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This is the Published version of the following publication

Mallya, Deepak Surendhra, Abdikheibari, Sara, Dumee, Ludovic, Muthukumaran, Shobha, Lei, Weiwei and Baskaran, Kanagaratnam (2023) Removal of natural organic matter from surface water sources by nanofiltration and surface engineering membranes for fouling mitigation – a review. Chemosphere, 321. ISSN 0045-6535

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Removal of natural organic matter from surface water sources by nanofiltration and surface engineering membranes for fouling mitigation – A review

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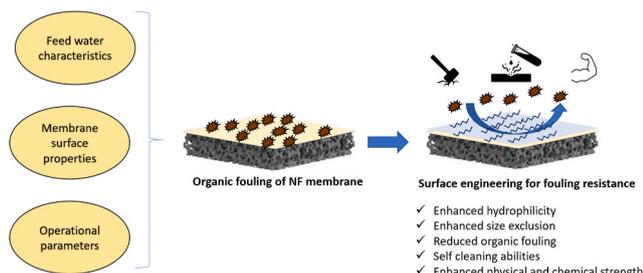
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HIGHLIGHTS

- Critical assessment on removal of NOM from water via NF membranes.
- Organic fouling mechanisms, factors and mitigation strategies are discussed.
- Surface engineering materials are evaluated for impact on antifouling performance.
- Insightful perspectives provided on surface-engineered NF membranes.
- Guidelines and outlooks presented for developing next-gen engineered NF membranes.

GRAPHICAL ABSTRACT



Abbreviations: NOM, natural organic matter; DBPs, disinfection by-products; NF, nanofiltration; HA, humic acid; FA, fulvic acid; Alum, aluminium sulfate; PAC, polyaluminium chloride; HMW, high molecular weight; LMW, low molecular weight; HS, humic substances; DOC, dissolved organic carbon; UV, ultraviolet; UV₂₅₄, ultraviolet absorbance at 254 nm wavelength; SUVA, specific ultraviolet absorbance; THMs, trihalomethanes; HAAs, haloacetic acids; ADWG, Australian drinking water guidelines; TFC, thin film composite; IP, interfacial polymerization; PIP, piperazine; MPD, metaphenylenediamine; PEI, poly(ethyleneimine); TMC, trimesoylchloride; PA, polyamide; MWCO, Molecular weight cut-off; MWD, molecular weight distribution; CP, concentration polarization; UF, ultrafiltration; PFASs, Per/poly fluoroalkyl substances; PHACUF, preserved humic acid components after UF; TMP, transmembrane pressure; MPs, microplastics; NPs, nanoplastics; PDA, poly(dopamine); PAA, poly(acrylic acid); SBMA, sulfobetaine methacrylate; AEMA, 2-aminoethyl methacrylate hydrochloride; AEPSPS, N-aminoethyl piperazine propane sulfonate; 1,3 - PS, 1, 3-propanesultone; MPDSAH, 3-(methacryloylamino)propyl-dimethyl-(3-sulfopropyl) ammonium hydroxide; PNIPAM, poly(N-isopropylacrylamide); PMDTA, 1,1,4,7,7-pentamethyl diethylenetriamine; PFTS, Perfluorodecyltrichlorosilane; HFBM, 2,2,3,4,4,4-hexafluorobutyl methacrylate; BiBB, α -bromoisobutyryl bromide; TEA, triethylamine; IPA, isopropanol; BpBr, 2-bromopropionyl bromide; BPY, 2-2'-bipyridyl; TEOA, triethanolamine; RO, reverse osmosis; TBO, toluidine blue O; AO7, anionic orange 7; CPC, C-phycocyanin; APC, allophycocyanin.

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<https://doi.org/10.1016/j.chemosphere.2023.138070>

Received 8 November 2022; Received in revised form 25 January 2023; Accepted 5 February 2023

Available online 10 February 2023

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ARTICLE INFO

Handling Editor: Kuan Shiong Khoo

Keywords:

Natural organic matter
Nanofiltration membranes
Drinking water production
Organic fouling mitigation
Surface engineering

ABSTRACT

Given that surface water is the primary supply of drinking water worldwide, the presence of natural organic matter (NOM) in surface water presents difficulties for water treatment facilities. During the disinfection phase of the drinking water treatment process, NOM aids in the creation of toxic disinfection by-products (DBPs). This problem can be effectively solved using the nanofiltration (NF) membrane method, however NOM can significantly foul NF membranes, degrading separation performance and membrane integrity, necessitating the development of fouling-resistant membranes. This review offers a thorough analysis of the removal of NOM by NF along with insights into the operation, mechanisms, fouling, and its controlling variables. In light of engineering materials with distinctive features, the potential of surface-engineered NF membranes is here critically assessed for the impact on the membrane surface, separation, and antifouling qualities. Case studies on surface-engineered NF membranes are critically evaluated, and properties-to-performance connections are established, as well as challenges, trends, and predictions for the field's future. The effect of alteration on surface properties, interactions with solutes and foulants, and applications in water treatment are all examined in detail. Engineered NF membranes containing zwitterionic polymers have the greatest potential to improve membrane permeance, selectivity, stability, and antifouling performance. To support commercial applications, however, difficulties related to material production, modification techniques, and long-term stability must be solved promptly. Fouling resistant NF membrane development would be critical not only for the water treatment industry, but also for a wide range of developing applications in gas and liquid separations.

1. Introduction

The decomposition of plants and aquatic organisms results in a complex matrix of organic compounds known as natural organic matter (NOM). A variety of substances, including humic acids (HA), fulvic acids (FA), proteins, amino acids, carbohydrates, fats, and transphilic acids, are found in the matrix. These substances differ in their molecular sizes, structures, and origins, giving rise to diverse properties (Metsämuuronen et al., 2014; Sillanpää, 2015). Although NOM is not harmful, its tendency to produce by-products that may be carcinogenic following the oxidative disinfection phases of water treatment mandates its removal from drinking water (Chaukura et al., 2020).

Over 700 distinct disinfection by-products (DBPs) can be produced when NOM reacts with routinely used disinfectants such as chlorine, ozone, or chlorine dioxide (Wawryk et al., 2021). Epidemiological studies indicate that human exposure to DBPs may be harmful to health due to their toxic, mutagenic, and carcinogenic characteristics (Kristiana et al., 2017). Water treatment systems are further stressed by the transport and interaction of NOM with other pollutants such as heavy metals (Joseph et al., 2019), fluorides, radionuclides (Santschi et al., 2017), emerging contaminants such as micro/nanoplastics (Sharma et al., 2021), per/polyfluoroalkyl substances (PFAS) (Gagliano et al., 2020), pharmaceutical compounds (Kim et al., 2020) and organic micropollutants (Li et al., 2021; Loganathan et al., 2022). Water distribution systems are negatively impacted by biological development that is sparked by the presence of organics in the water.

Globally, surface water from lakes, rivers, and reservoirs provides roughly 50% of the world's drinking water (Katsanou and Karapanagioti, 2019). NOM levels in surface water are significantly affected by water contamination, environmental activities, and climate change (Sillanpää et al., 2018b; Ndiweni et al., 2019). The chemistry and NOM concentration of surface water are strongly impacted by the increased frequency of unfavourable natural disasters including floods, droughts, and forest fires around the world, demanding the adaptation of drinking water quality management systems to shifting risk profiles (Khan et al., 2015). Due to these factors, the removal of NOM from drinking water is turning into a difficult process that necessitates the use of highly effective and dependable water treatment technologies that can handle the complex fluctuations of NOM and its rising concentrations in water sources around the globe.

Methods such as adsorption, coagulation, and flocculation involve the addition of chemicals to react with NOM and facilitate its removal. These methods suffer from lower removal efficiency, difficulties during operation and control of the treatment process, and the formation of secondary pollutants (Matilainen et al., 2010; Sillanpää et al., 2018a).

Using coagulants like aluminium sulfate (alum), polyaluminium chloride (PAC), and ferric chloride can only remove 40–60% of NOM from feed water, leaving substantial residual NOM in treated water that can considerably promote the development of DBPs. (Abdikhebari et al., 2020; Dayarathne et al., 2021). For instance, a conventional drinking water treatment plant in Victoria, Australia, removed only 57.5% of NOM, leaving behind 2.55 mg L⁻¹ of residual NOM in treated water (Abdikhebari et al., 2020). Most drinking water treatment facilities are based on conventional trains of operation, and such facilities generate large quantities of water treatment sludge, which requires further safe handling and costly disposal methods (Nguyen et al., 2022a, 2022b).

Nanofiltration (NF) membranes offer an advanced, compact, modular construction, environmentally friendly, and economically feasible solution to produce high-quality drinking water and address the issue of NOM problems during surface water treatment (Abdikhebari et al., 2020). Although NF membranes are increasingly being used for NOM removal, a major drawback of their operation during drinking water production is linked to surface fouling (Mallya et al., 2021). As a result of this phenomena, the membrane permeance is decreased, its performance and longevity are reduced, and membrane replacement is required frequently (Huang et al., 2020). Based on the characteristics of the foulants, fouling is classified into inorganic fouling or crystalline fouling (e.g., inorganic salt precipitates), organic fouling (e.g., humic substances, polysaccharides, and proteins), colloidal fouling (e.g., clay and flocs), and biofouling (e.g., bacteria and fungi) (Zahid et al., 2018; Pichardo-Romero et al., 2020). The primary foulant that influences the establishment of a fouling layer on the membrane surface during surface water treatment is NOM (Abdikhebari et al., 2020).

The essential component of developing next-generation fouling resistant NF membranes is the creation of antifouling membrane surfaces (Zhao et al., 2021). The fabrication of next-generation fouling-resistant NF membranes has been facilitated by the adaptability and efficacy of surface engineering membranes with appropriate polymers and nanomaterials (Mallya et al., 2021). A sustainable and efficient method for producing drinking water in developing nations, fouling-resistant membranes can drastically lower the expenses of operation and maintenance (Mallya et al., 2022). It is crucial to comprehend how NOM behaves during NF treatment and investigate cutting-edge surface engineering materials in order to create membranes that are fouling-resistant due to the rising concentration and characteristics of NOM in surface water. Recent works on the improvement of NOM removal and membrane fouling mitigation via pre-treatment, membrane modification, and cleaning were critically reviewed (Peters et al., 2021). The discussion in this study is restricted to ultrafiltration (UF) membranes, which allow significant fractions of

low-molecular-weight NOM to pass through yet result in additional problems downstream. A thorough update on the synthesis of fouling-resistant surface-engineered NF membranes is urgently needed, as is the development of an understanding of the mechanisms underlying the removal of NOM via NF membranes.

The last major reviews focusing on NF membrane fouling and its mitigation strategies date back to 2014–2015 (Metsämuuronen et al., 2014; Zhao and Yu, 2015) and the most recent reviews have focused on reverse osmosis (RO), ultrafiltration (UF) membrane fouling, and mitigation strategies (Choudhury et al., 2018; Peters et al., 2021; Zhao et al., 2021). According to an evaluation of different approaches to the synthesis of fouling-resistant RO membranes (Zhao et al., 2021), surface modification with hydrophilic polymers/nanomaterials post-interfacial polymerization (IP) has a higher level of industrial interest due to its straightforward operation and ability to be seamlessly incorporated into existing production lines. However, the manuscript is limited to the common mechanisms and functions of engineered membranes. Various antifouling, fouling release, and antimicrobial materials have been evaluated (Choudhury et al., 2018) to enhance membrane fouling resistance. Modification strategies include the construction of hydrophilic surface layers and antibacterial layers, and optimization of the membrane morphology and surface charge by incorporating emerging polymers/nanomaterials. Literature suggests that post-IP reaction surface engineering is very effective for synthesizing fouling-resistant membranes. No comprehensive review of surface-engineered membranes has been conducted, specifically focusing on the development of antifouling NF membranes. The literature lacks distinctive perspectives on nanomaterial/polymer interactions with membrane surfaces, as well as a thorough description of current advancements in surface-engineered NF membranes and their effects on the physico-chemical properties of the membrane. The challenges associated with surface-engineered NF membranes and future perspectives have been overlooked to date, and critical analysis of the prospect of this field is required.

This paper provides a state-of-the-art assessment on the fouling resistant surface-engineered NF membranes synthesised via post-IP reaction modification. To close a gap in the literature and aid in the creation of next-generation NF membranes, the mechanisms underlying the interactions of NOM with the NF membrane surface were thoroughly assessed and presented. Most importantly, we critically evaluated and compared different nanomaterials/polymers for providing fouling resistant properties to the NF membranes. This review paper primarily focuses on the surface engineering of membranes for improved antifouling performance, but also discusses the issue of NOM during surface water treatment via NF membranes, along with its related issues and mitigation techniques. In the first section, NF membrane synthesis and its properties are briefly introduced, followed by a critical discussion of the separation mechanisms involved during NOM removal. Organic fouling, a major challenge for NF membranes during surface water treatment, is reviewed, along with its influencing factors. A brief overview of alternative mitigation tactics is provided in the second section, with an emphasis on designing NF membranes that are resistant to organic fouling. The impact of surface engineering on membrane surface properties and performance along with potential application is comprehensively discussed. Finally, the challenges in surface engineering membranes, as well as insights into future perspectives on developing fouling resistant membranes for targeted applications and its complexity, are presented and discussed.

2. NF membranes for removal of NOM

This section briefly introduces the chemistry and properties of NF membrane synthesis, along with comprehensive discussions of NOM removal mechanisms via NF membranes, the issue of organic fouling, and the impact of controlling factors.

2.1. NF membrane synthesis and properties

The performance of NF membranes is dictated by the structure of the thin selective polyamide (PA) layer with interconnected sub-nanometric pores generated over a mesoporous non-selective support membrane, as shown in Fig. 1 (a) (Peng et al., 2022). The active PA layer is formed by IP reaction, which occurs at the interface between the aqueous and organic phases (He et al., 2015). Monomers such as piperazine (PIP), metaphenylenediamine (MPD), polyethyleneimine (PEI) at concentration 1–2 wt% in the aqueous phase and trimesoylchloride (TMC) at concentration 0.1–0.3 wt% in organic phase are commonly employed for IP reaction (Fig. 1 (a) and Fig. 1 (e)) (Du et al., 2022). The selective PA layer is usually 100–300 nm thick with a rough surface because of the protruding structures formed via the IP reaction, as shown in Fig. 1 (b–d). The PA layer dictates the membrane separation performance, while the mesoporous support (30–50 μm thick) enhances the mechanical strength of the membranes (Peng et al., 2022). Control over IP reaction parameters such as monomer concentration, solvents, chemical additives, nanomaterials, and post-treatment conditions enables desirable properties to the PA layer and enhances its performance (Mallya et al., 2021). Membrane properties such as electronegative charge, surface morphologies, molecular weight cut-off (MWCO), and hydrophobic/hydrophilic nature play a pivotal role in membrane separation performance (Mallya et al., 2021). These properties can be carefully engineered by controlling the IP reaction parameters and engineering the support membranes (Kahrizi et al., 2022; Wang et al., 2022). The pore size and MWCO of NF membranes fall in the range of 0.5–2 nm and 200–1000 Da, respectively (Du et al., 2022). Compared to RO membranes, NF membranes can operate at low operating pressures (3.5–16 bar), maintain higher permeation flux as well and retain divalent ions (>90%) but monovalent salt rejection is relatively low (30–60%) (Peydayesh et al., 2020; Shin et al., 2020). NF membranes also have high rejection (>80%) for NOM (Sengur-Tasdemir et al., 2021), persistent organic pollutants (Khoo et al., 2022), pharmaceuticals (Couto et al., 2020), hazardous chemicals in health care products and cosmetics (Wang et al., 2021). Generally, organic fouling and NOM removal via NF membranes are evaluated using lab-prepared HA solution as hydrophobic NOM surrogates, whereas bovine serum albumin (BSA) or sodium alginate (SA) are used as hydrophilic NOM surrogates (Chen et al., 2016; Abdikheibari et al., 2019). The separation of solutes in NF membranes is achieved via size exclusion and interactions between the membrane surface and solute molecules (Zuo et al., 2021). NF membranes mostly possess negative charge under neutral or alkaline environments and positive charge under highly acidic conditions (Mallya et al., 2022). The negative charge is linked to the deprotonation of the carboxylic groups present in the polymer structure at acidic pH, whereas the positive charge is due to the protonation of amine moieties at alkaline pH. This charge governs the electrostatic interactions of the membrane surface and multivalent ions, which influence the separation performance (Hoffman and Phillip, 2020; Kong et al., 2020).

2.2. NOM separation mechanisms

NOM is classified into three categories: hydrophobic fractions consisting of high molecular weight (HMW) humic substances (HS), which in turn are made up of HA, FA, and humin; hydrophilic (non-humic) fractions consisting of low molecular weight (LMW) substances such as proteins, carbohydrates, and polysaccharides; and transphilic fractions (intermediate properties) (Tshindane et al., 2019). Hydrophobic NOM is rich in aromatic carbon, phenolic structures, and conjugated double bonds, which contribute to the negative charge and brown colour of water, whereas hydrophilic NOM consists of more aliphatic carbon and nitrogenous compounds (Zularisam et al., 2007). Surface water predominantly contains humic substances; for instance, humic substances account for 45% of NOM in surface water, while low molecular weight (LMW) neutral compounds, building blocks, and biopolymers contribute

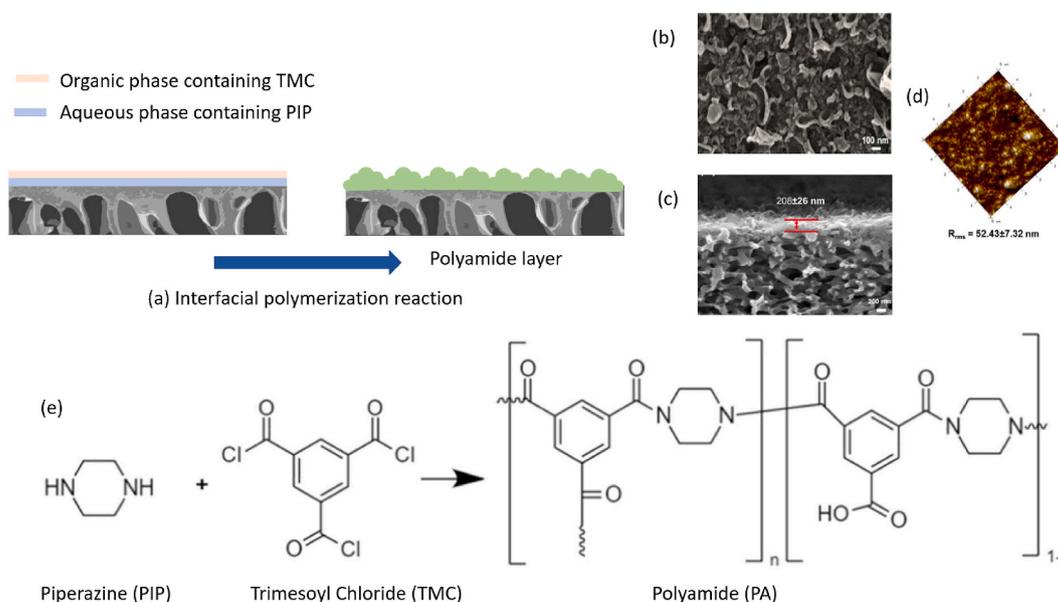


Fig. 1. (a) Schematic representation of IP reaction. (b) Surface and (c) Cross sectional scanning electron microscopic image of PA layer structure, (d) Atomic force microscopic image of membrane showing the membrane surface roughness. Reprinted with permission from Ref (Zarshenas et al., 2022), (e) IP reaction scheme with formation of the polyamide layer.

to 37%, 12%, and 6% of NOM, respectively (Abdikhebari et al., 2020). The separation of the neutral macromolecular components of NOM is mainly based on size exclusion and is governed by the MWCO of the membranes and the shape and molecular weight distribution (MWD) of the NOM (Metsämuuronen et al., 2014). The molecular size range of NOM compounds is in the colloidal range, varying from approximately 1 kDa–100 kDa, depending upon the source water (Ericsson and Trägårdh, 1997; Song et al., 2011).

A study employed two commercial membranes, NF-3 (1 kDa) and NF-4 (800 Da), to remove NOM using HA feed solution and real surface water (Yu et al., 2018). The DOC rejection was 89% and 94% respectively, for NF-3 and NF-4 membranes during tests with HA solution. The increased rejection from NF-4 was attributed to the reduced MWCO, which facilitated sieving of HMW humic compounds, which are prominent in HA (Yu et al., 2018). Removal of organic matter with molecular size (<10 kDa) was lower despite the fact that the pore size of the membranes used was less than 1 kDa, implying that NOM separation was dependent not only on the pore size of the membranes and the molecular size of NOM, but also on other properties such as charge and hydrophilicity (Yu et al., 2018). In addition, the results indicated that there was a greater difference between the rejections of the two membranes employed during surface water filtration compared to HA filtration. DOC removal results also suggested that the NF-3 and NF-4 membranes removed less organic matter from surface water at 45% and 70%, respectively (Yu et al., 2018). Comparing the two test waters, the surface water mainly consisted of biopolymers, humic substances, and LMW organic matter, whereas the HA solution was composed of hydrophobic components. Size exclusion is the major mechanism for the removal of large NOM components, while other properties of NOM need to be considered (Yu et al., 2018).

Hydrophobic/hydrophilic interactions of NOM with the membrane surface play a major role in the NOM removal mechanism (Mallya et al., 2022). NOM with a higher hydrophobicity is more likely to be deposited or adsorbed on the membrane surface and pores, making removal easier (Al-Amoudi, 2010). The deposition of NOM components onto the membrane leads to organic fouling, which decreases the flux, and the formation of a cake layer facilitates the removal of NOM owing to the additional filtering effect (Song et al., 2011). For instance, during filtration studies employing two different feed waters with similar MWD of organics, higher NOM removal was achieved for the feed water with a

higher content of hydrophobic NOM components due to adsorption and accumulation across the membrane surface (Cho et al., 1999). Membrane hydrophilicity/hydrophobicity also plays a vital role in the retention of organic (Abdikhebari et al., 2018). In the case of hydrophilic membranes, the surface absorbs water molecules, forming a water hydration layer that can effectively reject organics (Abdikhebari et al., 2018). For instance, a super-hydrophilic membrane exhibits excellent retention of the hydrophobic fraction of NOM (Shao et al., 2011; Abdikhebari et al., 2018). Hydrophobic membranes also show a higher removal of hydrophilic NOM (Xu et al., 2010). This was attributed to the deposition of hydrophobic organic foulants during the filtration process, which further increased repulsive interactions with the hydrophilic NOM. A schematic representation of the different separation mechanisms and interactions during NOM removal using the NF membrane is shown in Fig. 2 (j). Irrespective of membrane hydrophilicity/hydrophobicity, hydrogen bonding between NOM and the membrane surface may trigger NOM adsorption and deposition on the membrane, leading to enhanced NOM separation caused by size exclusion (Al-Amoudi, 2010).

Electrostatic repulsive forces between the membrane surface and organic moieties greatly influence NOM removal (Mallya et al., 2022). NF membranes with MWCO values of 500 Da was found to be able to remove 87% of organics, which were less than 1 kDa. LMW NOM possesses a higher negative charge, which facilitates its retention via repulsive forces (Abdikhebari et al., 2020). The agglomeration of negatively charged NOM species on top of the membrane may also boost the surface negative charge, which facilitates further repulsion of organic matter, increasing rejection (Schäfer et al., 2000; Jarusutthirak et al., 2007). The MWCO of the membrane represents the filtration performance based only on the size-exclusion principle, which is mostly applicable to HMW components. Charge interactions play a major role in the separation of LMW components of NOM (Lin et al., 2007). During the removal of NOM with a similar MWD, the presence of charged moieties enhanced the separation via electrostatic repulsion (Lin et al., 2006). Accordingly, in a study with a commercial NF 270 membrane employing three model compounds with similar MWD, namely phloroglucinol, resorcinol, and 3-hydrobenzoic acid, the rejection of 3-hydrobenzoic acid was the highest because of its negative charge (Lin et al., 2006). The other two compounds that had no electrostatic charge during the operation were separated mainly based on size exclusion. In the context

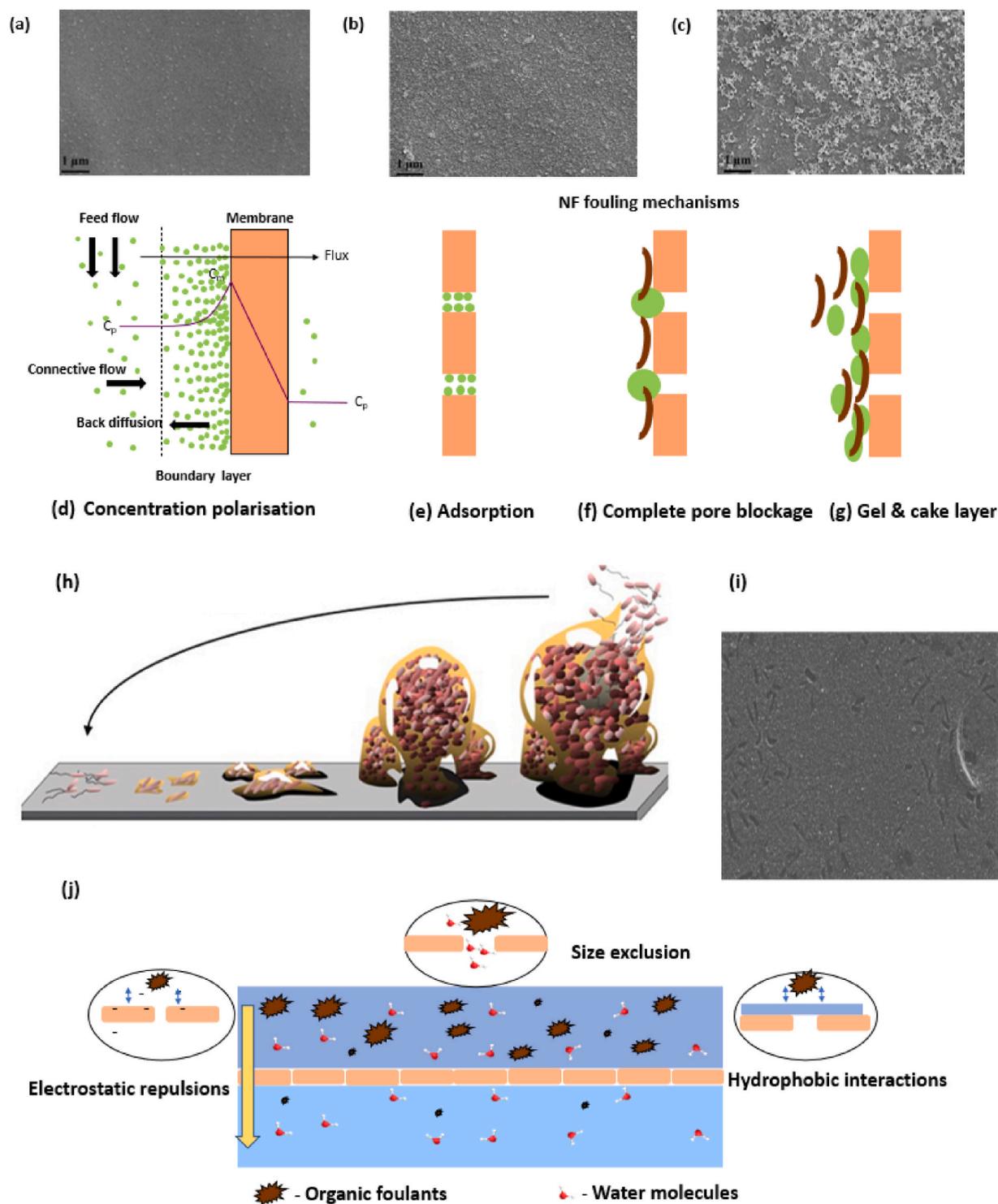


Fig. 2. Microscopic images of (a) fresh NF membrane, (b) NF membrane fouled with SA and (c) NF membrane fouled with BSA. Reprinted with permission from Ref (Abdikhebari et al., 2019), (d) Concentration polarization on NF membrane surface, (e) (f) and (g) representing the organic fouling mechanisms including adsorption, pore blockage and gel layer respectively, (h) Biofouling mechanism on NF membrane (Open resource; Credit: Bay Area Lyme Foundation), (i) microscopic image of biological cells on the membrane surface (j) Separation mechanisms of NOM via NF membrane.

of NOM characteristics, hydrophilic acids with aliphatic structures mostly possess greater negative charge densities than hydrophobic aromatic compounds (Meylan et al., 2007; Teixeira and Sousa, 2013). The separation of hydrophobic compounds is mainly governed by size exclusion and hydrophobic interactions, whereas hydrophilic compounds are separated by charge interactions (Abdikhebari et al., 2019; Mallya et al., 2022). The LMW neutral compounds of NOM are not

effectively separated compared to other fractions (Teixeira and Sousa, 2013). Recent study inferred that a commercial NF membrane, XN 45, was only able to remove 38% of LMW neutrals when compared to 98% removal of humic substances from a surface water source in Australia (Abdikhebari et al., 2020). NOM and the membrane surface charge characteristics facilitate the separation of smaller organic molecules through electrostatic interactions (Loganathan et al., 2020). Organics

with sizes comparable to or larger than membrane pores can be effectively retained by size exclusion (Yu et al., 2018). The fact that counterions with opposite charges could pass through the membrane and emerge on the permeate side owing to the electrostatic attraction phenomenon cannot be neglected (Van der Bruggen et al., 1999). It is also suggested that the polarity of the molecules is a governing factor in the permeation of NOM through membrane pores. Accordingly, a study described the effect of dipole moment on NOM rejection (Van der Bruggen et al., 1999). Molecules with high dipole moments are assumed to align in the direction of the membrane pores due to electrostatic interactions with the membrane, which inherently allows them to pass through the membrane and emerge in the permeate, reducing retention (Van der Bruggen et al., 1999). Comparing NOM molecules of similar sizes, polar molecules have a higher tendency to pass through the membrane and emerge in the permeate stream than non-polar molecules (Van der Bruggen et al., 1999).

In addition to the membrane surface properties and NOM characteristics, the concentration of organics is suspected to influence the efficacy of membrane filtration performance (Metsämuuronen et al., 2014). According to a report, NF was ineffective in rejecting NOM from surface water with a high organic content (DOC of 13–17 mg L⁻¹) due to the amplification of NOM diffusion across the membrane, which was facilitated by concentration polarization and deposition of NOM on the surface (Plourde-Lescelleur et al., 2015). Contradicting results were reported, in which NF membrane was able to remove more than 90% of NOM as DOC rejection during treatment of a river water containing very high concentration of NOM (160 mg L⁻¹) (Owusu-Agyeman et al., 2019). The higher DOC retention was attributed to size exclusion being the major mechanism of NOM removal. An increase in feed concentration did not significantly affect NOM retention. The effect of concentration is not clearly understood and is interdependent on the characteristics of NOM and NF operating conditions, such as the recovery rate and cross-flow velocity (Plourde-Lescelleur et al., 2015; Owusu-Agyeman et al., 2019).

The pH and ionic strength (IS) of the feed water strongly influence the PA layer properties, configuration, and charge properties of NOM, which ultimately controls the performance of the membranes (Luo and Wan, 2013; Su et al., 2017). The pH of the feed solution governs the surface charge of the membranes and organic molecules because of its tendency to protonate/deprotonate the functional groups present in them (Su et al., 2017). The presence of carboxyl and amine groups in the polymer structure contributes to the membrane charge (Abdikhebari et al., 2020). NF membranes exhibit amphoteric behaviour, and the membrane charge differs according to the pH of the feed solution (Siew et al., 2020). An acidic environment decreases the repulsive forces towards organic molecules owing to the neutralization of ionized carboxyl groups of NOM, increasing the NOM hydrophobicity and decreasing the negative charge (Braghetta et al., 1997, 1998). It has also been proposed that the variation in pH changes NOM configuration (Ghosh and Schnitzer, 1980). The reduced membrane charge along with the decreased size and negative charge of NOM leads to poor separation performance under acidic pH (Abdikhebari et al., 2020). Accordingly, reductions in DOC and UV₂₅₄ rejection (17.2 and 12.7%, respectively) were reported when the pH was decreased from 7 to 5 during filtration studies of natural surface water with lab made PA membranes (Abdikhebari et al., 2020). Under the same conditions, the commercial NF membrane XN 45 exhibited slight reductions. Similar results were reported during the removal of humic acid from water using NF membranes (Hong and Elimelech, 1997). It was reported that the rejection of humic acid at pH 4 and 8 is 89% and 93%, respectively. A few studies have also reported no difference in the rejection of organic molecules under varying pH values, despite the negative charge of the membrane and NOM (Verliefde et al., 2008; Owusu-Agyeman et al., 2019).

The IS of the solution is reported to affect the colloidal stability of NOM molecules according to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin et al., 1987). A high IS compresses the

electrical double layer of charged NOM, decreasing its hydrodynamic radius and reducing the electrostatic repulsive forces between the membrane surface and NOM molecules, which diminishes the rejection performance of the membranes (Hong and Elimelech, 1997). On the contrary, higher rejection of NOM has been reported when the IS of feed was as high as 0.05 M (Jarusutthirak et al., 2007). The higher rejection can be attributed to the densification (swelling) of the PA layer because of the lowered electrostatic repulsion between the polymer chains of the membrane matrix, which was more dominant than the double-layer compaction phenomenon (Kilduff et al., 2004; Wang et al., 2014).

To effectively remove NOM from water, factors such as the MWCO of membranes, membrane surface chemistry, solution characteristics, NOM properties, and hydrodynamic conditions must be considered. Table S1 summarizes the performance of the PA NF membranes and their respective physicochemical properties during the removal of NOM from surface waters or synthetic surrogate solutions. These results also suggest the versatile nature of NF membrane processes for handling water with varying chemistry and composition, and still achieve desirable removal rates for NOM.

2.3. Organic fouling mechanisms and controlling factors

Organic fouling occurs when organic foulants accumulate on the membrane surface, resulting in partial or complete blocking of the pores of NF membranes (Zhang et al., 2021; Du et al., 2022). Microscopic images of fresh membrane and membrane fouled with SA and BSA are shown in Fig. 2 (a – c), respectively. The images show significant deposition of foulants on the membrane surface. To overcome this issue, membranes must be cleaned at frequent intervals with either water or corrosive chemicals, and in many cases, the old membranes must be replaced, which makes the process very expensive (Huang et al., 2020). Organic fouling is usually classified as reversible or irreversible. In reversible fouling, the attached foulants can be effectively removed by washing the membranes with suitable cleaning agents, whereas irreversible fouling is caused by foulants that are chemically bonded to the membrane, causing permanent damage to the structural integrity (Zhao et al., 2019a). They are ineffective for physical cleaning procedures and require chemical cleaning or replacement of membranes.

Reversible fouling is governed by the phenomenon of concentration polarization (CP) which occurs at the surface of the membrane as represented in Fig. 2 (d) (Shon et al., 2013). The driving force, which is the applied pressure, causes water molecules and foulants to be pushed towards the membrane surface. The fouling phenomena are complex, with a combination of adsorption, complete pore blockage, and cake layer formation, as depicted in Fig. 2 (e – g) (Muthukumaran et al., 2014). Foulants smaller than the membrane pore size can be deposited into the membrane pores, which is the major factor causing irreversible fouling, whereas the deposition of larger foulants can significantly cause complete pore blockage and gel layer formation, leading to a severe decline in membrane permeance (Chang et al., 2011). Based on membrane selectivity, water molecules pass through the membrane while the foulants are retained and accumulate on the surface, forming a gel layer, as shown in Fig. 2 (g). This layer acts as a secondary barrier for transport through the membrane, leading to the build-up of permeation resistance, causing a decrease in flux (Baker, 2012). Reversible fouling can be handled by frequent cleaning of the membranes or by inducing turbulence at the membrane surface using feed spacers or rotating/vibrating membrane modules (Bagheri and Mirbagheri, 2018; Park et al., 2021b). These dynamic techniques are aimed at creating turbulence that decreases the effect of CP. The effect of shear stress enhances mixing, which decreases the thickness of the CP layer and improves the membrane antifouling performance (Bagheri and Mirbagheri, 2018; Park et al., 2021b).

Biofouling is another unavoidable consequence of organic fouling. The abundant availability of proteins near the membrane surface facilitates microbial colonization and leads to the formation of biofilms on

the membrane surface as shown in Fig. 2 (h), which adversely affects the membrane performance (Yadav et al., 2022). The biofouling mechanism is cyclic, as depicted in Fig. 2 (h), starting with the landing of the organics and bacteria on the membrane surface and the growth of bacterial cells that aggregate and tend to form a biofilm, which further releases free bacterial cells (Yadav et al., 2022). To overcome this issue of organic fouling and biofouling, frequent cleaning of the membranes is employed, which improves the membrane performance; however, irreversible fouling along with membrane degradation might cause a severe drop in membrane separation performance (Pichardo-Romero et al., 2020). Cleaning agents must be carefully chosen based on their compatibility with membranes because harsh chemicals (acids, bases, oxidants, and chlorine compounds) may permanently damage the membrane and degrade its performance (Yadav et al., 2022). Organic fouling and biofouling are interdependent and governed mainly by factors such as (1) membrane surface properties and NOM characteristics, (2) feed water characteristics, and (3) hydrodynamic conditions which are extensively discussed in the following sub-sections.

2.3.1. Membrane surface properties and NOM characteristics

Fouling and NOM removal mechanisms are controlled by foulant-membrane interactions, which are significantly influenced by membrane surface features such as membrane morphology (roughness), hydrophilicity/hydrophobicity, surface chemical composition, and surface charge (Abdikhebari et al., 2018; Zhao et al., 2021). Smooth and hydrophilic membranes exhibit a lesser propensity to foul than those with rough and hydrophobic surfaces (Jiang et al., 2017). Similar to this, during filtration trials using hydrophilic and hydrophobic water, a hydrophilic membrane showed less flux reduction and fouling (Feng et al., 2015). In a different investigation, under identical operating conditions, super-hydrophilic membranes displayed fouling layers with weak adhesion strength in comparison to super-hydrophobic membranes (Shan et al., 2016). This was due to the decreased affinity for both the hydrophobic and hydrophilic fractions of NOM. Membranes with inert properties have also functioned well (Mustafa et al., 2016). According to a study, the majority of hydrophilic membranes saw the greatest flow loss due to severe fouling brought on by polar interactions with foulants (Mustafa et al., 2016). It is impossible to ignore the propensity of extremely hydrophilic membranes to draw hydrophilic materials and make their adsorption on the membrane surface easier, which leads to fouling (Kwon et al., 2005; Jiang et al., 2017). The membrane negative charge, which can interact with negatively charged organic molecules, is just as important to fouling as other membrane characteristics like surface roughness and hydrophilicity (Abdikhebari et al., 2018). As a result, negatively charged hydrophobic membranes work better as filters than neutral hydrophilic membranes (Cho et al., 2000).

Research studies have indicated that hydrophilic NOM have a stronger impact on membrane fouling in relation to NOM properties (Her et al., 2004; Zazouli et al., 2010). For instance, autopsy of fouled membranes revealed that hydrophilic NOM with high mol-wt polysaccharides and proteins made up the majority of the organic fraction in the fouling layer of NF membranes (Her et al., 2000; Abdikhebari et al., 2020). A pilot research used hydrophilic and hydrophobic NOM including SA and HA solutions as the feed to compare the fouling effects of various NOM fractions (Zazouli et al., 2010). Individual alginate fouling causes a substantial flux reduction and is more detrimental than HA fouling (Zazouli et al., 2010). Similar findings have been observed for hydrophilic NOM components such as HMW polysaccharides and proteins, which induce significant membrane fouling (Her et al., 2004; Lee and Elimelech, 2006). Polysaccharide deposition on the membrane surface limits the ionizable groups on the polymer network, lowering the negative charge on the membrane surface. This lowers electrostatic repulsion between the membrane surface and organic species substantially (Cho et al., 1998). According to other studies, the electrostatic repulsion between the membrane surface and organic species can be augmented by the deposition of negatively charged foulants on the

membrane, enhancing rejection (Schäfer et al., 2000; Jarusutthirak et al., 2007). A study reported high flux decline for NF membrane at 54% after 54 h filtration experiment with surface water containing mostly hydrophilic fulvic acid like NOM (Abdikhebari et al., 2020). The analysis of fouled membranes revealed that the fouling layer was primarily composed of hydrophilic NOM derived from polysaccharides and fulvic acid-like organic materials. In general, the high molecular size of hydrophilic NOM and the tendency of alginic components to form a gel layer result in the formation of a dense fouling layer, leading to a significant flux decline (Lee and Elimelech, 2006).

The development of the fouling layer could potentially be caused by interactions between hydrophilic NOM moieties and the membrane surface via hydrogen bonding and dipole-dipole interactions (Abdikhebari et al., 2020). Highly hydrophilic membranes exhibit organic fouling by hydrophilic foulants through these interactions (Yamamura et al., 2014). Similarly, membrane autopsies of fouled commercial NE90 NF membranes subjected to pilot-scale organic fouling experiments with surface water from the Paldang Dam revealed that the initial organic fouling was caused by the deposition of hydrophilic NOM components, which decreased the negative charge of the membrane and triggered the accumulation of hydrophobic NOM (Chon and Cho, 2016). Filtration experiments were conducted with surface water containing mainly hydrophilic NOM and a synthetic feed of HA solution (Yu et al., 2018). It was observed that flux decline and fouling were more severe for surface water than for the HA solution. The membranes used were hydrophilic, which facilitated the deposition of hydrophilic NOM from surface water (Yu et al., 2018). Biopolymers present in surface water have also been identified as major foulants that cause the irreversible fouling of membranes (Kimura and Ando, 2016; Zheng et al., 2021). Contradicting studies have suggested that biopolymers could act as a controlling layer that can retain LMW organics through adsorption and size exclusion effects, decreasing fouling on NF membranes (Su et al., 2021a, 2021b).

The hydrophobic components of NOM can also cause severe fouling during operation. The intrinsic hydrophobicity of the membrane surface can trigger the deposition of hydrophobic NOM foulants (Jhaveri and Murthy, 2016; Abdikhebari et al., 2018). Accordingly, severe flux decline of 45% after 100 h of filtration with surface water was reported and linked to the fouling caused by the hydrophobic fraction of NOM (Nilson and DiGiano, 1996). Similarly, lake water with a high hydrophobic fraction causes a drastic flux decline when compared to water with lower hydrophobic constituents (Feng et al., 2015). Fouling caused by the hydrophilic fraction of NOM is reversible, whereas hydrophobic fractions lead to irreversible fouling (Amy, 2008). The hydrophilic nature of the hydrophilic NOM fraction can decrease irreversible adsorption on the membrane surface and facilitate complete flux recovery upon flushing with water (Abdikhebari et al., 2019). The deposition of hydrophobic foulants, such as compounds with alkyl and aromatic groups, makes the fouling layer less responsive to flushing with water and necessitates the use of chemical cleaning agents to induce oxidation and cleavage of protein molecules to remove them from the membrane surface and recover the water flux (Zhao et al., 2015; Tin et al., 2017).

2.3.2. Feed water characteristics

The impact of feed water chemistry, such as IS, pH, and specific ions, on the fouling potential of NF membranes has been evaluated in several studies (Abdikhebari et al., 2020; Wang et al., 2020). In general, high IS and low pH lead to severe fouling. The increased acidic nature of the feed solution, along with high IS, reduces the electrostatic repulsive forces between NOM and the membrane surface owing to the charge screening effect (Sillanpää, 2014). A lower pH transforms the structure of NOM into rigid coiled structures due to the decreased intermolecular interactions within them. This also increases the hydrophobic character of organic matter and leads to the deposition of a dense and thick fouling layer (De la Rubia et al., 2008; You et al., 2020). Accordingly, NF membrane flux decreased to 66% after operation of 6 h at pH 5 when compared to decrease to 89% at pH 7 during filtration studies with

surface water, which mainly comprised of hydrophilic NOM (Abdikhebari et al., 2020). Similarly, a study reported a severe flux decline at low pH (2–4) during filtration studies with Ngare Nanyuki surface water with high NOM content (Owusu-Agyeman et al., 2019). In a research study that used a hollow fibre NF membrane, a severe flux drop to 20% was reported after 100 h filtration experiment due to fouling of membrane caused by the hydrophobic fraction at high IS source water (Nilsson and DiGiano, 1996). Humic macromolecules tend to become coiled structures at high IS, leading to the formation of a dense fouling layer (Hong and Elimelech, 1997).

The presence of ions such as Na^+ and Ca^{2+} can increase the fouling propensity owing to the shielding effect of the charges between NOM and the membrane surface, thereby reducing its electrostatic repulsive forces (Zhao et al., 2015). The presence of Ca^{2+} destabilizes the colloidal stability and neutralizes the charge of organic moieties, leading to the extensive aggregation of NOM near the membrane surface (Song et al., 2020). Ca^{2+} ions can form complexes with NOM and the membrane surface, leading to the formation of a highly dense fouling layer (Emadzadeh et al., 2014; You et al., 2020). At higher permeation rates, Ca^{2+} has a strong tendency to convert reversible to irreversible fouling and severely impact membrane performance (You et al., 2020). Increasing the Ca^{2+} concentration to a moderate value of 1 mM shielded the electrostatic repulsion between the membrane and NOM, decreasing its rejection and slightly reducing the normalized flux of a commercial NF membrane (Abdikhebari et al., 2020). Concentrations above the critical value (2.5–3 mM) of Ca^{2+} ions can lead to complexation with NOM, which decreases the DOC content of the feed and, in turn, reduces fouling (Wang et al., 2017a; Miao et al., 2018).

Although several studies have been performed to understand the effect of Ca^{2+} ions on organic fouling, very few studies have elucidated the role of magnesium ions in organic fouling. Mg^{2+} ions are also ubiquitously present in surface waters (Wang et al., 2020). Limited work on Mg^{2+} has yielded contradictory results. (Arabi and Nakhla, 2009), reported that Mg^{2+} ions decreased membrane organic fouling. Another study compared organic fouling in the presence of Mg^{2+} and Ca^{2+} ions and concluded that the presence of Ca^{2+} caused severe fouling, while less fouling was observed in the presence of Mg^{2+} (Lee et al., 2006). Similarly, the effects of multivalent cations such as Ca^{2+} , Mg^{2+} and La^{3+} on the organic fouling of NF membranes were evaluated (Mahlangu et al., 2020). The study concluded that Ca^{2+} worsened membrane fouling through its complexation with organics and increased affinity of foulants for membrane surface, whereas Mg^{2+} and La^{3+} had less impact on organic fouling. A report concluded that the fouling propensities of Ca^{2+} and Mg^{2+} are comparable (Abrahamse et al., 2008). The effect of Mg^{2+} on polysaccharide fouling was investigated in a study that inferred that Mg^{2+} aggravates membrane fouling (Wang et al., 2020). The addition of Mg^{2+} promotes the crosslinking of alginate and increases its gelling tendency. It was reported that the Mg^{2+} reacts with carboxylic and hydroxyl groups of organic matter and the membrane, leading to development of dense gel layer on the membrane surface (Wang et al., 2020). In several water treatment facilities, feed water for nanofiltration is subjected to pre-treatment via ultrafiltration (UF) membranes (Li et al., 2020b). The permeate of the UF membrane consists of preserved humic acid components after UF (PHACUF), which, in the presence of Mg^{2+} ions, causes severe fouling (Song et al., 2021). This was attributed to the tendency of the Mg^{2+} ions to fully link with the carboxylic groups of the PHACUF moieties, causing a bridging effect and the formation of dense and large flocs. A recent study also suggested that the presence of other metal ions such as Al^{3+} , Fe^{3+} , and Cu^{2+} at critical concentrations caused severe flux decline, Cu^{2+} at a very low concentration of 5 μM , Al^{3+} and Fe^{3+} at 20 μM (Su et al., 2020).

Emerging contaminants, such as PFASs and Micro/nano plastics (MPs and NPs), in drinking water sources also tend to interact with NOM (Garg et al., 2021; Wu et al., 2021). Controlled studies confirmed that the interactions between HA, BSA, SA, and PFASs, influenced the organic fouling and removal of both organics and PFAS (Zhao et al.,

2016; Wang et al., 2018). The presence of NOM also leads to the aggregation of MPs and NPs through charge and hydrophobic interactions and bridging (Sharma et al., 2021). In addition to metal ions and emerging contaminants of concern, the presence of inorganic colloids, such as silica and alumina, along with NOM, can also severely affect membrane fouling (Schulz et al., 2016). Inorganic foulants are also deposited on the membrane surface, leading to a porous or compact layer, which in turn significantly impacts back diffusion during membrane cleaning (Teychene et al., 2016; Ma et al., 2019a). Understanding the interactions between organic foulants and various other moieties in water is important and can provide guidance on fouling control.

2.3.3. Hydrodynamic conditions

The shape of the membrane module and filtration type had a significant effect on the extent of fouling. Membrane modules used in industrial applications include flat sheets and tubular, hollow-fibre, and spiral wound (Wang and Liu, 2021). Flat sheet membrane modules have been extensively used in lab-based research because of their facile preparation and operation procedures (Baker, 2012). Hydrodynamic conditions during membrane filtration play a vital role and govern the extent and rate of fouling. Membranes can be operated under either constant transmembrane pressure (TMP) or constant flux modes (Miller et al., 2014). Owing to the fouling of the membranes, the resistance towards permeation increases, which reduces the flux in the constant TMP mode. In the constant TMP mode, a very high initial flux is achieved because of the clean surface of the membranes without a fouling layer. However, as the filtration proceeds, the membranes exhibit increased mass transfer resistance due to fouling, which reduces the permeate flux (Abdikhebari et al., 2018). Under constant flow conditions, the permeate flux was maintained constant by continuously varying the TMP. When the TMP is increased, the convective flow transports the organics towards the membrane with greater force and facilitates their deposition on the membrane surface (Hong and Elimelech, 1997). This greater force pushes the foulants into the pores, leading to complete pore blocking and irreversible fouling in many studies (Alborzfar et al., 1998; Seidel and Elimelech, 2002). In general, the accumulation of organics on the membrane surface can be decreased by enhancing the shear flow by either increasing the crossflow velocity or decreasing the TMP. High cross-flow velocities can induce turbulent flow regimes and high shear stress in the membrane system, which can mitigate fouling (Alborzfar et al., 1998). Accordingly, with an increase in cross flow velocity from 950 to 1300 L h^{-1} , flux decline was reduced from 35% to 26% (Alborzfar et al., 1998). The study also observed that an increase in operating pressure from 0.8 to 1 Mpa increased the flux decline by 58%. Another report suggested that, under constant crossflow velocity mode, increasing the flux by 3-times led to a 70% increase in fouling. This was because of the increased accumulation of NOM on the membrane surface under the effect of convective flux (Seidel and Elimelech, 2002). Contradicting results have also been reported when high cross-flow velocities were employed (Peters et al., 2021). The microbial cells present in feed water can be damaged under such conditions, triggering the release of extracellular polymeric materials. This, along with microalgal flocs, can lead to the formation of smaller colloidal substances that severely foul membranes (Wicaksana et al., 2012; He and Vidic, 2016).

Overall, the available literature varies significantly regarding the impact of factors affecting NF performance during the treatment of NOM-containing water. This was mainly attributed to the diverse nature of NOM and its complex physicochemical interactions with the membrane surface. The choice or synthesis of NF membranes is usually based on high NOM removal and antifouling performance, as well as considering NOM properties, feed water conditions, and NF operational parameters.

3. Fouling mitigation strategies

Fouling mitigation strategies, such as feedwater pre-treatment, membrane fouling monitoring, and cleaning, are briefly discussed. This is followed by a detailed section on recent advances in surface engineering of fouling-resistant NF membranes based on different types of engineering materials with a critical comparison of membrane performance.

3.1. Feedwater pre-treatment

Feedwater pre-treatment is a widely used strategy to improve feed water quality and prolong membrane life by mitigating the organic fouling of NF and RO membranes (Zhang et al., 2016b; Liu et al., 2022). Coagulation (Mariam and Nghiem, 2010), adsorption (Jamil et al., 2021), disinfection, oxidation (Park et al., 2017), ion exchange (López-Ortiz et al., 2018) and low-pressure membrane filtration (Li et al., 2020b) are few of the pre-treatment methods explored to mitigate organic fouling in NF membranes. Suitable methods are chosen based on various factors, such as NOM characteristics, feed water quality, pre-treatment efficiency, and the associated impact on membrane fouling, cost aspects, and quality of produced water. Fundamentally, the purpose is to reduce the amount of NOM entering the membrane stage, thereby decreasing fouling. Compared to other pre-treatment techniques, coagulation is an inherent part of most drinking water treatment plants (Sarkar et al., 2007; Lin et al., 2019). Pre-treatment methods have their own drawbacks as they can inherently change the properties of foulants and significantly affect membrane performance and fouling propensity (Chellam et al., 1997; Yuan et al., 2022). NF membrane-based surface water treatment plants require pre-treatment as a mandatory stage to remove larger particles and suspended and dissolved solids that are present in abundance in surface water (Lin et al., 2019).

3.2. Membrane fouling monitoring

Monitoring membrane fouling in real time and in situ is essential to evaluate the severity of fouling and initiate timely membrane cleaning (Jiang et al., 2017). During the NF operation, the fouling performance was evaluated by monitoring the flux decline with time (Ma et al., 2019b). During the filtration process, the foulants begin to deposit on the membrane surface, resulting in a significant flux decline during the first hours (0–8 h) of the experiments, followed by a gradual decline in flux (Abdikhebari et al., 2019). For instance, NF membrane exhibited a flux decline of 46% during 52 h filtration studies with surface water wherein, 25% decline was observed within the first 8 h (Abdikhebari et al., 2020). Autopsy of fouled membranes is also widely used to characterize and study foulant distribution and foulant types to comprehensively evaluate fouling (Chon and Cho, 2016; Li et al., 2020c). Techniques such as electrical impedance spectroscopy (Cen et al., 2015), optical coherence tomography (Gao et al., 2014), magnetic resonance imaging (Schork et al., 2018), ultrasonic time-domain reflectometry (Li et al., 2015) and fluorescence imaging (Park et al., 2020) can provide information on membrane fouling type, distribution, and fouling layer thickness. Other emerging techniques, such as Raman spectroscopy (Lamsal et al., 2012), infrared spectroscopy, and ultraviolet/visible reflectance spectroscopy (Gao et al., 2018) can provide information on the composition and concentration of foulants on the membrane surface. This in situ real-time monitoring of membrane fouling could help surface water treatment facilities to understand the extent and factors affecting the fouling conditions as well as predict the onset of fouling while offering relevant data (Rudolph et al., 2019). These methods have been applied to many different experimental scales and types of membrane modules (Rudolph et al., 2019). A single technique cannot provide all the information required to completely evaluate the fouling layer development. Each of these techniques has

advantages and disadvantages (Rudolph et al., 2019).

Recent advances in machine learning, artificial neural networks, deep learning models, and sophisticated control systems have created advanced fouling prediction models using these data that can evaluate diverse filtration conditions, focusing on improving NOM removal, reducing organic fouling, and producing high-quality drinking water (Park et al., 2019; Shim et al., 2021). Owing to the various factors impacting NF membrane fouling, the development of in situ real-time methods that provide quantitative and qualitative data on organic fouling and their integration with smart systems is necessary to optimize surface water treatment plants for the best performance along with plant and region-specific solutions.

3.3. Membrane cleaning

Periodic membrane cleaning is required to remove the cake layer formed during membrane fouling. Cleaning methods include physical, chemical, and biological approaches (Huang et al., 2020). Physical cleaning is based on hydraulic rinsing of the membranes by manipulating the flow conditions using methods such as sparging, sponge ball cleaning, and backwashing (Gul et al., 2021). Physical cleaning involving backflushing may severely impact the membrane structure owing to delamination, while rinsing the membranes might not be successful in removing the foulants deposited inside the pores (Gul et al., 2021). When air bubbles are used in sparging methods, the micro- and nanobubbles formed can help remove the foulant layers on the membrane surface while not being able to remove the foulants inside the pores (Wray et al., 2013; Bhoumick et al., 2021). Chemical cleaning utilizes detergents, surfactants, acidic/alkali solutions, disinfectants, and chelating agents, separately or in combination, to remove deposited foulants (Huang et al., 2020). The frequency and type of cleaning are governed by the NOM and membrane surface characteristics (Huang et al., 2020). The efficiency of cleaning depends on various factors, such as the concentration of cleaning agents, temperature and pH of cleaning solutions, cleaning time, and interaction among the cleaning agents, foulants, and membrane surface (Zhao et al., 2019a; Xu et al., 2020). Chemical agents should selectively remove fouling without significantly affecting the structural and chemical integrity of the membrane (Huang et al., 2020). In general, the use of cleaning agents is successful in removing foulants and recovering the water flux. In most cases, the chemical and physical properties of the membrane are altered by the interaction with cleaning agents, causing an increase in flux and a decline in solute rejection (Fujioka et al., 2015; Stolov and Freger, 2019). Exposure to commonly used NaOH cleaning solution leads to swelling of the active layer of NF membrane and increases the pore radii by 23%, leading to 5–7% decline in sulfate rejection (Wadekar et al., 2019). In this regard, rejection of neutral NOM moieties by alkali treated NF membranes drastically reduced by 27% due to the temporary expansion of polymeric chains and pores (Al-Amoudi and Lovitt, 2007; Kallioinen et al., 2016). This was attributed to the repulsive electrostatic interactions of the deprotonated carboxylic groups in the active surface layer under alkaline conditions, causing expansion of the polymer chain, which reduces organic retention (Kallioinen et al., 2016; Wadekar et al., 2019). Alkaline cleaning agents have been reported to effectively remove both the hydrophobic and hydrophilic fractions of NOM. Hydrophobic NOM is solubilized at an elevated pH during alkali cleaning, whereas hydrophilic proteins and polysaccharides are emulsified and removed from the fouling layer (Lee et al., 2001; Gwon et al., 2003). Alkali chelating agents, such as EDTA, with strong chelating capabilities are used in combination with NaOH to recover flux and completely remove the foulant layer formed in the presence of Ca^{2+} cations (Wang et al., 2005). This mechanism involves the disruption of intermolecular foulant-cation bridges that detach the foulant layer from the membrane surface (Li and Elimelech, 2004). Many studies have reported contradictory effects of alkaline cleaning on membrane flux and solute rejection, which implies that the cleaning efficiency is highly dependent on

membrane surface properties, cleaning chemical agents, and the nature of foulants (Al-Amoudi et al., 2007; Fujioka et al., 2015). Acidic cleaning solutions containing acids, such as hydrochloric acid, sulfuric acid, and citric acid, have also been explored for cleaning NF membranes. Acids tend to cause hydrolysis of amide bonds initiated by the protonation of N and O groups (Jun et al., 2019). For instance, a study reported that the exposure of NF membranes to highly acidic solutions resulted in an increase in the surface negative charge and permeate flux, while the PA layer was peeled off from the support during the operation owing to the lower stability of the amide bonds (Jun et al., 2018). Oxidizing agents such as NaOCl and H₂O₂ have also been extensively used to effectively clean membrane surfaces, as they have the tendency to degrade organic foulants (Gohil and Suresh, 2017; Ling et al., 2017). The membrane structure is significantly affected by exposure to oxidizing agents, which deteriorates the membrane separation performance after cleaning because of the low tolerance of NF membranes to oxidants (Goh and Ismail, 2020; Huang et al., 2020). Cleaning agents based on biological routes through enzymatic pathways have been widely explored for NF membrane cleaning owing to their ability to specifically degrade biological macromolecules, such as proteins, lipids, and polysaccharides (Lan et al., 2021; Zhang et al., 2022a). Emerging techniques, such as the application of an electric field to membranes during filtration, could also be explored (Ho et al., 2018). Challenges, such as heat generation and membrane degradation during the process, cannot be overlooked. Although different cleaning strategies have been reported, the choice of cleaning strategy is highly dependent on the membrane surface properties as well as the NOM components present in the specific feed water.

3.4. Surface engineering NF membranes for enhanced organic fouling resistance

The interactions between foulants and uncontaminated clean membranes determine the initial phase of fouling, implying that interaction forces are the most important determinant of the initial fouling rate (Abdikhebari et al., 2020). As a result, developing antifouling membranes requires surface engineering of the membrane to achieve specific interactions with foulants (Zhan et al., 2021; Zhao et al., 2021). Surface engineering of membranes after IP reaction is a highly preferred method over substrate modification and IP reaction additives as it successfully imparts new functionalities to the membrane surface while maintaining its bulk properties, such as membrane permeance and salt rejection performance, while providing desirable antifouling and organic removal properties (Zhao et al., 2021). Both lab-prepared and commercial membranes have been modified by various physical and chemical techniques. Physical methods that are relatively easy to perform include layer-by-layer assembly, dip coating, and filtration coating (Goh and Ismail, 2020). Chemical modification provides structural and long-term operational stability because of its strong covalent bonding and compatibility with the PA layer (Choudhury et al., 2018). Physical alterations based on weak van der Waals interactions with the membrane surface may result in modifier detachment during high-pressure operation (Goh and Ismail, 2020). Chemical modifications are mainly based on grafting macromolecules, polymers, and nanomaterials onto the PA layer (Choudhury et al., 2018). This involves strong anchoring of surface modification agents via chemical bonds onto the membrane PA layer via various mechanisms, such as cationic, anionic, free radical, redox, atom transfer radical polymerization (ATRP), plasma, enzymatic, and ultraviolet (UV) (Khoo et al., 2021).

Surface engineering post-IP reactions are based on the incorporation of materials that inhibit fouling (Abdikhebari et al., 2020). The versatile nature of foulant-membrane surface interactions can be altered by incorporating a wide range of suitable materials to impart antifouling properties to the membrane (Mi et al., 2017). The strategy is based on either passive or active mechanisms. The passive mechanism is based on the inhibition of foulants and bacterial attachment without changing the foulant properties, whereas the active mechanism focuses on degrading

the foulants and killing the bacteria (Choudhury et al., 2018; Vanagamudi et al., 2018b). Engineered materials, such as organic polymers, including hydrophilic neutral and charged polymers, zwitterionic polymers, polyelectrolytes, poly (dopamine), hyperbranched polymers, thermo-responsive, amphiphilic, and various inorganic nanomaterials, as well as combinations of organic/inorganic materials, have been explored to combat fouling for NF membranes. Fig. 3 shows schematics of the different surface engineering materials and the antifouling mechanisms discussed.

3.4.1. Neutral and charged hydrophilic polymers

Poly (vinyl alcohol) (PVA) is a water stable, neutrally charged hydrophilic polymer with high number of OH groups making it highly hydrophilic and biocompatible (Guo et al., 2019a). PVA is cheap and environmentally friendly, with a very high film-forming capability, facilitating various PVA and its derivatives for application in surface engineering NF membranes to mitigate organic fouling (Choudhury et al., 2018; Zhao et al., 2021). Commercially available NF membranes such as AFC30, AFC40, and AFC80 from PCI membranes are coated with neutral PVA layers (Otero-Fernández et al., 2020). In general, NF membranes coated with PVA exhibit smoother surfaces with low negative charges, increased hydrophilicity, and excellent antifouling and chlorine resistance properties (Ba et al., 2010; Ng et al., 2020). A study reported the performance of PVA-coated commercial NF 270 membranes for organic rejection (Dražević et al., 2013). The PVA-coated membrane exhibited, 5–30% increase in rejection of hydrophobic organics and decrease the rejection of hydrophilic solutes from 6 to 50%, while the rejection of NaCl was retained (Dražević et al., 2013). It was concluded that the PVA coating affected the solute/membrane interactions and the concentration of organics near the membrane surface, which improved the removal of hydrophobic organics and reduced the mass of the foulants adsorbed onto the membrane (Dražević et al., 2013). The PVA coating on the membranes also facilitates easy removal of foulants deposited on the membrane surface via cleaning strategies, and the PVA coatings can be regenerated (Ba et al., 2010; Suzuki et al., 2016). The PVA coating can also prevent the impact of chlorine-based cleaning agents on the PA layer, which can help retain the membrane with good transport properties even after multiple cleaning cycles (Liu et al., 2015a). The PVA coating requires cross-linking agents such as aldehydes and polyacids to prevent swelling and dissolution of PVA coating during operation (Guo et al., 2019a). Although various researchers have developed cross-linked PVA coating-based NF membranes, they exhibit low permeate flux because of the thick PVA layer, which restricts their widespread application (Table 1, entry 1) (Liu et al., 2015a; Zhu et al., 2020b).

Poly (ethylene glycol) (PEG) is another uncharged polymer with flexible long chains, a high exclusion volume, and hydrophilicity, which can restrict the attachment of organic foulants on the membrane surface (Shahkaramipour et al., 2017). When compared to PVA coating, PEG incorporation is based on grafting polymer brush-like molecules onto the PA layer, which provides steric hindrance to the organic foulants, avoiding its deposition on the membrane and maintaining high rejection performance (Kang et al., 2007; Shahkaramipour et al., 2017). Various studies have reported that PEG and its derivatives can be used as surface modification agents for commercial NF membranes (Tang et al., 2009; Van Wagner et al., 2011). The anchoring of PEG-based chains is dependent on the carboxylic and amine groups present on the PA layer; in many cases, another activation step is required to introduce more functional groups on the PA layer to improve its attachment (McCloskey et al., 2012). PDA was used as an activating agent to covalently attach amine-functionalized PEG to the polyamide matrix (McCloskey et al., 2012). The incorporation of PEG resulted in significantly decreasing the water permeance by 74.29%, and during 24 h fouling tests membrane flux was constant i.e., maintained excellent fouling resistance (Table 1, entry 2). PEG and its derivatives, such as polymers, hydrogels, and PEG-like polymers, have also been explored for the surface modification

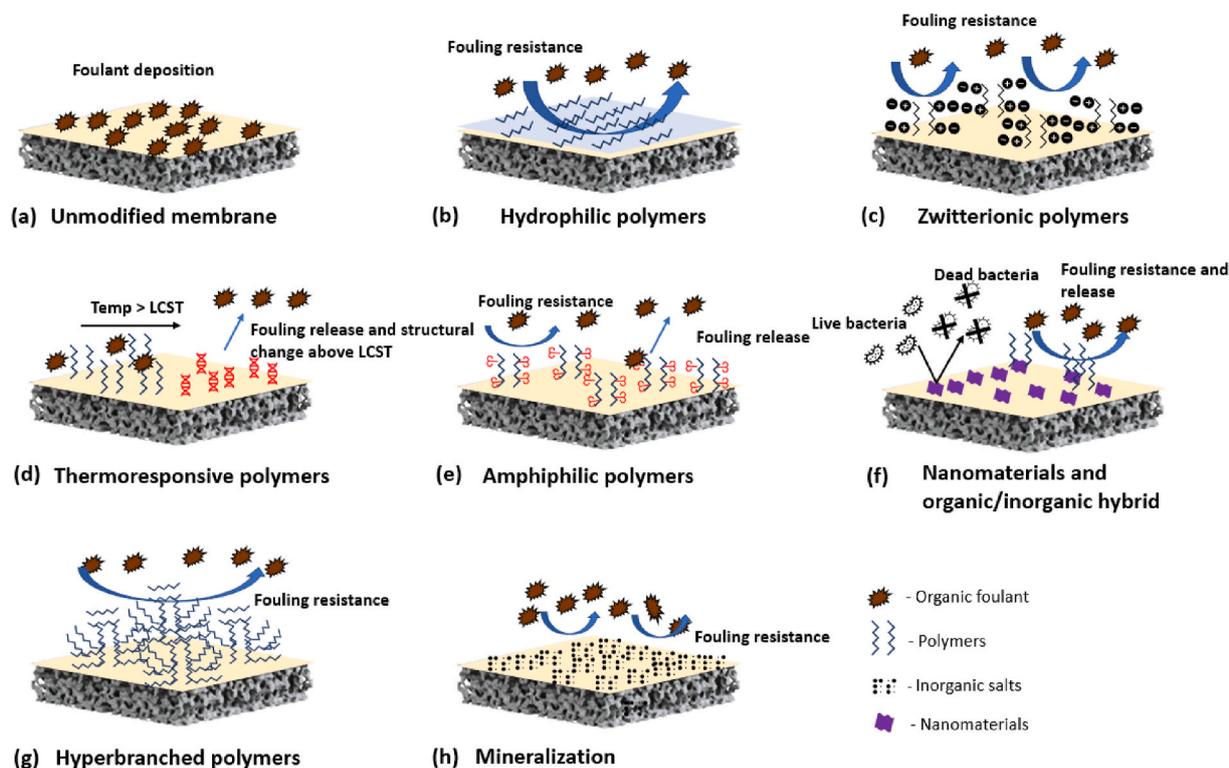


Fig. 3. Surface engineering of NF membranes using various materials discussed in this review. Adapted with permission from Ref (Xu et al., 2022a).

of membranes (Zou et al., 2011; Zhao et al., 2021). The high solubility of PEG in water, as well as the tendency of PEG-based materials to collapse under high salinity conditions, can lead to deterioration of the membrane surface, significantly impacting the membrane transport properties (Shahkaramipour et al., 2017).

Poly (acrylic acid) (PAA) is a hydrophilic anionic polymer with OH-groups, while polyethylene imine (PEI) is a branched cationic polymer with primary, secondary, and tertiary amide bonds that can be covalently bonded to the nascent PA layer (Bera and Jewrajka, 2016; Wang et al., 2017b). Owing to their hydrophilic properties and electrostatic interactions, PAA and PEI and their compounds have been widely utilized to modify NF membrane surfaces to impart very high hydrophilic properties (Himstedt et al., 2013; Bera and Jewrajka, 2016). The enhanced antifouling performance was attributed to the steric hindrance caused by PEI and its compounds towards organic foulants, formation of hydration layers, and a smoother membrane surface (Table 1, entries 3–5) (Bera and Jewrajka, 2016). It was also observed that upon incorporation of the modifiers, the flux and salt rejection were reduced, which was attributed to the increase in resistance to water transport and reduction in surface negative charge, respectively (Table 1, entry 5) (Choudhury et al., 2018). Grafted PAA is sensitive to the pH of the feed water, which affects its structure, leading to swelling, which could further deteriorate the separation performance (Himstedt et al., 2011). PAA has been employed with polyelectrolytes such as poly (allylamine hydrochloride) (PAH) to modify commercial NF90 membranes via a layer-by-layer assembly method, which enhanced the hydrophilicity, surface roughness and maintained nearly 100% normalized flux when compared to 85% for control membrane during 2 h filtration studies with HA solution (Table 1, entry 6). The membrane exhibited reduced flux owing to increased resistance to mass transfer due to multiple layers of polyelectrolytes (Baig et al., 2021).

3.4.2. Zwitterionic polymers

Post-activation by grafting of zwitterionic polymers has been widely used for surface engineering membranes because of its feasibility and

diversity in imparting antifouling properties (Wang et al., 2019; Guo et al., 2020a). Zwitterionic polymers are a class of materials with the same number of cations and anions in their polymer chains, and they exhibit high hydrophilicity (Zheng et al., 2017). In general, the incorporation of zwitterionic polymers results in enhanced membrane surface hydrophilicity, rougher surfaces, and electronegative charges, which play a key role in reducing the deposition of organic foulants (Lau and Yong, 2021). The enhanced surface charge, hydrophilicity, and tendency of zwitterionic polymers to bond with water molecules can lead to a thick water hydration layer over the membrane surface, inhibiting the deposition of organic foulants (Ding et al., 2021; Zhan et al., 2021). The unique zwitterionic structure and steric hindrance also play an important role in repelling organic foulants away (He et al., 2016). Zwitterionic polymers have been incorporated in many strategies, including self-assembly, solution polymerization, atom-transfer-radical polymerization (ATRP), solvent evaporation, and chemical vapor deposition (CVD) (Lau and Yong, 2021). For instance, zwitterion-modified NF membranes were prepared by employing PDA as an adhesive agent and sulfobetaine methacrylate (SBMA) monomers via surface-initiated atom-transfer radical polymerization (SI-ATRP), as shown in Fig. 4 (a) (Ding et al., 2021). The mechanisms underlying this modification technique and the interactions with the PA layer are shown in Fig. 4 (b). The modified membranes exhibited enhanced hydrophilicity, lower surface charge, and reduced pore size, retaining very high salt rejection of 99.1% for Na_2SO_4 and excellent flux recovery of 92.1% during fouling experiments with HA (Table 1, entry 7). It has been reported that the SBMA and hydration layers acted together as a buffer layer, as shown in Fig. 4 (a), which inhibited the deposition of organic foulants on the membrane surface with a 10% flux decline. When compared to PEG-based materials, the zwitterions can form eight times more hydrogen bonds, which can significantly increase the hydrophilicity and enhance the water permeance of the engineered membranes (Table 1, entries 8–11) (He et al., 2016).

Zwitterions also exhibit high stability under diverse filtration conditions (Shahkaramipour et al., 2017). In a recent study, SBMA and

Table 1

Summary of surface engineered membranes and impact on permeance, salt rejection and fouling recovery compared to control membrane without coating.

Entry	Surface engineering material	Modification method	Impact on membrane surface parameters (R -roughness, PAT - PA layer thickness, CA - contact angle, ZP - zeta potential at pH 7, ↑ - increases, ↓ - decreases	Membrane transport properties			Fouling performance (NOF-normalized flux, FRR- Flux recovery ratio) Value in [] refers for control membrane, with type of feed and filtration time.	Ref
				Permeance (L m ⁻² h ⁻¹ bar ⁻¹)	% ↑ or ↓ of permeance compared to control membrane	Na ₂ SO ₄ rejection (%)		
1	PVA	Contact coating	R ↓, PAT ↑, CA ↓, (-ve) ZP ↓ R = 3.2 nm (average), ZP = -19.2 mV, CA = 28.6°, PAT = 165 nm	8.83	↓ 6.38	99.4	NOF: 40% [15] HA FRR: 80% [40] HA	Zhu et al. (2020b)
2	PEG	Contact coating	CA ↓ CA = 40°	2.7	↓ 74.29		FRR: ~95% [30] Oil water emulsion (120 min)	McCloskey et al. (2012)
3	PEI	Dip coating	R ↓, PAT ↑, CA ~, (-ve) ZP ↓ R = 13 nm (average), ZP = 3 mV,	7	Similar	82	FRR: 81% [72] BSA (25 h)	Bera and Jewrajka (2016)
4	PEI-PEG	Dip coating	R ↓, PAT ↑, CA, (-ve) ZP ↓ R = 78 nm (average), ZP = -4 mV,	~8	Similar	84	FRR: 90% [72] BSA (25 h)	Bera and Jewrajka (2016)
5	PEI-dextran	Dip coating	R ↓, PAT ↑, CA ~, (-ve) ZP ↓ R = 13 nm (average), ZP = 1 mV,	~8.5	↓ 21	91	FRR: 88% [72] BSA (25 h)	Bera and Jewrajka (2016)
6	PAA and PAH	Dip coating and layer-by layer deposition	R ↓, PAT ↑, CA ↓ R = 250 nm (RMS), CA = 70.4°	5.71	↓ ~17	>98	NOF: ~100 [85] HA (2 h)	Baig et al. (2021)
7	PDA-SBMA	Surface initiated ATRP	R ↓, PAT ↑, CA ↓, (-ve) ZP ↓ R = 20.2 nm (average), ZP = -25 mV, CA = 18.4°, PAT = 93.3 nm	7.6	↓ 10	99.1	NOF: 39.5% [21.4] HA (3h) FRR: 92.1% [85.7] HA (3h)	Ding et al. (2021)
8	SBMA	Surface initiated ATRP	R ↓, PAT ↑, (-ve) ZP ↓ R = 13.1 nm (average), ZP = -30 mV, PAT = 170 nm	16.8	↑ 290	97.2	FRR: 95.5% [81] BSA (5h) FRR: 93% [86] HA (5h) FRR: 95% [85] SA (5h)	Guo et al. (2019b)
9	SBMA	Surface initiated ATRP	R ↑, PAT ↑, (-ve) ZP ↓ R = 27.29 nm (RMS), CA = 39°, PAT = 350 nm	10.7	↑ 137.8	98.6	FRR: 97.41% [90.3] HA (4h)	Guo et al. (2019c)
10	AEPPS	Amination reaction	R ↑, CA ↓, (-ve) ZP ↓ R = 52.9 nm (RMS), ZP = -40 mV, CA = 18°,	9.6	↑ 105.7	99.5	FRR: 95.5% [88.3] BSA (5h)	Mi et al. (2015)
11	1,3 - PS	Amination reaction	R ↑, CA ↓, (-ve) ZP ↓ R = 47.8 nm (RMS), ZP = -19.2 mV, CA = 36°, PAT = 110 nm	12	↑ 240	~13	FRR: 93.8% [77.1] BSA (16 h) FRR: 95.6% [82] for SA (16 h) FRR: 97.0% [92] for LYZ (16 h)	Mi et al. (2017)
12	SBMA and AEMA	In-situ chemical modification	R ↑, PAT ↓, CA ↓, (-ve) ZP ↓ R = 21.9 nm (average), ZP = -2 mV, CA = 12°, PAT = 35 nm	27.5	↑ 300	98.6	NOF: 90% [55] BSA (3h) FRR: 98% [79] BSA (3h)	Zhang et al. (2022b)
13	MPDSAHA	Ce induced graft polymerization	R ↓, CA ↓, R = 34.16 nm (RMS), CA = 35.5°, CA ↓	4.1	↓ 35	96	FRR: 95.5% [55] BSA (4h)	Li et al. (2014)
14	PDA	Contact coating	CA ↓ CA = 40°	8.0	↓ 23.1		FRR: 60% [30] Oil water emulsion (120 min)	McCloskey et al. (2012)
15	PDA	Contact coating	CA ↑ CA = 59.3°	~9.4	↓ 10.5	95	NOF: 85% [70] BSA (8 h)	Zhang et al. (2017)
16	Hyperbranched polyglycerol (hPG)	Contact coating	R ↓, CA ↓, (-ve) ZP ↑ R = 22 nm (RMS), ZP = -2 mV, CA = 31°	21.5	↑ 13	97	NOF: 65% [44] HA (12h) FRR: 75% [47] HA (12h)	An et al. (2020)
17	PNIPAM	ATRP reaction	R ↑, PAT ↑, CA ↓, (-ve) ZP ↓ R = 37.3 nm (average), ZP = -30 mV, CA = 40°, PAT = 96 nm	18.2	↑ 109.2	~98	NOF: 80% [65] BSA (0.5h) FRR: 100% [85] BSA (0.5h)	Xu et al. (2022a)
18	PFTS	Surface coating followed by covalent grafting	R ↑, CA ↓, (-ve) ZP ↓ R = 12.2 nm (average), ZP = -32 mV, CA = 65°	~4	↓ 50.5	80	NOF: ~88% [70] BSA (24h) NOF: ~86% [72] HA (24h) NOF: ~88% [75] SA (24h)	Ruan et al. (2018)
19	HFBM	Surface coating followed by	R ↑, CA ↓, (-ve) ZP ↓ R = 10.9 nm (average), ZP = -35 mV, CA = 64°	21.9	↑ 14.6	78.8	FRR: 99.4% [91.8] BSA (24h)	Zhang et al. (2016c)

(continued on next page)

Table 1 (continued)

Entry	Surface engineering material	Modification method	Impact on membrane surface parameters (R -roughness, PAT - PA layer thickness, CA - contact angle, ZP - zeta potential at pH 7, ↑ - increases, ↓ - decreases)	Membrane transport properties			Fouling performance (NOF-normalized flux, FRR- Flux recovery ratio) Value in [] refers for control membrane, with type of feed and filtration time.	Ref
				Permeance ($L m^{-2} h^{-1} bar^{-1}$)	% ↑ or ↓ of permeance compared to control membrane	Na ₂ SO ₄ rejection (%)		
20	TiO ₂	grafting via Michael addition Self-assembly	N/A	~10	↓ 6.99	~96	FRR: 99.8% [86.3] HA (24h) NOF: 85% [70] BSA (8h)	Zhang et al. (2017)
21	TiO ₂	PDA assisted coating	CA ↓ CA = 24.5°	~10	↓ 1.26	~95	NOF: 95% [70] BSA (8h)	Zhang et al. (2017)
22	Biogenic Ag	Covalent binding by bridging agent cysteamine	CA ↓ CA = 38°	4.97	↑ 31.48	~87	Modified membrane exhibited effective antibacterial ability inhibiting <i>P. aeruginosa</i> and <i>E. coli</i> growth	Liu et al. (2015b)
23	Ag-doped TiO ₂	Surface coating	R ↑, CA ↓ R = 13.7 nm (average), CA = 36°	0.6	~ ↓ 70	60	Bacterial growth reduced approximately 93% and 91% for the modified membrane when compared to control membrane for <i>E. coli</i> and <i>B. subtilis</i> , respectively.	Habib et al. (2020)
24	BN	Surface coating	R ↓, PAT ↑, CA ↓, (-ve) ZP ↑ R = 6 nm (RMS), ZP = -34.86 mV, CA = 25°, PAT = 54 nm	7.65	↑ 59	88.3	NOF: 99% [92] BSA (6h) FRR: 93% [89] BSA	Abdikhebari et al. (2019)
25	BN	Surface coating + IP reaction nanofiller	R ↑, CA ↓, (-ve) ZP ↑ R = 3.2 nm (average), ZP = -70 mV, CA = 20°	12.15	↑ 69		NOF: 95% [89] Surface water (6h) NOF: 80% [54] Surface water (52h)	Abdikhebari et al. (2020)

2-aminoethyl methacrylate hydrochloride (AEMA) were successfully grafted onto an NF membrane surface (Zhang et al., 2022b). The zwitterion-modified membrane exhibited higher hydrophilicity, higher surface area, and thinner PA layer. As a result, the membranes recorded nearly 300% increase in water permeance at $27.5 L m^{-2} h^{-1} bar^{-1}$ compared to $8.7 L m^{-2} h^{-1} bar^{-1}$ for control membrane while maintaining Na₂SO₄ rejection at 98.6% (Table 1, entry 12). The incorporation of zwitterions reduced the formation of an additional external layer over the nodular PA layer. Antifouling tests revealed that the normalized flux and flux recovery was at 90% and 98%, respectively, for the zwitterion modified membrane when compared to control membrane at 55% and 79% (Zhang et al., 2022b).

3.4.3. Polydopamine

PDA and its derivatives have been widely used to modify membrane surfaces and impart high antifouling properties (Kasemset et al., 2013; Karkhanechi et al., 2014). Dopamine is a mussel adhesive protein that exhibits excellent adhesive properties as well as self-polymerization in weak alkaline aqueous environments, leading to a strong adhesive PDA coating that is compatible with most organic and inorganic substrates (Jiang et al., 2013; Mi et al., 2021). Its inherent adhesive properties, along with its ability to form strong interfacial binding via covalent and hydrogen bonding, as well as electrostatic and hydrophobic interactions, endow great opportunities for its use in membrane surface modification (Zhao et al., 2021). PDA coatings also exhibit enhanced hydrophilicity due to various hydrophilic groups such as catechol, amino, and quinone, while functional groups, such as OH, NH, and C=O, serve as dual impacts, enhancing the hydrophilicity and acting as active sites for further modification (Guo et al., 2016; Mi et al., 2021). The antifouling properties of PDA-incorporated NF membranes are mainly attributed to the enhanced hydrophilicity of PDA, which keeps the organic foulants away from the surface through hydrophilic and electrostatic interactions (McCloskey et al., 2012; Zhang et al., 2017). In a few other cases, the purpose of PDA coating is to provide a strong adhesive layer to further

modify the membrane surface by immobilizing a suitable nanomaterial or further crosslinking with polymers for antifouling performance (Ang et al., 2019). Owing to these opportunities with PDA, membranologists extensively explore modifying the membrane surface with PDA coatings in various strategies, such as using an interlayer prior to IP reaction, post-IP reaction coating, and further cross-linking with other nanomaterials or polymers to enhance membrane performance and antifouling properties, which are not limited to NF membranes but are also widely used for RO membranes as well (Zhao et al., 2021). For instance, a study reported PDA modification of NF membranes resulted in fouling mitigation and increased flux during fouling experiments with BSA feed, resulting in normalized flux of 85% when compared to 70% for control membrane (Table 1, entry 14) (McCloskey et al., 2012). The major issues with PDA-incorporated NF membranes are their long self-polymerization time, alkaline pH, and uneven coating with unsatisfactory permeance, selectivity, and long-term stability, which restrict the commercial application of this technology (Baek et al., 2017). The use of ultraviolet irradiation (Baek et al., 2017), FeCl₃/H₂O₂ (Zhu et al., 2018), CuSO₄/H₂O₂ (Zhang et al., 2016a) have been used to increase the polymerization rate and support the formation of defect-free PDA coatings. A bottle neck exists between the permeance and rejection, as often the PDA coating adds up to the mass transfer resistance, which reduces the water flux by more than 10% (Table 1, entries 14–15) (Baek et al., 2017). Incorporating the PDA coating as a surface modifier to further incorporate nanomaterials or polymers would increase the membrane thickness and significantly reduce flux (Zhao et al., 2021). Therefore, to engineer PDA-incorporated membranes, the antifouling performance should be very high, with minimal flux reduction.

3.4.4. Hyperbranched polymers

Hyperbranched polymers (HBP) are reactive three-dimensional (3D) spherical macromolecules with unique physicochemical properties such as controllable size, monodispersity in water, abundant terminal functional groups, and nanovoids (Qiu et al., 2021). The inner voids of HBP,

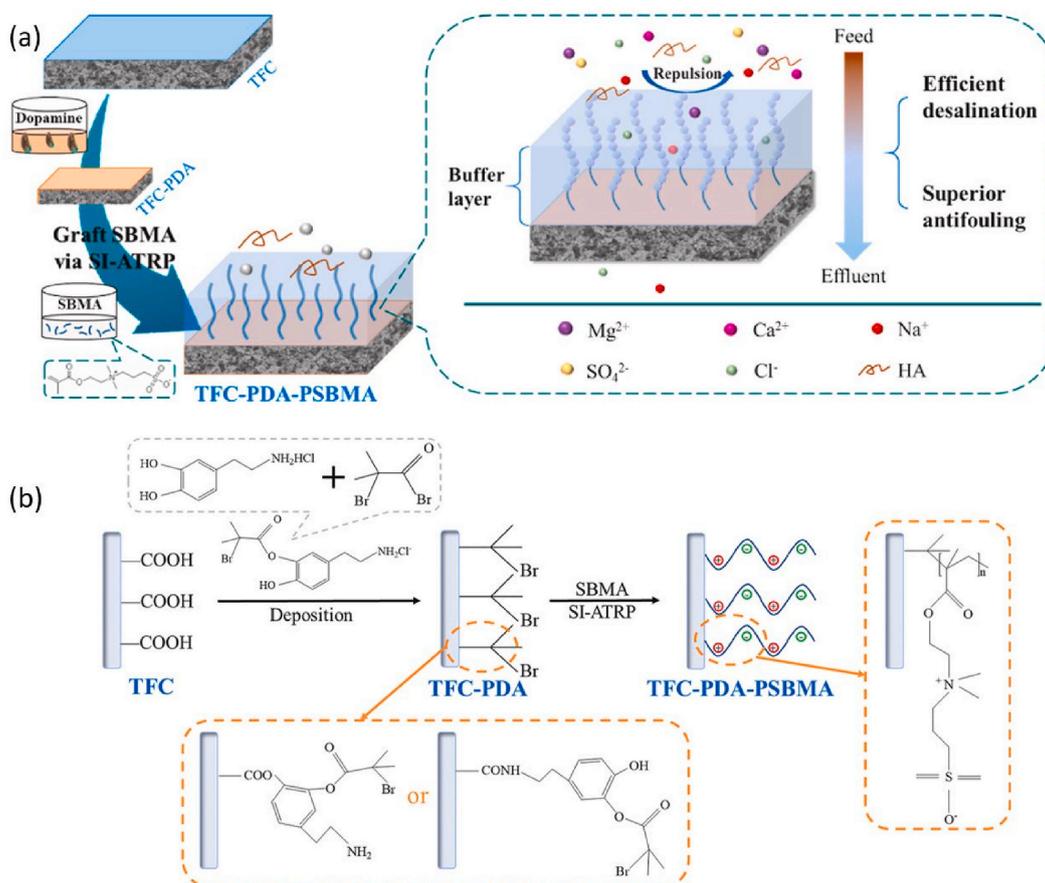


Fig. 4. (a) Synthesis of zwitterion modified NF membrane (b) Mechanisms of PDA and zwitterion modification of NF membrane. Reprinted with permission from Ref (Ding et al., 2021).

as well as the outer voids between the HBP molecules, acted as alternative selective water transport pathways, increasing the water permeance (Wei et al., 2013; Qiu et al., 2021). The steric hindrance and electrostatic interactions of HBP resulted in the maintenance of the required selectivity of NF membranes (Wei et al., 2013). The charge and molecular size of HBP can be suitably engineered by modulating the number of quaternary ammonium groups attached to them, resulting in enhanced permeance and molecular selectivity (Qiu et al., 2021). While most studies have focused on improving the permeance and salt rejection of NF membranes with HBP used as additives during IP reactions, only a few studies have focused on attaching HBP post-IP reactions (Wei et al., 2013; An et al., 2020; Qiu et al., 2021). Hyperbranched polyglycerol (hPG) has received increased attention for the synthesis of fouling resistant membranes because of its dendrimer-like structure, hydrophilicity, chemical stability, low toxicity, and easy synthesis strategy (Hasan and Pandey, 2015; Abbina et al., 2017). Grafting hPG on to the already formed PA layer, as shown in Fig. 5 (a) significantly enhanced the hydrophilicity of the membrane surface, leading to 13% increase in permeance while maintaining 97% rejection of Na₂SO₄ compared to control membrane (Table 1, entry 16) (An et al., 2020). hPG proved to be an excellent grafting agent to alleviate the organic fouling of membranes during filtration tests with HA and BSA, as shown in Fig. 5 (b–e) (An et al., 2020). The normalized flux at end of 12 h (HA) was increased to 65% and flux recovery to 75% when compared to control membrane with 44% and 47%, respectively (Fig. 5 (e)). Compared to BSA, HA fouling was severe with lower normalized flux and reversibility, indicating that different fractions of NOM interact differently during fouling of membranes, increasing the complexity of surface-engineered membranes. During fouling tests with BSA solution, the normalized flux was increased to 90% compared to 75% for control

membrane. The HBP coating exhibited an inherent thickness of 300–400 nm which could significantly increase the mass transfer resistance and reduce the permeance (Nikolaeva et al., 2015). Fig. 5 (f) and Fig. 5 (g) are microscopic images of the control and HBP-coated membranes, respectively, where an increase in the thickness of the selective layer is evident. There are challenges with the stability of the coating during filtration and cleaning, which need to be addressed for actual applications (Zhao et al., 2021).

3.4.5. Thermo-responsive polymers

Smart materials responding to temperature stimuli and self-cleaning properties have been explored for the synthesis of antifouling membrane surfaces (Yu et al., 2011; Vanangamudi et al., 2018a). Poly (N-isopropylacrylamide) (PNIPAM) is a low critical solution temperature (LCST) thermo-responsive polymer that exhibits a hydrophilic coiled structure at temperatures below 32 °C (LCST), which is favourable for antifouling surfaces (Xu et al., 2022a). Above the LCST, the polymer has a globular structure, which helps in the detachment of foulants owing to structural changes (Xu et al., 2022a). In a recent study, PNIPAM was incorporated into a bromine-containing polyamide NF membrane via ATRP, as shown in Fig. 6 (a) (Xu et al., 2022a). The modified membrane with 1 h polymerization time exhibited nearly double the permeance at 18.2 L m⁻² h⁻¹ bar⁻¹ when compared to 8.7 L m⁻² h⁻¹ bar⁻¹, while retaining high divalent salt rejection (Table 1, entry 17). This was mainly attributed to the improved surface hydrophilicity upon incorporation of PNIPAM (Zhao et al., 2020; Xu et al., 2022a). Further increasing the polymerization time resulted in extra resistance to water transport, reducing the permeance significantly (Xu et al., 2022a). In addition, PNIPAM incorporation significantly increases the deposition resistance and adhesion resistance of the foulants by reducing fouling

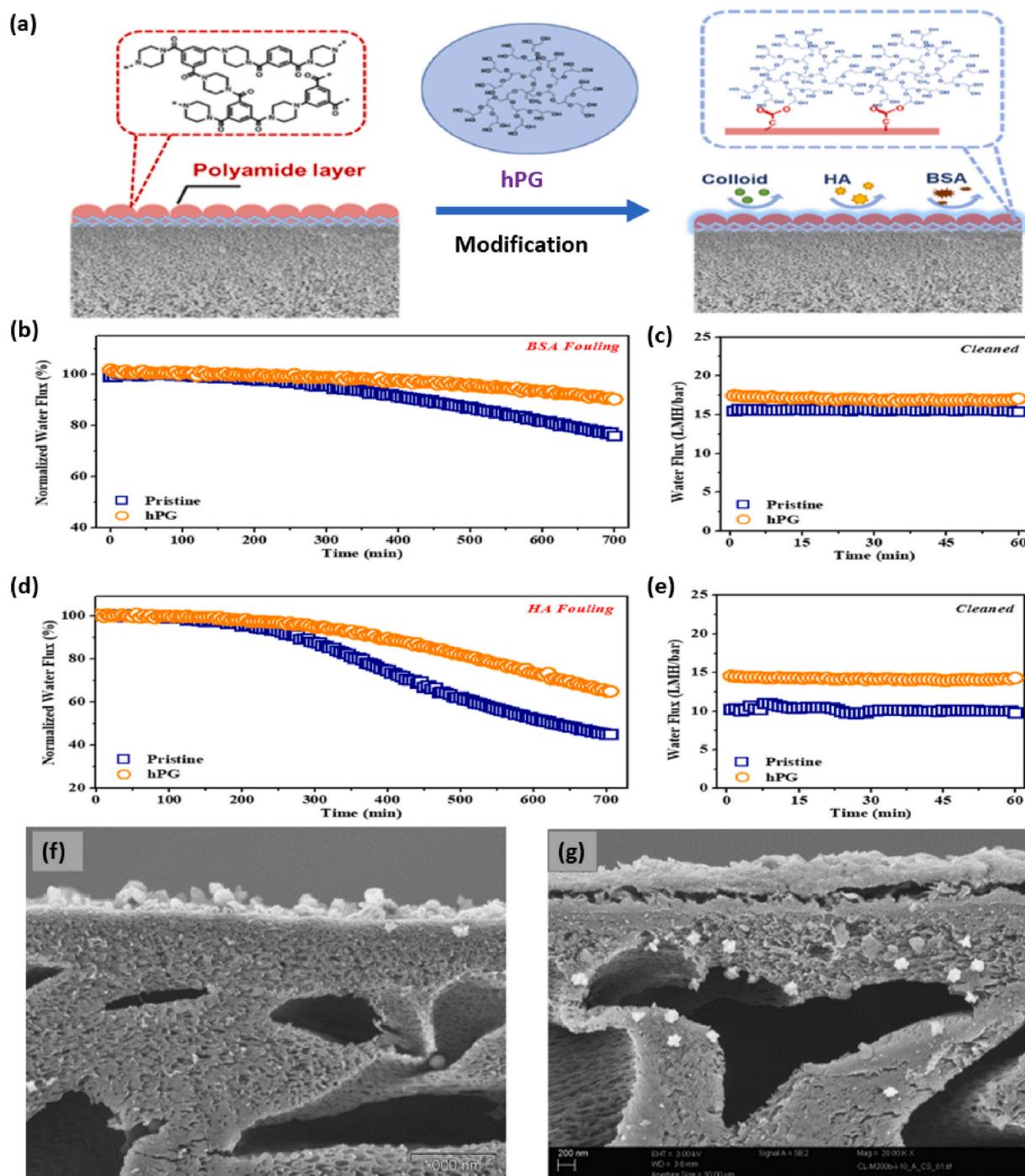


Fig. 5. (a) Synthesis of hyperbranched polymer incorporated membranes and its antifouling mechanisms, (b) and (c) Represents the fouling performance of the membranes during filtration/cleaning experiments with BSA, (d) and (e) Fouling performance of membranes during filtration/cleaning tests with HA, (f) and (g) represent the microscopic images of control and HBP coated membrane. Reprinted with permission from Ref (An et al., 2020).

and improving the recovery of flux during cleaning strategies (Zhao et al., 2020; Xu et al., 2022a). The incorporation of PNIPAM resulted in a significant increase in the normalized flux when compared to that of the control membrane, as shown in Fig. 6 (b), suggesting its enhanced antifouling performance (Xu et al., 2022a). The thermo-responsive nature of PNIPAM resulted in the formation of a buffer layer due to the shrinking of the polymer above the LCST (Fig. 6 (c)), which restricts the membrane-foulant interactions and enhances the detachment of pollutants, thus decreasing irreversible fouling (Xu et al., 2022a). In several water treatment facilities, the feed water temperature can exceed 32 °C, which can initiate spontaneous thermo-responsive behaviour on the

membrane and lead to poor membrane separation. The thermo-responsive properties can cause the PA layer to become unstable in actual industrial applications.

3.4.6. Amphiphilic polymers/surface

Amphiphilic polymers consist of both hydrophilic and hydrophobic components in their structures, which have been explored for use in antifouling membranes and fouling release coatings (Ruan et al., 2018). The hydrophilic component of the polymer facilitated the formation of a water hydration layer, mitigating the deposition of organic foulants, whereas the low surface energy of the hydrophobic part promoted

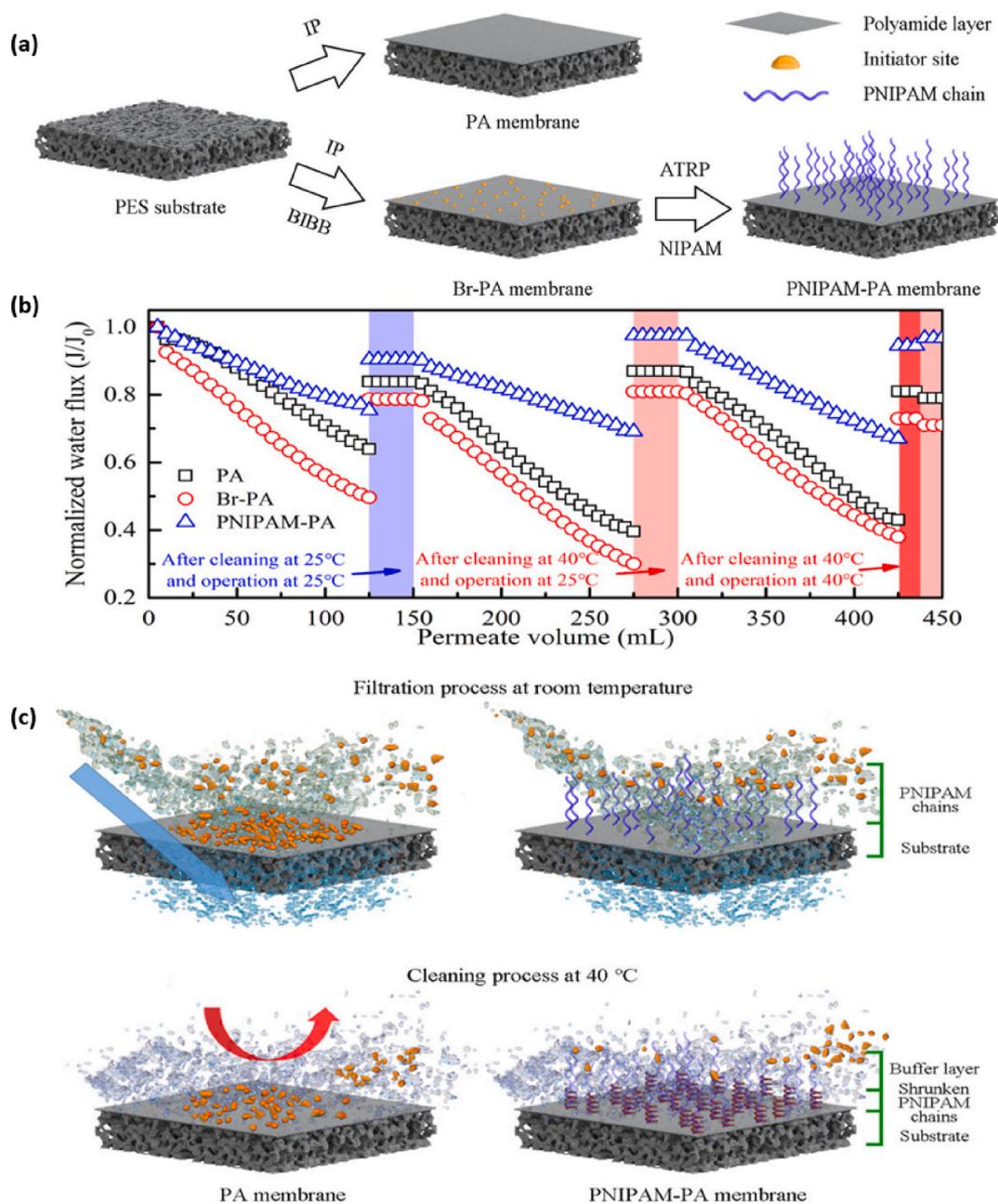


Fig. 6. (a) Schematic of synthesis process for thermo-responsive polymer incorporated NF membrane, (b) Fouling performance of membranes evaluated and (c) Schematic of fouling/cleaning mechanism of the PNIPAM incorporated membrane surface. Reprinted with permission from Ref (Xu et al., 2022a).

efficient removal of foulants during cleaning (Ruan et al., 2018). Owing to the presence of various fractions of NOM in surface water, researchers have recommended the use of amphiphilic polymers (Choudhury et al., 2018). Amphiphilic polymers are emerging materials that have been mostly used for RO membrane surface modification (Matin et al., 2016). Its unique properties can be explored for the surface engineering of NF membranes. Attaching both hydrophilic and low-surface-energy polymers can result in the formation of amphiphilic surfaces, which can improve antifouling membrane performance. In this regard, a study involved two-step modification of the NF membrane. First, triethanolamine (TEOA) with abundant hydrophilic groups was attached to the membrane surface, followed by the covalent grafting of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (PFTS) (Ruan et al., 2018). This amphiphilic surface resulted in an enhanced antifouling performance during filtration studies with HA, BSA, and SA solutions (Table 1, entry 18). The membranes also reported significant flux decline of 50.5%

when compared to control membrane owing to the addition of dual modification layers (Ruan et al., 2018). In another study, triethylenetetramine was attached to the carboxylic groups on a polyamide membrane, followed by grafting of 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBM) via a Michael addition reaction (Zhang et al., 2016c). The Amphiphilic membranes reported 14.6% higher permeance and excellent fouling resistance during filtration studies with BSA, HA, and oil/water emulsions (Table 1, entry 19).

3.4.7. Inorganic nanomaterial and mineralization

Various inorganic nanomaterials such as Cu (Ben-Sasson et al., 2016), Ag (Liu et al., 2015b), TiO₂ (Zhang et al., 2017), Fe (Karimnezhad et al., 2019), ZnO (Purushothaman et al., 2022), and silica (Liu et al., 2017a) have been widely used for the surface modification of membranes, mainly because of their biocidal properties, as well as improved hydrophilicity and organic fouling resistance. The general mechanism is

based on the liberation of metal ions, which facilitates antibacterial properties and hydrophilic surfaces for mitigating organic fouling (Choudhury et al., 2018). Ag and TiO₂ based nanomaterials are widely used for membrane surface modification owing to their easy in situ generation and high antibacterial performance (Table 1, entries 20–23). Inorganic nanomaterials suffer from poor compatibility with the polyamide matrix, leading to aggregation and leaching, which significantly reduces membrane separation performance (Mallya et al., 2021). Various studies have focused on the functionalization of inorganic nanomaterials or the use of bridging agents to improve their compatibility with the polymer matrix (Liu et al., 2015b; Zhang et al., 2017). For instance, biogenic AgNPs were grafted onto a selective polyamide layer via a cysteamine bridge for strong anchoring of AgNPs (Liu et al., 2015b). The modified membrane exhibited enhanced hydrophilicity, permeance, and antibacterial performance with good stability while

maintaining higher salt rejection (Table 1, entry 22). Hybrid inorganic nanomaterial structures have also been explored for modifying membrane surfaces to impart antibacterial and antifouling properties (Yi et al., 2019). For instance, Ag-doped TiO₂ nanoparticles were immobilized on commercial NF membranes using the dip-coating method (Habib et al., 2020). The hybrid nanomaterial-modified membranes exhibited enhanced hydrophilicity and antibacterial properties. Nevertheless, the membrane suffered from significant flux decline of 70% owing to the increase in hydraulic resistance due to additional coating of PVA and nanoparticles used for modifying the surface (Table 1, entry 23).

Emerging 2D nanosheet-based materials, such as graphene oxide (GO) and its compounds (Zhao et al., 2019b), BN (Abdikhebari et al., 2019), and MoS₂ (Mallya et al., 2022) have also been explored as surface engineering agents for NF membranes. The hydrophilicity and negative

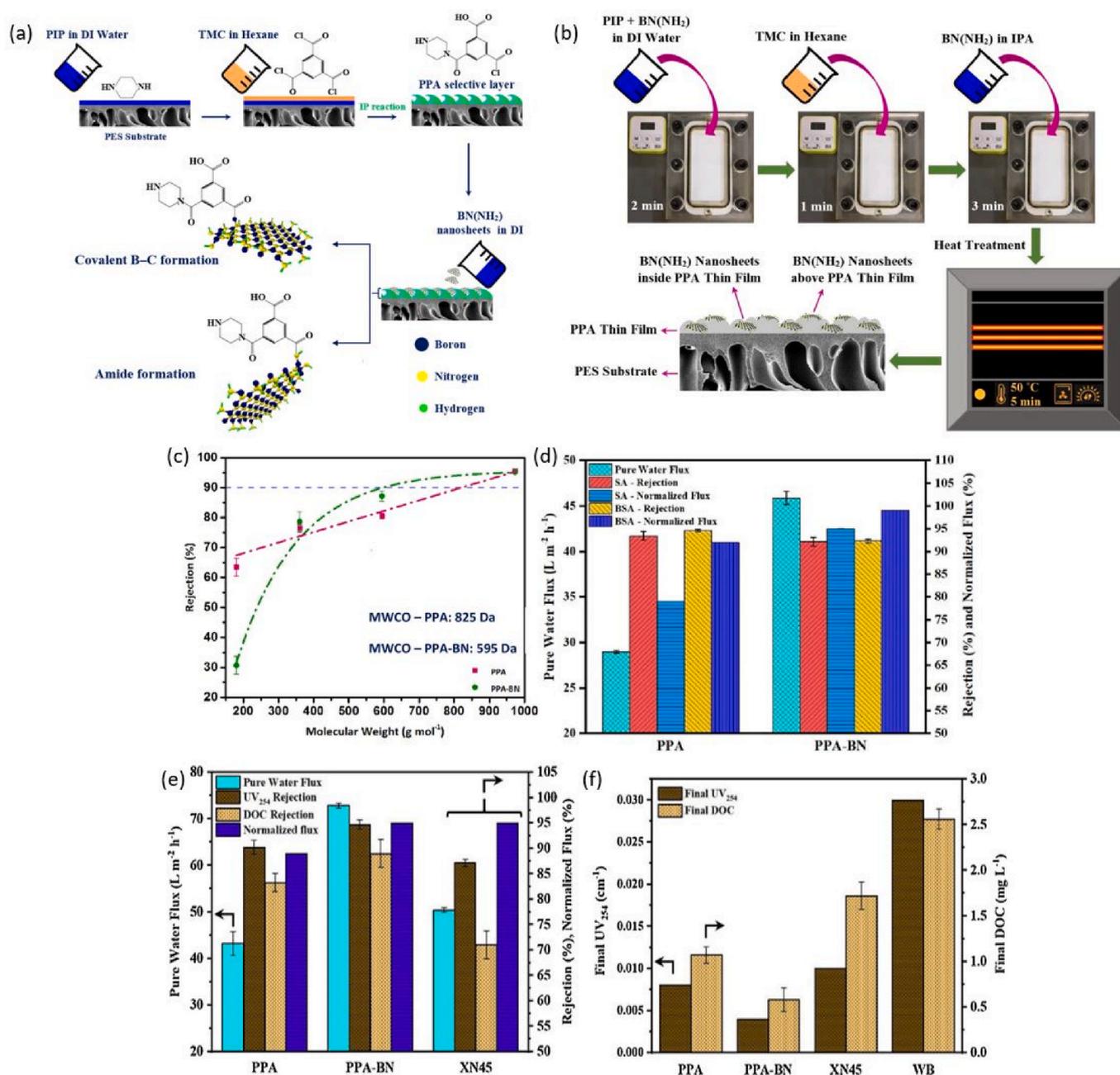


Fig. 7. (a) Synthesis of BN nanosheet decorated NF membrane, (b) Synthesis of dual modified NF membranes with BN nanosheets, (c) MWCO results and (d) NF performance data of BN decorated NF membrane compared to control membrane, (e) NF performance data and (f) NOM removal of commercial, control and dual modified membrane compared to conventional treatment plant. Reprinted with permission from Ref (Abdikhebari et al., 2019, 2020).

charge of the nanosheet, along with its seamless covalent integration with the PA matrix, enhanced the NF membrane performance. Suitable functionalization of 2D nanosheets has increased their compatibility with the polymer matrix (Mallya et al., 2021, 2022). In this regard, amine amine-functionalized BN nanosheets were decorated over already formed polyamide structure, as shown in Fig. 7 (a), which enhanced the membrane flux by 59% and 50% of total fouling resistance as well as maintained more than 92% NOM removal (Table 1, entry 24) (Abdikhebari et al., 2019). The reactive edges of the BN nanosheets facilitated covalent interactions between the electron-deficient B atoms and the polymer chains, and the amine functionalities led to reactions with unreacted TMC molecules (Abdikhebari et al., 2019). The modified membrane exhibited excellent long-term operational stability and recoverability without leaching of the nanosheets. Surface engineering with BN led to a significant decrease in the MWCO of the NF membrane from 825 Da to 595 Da, resulting in enhanced NOM rejection (Fig. 7 (c)). The membrane hydrophilicity and surface charge were enhanced, which resulted in a higher normalized flux and NOM rejection during filtration studies with BSA and SA, as shown in Fig. 7 (d). Compared to organic polymers, inorganic nanomaterials have lower compatibility with the polymer matrix; however, the modification strategy is simpler and less time-consuming (Choudhury et al., 2018). As mentioned, compatibility can be enhanced by attaching suitable functional groups to the 2D nanosheets, which can anchor strongly onto the polyamide layer (Mallya et al., 2021). In another research, amine-functionalized BN nanosheets were incorporated as nanofillers and surface modifiers to synthesize next-generation (Fig. 7 (b)) NF membranes for surface water treatment (Abdikhebari et al., 2020). The study reported that the dual modification strategy enhanced the hydrophilicity and negative charge by 60% and 40%, respectively, as well as 69% increase in flux, when compared to control membrane (Table 1, entry 25). The membranes exhibited stable filtration performance and enhanced antifouling and NOM removal performance, as shown in Fig. 7(e) and Fig. 7 (f). The NF-treated water showed a lower chlorine demand and higher removal of humic substances and lower molecular-sized NOM. Although 2D nanosheet materials have enhanced NF membrane performance, their tendency to form aggregates and leach during filtration cannot be overlooked.

As discussed, the surface charge, morphology, hydrophilicity, and functional groups of the membrane surface affect NOM fouling and removal performance (Ding et al., 2021). In particular, the free carboxylic groups present in the PA network play a vital role in exacerbating fouling as they tend to bridge with metal ions such as Ca^{2+} and Mg^{2+} which are abundantly present in hard surface water (Zhu et al., 2020a). Researchers have explored strategies to shield these free carboxylic groups as an easy method to improve antifouling performance (Han et al., 2016). This could also be achieved by incorporating salts such as CaCl_2 , NaHCO_3 , $\text{Ca}(\text{HCO}_3)_2$, FeCl_3 , CuSO_4 , NiSO_4 , $\text{Al}_2(\text{SO}_4)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, and CuSO_4 as additives during the IP reaction (Fan et al., 2014; Ghosh et al., 2019; Zhu et al., 2020a) or post-IP reaction activation of the membrane surface with the respective salts to facilitate mineralization. This endows the membrane surface with enhanced hydrophilicity and negative charge, as well as increased water flux and salt rejection (Choudhury et al., 2018).

3.4.8. Dual modification with organic polymers and inorganic nanomaterials

Surface-engineered membranes with inorganic nanomaterials suffer from leaching and compatibility issues with the polymer matrix of the NF membranes (Li et al., 2019). The synergistic use of organic polymers and nanomaterials has been explored to impart high antifouling properties (Rahaman et al., 2014). The three main strategies explored for this surface modification include a) attachment of organic polymers to the membrane surface and immobilization of inorganic nanomaterials on it (Zhang et al., 2016d). b) The inorganic nanomaterial is deposited on the membrane and further attached to the organic polymer to modify the

membrane surface (Rahaman et al., 2014). c) Modifying the inorganic nanomaterial with organic polymers before surface modification of the membrane (Zhang et al., 2016d). For instance, a study first coated the NF membrane surface with PVA, followed by attaching AgNPs in situ via thermal reduction (Zhang et al., 2016d). This method could successfully immobilize AgNPs in a simple and low-cost manner, as well as increase the release efficiency of Ag + while also reducing the leaching of AgNPs. The resulting membrane exhibited enhanced antibacterial performance but decreased permeance. The availability of several inorganic nanomaterials as well as organic polymers endows suitable properties for the membrane surface as well as good compatibility with the PA matrix, which could enhance the membrane separation and antifouling performance (Zhao et al., 2021).

4. Impact of surface engineering on PA layer properties and membrane performance

The incorporation of nanomaterials/polymers in surface-engineered NF membranes affects the PA layer properties, conclusively enhancing membrane performance. Their surface charge, hydrophilicity, and size/thickness influence membrane surface properties. The functional groups present in their structure cause further cross-linking of the PA layer, which leads to reduced pore size, improving the rejection properties of surface-engineered NF membranes. For instance, the attachment of BN nanosheets to the PA layer decreased the MWCO from 825 Da to 595 Da because of the partial coverage of the PIP-TMC network with BN nanosheets, as well as the formation of further amide and covalent C–B bonds (Abdikhebari et al., 2019). In another study, incorporation of PDA-SBMA declined the MWCO from 295.7 Da to 226.1 Da while enhancing the salt rejection to 99.1% and decreasing the water permeance by 10% (Ding et al., 2021). The majority of studies involving surface-engineered membranes exhibit a significant decline in water permeance, which could be attributed to the increased resistance to the transport of water due to the additional coating of the surface engineering materials. The decrease in permeance was also linked to the reduced pore size and free pore volume of the selective layer after surface modification (Abdikhebari et al., 2019). When compared to different studies reviewed in this work, membranes modified with PEG and PFTS exhibited highest decline in permeance at 74.29% and 50.5%, respectively, when compared to their control membranes (McCloskey et al., 2012; Ruan et al., 2018).

In terms of the surface roughness of surface-engineered NF membranes, both increasing and decreasing trends have been reported (Guo et al., 2019c; Zhang et al., 2022b). The increase in surface roughness is attributed to the confinement effect of nanosized CO_2 gas bubbles generated during the IP reaction in the PA layer, causing nanovoids and leaf-like turning structures (Mi et al., 2015; Zhang et al., 2022b). The covalent interactions between the reactive functional groups on the modifier materials and the PA layer structure cause alternative reaction pathways and cross-linking, leading to increased surface roughness (Abdikhebari et al., 2020). An increase in surface roughness increases the filtration area and supports the formation of a water hydration layer on the membrane surface, which results in an increase in water permeance and organic fouling resistance. This effect can also cause entrapment of foulants onto the rougher ridge-valley microstructures, further deteriorating membrane performance (Xu et al., 2022a). Many studies have also reported a reduction in surface roughness owing to surface engineering with nanomaterials/polymers (Table 1, entries 3–8). This was mainly attributed to the covering of the nodular structure of the PA layer with nanomaterials or polymer chains (Li et al., 2014). A few studies have also reported that surface engineering methods can interfere with the polymerization of PIP and TMC molecules, leading to thinner and smoother polyamide layers (Abdikhebari et al., 2019; Guo et al., 2019c). A smoother membrane surface can lead to a reduction in the area available for the adsorption of foulants, thereby restricting organic fouling of membranes (Baig et al., 2021; Ding et al., 2021).

Along with the improvement in antifouling properties, surface-engineered NF membranes also showed excellent resistance to biofouling (Liu et al., 2015b; Habib et al., 2020). This is achieved through a reduction in cell adhesion to the membrane surface through careful engineering of hydrophilicity, surface charge, and morphology. The incorporation of biocidal materials causes inactivation of microbes through interactions with their cell walls and DNA. The reactive oxygen species generated by biocides damage the cell, leading to its death (Li et al., 2020a). NF membranes were engineered by attaching zwitterions followed by immobilization of Ag nanoparticles, resulting in significant improvement in antifouling and antimicrobial properties without compromising the NF separation performance (Yi et al., 2019). Surface-engineered NF membrane exhibited higher release of Ag⁺ ions, disrupting the growth and metabolism of bacteria conclusively reducing 93.1% of *E. coli* and 95.7% of *S. aureus*, demonstrating great antimicrobial effects against different types of bacteria.

The intrinsic charge properties of the engineering materials affect the membrane surface charge. Several studies have reported that surface-engineered membranes show enhanced negative charge across the membrane surface, resulting in improved salt rejection, organic removal, and antifouling performance owing to electrostatic interactions (Abdikhebari et al., 2019; An et al., 2020). The availability of free carboxyl and amine groups on the PA layer governs the surface charge of the membrane and supports the attachment of various modifiers. The incorporation of polymers, such as zwitterionic and amphiphilic polymers, reduces the amount of free carboxyl groups and induces a shielding effect by decreasing the surface negative charge (Ruan et al., 2018; Zhang et al., 2022b). In such cases, the enhanced hydrophilicity, formation of a water hydration layer over the membrane surface, and steric hindrance due to the modifiers endow excellent antifouling performance (Bera and Jewrajka, 2016). Surface-engineered NF membranes with zwitterionic 1,3-PS decreased the surface negative charge (Mi et al., 2017). In spite of this, the membrane exhibited enhanced hydrophilicity, translating into excellent antifouling performance to proteins and polysaccharides with FRR >95% for BSA, and SA feed solutions. The improved hydrophilicity also enhances the solubilization and diffusion of water molecules, thereby increasing the permeance. Critical assessment of the various surface-engineered NF membranes reviewed in this paper revealed that the incorporation of zwitterionic polymers resulted in improved hydrophilicity of the membrane and exhibited the highest increase in water permeance. In particular, using SBMA and AEMA exhibited 300% increase in water permeance (Zhang et al., 2022b), while incorporation of SBMA and 1,3-PS exhibited 290% and 240% increases in water permeance, respectively, when compared to control membranes as well and maintained very high salt rejection (Mi et al., 2017; Guo et al., 2019b).

Surface-engineered NF membranes exhibit improved mechanical, chemical, and thermal stability. Decoration of BN nanosheets on already formed PA layer significantly enhanced the tensile strength and breaking elongation of the membrane (23.50% and 16.7%, respectively, compared to control) (Abdikhebari et al., 2019). The wrinkled topology of the BN nanosheets and its mechanical interlocking with polymer chains resulted in a reinforced polymer structure. The mechanical load can be partly transferred to the surface engineering material to preserve the underlying polymer structure, thereby boosting the mechanical strength and stability of the engineered NF membranes. The membrane modified with BN exhibited stable filtration performance during 52 h stability experiments owing to its excellent mechanical strength. Surface-engineered NF membranes also exhibit enhanced chlorine resistance owing to the shielding effect of the amide bonds of the PA layer during the chlorine exposure tests. The interactions of the functional groups present on the modifier materials, as well as the cross-linked structure, diminish the impact of chlorine on the degradation of the PA layer. For instance, membranes grafted with PVA after exposure to 31,200 ppm h of NaOCl exhibited increased water flux with higher salt rejection (Liu et al., 2015a). The grafting of PVA molecules at

the sites of amide linkages and amine groups reduced the number of chlorination sites. The dual effect of the reduction in chlorination sites and the protective coating layer of PVA restricts the attack of chlorine on the underlying polyamide layer (Liu et al., 2015a).

It is evident that the surface-engineered NF membranes significantly impact the PA layer properties and endow the membrane with suitable properties for enhanced permeance, selectivity, antifouling performance, mechanical and chemical stability. The properties of the engineering materials including size, hydrophilicity, charge and its interactions with polymer matrix influences the membrane surface properties and performance.

5. Potential for surface-engineered NF membranes for drinking water treatment and emerging applications

Surface-engineered NF membranes with high water permeance, salt rejection, and antifouling performance have been used in a wide range of applications in liquid separation. Drinking water treatment, desalination of seawater and brackish water, pharmaceuticals, manufacturing, food industries, resource recovery, and industrial wastewater treatment and reuse are important applications. Although the requirements and membrane performances vary for each application, membranes are required to showcase the standard transport properties and antifouling performance. The surface engineering of NF membranes and optimization of their performance for key specific applications are essential. The water permeance and selectivity of these surface-engineered NF membranes are highly dependent on the type of modifiers, engineering strategies, and their impact on membrane surface properties that determine specific applications. The selection of a particular surface-engineered NF membrane is based on the removal efficiency of the target component, as well as its impact on reducing the capital, operation costs, and energy requirements. In this section, a few important and emerging applications of NF membranes are summarized, with a critical focus on drinking water treatment.

Commercial NF membranes operate with permeance in the range of 5–12 L m⁻² h⁻¹ bar⁻¹ with Na₂SO₄ rejection >98% and Ca²⁺ and Mg²⁺ rejection around 70%. The surface-engineered NF membranes were compared in terms of their impact on the water permeance and desalination performance, as shown in Fig. 8. The majority of surface-engineered NF membranes fall within the recommended water permeance and salt rejection range. The type of surface modifier and functional groups present greatly impacted the membrane permeance and rejection performance. As shown in Fig. 8, the highest permeance was recorded for the membranes incorporating zwitterionic polymers. In particular, a study using SBMA and AEMA to engineer NF membranes recorded 300% increase in water permeance at 27.5 L m⁻² h⁻¹ bar⁻¹

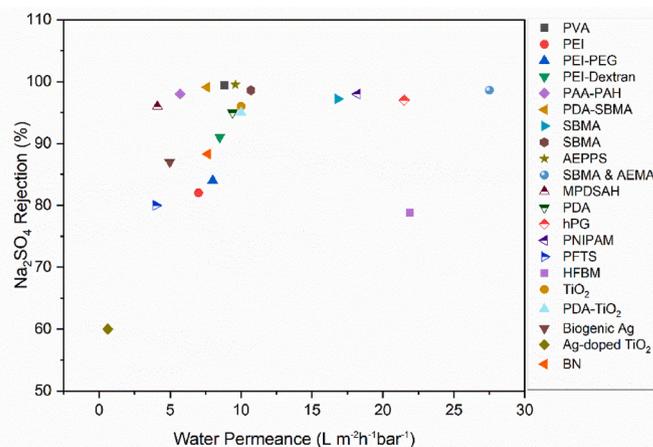


Fig. 8. Water permeance and Na₂SO₄ rejection performance of surface-engineered NF membranes reviewed in this review paper.

against the control membrane. Compared to other studies reviewed in this paper, this membrane exhibited both the highest value for water permeance and an increase post surface engineering. The membrane exhibited high salt rejection of 98.6% for Na_2SO_4 as well as excellent fouling resistance, with normalized flux maintained at 90% compared to 55% for the control membrane. Surface-engineered NF membranes with zwitterion polymers show enormous potential for suppressing organic fouling and exhibit enhanced water permeance and salt rejection (Mi et al., 2017; Zhang et al., 2022b). NF membranes incorporated HFBM and hPG also exhibited extraordinary water permeance values at 21.9, and 21.5 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ respectively with enhanced antifouling behaviour.

In terms of increase in water permeance, surface-engineered membranes incorporated with SBMA and 1,3-PS exhibited 290% and 240% increases in water permeance, respectively, when compared to control membranes as well and maintained very high salt rejection (Mi et al., 2017; Guo et al., 2019b). While Membranes modified with PEG and PFTS exhibited highest decline in permeance at 74.29% and 50.5%, respectively, when compared to their control membranes (McCloskey et al., 2012; Ruan et al., 2018). Another general trend observed in Fig. 8 is the lower permeance recorded for membranes modified with inorganic nanomaterials, such as Ag, TiO_2 and BN. Incorporating Ag-doped TiO_2 resulted in 70% decrease in water permeance to 0.6 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ with salt rejection at 60% for Na_2SO_4 (Habib et al., 2020). The majority of studies involving surface-engineered membranes exhibit a significant decline in water permeance, which is attributed to the increased resistance to the transport of water and reduction in pore size due to the additional coating of the surface engineering materials. This resulted in an increase in the salt rejection of the surface-engineered NF membranes. Highest salt rejection was reported for surface-engineered NF membranes incorporated with 1 wt% zwitterionic AEPPS polymer at 99.5% for Na_2SO_4 (Fig. 8), with water permeance enhanced by 105.7% from 4.67 to 9.6 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ (Mi et al., 2015). The membrane also exhibited good selective rejection of divalent ions over monovalent ions, with rejection of NaCl of 42%. The membrane's antifouling properties was simultaneously improved, with FRR ratio being as high as 95.5% for BSA. Lowest salt rejection was reported for Ag-doped TiO_2 and HFBM incorporated membranes at 60% and 78.8% for Na_2SO_4 respectively.

NF membranes are widely used in drinking water treatment plants to source water from surface and groundwater resources (Wang et al., 2022). This water contains high concentrations of hardness, causing ions such as Ca^{2+} and Mg^{2+} along with high sulfate and NOM concentrations, resulting in an unpleasant and distinctive taste. The presence of hardness ions also leads to severe scaling in piping and storage during water treatment, whereas high sulfate concentrations have been associated with intestinal discomfort and diarrhea (Wang et al., 2022). Surface-engineered NF membranes have reported high rejection rates for Ca^{2+} and Mg^{2+} supporting their application in solving the water hardness problem. A PNIPAM-incorporated NF membrane reported >95% rejection of MgSO_4 (Guo et al., 2019c). In another report, the SBMA-modified NF membrane exhibited rejections of 95% and 60% for MgSO_4 and CaCl_2 (Guo et al., 2019b).

Surface-engineered NF membranes with BN nanosheets exhibit exceptional operational versatility for handling NOM issues during drinking water production (Abdikhebari et al., 2020). Compared to the conventional treatment plant, the BN-incorporated NF membrane separated 650% and 341% more of UV_{254} and DOC. The engineered membrane was better in terms of pure water flux, NOM removal, and DBPs formation potential than the control and commercial membranes. The BN engineered membrane also exhibited stable performance under detrimental conditions, such as high concentrations of Ca^{2+} and low pH. BN engineered NF membranes also removed more than 93% of PFAS compared to 65% for commercial membrane supporting application of surface-engineered NF membranes for remediation of emerging contaminants such as PFAS and micropollutants (Abdikhebari et al., 2022).

Anthropogenic activities, such as mining, smelting processes, and industrial wastewater discharge, have led to the contamination of water sources with toxic heavy metal ions such as Hg^{2+} , Pb^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} (Kumar et al., 2022). Commercial and surface-engineered NF membranes are effective for removing heavy metals from water. The separation properties and mechanisms of heavy-metal cations are similar to those of hardness ions. Surface-engineered NF membranes can be tweaked to achieve particular interactions for the removal of target heavy metals through electrostatic interactions and adsorption (Wang et al., 2022). For instance, NF membranes modified with a surfactant-functionalized layer reported separation efficiency >98% for Zn^{2+} and Ni^{2+} , 96–98% for Cu^{2+} , >85% for Pb^{2+} (Xu et al., 2022b). NF membranes have been employed in various leather and textile industries to remove heavy metals and dyes from wastewater to promote zero liquid discharge (Pal et al., 2019; Tavangar et al., 2019). Hybrid processes involving NF and forward osmosis (FO) have improved effluent quality and reduced organic fouling in leather processing factories (Pal et al., 2019). Wastewater from textile industries contains high concentrations of dye components, which are hazardous to humans and the environment. NF membranes have been highly effective in removing more than 98% of these dyes from textile wastewater (Liu et al., 2017b; Yadav et al., 2022). In this context, surface-engineered NF membranes with diethanolamine exhibit high rejection of Congo red, methyl blue, sunset yellow, and neutral red at 99.6%, 99.8, 97.5 and 81.2%, respectively, while maintaining higher permeance and fouling resistance (Liu et al., 2017b). The incorporation of diethanolamine assists in modifying the membrane surface properties, thereby electrostatic interactions and steric hindrance, providing the membrane with high dye removal and antifouling properties (Liu et al., 2017b). A study reported surface-engineered nanofiber membranes with chitosan and proteins from egg white, which removed both cationic dye toluidine blue O (TBO) and anionic dye orange 7 (AO7) from aqueous solutions (Chen et al., 2022). Electrostatic interactions mainly governed the removal of dye molecules. The membrane exhibited very high absorption of 329.36 mg g^{-1} within 30 min for AO7, and 317.16 mg g^{-1} for TBO within 90 min. The repeated use of the engineered membranes did not significantly affect the removal of the dyes, supporting their potential as high-efficiency materials for dye wastewater treatment.

NF membranes have also been employed in a range of biotechnological applications, such as the separation of sucrose, glucose, and fructose from cane molasses (Luo et al., 2018), decolorization of molasses (Luo et al., 2019), fractionation of different proteins (Pruksasri et al., 2015) and enantiomers (Hadik et al., 2005). NF membranes are used in the pharmaceutical industry for the separation of active pharmaceutical ingredients from genotoxic impurities, as well as for the purification and recovery of antibiotics and drugs such as amoxicillin, diclofenac, ibuprofen, and paracetamol (Mallakpour and Azadi, 2022). In a particular study, coating NF membrane with chitosan resulted in enhancing the hydrophilicity and fouling resistance while maintaining high rejection for drug molecules including mebeverine (98%) and diphenhydramine (97%) (Kamrani et al., 2018). Surface-engineered NF membranes with 1,3-PS zwitterionic modification exhibited high rejection of erythromycin at 99% (Mi et al., 2017). Phycobiliproteins, such as C-phycoyanin (CPC) and allophycocyanin (APC), have been widely used as fluorescent markers in clinical diagnosis and as dyes in cosmetics and pharmaceuticals (Flores-Montero et al., 2019). Several protein components have very similar molecular masses and properties. The separation and purification of phycobiliproteins via column chromatography are laborious and costly (Liu et al., 2020). In this context, nanofiber membranes engineered with ethylenediamine and hexamethylenediamine show antibacterial and antioxidant properties, as well as high potential for separation of CPC and APC from complex algae feedstock (Liu et al., 2020).

Owing to the emerging applications of NF membranes, it is essential to develop surface-engineered NF membranes with suitable properties

and performances for tailored liquid separation applications. However, all applications require the membrane to have excellent antifouling performance, which can be engineered by understanding the mechanisms behind the interactions of particular foulants with the membrane surfaces in each application.

6. Challenges and future perspectives

The complex composition and variability of NOM in source water remains a critical challenge for water treatment facilities. Owing to the complex nature of NOM, various fractions such as polysaccharides, proteins, and humic substances are not uniform in terms of their surface properties and molecular weights. This leads to varying degrees of fouling potential and combined fouling owing to the interactions between different organic fractions (Tomaszewski et al., 2011; Shao et al., 2019). The interactions between the NOM fractions can lead to the formation of aggregates that have completely different fouling behaviours compared to the individual foulants, and few of the NOM fractions cannot be well defined due to their complex and overlapping behaviour with others (Wang and Tang, 2011; Arkhangelsky et al., 2016). For instance, it is well observed that in natural waters, protein-like and humic substances have similar characteristics and overlap, making it harder to characterize the fouling layer (Chen et al., 2002; Guo et al., 2020b). As a result, the lack of detailed characterization of NOM in feed water and fouling layer can significantly impact the understanding of the mechanisms behind organic fouling of membranes, NOM retention, and the quality of treated water. Understanding NOM characteristics, fouling mechanisms, and factors affecting fouling is essential for surface engineering membranes for enhanced antifouling and NOM removal performance.

Although surface-engineered NF membranes have shown enhanced performance, some critical challenges need to be addressed. The advantages and disadvantages associated with different surface engineering materials for developing advanced NF membranes are tabulated in Table S2. One of the major issues is the trade-off between the water permeance and rejection. Most studies have reported a significant decline in water permeance due to an inevitable increase in mass transfer resistance post surface engineering. In particular, the incorporation of macromolecules, such as hyperbranched polymers, amphiphilic polymers, and thermo-responsive polymers, results in a reduction in the permeance of the membrane owing to the bulky nature and thick coating layers. Coating with inorganic nanomaterials has also caused a significant decline in membrane permeance. Surface-engineered NF membranes should exhibit a balance between antifouling performance and reduction in the water permeance. Membranologists also highlight the importance of improving the selectivity and antifouling performance rather than water permeance of the membrane (Werber et al., 2016). The increase in water permeance can trigger extensive fouling as well have minimal impact on specific energy consumption. For instance, a study reported mere 16.6% reduction in specific energy consumption for a surface-engineered membrane compared to the commercial membrane with water permeance $15 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and $1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ respectively (Yang et al., 2020). It's worth noting that the majority of the energy calculation models of surface-engineered membranes have not considered the fouling and ageing of the membranes. It's essential to establish relevant techno-economic analysis of antifouling surface-engineered NF membranes to highlight environmental and economic advantages over existing commercial membranes and fouling mitigation strategies such as feed water pre-treatment and membrane cleaning. The future studies should also focus on development of guidelines based on cost analysis for recommending the permeance, selectivity, and antifouling performance of surface-engineered membranes.

Most nanomaterials and polymers used for surface-engineered NF membranes use complex, costly, and time-consuming synthesis methods. They use hazardous chemicals for their synthesis, which are

dangerous to humans and the environment (Mi et al., 2017; Zhang et al., 2022b). For instance, the best-performing zwitterion polymer-modified membranes require the excessive use of chemicals such as 2-bromopropionyl bromide, 2-bromoisobutyl bromide, and copper bromide, which can cause severe skin burns and eye damage, as well as cause detrimental effects on aquatic life (Khoo et al., 2021; Zhang et al., 2022b). Large volumes of various organic solvents used during modification generate waste for careful handling and disposal (Mallya et al., 2021; Park et al., 2021a). Commercially used IP reaction monomers for NF and RO membranes, such as MPD, PIP, and TMC, are highly toxic and are derived from petrochemicals that are not sustainable. Organic solvents are also used in high volumes during IP reactions, generating a large amount of waste (Mallya et al., 2021; Park et al., 2021a). In terms of the synthesis process, most surface engineering methods are time consuming, ranging from a few hours to days of contact in a controlled environment, and require the use of energy-intensive processes such as UV and plasma, restricting its industrial scale-up (Baek et al., 2017; Reis et al., 2017a, 2017b). There is a need to develop feasibility studies to evaluate the industrial scale-up opportunities for surface-engineered NF membranes. Future research should focus on developing environmentally friendly methods to synthesize materials and engineer membranes using simple and cost-effective procedures.

The long-term stability of the surface-engineered membranes is an important parameter for industrial applications. Most studies have focused on lab-prepared membranes and evaluated their performance in short-term experiments in lab-scale filtration units. Data from actual long-term experiments and fouling/cleaning cycles are required to confirm their industrial application. There is a lack of correlation between the short-term and long-term performance of surface-engineered membranes. The delamination of the modified surface during operation is a major issue for these membranes. Physically coated and covalently grafted polymers/nanomaterials have reportedly detached from the membrane surface during operation owing to their poor stability. For instance, hydrophilic polymers such as PEG and PVA have a tendency to be easily washed away during high-pressure operation owing to the large drag force and reactivity towards water (Shahkaramipour et al., 2017; Guo et al., 2019a). This leaves the membrane surface exposed to foulants, causing significant fouling, thereby reducing membrane performance. Inorganic nanomaterials have shown a tendency to form aggregates and unselective voids, leading to compromised membrane integrity and causing significant degradation of membrane stability during extended filtration conditions. Environmental issues associated with the leaching of inorganic nanomaterials cannot be overlooked. The reorientation and reactivity of attached polymers, such as zwitterionic, amphiphilic, and thermo-responsive polymers, can significantly deteriorate membrane performance (Choudhury et al., 2018). For instance, it is essential to maintain the recommended process conditions such as pH, temperature, and ionic content in the feed water to support the performance of engineered NF membranes. Any changes in the conditions can induce reorientation and varied reactivity of the engineering material with the foulants, impacting the transport and antifouling performance. Hence, long term stability tests and pilot scale experiments are required to ascertain the stability and performance of surface-engineered NF membranes. Comprehensive techno-economic analysis at the pilot scale is essential to support the feasibility of industrial applications of surface-engineered NF membranes and justify their performance. Pilot-scale studies will assist membranologists in gaining more information on the feasibility, profitability, fouling, and filtration performance of surface-engineered membranes with actual feedwater for specific applications, replacing the synthetic feed materials often utilized for lab studies.

From the prospects of application of surface-engineered NF membranes in drinking water treatment, the literature should be updated with studies evaluating the removal performance of problematic NOM and emerging contaminants such as PFAS, micropollutants, heavy metals, and pharmaceuticals. The majority of existing studies only

report desalination and antifouling performance with limited salts and modal organic foulants. There is a lack of studies pertaining to the performance analysis and fouling behaviour of surface-engineered membranes in contact with surface water. Because of the extensive use of surface water in various countries for drinking water production, more research should focus on surface engineering NF membranes to optimize NOM removal, antifouling performance, and DBPs reduction during drinking water production. From the perspective of NOM fouling and removal, inorganic nanomaterials such as BN nanosheet-incorporated membranes have performed exceedingly well. The issues with the lower compatibility of nanomaterials with polymer matrices hinder their application. Membranologists should focus on improving the compatibility of these nanomaterials with covalent functionalization and using inorganic/organic hybrid nanoarchitectures to engineer membranes. From an industrial point of view, the incorporation of hydrophilic polymers is a relatively easy strategy because of its simple procedure and easy integration into existing membrane production facilities. Various commercial NF and RO membranes have used coating layers of hydrophilic polymers such as PVA. From a thorough review of the various mechanisms behind NOM interactions with membrane surfaces, it is evident that the incorporation of hydrophilic polymers is not a foolproof solution to mitigate the organic fouling of NF membranes. Specific interactions of NOM with hydrophilic polymers can trigger more fouling (Zhao et al., 2021). Thus, more research should be focused on the use of amphiphilic polymers that contain both hydrophilic and low-surface-energy groups that can perform well and alleviate organic fouling in NF membranes.

From this comprehensive review, it is evident that engineering next-generation fouling resistant NF membrane is critical for securing water for the future. Recent advances in emerging nanomaterials and polymers have significantly diversified the pool of materials available for engineering NF membranes to enhance their performance. There is a critical need to develop guidelines for selecting engineering materials, and a comprehensive performance evaluation is necessary to develop NF membranes for targeted liquid separation applications. Membrane manufacturers should focus on implementing a circular economy approach to solve the waste membrane modules generated after their lifespan. The approach does not involve a single-step solution, but rather follows a chain of processes and optimizations. Material scientists and membranologists have focused on developing antifouling membranes using various approaches including surface engineering. This is followed by the optimization of the process and control, including pre-treatment, membrane fouling monitoring, and membrane cleaning. The application of machine learning and artificial intelligence in developing advanced fouling models and performance predictions is crucial for optimizing NF membranes for enhanced antifouling and NOM removal. Although several surface-engineered membranes show enhanced antifouling performance, pre-treatment and membrane cleaning are unavoidable. In this regard, surface engineering of NF membranes and the regeneration of membranes in situ using simple procedures are of the most importance. More research should be focused on cost-effective end-of-life membrane regeneration as well as recycling (direct and indirect) before reaching landfills. Owing to emerging NF membrane applications such as the treatment of groundwater, surface water, brackish water, and water reuse, it is highly relevant to have a comprehensive approach to solve the fouling problem and reduce the waste generated due to the used membrane as well as reduce the energy and economic requirements.

7. Conclusions

Due to the increasing concentration of NOM in surface water and its interaction with emerging pollutants, it is necessary to eliminate these contaminants in order to create safe and high-quality drinking water. Due to the extraordinary rise in the demand for freshwater and the development of new membrane materials with improved performance,

NF membrane-based water treatment plants will in particular see significant growth. The development of fouling-resistant and long-lasting NF membranes is necessary since the membrane's performance is severely impacted by the inevitable organic fouling that occurs during surface water treatment. Understanding fouling mechanisms and interactions between NOM and membrane surface is crucial for the development of NF membranes that are fouling-resistant. Considering mechanisms including size exclusion, electrostatic interactions, steric hindrance, and hydrophilic/hydrophobic interactions, current study provides a thorough assessment of the removal of NOM during surface water treatment using NF. With regard to the influencing variables and solutions for fouling mitigation, the crucial topic of organic fouling is thoroughly covered. Surface-engineered NF membranes post-IP reaction facilitated the optimization of membrane surface properties, including chemistry, morphology, hydrophilicity, and charge, to enhance antifouling performance. Various materials, including polymers, inorganic nanomaterials, and hybrid inorganic/organic materials, have been explored and reviewed based on their strategies, syntheses, and applications. A systematic review of the effect of surface engineering on membrane surface properties and performance is undertaken along with recent advancements in this sector. The effectiveness of the surface-engineered NF membranes for water filtration is assessed by comparing them to commercial and control membranes. Surface-engineered NF membranes with improved permeance, selectivity, antifouling, and antimicrobial property were created by engineering materials with its special features. While preserving outstanding antifouling and chemical stability qualities, zwitterion-based surface-engineered NF membranes stand out among these materials as having significant potential for addressing the trade-off between permeance and salt rejection. With a 300% increase in permeance at $27.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ compared to the control membrane with 98.6% Na_2SO_4 and outstanding antifouling performance, the surface-engineered NF membrane with SBMA and AEMA outperformed previous membranes. However, difficulties in the design and manufacture of surface-engineered NF membranes limit their industrial applicability, and this is thoroughly examined. Future views include the production of engineering materials using economical and environmentally friendly processes as well as the simple modification of membrane surfaces to work with selective layers. The transition of surface-engineered NF membranes into the industrial sector would be supported by improvements in post IP reaction modification procedures. In addition to the water purification area covered in this paper, applications of fouling-resistant NF membranes would grow exponentially in gas and other liquid separations.

Credit authors statement

Deepak Surendhra Mallya: Conceptualization, Visualization, Writing – original draft, Writing – review & editing. Sara Abdikhebari: Conceptualization, Writing – review & editing. Ludovic F. Dumée: Writing – review & editing. Shobha Muthukumaran: Supervision, Writing – review & editing. Weiwei Lei: Writing – review & editing. Kanagaratnam Baskaran: Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

Mr. Mallya acknowledges Deakin University for his PhD scholarship,

and the partial financial support from Khalifa University through project RC2-2019-007 is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.138070>.

References

- Abbina, S., Vappala, S., Kumar, P., Siren, E.M.J., La, C.C., Abbasi, U., Brooks, D.E., Kizhakkedathu, J.N., 2017. Hyperbranched polyglycerols: recent advances in synthesis, biocompatibility and biomedical applications. *J. Mater. Chem. B* 5, 9249–9277.
- Abdikhebari, S., Baskaran, K., Guijt, R., Lei, W., Dumée, L.F., 2022. Cross-linked boron nitride-piperazine amide thin film nanocomposite membranes for rejection and concentration of per- and poly-fluoroalkyl substances (PFAS). *Environ. Qual. Manag.* 31, 425–432.
- Abdikhebari, S., Dumée, L.F., Jegatheesan, V., Mustafa, Z., Le-Clech, P., Lei, W., Baskaran, K., 2020. Natural organic matter removal and fouling resistance properties of a boron nitride nanosheet-functionalized thin film nanocomposite membrane and its impact on permeate chlorine demand. *J. Water Proc. Eng.* 34, 101160.
- Abdikhebari, S., Lei, W., Dumée, L.F., Barlow, A.J., Baskaran, K., 2019. Novel thin film nanocomposite membranes decorated with few-layered boron nitride nanosheets for simultaneously enhanced water flux and organic fouling resistance. *Appl. Surf. Sci.* 488, 565–577.
- Abdikhebari, S., Lei, W., Dumée, L.F., Milne, N., Baskaran, K., 2018. Thin film nanocomposite nanofiltration membranes from amine functionalized-boron nitride/poly-piperazine amide with enhanced flux and fouling resistance. *J. Mater. Chem. B* 6, 12066–12081.
- Abrahamse, A., Lipreau, C., Li, S., Heijman, S., 2008. Removal of divalent cations reduces fouling of ultrafiltration membranes. *J. Membr. Sci.* 323, 153–158.
- Al-Amoudi, A., Lovitt, R.W., 2007. Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. *J. Membr. Sci.* 303, 4–28.
- Al-Amoudi, A., Williams, P., Mandale, S., Lovitt, R.W., 2007. Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability. *Separ. Purif. Technol.* 54, 234–240.
- Al-Amoudi, A.S., 2010. Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: a review. *Desalination* 259, 1–10.
- Alborzfar, M., Jonsson, G., Grøn, C., 1998. Removal of natural organic matter from two types of humic ground waters by nanofiltration. *Water Res.* 32, 2983–2994.
- Amy, G., 2008. Fundamental understanding of organic matter fouling of membranes. *Desalination* 231, 44–51.
- An, X., Zhang, K., Wang, Z., Ly, Q.V., Hu, Y., Liu, C., 2020. Improving the water permeability and antifouling property of the nanofiltration membrane grafted with hyperbranched polyglycerol. *J. Membr. Sci.* 612, 118417.
- Ang, M.B.M.Y., Trilles, C.A., De Guzman, M.R., Pereira, J.M., Aquino, R.R., Huang, S.-H., Hu, C.-C., Lee, K.-R., Lai, J.-Y., 2019. Improved performance of thin-film nanocomposite nanofiltration membranes as induced by embedded polydopamine-coated silica nanoparticles. *Separ. Purif. Technol.* 224, 113–120.
- Arabi, S., Nakhla, G., 2009. Impact of magnesium on membrane fouling in membrane bioreactors. *Separ. Purif. Technol.* 67, 319–325.
- Arkhangelsky, E., Wicaksana, F., Al-Rabiah, A.A., Al-Zahrani, S.M., Wang, R., 2016. Understanding the interaction between biomacromolecules and their influence on forward osmosis process. *Desalination* 385, 12–23.
- Ba, C., Ladner, D.A., Economy, J., 2010. Using polyelectrolyte coatings to improve fouling resistance of a positively charged nanofiltration membrane. *J. Membr. Sci.* 347, 250–259.
- Baek, Y., Freeman, B.D., Zydney, A.L., Yoon, J., 2017. A facile surface modification for antifouling reverse osmosis membranes using polydopamine under UV irradiation. *Ind. Eng. Chem. Res.* 56, 5756–5760.
- Bagheri, M., Mirbagheri, S.A., 2018. Critical review of fouling mitigation strategies in membrane bioreactors treating water and wastewater. *Bioresour. Technol.* 258, 318–334.
- Baig, U., Waheed, A., Salih, H.A., Matin, A., Alshami, A., Aljundi, I.H., 2021. Facile modification of NF membrane by multi-layer deposition of polyelectrolytes for enhanced fouling resistance. *Polymers* 13, 3728.
- Baker, R.W., 2012. *Membrane Technology and Applications*. John Wiley & Sons.
- Ben-Sasson, M., Lu, X., Nejat, S., Jaramillo, H., Elimelech, M., 2016. In situ surface functionalization of reverse osmosis membranes with biocidal copper nanoparticles. *Desalination* 388, 1–8.
- Bera, A., Jewrajka, S.K., 2016. Tailoring polyamide thin film composite nanofiltration membranes by polyethyleneimine and its conjugates for the enhancement of selectivity and antifouling property. *RSC Adv.* 6, 4521–4530.
- Bhoomick, M.C., Roy, S., Mitra, S., 2021. Synergistic effect of air sparging in direct contact membrane distillation to control membrane fouling and enhancing flux. *Separ. Purif. Technol.* 272, 118681.
- Braghetta, A., DiGiano, F.A., Ball, W.P., 1997. Nanofiltration of natural organic matter: pH and ionic strength effects. *J. Environ. Eng.* 123, 628–641.
- Braghetta, A., DiGiano, F.A., Ball, W.P., 1998. NOM accumulation at NF membrane surface: impact of chemistry and shear. *J. Environ. Eng.* 124, 1087–1098.
- Cen, J., Vukac, M., Barton, G., Kavanagh, J., Coster, H.G.L., 2015. Real time fouling monitoring with electrical impedance spectroscopy. *J. Membr. Sci.* 484, 133–139.
- Chang, E.-E., Yang, S.-Y., Huang, C.-P., Liang, C.-H., Chiang, P.-C., 2011. Assessing the fouling mechanisms of high-pressure nanofiltration membrane using the modified Hermia model and the resistance-in-series model. *Separ. Purif. Technol.* 79, 329–336.
- Chaukura, N., Marais, S.S., Moyo, W., Mbali, N., Thakalekoala, L.C., Ingwani, T., Mamba, B.B., Jarvis, P., Nkambule, T.T., 2020. Contemporary issues on the occurrence and removal of disinfection byproducts in drinking water—a review. *J. Environ. Chem. Eng.* 103659.
- Chellam, S., Jacangelo, J.G., Bonacquisti, T.P., Schauer, B.A., 1997. Effect of pretreatment on surface water nanofiltration. *J. - Am. Water Works Assoc.* 89, 77–89.
- Chen, J., Gu, B., LeBoeuf, E.J., Pan, H., Dai, S., 2002. Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. *Chemosphere* 48, 59–68.
- Chen, J., Li, Z., Wang, C., Wu, H., Liu, G., 2016. Synthesis and characterization of gC 3 N 4 nanosheet modified polyamide nanofiltration membranes with good permeation and antifouling properties. *RSC Adv.* 6, 112148–112157.
- Chen, Y.-S., Ooi, C.W., Show, P.L., Hoe, B.C., Chai, W.S., Chiu, C.-Y., Wang, S.S.-S., Chang, Y.-K., 2022. Removal of ionic dyes by nanofiber membrane functionalized with chitosan and egg white proteins: membrane preparation and adsorption efficiency. *Membranes* 12, 63.
- Cho, J., Amy, G., Pellegrino, J., 1999. Membrane filtration of natural organic matter: initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes. *Water Res.* 33, 2517–2526.
- Cho, J., Amy, G., Pellegrino, J., 2000. Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane. *J. Membr. Sci.* 164, 89–110.
- Cho, J., Amy, G., Pellegrino, J., Yoon, Y., 1998. Characterization of clean and natural organic matter (NOM) fouled NF and UF membranes, and foulants characterization. *Desalination* 118, 101–108.
- Chon, K., Cho, J., 2016. Fouling behavior of dissolved organic matter in nanofiltration membranes from a pilot-scale drinking water treatment plant: an autopsy study. *Chem. Eng. J.* 295, 268–277.
- Choudhury, R.R., Gohil, J.M., Mohanty, S., Nayak, S.K., 2018. Antifouling, fouling release and antimicrobial materials for surface modification of reverse osmosis and nanofiltration membranes. *J. Mater. Chem. B* 6, 313–333.
- Couto, C.F., Santos, A.V., Amaral, M.C.S., Lange, L.C., de Andrade, L.H., Foureaux, A.F.S., Fernandes, B.S., 2020. Assessing potential of nanofiltration, reverse osmosis and membrane distillation drinking water treatment for pharmaceutically active compounds (PhACs) removal. *J. Water Proc. Eng.* 33, 101029.
- Dayarathne, H.N.P., Angove, M.J., Aryal, R., Abuel-Naga, H., Mainali, B., 2021. Removal of natural organic matter from source water: review on coagulants, dual coagulation, alternative coagulants, and mechanisms. *J. Water Proc. Eng.* 40, 101820.
- De la Rubia, A., Rodríguez, M., León, V.M., Prats, D., 2008. Removal of natural organic matter and THM formation potential by ultra- and nanofiltration of surface water. *Water Res.* 42, 714–722.
- Derjaguin, B.V., Churaev, N.V., Muller, V.M., 1987. *The theory of stability of lyophobic colloids—landau—verwey—overbeek (DLVO) theory of stability of lyophobic colloids*. In: Derjaguin, B.V., Churaev, N.V., Muller, V.M. (Eds.), *Surface Forces*. Springer US, Boston, MA, pp. 293–310.
- Ding, J., Liang, H., Zhu, X., Xu, D., Luo, X., Wang, Z., Bai, L., 2021. Surface modification of nanofiltration membranes with zwitterions to enhance antifouling properties during brackish water treatment: a new concept of a “buffer layer”. *J. Membr. Sci.* 637, 119651.
- Dražević, E., Košutić, K., Dananić, V., Pavlović, D.M., 2013. Coating layer effect on performance of thin film nanofiltration membrane in removal of organic solutes. *Separ. Purif. Technol.* 118, 530–539.
- Du, Y., Pramanik, B.K., Zhang, Y., Dumée, L., Jegatheesan, V., 2022. Recent advances in the theory and application of nanofiltration: a review. *Curr. Pollut. Rep.* 8, 51–80.
- Emadzadeh, D., Lau, W., Matsuura, T., Hilal, N., Ismail, A., 2014. The potential of thin film nanocomposite membrane in reducing organic fouling in forward osmosis process. *Desalination* 348, 82–88.
- Ericsson, B., Trägårdh, G., 1997. Treatment of surface water rich in humus—membrane filtration vs. conventional treatment. *Desalination* 108, 117–128.
- Fan, X., Dong, Y., Su, Y., Zhao, X., Li, Y., Liu, J., Jiang, Z., 2014. Improved performance of composite nanofiltration membranes by adding calcium chloride in aqueous phase during interfacial polymerization process. *J. Membr. Sci.* 452, 90–96.
- Feng, G., Chu, H., Dong, B., 2015. Characterizing dissolved organic matter fouling of nanofiltration membranes and evaluating effects of naproxen retention. *Desalination Water Treat.* 56, 2835–2847.
- Flores-Montero, J., Kalina, T., Corral-Mateos, A., Sanoja-Flores, L., Pérez-Andrés, M., Martín-Ayuso, M., Sedek, L., Rejlova, K., Mayado, A., Fernández, P., van der Velden, V., Bottcher, S., van Dongen, J.J.M., Orfao, A., 2019. Fluorochrome choices for multi-color flow cytometry. *J. Immunol. Methods* 475, 112618.
- Fujioka, T., Khan, S.J., McDonald, J.A., Nghiem, L.D., 2015. Rejection of trace organic chemicals by a nanofiltration membrane: the role of molecular properties and effects of caustic cleaning. *Environ. Sci.: Water Res. Technol.* 1, 846–854.
- Gagliano, E., Sgroi, M., Falciglia, P.P., Vagliasindi, F.G.A., Roccaro, P., 2020. Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. *Water Res.* 171, 115381.
- Gao, F., Wang, J., Zhang, H., Jia, H., Cui, Z., Yang, G., 2018. Role of ionic strength on protein fouling during ultrafiltration by synchronized UV-vis spectroscopy and electrochemical impedance spectroscopy. *J. Membr. Sci.* 563, 592–601.

- Gao, Y., Haavisto, S., Li, W., Tang, C.Y., Salmela, J., Fane, A.G., 2014. Novel approach to characterizing the growth of a fouling layer during membrane filtration via optical coherence tomography. *Environ. Sci. Technol.* 48, 14273–14281.
- Garg, S., Wang, J., Kumar, P., Mishra, V., Arafat, H., Sharma, R.S., Dumée, L.F., 2021. Remediation of water from per-/poly-fluoroalkyl substances (PFAS) – challenges and perspectives. *J. Environ. Chem. Eng.* 9, 105784.
- Ghosh, B., Ghosh, A., Bindal, R., 2019. Influence of metal salts in reaction medium on performance enhancement of novel aliphatic–aromatic-based polyamide thin-film composite osmosis membranes. *Separ. Sci. Technol.* 54, 1363–1375.
- Ghosh, K., Schnitzer, M., 1980. Macromolecular structures of humic substances. *Soil Sci.* 129, 266–276.
- Goh, P.S., Ismail, A.F., 2020. Chemically functionalized polyamide thin film composite membranes: the art of chemistry. *Desalination* 495, 114655.
- Gohil, J.M., Suresh, A.K., 2017. Chlorine attack on reverse osmosis membranes: mechanisms and mitigation strategies. *J. Membr. Sci.* 541, 108–126.
- Gul, A., Hruza, J., Yalcinkaya, F., 2021. Fouling and chemical cleaning of microfiltration membranes: a mini-review. *Polymers* 13, 846.
- Guo, H., Deng, Y., Tao, Z., Yao, Z., Wang, J., Lin, C., Zhang, T., Zhu, B., Tang, C.Y., 2016. Does hydrophilic polydopamine coating enhance membrane rejection of hydrophobic endocrine-disrupting compounds? *Environ. Sci. Technol. Lett.* 3, 332–338.
- Guo, M., Wang, S., Gu, K., Song, X., Zhou, Y., Gao, C., 2019a. Gradient cross-linked structure: towards superior PVA nanofiltration membrane performance. *J. Membr. Sci.* 569, 83–90.
- Guo, Y.-S., Ji, Y.-L., Wu, B., Wang, N.-X., Yin, M.-J., An, Q.-F., Gao, C.-J., 2020a. High-flux zwitterionic nanofiltration membrane constructed by in-situ introduction method for monovalent salt/antibiotics separation. *J. Membr. Sci.* 593, 117441.
- Guo, Y.-S., Mi, Y.-F., Ji, Y.-L., An, Q.-F., Gao, C.-J., 2019b. One-step surface grafting method for preparing zwitterionic nanofiltration membrane via in situ introduction of initiator in interfacial polymerization. *ACS Appl. Polymer Mater.* 1, 1022–1033.
- Guo, Y.-S., Weng, X.-D., Wu, B., Mi, Y.-F., Zhu, B.-K., Ji, Y.-L., An, Q.-F., Gao, C.-J., 2019c. Construction of nonfouling nanofiltration membrane via introducing uniformly tunable zwitterionic layer. *J. Membr. Sci.* 583, 152–162.
- Guo, Y., Li, T.-y., Xiao, K., Wang, X.-m., Xie, Y.F., 2020b. Key foulants and their interactive effect in organic fouling of nanofiltration membranes. *J. Membr. Sci.* 610, 118252.
- Gwon, E.-m., Yu, M.-j., Oh, H.-k., Ylee, Y.-h., 2003. Fouling characteristics of NF and RO operated for removal of dissolved matter from groundwater. *Water Res.* 37, 2989–2997.
- Habib, Z., Khan, S.J., Ahmad, N.M., Shahzad, H.M.A., Jamal, Y., Hashmi, I., 2020. Antibacterial behaviour of surface modified composite polyamide nanofiltration (NF) membrane by immobilizing Ag-doped TiO₂ nanoparticles. *Environ. Technol.* 41, 3657–3669.
- Hadik, P., Szabó, L.P., Nagy, E., Farkas, Z., 2005. Enantioseparation of d,l-lactic acid by membrane techniques. *J. Membr. Sci.* 251, 223–232.
- Han, J.-L., Xia, X., Tao, Y., Yun, H., Hou, Y.-N., Zhao, C.-W., Luo, Q., Cheng, H.-Y., Wang, A.-J., 2016. Shielding membrane surface carboxyl groups by covalent-binding graphene oxide to improve anti-fouling property and the simultaneous promotion of flux. *Water Res.* 102, 619–628.
- Hasan, A., Pandey, L.M., 2015. Polymers, surface-modified polymers, and self assembled monolayers as surface-modifying agents for biomaterials. *Polym.-Plast. Technol. Eng.* 54, 1358–1378.
- He, C., Vidic, R.D., 2016. Application of microfiltration for the treatment of Marcellus Shale flowback water: influence of floc breakage on membrane fouling. *J. Membr. Sci.* 510, 348–354.
- He, L., Dumée, L.F., Feng, C., Velleman, L., Reis, R., She, F., Gao, W., Kong, L., 2015. Promoted water transport across graphene oxide–poly (amide) thin film composite membranes and their antibacterial activity. *Desalination* 365, 126–135.
- He, M., Gao, K., Zhou, L., Jiao, Z., Wu, M., Cao, J., You, X., Cai, Z., Su, Y., Jiang, Z., 2016. Zwitterionic materials for antifouling membrane surface construction. *Acta Biomater.* 40, 142–152.
- Her, N., Amy, G., Jarusutthirak, C., 2000. Seasonal variations of nanofiltration (NF) foulants: identification and control. *Desalination* 132, 143–160.
- Her, N., Amy, G., Park, H.-R., Song, M., 2004. Characterizing algal organic matter (AOM) and evaluating associated NF membrane fouling. *Water Res.* 38, 1427–1438.
- Himstedt, H.H., Du, H., Marshall, K.M., Wickramasinghe, S.R., Qian, X., 2013. pH responsive nanofiltration membranes for sugar separations. *Ind. Eng. Chem. Res.* 52, 9259–9269.
- Himstedt, H.H., Marshall, K.M., Wickramasinghe, S.R., 2011. pH-responsive nanofiltration membranes by surface modification. *J. Membr. Sci.* 366, 373–381.
- Ho, K.C., Teow, Y.H., Mohammad, A.W., Ang, W.L., Lee, P.H., 2018. Development of graphene oxide (GO)/multi-walled carbon nanotubes (MWCNTs) nanocomposite conductive membranes for electrically enhanced fouling mitigation. *J. Membr. Sci.* 552, 189–201.
- Hoffman, J.R., Phillip, W.A., 2020. Dual-functional nanofiltration membranes exhibit multifaceted ion rejection and antifouling performance. *ACS Appl. Mater. Interfaces* 12, 19944–19954.
- Hong, S., Elimelech, M., 1997. Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *J. Membr. Sci.* 132, 159–181.
- Huang, J., Luo, J., Chen, X., Feng, S., Wan, Y., 2020. How do chemical cleaning agents act on polyamide nanofiltration membrane and fouling layer? *Ind. Eng. Chem. Res.* 59, 17653–17670.
- Jamil, S., Loganathan, P., Khan, S.J., McDonald, J.A., Kandasamy, J., Vigneswaran, S., 2021. Enhanced nanofiltration rejection of inorganic and organic compounds from a wastewater-reclamation plant's micro-filtered water using adsorption pre-treatment. *Separ. Purif. Technol.* 260, 118207.
- Jarusutthirak, C., Mattaraj, S., Jiratananon, R., 2007. Factors affecting nanofiltration performances in natural organic matter rejection and flux decline. *Separ. Purif. Technol.* 58, 68–75.
- Jhaveri, J.H., Murthy, Z., 2016. A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes. *Desalination* 379, 137–154.
- Jiang, J., Zhu, L., Zhu, L., Zhang, H., Zhu, B., Xu, Y., 2013. Antifouling and antimicrobial polymer membranes based on bioinspired polydopamine and strong hydrogen-bonded poly(N-vinyl pyrrolidone). *ACS Appl. Mater. Interfaces* 5, 12895–12904.
- Jiang, S., Li, Y., Ladewig, B.P., 2017. A review of reverse osmosis membrane fouling and control strategies. *Sci. Total Environ.* 595, 567–583.
- Joseph, L., Jun, B.-M., Flora, J.R.V., Park, C.M., Yoon, Y., 2019. Removal of heavy metals from water sources in the developing world using low-cost materials: a review. *Chemosphere* 229, 142–159.
- Jun, B.-M., Kim, S.H., Kwak, S.K., Kwon, Y.-N., 2018. Effect of acidic aqueous solution on chemical and physical properties of polyamide NF membranes. *Appl. Surf. Sci.* 444, 387–398.
- Jun, B.-M., Lee, H.K., Park, Y.-I., Kwon, Y.-N., 2019. Degradation of full aromatic polyamide NF membrane by sulfuric acid and hydrogen halides: change of the surface/permeability properties. *Polym. Degrad. Stabil.* 162, 1–11.
- Kahrizi, M., Gonzales, R.R., Kong, L., Matsuyama, H., Lu, P., Lin, J., Zhao, S., 2022. Significant roles of substrate properties in forward osmosis membrane performance: a review. *Desalination* 528, 115615.
- Kallioinen, M., Sainio, T., Lahti, J., Pihlajamäki, A., Koivikko, H., Mattila, J., Mänttari, M., 2016. Effect of extended exposure to alkaline cleaning chemicals on performance of polyamide (PA) nanofiltration membranes. *Separ. Purif. Technol.* 158, 115–123.
- Kamrani, M., Akbari, A., Yunesnia lehi, A., 2018. Chitosan-modified acrylic nanofiltration membrane for efficient removal of pharmaceutical compounds. *J. Environ. Chem. Eng.* 6, 583–587.
- Kang, G., Liu, M., Lin, B., Cao, Y., Yuan, Q., 2007. A novel method of surface modification on thin-film composite reverse osmosis membrane by grafting poly (ethylene glycol). *Polymer* 48, 1165–1170.
- Karimnezhad, H., Navarchian, A.H., Tavakoli Gheini, T., Zinadini, S., 2019. Incorporation of iron oxyhydroxide nanoparticles in polyacrylonitrile nanofiltration membrane for improving water permeability and antifouling property. *React. Funct. Polym.* 135, 77–93.
- Karkhanechi, H., Takagi, R., Matsuyama, H., 2014. Biofouling resistance of reverse osmosis membrane modified with polydopamine. *Desalination* 336, 87–96.
- Kasemset, S., Lee, A., Miller, D.J., Freeman, B.D., Sharma, M.M., 2013. Effect of polydopamine deposition conditions on fouling resistance, physical properties, and permeation properties of reverse osmosis membranes in oil/water separation. *J. Membr. Sci.* 425–426, 208–216.
- Katsanou, K., Karapanagioti, H.K., 2019. Surface water and groundwater sources for drinking water. In: Gil, A., Galeano, L.A., Vicente, M.A. (Eds.), *Applications of Advanced Oxidation Processes (AOPs) in Drinking Water Treatment*. Springer International Publishing, Cham, pp. 1–19.
- Khan, S.J., Deere, D., Leusch, F.D.L., Humpage, A., Jenkins, M., Cunliffe, D., 2015. Extreme weather events: should drinking water quality management systems adapt to changing risk profiles? *Water Res.* 85, 124–136.
- Khoo, Y.S., Goh, P.S., Lau, W.J., Ismail, A.F., Abdullah, M.S., Mohd Ghazali, N.H., Yahaya, N.K.E.M., Hashim, N., Othman, A.R., Mohammed, A., Kerisnan, N.D.A.P., Mohamed Yusoff, M.A., Fazlin Hashim, N.H., Karim, J., Abdullah, N.S., 2022. Removal of emerging organic micropollutants via modified-reverse osmosis/nanofiltration membranes: a review. *Chemosphere* 305, 135151.
- Khoo, Y.S., Lau, W.J., Liang, Y.Y., Yusof, N., Fauzi Ismail, A., 2021. Surface modification of PA layer of TFC membranes: does it effective for performance improvement? *J. Ind. Eng. Chem.* 102, 271–292.
- Kilduff, J.E., Mattaraj, S., Belfort, G., 2004. Flux decline during nanofiltration of naturally-occurring dissolved organic matter: effects of osmotic pressure, membrane permeability, and cake formation. *J. Membr. Sci.* 239, 39–53.
- Kim, S., Muñoz-Sennache, J.C., Jun, B.-M., Park, C.M., Jang, A., Yu, M., Hernández-Maldonado, A.J., Yoon, Y., 2020. A metal organic framework-ultrafiltration hybrid system for removing selected pharmaceuticals and natural organic matter. *Chem. Eng. J.* 382, 122920.
- Kimura, K., Ando, N., 2016. Maximizing biopolymer removal by coagulation for mitigation of fouling in the following membrane process. *Separ. Purif. Technol.* 163, 8–14.
- Kong, Q., Xu, H., Liu, C., Yang, G., Ding, M., Yang, W., Lin, T., Chen, W., Gray, S., Xie, Z., 2020. Fabrication of high performance TFN membrane containing NH₂-SWCNTs via interfacial regulation. *RSC Adv.* 10, 25186–25199.
- Kristiana, I., Liew, D., Henderson, R.K., Joll, C.A., Linge, K.L., 2017. Formation and control of nitrogenous DBPs from Western Australian source waters: investigating the impacts of high nitrogen and bromide concentrations. *J. Environ. Sci.* 58, 102–115.
- Kumar, P., Mishra, V., Yadav, S., Yadav, A., Garg, S., Poria, P., Farooqi, F., Dumée, L.F., Sharma, R.S., 2022. Heavy metal pollution and risks in a highly polluted and populated Indian river-city pair using the systems approach. *Environ. Sci. Pollut. Control Ser.* 29, 60212–60231.
- Kwon, B., Lee, S., Cho, J., Ahn, H., Lee, D., Shin, H.S., 2005. Biodegradability, DBP formation, and membrane fouling potential of natural organic matter: characterization and controllability. *Environ. Sci. Technol.* 39, 732–739.
- Lamsal, R., Harroun, S.G., Brosseau, C.L., Gagnon, G.A., 2012. Use of surface enhanced Raman spectroscopy for studying fouling on nanofiltration membrane. *Separ. Purif. Technol.* 96, 7–11.

- Lan, Y., Hiebner, D.W., Casey, E., 2021. Self-assembly and regeneration strategy for mitigation of membrane biofouling by the exploitation of enzymatic nanoparticles. *Chem. Eng. J.* 412, 128666.
- Lau, S.K., Yong, W.F., 2021. Recent progress of zwitterionic materials as antifouling membranes for ultrafiltration, nanofiltration, and reverse osmosis. *ACS Appl. Polymer Mater.* 3, 4390–4412.
- Lee, H., Amy, G., Cho, J., Yoon, Y., Moon, S.-H., Kim, I.S., 2001. Cleaning strategies for flux recovery of an ultrafiltration membrane fouled by natural organic matter. *Water Res.* 35, 3301–3308.
- Lee, S., Ang, W.S., Elimelech, M., 2006. Fouling of reverse osmosis membranes by hydrophilic organic matter: implications for water reuse. *Desalination* 187, 313–321.
- Lee, S., Elimelech, M., 2006. Relating organic fouling of reverse osmosis membranes to intermolecular adhesion forces. *Environ. Sci. Technol.* 40, 980–987.
- Li, N., Yu, L., Xiao, Z., Jiang, C., Gao, B., Wang, Z., 2020a. Biofouling mitigation effect of thin film nanocomposite membranes immobilized with laponite mediated metal ions. *Desalination* 473, 114162.
- Li, Q., Elimelech, M., 2004. Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms. *Environ. Sci. Technol.* 38, 4683–4693.
- Li, T., Zhang, Y., Gui, B., Gao, K., Zhao, Q., Qu, R., Liu, T., Hoffmann, M., Staaks, C., Dong, B., 2020b. Application of coagulation-ultrafiltration-nanofiltration in a pilot study for Tai Lake water treatment. *Water Environ. Res.* 92, 579–587.
- Li, X., Cao, Y., Kang, G., Yu, H., Jie, X., Yuan, Q., 2014. Surface modification of polyamide nanofiltration membrane by grafting zwitterionic polymers to improve the antifouling property. *J. Appl. Polym. Sci.* 131.
- Li, X., Li, A., Li, Z., Sun, H., Shi, P., Zhou, Q., Shuang, C., 2021. Organic micropollutants and disinfection byproducts removal from drinking water using concurrent anion exchange and chlorination process. *Sci. Total Environ.* 752, 141470.
- Li, X., Zhang, H., Hou, Y., Gao, Y., Li, J., Guo, W., Ngo, H.H., 2015. In situ investigation of combined organic and colloidal fouling for nanofiltration membrane using ultrasonic time domain reflectometry. *Desalination* 362, 43–51.
- Li, Y., Li, M., Xiao, K., Huang, X., 2020c. Reverse osmosis membrane autopsy in coal chemical wastewater treatment: evidences of spatially heterogeneous fouling and organic-inorganic synergistic effect. *J. Clean. Prod.* 246, 118964.
- Li, Y., Yang, S., Zhang, K., Van der Bruggen, B., 2019. Thin film nanocomposite reverse osmosis membrane modified by two dimensional laminar MoS₂ with improved desalination performance and fouling-resistant characteristics. *Desalination* 454, 48–58.
- Lin, D., Tang, X., Xing, J., Zhao, J., Liang, H., Li, G., 2019. Application of peroxymonosulfate-based advanced oxidation process as a novel pretreatment for nanofiltration: comparison with conventional coagulation. *Separ. Purif. Technol.* 224, 255–264.
- Lin, Y.-L., Chiang, P.-C., Chang, E., 2006. Reduction of disinfection by-products precursors by nanofiltration process. *J. Hazard Mater.* 137, 324–331.
- Lin, Y.-L., Chiang, P.-C., Chang, E.E., 2007. Removal of small trihalomethane precursors from aqueous solution by nanofiltration. *J. Hazard Mater.* 146, 20–29.
- Ling, R., Yu, L., Pham, T.P.T., Shao, J., Chen, J.P., Reinhard, M., 2017. The tolerance of a thin-film composite polyamide reverse osmosis membrane to hydrogen peroxide exposure. *J. Membr. Sci.* 524, 529–536.
- Liu, B.-L., Chai, W.S., Show, P.L., Chen, J.-Y., Chang, Y.-K., 2020. Evaluation of dynamic binding performance of C-phycoerythrin and allophycocyanin in *Spirulina platensis* algae by aminated polyacrylonitrile nanofiber membrane. *Biochem. Eng. J.* 161, 107686.
- Liu, C., Lee, J., Small, C., Ma, J., Elimelech, M., 2017a. Comparison of organic fouling resistance of thin-film composite membranes modified by hydrophilic silica nanoparticles and zwitterionic polymer brushes. *J. Membr. Sci.* 544, 135–142.
- Liu, M., Chen, Q., Lu, K., Huang, W., Lü, Z., Zhou, C., Yu, S., Gao, C., 2017b. High efficient removal of dyes from aqueous solution through nanofiltration using diethanolamine-modified polyamide thin-film composite membrane. *Separ. Purif. Technol.* 173, 135–143.
- Liu, M., Chen, Q., Wang, L., Yu, S., Gao, C., 2015a. Improving fouling resistance and chlorine stability of aromatic polyamide thin-film composite RO membrane by surface grafting of polyvinyl alcohol (PVA). *Desalination* 367, 11–20.
- Liu, S., Fang, F., Wu, J., Zhang, K., 2015b. The anti-biofouling properties of thin-film composite nanofiltration membranes grafted with biogenic silver nanoparticles. *Desalination* 375, 121–128.
- Liu, W., Zhao, C., Zhou, S., Liu, B., Cheng, X., Xue, Z., Zhu, T., 2022. Effects of UV/Fe(II)/sulfite pre-treatment on NOM-enhanced Ca²⁺ scaling during nanofiltration treatment: fouling mitigation, mechanisms, and correlation analysis of membrane resistance. *Water Res.* 223, 119025.
- Loganathan, P., Gradziński, M., Bustamante, H., Vigneswaran, S., 2020. Progress, challenges, and opportunities in enhancing NOM flocculation using chemically modified chitosan: a review towards future development. *Environ. Sci.: Water Res. Technol.* 6, 45–61.
- Loganathan, P., Kandasamy, J., Jamil, S., Ratnaweera, H., Vigneswaran, S., 2022. Ozonation/adsorption hybrid treatment system for improved removal of natural organic matter and organic micropollutants from water – a mini review and future perspectives. *Chemosphere* 296, 133961.
- López-Ortiz, C.M., Sentana-Gadea, I., Varó-Galvañ, P., Maestre-Pérez, S.E., Prats-Rico, D., 2018. The use of combined treatments for reducing parabens in surface waters: ion-exchange resin and nanofiltration. *Sci. Total Environ.* 639, 228–236.
- Luo, J., Guo, S., Qiang, X., Hang, X., Chen, X., Wan, Y., 2019. Sustainable utilization of cane molasses by an integrated separation process: interplay between adsorption and nanofiltration. *Separ. Purif. Technol.* 219, 16–24.
- Luo, J., Guo, S., Wu, Y., Wan, Y., 2018. Separation of sucrose and reducing sugar in cane molasses by nanofiltration. *Food Bioprocess Technol.* 11, 913–925.
- Luo, J., Wan, Y., 2013. Effects of pH and salt on nanofiltration—a critical review. *J. Membr. Sci.* 438, 18–28.
- Ma, B., Wu, G., Li, W., Miao, R., Li, X., Wang, P., 2019a. Roles of membrane-foulant and inter/intrafoulant species interaction forces in combined fouling of an ultrafiltration membrane. *Sci. Total Environ.* 652, 19–26.
- Ma, M.-Q., Zhang, C., Zhu, C.-Y., Huang, S., Yang, J., Xu, Z.-K., 2019b. Nanocomposite membranes embedded with functionalized MoS₂ nanosheets for enhanced interfacial compatibility and nanofiltration performance. *J. Membr. Sci.* 591, 117316.
- Mahlangu, O.T., Mamba, B.B., Verliefde, A.R., 2020. Effect of multivalent cations on membrane-foulant and foulant-foulant interactions controlling fouling of nanofiltration membranes. *Polym. Adv. Technol.* 31, 2588–2600.
- Mallakpour, S., Azadi, E., 2022. Nanofiltration membranes for food and pharmaceutical industries. *Emergent Mater.* 5, 1329–1343.
- Mallya, D.S., Dumeé, L.F., Muthukumar, S., Lei, W.W., Baskaran, K., 2021. 2D nanosheet enabled thin film nanocomposite membranes for freshwater production – a review. *Mater. Adv.* 2, 3519–3537.
- Mallya, D.S., Yang, G., Lei, W., Muthukumar, S., Baskaran, K., 2022. Functionalized MoS₂ Nanosheets Enabled Nanofiltration Membrane with Enhanced Permeance and Fouling Resistance. *Environmental Technology & Innovation*, 102719.
- Mariam, T., Nghiem, L.D., 2010. Landfill leachate treatment using hybrid coagulation-nanofiltration processes. *Desalination* 250, 677–681.
- Matilainen, A., Vepsäläinen, M., Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment: a review. *Adv. Colloid Interface Sci.* 159, 189–197.
- Matin, A., Shafi, H., Wang, M., Khan, Z., Gleason, K., Rahman, F., 2016. Reverse osmosis membranes surface-modified using an initiated chemical vapor deposition technique show resistance to alginate fouling under cross-flow conditions: filtration & subsequent characterization. *Desalination* 379, 108–117.
- McCloskey, B.D., Park, H.B., Ju, H., Rowe, B.W., Miller, D.J., Freeman, B.D., 2012. A bioinspired surface fouling-resistant surface modification for water purification membranes. *J. Membr. Sci.* 413–414, 82–90.
- Metsämuuronen, S., Sillanpää, M., Bhatnagar, A., Mänttäri, M., 2014. Natural organic matter removal from drinking water by membrane technology. *Separ. Purif. Rev.* 43, 1–61.
- Meylan, S., Hammes, F., Traber, J., Salhi, E., von Gunten, U., Pronk, W., 2007. Permeability of low molecular weight organics through nanofiltration membranes. *Water Res.* 41, 3968–3976.
- Mi, Y.-F., Zhao, F.-Y., Guo, Y.-S., Weng, X.-D., Ye, C.-C., An, Q.-F., 2017. Constructing zwitterionic surface of nanofiltration membrane for high flux and antifouling performance. *J. Membr. Sci.* 541, 29–38.
- Mi, Y.-F., Zhao, Q., Ji, Y.-L., An, Q.-F., Gao, C.-J., 2015. A novel route for surface zwitterionic functionalization of polyamide nanofiltration membranes with improved performance. *J. Membr. Sci.* 490, 311–320.
- Mi, Z., Liu, Z., Jin, S., Zhang, D., Wang, D., 2021. Positively charged nanofiltration membrane prepared by polydopamine deposition followed by crosslinking for high efficiency cation separation. *Polym. Test.* 93, 107000.
- Miao, R., Li, X., Wu, Y., Wang, P., Wang, L., Wu, G., Wang, J., Lv, Y., Liu, T., 2018. A comparison of the roles of Ca²⁺ and Mg²⁺ on membrane fouling with humic acid: are there any differences or similarities? *J. Membr. Sci.* 545, 81–87.
- Miller, D.J., Kasemset, S., Paul, D.R., Freeman, B.D., 2014. Comparison of membrane fouling at constant flux and constant transmembrane pressure conditions. *J. Membr. Sci.* 454, 505–515.
- Mustafa, G., Wynn, K., Buekenhoudt, A., Meynen, V., 2016. New insights into the fouling mechanism of dissolved organic matter applying nanofiltration membranes with a variety of surface chemistries. *Water Res.* 93, 195–204.
- Muthukumar, S., Jegatheesan, J.V., Baskaran, K., 2014. Comparison of fouling mechanisms in low-pressure membrane (MF/UF) filtration of secondary effluent. *Desalination Water Treat.* 52, 650–662.
- Ndiweni, S.N., Chys, M., Chaukura, N., Van Hulle, S.W., Nkambule, T.T., 2019. Assessing the impact of environmental activities on natural organic matter in South Africa and Belgium. *Environ. Technol.* 40, 1756–1768.
- Ng, Z.C., Lau, W.J., Ismail, A.F., 2020. GO/PVA-integrated TFN RO membrane: exploring the effect of orientation switching between PA and GO/PVA and evaluating the GO loading impact. *Desalination* 496, 114538.
- Nguyen, M.D., Adhikari, S., Mallya, D.S., Thomas, M., Surapaneni, A., Moon, E.M., Milne, N.A., 2022a. Reuse of aluminium-based water treatment sludge for phosphorus adsorption: evaluating the factors affecting and correlation between adsorption and sludge properties. *Environ. Technol. Innovat.* 27, 102717.
- Nguyen, M.D., Thomas, M., Surapaneni, A., Moon, E.M., Milne, N.A., 2022b. Beneficial reuse of water treatment sludge in the context of circular economy. *Environ. Technol. Innovat.* 28, 102651.
- Nikolaeva, D., Langner, C., Ghanem, A., Rehim, M.A., Voit, B., Meier-Haack, J., 2015. Hydrogel surface modification of reverse osmosis membranes. *J. Membr. Sci.* 476, 264–276.
- Nilson, J.A., DiGiano, F.A., 1996. Influence of NOM composition on nanofiltration. *J. - Am. Water Works Assoc.* 88, 53–66.
- Otero-Fernández, A., Díaz, P., Otero, J.A., Ibáñez, R., Maroto-Valiente, A., Palacio, L., Prádanos, P., Carmona, F.J., Hernández, A., 2020. Morphological, chemical and electrical characterization of a family of commercial nanofiltration polyvinyl alcohol coated polyepiperazineamide membranes. *Eur. Polym. J.* 126, 109544.
- Owusu-Agyeman, I., Reinwald, M., Jeihanipour, A., Schäfer, A.I., 2019. Removal of fluoride and natural organic matter from natural tropical brackish waters by nanofiltration/reverse osmosis with varying water chemistry. *Chemosphere* 217, 47–58.

- Pal, P., Sardar, M., Pal, M., Chakraborty, S., Nayak, J., 2019. Modelling forward osmosis-nanofiltration integrated process for treatment and recirculation of leather industry wastewater. *Comput. Chem. Eng.* 127, 99–110.
- Park, M., Anumol, T., Simon, J., Zraick, F., Snyder, S.A., 2017. Pre-ozonation for high recovery of nanofiltration (NF) membrane system: membrane fouling reduction and trace organic compound attenuation. *J. Membr. Sci.* 523, 255–263.
- Park, S.-H., Alammari, A., Fulop, Z., Pulido, B.A., Nunes, S.P., Szekely, G., 2021a. Hydrophobic thin film composite nanofiltration membranes derived solely from sustainable sources. *Green Chem.* 23, 1175–1184.
- Park, S., Baek, S.-S., Pyo, J., Pachepsky, Y., Park, J., Cho, K.H., 2019. Deep neural networks for modeling fouling growth and flux decline during NF/RO membrane filtration. *J. Membr. Sci.* 587, 117164.
- Park, S., Jeong, Y.D., Lee, J.H., Kim, J., Jeong, K., Cho, K.H., 2021b. 3D printed honeycomb-shaped feed channel spacer for membrane fouling mitigation in nanofiltration. *J. Membr. Sci.* 620, 118665.
- Park, S., Kim, S., Park, J., Cho, K.H., 2020. Real-time monitoring the spatial distribution of organic fouling using fluorescence imaging technique. *J. Membr. Sci.* 597, 117778.
- Peng, L.E., Yang, Z., Long, L., Zhou, S., Guo, H., Tang, C.Y., 2022. A critical review on porous substrates of TFC polyamide membranes: mechanisms, membrane performances, and future perspectives. *J. Membr. Sci.* 641, 119871.
- Peters, C.D., Rantissi, T., Gitis, V., Hankins, N.P., 2021. Retention of natural organic matter by ultrafiltration and the mitigation of membrane fouling through pre-treatment, membrane enhancement, and cleaning - a review. *J. Water Proc. Eng.* 44, 102374.
- Peydayesh, M., Mohammadi, T., Nikouzad, S.K., 2020. A positively charged composite loose nanofiltration membrane for water purification from heavy metals. *J. Membr. Sci.* 611, 118205.
- Pichardo-Romero, D., Garcia-Arce, Z.P., Zavala-Ramírez, A., Castro-Muñoz, R., 2020. Current advances in biofouling mitigation in membranes for water treatment: an overview. *Processes* 8, 182.
- Plourde-Lescelleur, F., Papineau, I., Carrière, A., Gadbois, A., Barbeau, B., 2015. NOM removal: evaluating five process alternatives to alum coagulation. *J. Water Supply Res. Technol. - Aqua* 64, 278–289.
- Pruksasri, S., Nguyen, T.-H., Haltrich, D., Novalin, S., 2015. Fractionation of a galactooligosaccharides solution at low and high temperature using nanofiltration. *Separ. Purif. Technol.* 151, 124–130.
- Purusothaman, M., Arvind, V., Saikia, K., Vaidyanathan, V.K., 2022. Fabrication of highly permeable and anti-fouling performance of Poly(ether ether sulfone) nanofiltration membranes modified with zinc oxide nanoparticles. *Chemosphere* 286, 131616.
- Qiu, Z.-L., Yu, W.-H., Shen, Y.-J., Zhu, B.-K., Fang, L.-F., 2021. Cationic hyperbranched poly(amido-amine) engineered nanofiltration membrane for molecular separation. *J. Membr. Sci.* 629, 119275.
- Rahaman, M.S., Thérien-Aubin, H., Ben-Sasson, M., Ober, C.K., Nielsen, M., Elimelech, M., 2014. Control of biofouling on reverse osmosis polyamide membranes modified with biocidal nanoparticles and antifouling polymer brushes. *J. Mater. Chem. B* 2, 1724–1732.
- Reis, R., Duke, M., Merenda, A., Winther-Jensen, B., Puskar, L., Tobin, M.J., Orbell, J.D., Dumée, L.F., 2017a. Customizing the surface charge of thin-film composite membranes by surface plasma thin film polymerization. *J. Membr. Sci.* 537, 1–10.
- Reis, R., Duke, M.C., Tardy, B.L., Oldfield, D., Dagastine, R.R., Orbell, J.D., Dumée, L.F., 2017b. Charge tunable thin-film composite membranes by gamma-ray triggered surface polymerization. *Sci. Rep.* 7, 1–10.
- Ruan, H., Li, B., Ji, J., Sotto, A., Van der Bruggen, B., Shen, J., Gao, C., 2018. Preparation and characterization of an amphiphilic polyamide nanofiltration membrane with improved antifouling properties by two-step surface modification method. *RSC Adv.* 8, 13353–13363.
- Rudolph, G., Virtanen, T., Ferrando, M., Güell, C., Lipnizki, F., Kallioinen, M., 2019. A review of in situ real-time monitoring techniques for membrane fouling in the biotechnology, biorefinery and food sectors. *J. Membr. Sci.* 588, 117221.
- Santschi, P., Xu, C., Zhang, S., Schwehr, K., Lin, P., Yeager, C., Kaplan, D., 2017. Recent advances in the detection of specific natural organic compounds as carriers for radionuclides in soil and water environments, with examples of radioiodine and plutonium. *J. Environ. Radioact.* 171, 226–233.
- Sarkar, B., Venkateswralu, N., Rao, R.N., Bhattacharjee, C., Kale, V., 2007. Treatment of pesticide contaminated surface water for production of potable water by a coagulation-adsorption-nanofiltration approach. *Desalination* 212, 129–140.
- Schäfer, A., Fane, A.G., Waite, T., 2000. Fouling effects on rejection in the membrane filtration of natural waters. *Desalination* 131, 215–224.
- Schorf, N., Schuhmann, S., Arndt, F., Schütz, S., Guthausen, G., Nirschl, H., 2018. MRI investigations of filtration: fouling and cleaning processes. *Microporous Mesoporous Mater.* 269, 60–64.
- Schulz, M., Soltani, A., Zheng, X., Ernst, M., 2016. Effect of inorganic colloidal water constituents on combined low-pressure membrane fouling with natural organic matter (NOM). *J. Membr. Sci.* 507, 154–164.
- Seidel, A., Elimelech, M., 2002. Coupling between chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes: implications for fouling control. *J. Membr. Sci.* 203, 245–255.
- Sengur-Tasdemir, R., Urper-Bayram, G.M., Turken, T., Ates-Genceli, E., Tarabara, V.V., Koyuncu, I., 2021. Hollow fiber nanofiltration membranes for surface water treatment: performance evaluation at the pilot scale. *J. Water Proc. Eng.* 42, 102100.
- Shahkarampour, N., Tran, T.N., Ramanan, S., Lin, H., 2017. Membranes with surface-enhanced antifouling properties for water purification. *Membranes* 7.
- Shan, L., Fan, H., Guo, H., Ji, S., Zhang, G., 2016. Natural organic matter fouling behaviors on superwetting nanofiltration membranes. *Water Res.* 93, 121–132.
- Shao, J., Hou, J., Song, H., 2011. Comparison of humic acid rejection and flux decline during filtration with negatively charged and uncharged ultrafiltration membranes. *Water Res.* 45, 473–482.
- Shao, S., Fu, W., Li, X., Shi, D., Jiang, Y., Li, J., Gong, T., Li, X., 2019. Membrane fouling by the aggregations formed from oppositely charged organic foulants. *Water Res.* 159, 95–101.
- Sharma, V.K., Ma, X., Guo, B., Zhang, K., 2021. Environmental factors-mediated behavior of microplastics and nanoplastics in water: a review. *Chemosphere* 271, 129597.
- Shim, J., Park, S., Cho, K.H., 2021. Deep learning model for simulating influence of natural organic matter in nanofiltration. *Water Res.* 197, 117070.
- Shin, M.G., Kwon, S.J., Park, H., Park, Y.-I., Lee, J.-H., 2020. High-performance and acid-resistant nanofiltration membranes prepared by solvent activation on polyamide reverse osmosis membranes. *J. Membr. Sci.* 595, 117590.
- Shon, H., Phuntsho, S., Chaudhary, D., Vigneswaran, S., Cho, J., 2013. Nanofiltration for water and wastewater treatment-a mini review. *Drink. Water Eng. Sci.* 6, 47–53.
- Siew, Y.W., Zedda, K.L., Velizarov, S., 2020. Nanofiltration of simulated acid mine drainage: effect of pH and membrane charge. *Appl. Sci.* 10, 400.
- Sillanpää, M., 2015. *Natural Organic Matter in Water: Characterization and Treatment Methods*. Butterworth-Heinemann, Oxford.
- Sillanpää, M., 2014. *Natural Organic Matter in Water: Characterization and Treatment Methods*. Butterworth-Heinemann.
- Sillanpää, M., Ncibi, M.C., Matilainen, A., 2018a. Advanced oxidation processes for the removal of natural organic matter from drinking water sources: a comprehensive review. *J. Environ. Manag.* 208, 56–76.
- Sillanpää, M., Ncibi, M.C., Matilainen, A., Vepsäläinen, M., 2018b. Removal of natural organic matter in drinking water treatment by coagulation: a comprehensive review. *Chemosphere* 190, 54–71.
- Song, H., Shao, J., He, Y., Hou, J., Chao, W., 2011. Natural organic matter removal and flux decline with charged ultrafiltration and nanofiltration membranes. *J. Membr. Sci.* 376, 179–187.
- Song, Y., Li, X., Li, C., Li, J., Dong, Z., Zhang, M., Qi, P., Bai, X., Jiang, K., 2020. Exploring and comparing the roles of Ca²⁺ and Mg²⁺ in small-sized natural organics-induced charged nanofiltration membrane fouling. *Separ. Purif. Technol.* 251, 117415.
- Song, Y., Li, X., Sun, Y., Wang, Y., Bai, X., Zhang, X., Zhang, N., Jiang, K., 2021. Nanofiltration fouling behaviors with different membrane materials induced by residual natural organics left over after ultrafiltration unit encountered with divalent cations. *Chem. Eng. J.* 413, 127398.
- Stolov, M., Freger, V., 2019. Degradation of polyamide membranes exposed to chlorine: an impedance spectroscopy study. *Environ. Sci. Technol.* 53, 2618–2625.
- Su, X., Song, Y., Li, T., Gao, C., 2017. Effect of feed water characteristics on nanofiltration separating performance for brackish water treatment in the Huanghuai region of China. *J. Water Proc. Eng.* 19, 147–155.
- Su, Z., Liu, T., Li, X., Graham, N., Yu, W., 2021a. Beneficial impacts of natural biopolymers during surface water purification by membrane nanofiltration. *Water Res.* 201, 117330.
- Su, Z., Liu, T., Li, X., Graham, N.J., Yu, W., 2020. Tracking metal ion-induced organic membrane fouling in nanofiltration by adopting spectroscopic methods: observations and predictions. *Sci. Total Environ.* 708, 135051.
- Su, Z., Yu, W., Liu, T., Li, X., Graham, N.J.D., Lu, Y., Wiesner, M.R., 2021b. Discovery of welcome biopolymers in surface water: improvements in drinking water production. *Environ. Sci. Technol.* 55, 2076–2086.
- Suzuki, T., Tanaka, R., Tahara, M., Isamu, Y., Niinae, M., Lin, L., Wang, J., Luh, J., Coronell, O., 2016. Relationship between performance deterioration of a polyamide reverse osmosis membrane used in a seawater desalination plant and changes in its physicochemical properties. *Water Res.* 100, 326–336.
- Tang, C.Y., Kwon, Y.-N., Leckie, J.O., 2009. Effect of membrane chemistry and coating layer on physicochemical properties of thin film composite polyamide RO and NF membranes: II. Membrane physicochemical properties and their dependence on polyamide and coating layers. *Desalination* 242, 168–182.
- Tavangar, T., Jalali, K., Alaei Shahmirzadi, M.A., Karimi, M., 2019. Toward real textile wastewater treatment: membrane fouling control and effective fractionation of dyes/inorganic salts using a hybrid electrocoagulation – nanofiltration process. *Separ. Purif. Technol.* 216, 115–125.
- Teixeira, M.R., Sousa, V.S., 2013. Fouling of nanofiltration membrane: effects of NOM molecular weight and microcystins. *Desalination* 315, 149–155.
- Teychene, B., Collet, G., Gallard, H., 2016. Modeling of combined particles and natural organic matter fouling of ultrafiltration membrane. *J. Membr. Sci.* 505, 185–193.
- Tin, M.M.M., Anioke, G., Nakagoe, O., Tanabe, S., Kodamatani, H., Nghiem, L.D., Fujioka, T., 2017. Membrane fouling, chemical cleaning and separation performance assessment of a chlorine-resistant nanofiltration membrane for water recycling applications. *Separ. Purif. Technol.* 189, 170–175.
- Tomaszewski, J.E., Schwarzenbach, R.P., Sander, M., 2011. Protein encapsulation by humic substances. *Environ. Sci. Technol.* 45, 6003–6010.
- Tshindane, P., Mamba, P.P., Moss, L., Swana, U.U., Moyo, W., Mota, M.M., Chaukura, N., Mamba, B.B., Nkambule, T.T., 2019. The occurrence of natural organic matter in South African water treatment plants. *J. Water Proc. Eng.* 31, 100809.
- Van der Bruggen, B., Schaep, J., Wilms, D., Vandecasteele, C., 1999. Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J. Membr. Sci.* 156, 29–41.
- Van Wagner, E.M., Sagle, A.C., Sharma, M.M., La, Y.-H., Freeman, B.D., 2011. Surface modification of commercial polyamide desalination membranes using poly(ethylene glycol) diglycidyl ether to enhance membrane fouling resistance. *J. Membr. Sci.* 367, 273–287.

- Vanangamudi, A., Dumée, L.F., Duke, M.C., Yang, X., 2018a. Dual functional ultrafiltration membranes with enzymatic digestion and thermo-responsivity for protein self-cleaning. *Membranes* 8, 85.
- Vanangamudi, A., Saeki, D., Dumée, L.F., Duke, M., Vasiljevic, T., Matsuyama, H., Yang, X., 2018b. Surface-engineered biocatalytic composite membranes for reduced protein fouling and self-cleaning. *ACS Appl. Mater. Interfaces* 10, 27477–27487.
- Verliefde, A.R., Cornelissen, E., Heijman, S., Verberk, J., Amy, G., Van der Bruggen, B., Van Dijk, J., 2008. The role of electrostatic interactions on the rejection of organic solutes in aqueous solutions with nanofiltration. *J. Membr. Sci.* 322, 52–66.
- Wadekar, S.S., Wang, Y., Lokare, O.R., Vidic, R.D., 2019. Influence of chemical cleaning on physicochemical characteristics and ion rejection by thin film composite nanofiltration membranes. *Environ. Sci. Technol.* 53, 10166–10176.
- Wang, J., Liu, X., 2021. Forward osmosis technology for water treatment: recent advances and future perspectives. *J. Clean. Prod.* 280, 124354.
- Wang, J., Mo, Y., Mahendra, S., Hoek, E.M., 2014. Effects of water chemistry on structure and performance of polyamide composite membranes. *J. Membr. Sci.* 452, 415–425.
- Wang, J., Wang, L., Xu, C., Zhi, R., Miao, R., Liang, T., Yue, X., Lv, Y., Liu, T., 2018. Perfluorooctane sulfonate and perfluorobutane sulfonate removal from water by nanofiltration membrane: the roles of solute concentration, ionic strength, and macromolecular organic foulants. *Chem. Eng. J.* 332, 787–797.
- Wang, J., Zhang, S., Wu, P., Shi, W., Wang, Z., Hu, Y., 2019. In situ surface modification of thin-film composite polyamide membrane with zwitterions for enhanced chlorine resistance and transport properties. *ACS Appl. Mater. Interfaces* 11, 12043–12052.
- Wang, K., Wang, X., Januszewski, B., Liu, Y., Li, D., Fu, R., Elimelech, M., Huang, X., 2022. Tailored design of nanofiltration membranes for water treatment based on synthesis–property–performance relationships. *Chem. Soc. Rev.* 51, 672–719.
- Wang, R., Liang, D., Liu, X., Fan, W., Meng, S., Cai, W., 2020. Effect of magnesium ion on polysaccharide fouling. *Chem. Eng. J.* 379, 122351.
- Wang, T., Yen, Y.-J., Hsieh, Y.-K., Wang, J., 2017a. Size effect of calcium-humic acid non-rigid complexes on the fouling behaviors in nanofiltration: an LA-ICP-MS study. *Colloids Surf. A Physicochem. Eng. Asp.* 513, 335–347.
- Wang, Y.-N., Tang, C.Y., 2011. Fouling of nanofiltration, reverse osmosis, and ultrafiltration membranes by protein mixtures: the role of inter-foulant-species interaction. *Environ. Sci. Technol.* 45, 6373–6379.
- Wang, Y., Wang, Z., Han, X., Wang, J., Wang, S., 2017b. Improved flux and anti-biofouling performances of reverse osmosis membrane via surface layer-by-layer assembly. *J. Membr. Sci.* 539, 403–411.
- Wang, Y., Zucker, I., Boo, C., Elimelech, M., 2021. Removal of emerging wastewater organic contaminants by polyelectrolyte multilayer nanofiltration membranes with tailored selectivity. *ACS ES&T Engineering* 1, 404–414.
- Wang, Z., Zhao, Y., Wang, J., Wang, S., 2005. Studies on nanofiltration membrane fouling in the treatment of water solutions containing humic acids. *Desalination* 178, 171–178.
- Wawryk, N.J.P., Craven, C.B., Blackstock, L.K.J., Li, X.-F., 2021. New methods for identification of disinfection byproducts of toxicological relevance: progress and future directions. *J. Environ. Sci.* 99, 151–159.
- Wei, X., Kong, X., Yang, J., Zhang, G., Chen, J., Wang, J., 2013. Structure influence of hyperbranched polyester on structure and properties of synthesized nanofiltration membranes. *J. Membr. Sci.* 440, 67–76.
- Werber, J.R., Deshmukh, A., Elimelech, M., 2016. The critical need for increased selectivity, not increased water permeability, for desalination membranes. *Environ. Sci. Technol. Lett.* 3, 112–120.
- Wicakana, F., Fane, A.G., Pongpairaj, P., Field, R., 2012. Microfiltration of algae (*Chlorella sorokiniana*): critical flux, fouling and transmission. *J. Membr. Sci.* 387–388, 83–92.
- Wray, H.E., Andrews, R.C., Bérubé, P.R., 2013. Surface shear stress and membrane fouling when considering natural water matrices. *Desalination* 330, 22–27.
- Wu, J., Jiang, R., Liu, Q., Ouyang, G., 2021. Impact of different modes of adsorption of natural organic matter on the environmental fate of nanoplastics. *Chemosphere* 263, 127967.
- Xu, D., Zheng, J., Zhang, X., Lin, D., Gao, Q., Luo, X., Zhu, X., Li, G., Liang, H., Van der Bruggen, B., 2022a. Mechanistic insights of a thermoresponsive interface for fouling control of thin-film composite nanofiltration membranes. *Environ. Sci. Technol.* 56, 1927–1937.
- Xu, H., Xiao, K., Wang, X., Liang, S., Wei, C., Wen, X., Huang, X., 2020. Outlining the roles of membrane-foulant and foulant-foulant interactions in organic fouling during microfiltration and ultrafiltration: a mini-review. *Front. Chem.* 8, 417.
- Xu, P., Bellona, C., Drewes, J.E., 2010. Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation: membrane autopsy results from pilot-scale investigations. *J. Membr. Sci.* 353, 111–121.
- Xu, S.-J., Shen, Q., Luo, L.-H., Tong, Y.-H., Wu, Y.-Z., Xu, Z.-L., Zhang, H.-Z., 2022b. Surfactants attached thin film composite (TFC) nanofiltration (NF) membrane via intermolecular interaction for heavy metals removal. *J. Membr. Sci.* 642, 119930.
- Yadav, D., Karki, S., Ingole, P.G., 2022. Current advances and opportunities in the development of nanofiltration (NF) membranes in the area of wastewater treatment, water desalination, biotechnological and pharmaceutical applications. *J. Environ. Chem. Eng.* 10, 108109.
- Yamamura, H., Okimoto, K., Kimura, K., Watanabe, Y., 2014. Hydrophilic fraction of natural organic matter causing irreversible fouling of microfiltration and ultrafiltration membranes. *Water Res.* 54, 123–136.
- Yang, Z., Sun, P.-F., Li, X., Gan, B., Wang, L., Song, X., Park, H.-D., Tang, C.Y., 2020. A Critical Review on Thin-Film Nanocomposite Membranes with Interlayered Structure: Mechanisms, Recent Developments, and Environmental Applications. *Environmental Science & Technology*.
- Yi, M., Lau, C.H., Xiong, S., Wei, W., Liao, R., Shen, L., Lu, A., Wang, Y., 2019. Zwitterion–Ag complexes that simultaneously enhance biofouling resistance and silver binding capability of thin film composite membranes. *ACS Appl. Mater. Interfaces* 11, 15698–15708.
- You, X., Teng, J., Chen, Y., Long, Y., Yu, G., Shen, L., Lin, H., 2020. New insights into membrane fouling by alginate: impacts of ionic strength in presence of calcium ions. *Chemosphere* 246, 125801.
- Yu, S., Liu, X., Liu, J., Wu, D., Liu, M., Gao, C., 2011. Surface modification of thin-film composite polyamide reverse osmosis membranes with thermo-responsive polymer (TRP) for improved fouling resistance and cleaning efficiency. *Separ. Purif. Technol.* 76, 283–291.
- Yu, W., Liu, T., Crawshaw, J., Liu, T., Graham, N., 2018. Ultrafiltration and nanofiltration membrane fouling by natural organic matter: mechanisms and mitigation by pre-ozonation and pH. *Water Res.* 139, 353–362.
- Yuan, Z.-y., Li, Y.-f., Li, T.-y., Yao, J.-l., Zhang, J.-f., Wang, X.-m., 2022. Identifying key residual aluminum species responsible for aggravation of nanofiltration membrane fouling in drinking water treatment. *J. Membr. Sci.* 659, 120833.
- Zahid, M., Rashid, A., Akram, S., Rehan, Z., Razzaq, W., 2018. A comprehensive review on polymeric nano-composite membranes for water treatment. *J. Membr. Sci. Technol.* 8, 179–198.
- Zarshenas, K., Dou, H., Habibpour, S., Yu, A., Chen, Z., 2022. Thin film polyamide nanocomposite membrane decorated by polyphenol-assisted Ti3C2Tx MXene nanosheets for reverse osmosis. *ACS Appl. Mater. Interfaces* 14, 1838–1849.
- Zazouli, M.A., Nasser, S., Ulbricht, M., 2010. Fouling effects of humic and alginic acids in nanofiltration and influence of solution composition. *Desalination* 250, 688–692.
- Zhan, Z.-M., Zhang, X., Fang, Y.-X., Tang, Y.-J., Zhu, K.-K., Ma, X.-H., Xu, Z.-L., 2021. Polyamide nanofiltration membranes with enhanced desalination and antifouling performance enabled by surface grafting polyquaternium-7. *Ind. Eng. Chem. Res.* 60, 14297–14306.
- Zhang, C., Ou, Y., Lei, W.-X., Wan, L.S., Ji, J., Xu, Z.K., 2016a. CuSO₄/H₂O₂-Induced rapid deposition of polydopamine coatings with high uniformity and enhanced stability. *Angew Chem. Int. Ed. Engl.* 55, 3054–3057.
- Zhang, J., Northcott, K., Duke, M., Scales, P., Gray, S.R., 2016b. Influence of pre-treatment combinations on RO membrane fouling. *Desalination* 393, 120–126.
- Zhang, J., Zhang, H., Wan, Y., Luo, J., 2022a. Chemoenzymatic cascade reaction for green cleaning of polyamide nanofiltration membrane. *ACS Appl. Mater. Interfaces* 14, 12204–12213.
- Zhang, J., Zhou, F., Li, S., Wan, Y., Luo, J., 2021. Surface functionalization of nanofiltration membrane by catechol-amine codeposition for enhancing antifouling performance. *J. Membr. Sci.* 635, 119451.
- Zhang, R.-X., Braeken, L., Liu, T.-Y., Luis, P., Wang, X.-L., Van der Bruggen, B., 2017. Remarkable anti-fouling performance of TiO₂-modified TFC membranes with mussel-inspired polydopamine binding. *Appl. Sci.* 7, 81.
- Zhang, R., Li, Y., Su, Y., Zhao, X., Liu, Y., Fan, X., Ma, T., Jiang, Z., 2016c. Engineering amphiphilic nanofiltration membrane surfaces with a multi-defense mechanism for improved antifouling performances. *J. Mater. Chem.* 4, 7892–7902.
- Zhang, X., Tian, J., Xu, R., Cheng, X., Zhu, X., Loh, C.Y., Fu, K., Zhang, R., Wu, D., Ren, H., Xie, M., 2022b. In situ chemical modification with zwitterionic copolymers of nanofiltration membranes: cure for the trade-off between filtration and antifouling performance. *ACS Appl. Mater. Interfaces* 14, 28842–28853.
- Zhang, Y., Wan, Y., Shi, Y., Pan, G., Yan, H., Xu, J., Guo, M., Qin, L., Liu, Y., 2016d. Facile modification of thin-film composite nanofiltration membrane with silver nanoparticles for anti-biofouling. *J. Polym. Res.* 23, 105.
- Zhao, C., Tang, C.Y., Li, P., Adrian, P., Hu, G., 2016. Perfluorooctane sulfonate removal by nanofiltration membrane—the effect and interaction of magnesium ion/humic acid. *J. Membr. Sci.* 503, 31–41.
- Zhao, D., Qiu, L., Song, J., Liu, J., Wang, Z., Zhu, Y., Liu, G., 2019a. Efficiencies and mechanisms of chemical cleaning agents for nanofiltration membranes used in produced wastewater desalination. *Sci. Total Environ.* 652, 256–266.
- Zhao, D., Yu, S., 2015. A review of recent advance in fouling mitigation of NF/RO membranes in water treatment: pretreatment, membrane modification, and chemical cleaning. *Desalination Water Treat.* 55, 870–891.
- Zhao, F., Xu, K., Ren, H., Ding, L., Geng, J., Zhang, Y., 2015. Combined effects of organic matter and calcium on biofouling of nanofiltration membranes. *J. Membr. Sci.* 486, 177–188.
- Zhao, G., Hu, R., He, Y., Zhu, H., 2019b. Physically coating nanofiltration membranes with graphene oxide quantum dots for simultaneously improved water permeability and salt/dye rejection. *Adv. Mater. Interfac.* 6, 1801742.
- Zhao, S., Liao, Z., Fane, A., Li, J., Tang, C., Zheng, C., Lin, J., Kong, L., 2021. Engineering antifouling reverse osmosis membranes: a review. *Desalination* 499, 114857.
- Zhao, Y., Wen, J., Sun, H., Pan, D., Huang, Y., Bai, Y., Shao, L., 2020. Thermo-responsive separation membrane with smart anti-fouling and self-cleaning properties. *Chem. Eng. Res. Des.* 156, 333–342.
- Zheng, L., Sundaram, H.S., Wei, Z., Li, C., Yuan, Z., 2017. Applications of zwitterionic polymers. *React. Funct. Polym.* 118, 51–61.
- Zheng, X., Khan, M.T., Cao, X., Croue, J.-P., 2021. Importance of origin and characteristics of biopolymers in reversible and irreversible fouling of ultrafiltration membranes. *Sci. Total Environ.* 784, 147157.
- Zhu, J., Tsehaye, M.T., Wang, J., Uliana, A., Tian, M., Yuan, S., Li, J., Zhang, Y., Volodin, A., Van der Bruggen, B., 2018. A rapid deposition of polydopamine coatings induced by iron (III) chloride/hydrogen peroxide for loose nanofiltration. *J. Colloid Interface Sci.* 523, 86–97.
- Zhu, X., Tang, X., Luo, X., Cheng, X., Xu, D., Gan, Z., Wang, W., Bai, L., Li, G., Liang, H., 2020a. Toward enhancing the separation and antifouling performance of thin-film composite nanofiltration membranes: a novel carbonate-based preoccupation strategy. *J. Colloid Interface Sci.* 571, 155–165.
- Zhu, X., Yang, Z., Gan, Z., Cheng, X., Tang, X., Luo, X., Xu, D., Li, G., Liang, H., 2020b. Toward tailoring nanofiltration performance of thin-film composite membranes:

- novel insights into the role of poly(vinyl alcohol) coating positions. *J. Membr. Sci.* 614, 118526.
- Zou, L., Vidalis, I., Steele, D., Michelmore, A., Low, S.P., Verberk, J.Q.J.C., 2011. Surface hydrophilic modification of RO membranes by plasma polymerization for low organic fouling. *J. Membr. Sci.* 369, 420–428.
- Zularisam, A., Ismail, A., Salim, M., Sakinah, M., Ozaki, H., 2007. The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes. *Desalination* 212, 191–208.
- Zuo, K., Wang, K., DuChanois, R.M., Fang, Q., Deemer, E.M., Huang, X., Xin, R., Said, I. A., He, Z., Feng, Y., Shane Walker, W., Lou, J., Elimelech, M., Huang, X., Li, Q., 2021. Selective membranes in water and wastewater treatment: role of advanced materials. *Mater. Today* 50, 516–532.