



Antifouling Membrane Modification for Water Desalination: Study of Synthesis and Modification

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Received: September 02, 2025

Accepted: September 19, 2025

Online Published: October 31, 2025

ABSTRACT

One of the most important ingredients on earth that everyone needs is water. Consumption of large amounts of water is needed in various human activities such as agriculture, power generation, sanitation, drinking water needs and others. Membrane technology has developed into an indispensable platform technology for water purification, including seawater and brackish water desalination, due to its energy-saving and cost-effective qualities. However, membrane fouling, which results from the non-specific interaction between the membrane surface and foulants, severely impedes the effective deployment of membrane technology. Therefore, this review aims to provide a complete overview of the fabrication and modification of polymer or biopolymer based membranes as an antifouling membrane that focused on the method and performance of antifouling membrane, including water flux, salt rejection, and fouling properties. This review will first outline the main foulants and the primary mechanisms of membrane fouling, followed by a discussion of the development of antifouling membranes, including antifouling tactics and preparation methods. In the final site, the author will be show about the application, challenges and potential future of the antifouling membrane for water desalination.

Keywords: Membrane, Antifouling, Desalination, Modification, Water Flux, Salt Rejection

I. INTRODUCTION

A basic human need is clean drinking water, but only 71% of the world's population has access to it. On the other hand, 844 million people lack access to basic water utilities. Some of the most important global concerns facing humanity in the 21st century include water scarcity and pollution, which have a significant impact on the sustainable growth of industrial and societal activities (Houtman, 2010). The shortage of clean water is caused by many factors, such as the rapid increase in human population over the last few decades which has resulted in a drastic increase in demand for clean water, unequal distribution of clean water, as well as climate change and rainfall accompanied by decrease in the amount of surface and ground water reserves. Global water resources can be divided into two categories: conventional water resources (CWRs) and unconventional water resources (UCWRs). CWRs include natural freshwater resources (e.g., groundwater, rivers and lakes) that can provide clean water directly for drinking or industrial applications without complex treatment. UCWRs are water resources

that are not available for direct use because of the difficulty in purification (e.g., polluted water, wastewater, seawater and brackish water) or collection (e.g., rain and dew)(Zhang et al., 2016)(Lawler, 2016).

Therefore, the latest innovations and solutions are needed to overcome this case. Recently, a number of technologies have been developed for sustainable water purification such as flocculation, flotation, adsorption, distillation, and oxidation processes. However, the complex pollutants in UCWRs (such as inorganic salts, organic materials, and microbes) call for improved technology (Zhang et al., 2016). Desalination of seawater and brackish water is the new approach to produce potable fresh water, which can be utilized for agricultural and industrial applications. The area of the earth's waters is estimated at 361 million km², which indicates that the outer seas of the earth control about 71% of the total area of the earth (Nurman & Ginting, 2022). This is the basis that the potential for desalinating sea water into fresh water is the right solution. Several large-scale desalination plants or industries have been built around the world in recent years, and this trend is expected to continue (P. Jia et al., 2021; Kuzmenkov et al., 2021; Potla et al., 2018; Rong et al., 2022; Warsinger et al., 2015).

Desalination is a technique for removing salt content from water, which was first discovered by Thomas Jefferson in 1791. Generally, seawater and brackish water are treated by desalination. Several seawater desalination methods have been researched and developed to obtain fresh water from salty seawater because it contains salt. Various forms of salt that can be removed during the desalination process include NaSO₄, NaCl, MgCl₂, LiCl and MgSO₄. There are three techniques or criteria for seawater desalination that have been carried out for a long time, namely thermal desalination, electric and pressure desalination (Mayyahi, 2018; Yasin et al., 2021; Zhou et al., 2020). Until now, the three desalination techniques are still used, but each has its weaknesses, especially in terms of energy requirements in the operation process. Therefore, a desalination technique that has high performance and efficiency, and is low cost is needed to convert seawater into fresh water.

Currently, desalination using membrane materials is a desalination technique that is being developed. Reverse osmosis (RO) is a desalination technique approach using selective membranes that can absorb water molecules but reject salts and organic compounds [10]. However, since membrane water treatment technology was developed, membrane fouling has consistently been a problem which reduces the efficiency of the process, reduces water permeation flux, decreases product water quality, and increases energy consumption. Membrane fouling is a widespread issue in a wide range of water purification applications, including the treatment of industrial and municipal wastewater, the manufacture of ultra-pure and drinkable water, and the desalination of seawater and brackish water. Membrane fouling, which can result in a short or long-term flow drop, can be brought on by pore clogging, cake formation, organic adsorption, inorganic precipitation, and biological fouling (Zhang et al., 2016)

To reduce membrane fouling, any approaches have been developed, including raw water pre-treatment, improving operating conditions, cleaning membranes, and developing antifouling membranes. Treatment of raw water has been carried out in several studies using chlorine (Xing et al., 2021) , but the results of research [14]–[16] showed that chlorine can damage membranes which has implications for decreasing membrane performance. According to Guo et al (Guo et al., 2016) that during the uv-chlorination process, disinfection products were formed of the water collected after filtration unit in a drinking water treatment plant, including trihalomethanes (THMs), haloacetonitriles (HANs) and halonitromethanes (HNMs). Besides that, pre-treatment of raw water necessitates additional unit activities (such as air

flotation tanks, flocculation basins, and activated sludge tanks), which take up space and use energy (Zhang et al., 2016).

Membrane cleaning is also widely used to overcome membrane fouling. Although simple physical cleaning of membranes can reduce the small amount of foulants, but large proportions of foulants can only be reduced by complex chemical cleaning, which can degrade the membrane matrix material (Ren et al., 2018). Therefore, In order to solve the membrane fouling problem fundamentally, most research and development efforts have focused on three aspects of membrane fouling, including the behaviour of different kinds of foulant and the corresponding fouling mechanisms, antifouling strategies, and developing various modification method of antifouling membrane. Various methods, such as surface coating, surface grafting, surface bioadhesion, physical blending and surface segregation, have been explored to prepare different kinds of antifouling membranes (Ding et al., 2017; Kadhom et al., 2016; Silva et al., 2017; Tayefeh et al., 2015; Tiraferri et al., 2012).

In this review, the author will be focused to the latest effort in exploring advanced method for fabrication of antifouling membrane for water desalination, including surface coating, surface grafting, physical blending and surface segregation. This article review is compiled from the latest articles in the last 5 years. Articles were obtained from journals published by sciencedirect, membranes journal, MDPI, and others. Reviews are arranged based on the order of taking references and the order of topics.

II. METHODS

This review article combines a systematic literature review approach with narrative synthesis analysis to gain a comprehensive understanding of the development, mechanisms, modifications, and future prospects of biopolymer-based membranes for Direct Methanol Fuel Cells (DMFC) applications. The literature search process was conducted during the period of September–December 2025 through several of the most relevant international scientific databases, namely Scopus, Web of Science, ScienceDirect, SpringerLink, Wiley Online Library, and MDPI. The keywords used included a combination of phrases such as biopolymer membrane, biomass-based membrane, proton exchange membrane, direct methanol fuel cell, methanol crossover, chitosan membrane, cellulose-based PEM, and membrane modification for DMFC. The search was conducted using Boolean operators (AND/OR) and a publication year filter to obtain the latest research developments.

III. RESULTS AND DISCUSSION

Mechanisms for Membrane Fouling

Fouling is considered as one of the main drawbacks of using membrane technologies. Membrane fouling occurs due to the adhesion or adsorption of solid particles, colloidal and oligo-/polymer compounds on the membrane surface (Zhao et al., 2020). Fouling causes the impairment of membrane performance, which is manifested in membrane flux, thus decreasing lifetime and increasing cost (Shokri et al., 2021). The adsorbed layer of dissolved substances on the membrane surface often has to be removed using aggressive chemicals to recover membrane performance (Lu et al., 2017).

Membrane fouling can be separated into two types: (1) reversible fouling brought on by polarization of the concentration and cake formation, and (2) irreversible fouling brought on by foulant adsorption. After rinsing procedures, reversible fouling is easily removeable.

However, due to interactions between foulants and membrane surfaces, irreversible fouling cannot be eliminated by physical cleaning (Loske, 2020). In many circumstances, foulants interact physically with the membrane surface in addition to chemically deteriorating the membrane components. Fundamentally, fouling is brought on by interactions between foulants and the membrane surface, whether they are specialized or general. In contrast to non-specific interactions, which include van der Waals, hydrophobic, hydrogen bonding, and electrostatic interactions between the foulant molecules and the membrane surface, specific interactions are covalent bonding and coordination interactions formed between specific functional groups (such as amino-carboxyl and metal-carboxyl).

According to their intrinsic properties, membrane foulants can generally be classified into three groups: inorganic foulants, organic foulants, and biofoulants. Inorganic foulants mostly consist of inorganic scales and colloidal inorganic materials such as silica, aluminum silicate minerals, and ferric oxide/hydroxide colloids. Organic foulants mainly include oils, biomacromolecules such as BSA, and natural organic matter (NOM) such as HA and SA, whereas microorganisms that make up biofoulants include algae, bacterial cells like Gram-negative *Escherichia coli* (*E. coli*), and Gram-positive *Staphylococcus aureus* (*S. aureus*)(Zhang et al., 2016).

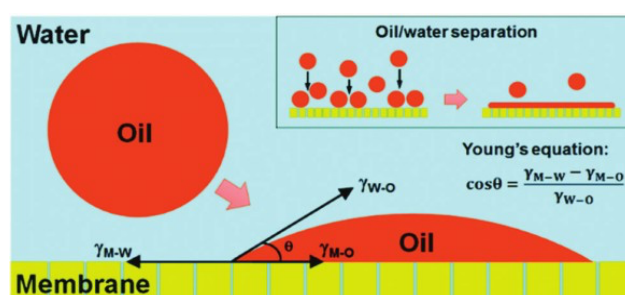


Figure 1. Schematic representation of the process of spreadable oil fouling

Spreadable foulants have fairly complicated fouling mechanisms. One common class of spreadable foulants is oil, which includes free oil, emulsified oil, and dissolved oil. Because oil foulants easily distort and agglomerate in an aqueous solution, they are far more unstable than protein molecules. Oil foulants quickly deposit on filtration membranes due to their significant hydrophobicity, which is a result of the hydrophobic interaction between the oil and the components of the membrane. Oil droplets distort, infiltrate, and spread out along the membrane-oil-water three-phase interface as they come into contact with the underwater membrane surface (Figure. 1). The behavior of oil fouling is greatly influenced by the oil's wettability on the membrane surface (Lu et al., 2017).

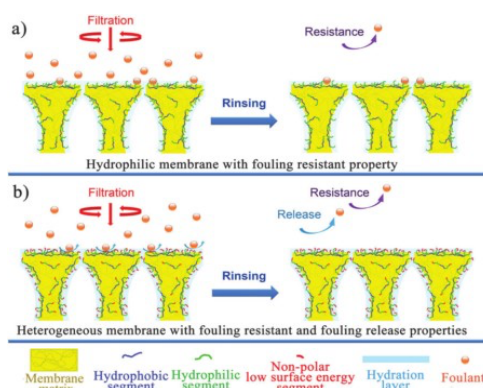


Figure 2. Comparison of the antifouling mechanisms for membranes with two types of surfaces

Membrane fouling is often caused by different varieties of foulants. Therefore, in many applications, either fouling resistance or fouling release is not sufficient to render membranes with excellent performance. More recently, a novel perspective has been proposed to construct amphiphilic surfaces consisting of both hydrophilic moieties with a fouling-resistant attribute and hydrophobic moieties with a fouling release attribute. Figure 2 showed the schematic representation for the comparison of antifouling mechanisms for membranes with two types of surfaces (hydrophilic membranes and heterogeneous membranes). According to the two type of mechanism, because non-polar low surface energy microdomains and hydrophilic domains on heterogeneous membrane surfaces work together synergistically, different foulants in the feed solution can be easily resisted and evicted from the membrane surface; they can diffuse back to the bulk feed solution at low hydrodynamic shear force, achieving both low permeate water flux decline and high water flux recovery during the filtration process (Y. Shen & Badireddy, 2021).

Fabrication of Antifouling Membrane

Modification of polymer membranes by surface coating method has been carried out in several studies (Bai et al., 2019; Ji et al., 2022; Y. Liang et al., 2023; Ni et al., 2014). Research conducted by Bai et al (Bai et al., 2019) reported the synthesis of an antifouling membrane through the nanomaterial coating method in polysulfone pristine membrane. In the study, the antifouling properties of CNCs and CNFs, modified ultrafiltration (UF) membranes from polysulfone, were directly compared. Atomic force microscopy (AFM) was used to analyze the membrane surface morphology, and the results showed that the CNF-coating membranes had rougher surfaces than the CNC-coating membranes. Pure water flux measurements showed that the flow of the CNC-coating membranes was marginally lower than that of the CNF-coating membranes. Antifouling properties were evaluated and compared for the two types of membranes by filtration of NOM foulant models, humic acid (HA) and bovine serum albumin (BSA). The results showed that the antifouling properties of the modified membranes were enhanced through the coating of either CNCs or CNFs to a control PES membrane.

Another study, a Janus membrane with antiwetting and antifouling properties was prepared for complicated wastewater treatment. The membrane was fabricated by directly depositing coating gallic acid (GA) and polyethyleneimine (PEI) onto one side of the PVDF/polydimethylsiloxane (PDMS) blend membrane. The obtained Janus membrane performs excellent antiwetting and antifouling properties because of its asymmetric wettability. When the 36 h DCMD test was carried out using the Janus membrane to treat feed solution containing 1000 mg/L crude oil, 0.3 mM SDS and 3.5 wt% NaCl, a relatively stable flux of $15.7 \pm 0.2 \text{ Kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ was maintained, as well as the very small conductivity of $0.3 \pm 0.0 \text{ } \mu\text{S/cm}$ in the permeate side was kept. In addition, the as-prepared Janus membrane maintained stable when pH ranged from 1.0 to 11.0. Therefore, this Janus membrane can be a strong candidate in DCMD process to treat wastewater containing complicated contaminants (Ji et al., 2022).

In another study by Mo et al (Mo et al., 2021), a new coating method called bio-inspired coating was introduced. This research is quite unique because development of this method was inspired by the antifouling properties of scaly fish which can effectively reduce the contact area with protein membranes resulting from the secretion of fouling organisms and prevent further adhesion between the fouling organisms and the bio-inspired coating. Referring to the antifouling properties of scaly fish, Mo and Co-researchers synthesized an antifouling membrane from a composite layer of phenylmethylsilicone oil (PSO/PDMS) coated with silica

material. This membrane was prepared and modified with a single layer polystyrene (PS) microsphere arrangement (PSO/PDMS-PS) as illustrated in Figure 3.

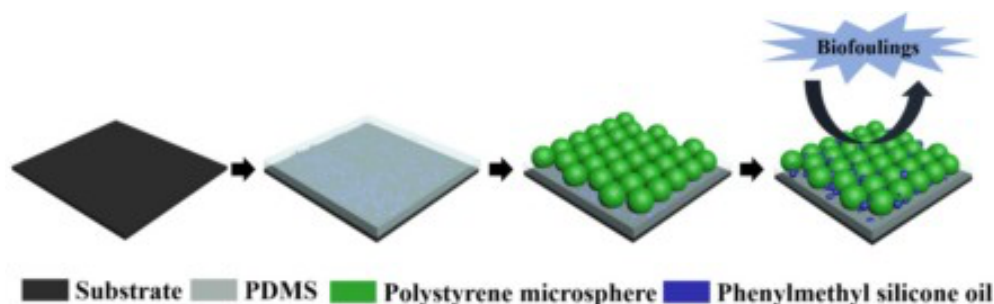


Figure 3. Schematic illustration of the fabricating process of (PSO/PDMS-PS) composite coating

Application of Antifouling Membrane for Water Desalination

Desalination of seawater or brackish water is a technology that has great potential for expanding the world's water supply in the coming decades since it can provide high-quality water without harming the environment of freshwater lakes and rivers. Many different water desalination systems have been developed, including thermal technologies (such as multi-effect evaporation (MED) and multi-stage flash (MSF)) and membrane technologies (such as NF, RO, FO, MD, and ED). In membrane technology, antifouling membrane fabrication results have also been widely applied to desalination processes as shown in Table 1.

Table 1. The Application of Antifouling Membrane for Water Purification

Type of antifouling membrane	Modification	Water flux	salt rejection	Application	Ref.
PA Membrane (Surface Patterned)	Surface patterned	9-9,5 LMH	75 – 85 % (Na ₂ SO ₄)	NF, Desalination	(Ward et al., 2021)
HPMC/PVP blend membrane	Polymer Blending	4.86 kg/m ² h	99.9%	Pervaporative Desalination	(Unlu, 2020)
GA/CA Heterogenous Membrane	Blended to 2D nanochannel	reaches 0.55 W/m ²	salinity gradient of 500-fold	Seawater Desalination	(P. Jia et al., 2021)
PA/TiO ₂ NC membrane	Interfacial Polymerization	40 to 65 L/m ² h	above 96% (NaCl)	Desalination	(Mayyahi, 2018)
CA Nanocrystals/PA membrane	Embedded materials	30 to 63 ± 10 L/m ² ·h	96 %	Reverse Osmosis	(Asempour et al., 2018)
GO-TEOA membranes	Surface Grafting	18 LMH	85 % (NaCl dan Na ₂ SO ₄)	Desalination	(Nakagawa et al., 2018)
gelatin-coated magnetite nanoparticles	Surface coating	1.54 LMH.	-	Desalination	(Azadi et al., 2020)

(MNPs) membrane					
PES/CA/PVP)/Ti O2 MMM	Blended nanoparticle	55-89,6 LMH (overall membrane)	70,5 – 76,8 % in all concentration of salt	Desalination	(Batoool et al., 2021)

IV. CONCLUSION

Although much has been accomplished, there are still pressing needs and formidable obstacles to be overcome in order to develop more durable antifouling membranes for sustainable water filtration, especially for water desalination. Due to the complexity of both foulants and membranes, membrane fouling mechanisms are quite complicated. The porous structure, varied surface physicochemical qualities, and unique operational circumstances of membranes make membrane fouling more complex than that of ordinary impermeable surfaces. Antifouling techniques have been developed with improved understanding of the fouling mechanisms of varied foulants. It has been qualitatively well established that there are correlations between membrane features and antifouling properties (such as hydrophilicity-fouling resistance, surface energy-fouling release, and biotoxicity-antimicrobial property). However, since functional moieties and antifouling property don't have a clear quantitative relationship, exact modulation of the antifouling property is still very difficult. Even though a wide range of antifouling membranes have been successfully manufactured in labs and exhibit a great deal of potential for sustainable water purification, only a small number of methods have been implemented on a large scale due to difficult modification conditions, difficult processing steps, and a high cost. The application of antifouling membranes is also restricted by the antifouling modifiers' long-term stability and their universality. Therefore, creating a simpler and more manageable process for creating membranes with adaptable and long-lasting antifouling qualities is crucial for environmentally friendly water filtration.

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