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Review

Nanofiltration as an advanced wastewater treatment technique: a comprehensive review

Djadjiti Namla[1,2] · Mohammad Oves[3] · Majed Ahmed Alshaeri[1] · Saleh M. Al-Maaqar[1] · Hamdy Nasr Youssef Issa[1] · George Mangse[2]

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Abstract

Nanofiltration (NF) is a membrane-based filtration method that has gained prominence in modern technology because of its superior separation efficiency, cost-effectiveness, and ease of operation. With pore sizes ranging from 1 to 10 nm, and a molecular weight cut-off (MWCO) ranging from 100 to 2000 Da, NF membranes bridge the gap between reverse osmosis (RO) and ultrafiltration (UF) processes—and effectively removing a wide range of contaminants including suspended particles, oil emulsions, bacteria, cells, colloidal haze, viruses, macromolecules, proteins, sub-molecular organic groups, monovalent and divalent ions, and heavy metals. To enhance membrane selectivity and permeability, NF membranes have been fabricated from a variety of materials including polymer thin films, metals, polymers with inorganic nanofillers, carbon compounds, metal composites, and nano-semiconductors. Each of these materials contributes unique properties to NF membranes, such as high aspect ratios, biocompatibility, chemical resistance, and thermal stability, making them valuable in various separation processes. Despite the advancements in NF membrane materials, challenges such as membrane fouling and low permeate flux persist. This review provides an in-depth examination of NF as an innovative solution for wastewater treatment, focusing on its principles, applications, and recent advancements in NF technology. This highlights the challenges of current wastewater treatment methods and explores how NF offers a viable alternative for improving treatment efficiency and sustainability. This review also discusses the potential of integrating various membrane materials to optimize NF performance and outlines future trends and challenges in the widespread adoption of NF in wastewater management systems.

Article highlights

- Advanced NF membranes enhance performance, energy efficiency, and sustainability in water treatment.
- Challenges like fouling and low water flow hinder NF's adoption, despite versatile, reusable filters.
- Hollow fiber (HF) membranes offer unique advantages for NF systems.

Keywords Nonfilter · Permeability · Sustainability · Biocompatibility · Membrane technology

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✉ Mohammad Oves, owais.micro@gmail.com | [1]Department of Biological Sciences, Faculty of Sciences, King Abdul Aziz University, Jeddah, Saudi Arabia. [2]Department of Bioechmistry and Biotechnology,, Faculty of Sciences, Nile University of Nigeria, Abuja, Nigeria. [3]Center of Excellence in Environmental Studies, King Abdul Aziz University, Jeddah, Saudi Arabia.

1 Introduction

The designing and development of a high-performance nanofiltration (NF) system is tailored to the membrane materials. However, the successful customization of NF systems depends on a thorough understanding of how membrane manufacturing techniques and parameters shape the membrane's composition, structure, and overall performance of the membrane [1]. Not only do membranes serve as a selective layer for reaction components, but they also possess the ability to function as catalyst supports and exhibit their catalytic activity [2]. This versatile technology has garnered widespread use in waste treatment on a global scale [3–5]. enormous materials such as metals, polymers with inorganic nanofillers, carbon compounds, metal composites, polymer thin films, and nano-semiconductors are being used in the synthesis of nano-membranes for NF systems. Graphene, a carbon-based compound with a distinctive nanostructure, has emerged as a promising material for fabricating thin and flexible nano-membranes with exceptional chemical stability and mechanical strength [6]. In addition to their applications in wastewater treatment, these materials have been extensively used in various industries, including the food and beverage industry, pharmaceuticals, and water softening [7]. While their unique nano-channels not only promote ion mobility but also facilitate efficient molecule filtration, many of these materials such as graphene oxide (GO) serve as ideal two-dimensional water channels [8, 9].

The critical strength of NF lies in its ability to remove a wide range of contaminants from suspended solids, organic matter, heavy metals, and pathogens while retaining important minerals that are lost [10]. Consequently, NF is a suitable alternative for purifying industrial wastewater, municipal discharge, agricultural runoffs, and other contaminated water sources [11].

Other utilization fields of NF systems include medicine alongside wastewater treatment. For instance, it is applied in the fermentation processes where amino acids and lipids are obtained from blood or any other cell culture [12]. Specifically, NF membranes can selectively separate these biomolecules due to the molecular size and charge of each of them, which allows the isolation of groups used for medical purposes [13].

In addition, NF has been used in the de-tarring of feed kids and non-thermal solvent removal and control operations [14]. These applications highlight the flexibility that NF technology offers in tackling some of the most critical bottlenecks associated with liquid separation and purification.

1.1 Background on wastewater treatment

Ancient methods evolved into sophisticated sewer systems in Paris and London [15]. Modern wastewater treatment is crucial for health, resource preservation, and ecological balance [16]. Freshwater scarcity is worsened by climate change and industrial expansion [17]. Hence, untreated wastewater discharge leads to eutrophication, posing pollution risks [18].

Industries, particularly textiles, contribute to water pollution through the discharge of wastewater containing synthetic dyes, hazardous metals, and chlorine [19], which negatively impact aquatic ecosystems by reducing light penetration, inhibiting photosynthesis, and causing oxygen depletion, ultimately leading to the death of aquatic organisms [20]. Nanofiltration serves as a contemporary solution to efficiently remove contaminants, ensuring that discharged water meets environmental standards and safeguards against the detrimental effects of untreated wastewater on ecosystems and human health [21]. Features including a pore size between 1 and 10 nm, typically possessing charged surfaces in aqueous settings, and a molecular weight cut-off (MWCO) ranging from 100 to 2000 Da, have made NF membrane-based technology widely used. These properties make NF membranes particularly effective for the selective exclusion of biomolecules. Consequently, NF membranes find applicability in diverse areas such as decolorization, desalination, concentration, and the separation of biomolecules represents in the Fig. 1.

1.2 Recent advances in water treatment

Traditional wastewater treatment methods, while effective in removing solids and organic matter, have limitations in addressing emerging contaminants and other pollutants [22–24]. The Industrial Revolution intensified the need for advanced treatment due to increased wastewater volume and complexity [25–27]. Factors such as the presence of emerging contaminants [23, 28, 29], growing water scarcity, climate change [30, 31], aging infrastructure, energy consumption [32, 33], and public health concerns [34–36] necessitate the development of advanced wastewater treatment techniques. Key advancements include the activated sludge process [37, 38], secondary treatment involving biological oxidation,

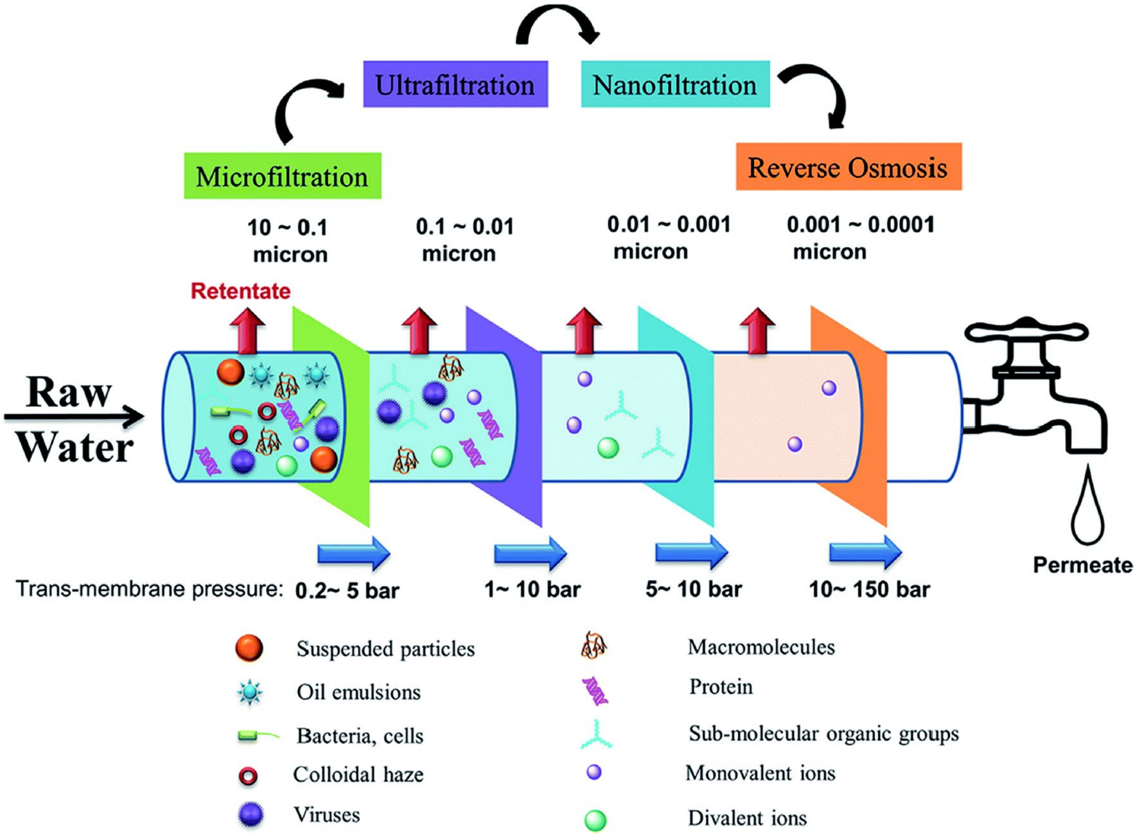


Fig. 1 Pressure-driven membrane processes for water treatment technologies, showing the particles effectively captured by each process along with the pore sizes of the membranes used for each process [18]

chemical precipitation, and physical separation [39–41], and tertiary treatment for nutrient removal and overall water quality improvement [27, 42]. Recent innovations focus on enhancing sludge dewatering through compound conditioning [43, 44]. Tertiary treatment focuses on removing nutrients like nitrogen and phosphorus, which contribute to harmful algal blooms (eutrophication) in water bodies [22, 24, 45, 46]. Advanced techniques like activated carbon adsorption, membrane filtration (including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis), and advanced oxidation processes are employed for this purpose [27, 47–49]. The increasing prevalence of emerging contaminants, such as pharmaceuticals and personal care products, has underscored the importance of tertiary treatment in safeguarding aquatic ecosystems and human health [50, 51].

2 Nanofiltration (NF)

NF development began in the 1960s when researchers recognized a distinct selectivity region between reverse osmosis and UF membranes [52]. This realization led to the development of NF membrane technology, which has found plentiful practical applications across various industries due to its unique selectivity range [53]. Nanofiltration is a membrane-based filtration process that operates on the principle of size exclusion [54]. It can remove particles, organic matter, and certain ions from water, allowing smaller molecules to pass through [55]. NF membranes have pore sizes ranging from 1 to 10 nm, allowing for separating dissolved solids and divalent ions.

2.1 Principles of nanofiltration

Nanofiltration, a versatile process, measures Van der Waals forces via a small tip (< 100 Å) scanning across the membrane, linking surface roughness to fouling susceptibility [56]. Permporometry gauges porous membrane traits, ruling out non-porous polymeric membranes [57]. This variant permits the passage of non-ionized organic compounds (< 200 g/mol) and monovalent salts while impeding non-ionized organics (> 250 g/mol) and ionized multivalent salts [57].

NF utilizes two separation mechanisms, often known as the dielectric mechanism: electrical repulsion for charged species and size-based separation for uncharged solutes [58, 59]. Hence, ion selectivity and rejection rates are significantly influenced by the dielectric effect [53]. The dielectric effect arises due to the difference in dielectric constants between the membrane material and the aqueous solution, affecting the distribution of ions near the membrane surface [60]. Ions with a higher charge density possibly experience stronger interactions with the electric field, leading to increased rejection rates. This effect is crucial in separating multivalent ions from monovalent ions and influences the membrane's ability to retain organic molecules [61]. The dielectric exclusion mechanism complements steric and Donnan exclusion effects, also known as the Gibbs-Donnan effect in NF, enhancing selectivity based on ion valence and size [62]. Membranes, often polyamide (PA) or polyether sulfone (PES), operate through size exclusion, electrostatic interactions, and solute diffusion under applied pressure, facilitating solvent flow while retaining larger solutes [53].

Building on the characteristic features of NF membranes, including their sub-nanometer scale pore size and electric charge properties, various pore flow models have been extensively studied to explain ion transport within these membranes. These models include the Teorell-Meyer-Sievers (TMS) model [63, 64], the steric-hindrance pore (SHP) model [65, 66], the electrostatic and steric-hindrance (ES) model [67], and the Donnan steric pore model (DSPM) [68]. As research advanced on the impact of nanoconfined environments on the dielectric constant of water, the dielectric exclusion mechanism was integrated with the DSPM model to account for the dielectric properties of materials on ion transport [68, 69]. The refined DSPM-DE model has been effectively employed to describe ion transfer processes and predict membrane separation performance in mixed component systems. The DSPM-DE model accurately describes ion partitioning and transfers in NF membranes by integrating dielectric exclusion with Donnan exclusion and size-sieving effects [69]. From this model, the Nernst–Planck equation accounts for ionic diffusion, electromigration, and convection within the membrane pores.

$$J_i = J_V K_{i,c} c_i - D_{i,p}\frac{\mathrm{d}c_i}{\mathrm{d}x} - z_i c_i D_{i,p}\frac{F}{RT}\frac{d\Psi}{dx}$$

where J_i represents the solute flux of species *i*, J_V denotes the water flux through the membrane, and $K_{i,c}$ is the hindrance factor. C*i*, $D_{i,p}$, and *zi* correspond to the concentration, intrapore diffusion coefficient, and valence of species *i*, respectively. F is the Faraday constant, and Ψ represents the membrane potential.

The partitioning of ions at the interfaces between the membrane and external solutions adheres to the principles of Donnan equilibrium and Born solvation theory as described by the following equations:

$$\frac{c_{i,(0^+)}}{c_{i,(0^-)}} = \varphi_i \exp\left(-z_i \Delta\psi_{D,(0^+|0^-)}\right)\exp(-\Delta \mathrm{W}_{\mathrm{i,Born}})$$

$$\frac{c_{i,(L^-)}}{c_{i,(L^+)}} = \varphi_i \exp\left(-z_i \Delta\psi_{D,(\mathrm{L}^-|\mathrm{L}^+)}\right)\exp(-\Delta \mathrm{W}_{\mathrm{i,Born}})$$

Born effect

$$\Delta \mathrm{W}_{\mathrm{i,Born}} = \frac{(z_i e)^2}{8\pi\varepsilon_0 kTr_{i,\mathrm{cov}}}\left(\frac{1}{\varepsilon_p} - \frac{1}{\varepsilon_b}\right)$$

where $\Delta\psi_D$ represents the Donnan potential, while ε_p and ε_b are the dielectric constants of the pore solution and the bulk solution, respectively.

This model incorporates various membrane structural parameters, such as the ratio of effective membrane thickness to porosity (Δx/Ak), volume charge density (Xd), and dielectric constant (ε), to better capture realistic ion transfer behavior [60, 64], The thin-film composite (TFC) NF membranes based on size sieving, Donnan exclusion, and dielectric exclusion effects represents in the Fig. 2. Such arrangement enables the prediction of membrane functionality based on specific structural parameters, including flow, ion rejection, and selectivity [62]. To assess the impact of different ion selectivity processes, the contributions of ion flux driven by diffusion, convection, and electromigration can be individually quantified [62]. Altogether, these increasingly sophisticated models, which closely align with the detailed characteristics of polymeric membrane structures, offer a deeper understanding of the ion selectivity mechanisms governed by multifactor coupling and provide valuable guidance for designing advanced ion-selective NF membranes [62].

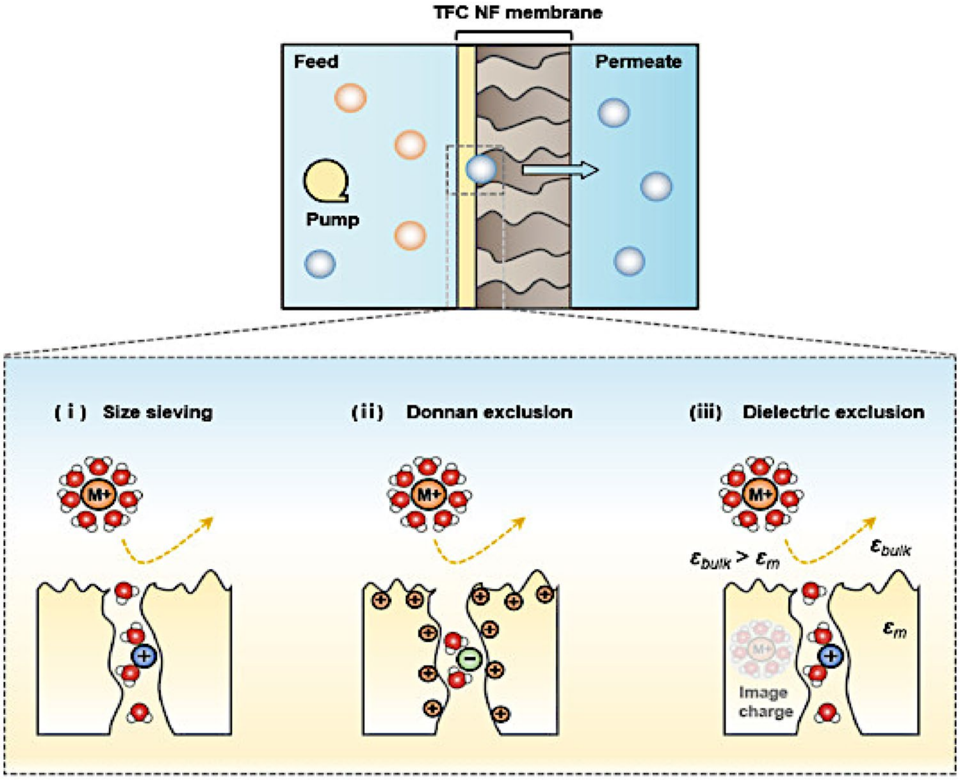


Fig. 2 The ion separation mechanism of thin-film composite (TFC) NF membranes involves size sieving, Donnan exclusion, and dielectric exclusion effects [60]

2.2 Materials used for nanofiltration membrane

2.2.1 Traditional polymer-based materials

Various materials have been employed for the fabrication of NF membranes. These integral materials to membranes in filtration are classified into polymer thin films, metals, polymers with inorganic nanofillers, carbon compounds, metal composites, and nano-semiconductors [61]. Ultra-thin materials extensively applied in filtration significantly influence the efficiency of the filtration process [61]. Polymer thin films like polyethylene terephthalate (PET) find widespread use in crafting nano-membranes for filtration, providing flexibility and durability suitable for diverse filtration applications [62]. Metals, such as aluminum, and other metal composites contribute to NF membrane fabrication, offering enhanced mechanical strength and chemical resistance crucial for efficient filtration processes [63].

Combining polymers with inorganic nanofillers creates hybrid NF membranes for filtration, reinforcing structural integrity and overall performance [64]. Utilization of organic membranes, featuring materials like polyacrylonitrile (PAN), polyvinylchloride (PVC), PA, and polysulfide (PS), is common due to their chemical stability and compatibility with diverse filtration processes [64, 65]. The preparation of NF membrane with interfacial polymerization and employed sysnthetic compunds piperazin (PIP), trimesoyl chroride (TMC) and regulated by g-C3N4, more details in Fig. 3.

Metal-based NF membranes, constructed from various metals and oxides like gold (Au), palladium (Pd), aluminum oxide (Al_2O_3), titanium dioxide (TiO), and zinc oxide (ZnO), address specific filtration needs, including chemical resistance and selective permeability [66–68]. Semiconductor-made membranes, incorporating materials including germanium sulfide (Ge_2S_3) and molybdenum disulfide (MoS_2), play a vital role in filtration technology, offering advanced functionalities like selective adsorption and separation capabilities, thereby enhancing overall filtration efficiency [69, 70].

Anodization, lithography, micromachining, chemical vapour deposition, layer-by-layer deposition, sol–gel processing, and the fundamentals of 3D printing remain the most used processes for the synthesis of NF membranes [71]. Lithography plays a critical role in various industries, especially as there is a growing demand for smaller features and high resolution [72]. There are two main types of lithography, masked and maskless [73]. Masked lithography utilizes

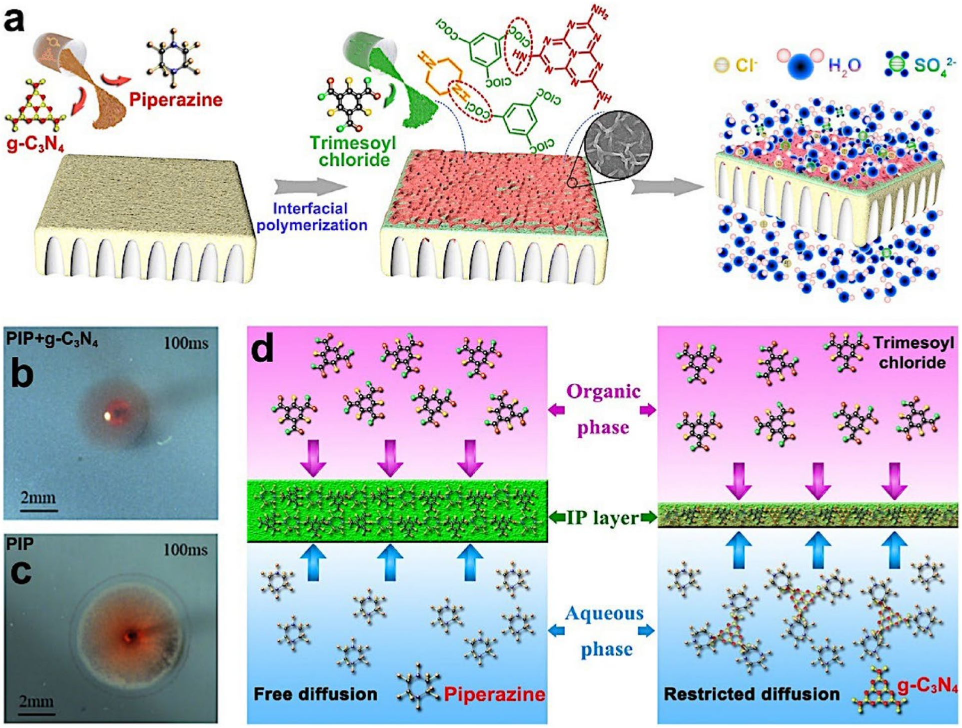


Fig. 3 Preparation of NF membranes regulated by g-C3N4 [2] **a** Diagram depicting the procedure for preparing the g-C3N4-regulated membrane. **b** Photographic representation capturing the PIP + g-C3N4 + TMC reaction after 100 ms. **c** Photographic representation capturing the PIP + TMC reaction after 100 ms. **d** Illustrations comparing the unhindered and constrained diffusion of PIP during the IP process with and without g-C3N4

a mask to transfer patterns onto a base material, whereas maskless lithography uses serial writing to create diverse designs without the use of a mask [74]. Examples of masked techniques include photolithography (with a minimum feature size of 2–3 µm) and nanoimprint lithography (with a minimum feature size of 6–40 nm) [71]. Anodization is another technique of membrane fabrication which is mostly done using Al_2O_3. There are two types of steady-state anodization: soft and hard [75]. When comparing these processes, the hard anodizing reaction is more vigorous, resulting in faster growth of the porous anodic Al_2O_3 coating [75] re-present in the Fig. 4. However, this increased activity generates more heat, necessitating additional cooling equipment [61]. In addition to steady-state anodization, there are two non-steady-state types: periodic and pulsed [76]. The periodic anodizing method is superior in controlling the porous structure within the anodic Al_2O_3 coating compared to the alternative method [77].

During the anodizing process, a layer must be applied to the aluminum [78]. The properties of the anodic layer, such as the thickness of the barrier layer and the size of the pores, are influenced by the voltage applied [77, 78]. Voltage and current also impact the surface appearance of aluminium [78]. Electric polishing involves low voltages and strong currents, resulting in the formation of a porous layer as voltage rises and current decreases. Conversely, a thick layer of

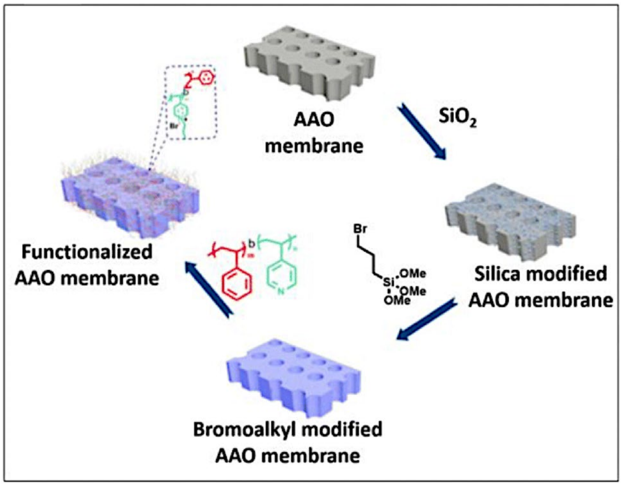


Fig. 4 Schematic illustration of grafting to strategy for preparing poly(styrene)-block-poly(4-vinylpyridine)/AAO composites [75]

aluminium oxide forms when the current is low, and the voltage is high [79]. Anodic aluminium oxide patterns develop over time when aluminium undergoes anodization in acid solutions under an electric field [77–79].

Nano-modifiers have been incorporated into NF systems. The integration of these materials into NF not only enhances the performance of the membrane, encompassing water permeability, salt rejection, and contaminant removal selectivity [80], but also elevates the inherent characteristics of these membranes, including hydrophilicity, porosity, antifouling properties, antimicrobial properties, as well as mechanical, thermal, and chemical stability [81]. However, limitations such as fouling and chemical instability have prompted the exploration of novel materials.

2.2.2 Emerging materials in nanofiltration membranes

Cellulose nanocrystals (CNC), MXene, porous organic polymers (POPs), and other emerging nanoparticles enhance performance in terms of permeability, selectivity, and resistance to fouling [79]. CNCs are derived from natural cellulose and possess high strength, stiffness, and biodegradability. Their introduction into NF membranes improves mechanical properties and increases hydrophilicity, which enhances water flux while maintaining high selectivity [82]. CNCs can also serve as a platform for functionalization, enabling further enhancement of membrane performance through the introduction of specific chemical functionalities [83].

MXenes, a family of two-dimensional transition metal carbides, nitrides, and carbonitrides, have emerged as promising materials in NF membranes due to their unique properties, such as high electrical conductivity, hydrophilicity, and surface charge tunability. These properties facilitate efficient ion rejection and improve antifouling characteristics when incorporated into NF membranes [84]. POPs are another class of novel materials that have been successfully integrated into NF membranes. These materials feature a highly porous structure, allowing for fine-tuning of pore size and surface chemistry [85]. This adaptability results in NF membranes with enhanced selectivity and high permeability. Moreover, the stability of POPs under harsh conditions makes them suitable for various industrial applications [86].

Nanofiltration membranes featuring interlayer structures, where varied materials are layered to create a composite membrane, represent a significant advancement in the field. These interlayered NF membranes often combine the advantages of various materials, such as the mechanical strength of CNCs, the conductivity of MXenes, and the porosity of POPs, leading to membranes with superior performance characteristics. For instance, the use of a thin layer of MXene sandwiched between CNC layers can result in a membrane with both high flux and excellent ion rejection [84]. Also incorporating a selective layer between the support and active layer can enhance rejection while reducing fouling [85]. Functionalized layers can be used as well to improve hydrophilicity, antifouling properties, or specific molecule separation [85, 86].

However, there are misclassification issues surrounding the novel NF membranes. To fill the gap in knowledge of hybrid NF systems, we introduce a new classification method for this hybridization approach, taking into account both synergistic material interactions and functional roles:

(i) Polymetric Materials: Most NF membranes are based on polysulfone, polyamide, polyethersulfone.
(ii) Inorganic Materials: Utilizing growth of inorganic materials including carbon nanotubes, graphene oxide, and metal–organic frameworks (MOFs) to improve membrane mechanical strength, thermal stability and selectivity.
(iii) Active Layer Materials: Polymeric active layers: usually formed by interfacial polymerization, allowing tuning of membrane pore size and surface charge.
(iv) Hybrid Active Layers: Usage of inorganic and polymer hybrid active layers to enhance selectivity and antifouling properties and permeability.
(v) Functionalizing Agents: Surface Modifiers: These include surfactants, polymers and nanoparticles that can be used to modify the surface nature of the membrane, enhance hydrophilicity, reduce fouling and improve selectivity.
(vi) Biomimetic Materials: Biomimetic materials, inspired by natural systems, can provide unique properties like self-cleaning and antifouling capabilities.
(vii) Hybrid NF Systems: There are three types of hybrid NF systems depending on the polymer-inorganic combinations that show various functionalities. And based on the latter criterions, these systems are mainly: (a) Polymer-Inorganic Hybrid systems in which various materials are employed in the fabrication of the membranes, (b) Functionalized Membranes: these particular hybrid NF systems involve embedding distinct functionalizing agents within them, improving their specific features like selectivity, antimicrobial activity and antifouling, and (c) Membranes Assembled in Layers: created by depositing many layers of different materials (only one at a time), giving control over the membrane structure and properties.

2.3 Applications of nanofiltration in wastewater treatment

According to recent studies, NF systems are viable substitutes for pressure-driven reverse osmosis in integrated membrane systems [87]. The use of these systems is low-cost and consumes little energy. Saravanan et al. [88] explored the efficiency of a nanofiltration system made up of a reverse osmosis (RO) system combined with a hybrid organic polyimide membrane. Working conditions of their experiment include pressure, temperature, pH value of the wastewater, and volume reduction factor. They observed an 89% improvement in filter efficiency which clearly shows that total hardness, sulfate, and chemical oxygen demand (COD) are much reduced. The authors stress the importance of ecofriendly treatment in leather industries and point out that nanofiltration as well as RO processes help assuage environmental impact. In addition, they concluded that organic polyamide membranes give a more environmentally friendly touch to filtering, contributing to further purities.

Suwaileh et al. [89] examined the application of a membrane distillation (MD) method integrated with an electrodialysis (ED) system to generate cost-effective high-quality water, specifically tailored for irrigation (Fig. 5).

Meanwhile, in their experimental work, Kim et al. [84] explored a hybrid approach that combines fertilizer-drawn forward osmosis (FDFO) with nanofiltration (NF) for the treatment of water impacted by mining activities. Notably, the FDFO–NF hybrid system exhibited markedly reduced energy consumption (1.08 kWh/m3) in comparison to MF–RO and UF–RO systems operating under similar feed conditions.

2.4 Industrial applications of nanofiltration beyond water treatment

A particularly intriguing feature of NF membranes is their capability to allow the passage of monovalent ions, like sodium chloride (NaCl), through the membrane while blocking divalent [90] and multivalent ions, such as sodium sulfate (Na_2SO_4) [91]. This adaptability creates abundant opportunities for specialized process applications across various industries [92]. Given the primary focus of filtration on process applications, progress has been made to incorporate NF membranes into an already diverse product range that includes ultrafiltration and microfiltration membranes [91–93] and NF membrane used in various purposes given in the Table 1 and in Fig. 6.

According to Abdel-Fatah [91], the reported applications of NF include:

- Applications in pharmaceutical and biotechnology sectors, and purification of spent clean-in-place (CIP) chemicals.
- Implementation in the chemical industry.

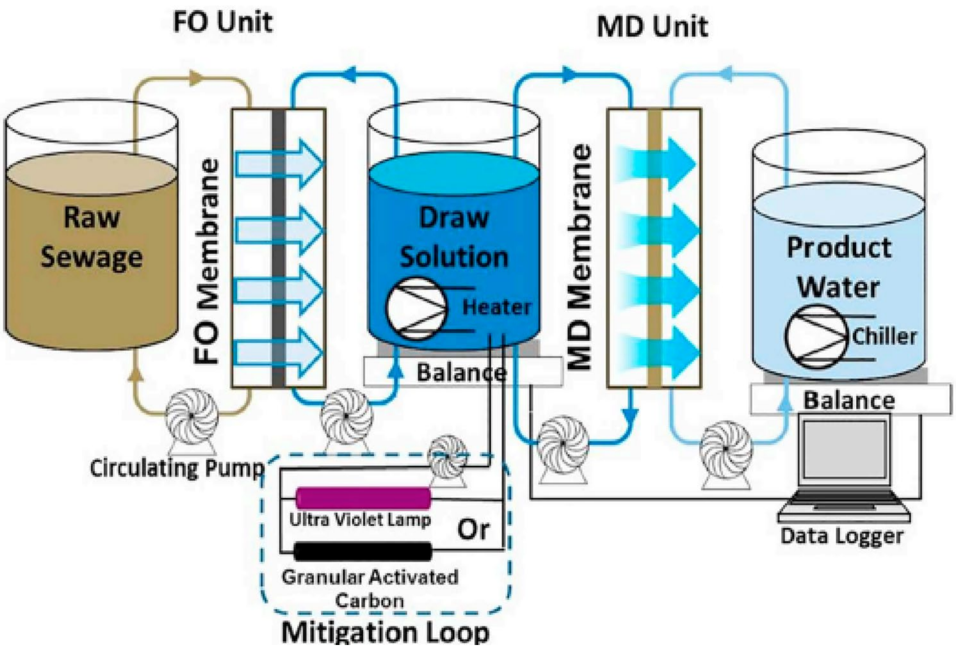


Fig. 5 The design of the forward osmosis (FO)–membrane distillation (MD) process is composed of an FO membrane channel, a direct contact MD membrane compartment, pumps, and temperature monitoring sensors [89]

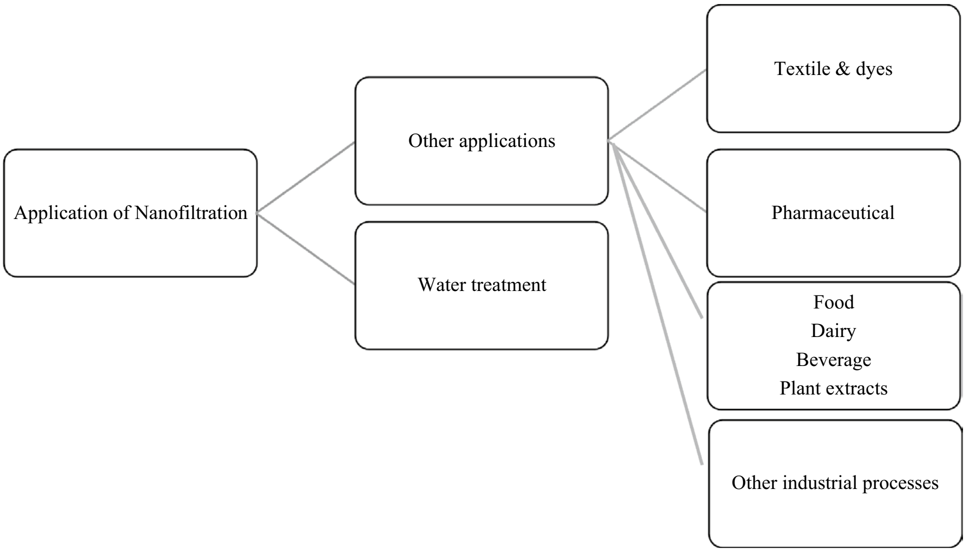
Table 1 Other areas of Nanofiltration applications other than water treatment

Area of application	Applications	Description	Benefits	References
Textile and Dyes	Dyes Desalting and Concentration: NF serves as an effective method for textile wastewater treatment	Desalinate and concentrate dyes in textile wastewater, improving dye quality	Improves dye purity, reduces wastewater treatment costs, and promotes sustainability by enabling dye recovery and reuse	[19, 105]
Dyes Penetration Removal:	NF is used to recover dyes, ensuring compliance with discharge regulations following penetration testing with fluorescent dyes	NF membranes are applied after penetration testing to remove residual dyes from wastewater, ensuring compliance with environmental regulations	Ensures regulatory compliance, reduces environmental pollution, and allows for the potential reuse of recovered dyes	[19, 22, 105]
Optical Brightening Agent Concentration and Desalination	NF is used to concentrate optical brightening agents for color enhancement, promoting their reuse in the process	. NF membranes concentrate optical brightening agents in textile processes, reducing the need for fresh chemicals and enhancing color brightness in textiles	Reduces chemical costs, enhances product quality, and promotes the reuse of brightening agents, reducing waste and environmental impact	[96]
Pharmaceutical	NF captures fibrinogen and clotting compounds efficiently upon separating blood serum and plasma, nanofiltration	NF membranes are used in blood serum processing to separate and capture valuable proteins like fibrinogen and clotting factors	Enables efficient protein separation, supports the production of high-quality blood products, and enhances medical research and pharmaceutical production	[99]
Antibiotic Production	NF membranes are a compelling technology for separating, concentrating, and manufacturing hormones and antibiotics	NF is applied in the pharmaceutical industry for the separation and concentration of antibiotics and hormones, improving production efficiency and product purity	Increases production efficiency, reduces production costs, and ensures high purity of pharmaceutical products, benefiting both manufacturers and patients	[100, 101]
Food, Dairy, Beverage, and Plant Extracts	NF is a quicker and more cost-effective alternative to traditional boiling methods for thick maple syrup	NF concentrates maple syrup more efficiently than traditional methods, reducing processing time and energy consumption	Reduces production time and energy costs, increases product yield, and maintains syrup is natural flavor and quality	[102]
Concentration and Demineralization of Lactose	NF membranes can concentrate and demineralize lactose to varying purification levels as needed in the process	NF membranes are used in dairy processing to concentrate and remove minerals from lactose, producing high-purity lactose for various applications	Provides a flexible and efficient method for lactose processing, improving product quality and expanding its use in different food products	[103]
Plant Extracts	NF enhances the overall product yields of plant extract through the concentration of plant hormones like gibberellins	NF membranes concentrate valuable plant hormones and compounds from extracts, improving product yield and quality	Increases yield, reduces waste, and supports the production of high-quality plant-based products for pharmaceuticals, cosmetics, and food industries	[102, 104]
Industrial Processes	Seawater Sulfate Removal: NF selectively eliminates seawater sulfate, crucial for scaling prevention in oilfield waterflood operations	NF membranes are applied in oilfield operations to remove sulfate from seawater, preventing scaling and maintaining the efficiency of waterflood operations	Prevents scaling, reduces maintenance costs, and enhances the longevity and efficiency of oilfield equipment, contributing to more sustainable oil extraction processes	[42, 108]
Brine Recovery	NF membranes selectively reject sulfate while permitting sodium chloride passage, providing an effective brine recovery solution in industries	NF is used to recover brine solutions in various industrial processes, separating valuable salts from unwanted contaminants	Enhances resource recovery, reduces waste, and lowers operational costs by enabling the reuse of recovered brine	[1, 121]

Table 1 (continued)

Area of application	Applications	Description	Benefits	References
Dissolved Natural Organic Matter Removal from Surface Water	NF effectively eliminates natural organic matter from surface water, facilitating NOM-enriched water production or industrial processes	NF membranes are employed to remove dissolved organic matter from surface water, improving water quality for industrial and municipal use	Improves water quality, reduces treatment costs, and enables the use of surface water in various applications, from drinking water production to industrial processes	[9]

Fig. 6 Nanofiltration Applications Other than Water Treatment



- Desalination within the food industry (including dairy, juice processing, soft drinks, sugar production, fish meal, beverage products, meat processing, baker's yeast, and olive processing).
- Partial desalination of whey.
- Desalination of textile dyes and optical brighteners.
- Removal of metals, nickel, and chrome plating in metal finishing industries and the leather industry.

2.5 Reusability of nano-membrane filter

Among the myriad advantages of nano-membrane filters, their reusability stands out as a crucial feature, significantly contributing to sustainable water treatment practices. However, the mechanism of reusability of NF membranes has been attributed to many factors including operational conditions, cleaning protocols, and fouling control [11]. The unique pore size (1–10 nm) of NF membranes enables selective permeability [56]. This structure allows for the rejection of multivalent ions and organic molecules while permitting the passage of monovalent ions [56]. This selectivity eventually reduces the risk of severe fouling often associated with larger molecules and particles, a common issue in tighter membranes like RO, MF, and UF [53, 57, 59]. Operating at lower pressures compared to RO, UF, and MF, NF membranes experience less compressive force on the membrane surface. This minimizes fouling caused by particle accumulation and biofilm formation. Additionally, NF membranes exhibit superior resistance to organic fouling due to their ability to reject hydrophobic contaminants [79]. The durability of NF membranes extends to their resistance to harsh chemicals and high-pH cleaning solutions [80]. This characteristic simplifies the cleaning process, extends membrane life, and improves cost efficiency [94]. Consequently, NF membranes require less frequent cleaning and maintenance, enhancing operational efficiency and lifespan [80, 91]. Beyond fouling resistance, NF membranes demonstrate higher tolerance to variations in feed water quality, including fluctuations in pH and temperature [67, 94]. These parametric variations have been found to reduce the need for stringent pretreatment [67–69, 94]. Finally, NF systems consume less energy due to their lower operating pressures compared to RO [94]. Xu et al. [95] fabricated carbon-decorated titanium nano-membranes (C/TiNMs) for efficient protein adsorption, elution, and selective isolation. Titanium foils were anodized to form TiO_2 nanotube arrays, followed by carbon decoration through annealing. The resulting C/TiNMs exhibited amphiphilic properties and enhanced protein adsorption capacities compared to bare TiNMs. Protein adsorption was pH-dependent, with optimal conditions near protein isoelectric points. Elution efficiency was achieved using alkaline buffers, and circular dichroism analysis indicated preserved protein secondary structure during adsorption/desorption cycles. The multiple adsorption and elution cycles, together with the high adsorption efficiency for proteins maintained by the C/TiNM display its robust reusability. UV-induced self-cleaning enhanced membrane recyclability [94].

Nano-membrane filters with intricate nanostructures enable precise control over pore size and surface properties. Tamboli et al. [96] synthesized recyclable titanium nanofibers, doped with cerium and nickel doped. The reusability test showed that the catalyst is active even after five runs of hydrolytic reaction, implying the as-prepared NiO-doped TiO_2 nanofibers could be considered as a potential candidate catalyst for a portable hydrogen fuel system.

The carefully engineered nanoarchitecture ensures superior filtration efficiency and plays a pivotal role in enhancing the filter's durability and reusability [97].

Nano-membranes are often crafted from robust materials, such as graphene oxide, carbon nanotubes, or polymers, providing excellent chemical and physical stability [71]. This inherent resilience allows the filters to withstand repeated use without compromising their structural integrity [98]. The filters can endure harsh chemical cleaning processes, making them suitable for multiple cycles of filtration and reuse [98].

The reusability of nano-membrane filters aligns with the principles of sustainable development by minimizing waste generation [99]. Conventional water filtration methods often rely on disposable filters, contributing to environmental pollution [100]. In contrast, the ability to reuse nano-membrane filters reduces the demand for new filter production and disposal, promoting an eco-friendly approach to water treatment [101].

While the initial investment in nano-membrane filter technology might be higher than traditional filtration methods, the long-term cost benefits are significant [71, 99]. The filters' reusability reduces operational costs associated with frequent replacements, maintenance, and disposal of used filters [102]. This cost-effectiveness makes nano-membrane filters an attractive option for industrial and domestic water treatment applications [102].

2.6 Advantages and limitations of nanofiltration

The emergence of nanofiltration membranes represents a recent advancement, bridging the gap between two established technologies: reverse osmosis and ultrafiltration separation processes [103]. Nanofiltration stands out as a water-softening method due to its unique advantage [104]. In addition, it retains calcium and magnesium ions while allowing small hydrated monovalent ions to pass through without introducing additional sodium [85]. This is the most prominent characteristic of ion exchangers. Diverse separation processes require continuous heating or cooling, but NF can continue to be conducted at room temperature [105]. One of the benefits of this process is its mild molecular separation, often omitted in other procedures such as centrifugation [106]. Nanofiltration can manage large volumes and ensure continuous product streams but is less well-known in the industry [107]. This is explained by the pores in its membrane are limited to only a few nanos [108]. Over the years, different studies have investigated various membranes that have been synthesized for the removal of fluorides, dyes, and others. Some examples are given in Table 2 below.

The advantages of NF in wastewater treatment include high removal efficiency, low energy consumption, and the ability to operate at lower pressures compared to other membrane processes such as reverse osmosis [109]. NF can effectively remove contaminants such as heavy metals, organic compounds, and micropollutants from wastewater streams [110].

Many of the difficulties associated with the use of NF include fouling, scaling, and insufficient contaminant removal [111]. The NF/RO membranes can be easily fouled by all kinds of particulates in the feedwater: refractory organics, traces of synthetic organic compounds generated during disinfection treatments, and soluble microbial products produced from biological treatment processes [112]. Charged pharmaceuticals like diclofenac and salicylic acid were also effectively removed by both NF (92%, 93%) and RO membranes (92%, 95%). Nonetheless, NF (12%, 45%, 19%, 87%) and RO membranes (43%, 99%, 71%, 84%) do not reject such noncharged compounds as well [113].

In conclusion, nanofiltration has been an effective technique in wastewater treatment systems. However, there are enormous advantages to incorporating nanofiltration (NF) as the initial treatment step before reverse osmosis (RO). Firstly, it reduces the pressure requirements of RO so energy can be saved [114]. Furthermore, NF is effective in removing a sizable portion of low-molecular-weight organics from solution bills [115]. This results in less organic and biofouling fouling during the following RO process [116]. Less fouling means longer life for RO membranes, eliminating the need so often to replace them and reducing overall energy [117].

2.7 Recent advances in NF technology

In the past few decades, the research effort has been concentrated on developing high-throughput membrane filtration systems for NF-based wastewater treatment. However, some of the most recent studies that have reported on the treatment of water using NF membrane-based treatment systems to remove refractory organics are summarized below [118, 119].

Table 2 Membranes are synthesized and used for the removal of various pollutants

Membranes	Pollutants	Treatment efficiencies [%]	Advantages	Limitations	References
ZIF-67@wood composites	Congo red dye	99.28	High efficiency for dye removal	Potential for fouling	[53]
MOF-based macroporous membrane	Uranium	80.60	Effective for heavy metal removal	May require high pressure	[52]
La-Mn-Fe tri-metal oxide	Fluoride	99.33	Excellent selectivity	Possible chemical interactions	[1]
Submerged membrane adsorption hybrid system (SMAHS)	Total organic carbon	83	Integrates adsorption for efficiency	Complex system setup	[120]
Submerged low-pressure ultrafiltration membrane (AMT SUAIR-200 K)	Phosphate	50	Suitable for low-pressure systems	Lower efficiency for certain pollutants	[121]
Flat-sheet submerged NF	Diclofenac	92	High removal rate for pharmaceuticals	May require frequent cleaning	[125]
Flat-sheet submerged NF	Salicylic acid	95	High flux and low energy required	Fouling, polarization, and cleaning issues	[125]
NF-membrane bioreactor	Total organic carbon	90	Combines NF and biological treatment	Higher complexity and maintenance	[129]
TW30-nano-membrane	TDS	93	General-purpose use	Sensitive to high turbidity	[130]
TW30-nano-membrane	Calcium	96.1	Effective removal of mulivalent Ca^{+2}	Fouling, pH sensitivity, Limited removal of dissolved solids	[130]
TW30-nano-membrane	Magnesium	98.7	Effective removal of Mg^{2+}	Fouling, pH sensitivity, Limited removal of dissolved solids	[130]
TW30-nano-membrane	Chlorine	90.3	Low energy needed, Preservation of minerals, Reduction in chlorine level	Fouling, pH sensitivity, Limited removal of dissolved solids	[130]
Organic-polyamide nano-porous	COD	89	High selectivity	Specific pH conditions needed	[95]
Organic-polyamide nano-porous	Water hardness	88	Reduced chemical usage,	Fouling & pressure required	[95]

2.7.1 Advancements in NF materials and design

The materials used in the NF membrane system and the designing have been recently improved as new contaminants have emerged over time. The novel NF materials include inorganic (metal–organic framework, graphene, carbon nanotubes) and polymeric (blends, functionalized) materials. These materials are often combined for synergistic effects [53]. While the New NF system designs involve layer-by-layer assembly, 3D printing, electrospinning, and surface modification to enhance selectivity, permeability, and resistance to fouling [47, 50, 53, 108].

Tay et al. [118] investigated the feasibility of a novel nanofiltration membrane bioreactor (NF-MBR) followed by RO for water reclamation at 90% recovery and compared it with an ultrafiltration MBR (UF-MBR) + RO process as a baseline. The NF-MBR had higher organic and inorganic removal than the UF-MBR; due to the long retention time which promoted biodegradation. Also, the authors observed that the fouling of the NF-MBR was reversible and could be cleaned for physical reasons and its permeability restored. Finally, when they compared the NF-MBR + RO system to the UF-MBR, it employed about the same amount of energy as the UF- MBR + RO system at a 75% recovery level. Therefore, they concluded that the NF-MBR + RO process is suitable for achieving high recovery rates in water reclamation. The development of hybrid systems like NF-MBR coupled with RO is promising, focusing on increasing recovery rates, and reducing energy consumption. However, future research may explore optimizing the biodegradation process within NF-MBRs, enhancing membrane materials for better fouling resistance, and integrating advanced cleaning methods to maintain permeability.

2.7.2 Enhanced NF systems and applications

Integrating other treatment techniques with NF with has led to novel opportunities. The hybrid systems combining NF with advanced oxidation processes, forward osmosis (FO), and membrane distillation (MD) offer complementary advantages in pollutants removal [107]. For instance, FO-NF hybrid systems efficiently handle high salinity waters, achieving lower energy consumption and higher recovery rates compared to standalone processes.

A comparative study by Mousavi and Kargari [119] investigated the use of three types of nanofiltration (NF) membranes including thin-film nanocomposite with a molecular weight cut-off of 30 Daltons (TW30), nanofiltration element with a nominal molecular weight cut-off of 90 and 7 Daltons (NE90), and (NE7) to treat RO concentrate from a petrochemical complex. In terms of eliminating total dissolved solids (TDSs), the TW30 membrane was remarkably effective, achieving a rejection rate of 93% at a flux level off 2.84 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-l}$ when operated under 10 bar pressure. Moreover, the TW30 membrane had impressive removal percentages for divalent ions like calcium (96.1%) and magnesium (98.7%), while that of chloride was a respectable 90.3%. Despite the NE90 and NE70 membranes having a lower removal rate, they had a higher flux. Such quantitative insights underline the potential of NF systems in resource-intensive industries. Hence, prospective developments could be focused on designing NF membranes with even finer molecular weight cut-offs and enhancing selectivity for specific contaminants. This could lead to the fabrication of membranes that maintain high flux while improving rejection rates, particularly for challenging industrial waste streams, especially pharmaceutical industries.

Recently, studies have proven that hybrid systems are effective for the sustainable removal of all kinds of micropollutants in ROCs. Devaisy et al. [120] proposed two successful approaches for micropollutant removal from ROCs: a combined system of microfiltration (MF) and granular activated carbon (GAC), or treatment with NF. Both methods were equally efficient at eliminating these compounds. The authors proposed a design that combines permeating from an MF-GAC hybrid system or the NTR 729HF membrane (NF) filter with RO filtration. The integration of multiple filtration technologies to maximize micropollutant removal efficiency is prospective. Hence, future research should focus on developing more compact and energy-efficient hybrid systems, optimizing the sequence and combination of filtration stages to manage a broader spectrum of pollutants.

Zhang et al. [121] introduced a novel quick test method, which included using a syringe filter to load powdered activated carbon (PAC) quickly into water samples for filtration. The method is contrasted with typical batch tests, demonstrating remarkably similar sorption patterns for 14 commonly detected organic micropollutants (OMPs); total OMPs; and dissolved organic matter (DOM) fractions in treated wastewater. In both methods, UV254 was found to be a good indicator of OMP loss. According to the authors, the shortened adsorption time of 45 s for the quick test which is compensated by the higher dosage of PAC, has been much discussed as a practical and convenient substitute for conventional batch tests requiring between 25 and 60 min of contact time. The focus will shift toward developing rapid, on-site testing methods that can quickly and accurately assess water quality. In the future, advancements may involve further refinement of this quick test method, potentially integrating it with other rapid detection technologies to provide comprehensive water analysis in real-time.

In their experimental research, Virga et al. [122] made use of polyelectrolyte multilayers (PEM) based NF, in crosslinked PAH (Poly (allylamine hydrochloride)), PSS (poly (sodium 4-styrene sulfonate) or regenerated cellulose acetates) to investigate the effect of surface chemistry on fouling of NF membranes. They proceeded through three main stages: adsorption of surfactants on model interfaces, fouling by produced water stabilized with the same surfactant as PEM-based NF membranes, and fouling of turbid groups formed using that very same surfactant without oil. Their study showed that fouling of PEM-based NF membranes during PW treatment is primarily attributed to membrane active layer fouling caused by surfactant uptake within the PEM coating, rather than cake layer formation. The findings challenge the notion that membrane surface chemistry determines fouling extent, suggesting that the surfactant interaction with the bulk of the PEM is the critical factor. The results then proposed that a denser multilayer or the use of slightly bulkier surfactants could mitigate fouling issues during wastewater treatment by preventing surfactant penetration into the PEM. Developing PEM-based membranes with enhanced resistance to fouling, potentially through the design of denser multilayers or the use of modified surfactants that reduce penetration into the PEM would be the future trend. Hence, prospective research may also focus on understanding the interactions between membrane materials and specific contaminants to design more targeted fouling mitigation strategies.

In addition to increasing the quantity of water available for reuse in irrigation, it also adds valuable nutrients [112]. Membrane GAC adsorption hybrid systems have been shown by economic analysis to be economically feasible for removing organic substances and micropollutants [123].

Abdullah et al. [124] fabricated a novel NF-like thin-film composite (TFC) membrane using a hydrophilic coated polyacrylonitrile/polyphenyl-sulfone (PAN/PPSU) substrate without non-woven fabric, aiming to enhance membrane performance in water and wastewater treatment through engineered osmosis. Testing the best-performing TFC membrane, with the hydrophilic coating layer, using aerobically treated palm oil mill effluent (AT-POME) as a feed solution and 4 M $MgCl_2$ as a draw solution, revealed substantial performance enhancements. However, when compared to the TFC membrane without the coating layer, the coated TFC membrane achieved a 67% higher forward osmosis (FO) water flux, and a 41% higher pressure retarded osmosis (PRO) water flux. Notably, the coated TFC membrane demonstrated excellent color rejection ($>97\%$) during AT-POME treatment, surpassing the performance of commercial NF90 and NF270 membranes in terms of water flux and reverse solute flux. Prospective experiments could focus on further enhancing the performance of TFC membranes by experimenting with different coating materials and methods to improve both water flux and selectivity while minimizing reverse solute flux, making these membranes more effective for a wider range of applications in wastewater treatment and desalination.

Dee et al. [125] evaluated the efficiency of membranes made with 2D boron nitride nanosheets (BNNS) in the filtration of 14 ± 4 nm magnetic nanoparticles magnetite (MNPs). Their results revealed an impressive capture rate of 100%, with no MNPs left in the filtration. This highlights the effectiveness of magnetic nanocomposite membranes in water remediation. The integration of advanced nanomaterials like BNNS in filtration membranes is expected to grow, focusing on enhancing the selectivity and durability of these membranes. Indeed, future research may explore the scalability of such materials and their application in industrial-scale water treatment processes, including the removal of a broader range of contaminants. Similarly, Jiang, et al. [126] investigated the efficiency of 3D boron nitride (BN) integrated into a polymer nanofiber (NF) membrane system of polyacrylonitrile (PAN), aiming to enhance its absorption capacity for pollutant removal. The membrane was evaluated against Congo red (CR), basic yellow 1 (BY), and rhodamine B (Rh B). The dyes and pollutants were eliminated from the water through heating, leveraging the high heat resistance of 3D BN. Further development of 3D BN-integrated membranes with improved pollutant absorption capacities, particularly for industrial wastewater containing complex organic contaminants seems to prosper in the future. However, prospective research may also focus on the thermal properties of such membranes to optimize their performance under various environmental conditions.

Mohanadas et al. [127] assessed and compared the separation performance of different membranes, comparing the pressure-driven performance between membrane filtration and membrane distillation (MD). Their results showed that both membranes could overcome fouling. However, in MD, wetting occurred due to feed penetration into membrane pores, leading to flux reduction. The fabrication of novel membranes resistant to wetting while maintaining high flux would improve MD technology in the future. Therefore, future advancements may include the design of membranes with enhanced pore structures or surface coatings that prevent wetting and fouling, making MD a more reliable option for various water treatment applications.

In their experimental study, Ismael, et al. [128] explored the application of vacuum membrane distillation (VMD) beyond seawater desalination and addressed the challenges associated with experimental testing on a pilot or large-scale using machine learning techniques as a valuable tool for predicting membrane performance. Their novel hybrid model combines a spotted hyena optimizer (SHO) with a support vector machine (SVR) to predict flux pressure in VMD. The SVR-SHO hybrid model is validated using experimental data and compared against other machine learning tools, including artificial neural networks (ANNs), classical SVR, and multiple linear regression (MLR). Results indicate that the SVR-SHO hybrid model achieves high accuracy in predicting flux pressure, with a correlation coefficient (R) of 0.94, compared to other models. The use of machine learning in membrane technology is expected to grow, with future trends focusing on developing more sophisticated predictive models to optimize the membrane design and operational conditions of NF systems. This could lead to more efficient and tailored membrane systems, particularly for complex and large-scale water treatment processes.

3 Hollow fiber membranes: new directions in nanofiltration technology

As research continues, novel materials and membrane structures are expected to emerge, addressing challenges such as fouling, energy consumption, and scaling. The combination of advanced materials, innovative fabrication techniques, and interlayer structures holds the promise of developing NF membranes with superior performance and broader applications. Hollow fiber (HF) membranes remain one of the most burgeoning areas of NF systems. These membranes are characterized by their high surface area-to-volume ratio which in turn favors filtration processes [129]. The fundamental characteristic of HF membranes is their tubular geometry, which enables higher packing density (up to 10,000 m^2/m) in the filtration modules and thus higher throughput and more compact systems [130]. They are especially useful there given that large-scale water treatment and industries usually do not have the luxury of space and time [131].

The introduction of the HF-NF membranes comes with a desire to improve performance factors including permeability, selectivity, and fouling [83, 84, 128, 132]. Development of the technology in material science has made it possible to control the pore size distributions and surface chemistry of the HF membranes which are the key parameters for optimization of NF processes [133, 134]. HF-NF membranes offer many advantages for water treatment [134–136]. Their high surface area-to-volume ratio and unique geometry contribute to efficient filtration and reduced fouling [83, 84, 137]. In contrast, their ability to withstand harsh conditions and manage high suspended solids enhances operational durability. HF-NF membranes can be customized through various preparation methods to suit specific needs, and their effectiveness in removing natural organic matter makes them well-suited for drinking water treatment [138–140].

Altogether, the versatility of membrane structure also enables the introduction of new materials, like advanced polymers and nanomaterials, to optimize the nature of HF-NF membranes [141, 142]. The future trends in this field are expected to feature innovations in the use of HF membranes in combination with other technologies, these include Hybrid filtration and Smart membranes [142]. Such integration could pave the way for the innovation of composite NF membranes that would work as an all-in-one solution to various problems which include contaminants rejection, energy loss, and membrane deterioration. Nevertheless, studies are ongoing to contribute to the development of hollow fiber membranes and their application in NF in terms of elaboration of novel approaches to different separations.

Most recently, NF experienced a breakingthrough milestone with the incorporation of artificial intelligence (AI). In fact, machine learning algorithms can optimize the membrane operational parameters, design, and ensuring consistent performance under varying feedwater conditions [10, 128]. However, the future of NF technology relies on the customization based on specific applications. Because specially designed membranes capable of selectively removing emerging contaminants, such as polyfluoroalkyl substances (PFAS), microplastics, and pharmaceuticals, represent a significant leap forward for sustainable water treatment.

4 Conclusion

The use of NF in wastewater treatment, especially with combined membrane systems, has been shown to work well in lowering total hardness, sulfate, and chemical oxygen demand (COD). NF systems, which often use natural polyamide membranes, provide an expensive and energy-saving choice for old ways. This technology has also been used in different mixed systems like membrane distillation and electrodialysis. This shows how flexible it is in solving various water treatment problems. NF has many advantages, including the removal of many pollutants, using little energy, and can operate at normal room temperature. Its ability to split tiny molecules, gentle working conditions, and managing substantial amounts make it a well-known way to soften hard water. However, problems such as plugging, slimming and the inability to get rid of unwanted substances that are not charged create barriers to their use by different people. Recent progress in NF technology has focused on making membranes work better, trying innovative technologies such as the use of boron nitride nanosheets and creating mixed systems to remove tiny pollutants. These improvements have been made to improve NF-based wastewater treatment and last longer. Using NF before reverse osmosis has been pointed out to lower pressure needs, save energy, and make membranes last longer.

Prospective studies about the NF technology should be focused onto developing tailored NF membranes for targeted contaminants, especially emerging pollutants—and the ability of these novel membranes to effectively recover resources from wastewater also should be considered. Additionally, scaling up novel configurations, such as hollow fiber NF membranes, and exploring the synergies between NF and advanced oxidation processes can further expand its applicability. The integration of AI-driven optimization tools will mark a sea change in the design and operational efficiency of NF systems, thereby fostering their adoption across diverse industries.

Finally, the few advancements reviewed here show not only the versatility and potential in NF technology but can also be considered as a foundation to addressing some of the most vital water management challenges of our century. Further innovation and interdisciplinary collaboration thus are required to unlock fully the potential of NF in achieving sustainability.

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Declarations

Competing interests The authors declare no competing interests.

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