colleagues [92], [93] utilized an initiated chemical vapor deposition (CVD) technique to deposit amphiphilic copolymer films on RO membranes, resulting in significant reductions in protein and organic foulant adsorption as well as bacterial attachment in both static flow and cross-flow filtration conditions.

2.3.3 Membrane Cleaning Strategies

Membrane cleaning is vital for restoring water flux and salt rejection levels in water and wastewater treatment processes. It involves physical, chemical, and sometimes biological methods, with effectiveness gauged by hydraulic resistance removal and flux recovery. It's advisable to commence cleaning at a 10% flux decline to prevent irreversible fouling buildup [9].

In physical cleaning techniques, foulants are removed from the membrane surface by applying mechanical forces. Although they work well to remove loosely bound cake layers, over time their effectiveness deteriorates, and some fouling becomes irreversible. Depending on particular configurations and force application modes, conventional techniques in this category include CO₂ back permeation, sponge ball cleaning, flushing, and backwashing [9].

Generally speaking, physical cleaning takes less time to complete than chemical cleaning. It does not involve the use of chemicals, thereby eliminating chemical waste production, and is gentler on the membrane. Chemical cleaning, on the other hand, is usually more effective because it can remove nonreversible foulants [32].

Chemical cleaning is a vital aspect of membrane maintenance, requiring careful consideration of various factors such as fouling type, foulant components, and economic viability. Effective chemical agents interact with foulants to diminish cohesion forces and adhesion to the membrane surface, facilitating their removal. Common agents like acids are employed for scaling [94], while alkaline solutions combat organic and biofouling [95], [96]. Chelating agents such as ethylene diamine tetra acetic acid (EDTA) are also utilized,

with their efficacy influenced by solution pH [97]. Operational parameters like cleaning time, crossflow velocity, and temperature further impact cleaning efficiency [98]. Surfactants like sodium dodecyl sulfate (SDS) prove effective against organic and colloidal fouling due to their dual hydrophobic and hydrophilic nature, and combining chemical with physical cleaning methods can enhance overall efficacy by loosening fouling layers and promoting their removal through fluid shear [35], [99].

Research has explored the effectiveness of different chemical agents in treating various fouling types [100], [101], [102]. For instance, acid and alkaline cleaning may struggle with removing calcium salt scales in the presence of trace organic materials [103], whereas sodium chloride can effectively eliminate alginate gel layers from membrane surfaces [104]. Novel cleaning techniques like backwash cleaning with high salinity solutions, thermo-responsive polymer agents, and one-step cleaning with free nitrous acid show promise in efficiently tackling fouling [96], [105], [106]. However, combining chemical cleaning agents may not always yield optimal results, highlighting the need for customized approaches tailored to specific membrane operation conditions.

While chemical cleaning methods offer efficient fouling removal, they pose challenges such as the need for significant quantities of chemicals, potential membrane damage, and the generation of environmentally harmful waste streams. Additionally, incomplete foulant removal due to irreversible fouling can impact membrane properties [44], necessitating further research to refine cleaning protocols and mitigate environmental consequences.

Due to the potential effectiveness of amphiphilic compounds like sodium dodecyl sulfate (SDS) and ethylene diamine tetra acetic acid (EDTA) [35] in combating fouling in

membrane filtration systems, we investigated the use of certain polymeric amphiphiles. Additionally, poly(ethyleneimine) [has been identified as an amphiphilic bioactive material with antibacterial properties, making it promising for addressing biofouling. Other compounds such as polyguanidine and N-halamine have also shown antimicrobial potential [107], all sharing amino functionalities. Poly(ethyleneimine) and polyguanidine further feature alternating hydrophobic alkyl units. Previous research by Khan et al. (2010) demonstrated the efficacy of poly(isobutylene-alt-maleic acid-graft-oligoethyleneamine) [PIMA-OEA] complexes in gene transfection, with minimal cytotoxicity and adverse effects. Thus, polyethyleneamines have been incorporated into the synthesis of amphiphilic polymers, offering an environmentally friendly alternative for cleaning fouling.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Materials

All commercial Seawater Reverse Osmosis (SWRO) membranes used in this research (Table 1) were obtained from a local desalination plant in Jubail, Saudi Arabia. These SWRO membranes are characterized with a near to 100% salt rejection and high Boron rejection (>90%). Operating at a pressure of 20 bars and a feed temperature of 25°C, they demonstrated a permeate flux of approximately 40 LMH.

Table 1. Membrane specifications provided by the supplier.

Specification	LG SW 400 R G2
Active Membrane Area (ft ²)(m ²)	400 (37)
Permeate Flow Rate (GPD)(m ³ /d)	9000 (34.1)
Stabilized Salt Rejection (%)	99.88
Minimum Salt Rejection (%)	99.75
Boron Rejection (%)	93
Feed Spacer Thickness (mil)	34
Element Length (in/mm)	40 (1016)
Element Diameter (in/mm)	7.9 (200)
Inner Diameter (in/mm)	1.125 (28.6)
Weight (kg/lbs)	16 (35)
Max. Applied Pressure (psi/bar)	1200 / 82.7
Max. Chlorine Concentration (ppm)	< 0.1
Max. Operating Temperature (°C/°F)	45 / 113
pH Range Continuous (Cleaning)	2-11 (2-13)
Max. Feedwater Turbidity (NTU)	1.0
Max. Feedwater SDI (15 mins)	5.0
Max. Feed Flow (gpm)(m ³ /h)	75 (17)
Min. Ratio of Concentrate to Permeate Flow	5:1
Max. Pressure Drop (ΔP) per Element (psi/bar)	15 / 1.0

The reagents and chemicals that were utilized include poly(isobutylene-alt-maleic anhydride) [PIMA], organic amines (pentaethylenhexamine [PEHA], tetraethylenepentaamine [TEPA], triethylenetetraamine [TETA]), dimethyl sulfoxide

(DMSO), sodium hydroxide (NaOH), hydrogen chloride (HCl), all sourced from Sigma Aldrich. Additionally, high-purity sodium alginate (95% purity, Sigma Aldrich, Inc.) served as the model foulant (see **Figure 3**). These chemicals and reagents were of pure standards and were used without further treatment or purification. All solutions prepared during this were prepared using deionized (DI) water.

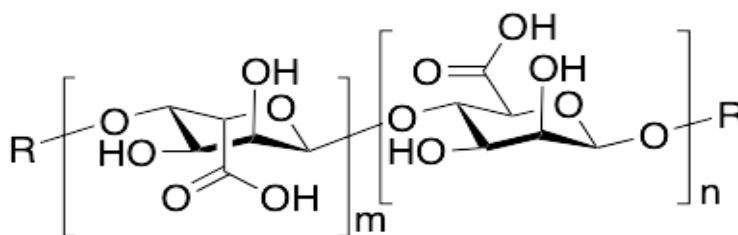


Figure 3. Schematic sketch of an alginate molecule with the abundance of O atoms and OH groups.

3.2 Synthesis of Comb-shaped Amphiphilic Polymers

For the synthesis of the target polymers, a method similar to that described by Khan *et al.* (2010) [108] was adopted with minor changes. The synthesis began with the combination of 100 mL of dimethyl sulfoxide (DMSO) and 2g of poly(isobutylene-alt-maleic anhydride) [PIMA] at room temperature. Meticulous stirring was employed to ensure complete dissolution of the polymer. In a separate flask, a solution was prepared by combining twenty-fold excess of the ethylene amine-based compound with 150 mL of DMSO. The polymer solution was gradually introduced into this flask while maintaining a temperature of 60°C, and the mixture was stirred for a duration of 72 hours.

At the completion of reaction, the reacted mixture was cooled to 30°C and the crude product was precipitated in acetone (2L). Following dissolution in water, a 2-day dialysis process was employed using a membrane dialysis method with a tubing of 14 kDa

PIMA + H₂N[CH₂CH₂NHCH₂CH₂NH₂]_m $\xrightarrow[72\text{h}]{\text{DMSO, } 60^{\circ}\text{C}}$ Comb-shaped polymer product

m = 0 (EDA)
 = 2 (TETA)
 = 3 (TEPA)
 = 4 (PEHA)

3.3 Polymer Characterization

3.4 Membrane Fouling

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using two pumps: an auxiliary pump and a high-pressure pump. Three stainless steel membrane cells were arranged in parallel, with the feed evenly distributed among them. Each cell was equipped with a thin permeate tube made of Teflon connected to its top portion. Circular membranes with an approximate diameter of 3.5cm were utilized for the study.

Prior to fouling, the membranes were compacted at 20 bars for 2–3 hours using deionized water, with a feed temperature maintained at around 25°C. The stabilized permeate flux was measured for all cells. Subsequently, 100 mg of CaCl_2 dissolved in 100 mL of deionized water was introduced into the feed, and the system was allowed to equilibrate. Following this, 200 mL of a previously prepared 100 ppm sodium alginate solution was added to the feed, initiating the fouling run.

3.5 Membrane Cleaning and Filtration Test

The fouled membranes were subjected to cleaning using the same cross-flow setup immediately following the fouling runs, following a standard cleaning protocol. Initially, the cells were flushed with deionized (DI) water at intermediate cross-flow velocities for approximately 1 hour. Subsequently, a specific cleaning solution was circulated through one of the cells while the others remained closed. The cleaning solution was heated to the desired temperature, typically around 40°C, using a hot plate, and the recirculating chiller was set to approximately 45°C. The cleaning solution circulated through the cell for 2 hours at a pump speed of approximately 20. Following this, the cell underwent a 15-minute flush with DI water to remove any excess cleaning agent that may have deposited on the membrane surface.

It's standard procedure to verify the filtration performance of the membranes post-cleaning runs. This serves to validate the effectiveness of the cleaning agents and ensure that the filtration efficiency and flux of the membranes have been fully or nearly restored to pristine levels. Utilizing the same cross-flow filtration setup employed for fouling and cleaning, the operating pressure remained at 20 bars with a cross-flow velocity of approximately 25. The feed temperature was maintained at around 24°C using a constant temperature circulating bath (Polystat, Inc.). Following this, the membrane water permeation flux was measured under the specified conditions after operating the setup for approximately 2 hours.

3.6 Post-Fouling Membrane Characterization

3.6.1 Surface Wettability

The contact angle measurement was employed to assess changes in membrane hydrophilicity and wetting properties, so as to provide evidence of fouling, post-cleaning. Measurements were conducted using a Kruss goniometer DSA25 (Kruss GmbH, Germany). For this test, samples were cut into small rectangular shapes and positioned on a glass slide. A syringe tip is then carefully placed near the sample surface to dispense a liquid drop (e.g., distilled water) of approximately 2 μL onto it. Images of the drop are captured by a camera, and specialized software determines the contact angles. By comparing the contact angles of cleaned membranes to those of pristine membranes, the cleaning efficiency of the chemicals can be assessed.

3.6.2 Surface Morphology/Composition (SEM/EDX)

Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) analysis was performed using a JEOL JSM-6610LV Scanning Electron Microscope (JEOL Ltd., Japan). This SEM is equipped with an Oxford Instruments X-Max^N 50 EDX detector for elemental analysis. To ensure compatibility with SEM/EDX analysis, samples were prepared following standard procedures. Initially, the samples were affixed onto aluminum stubs using double-sided carbon adhesive tape. Non-conductive samples underwent sputter-coating with a thin layer of gold using a Quorum Q150T ES sputter coater. This process enhances surface conductivity and minimizes charging effects during imaging. The entire sample surface was scanned, and images at varying magnifications were captured. By comparing the surface morphologies of pristine and treated membranes, the effect of the chemicals on the fouled membrane was studied.

3.6.3 Surface Topography

Atomic Force Microscopy (AFM) analysis was conducted using a Nanosurf Flex AFM 5 (Nanosurf AG, Switzerland) equipped with an Isostage System and C3000 Controller. Samples were prepared and mounted onto a substrate using standard procedures. The AFM probe scanned the sample surface to produce high-resolution images illustrating surface topography and morphology. AFM offers valuable insights into nanoscale features, particularly surface roughness, complementing the comprehensive characterization of the membranes.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Polymer Characterization

The successful synthesis of all polymers was primarily validated through Fourier transform infrared spectroscopy (FTIR) spectra, with nuclear magnetic resonance (NMR) spectroscopy providing additional confirmation, as illustrated in **Figures 4** and **5**, respectively. Distinct spectral data from the starting material, poly[isobutylene-*alt*-(maleic anhydride)], and the products (PIMA-TETA, PIMA-TEPA, and PIMA-PEHA), affirmed the grafting of ethylene amine compounds and justified the formation of the new compounds.

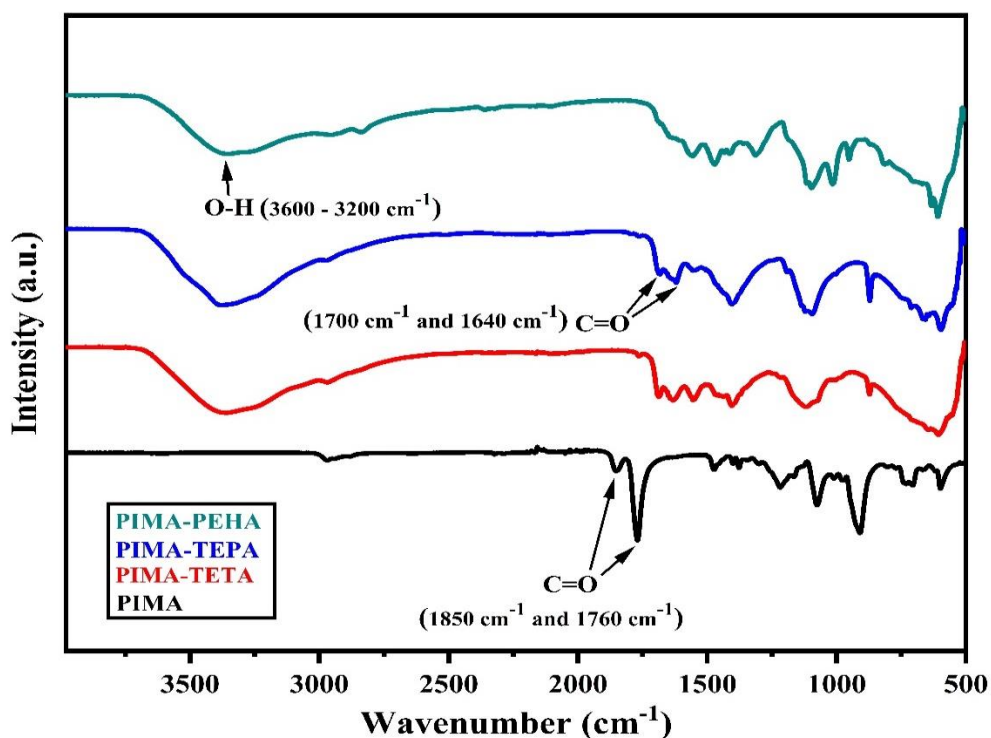


Figure 4. FTIR spectrum for poly[isobutylene-*alt*-(maleic anhydride)] (PIMA) and the products (PIMA-TETA, PIMA-TEPA, and PIMA-PEHA)

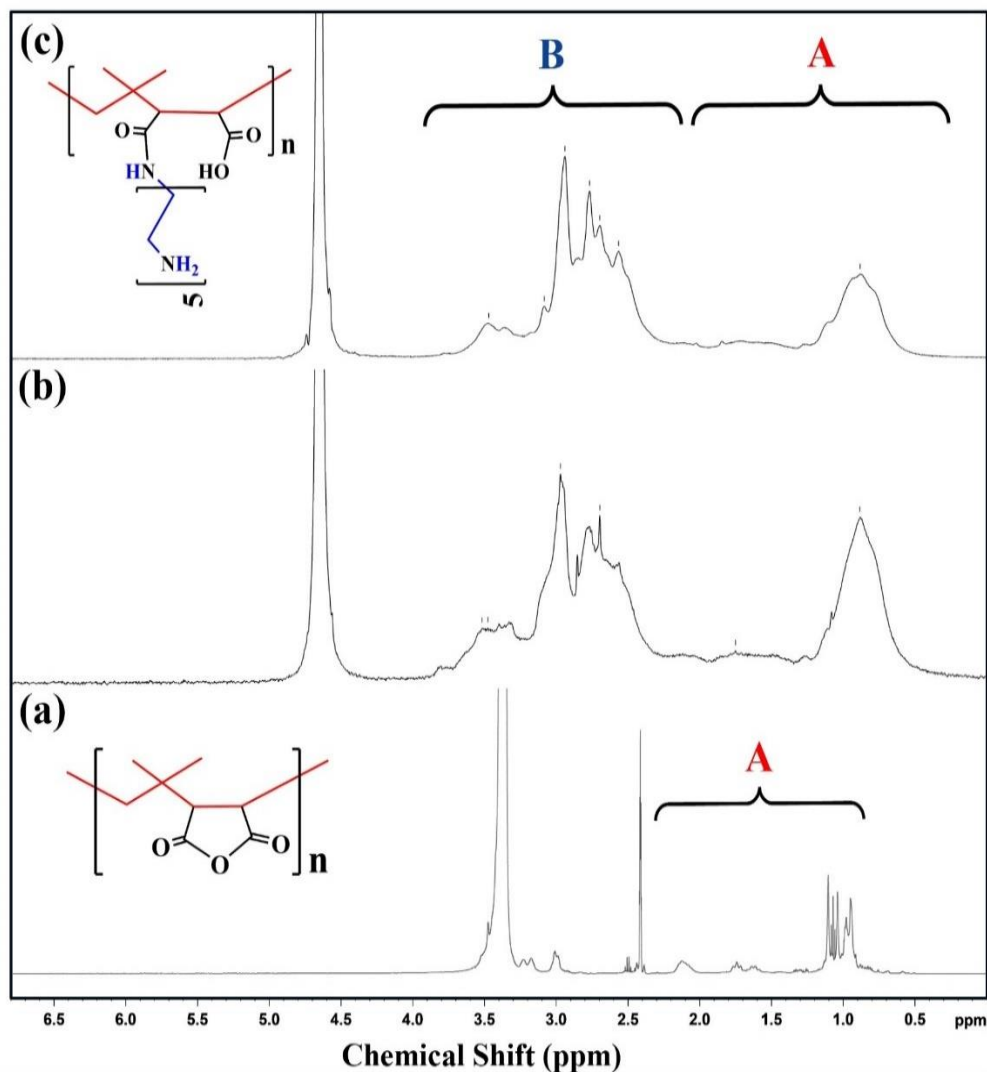


Figure 5. NMR spectrum for (a) poly[isobutylene-*alt*-(maleic anhydride)] (PIMA) in DMSO-d₆, (b) PIMA-TEPA in D₂O, and (c) PIMA-PEHA in D₂O.

4.2 Membrane Fouling

The membranes were initially compacted at approximately 25 bars using deionized (DI) water for 2 – 3 hours. Post-compaction, adjustments were made to the pump speed and operational pressure, setting them to 30 and approximately 20 bars, respectively. Permeate flux measurements were conducted for all three cells by collecting permeate in glass vials. Subsequently, the feed was equilibrated with CaCl₂ at a concentration of 100 ppm, as

calcium is known to exacerbate organic fouling. Next, 100 mg/L of sodium alginate that had been separately dissolved in DI water was added to the feed. Permeate from all cells was collected at regular hourly intervals, and flux was calculated accordingly.

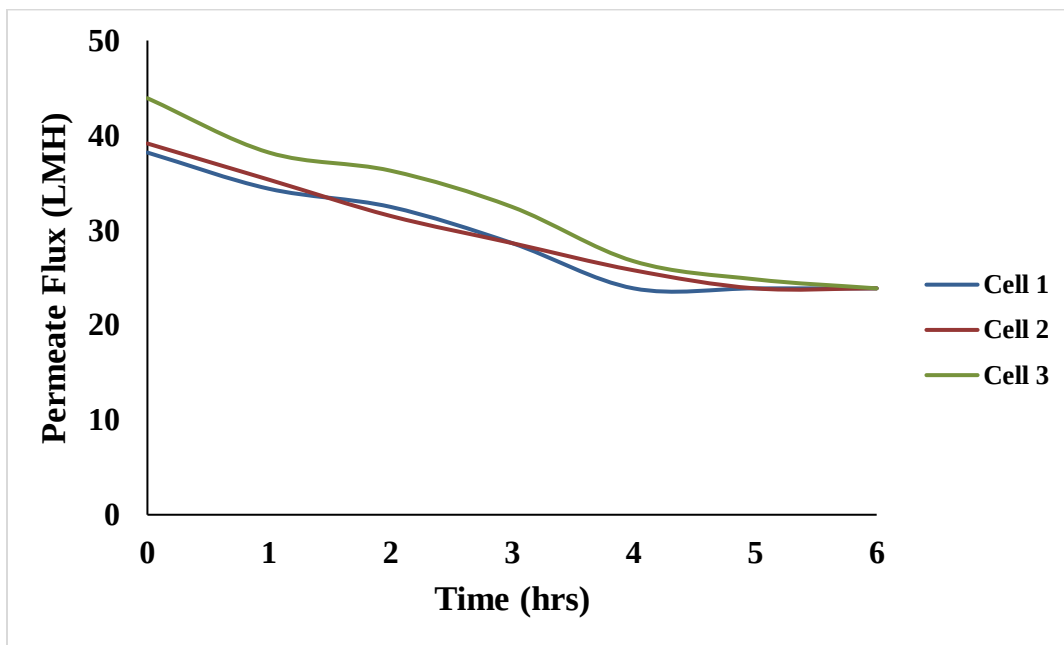


Figure 6. Variation of permeate flux with time for the membranes in the presence of alginate feed. Note the significant flux decline in a period of 6 hours.

Figure 6 illustrates the flux variation over time following the introduction of 100 mg/L alginate into the feed. The flux exhibited a rapid decline, decreasing by approximately 35-40% within 6 hours. This substantial reduction can be attributed to the presence of Ca^{2+} ions, which are known to facilitate the formation of a gel-like fouling layer by bridging successive alginate layers. Elimelech and colleagues [109] conducted fouling experiments with alginate in the presence and absence of Ca, as well as with Mg. The formation of alginate gel in the presence of calcium ions aligns with the "egg-box" model [110], wherein calcium ions selectively bind to the carboxylic groups of alginate molecules, forming bridges between adjacent alginate molecules and creating an egg-box-shaped gel network.

This preferential complexation of calcium with alginate, leading to gel formation, has been corroborated by various studies. For instance, Davis et al. [111] observed increased selectivity of alginate for calcium and cadmium over magnesium, resulting in alginate gel network formation. Additionally, Bruus et al. [112] noted enhanced stability of biological flocs formed with alginate in the presence of calcium ions compared to magnesium ions, suggesting a preference for alginate gel formation in the presence of calcium ions.

4.3 Membrane Cleaning

4.3.1 Identification of Most Effective Chemical Agent

A key measure of cleaning effectiveness is the flux recovery ratio following the implementation of the cleaning procedure. As depicted in **Figure 7**, the flux recovery rates for the fouled membranes vary based on the applied cleaning methods. Flushing with DI water alone at a high cross-flow velocity results in approximately 60% flux recovery, revealing the presence of the alginate fouling layer across the entire membrane surface. This indicates a substantial level of irreversible fouling, with the fouling layer strongly bonded to the membrane surface. Similar observations have been documented in prior studies on organic and biofouling, where flushing with DI water alone removes only the loosely bound fouling layer at the surface, leaving the denser, more tightly packed layer unaffected by shear forces alone.

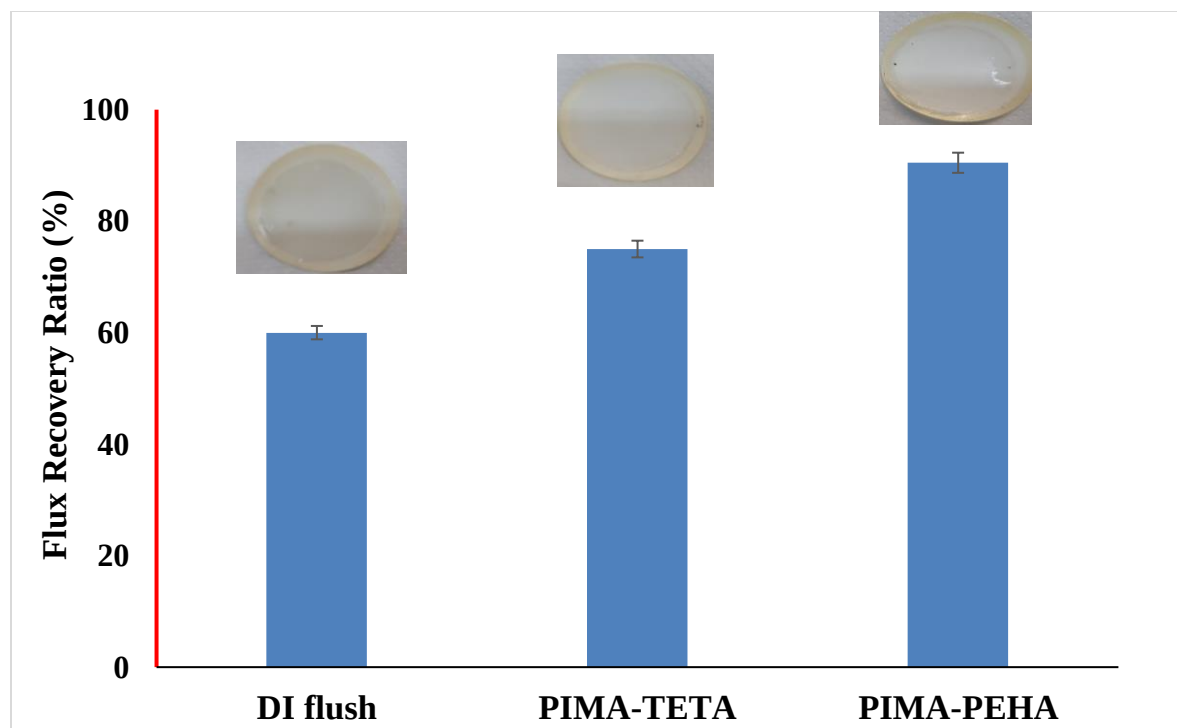


Figure 7. Flux recovery for the fouled membranes after the application of different cleaning regimes: DI flush, PIMA-TETA and PIMA-PEHA. The conditions for the cleaning agents were concentration of 2.5 g/L, pH of ~11, and temperature 40°C. The inset shows sample images after the cleaning step.

In contrast, cleaning with polymers featuring a surfactant-like molecular structure demonstrates greater effectiveness, evident from the visibly cleaner membrane surface and higher recovery levels (**Figure 7**). Notably, cleaning with a 2.5 g/L PIMA-TETA solution at a pH of 11 and a temperature of 40°C yielded a flux recovery of approximately 75%. Conversely, the polymer with a higher amine ratio, PIMA-PEHA-based, proved even more effective, achieving a recovery rate exceeding 90%. Despite sharing a similar backbone in the form of poly[isobutylene-alt-(maleic anhydride)] (PIMA), the variance in the number of amine groups results in divergent cleaning efficiencies. PIMA-TETA comprises a total of four amines, including two primary and two secondary amines. Conversely, PIMA-PEHA consists of five ethylene groups (-CH₂CH₂-) linked together in a chain by four secondary amine groups (-NH-) and capped with primary amine groups (-NH₂) at each

end. Leveraging the Lewis basicity of the amine groups, PIMA-PEHA functions as a hexadentate ligand akin to the commercial chelating agent EDTA, enabling it to form six bonds with a central metal atom.

4.3.2 Cleaning Parameter Optimization

Alkaline solutions facilitate the cleaning of organic-fouled membranes through hydrolysis and solubilization mechanisms. By elevating the solution pH, alkaline solutions enhance the negative charge and solubility of the organic foulant. For instance, deprotonation of carboxylic functional groups within the organic foulant under alkaline conditions significantly increases solubility by nearly three orders of magnitude. Following the successful application of PIMA-PEHA at a pH of approximately 11.4, further investigation into the impact of pH on cleaning efficiency was conducted. The fouled membranes were subjected to cleaning at two distinct pH levels: 8 and 9.4. **Figure 8** illustrates the flux recovery observed for membranes cleaned at these pH values while maintaining consistent conditions otherwise. Notably, membranes cleaned at a pH of 9.4 exhibit a flux recovery exceeding 75%, whereas cleaning at a pH of 8 yields a negative recovery.

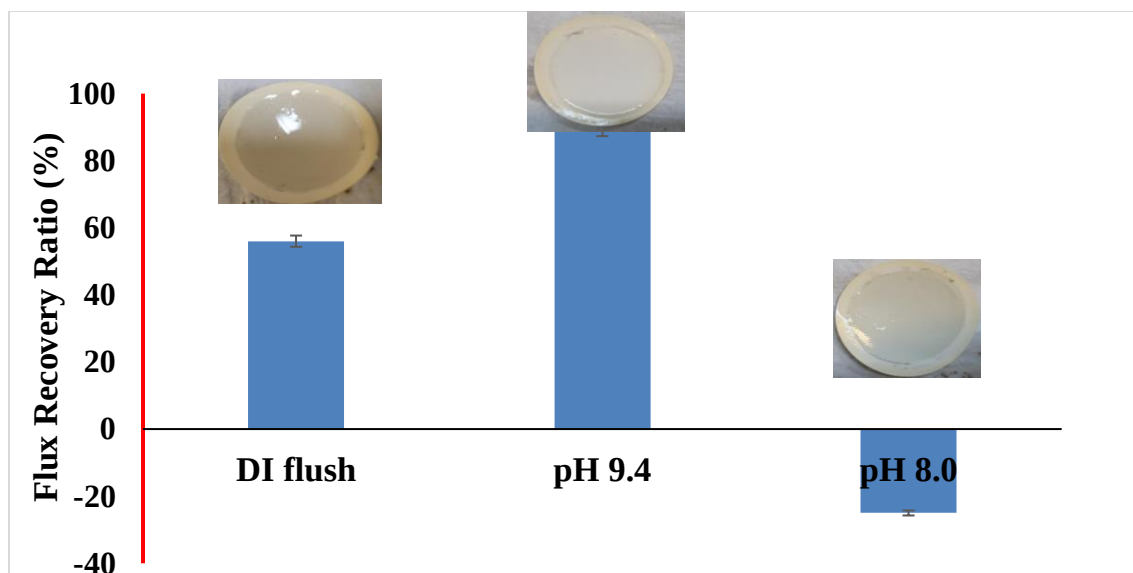


Figure 8. Flux recovery after cleaning with PIMA-PEHA at different pH. Note the high recovery at a pH of 9.4 and the negative recovery for a pH of 8. The inset shows the membranes after cleaning.

The images of the samples vividly illustrate the contrasting effectiveness of different pH values. While the membrane cleaned at pH 9.4 displays a remarkably clean surface, closely resembling the virgin membrane, the sample cleaned at pH 8 exhibits a conspicuous fouling layer akin to the surface flushed with DI alone.

The negative recovery indicates a decrease in flux following the implementation of the cleaning protocol. This decline is attributed to the adsorption of cleaning agent molecules on the membrane surface, subsequently altering surface characteristics such as hydrophobicity, pore size, and chemistry. Similar trends have been noted in recent studies on membrane fouling and cleaning. For instance, Zhao et al. [113] examined the cleaning efficiencies and mechanisms of various agents for NF membranes in produced water desalination, observing a flux decline of approximately 25% with the surfactant cetyltrimethylammonium chloride (CTAC).

4.4 Membrane Characterization

4.4.1 Surface Wettability

Assessing changes in surface hydrophilicity/hydrophobicity post-fouling and cleaning is vital, with the contact angle goniometer serving as a valuable and standard tool for this purpose. **Figure 9** illustrates the average contact angle (CA) values and water droplet images following cleaning of the fouled membranes using various protocols. The membrane flushed solely with DI exhibits a contact angle exceeding 70°, indicating significant fouling irreversibility likely attributed to high initial fluxes. Visual inspection reveals a continuous grayish layer of alginate, corroborating this observation. This aligns with findings by Alnajjar et al. [114], who investigated the efficacy of saturated CO₂ against alginate fouling and noted that even after DI flushing, a complete fouling layer remained visible.

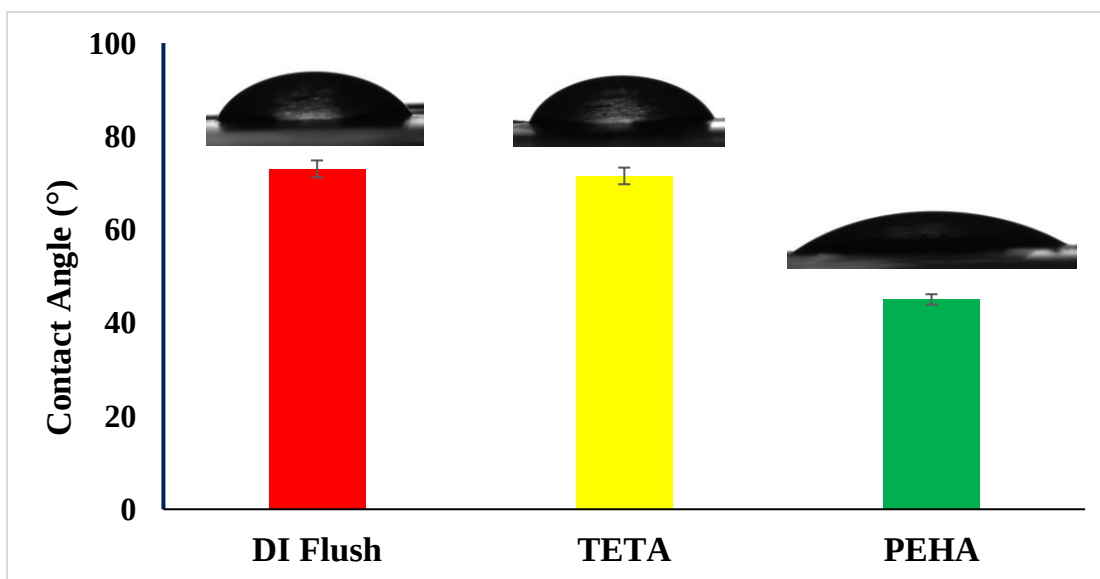


Figure 9. Images of water droplets on the membranes after cleaning runs (a) DI Flush (b) TETA 2.5 g/L (c) PIMA-PEHA 2.5 g/L. Note the similarity between DI flush and PIMA-TETA and the restoration of original wetting behavior by PIMA-PEHA.

Interestingly, the membrane treated with PIMA-TETA for 2 hours exhibited similar wetting behavior to the one treated with DI, with an average contact angle of approximately 71°. Subsequent SEM images confirmed the presence of a fouling layer on the membrane surface. While PIMA-TETA cleaning resulted in better flux recovery compared to DI alone, it failed to eliminate the foulant layer next to the membrane surface. In contrast, PIMA-PEHA cleaning effectively restored the original wetting behavior of the membrane surface and removed most of the foulants next to the membrane surface, as evidenced by flux recovery and SEM images.

There are two types of interactions that explain the above trend: membrane - foulant and foulant - foulant. The initial foulant deposition on the membrane surface is primarily determined by interactions between the membrane surface and foulant molecules. Subsequently, the fouling layer thickens due to interactions between foulant molecules on the membrane surface and in bulk solution.

After determining PIMA-PEHA as the most efficient cleaning agent, the influence of pH on its efficacy was investigated. **Figure 10** illustrates the average contact angle values following cleaning with PIMA-PEHA at pH 8 and 9.4. Intriguingly, the membrane cleaned at pH 8 exhibits a higher contact angle (approximately 83°) than even the sample flushed with DI alone (around 73°). This, coupled with the negative flux recovery observed (**Figure 8**), suggests a distinct phenomenon occurring on the membrane surface. In contrast, cleaning at pH 9.4 proves as effective as cleaning at pH 11, with the wetting behavior resembling that of the original membrane (approximately 45°).

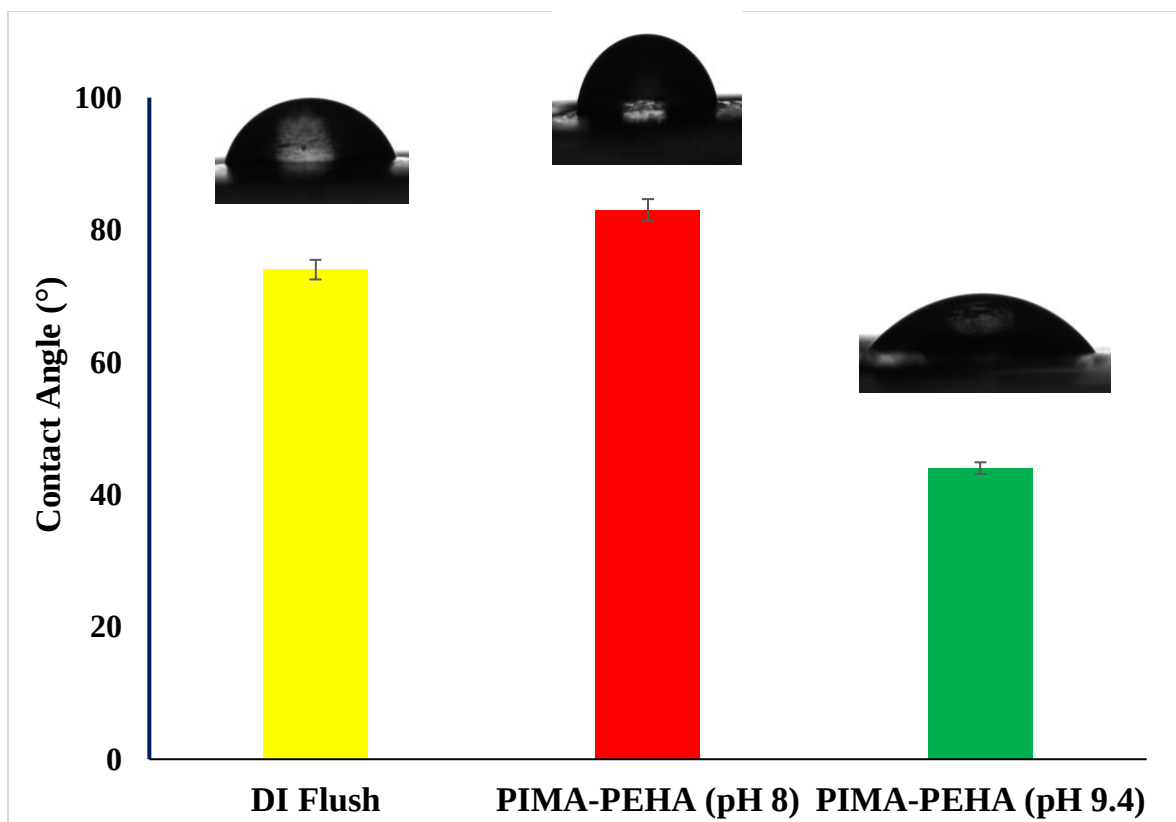


Figure 10. Average contact angle values for the membranes after cleaning with HEXA at two different pH, 8 and 9.4. Notice the increase in CA after cleaning with PIMA-PEHA at a pH of 8.

4.4.2 Surface Morphology/Composition (SEM/EDX)

SEM serves as a valuable tool for examining the surface morphology of membranes post-fouling and cleaning, offering insights into the extent and effectiveness of foulant removal.

Figure 11 presents a compilation of SEM images depicting membranes cleaned with various protocols. The sample treated solely with DI water (**Figure 11 a – c**) exhibits a continuous fouling layer on the surface, obscuring the original polyamide morphology. Additionally, dispersed crystals of calcium salts are evident throughout the surface. This observation aligns with prior research, indicating that hydraulic cleaning predominantly eliminates the loosely adhered fouling layer from the surface. Similar outcomes are observed in cases of biofouling [115].

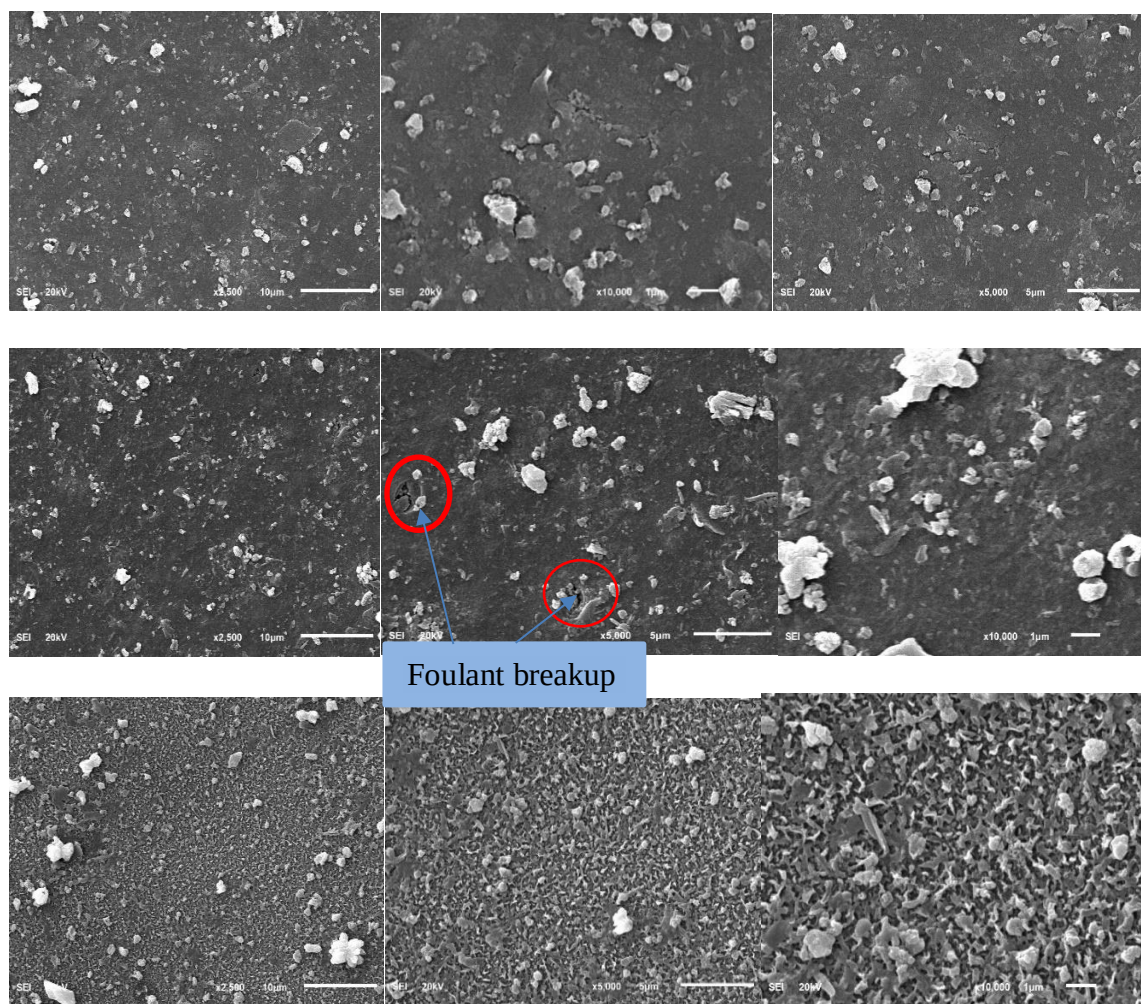


Figure 11. SEM images of the fouled membranes after cleaning with different regimes: DI flush (top row), 2.5g/L PIMA-TETA at pH 11 and 40°C (middle row), 2.5 g/L HEXA at pH 11 and 40°C (bottom row). Note the visibility of the

After cleaning with PIMA-TETA at an alkaline pH and 40°C for 2 hours, SEM analysis reveals an almost continuous fouling layer on the membrane surface (**Figure 7 d – f**). The characteristic ridge and valley structure of polyamide remains obscured, indicating incomplete fouling removal. However, notable breakup of the deposited alginate layer is observed in certain regions (**Figure 7e**). Additionally, EDX analysis unveils significant differences in the surface composition of these membranes (**Figure 8**). The C:O ratio serves as a reliable indicator of cleaning efficacy and foulant removal. Given the high oxygen content of sodium alginate molecules due to the presence of numerous O radicals

and OH groups (**Figure 3**), variations in the C:O ratio provide valuable insights into the effectiveness of cleaning protocols.

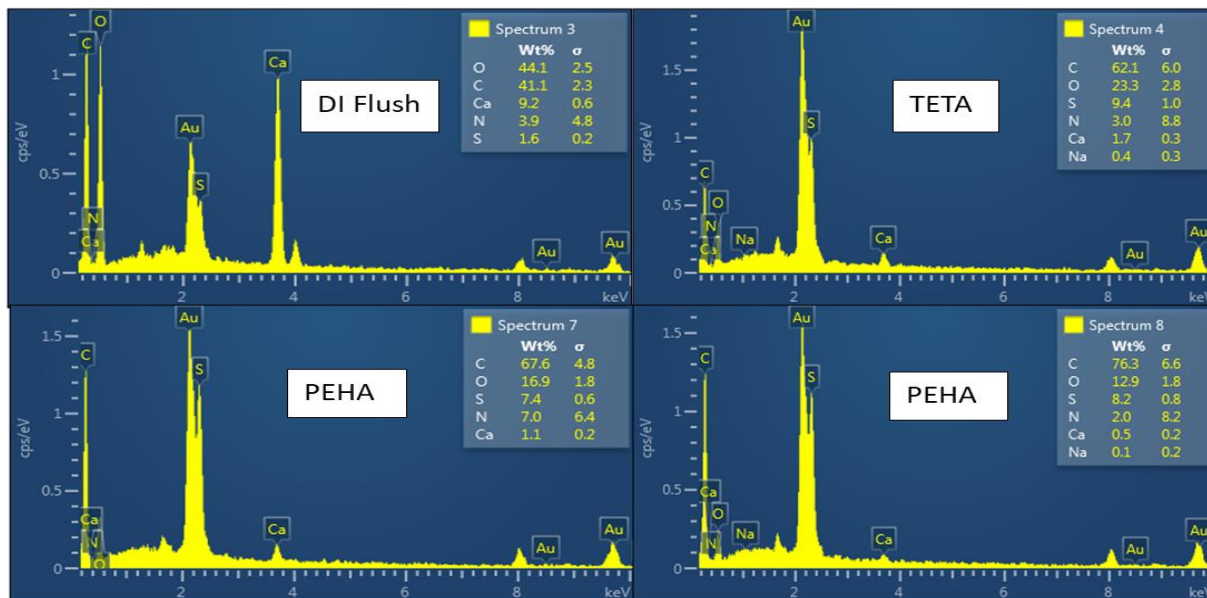


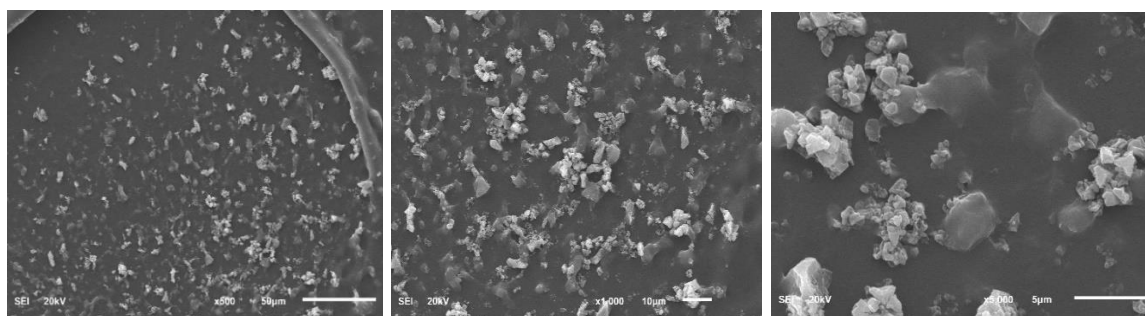
Figure 12. Findings from EDX analysis of the membranes cleaned with different regimes. Notice the difference in C:O ratios for the samples, lowest for the DI flush (~ 1), higher for the PIMA-TETA (~ 2.5), and the highest for PIMA-PEHA cleaned ($\sim 4 - 6$). The ratio approaches that of the virgin membrane with effective cleaning.

The observed trends are consistent with both the flux recovery data and the SEM images presented earlier. For instance, the membrane flushed with DI alone exhibits a C:O ratio of approximately 1, with the oxygen content (around 44%) slightly surpassing that of carbon (about 41%). Additionally, the relatively high calcium content (9.2%) suggests the presence of Ca ions acting as bridges between alginate layers, confirming the existence of a thick fouling layer on the surface. Cleaning with the polymer agents induces changes in surface chemistry due to enhanced foulant removal. Following cleaning with PIMA-TETA, the C:O ratio increases to approximately 2.7:1, while the calcium content decreases to 1.7%. Although SEM images (Figure 11) still reveal a continuous fouling layer and the

absence of polyamide morphology, these alterations underscore PIMA-TETA's effectiveness in removing multiple layers of fouling.

Cleaning with PIMA-PEHA at a pH of 11 nearly restored the original surface chemistry of the RO membranes. As depicted in **Figure 12 c & d**, the C:O ratio increased to approximately 4:1, and in certain regions, even to 6:1. This coincided with a noticeable decrease in the presence of Ca, dropping to less than 1% in select areas. Another significant change was the substantial increase in S content, rising from a mere 1.6% for the membrane flushed with DI alone to about 8% for the one cleaned with PIMA-PEHA. Since the remaining foulant on the membrane surface was minimal, the EDX rays penetrated a considerable portion of the polysulfone support layer in the membrane. There was some variation in the N content, attributable to two potential sources: (i) the polyamide active layer, and (ii) the cleaning polymer with amine groups.

Figure 13 Illustrates SEM images of the membranes following cleaning with PIMA-PEHA at pH values of 8 and 9.4, respectively. The membrane cleaned at pH 8 displays a completely distinct morphology.



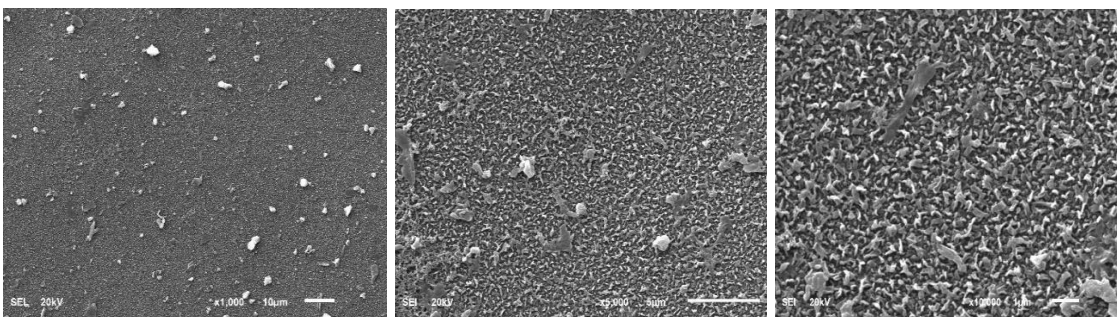
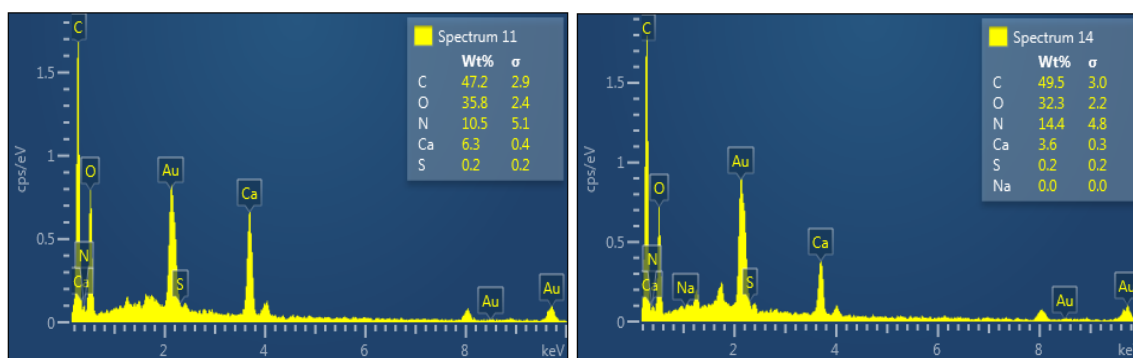


Figure 13. SEM images of the membranes cleaned with PIMA-PEHA at pH 8 (top row) and pH 9.4 (bottom row) after alginate fouling. Note the cleaning ineffectiveness at a pH of 8 and the high efficacy at 9.4.

EDX analysis was conducted on the samples treated with PIMA-PEHA solution at pH values of 8 and 9.4. **Figure 14** displays the outcomes of this analysis. In the membrane cleaned at a nearly neutral pH, the C:O ratio ranges from 1.3 to 1.5, only marginally higher than that of the DI flush sample. Notably, there is a significant presence of nitrogen (10 – 15%), despite the original PA morphology being entirely absent. This observation, along with the presence of white deposits (**Figure 13**), suggests the deposition of the cleaning polymer on the membrane surface.



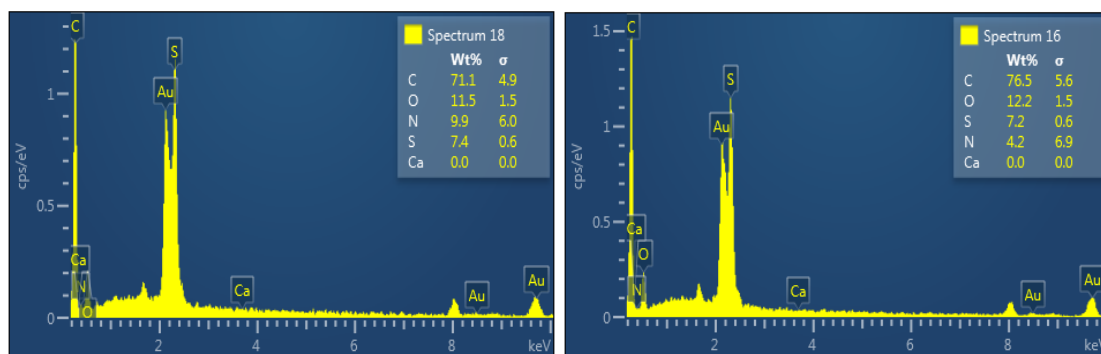
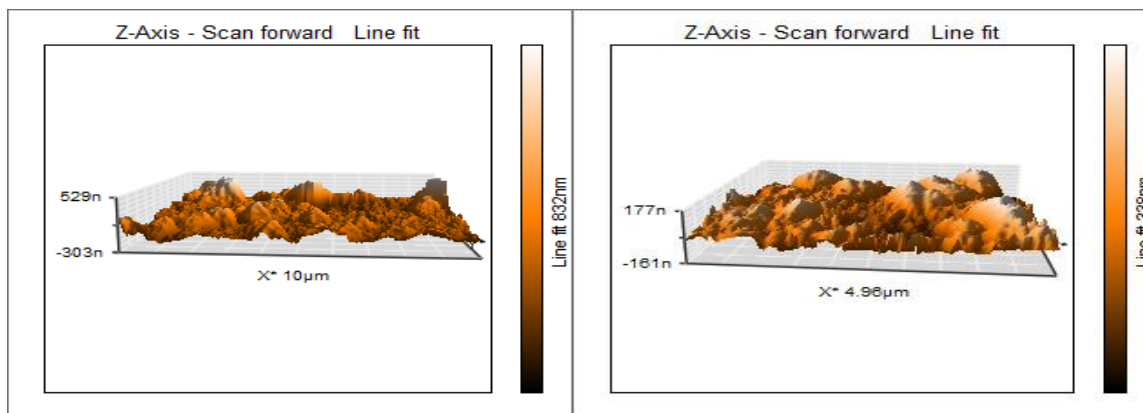


Figure 14. Results of EDX analysis for the membranes cleaned with PIMA-PEHA at pH 8 (top row) and 9.4 (bottom row). Note the unusually high N content for the pH 8 sample which is probably due to cleaning polymer deposition. On the other hand, the composition is nearly identical to a virgin membrane after cleaning at pH 9.4.

4.4.3 Surface Topography

AFM serves as a valuable tool for examining membrane surface roughness. In **Figure 15**, representative 3D images depict membranes treated with various cleaning protocols. The sample flushed with DI alone exhibits substantial variations in topography, featuring regions with prominent peaks adjacent to flat areas (**Figure 15 – first row**). The average roughness values measure approximately 100 nm, significantly surpassing those of the original membrane. These AFM images correspond well with earlier SEM images, with the peaks likely corresponding to the salt crystals observed in the latter.



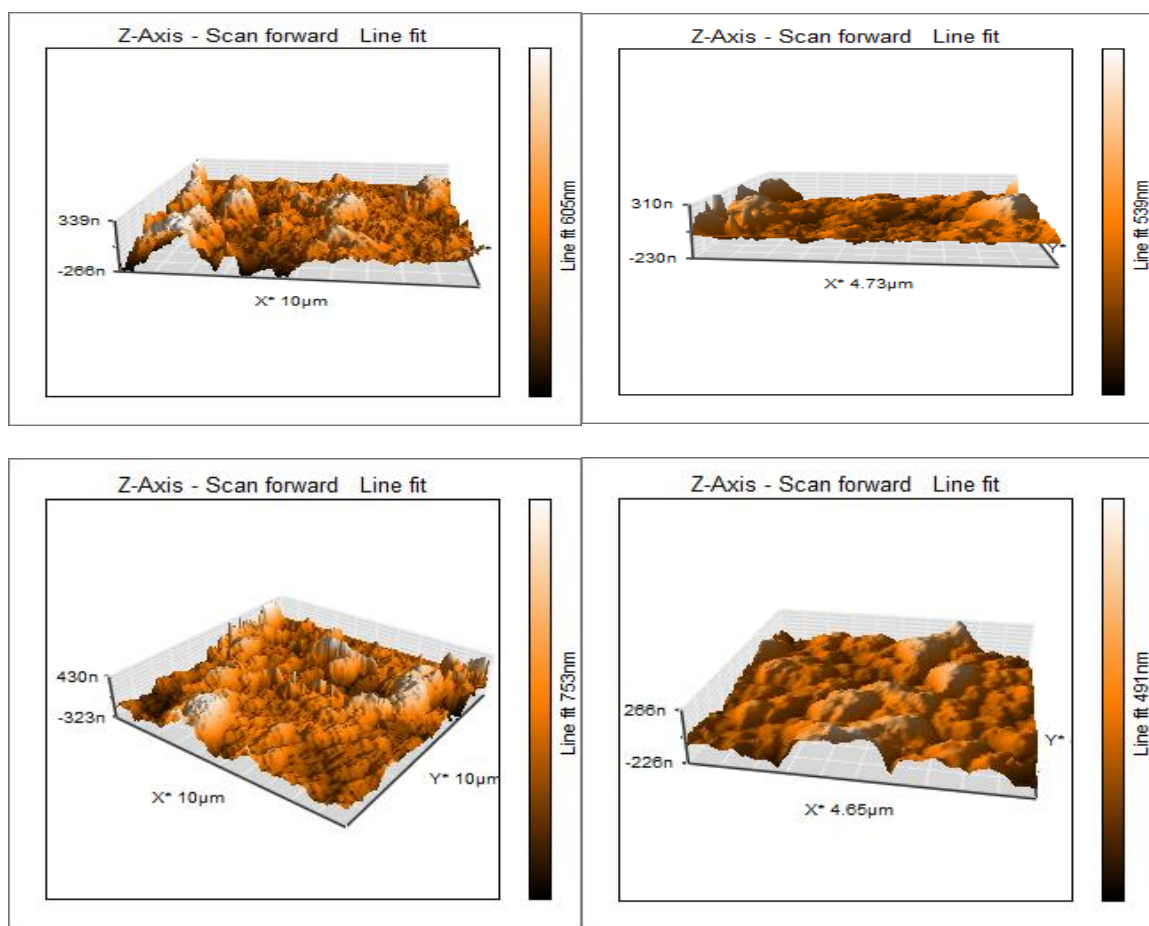


Figure 15. Surface roughness of the membranes cleaned with DI flush (top row), PIMA-TETA (middle row), and PIMA-PEHA (bottom row) measured by atomic force microscopy (AFM). A lower surface roughness was observed for the PIMA-HEXA cleaned membrane.

CHAPTER 5

CONCLUSION

In conclusion, the present work advances the understanding of comb-shaped amphiphilic polymers' synthesis and their application in mitigating fouling in seawater reverse osmosis membranes. The successful synthesis of polymers, including PIMA-TETA, PIMA-TEPA, and PIMA-PEHA, was confirmed through FTIR and NMR spectroscopy. Results showed significant flux decline due to alginate fouling, but polymer cleaning agents, particularly PIMA-PEHA, effectively restored membrane flux. Surface analysis such as SEM/EDX and AFM confirmed the efficacy of cleaning agents. This research provides practical insights into effective cleaning strategies for SWRO membranes, contributing to sustainable water treatment solutions. Future studies could explore the scalability and long-term performance of the synthesized polymers in real-world desalination applications. Continued interdisciplinary collaboration is vital for further advancements in membrane technology to address global water scarcity challenges.

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