PROGRESS IN THIN FILM COMPOSITE MEMBRANES FOR REVERSE OSMOSIS AND NANOFILTRATION IN DESALINATION APPLICATIONS

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ABSTRACT: Through reverse osmosis (RO), polymeric membranes can be used to successfully remove salt from brackish and seawater. Two different methods were used to make these polymeric RO membranes: phase inversion was used for asymmetric membranes like cellulose acetate membranes, and interfacial polymerization was used for thin film composite (TFC) membranes. Even though the water that comes out of the TFC-RO process is very good, TFC membranes can get blocked. After a lot of research in both academia and industry, most people now agree that hydrophilicity, surface charge, and surface irregularity are the main things that affect how easily the TFC membrane gets fouled. Because of this, a lot of recent research has worked on changing these features to make TFC membranes for desalination applications that have better flow, reject more salt, and get less contaminated. Within this research, the authors look at all the latest research in the area, focusing on how to make TFe RO and nanofiltration membranes work better in desalination applications by changing the membranes themselves. After that, the authors would talk about a new way to make TFC membranes on a porous polysulfone base. This new method involves the interfacial polymerization of surface modifying macromolecules (SMMs). The organic liquid of the TFC system was used to make hydrophilic SMMs (LSMMs) both outside and inside the system. Shortly after the in-situ LSMM made the membrane, the flux drop went down for a long time. The ex-situ LSMM lowered salt rejection by a large amount and decreased nux by a moderate amount. The in-situ LSMM increased salt rejection but caused flux decline rates to change depending on the concentration of the LSMM.

Keywords: Reverse osmosis, thin film composite (TFC) membrane, fouling, desalination

1. INTRODUCTION

Water treatment and saltwater desalination often make use of thin film composite (TFC) membranes made of aromatic polyamide (PA) as a reverse osmosis (RO) membrane. The TFC membrane is an asymmetrical structure made up of a fabric, a polysulfone (PS) porous support layer, and a dense but extremely thin salt rejection barrier layer J. The thin layer is created by poly condensation, also known as interfacial polymerization (IP), as opposed to the porous support layer, which is usually made of PS and created through phase inversion. Composite membranes can be made utilizing a multitude of processes to create the ultrathin barrier layer. These strategies encompass the following: polymerization at the interface; first, create a thin dense layer; then, laminate it with the microporous support layer.

The gaseous phase monomer plasma (plasma polymerizing) is used to immediately apply the barrier film on the microporous support layer following its dip coating and drying. After that, a polymer solution is added. The industrial manufacture of polyamide TFC membranes makes use of IP, the most commonly used of these approaches. A large number of RO TFC membranes have been successfully manufactured using a variety of polymers, including polyurea, polyamides, polyureaamides, polyether-amides, polybenzhydrazides, and polybenzimidazole.

These TFC membranes have a low water permeability and a strong ability to reject salt. One of the most popular commercial RO TFC membranes, the FT-30, is made by Dow-Pilmtec

Co. A polyfunctional amine, like I, 3-phenylenediamine (MPD), and an acid chloride, like 1, 3, 5 benzenetricarbonyl trichloride (TMC), both dissolved in hydrocarbon solvents, undergo an interfacial polymerization (poly condensation) reaction to produce these membranes. A thin layer of lipid bilayers arises on top of the porous substrate membrane during polymerization because water and hydrocarbon solvents are incompatible. The stiff cross-linked structure of membranes, which is made up of several polyamides, is responsible for their limited water permeability.

Because the shape and surface chemistry of a membrane have such a profound impact on its performance, scientific and technological methods agree that surface modification is necessary to manage surface attributes. Improving the performance and resilience to contamination and chlorine attack of TFC membranes will boost their application. A lot of people are interested in finding ways to make TFC membranes that are more resistant to contamination and chlorine attack, and that also have better performance (more flux and separation). Both chemical and physical modifications to the thin films and the creation of new polymeric materials for the TFC-RO membranes are viable options in this situation. Researchers are looking at a number of chemical modification strategies that could change the surface properties of the membrane.

These techniques can change the surface morphology (including roughness) or chemistry (including hydrophilicity), which in turn affects the transport capacity. Grafting, coating, and mixing of hydrophilic/hydrophobic surface modifying macromolecules are among the many described methods for membrane surface modification. Their publication is complete. A variety of polymers, including aromatic polyamides, have been added to active layer materials in order to increase water permeability. These include hydrophilic sulfonic acid or carboxylic acid groups, poly(vinyl alcohol) (PVA) and poly(vinyl phenol), among others. These modification procedures usually enhance the water nux of the TFC membrane, which reduces its salt rejection. The present state of knowledge regarding the solvent transport mechanism across the membrane allowed for the demonstration that hydrophilic groups, rigid backbones, and specific levels of crosslinking are the components of high-performance transdermal fuel cell (TFC) membranes.

2. IP REACTION TFC MEMBRANES IMPROVED WITH NEW MONOMERS

A number of methods for fabricating TFC membranes from monomers for the IP reaction have been discovered in more recent studies. In order to create the TFC-RO membrane using IF, Li et al. produced 3 unique monomers: tri-and tetra-functional biphenyl acid chloride (BTRC), 3,4',5-biphenyl triacyl chloride (BTRC), and 3,3',5,5'-biphenyl tetraacyl chloride (BTEC). Membranes made of BTRC and BTEC have a higher salt rejection rate than TFC membranes made of TMC. Strongly cross-linked aromatic FA are thought to include functional acylamide (-CONH-) bonds, which could explain this phenomenon. One of the most efficient materials for making the thin active layers of TFC membranes is FA-urethane, which is formed when an aromatic polyamine reacts with a haloformyloxy-substituted acyl chloride.

When desalinating brackish water, the TFC membrane showed remarkable solute rejection and permeability properties. It was made by IPing 5-chloroformyloxyisophthaioyl chloride (CFIC) with MPD. In order to build TFC membranes, Zhou et al. employed CFIC-MPD IP. The surface of these membranes is thick, and they have a granular structure that is finely distributed. The membranes have urethane and amide functional groups on their surfaces. When subjected to same working circumstances as the MPD/TMC membranes, the MPD/CFIC membranes reject a higher flux and salinity.

The amide (-CONH-), urethane (-OCONH-), and hydroxyl (-OH) functional groups were thought to be responsible for this. By utilizing CPIC and MPD IP, Lin et al. have developed a RO-TFC seawater membrane on a PS substrate. A dense, smooth surface with little cross-linking structure was described by them as the membrane's surface.

Adding trace amounts of isopropyl alcohol to the aqueous phase of the IP process (less than 6% by weight) significantly increased water flow while marginally improving salt rejection. By mixing IP in the aqueous phase with TMC in the organic solution, Zhou et al. were able to create TFC membranes. The IP was between MPD and m-phenylenediamine-5-sulfonic acid (SMPD). There was shown to be a strong correlation between the membrane efficacy and the SMPD to MPD ratio. As the SMPD:MPD ratio grew, their research showed a flattening of the surface, a decrease in NaCI rejection, an increase in flow, and an expanded linear section of the membrane barrier layer containing pendant-COOH. The same team also made TFC membranes with MPD using IP in PS support films and 5-isocyanate-isophthaloyl chloride (ICIC+IPC). The resulting membranes have grain structures that are thick and finely distributed. It was found that as the mass ratio of IPC/ICIC grows, the permeate flux increases and the NaCI rejection lowers.

Nanofiltration (NF) membranes were constructed by Thng et al. using IP oltriethanolamine and TMC on the PS supporting membrane. The amphoteric surface properties and good long-term stability were demonstrated by the membranes created with their dense and uneven active layer. The impact of the seed solution's pH on water flow and the rejection of NaCI and other tested salts was thus realized.

Impact of Hydrophilicity on TFC Membrane Performance

The main reason why TFC-RO membranes are more hydrophilic and can potentially have a higher water flow rate is because aromatic polyamides have their acyl chloride groups hydrolyzed. Carboxylic acid groups have a significant effect on salt rejection and water flux because they raise the negative charges of the PA network. As a basic property of membranes, hydrophilicity is anticipated to outstrip other important factors impacting membrane performance, including interactions with solvents or solutes, density, free volume, mobility of polymer chains, and film thickness. As a result, maintaining the active layer's functional group presence is crucial for TFC membrane function.

There have been several attempts to improve the hydrophilicity of membrane surfaces by means of surface modification, and each of these approaches has had its pros and cons. To make a membrane hydrophilic, one must first expose it to a solvent that dissolves in water, be it an acid, an alcohol, or a mix of the two.

Despite improving the flux without changing the chemical structure, the hydrophilizing agent finally leaches through water penetration, resulting in a decrease in the water flux. Due to their respective roles in promoting partial hydrolysis and skin modification, acid and alcohol, when applied together, can enhance surface characteristics. As a result, the membrane's flow and rejection will be improved. It was postulated that extra charges are generated when the water-acidic interaction is accelerated due to the existence of hydrogen bonds on the surface of the membrane. Through the use of ethanol, 2-propanol, hydrofluoric acid, and hydrochloric acid, Kulkarni et al. hydrophiled a TFC-RO membrane. Even without a change in salt rejection, they found that increasing hydrophilicity significantly increases water flow.

A commercial PATFC-RO membrane was grafted with methacrylic acid and poly(ethylene glycol) methacrylate to create a hydrophilic, charged TFC membrane.

Ethylene glycol containing amino acids greatly enhances water permeability through the membrane and prevents improved performance through increased hydrophilicity. Applying an oxygen plasma treatment to the PA-TFC-RO membrane would boost its water permeability and hydrophilicity by introducing carboxylic groups to the membrane's surface. The hydrophilization approach was introduced by Karikov et al. for the hydrophobic support and pore mouth of the TFC active membrane layer.

A hot chromic acid solution was used to oxidize the membrane after it had been prewet with acetone. Liu et al. discovered that TFC polyamide membranes made with MPD from IP of TMC, ICIC, or CFIC changed in surface properties and separation efficacy. Although adding an isocyanato group to polyacyl chloride decreases chlorine stability, their results imply that the TFC

membrane's hydrophilicity, water permeability, and surface uniformity are improved. Adding a chloroformyloxy group to the composite membrane decreases its water permeability but increases its salt rejection rate and surface roughness. Despite the reversed order of surface roughness, the produced membranes were hydrophilic in the following order: MPDICIC > MPD-TFMC > MPD-CFIC. To create TPC NF membranes with hydrophilic surface functional groups that were neutral or negatively charged, Reddy et al. used comparable monomers. The researchers found that the hydrophilicity, water permeability, and salt rejection of the membranes made from the calcium and sulfate salt-containing feed water followed the following sequence:

MPD-ICIC>MPD-TMC>MPD-CFIC. In addition, they claimed that the urea bond and pendant -NHCOOH groups made the MPD-CFIC membrane less chlorine resistant than the MPD-ICIC and MPD-TMC membranes. The authors Jin et al. contend that the dispersion of monomers during the IF process is responsible for the PA film's elevated pendant (free) acid group content at either lower or greater MPD concentrations, longer polymerization reaction times, or lower reaction temperatures. Consequently, these free acid groups exerted a substantial influence on the PA thin film's hydrophilicity. The TFC membrane was created by Chena and coworkers employing IF to synthesis sulfonated cardo poly (aryleneether sulfone) (SPES-NH). The water phase contained MPD and SPES-NH. The resultant membrane could reject a lot of salt and flow really well because to its stiff polymer backbone and strong hydrophilic sulfonic group.

The Emergence of Nanotechnology in Maklng TFC Membranes

Further research is required to ascertain the prospective applications of functional group materials in water treatment and desalination, as nanotechnology has produced a new generation of these materials. Extensive research on membranes made from carbon nanotubes and zeolite films for filtration and desalination has unveiled compelling new possibilities. The synergistic advantages of polymeric materials and nanoparticles are enhanced through mixed matrix or nanocomposite membranes. Moreover, mixed matrix membranes have enhanced mechanical, chemical, and thermal durability, with superior sorption and separation properties. The incorporation of zeolite nanoparticles into the thin layer of TFC-RO membranes resulted in a threefold increase in water flow while preserving salt rejection. Some proposed that biofouling might be mitigated by integrating an innovative anti-fouling membrane made of TiO nanoparticles into TFC membranes to diminish the decline of RO permeability.

Jadav and Singh produced nanocomposite membrane films by in situ incorporating two types of silica nanoparticles (3 nm and 16 nm in diameter) into PA films. The nano-composite membranes are allegedly more thermally stable than pure FA membranes. Both nano-composite membranes exhibited maximal separation efficiency and flux productivity at a particular silica loading level. Enhanced silica incorporation into the polymer leads to thicker membrane films characterized by larger pore diameters and increased pore number density. This has been proved.

Performance Enhancement usingChemical Additives in TFC Membranes

Numerous research were undertaken to enhance the performance of the TFC membrane by integrating various chemical additives before, during, and after the IP reaction in the manufacturing process. The TFC flow in RO applications is enhanced by 30–70% through the immersion of newly manufactured TFC membranes in solutions comprising various organic compounds, such as glycerol, sodium lauryl sulfate, and the salt of triethylamine with camphorsulfonic acid. The physical attributes (abrasion resistance) and flux stability of the TFC were enhanced by utilizing an aqueous solution including PYA and a buffer solution as a post-treatment phase in the TFC membrane fabrication process.

Recently, a PYA-based amine molecule including a side chain amino group has been utilized as the aqueous phase monomer instead of MPD to produce high-flow TFC membranes for low-pressure applications. TFC membranes exhibiting

superior performance are synthesized by integrating alcohols, ethers, sulfur-containing chemicals, monohydric aromatic compounds, and, notably, dimethyl sulfoxide (DMSO) into the aqueous phase. The incorporation of DMSO into the IP system can yield TFC membranes exhibiting a water flow fivefold larger than that of traditional TFC water flux, while maintaining a negligible decrease in rejection efficiency. Yoon et al. have recently developed an electrospun polyacrylonitrile nanofibrous scaffold to serve as a midlayer support in thin film nanofibrous composite (TFNC) membranes for nanofiltration applications.

By IPing polyamides with different concentrations of bipiperidine (PIP) and piperazines, a barrier layer was formed. Their research's results indicated that the TFNC membranes exhibited a permeate flux exceeding 2.4 times that of TFC membranes with identical chemical compositions, attributable to a larger open pore structure and reduced hydraulic resistance of the nanofibrous support, while sustaining a rejection rate of approximately 98%. Wu et al. [65J] utilized an alternative approach to produce thermally stable composite nanofiltration membranes using the interfacial polymerization of PIP and TMC on a poly(phthalazinone ether amide) ultrafiltration membrane. The rejection of Na2SO4 was found to increase with longer immersion periods in the aqueous phase during the IP process, even while the permeate flux diminished. Ultimately, Louie et al. established that the gas flow (0" N" and Hz) over the membrane surface during the water reverse osmosis process could be diminished by treating the thin-film composite membrane with n-butanol followed by dehydration.

Nonetheless, the chlorine resistance of the TFC-RO membrane can be improved with chemical treatments, such as argon plasma treatment, which facilitates cross-linking at the nitrogen sites on the surface of the TFC membrane. Lang et al. produced a more chlorine-resistant PYA RO-TFC membrane by employing malic acid as a cross-linker and acetic acid as a catalyst. Likewise, surface modification with poly(ethylene glycol) (PEG) and its derivatives has been implemented to create fouling-resistant TFe membranes. This can be accomplished by attaching PEG chains to TFCRO membranes. In contrast, Louie et al. created anti-fouling membranes by coating commercial TFC-RO membranes with a polyetherpolyamide solution (PEBAX 1657).

The use of Surface Modifying Macromolecules (SMMs) inTFC Membranes

To modify membrane surfaces in an unexpected way, an active component can be incorporated. We hypothesize that additives may migrate to the top film surface during membrane production, changing the surface chemistry while bulk features are preserved. This is the basis of our technique.

Using this approach, even very small concentrations of chemicals can change the surface chemistry of the membranes. This method of membrane surface modification has recently gained attention due to the incorporation of hydrophobic SMMs into a basic polymer, even though blending is typically used. By integrating hydrophilic SMMs (LSMMs) generated by in-situ polymerization with the polycondensation reaction in the organic solvent of the TFC system, Abu Tarboush et al. improved the flux stability of the PA-TFC-RO membrane.

To build TFC RO membranes on porous PS substrates, a novel approach to interfacial polymerization based on LSMMs was utilized. Despite a smoother surface due to increased LSMM concentrations, scanning electron micrographs show that TFC membranes have more surface heterogeneity than the control PS membrane. See Figures I-A and I-B for examples of both the ex-situ and in-situ synthesis of the LSMMs before to and during the IP process, respectively.

The experimental data presented by Abu Tarboush et al. indicated that both LSMMs may be successfully absorbed by the aromatic PA layer of the TFC membrane. By increasing the solvent's hydrophobicity, we were able to decrease flow rate while improving NaCl separation in a number of different solvents, including hydrocarbons and esters. The in-situ LSMM-incorporated membrane outperformed the ex-situ membrane. When LSMM was added in situ, the stability of the membrane desalination efficacy was much

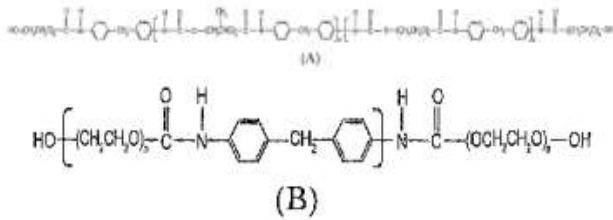improved. The developed in-situ LSMM membrane showed a decreased flow rate over a long time of operation.

Figure 1 LSJvlI\.1 formula. (A): LSIv1M made ex-situ, (B) chemical block for LSIv1M made in-situ

3. CONCLUSION

Reverse osmosis (RO) and nanofiltration (NF) have been the subject of much research for the past fifty years as potential methods for purifying water. An extremely effective commercial reverse osmosis membrane, the FT-30, was created by Dow-Filmtec Co. Most membranes have a thin layer of polyamide (PA) made by combining m-phenylenediamine (MPD) in the water phase with trimesoyl chloride (TMC) in the organic phase through interfacial polymerization (IP). Countless research groups across the globe have created the PA layer by combining various diamines and tri-chlorides, including aromatic, aliphatic, alicyclic, and more. However, further work will necessitate the use of a variety of monomers. When polymericand/or small molecular chemical compounds were added to thin-film-composite (TFC) membranes during interfacial polymerization, their functionality was improved. Polyethylene glycol is used to decrease contamination, while malic acid is used as a crosslinker to increase chlorine resistance. A variety of nanoparticles, including zeolite, titanium oxide (TiO2), carbon nanotubes (CNTs), alumina (Al2O3), and metallic silver (Ag), have been used to produce high-flow reverse osmosis/nanofiltration membranes in recent years. Membranes for high-flow reverse osmosis and nanofiltration were made using carbon nanotubes. In order to reduce microbial proliferation on membrane surfaces and resolve membrane biofouling, it is commonly acknowledged that the appropriate integration of Ag nanoparticles is crucial. The PAskin layer of the TPC membrane

can be utilized to incorporate hydrophilic surface modifying macromolecules (iLSMMs), which can be synthesized using a new approach to in-situ polymerization's organic phase. Recently, PA was used to coat an electrospun nanofiber membrane, which acts as a support. Our main goal is to create ROINF membranes that are more resistant to chlorine and have less pollution. To create RO/NF membranes of the future with improved flow and less pollution, additional basic research on TFC RO and NF membranes is required.

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