

Nanofiltration Membranes for Water Treatment: A Review of Fabrication Methods and Performance Evaluation

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ABSTRACT

The increasing global water crisis, due to the shortage of fresh water and pollution caused by industry, agriculture, and pharmaceutical companies, has increased the need for water purification technologies. Presently, 2.2 billion people are estimated not to have access to safe drinking water, with water pollution having become an issue in every part of the world. Nanofiltration (NF) membranes can play a crucial role in solving the problem since they fill in the gap between reverse osmosis (RO) and ultrafiltration (UF) processes by being able to remove ions under pressure as low as 5-15 bar (whereas RO requires up to 10-80 bar). Importantly, the development of molecular engineering technologies, such as the creation of Janus microporous frameworks, cationic triazolyl heterocyclic compounds, sulfonated macrocyclic compounds (Noria), and different types of MOFs, succeeded in breaking the

permeability-selectivity dilemma. Machine learning techniques, specifically those of an ensemble nature, e.g., Random Forest, XGBoost, show great promise in predicting membrane performance and optimizing membrane fabrication, yielding accuracy levels greater than 0.85 R^2 when predicting salt/dye separation performance. The global NF membrane market estimated to be valued at around \$1.2 billion in 2024 is anticipated to experience a CAGR of 12-15% from 2024 to 2030, owing to the growing demand for water treatment in water-stressed regions and regulatory requirements. Some issues remain to be resolved, such as the problem of membrane fouling (that may lead to loss of membrane flux of between 30% and 70%), scalable manufacturing process, and chemical stability in the long term.

Keywords: Nanofiltration Membranes; Water Treatment; Membrane Fabrication; Interfacial Polymerization; Thin-Film Nanocomposite; Fouling Resistance; Selectivity And Permeability; Metal-Organic Frameworks; Covalent Organic Frameworks;

Introduction

The global water crisis is arguably one of the greatest concerns in the 21st century. Increased population growth, projected to surpass 9.7 billion by 2050, coupled with industrial, agricultural activities, and climatic change have led to increased water scarcity and contamination of water resources with complex contaminants. According to a recent report, 4 billion people face severe water scarcity for at least a month every year, and this number is expected to increase due to changes in climate conditions. Examples of these contaminants include PhACs, EDCs, PCPs, PFAS, microplastics, heavy metals, and OMPs[1]. Conventional methods of treatment, such as coagulation, flocculation, sedimentation, sand filtration, and biodegradation, are not sufficient in the elimination of some of these pollutants from contaminated water. Most conventional treatment processes of activated sludge can eliminate only 20-60% of pharmaceutical compounds from water. PFAS compounds cannot be degraded biologically. In addition, membrane-based technologies have been shown to be the preferred advanced treatments[2].

Membrane filtration techniques have made water purification easier through physical separation of impurities without any changes in phase or chemicals[3]. Membrane filtration for water treatment has generated revenues above \$12 billion in the global market in 2024 and maintains an annual growth rate of 8%-10%. Membrane filtration includes four types: microfiltration (MF; pore size 0.1-10 μm ; operation pressure 0.1-2 bar); ultrafiltration (UF; pore size 0.01-0.1 μm ; operation pressure 1-5 bar); nanofiltration (NF; pore size 0.5-10 nm; operation pressure 5-15 bar); and reverse osmosis (RO; pore size <0.5 nm; operation pressure 10-80 bar). Every type of filtration targets particular contaminants, with NF being a vital link[4].

Nanofiltration is a distinct process that lies between UF and RO processes, with pores having dimensions of 0.5-10 nm or more specifically 1-10 nm, and MWCO of 200-1000 Da. As opposed to RO, which blocks virtually all the dissolved solutes at very high pressures (10-80 bars), NF works under relatively low pressures (5-15 bars) but still enables the selective rejection of multivalent ions like Ca^{2+} , Mg^{2+} , SO_4^{2-} while passing through monovalent ions (Na^+ , Cl^- , K^+)[5]. The ability of NF process to selectively separate monovalent and multivalent ions, along with other organic

compounds larger than 300 Da, makes NF process suitable for applications such as partial demineralization. Some common uses include softening of drinking water (removing hardness causing calcium and magnesium ions), demineralization of brackish waters (removal of salinity from 3,000-10,000 ppm TDS), resource extraction, and pre-treatment of RO process[6].

The unique features of NF over other membrane-based technology methods are: (1) much less energy usage as compared to RO – while the typical energy requirement for NF ranges between 0.5-1.5 kWh/m³, that of seawater RO is between 3-8 kWh/m³; (2) the ability to remove divalent ions and let monovalent ions through, thereby making NF suitable for use in water softening, as opposed to desalination; (3) high rejection rate of organic micropollutants, such as pesticides (>95% for those over 300Da), pharmaceuticals (70-99% dependent upon size and charge), and endocrine disruptors; (4) high water flux (between 20-100 LMH as compared to 10-40LMH in RO at equivalent pressures); (5) less expensive capital investments owing to lower pressures and cheaper pumping equipment; and (6) possible resource recovery as opposed to merely removing contaminants[7].

However, NF membranes have a number of shortcomings: (1) their tendency to suffer from fouling, leading to a decrease in permeate flow rate by 30-70% in several weeks or months of operation due to inadequate pretreatment; (2) weak resistance to aggressive chemical cleansing, especially chlorine, which negatively impacts polyamide active layers; (3) inability to reject very small molecular weight impurities (<150 Da), such as certain pesticides and disinfection byproducts; (4) difficulties with handling the concentrate stream, as NF technology generates a concentrated brine stream with highly concentrated impurities (about 10-25% of the feed flow rate); and (5) high membrane replacement expenses (usually about 20-30% of total operating costs) [8], [9].

The purpose of this review is to present a detailed overview of recent developments in the synthesis and characterization of NF membranes, focusing primarily on innovative information released during 2024-2026. In particular, special emphasis will be placed on molecular design approaches aimed at overcoming conventional performance barriers and novel materials like MOFs, COFs, MXenes, and CTFs; state-of-the-art analytical techniques, namely positron annihilation spectroscopy, AFM, and molecular dynamics simulations; as well as the use of artificial intelligence in predicting membrane characteristics and performance.

Fundamentals of Nanofiltration

Principles of Nanofiltration

The processes behind NF separation rely on the interaction of several factors that include size exclusion, Donnan exclusion, dielectric exclusion, and hydrophobic interaction[10].

Size Exclusion (Steric Hindrance): If a solute is larger than the pore of the membrane, the solute will be hindered by the process of diffusion. It plays a major role in the separation of neutral solutes, and it is determined by the ratio of solute molecule sizes (Stokes radius, molecular length) to that of pores. When it comes to spheres, an increase in the rejection factor becomes more prominent when the solute radius is greater than 30%-40% of the pore radius[11].

Donnan Exclusion (Charge-Based Separation): When the transported solute species are charged, the interaction forces between these solute species and the charge on the membrane surface will play a role in the transport process. Membrane surfaces with negative charge (the charge on commercial NF membranes at neutral pH, zeta potential values between -10 and -40 mV) will repel anions but attract cations[12]. The resulting ion distribution in the vicinity of the membrane surface results in ion repulsion via the Donnan effect at the membrane/solution interface that acts against the diffusion of the co-ions (ions having the same sign as the surface charge) from the solution into the membrane[13].

Dielectric Exclusion: The movement of the ions from the high-dielectric bulk phase (bulk water with a dielectric constant of ~80) to the low-dielectric phase (membrane pores, with dielectric constant of ~2-10) will be energetically unfavorable. This effect contributes especially to divalent ions and pores less than 2 nm in size[14].

Hydrophobic Interactions: The non-polar nature of the substance may contribute to its interaction with the hydrophobic surface of the membrane pores, which impacts both rejection and permeability. Such interactions are represented by the solute log P value, and substances with $\log P > 3$ demonstrate considerable hydrophobic interactions[15].

NF Membrane Properties

Pore size range: 0.5 -10 nm (typically 1 – 10 nm), related to MWCO 200 – 1000 Da. Currently, membranes with sub-20 nm nanofilm polyamides with controllable microporous structure can be developed. Pore size distribution (ideally narrow, geometric SD <1.3) plays an important role in selectivity properties. Various techniques for membrane characterization include retention experiments with neutral organic compounds such as glycerol, glucose, raffinose, or polyethylene glycols with different molecular weights, positron annihilation lifetime spectroscopy, and atomic force microscopy[16].

Surface Charge: Commercial NF membranes generally exhibit negative surface charges under neutral pH conditions (pH 6-8) owing to the dissociation of carboxylic acids resulting from acyl chloride residues (pKa ~3-5), sulfonic acid groups, and anion adsorption[7]. The isoelectric point (IEP) usually falls within the pH range of 3-5; that is, the surface is positively charged when $\text{pH} < 3-5$ and negatively charged when $\text{pH} > 3-5$. However, positively charged membranes ($\text{IEP} > 7$) have been designed for specific purposes such as removing heavy metals (which are normally present in the cation form) and cationic dye substances. Zeta potentials are used to determine membrane surface charge, with values generally varying between -40 mV and +30 mV based on pH and ionic strength[17].

Hydrophilicity/hydrophobicity: Hydrophilic surfaces (water contact angles <50°) enhance water passage by minimizing the energy needed for water sorption while preventing the absorption of hydrophobic substances on the surface, thus reducing fouling tendencies. Commercial NF membranes show contact angles between 20°

(highly hydrophilic, for example, NF270) and 70° (moderately hydrophobic)[18]. Surface hydrophilicity depends on the chemical composition of the surface material (hydrophilic groups include carboxylic, hydroxylic, amine, and sulfonic groups; aromatic groups, alkane chains, and aromatic rings are hydrophobic groups) and surface morphology (Wenzel model)[19].

Surface Roughness: Typically, the polyamide NF membranes have a characteristic surface topography of “ridges and valleys” with RMS roughness values of 20 to 150 nm. Increased roughness provides increased filtering area and flux, but fouling can occur on the valley surfaces. Roughness can be altered by changing interfacial polymerization parameters, including concentration, reaction time, and post-processing[20].

Thickness of Selective Layers: NF membranes have an extremely thin selective layer composed of polyamide that measures 10 to 200 nm in thickness. Thin selective layers have low hydraulic resistance (the flux is inversely proportional to the thickness), but there is a high possibility of having defects in the thin layers, making them mechanically weaker[16].

Transport Mechanisms

Solution-Diffusion Model: Initially developed for the dense RO membranes, this model considers transport across the selective layer through three steps: (a) Sorption of the permeating substance in the membrane at the feed interface, (b) Diffusion across the membrane driven by chemical potential gradient, and (c) Desorption at the permeate interface[21]. In NF process, this model applies only to neutral substances transported in dense selective layers. Water flux can be represented as $J_w = A(\Delta P - \Delta \pi)$, where A is the water permeability coefficient, ΔP is the applied pressure, and $\Delta \pi$ is osmotic pressure difference. Solute flux is expressed as follows: $J_s = B(C_f - C_p)$, where B is the solute permeability coefficient, C_f is feed concentration, and C_p is permeate concentration[22], [23].

Extended Nernst-Planck Equation: In the case of charged nanofiltration (NF) membranes, for the movement of ions, the extended Nernst-Planck equation is a better choice because it accounts for diffusion, electromigration, and convection processes. The Donnan Steric Pore Model with Dielectric Exclusion (DSPM-DE) takes into consideration all three transport mechanisms in addition to steric hindrance effects (which depend on the solute radius to pore radius ratio) and dielectric exclusion terms. It can reasonably predict rejection in single-salt solutions (NaCl, Na₂SO₄, CaCl₂, and MgSO₄) and mixed salts[24].

Pore-Flow Model for Organic Solutes: In case of organic solutes in NF membranes with an open structure (MWCO > 500 Da), the convective transport due to the pore flow becomes predominant over diffusion. Hagen-Poiseuille equation (laminar flow in a cylindrical tube) along with steric exclusion factor is used for estimation of the permeation rate of water, whereas solute rejection is determined by the ratio of molecular diameter of the solute to the pore diameter and its interaction with the membrane material[25].

Computational Progresses Recently Made: Computational studies involving molecular dynamics simulation have shown water and ion transfer in polyamide nanofilm in atomic detail. It was found that water permeates by means of

interconnected free volume sites (cavities with diameter 0.5-1.5 nm connected by narrower regions), with the passage of water molecules between cavities at a picosecond time scale. Ions face restrictions not only sterically, but also electrostatically because of their interactions with carboxyl groups on the pore wall[26].

Materials Used in Nanofiltration Membranes

Polymer-Based Membranes

Polymeric substances constitute the major commercial material used in the manufacture of NF membranes, contributing to about 85-90% of the total NF market share because of their ease of processing and affordability (\$20-50/m²)[27].

Polysulfone (PSf) and Polyethersulfone (PES): These amorphous thermoplastics function mainly as substrate layers in thin film composite membranes. Their high thermal stability (glass transition temperature between 185-220°C), strong mechanical properties (tensile strength ranging between 70-80 MPa), resistance to extremely low/high pH (pH 1-13), and tolerance to chlorine concentrations up to 2000 ppm-hrs render them as appropriate substrates. The fabrication of PSf and PES substrates is done through phase inversion methods, resulting in porosity levels between 60-80%, while the surface pores range between 20-100 nm[28], [29].

Polyamide (PA): Polyamide is the selective layer of the latest generation of TFC NF membranes, formed through interfacial polymerization involving diamine (commonly piperazine, m-phenylenediamine, or new diamines such as 1,3,5-triaminobenzene) and tricarboxylic acid chloride (TMC). The thickness of the polyamide layer varies between 20 and 200 nm, with pore size and charge depending on the level of crosslinking density (proportion of trivalent and monovalent reactive groups)[30]. The most recent advances in molecular engineering have resulted in the development of cationic triazolyl heterocyclic polyamide (CTHP) nanofilms, which exhibit remarkable ion selectivity due to triazole groups providing permanent positive charges and enlarged free volume via contorted molecules[31].

Polyetherimide (PEI): PEI membranes have better resistance to chemicals than PSf/PES membranes but are more costly and harder to work with. PEI membranes find application in SRNF technology[32]. **Cellulose Acetate (CA):** As historically significant as the first NF membrane material, CA provides superior chlorine resistance compared to polyamide but poor pH stability (pH 4-7) and compactability under pressure. CA membranes continue to be used in certain applications due to their chlorine resistance[33]. **Polybenzimidazole (PBI):** PBI membranes provide excellent thermal and chemical resistance as well as positive surface charge in neutral pH (rare for polymer). PBI membranes are thus useful for heavy metals removal and high-temperature processes, although expensive[34].

Inorganic Membranes

Inorganic NF membranes, constituting a mere 5-10% of the total NF membranes' market share, possess distinct characteristics suitable for harsh conditions where polymer membranes fail. **Ceramic Membranes:** Ceramic membranes can be made by sol-gel and chemical vapor deposition methods from various metal oxides (α -Al₂O₃, γ -Al₂O₃, TiO₂, ZrO₂, SiO₂) and provide excellent chemical resistance (pH 0-

14) and thermal stability (up to 400°C). The rigid structure of ceramic membranes ensures reliable operation at high pressures due to a clearly defined pore size distribution (0.5 nm minimum for TiO₂ and SiO₂ membranes)[35]. The permeability rates of ceramic NF membranes are 5-20 LMH/bar and MWCO 200-1000 Da. However, higher costs (in comparison with polymeric ones – \$200-500 versus \$20-50 per m²) and fragility make them less commonly used. Recently developed membranes based on TiO₂-ZrO₂ mixed oxides exhibit better selectivity and hydrothermal stability[36].

Zeolite-based Membranes: Zeolites are crystalline aluminosilicates that have uniform pores with diameters between 0.3 nm and 1.0 nm, allowing precise separation of molecules. The zeolite membranes are characterized by high thermal stability and chemical resistance; separation occurs mainly by size exclusion and preferential adsorption[37]. Zeolites are also hydrophilic and capable of ion exchange. However, creating large areas without intercrystalline channels is still difficult to obtain. Recently, much effort has been put into developing zeolite nanosheet membranes.

Silica-Based Membranes: Membranes based on microporous silica prepared by sol-gel or chemical vapor deposition techniques can produce pores smaller than 1 nm, allowing nanofiltration and even reverse osmosis. Modification with hydrophobic organosilica precursors, such as bridged silsesquioxanes, enhances their hydrothermal resistance, which was a limitation of the use of silica membranes[38].

Carbon-based Nanomaterials

Carbon Nanotubes (CNTs): The hydrophobicity of the inner surface of carbon nanotubes (single-wall diameters ranging from 0.8 to 2.0 nm, while multi-wall diameters range from 2 to 50 nm) allows water molecules to pass through the nanotubes due to a slip length of several tens or hundreds of nanometers, resulting in an enormous theoretical water permeability order of magnitude larger than that of polymer membranes. Water fluxes in vertically aligned carbon nanotube membranes were measured at 10,000-100,000 LMH/bar; however, fabricating defect-free membranes on a large scale is difficult[39].

Graphene Oxide (GO): The presence of oxygenated functional groups (epoxide, hydroxyl, and carboxyl) in GO provides hydrophilic properties and negative surface charges that enhance permeability and rejection of anionic dyes. Nanochannels are created due to the layered structure of GO having interlayer spacing of 0.6 to 1.5 nm depending on the hydration status, resulting in size selective transport properties. Water permeabilities in GO membranes range between 10 to 100 LMH/bar with a molecular weight cutoff (MWCO) of 300 to 500 Da. Swelling issues can occur when the material is hydrated; therefore, reducing rejection and stability of GO under pressure can be improved by crosslinking using divalent ions (Ca²⁺, Mg²⁺) or polymers[40], [41].

MXenes (Ti₃C₂Tx): Since 2020, novel materials referred to as MXenes, which are 2D transition metal carbides and nitrides, have been developed for NF applications. The features of MXene nanosheets include metallic conductivity, hydrophilicity (contact angles 20-40°), and interlayer spacing that ranges between 0.5-1.5 nm. With MXene membranes, water permeabilities range between 100 and 1000 LMH/bar with dye rejections of more than 90%[42].

Metal-Organic Frameworks (MOFs)

The MOF structure is considered especially attractive for use in NF membranes due to their unusually high surface areas (1,000-7,000 m²/g), tunable pore sizes (0.3-5.0 nm, depending on the selection of the metal node and organic linker), and internal surface functionalities[43].

MOF Types for NF:

UiO-66 (Zr-based): High stability in chemicals and temperatures (highly stable in water and pH range between 1-11, up to 300°C). The pores of this compound have sizes of ~0.6 nm and 1.2 nm (two cage types). Incorporation of UiO-66-NH₂ into polyamide membrane matrix improved water permeation from 8.65 to 305.4 LMH with retention of more than 97.5% dye rejection rate. Amine groups of UiO-66-NH₂ compounds form a covalent bond with TMC during interfacial polymerization and anchor the metal-organic framework in the polyamide matrix. **ZIF-8 (Zinc-based):** Highly hydrophobic; with pores of sizes ~0.34 nm and aperture of 0.44 nm. ZIF-8 demonstrates remarkable abilities of capturing CO₂, which has led to its incorporation into polyamide membranes for organic solvent nanofiltration[44]. **MIL-101 (Iron or Chromium based):** Pores of large sizes (2.9-3.4 nm), very high surface area (3,000-4,000 m²/g). MIL-101 nanoparticle embedded in polyamide layers can increase water transport channels. **MIL-53 (Al or Fe-based):** The exhibits “breathing” phenomenon—porous structure modification based on pressure, temperature, or adsorption of foreign molecules, which facilitates stimuli-responsive separation[44]. **MOF-Polymer Interface Design:** The successful addition of MOF nanoparticles demands the suppression of nanofiller agglomeration (usually restricting loading at 0.05–0.5 wt% for TFN membranes) and compatibility between the MOFs and the polymers. Methods include: (1) MOF surface functionalization with moieties capable of reacting with the polymer precursors; (2) MOF in situ synthesis within polymer matrices; and (3) direct conjugation of MOFs onto the polymer chains[45].

Covalent Organic Frameworks (COFs)

Composed of light elements (carbon, hydrogen, nitrogen, oxygen, boron) and covalently bonded, COFs feature regular porous architecture (generally 1-5 nm), ultralow density (0.5-1.5 g/cm³), and high stability against chemical alteration. In contrast to MOFs, metal-free COFs negate metal leakage issues. COF-based membranes can be constructed as: (1) pure COF membranes formed by in situ synthesis on supporting substrates; (2) hybrid membranes with COF nanoparticles embedded in polymer matrices; and (3) COF laminates assembled using exfoliated COF nanosheets. Imine-linked COFs like TAPB-PDA have water permeability rates of 20-50 LMH/bar with more than 95% dye rejection[46].

Nanocomposite Membranes with Macrocyclic Molecules

Sulfonated Noria: Noria is a macrocyclic compound with a molecular weight of approximately 1,200 Da and particle size of about 5.9 nm. It comprises six repeated units that form a rigid ring-like shape. The process of sulfonation attaches sulfonic acid groups (-SO₃H), resulting in high negativity and hydrophilicity. The incorporation of S-Noria into polyamide layers at high concentrations (20 wt%) has

led to an increase in membrane permeability by 3.4 times with only ~98% rejection of Na₂SO₄[47].

Calixarenes and Cyclodextrins: Calixarenes and cyclodextrins are cyclic oligomers that contain four to eight phenol units (calixarenes) and six to eight glucose units (cyclodextrins). They have been used to design molecular recognition sites on NF membranes, allowing them to specifically bind solutes. The application of β -cyclodextrin with an internal cavity diameter of ~0.65 nm and cavity depth of ~0.79 nm has made it possible to complex aromatic compounds[48].

Zwitterionic Polymers

In zwitterionic polymers, there are equimolar amounts of cationic and anionic moieties (for example, sulfobetaines, carboxybetaines, and phosphorylcholines), thus producing a highly hydrated layer due to the electrostatic interactions between water molecules. Grafting zwitterionic polymers results in a reduction in protein deposition by more than 95% on these modified surfaces, as well as a 2–3-fold decrease in bacterial binding. Water permeability is reduced by 10-30% due to hydraulic resistance, although the longevity of these membranes is considerably increased[49].

Fabrication Methods of Nanofiltration Membranes

Phase Inversion Technique

The phase inversion technique continues to be the most common route for asymmetric polymeric support membrane fabrication, with about 70-80% of commercial NF supports manufactured using the phase inversion technique[50].

Immersion Precipitation (Non-Solvent Induced Phase Separation – NIPS): Polymer solution (containing 15-25 wt% of polymer dissolved in solvent such as N-methyl-2-pyrrolidone, dimethyl formamide or dimethyl acetamide) is cast on a substrate (nonwoven polyester fiber web or glass plate) to a thickness of 150-300 μ m[51]. This is immediately followed by immersion of cast film into non-solvent bath (usually water or its mixture with co-solvent/surfactant), leading to a solvent/non-solvent exchange reaction and precipitation of polymer. Membrane formed is characterized by formation of a dense skin layer (with thickness of 0.1-1 μ m) supported by porous layer having finger-like or spongy macro voids[52]. **Polymer concentration:** Higher concentration increases skin layer thickness and reduces pore size (MWCO decreases from 100 kDa to 20 kDa as PSf concentration increases from 15% to 25%)[53].

Solvent/non-solvent pair: Diffusion rate mutual affects the morphology, where high diffusion (e.g., DMF/Water) results in finger-shaped macrovoids while low diffusion (e.g., NMP/Water with co-solvents) yields sponge-shaped structures with greater mechanical strength. **Coagulation bath temperature:** High temperatures lead to fast diffusion rates, thus producing large pores, high flux, and reduced selectivity. Typically, the temperature ranges between 10-50°C. **Other additives:** Porogen agents (PVP, PEG, LiCl, Water) increase porosity and interconnectivity. PVP in 5-15 wt% may double the water flux but decrease tensile strength by 20-30%[54], [55].

Thermally Induced Phase Separation (TIPS): In TIPS process, a polymer is dissolved in a diluent such as diphenyl ether, dibutyl phthalate, glycerol trioleate under high temperatures (150-250°C). The solution is homogeneously mixed and cast

and then cooled down for phase separation to occur between the polymer-rich and polymer-poor regions. Afterwards, the diluent is extracted, leading to formation of the porous structure. With TIPS, it is possible to fabricate membranes with better pore structure uniformity (narrow pore size distribution), high porosity (up to 85%) and wide material suitability (polypropylene, polyethylene, polyvinylidene fluoride). Nevertheless, TIPS requires higher temperatures and solvent extraction which results in increased costs[56].

Vapor-Induced Phase Separation (VIPS): The cast polymer film is subjected to humid air (50-90% relative humidity) prior to immersion into a nonsolvent bath. The uptake of water vapor from humid air causes slow phase separation, resulting in sponge-like membranes that have smaller pore size on the surface and greater selectivity compared to NIPS. VIPS is especially suitable for the fabrication of NF-grade supports without an additional selective layer formation process[57].

Advances in Phase Inversion Techniques: (1) Multi-layer co-casting to produce gradient membrane; (2) use of environmentally friendly green solvents (Cyrene, dimethyl isosorbide, and ionic liquids) as substitutes for hazardous aprotic solvents; (3) nanoparticle incorporation during casting for simultaneous preparation and functionalization of the membrane; (4) electrospray assisted phase inversion technique[58].

Interfacial Polymerization

The interfacial polymerization (IP) technique serves as the basis for the production of thin-film composite (TFC) membranes that make up more than 80% of all the membranes used for nanofiltration in industry. This method was developed by Cadotte in the 1970s and is characterized by producing a very thin, defect-free layer of polyamide on a porous substrate[59].

Piperazine (PIP): Most popular NF diamine. PIP forms very cross-linked and negatively charged polyamide with MWCO 200-400 Da. Rejection: Na_2SO_4 >98%, NaCl 20-60%. **m-Phenylenediamine (MPD):** More reactive than PIP; denser polyamide with MWCO 100-200 Da. RO-like rejection properties (NaCl >99%) are common for MPD-based membranes, though the flux is lower compared to pure RO. MPD is mainly used for RO applications; however, when used in combination with PIP, membranes show intermediate NF properties. **Novel Diamines:** 1,3,5-Triaminobenzene forms polyamide with greater crosslinking density. 1,4-Cyclohexanediamine is used to introduce aliphatic regions, thus increasing free volume in the membrane. Diamines with triazole moiety form positively charged membranes called CTHPs. **Trimesoyl Chloride (TMC):** Standard trifunctional acyl chloride. Increasing content of TMC causes greater cross-linking (smaller pores) but increased surface roughness. **Isophthaloyl Chloride (IPC):** Bifunctional; forms less crosslinked, more open structure. Mixing TMC and IPC allows for regulation of crosslinking density[60], [61].

Process Control Parameters:

Monomer concentration: Increase in PIP from 0.5% to 5% decreases MWCO from 500 Da to 200 Da, while flux decreases by 40-60%. Increase in TMC from 0.05% to 0.5% results in the same effects[62]. **Time for reaction to occur:** Time needed to

conduct IP reaction is about 10-60 seconds. Higher times will increase thickness of film and degree of crosslinking. However, diminishing effect is reached after 60 second[63]. **Organic solvent:** Hexane is commonly used due to low price and low toxicity, but cyclohexane provides a smooth surface. Isopar-G (branched paraffins) slows down TMC diffusion, leading to production of thin films[61]. **Additives:** Surfactants (sodium dodecyl sulfate, Triton X-100) decrease interfacial tension, resulting in even distribution of aqueous layers. Acids' acceptors (Na_2CO_3 , Na_3PO_4 , triethylamine) neutralize HCl formed during IP reaction and prevent corrosion of support materials, as well as accelerating reaction. Co-solvent in aqueous layer (acetone, dimethyl sulfoxide) increases concentration of monomers in organic layer[64]. **Support properties:** Porosity, pore size, and hydrophobicity of support affect the process. Hydrophilic support promotes even distribution of aqueous layer. Support surface pores larger than 100 nm might cause local thickening[65].

Recent Advances in Interfacial Polymerization:

Ionic liquid-assisted IP: The solubility of aromatic diamines in ionic liquids (such as 1-ethyl-3-methylimidazolium acetate), which do not dissolve in water, enlarges the pool of chemicals used. The use of this strategy made it possible to synthesize thin polyamide films (<20 nm) with increased permeability[66]. **Controlled diffusion of monomers:** Monomer slow delivery by nanocarriers (mesoporous silica nanoparticles, cyclodextrin), prevents creation of films with defects. The inclusion of PIP into cyclodextrin cavities results in reduced concentration of PIP at the interface leading to slower reactions and formation of thin selective layers (15-30 nm)[67]. **Organic phase additives:** Introduction of surfactants or cosolvents to the organic phase controls the rate of monomers dissolution and diffusion. Addition of 0.1-1% dimethyl sulfoxide into TMC/hexane mixture enhances PIP concentration in the organic phase[68]. **Support layer modification:** Prior to IP, pretreating PSf supports with hydrophobic diamines such as 1,6-hexanediamine (0.1 wt %) increases the water flux from 25.8 to 95.4 LMH at 15 bar. This hydrophobic diamine lowers the support surface energy, favoring the development of an aqueous layer that is thinner and more uniform[69]. **Post-polymerization processes:** Heat treatments (50-90°C) help create further crosslinks. Post polymerization treatments involving chemical modification using acids (pH 2-3) or bases (pH 10-11) convert residual acyl chloride groups into carboxyl groups. Grafting hydrophilic polymers onto acyl chloride groups provides better antifouling behavior[70]. **IP continuous processes:** Roll-to-roll IP fabrication processes, which use slot die coating, spray coating, or meniscus coating methods, help manufacture membranes at very high throughput rates (line speeds of up to 10 m/min). It is possible to form ultrathin polyamide films (as low as 10 nm) and transfer them onto supports[68].

Layer-by-Layer Assembly

The layer-by-layer assembly technique entails the sequential deposition of polyelectrolytes bearing opposite charges onto a substrate membrane. With each cycle of deposition, two layers of polyelectrolytes are formed. This technique offers great precision in regulating the thickness of selective layers (5-50 nm), the concentration of charge, and pore size[71].

Electrospinning

Electrospinning creates nanofiber mats with extremely high porosity (as much as 90%), high surface area (10-100 m²/g), and porous interconnections[72].

NF membrane application: Although the electrospun mats find applications in NF as a support layer because of its open structure (porosity of 0.5-5 µm), the electrospun nanofiber membranes can also be used as NF membranes if: The fiber diameters are lowered (<100 nm) with enhanced packing density (electrospinning time >2 hours). The fibers are cross-linked/thermally treated (to lower the pores). A selective layer (via IP/LB) is coated on the electrospun support[73].

Advanced and Hybrid Techniques

3D Printing (Additive Manufacturing): Extrusion-based 3D printing (fused deposition modeling) and vat photopolymerization (stereolithography) allow for creating membrane modules with optimal hydrodynamics and customized support structures. Using 3D-printed spacers with triply periodic minimal surfaces results in pressure drop reduction by 30-50% relative to commercial net spacers and higher mass transfer. Although still in early stages, 3D printing holds promise for rapid prototyping and production of membrane modules tailored to on-site decentralized water treatment needs[74].

Modification Strategies for Performance Enhancement

Surface Modification

Surface modification involves the improvement of membrane properties without changing the bulk structure of the selective layer.

Hydrophilic coating: Coating with hydrophilic polymers such as polydopamine, poly(vinyl alcohol), PEG, chitosan, tannic acid prevents the adsorption of hydrophobic solutes[75].

Polydopamine (PDA): The monomer dopamine undergoes spontaneous polymerization in an alkaline medium with pH = 8.5, presence of air, and reaction time of 2-24 hours. PDA coating is formed due to the above reactions that occur in an aqueous medium to coat any surface[76]. The thickness of PDA film is dependent on the concentration of dopamine (0.5-5 mg/mL) and reaction time and varies between 2-50 nm. PDA coating lowers the contact angle to 40-50° from 70°, increases permeate flux by 10-30% and increases fouling resistance (fluctuate flux recovery >90%).

Poly(vinyl alcohol) (PVA): Crosslinked PVA coating by glutaraldehyde or citric acid results in formation of secondary selective layer, lowering MWCO and improving rejection.

Tannic Acid (TA): TA/Fe³⁺ complexation with the coordination creates hydrophilic layers with anti-bacterial effects. The TA/Fe³⁺ layer (5 repetitions) inhibits bacteria adhesion by 99% relative to bare membranes[77].

Zwitterionic Polymerization: Hydrophilic polymers with zwitterionic properties such as sulfobetaine and carboxybetaine form hydration layers due to the electrostatic attraction of water molecules.

Surface-initiated polymerization: Atom Transfer Radical Polymerization (ATRP) or Reversible Addition Fragmentation Chain Transfer (RAFT) via immobilized initiators leads to zwitterionic brushes.

Grafting of Poly(sulfobetaine methacrylate) (PSBMA): Grafting PSBMA reduces the bovine serum albumin adsorption from 50 µg/cm² to below 1 µg/cm². **Grafting-to":** The

grafting is achieved via pre-polymerized zwitterionic polymers containing functional end groups (such as dopamine, thiol, aldehyde), etc., on the membrane surface[78], [79].

Nanomaterials Incorporation

Incorporating nanofiller modifies TFC membranes into thin-film nanocomposite (TFN) membranes that show better performance. Porous Nanofillers (MOFs, COFs, Zeolites, Mesoporous Silica): Additional water flow channels in pores contribute to reduced effective selective layer thickness. The increase ratio of water flux J/J_0 depends on the pore volume of nanofillers[29].

UiO-66-NH₂ (porosity ~40%, pore size 0.6/1.2 nm): Loading at 0.1 wt% raised flux from 8.65 to 305.4 LMH (35-fold increase), with retention capability unchanged. ZIF-8 (porosity ~50%, pore size 0.34 nm): Loading at 0.05 wt% caused an 80-120% increase in flux, retaining >90% NaCl rejection capability. S-Noria (macrocycle, internal cavity ~1 nm): Loading at 10 wt% caused a 3.4-fold increase in flux, retaining >98% Na₂SO₄ rejection capability[80].

Antifouling and Antimicrobial Effects via Nanofillers:

Hydrophilic nanofillers: S-Noria, SiO₂, TiO₂: Enhances surface hydrophilicity, minimizing foulant adhesion. S-TFN membranes have exhibited milder flux degradation (30% decrease as opposed to 50% reduction in TFC membranes) during organic foulant testing. Photocatalytic nanofillers: TiO₂, ZnO, g-C₃N₄: Produces reactive oxygen species upon exposure to UV/visible radiation, leading to organic foulant decomposition[81]. The TiO₂-TFN membranes were able to recover 90% flux following UV illumination without employing any chemical cleaning process. Antimicrobial nanofillers: Ag, CuO, chitosan, quaternary ammonium-functionalized SiO₂: Kills bacteria either on contact or through ion secretion, preventing biofilm development[82]. Electrically Conductive Nanofillers: CNT, Graphene, MXene: Facilitates electrical-assisted foulant removal. Application of 1-2 V (AC or DC) voltage produces electric field strength that pushes negatively charged foulants away from the membrane or induces reactive oxygen species generation [83].

Chemical Functionalization

Charge Tuning Membrane surface charge influences the effectiveness of Donnan exclusion for ionic solutes. Forming positive charge: Quaternization involves the addition of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) that results in the formation of permanent positive charge (quaternary ammoniums). Positively charged surfaces (zeta potential +20 to +40 mV at pH 7) have higher rejection rates of divalent cations such as Ca²⁺, Mg²⁺, and heavy metals as well as anionic dyes[83]. High levels of positive charge led to the rejection rate of more than 99% for divalent cations with nine times better monovalent/divalent cation selectivity of CTHP membranes. Forming negative charge: The hydrolysis reaction leads to the formation of carboxylic groups from residual acyl chloride groups (pK_a ~3-5). Treatment with base (0.1-1 M NaOH; 10-60 min; 25-50°C) converts 30%-80% of residual acyl chloride to carboxyl group. Negative charge leads to increased rejection of SO₄²⁻, HPO₄²⁻, and cationic dyes as it rises from (zeta potential -30 to -50 mV).

Amphoteric surfaces: Membranes with both positive and negative charge sites, such as zwitterionic polymers and amino acid functional groups, will show reversed charge at their isoelectric points[7].

Hydrophilicity Improvement: The introduction of hydrophilic functional groups minimizes the water contact angle, favoring water uptake and transport and minimizing adsorption of hydrophobic solutes. Hydroxyl groups (-OH): By means of plasma modification, dopa-polymerization technique, or grafted poly(vinyl alcohol). Water contact angle decreased from 70° to 40-50°. Carboxyl groups (-COOH): By means of hydrolysis (similar to hydroxyl groups), or grafting of poly(acrylic acid). Contact angle decreased from 70° to 50-60°. Amine groups (-NH₂): By means of plasma treatment (ammonia plasma) or grafted polyethylenimine (PEI). Contact angle decreased from 70° to 45-55°. The amine groups give additional positive charge for pH<9. Sulfonic groups (-SO₃H): By means of S-Noria technique or grafted poly(sodium styrenesulfonate). Decrease in contact angle: 70° to 35-45°. Sulfonic groups stay extremely hydrophilic and negative charged in broad pH range. Poly(ethylene glycol) (PEG): The polymer chains of PEG (MW 200-2000 Da) form a sterical hydration shell due to hydrogen bonding[84].

Crosslinking Enhancement: Increased cross-linking in polyamide chains leads to decreased porosity and increased chemical stability. Heating (50-90°C): Promotes more condensation reactions between the carbonyl and amino functional groups resulting in enhanced cross-linking. Heating (70°C, 10 minutes) results in a decrease of MWCO from 400 to 250 Da, but flux decreases by 20-40%. Cross-linking with chemicals: Cross-linking through reaction with bifunctional reagents such as glutaraldehyde and epichlorohydrin increases cross-links. Treatment with glutaraldehyde (0.1-1 wt%, 30-60 min) enhances membrane solvophilicity to organic solvents. Photo-cross-linking with UV radiation (254 nm): Irradiation of membranes with functional groups sensitive to photo[85], [86].

Performance Evaluation of Nanofiltration Membranes

Permeability and Water Flux

Measurement Methods:

Dead-end filtration: Application of constant pressure (5-20 bar) to a stirred cell with a volume of 10-500 ml and membrane area of 10-50 cm². Easier and quicker than cross-flow filtration and less realistic, because no feed recirculation, foulant deposition, or effect of cross-flow is taken into account. Cross-flow filtration: Feed recirculates over the membrane surface with cross-flow rate from 0.1 to 1 m/s. Allows for extended studies of fouling phenomena. Test conditions are standard: temperature 25°C, pressure 10 bar, cross-flow rate 0.5 m/s. Normalization: The water flux (J , l·m⁻²·h⁻¹) is determined using the formula $J=Q/(A \cdot t)$, where Q – permeate flow (l); A – membrane area (m²); t – time (hours). Pure water permeability (PWP, l·m⁻²·h⁻¹·bar⁻¹)[87], [88]

Table 1: Typical Performance Ranges for Commercial NF Membranes:

Membrane	MWCO (Da)	PWP (LMH/bar)	Na ₂ SO ₄ Rej (%)	NaCl Rej (%)	Contact Angle (°)
NF270 (DuPont)	200-400	8-12	>98	40-60	25-35
NF90 (DuPont)	150-300	5-8	>99	85-90	30-40
NF245 (DuPont)	300-500	10-15	>95	20-40	20-30
TS80 (Toray)	200-300	6-10	>99	80-85	30-40
TS40 (Toray)	200-300	8-12	>98	50-70	25-35
NTR-7450 (Nitto)	300-500	10-20	>95	20-40	20-30

Recent Laboratory Performance Data:

S-TFN membrane (S-Noria in polyamide): 3.4× more PWP than control TFC (control PWP ~10 LMH/bar, new design PWP ~34 LMH/bar), 98.1% rejection for Na₂SO₄ (control 98.5%). CTHP membrane (cationic triazolyl polyamide): PWP 12-15 LMH/bar, >99% rejection for MgCl₂, 9× greater selectivity to MgSO₄/NaCl. MOF-TFN (UiO-66-NH₂ in PIP-TMC): PWP rose from 8.65 to 305.4 LMH/bar (increase 35 times at 0.1%) while dye rejection remained >97.5%. Hydrophobic diamine functionalization: PWP increase 3.7× (from 25.8 to 95.4 LMH/bar at 15 bar), salt and drug rejections remained unchanged. Janus microporous polyamide: Methanol permeance 32.5, acetone 78.7, hexane 47.4 LMH/bar – exceptional performance in organic solvent nanofiltration[89].

Factors Affecting Flux:

Transmembrane pressure: Linear relation under certain conditions ($J = \text{PWP} \times \Delta P$). Non-linear above a critical pressure due to membrane compaction. For NF, linear region usually lies between 5 and 25 bar. Temperature: Viscosity of water drops by 2% per degree Celsius; flux rises by 3-5% per degree Celsius. Standard test condition is 25°C; flux at 40°C is 50-70% more than at 20°C. Feed concentration: The feed solute concentration increases the osmotic pressure, lowering the driving pressure ($\Delta P - \Delta \pi$). For brackish water (TDS of 3,000 ppm), $\Delta \pi$ is roughly 2 bar; while for seawater (TDS 35,000 ppm), $\Delta \pi$ is approximately 28 bar (above the pressure limit for NF). Fouling: Decrease in flux over time. Initial decrease due to pore clogging (occurs over first few hours) followed by decrease due to cake formation (over days to weeks). Resistance of support layer: Support contributes 10-40% of the total hydraulic resistance for TFC membranes[90].

Selectivity and Rejection Efficiency

Salt Rejection Measurement:

For single salt solutions: Normal concentration range 500-2,000 ppm (mg/L) for NF tests. The formula to find rejection $R = (C_f - C_p)/C_f \times 100\%$ where C_f = Feed concentration while C_p = Concentration of Permeate (using conductivity to measure total dissolved solids or ion chromatography for individual ions). For mixed salts solution: Closer to practical applications as found in natural water. For permselectivity S or selectivity $\alpha = (R_{\text{divalent}})/(R_{\text{monovalent}})$, $S = (C_f \text{NaCl}/C_p \text{NaCl})/(C_f \text{MgSO}_4/C_p \text{MgSO}_4)$ [91].

Table 2: Typical Rejection Values:

Salt	Commercial NF (typical)	Recent Advanced Membranes
Na ₂ SO ₄	95-99%	>99% (S-TFN, CTHP)
MgSO ₄	90-98%	>99% (CTHP)
CaCl ₂	40-80%	>95% (CTHP)
NaCl	20-80%	50-80% (varies by membrane)
MgCl ₂	50-90%	>99% (CTHP positive charge)

Organic Pollutant Removal:

Pharmaceutical compounds (PhACs): Carbamazepine (MW 236 Da): NF90 rejection rate is 95-99%, NF270 rejection rate is 60-85%. Diclofenac (MW 296 Da): more than 90% rejection rate for both. Ibuprofen (MW 206 Da): NF270 rejection rate is 40-70% (pH dependent – higher rejection when pH is above pKa due to deprotonation). Pesticides: Atrazine (MW 216 Da): NF90 rejection rate is 85-95%, NF270 rejection rate is 50-80%. The systematic examination of 15 commercially available NF/RO membranes demonstrated that NF90, NF270, NFX, and TS80 are top-performing membranes, with a permeance of 3-7 LMH/bar and greater than 90% retention for most studied OMPs (MW >200 Da). Endocrine disruptors (EDCs): Bisphenol A (MW 228 Da): NF rejection rate is typically 80-95%. Nonylphenol (MW 220 Da): more than 90% rejection rate due to hydrophobic adsorption. PFAS compounds: Perfluorooctanoic acid (PFOA, MW 414 Da): NF rejection rate is 90-99% (dependant on the membrane charge – higher rejection rate for negatively charged membranes[92], [93])

Salts/Organics Separation for High-Salinity Wastewater:

When using NF membranes with MWCO less than 500 Da, salinity separation factor more than 3.7 is achieved (organic rejection >90%, salt rejection <30%) to concentrate organics and recover them from high-salinity organic wastewater (e.g., coal chemical, textile dyeing)[94].

Fouling and Fouling Resistance

Fouling types:

Organic fouling: Causal agents: humic and fulvic acids, bovine serum albumin, lysozyme, sodium alginate, dextran, etc. Organic foulants adhere by hydrophobic interaction, hydrogen bonding, and electrostatic attraction due to opposite charges. Flux loss: 30-70% after weeks to months. Inorganic scaling: Causal agents: precipitates formed due to supersaturation (calcium carbonate, calcium sulfate, barium sulfate, silicates, tricalcium phosphate, etc.). Calcium carbonate scaling is prevented by adding acids to lower pH (6-7) or by using antiscalants. Biofouling: The most difficult type of fouling. Microorganisms adhere, secrete EPS and create biofilms after days to weeks. *Pseudomonas aeruginosa*, *Escherichia coli*, *Bacillus subtilis*, etc. are some bacteria causing biofouling. Colloidal fouling: Foulant particles (<1 µm) such as clay, silica colloids, metal oxides, and others that bypass pre-filtration equipment[95].

Fouling Mechanisms:

Pore Blocking: Particles bigger than the membrane pores occlude the entrance of the pores. Pore blocking results in quick flux decline (minutes to hours) and is worse for membranes that have larger pores (loose NF). **Cake Formation:** Solutes get deposited on the membrane surface, creating a porous or gelatinous film. Cake formation introduces hydraulic resistance (R_{cake}) and can lead to extra filtering resistance. Cake buildup leads to slower flux decrease (hours to days). Tight NF membranes (MWCO <300 Da) build up dense cakes; loose NF membranes (MWCO >1000 Da) are more susceptible to pore blocking. **Concentration Polarization:** Retained solutes tend to accumulate near the membrane surface, resulting in an enriched layer called a boundary layer. The concentration polarization factor (C_m/C_b) is normally between 1.1 and 1.5 for NF under standard crossflow velocities (0.1-1 m/s)[96].

Quantifying Fouling Resistance:

Flux decrease ratio (FDR): $FDR = [(J_{\text{initial}} - J_{\text{fouled}})/J_{\text{initial}}] \times 100\%$. Common values for unmodified membranes: 40-70% in 24-48 hrs. **Flux recovery ratio (FRR):** $FRR = J_{\text{cleaned}}/J_{\text{initial}} \times 100\%$, where J_{cleaned} = flux after physical or chemical cleaning. FRR >90% implies high cleanability. S-TFN membrane showed FRR >95% after rinse compared to 80% for control TFC. **Hydraulic resistance (R_{total}):** $R_{\text{total}} = \Delta P/(\mu J)$, where μ = viscosity. $R_{\text{total}} = R_m + R_{\text{foulant}} + R_{\text{cake}}$. R_m (membrane resistance) is a constant value; R_{foulant} and R_{cake} increase as fouling progresses. **Critical flux:** Below this flux, there is no fouling. Critical flux for NF membranes lies between 20-50 LMH, depending on feed water composition[97].

Fouling Mitigation Strategies:

Hydrophilic surface modification: Minimizes hydrophobic fouling. Hydrophobic PDA coating decreased the decline in flux from 60% to 30% in humic acid fouling experiments. **Zwitterionic modification:** Forms hydration shell preventing foulant adsorption. Grafting of zwitterionic PSBMA chains decreased protein fouling by 95% and bacterial fouling by 99%. **Low-fouling feed spacers:** Spacer design minimizes dead zones prone to foulant accumulation. 3D-printed spacers with triply periodic minimal surfaces achieved 40% lower pressure drop and 15-20% higher FRR. **Air sparging:** Air injection produces two-phase fluid flow, enhancing shear force at the membrane interface. Air sparging (10-20% air holdup) increased the critical flux by 30-50%. **Backwashing:** Permeate flow is periodically reversed to remove foulants. NF membranes should be backwashed every 15-60 minutes for 10-60 seconds at 1-2 bar pressure (under membrane burst pressure). **Chemical cleaning:** Periodic chemical cleaning with NaOH (pH 11-12, organic foulant removal), acid (pH 2-3, scale removal), and NaOCl (200-500 ppm, disinfection and organic foulant oxidation). Frequency: once per day to once per week, depending[98].

Mechanical and Chemical Stability

Mechanical Stability:

Tensile Strength:

Phase inversion membranes: 50-100 MPa. TFC membranes: tensile strength depends on the support; the selective layer does not contribute much. Electrospun supports: 1-

10 MPa (should be handled delicately). Elongation at Break: Phase inversion membranes: 10-50%. Electrospun membranes: 50-200% (more flexible). Compaction Resistance: Polymeric membranes will experience compaction upon pressure application (creep). Loss in flux from compaction: 10-30% after 100 hours of filtration. Compaction becomes worse with an increase in temperature. Burst Pressure: TFC membranes can withstand 30-40 bar of pressure (higher than NF applications)[29].

Long-Term Performance Data:

Conducted continuous one-month tests on NF membranes processing real industrial wastewater with separation factors consistently maintained above 3.3. The flux decreased by 20-30% over 30 days but recovered after cleaning chemicals. Conducted five-year-long field study on NF for softening drinking water. Flux decreased by 40% during 5 years with repeated maintenance (backwash per week, chemical cleaning per month). Membrane replaced within 7-10 years. Aging test at high temperature/pressure/pH allows predicting the lifespan of the membrane. Lifespan estimation from Arrhenius modeling equals to 5-15 years for NF membranes[99].

Applications of Nanofiltration in Water Treatment

Drinking Water Purification

NF is an effective method for the removal of hardness (Ca^{2+} , Mg^{2+}), natural organic matter (NOM) and micropollutants from water sources. The highly selective removal of divalent ions while maintaining minerals (Na^+ , K^+ , HCO_3^-) in the process makes NF a promising technology in drinking water treatment for households and municipal softening plants. Municipal Softening – Case Study (France, Netherlands): NF softening plants using Seine River or Meuse River surface water and NF90 membranes deliver the following performance: hardness from 250-350 mg/L (as CaCO_3) reduced to 80-120 mg/L; TOC reduction >90%; atrazine and other pesticides removed >95%; flux 20-30 LMH at 8-10 bar pressure. Power consumption 0.5-0.7 kWh/m³. Removal of Natural Organic Matter (NOM): NOM (humic substances, fulvic acids) interact with chlorine, forming DBPs (disinfection by-products) trihalomethanes, haloacetic acids. NF reduces NOM concentration by >90%, decreasing DBP formation potential by 80-95%. Heavy Metals Removal: NF can remove >95% of Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Cr^{3+} , As(V) (arsenate). As(III) (arsenite) is neutral in the pH range 6-8 and therefore not efficiently removed (50-80%), but its conversion to arsenate before NF improves efficiency[100]. Removal of Fluoride: NF removes fluoride concentration from 5-10 mg/L (fluoride contamination by geogenic factors) to <1.5 mg/L (World Health Organization guideline). Rejection is a function of pH (more at pH>7 owing to deprotonation to F^- , which interacts with the membrane charge). Point-of-Use Systems: NF membranes in gravity-driven or low-pressure systems offer drinking water in off-grid locations. Gravity-driven NF (0.5 bar, 2 m height) prototype can operate at 5-10 LMH with >95% bacterial rejection and >80% hardness rejection[101].

Wastewater Treatment

Industrial Effluents - Textile Wastewater: Textile effluents are composed of synthetic dyes (50-500 mg/L), salts (NaCl, Na₂SO₄, 5-50 g/L), surfactants, and heavy metals. NF provides: dye rejection 95-99%, salt passage 50-80% (facilitating dye concentration and salt recovery). In a MOF-based TFN membrane setup, NF provided dye rejection up to 97.5% at 10 bar pressure with improved flux of 305 LMH. Dual-stage NF process includes: first-stage for concentrating dye (retentate) while allowing salt passage; second-stage for recovery of salt (permeate). **Industrial Effluents - Pharmaceutical Production:** Pharmaceutical industry wastewaters include antibiotics, analgesics, hormones, and organic solvents. NF provides: active pharmaceutical ingredients (API) rejection rate more than 95%, solvent passage for recovering solvent[102]. **Novel solvent resistant NF membranes** (crosslinked polyamide, PBI) directly treat organic solvent streams. **Industrial Effluents Oil & Gas Produced Water:** Produced water effluents contain oil droplets in amounts ranging from 10-100 million barrels per day globally with concentrations of 10-1000 ppm along with dissolved organics (such as BTEX, phenols) and high salinity levels of 10-300 g/L TDS. Nanofiltration (combined with pre-treatment) provides: oil & grease <5 ppm (down from >100 ppm), TOC reductions >80% as well as partial de-salination making the produced water suitable for beneficial reuse. Problems include high foulability, wide range in influent water quality, high temperatures (40-80°C). **Industrial Effluents Coal Chemical Effluent:** Highly saline effluents from the process of coal gasification and coking operations contain COD 1,000-10,000 mg/L, TDS of 5-50 g/L, and a variety of toxins (phenols, cyanides, PAHs). Nanofiltration with MWCO <500 Da enables achieving separation ratios >3.7 for salt/organic matter separation allowing organics to be concentrated for either incineration or anaerobic digestion and salt recovery for ZLD processes[103].

Challenges and Limitations

Membrane Fouling

Fouling continues to be the main problem, resulting in flux decrease (30-70% during weeks and months), higher energy requirements (20-50% greater costs for pumping flux), regular cleaning (every day to week), lower lifespan of membranes (5-10 years compared to 10-15 without fouling), and higher operation costs (20-40% of total O&M). Although research on development of antifoulants continues, there is no general way to avoid fouling due to the variety of compositions. **Economic Impact:** In case of a 10,000 m³/day NF system, fouling cost (cleaning chemicals, manual labor, loss of productivity, higher energy costs, early membrane replacement) will be \$0.05-0.15 per cubic meter of treated water (15-30% of the whole operating costs)[104].

Permeability-Selectivity Trade-Off

Inverse relationship between permeability and selectivity is the main drawback of membranes. As for the traditional thin film composite (TFC) membranes, increasing water permeability (decreasing thickness of selective layer or degree of cross-linking) always decreases salt rejection, as both are determined by one structural factor - free volume/pore size. Even though some recent techniques in molecular engineering have shown an ability to increase both permeability and rejection rate simultaneously (such

as those used for creation of S-TFN membranes that showed a 3.4x improvement in permeability with rejection maintained), these results usually are achieved in laboratory conditions and cannot be easily extrapolated into industrial practice. The "upper bound" of NF membranes is still being increased due to the development of new materials and fabrication techniques[105].

High Fabrication Cost

High price of NF membranes when compared to other purification techniques can serve as a serious obstacle in their implementation, especially in developing countries. Estimated prices: polymeric NF membranes - \$20-50/m²; ceramic NF membranes - \$200-500/m²; MOF-TFN membranes - \$50-100/m² (high cost of nanofiller). Introduction of nanomaterials (such as MOFs, CNTs, GO) into the design of membranes leads to additional costs: for example, UiO-66 costs about \$50-100/gram (lab-scale synthesis, but bulk production might decrease prices considerably). For comparison, UF membranes cost about \$10-30/m², while MF membranes - \$5-15/m²[106].

Scaling-Up Issues

Small-scale laboratory performance (dead-end cell, 10-50 cm²) is not always transferable to industrial scale membrane modules (spiral-wound, 5-50 m²). Some issues in scaling up include: Defect-free large area production: Production of polyamide layers of high-quality over a large substrate surface without pinholes and cracks. Nanoparticle dispersion: Dispersion of nanofillers at levels of 0.05-0.5 wt% in large baths (100-1,000 L) without nanoparticle agglomeration. Module engineering: Hydrodynamic conditions in spiral-wound modules (pressure drop, concentration polarization effects) do not coincide with flat sheet test results. Computational fluid dynamics are needed to optimize module design. Quality assurance: Nondestructive quality assessment of large area membranes and modules is not easy. Electrical impedance spectroscopy and fluorescent microscopy look promising but are still experimental[107].

Concentrate Management

NF provides a reject stream (concentrate) of 2-10 times the concentration of contaminants in the feed stream. For a plant operating with 90% recovery, the concentrate volume is 10% of the feed volume, but its contaminant content is 90% of that in the feed stream. The following methods can be employed for the management of NF concentrates: deep well injection (geological and ground water contamination issues); evaporation ponds (space demanding and only applicable in arid areas); zero liquid discharge with thermal or membrane brine concentration (\$1-5/m³ treated); and beneficial use (examples: concentrate for salts production, fish farming, and irrigation of halophytic crops)[108].

Chemical Stability and Cleaning Limitations

The polyamide NF membranes deteriorate when exposed to oxidants such as chlorine (common disinfectant), ozone, and permanganate. An oxidation exposure level of more than 1,000 ppm·hours results in salt rejection reduction by 10-50%. This implies

that there will be very few cleaning and pretreatment agents because the NF membranes cannot withstand chemicals such as chlorinated cleaning solutions. NF membranes can only be cleaned using pH levels ranging from 11-12 (NaOH solution) and 2-3 (acid solution), but this deteriorates them over time[109].

Conclusion

NF membrane technology has developed into one of the key membrane technologies today due to breakthroughs in terms of materials science, manufacturing processes, and fundamental studies of transport processes. NF membranes are used today in municipal drinking water treatment and other applications with the global market expected to continue growing at 12-15% per year. Mechanisms underlying NF separation (mechanism of size exclusion, Donnan exclusion, and dielectric exclusion) are understood well, making membrane engineering possible. Extended Nernst-Planck and DSPM-DE equations reliably predict rejection for individual salts and mixes of ions. Despite the leading position of polyamide TFC membranes in the market (80% market share), innovative materials, such as MOFs, COFs, GO, 2D MXenes, and macrocyclic S-Noria, have been reported with remarkable performance levels. Each of these materials brings something new: MOFs increase permeability, S-Noria is an anti-fouling material, and CTHP is highly selective for cations.

While interfacial polymerization has been widely used for fabricating selective layers, new methods in the monomer design (containing triazole rings, macrocycles) and synthesis processes (ionic liquids, monomer diffusion control) allow gaining extraordinary control over membrane properties. Phase inversion, LbL assembly, and electrospinning can be applied as alternative membrane supports and for particular applications. Breakthroughs in performance: Modern approaches in molecular engineering have broken the long-standing rule of permeability/selectivity trade-offs. S-TFN membranes demonstrate 3.4× increase in permeability while maintaining high selectivity; CTHP membranes demonstrate 9× improvement in monovalent/divalent selectivity; MOF-TFN membranes exhibit 35× increase in permeability while maintaining high rejection rate for dyes. Fouling: Even with the development of advanced antifouling materials (zwitterionic polymers, coating with PDA, hydrophilic nanofillers), fouling reduces the flux by 30-70%. Combined approach (hydrophilic surface, anti-microbial properties, and electro-assistance) seems to be promising in controlling the fouling issue.

ML models predict membranes' performances with $>0.85 R^2$ accuracy, identify structural parameters affecting separation processes, and allow reducing the number of required experiments for optimization of fabrication processes by 50-80%. Sustainability is important: Use of green solvents, bio-based monomers, and recyclable membrane materials limits the environmental footprint. The energy requirement (0.5-1.5 kWh/m³ in NF) is much less than RO (3-8 kWh/m³ in seawater), yet improvements are required using renewable power and low pressure. Application areas have widened: Besides water purification, NF offers resource recovery (lithium from brine, nutrients from wastewater, organics from industry effluent). Combined NF systems (NF-RO, NF-MD, NF-electrochemistry) compensate for NF's limitations and enable ZLD.

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