



## A review of recent advance in fouling mitigation of NF/RO membranes in water treatment: pretreatment, membrane modification, and chemical cleaning

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### ABSTRACT

Currently, nanofiltration (NF) and reverse osmosis (RO) membranes are the most widely employed in surface water treatment, but membrane fouling has always been an important problem in the process of its application and scientific community paid wide attentions to this issue. This paper aims at reviewing the recent reports about fouling mitigation of NF/RO membranes, mainly focusing on the feed water pretreatment and membrane modification. In generally, high-quality feed water can ensure long-term stability of the membrane systems through altering size distribution of foulant, reducing its affinity to membrane surface and removing microbial nutrient source. Membrane modification can also effectively enhance anti-fouling capacity of NF/RO membranes by tailoring surface hydrophilicity, roughness, zeta potential, and functional groups so as to reduce the interaction between membrane surface and foulants. Besides, in order to recover the membrane flux of NF/RO systems, chemical cleaning is inevitable. The interaction mechanisms between chemical agent and foulant cake layer on the membrane surface and existing problems in chemical cleaning progress are also summarized. At last, the future research direction in this field is identified.

*Keywords:* Membrane fouling; Pretreatment; Membrane modification; Chemical cleaning

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### 1. Introduction

Nanofiltration (NF) and reverse osmosis (RO) processes are widely used in systems for seawater desalination, drinking water purification, and wastewater reuse, because they are capable of removing a broad range of contaminants in a single treatment step [1]. The NF/RO membranes have similar structures and parallel fouling properties except different selective layer thickness [2,3]. In current review, NF and RO membranes are discussed together.

One of major problems for NF/RO membranes in water treatment is fouling by inorganic salt scaling, colloidal or dissolved organic matter (DOM), and biofilm formation [4–8]. In addition to increasing hydraulic resistance, adsorption of dissolved organic compounds can form conditioning layer for bacterial adhesion and subsequent development of hydraulically poorly permeable biofilm [4,9], thereby causing various negative effects on membrane performance such as flux and permeate quality decline, increment of energy consumption and operation costs, and membrane degradation [10–12].

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Membrane fouling is strongly dependent on the pH, ionic strength, ionic composition (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ), and type and concentration of foulants in the feed water [13]. Many existing literatures showed that fouling was enhanced by low pH, high divalent ion concentration, and high ionic strength [14–20]. In these conditions, charge property of organic matters decreases through the neutralization of functional groups as well as organic-calcium complexation [17]. That will result in the destabilization of organic matters and promoted deposition on the membrane surface through enhancing the foulant-membrane interaction as well as foulant–foulant interactions that have been confirmed by atomic force microscopy interaction force measurements [15,18]. Many studies have shown that bridging between carboxyl groups on the membrane surface and foulant by divalent cations greatly increases fouling rate [5,21,22]. Jin et al. [21] suggested that selective removal of calcium ions via pretreatment can significantly reduce the fouling capacity of carboxylic rich macromolecules. However, in the presence of alum, calcium and alum had synergistic effects in lowering the resistance and making the cake layer more compressible [23]. In addition, Yu et al. [24] indicated that flux decline curves obtained at the seawater-level ionic strength was almost identical regardless of the variations of calcium concentration in the feed water due to the electrostatic interaction being effectively screened under such high ionic strength conditions and the enhanced acid-base interaction masking the effect of calcium concentration. Mo et al. [25] found that a critical calcium concentration is existent above which the initial rate of fouling will decrease.

Besides, there have been a limited number of studies that focus on combined fouling by both inorganic colloids and DOM. Studies revealed that combined fouling by organic and inorganic colloidal foulants may be influenced by three hypothesized mechanism i.e. increased hydraulic resistance, cake-enhanced concentration polarization [26], and changes in colloid surface properties due to organic adsorption [27]. Ang and Elimelech [15] showed that membrane fouling by BSA could be significantly enhanced in the presence of alginate. Wang and Tang [28] found the flux decline caused by the protein mixture was much more extensive compared to that of a single protein due to the electrostatic attraction between the oppositely charged molecules. Moreover, Wang and Tang [29] also systematically studied NF membrane fouling by oppositely charged alginate and lysozyme and found the same phenomena.

Pore blocking has been reported as an important fouling mechanism for porous MF/UF membranes,

but it is unlikely to be important for nonporous NF/RO membranes [30]. The fouling of NF/RO membrane is strongly influenced by the macroscopic physiochemical properties of the membrane surface, including surface charge, roughness, hydrophilicity, and surface functional groups specially interacting with foulants. Previous studies suggested that smooth and hydrophilic membrane with favorable electrostatic interaction is preferred for improving anti-fouling performance [11,12,28,31]. Li et al. [31] found ESPA1 membrane, which has the higher negative charge and hydrophilicity, showed the highest overall fouling rate compared to LFC1 and LFC3, and the author attributed this phenomena to its very rough surface morphology. Meanwhile, Tang et al. [32–34] analyzed the physiochemical properties of 17 widely used commercial NF/RO polyamide membranes and found a neutral polyvinyl alcohol (PVA) coating layer on some commercial membrane surfaces. In addition, the selective layer of most commercial NF/RO membranes is formed by interfacial polymerization that gives the membrane surface carboxyl and amine groups [3]. Carboxyl and amine groups change their protonation states with pH, which largely determines membrane surface charge. High negatively charged membrane performed well with less fouling if the feed water containing negatively charged organics or colloids [35].

Specific interactions between functional groups on the foulant molecules and those on the membrane surface can contribute greatly to organic fouling [36]. Contreras et al. [37] have investigated the adsorption of organic foulants on seven different common membrane surface functionalities using self-assembled monolayers. It turned out that surfaces modified with hydroxyl and ethylene-glycol functional groups can reduce membrane fouling [37]. After that, Mo et al. [22] found higher density of carboxyl group resulted in higher foulant-membrane surface intermolecular forces. Therefore, surface modification may be an effective strategy to enhance anti-fouling capacity of NF/RO membranes [37], which will be discussed in detail in Section 3. Previous fouling studies have demonstrated that initial stage of membrane fouling is controlled by the interaction between foulant and virgin membrane surface, while the interaction between foulant and deposited foulant become dominant once the membrane surface was fully covered by the foulant cake layer [17,28,38].

Prior studies showed that higher initial flux tended to promote severe membrane fouling as a result of increased permeate drag force, enhanced concentration polarization, and made foulant layer more dense [17]. Severe membrane fouling occurs only if the flux exceeds the critical flux [39]. In general, a higher

temperature is favorable to the membrane filtration due to the reduction of feed viscosity and concentration polarization [40]. However, that is dependent on the type of foulant. For example, higher temperature can trigger denaturation of protein and expose its inner hydrophobic portions to the surrounding, which increases the tendency of aggregation or adsorption to the membrane surface [41].

The following contents will discuss recent advance in fouling mitigation of NF/RO membranes in water treatment, mainly focusing on feed water pretreatment, membrane modification, and chemical cleaning.

## 2. Feed water pretreatment

Due to fouling propensity of NF/RO membranes, high-quality feed water is required to ensure long-term stability of membrane systems. Pretreatment can reduce fouling potential, increase membrane life, and maintain performance level by altering the physical, chemical, and/or biological properties of the feed water [42]. In this section, prevailing feed water pretreatment processes are presented in order to further elucidate the impact and implication of main pretreatment processes on fouling mitigation of NF/RO membranes.

### 2.1. Coagulation

Aqueous particulate and colloidal matters are typically negatively charged, and thus stay separated because same charges repulse each other. The role of coagulants is to effectively neutralize same charges and allow the suspended solids to group together in flocs. Therefore, coagulants are typically positively charged molecules. Two types of coagulants are available in commercial market: inorganic salt and organic macromolecules. Inorganic coagulants are commonly iron or aluminum salts such as ferric chloride or aluminum sulfate [43,44]. Effective coagulation of particles occurs through the combination of charge neutralization and sweep flocculation if the coagulation is controlled at neutral pH [45,46]. In comparison, organic coagulants, which are typically cationic and low molecular weight, are different from inorganic coagulants due to their adsorption behaviors and bridging effects [47]. However, use of organic coagulants in pretreatment for membrane filtration has been less frequently reported in the literatures.

Coagulation has been successfully used combined with MF or UF membranes to prevent fouling during feed water pretreatment [48]. The primary objective of inline coagulation is to change the surface chemistry

of the suspended particles so that they can attach well to the filtration media. Shon et al. [49] investigated the effect of flocculation followed by adsorption pretreatment on the organic molecular distribution of the permeate and on the surfaces of UF and NF membranes. Results showed that flocculation followed by adsorption pretreatment can alleviate the membrane fouling effectively [49].

The coagulant not only removes main membrane foulants but also forms a cake structure layer that is more porous than the supporting membrane, thus avoiding permeate flux decline [50]. However, successful coagulation and membrane filtration are sensitive to coagulant type and dose, and doses above or below the optimal dose can lead to permeate flux decline. Ferric chloride has been shown to be the most successful coagulant in NF/RO pretreatment applications, and a dual coagulation strategy is recommended for treating seawater with moderate to high levels of algae or with humic substances [51]. Aluminum is not as commonly used in pretreatment coagulation prior to membrane filtration because membrane permeability declined when the feed water contained residual aluminum at 18 µg/L or more [52,53]. Therefore, control of residual aluminum in the pretreatment processes prior to NF/RO systems is crucial for fouling mitigation.

### 2.2. Activated carbon adsorption

Adsorption is an important way to remove soluble non-polar organics present in water, natural organic matter as well as emerging pollutants such as endocrine disrupting compounds [54]. In spite of a low adsorption capacity and slow adsorption kinetics of most commercially available activated carbon, it is a well-established process for the removal of DOM from water due to its strong tendency to uptake hydrophobic organic compounds even at low concentrations [55].

Activated carbon adsorption, either in granular or powder form, has also been considered as a feasible mean for reducing membrane fouling, either alone or in combination with other pretreatment processes. Kim et al. [56] investigated granular activated carbon adsorption as a pretreatment for the secondary effluent, in combination with either dual media filtration (sand and anthracite) or dual media filtration and flocculation. Although TOC removal efficiency was up to 75–90%, the flux decline of RO membrane was rapid because the activated carbon could remove the soluble contaminants rather than particulate matters [56]. Meier and Melin [57] tested a hybrid process

combining powder activated carbon (PAC) recirculation with NF membrane for secondary effluent reclamation, which lead to a reduction of membrane fouling caused by small neutral and amphiphilic substances. Gur-Reznik et al. [58] studied the adsorption of DOM onto GAC as a pretreatment for RO system of membrane bioreactor (MBR) effluents in laboratory and pilot scales. The results showed GAC pretreatment in pilot-scale columns can stabilize permeability and increase permeate quality of the RO membrane by removing 80–90% DOM which is mainly composed of hydrophobic and biodegradable components [58].

In most cases, activated carbon contactor, where the influent water is put in contacting with activated carbon (either a GAC filter or a PAC suspension), usually combines with a low-pressure-driven membrane filtration as pretreatment for NF/RO systems. Moreover, its effectiveness was affected by the particle size, operating flux, operating mode, and feed water chemistry [59]. Thus, a lot of research work should be further carried out on the combined process of activated carbon adsorption with low-pressure membranes filtration.

### 2.3. Filtration

Although conventional filtration pretreatment has been widely used in NF/RO plants, fluctuation of feed water quality during events such as algal bloom or chemical contamination can lead to deteriorations of effluent water quality in conventional filtration pretreatment [60]. Colloids and suspended particles often pass through conventional filtration pretreatment and contribute to irreversible fouling of NF/RO membranes. As membrane costs decrease and raw water qualities decline, the use of large pore size membranes, such as MF and UF, prior to NF/RO stage has become a more practicable alternative to conventional pretreatment [48]. Currently, UF membranes represent perhaps the best balance between contaminant removal and productivity due to UF membranes have smaller pore sizes than MF membranes and higher flux than NF membranes. UF can provide high permeate flux and constant water quality ensures that RO plants can operate on a continuous basis, at higher permeate fluxes and recovery rates than conventional pretreatment [48]. However, each membranes have their own characteristics, and each treatment plant must choose pretreatment based on specific contaminant removal requirements. MF membranes are the appropriate choice for removal of larger particulate matter at higher permeate fluxes [61], while NF membranes are used to remove DOM, particulate materials, colloids, and bivalent salts.

The combination of UF with coagulation at low dose helped in controlling the RO membrane fouling in the downstream [62–64]. Membrane pretreatment can lower turbidity to less than 0.05 NTU and is particularly advantageous to NF/RO systems for treating surface water [65,66]. The reason is that surface water tends to have more organic colloidal and suspended solids, as well as a higher fluctuation due to algal blooms and chemical pollution. In addition, the MBR process has been applied to reclaim municipal wastewater due to the strong removal ability of organic and particulate matters, and the subsequent NF/RO systems can be operated at a high and stable permeate flux in long-term operation [67,68]. Herzberg et al. [61] found pretreatment of the secondary effluents with MF can reduce fouling of RO membranes due to removal of particulate/colloidal matter and can impact biofilm mechanic properties and cleaning strategies which is in favor of the subsequent RO membranes. Moreover, Jeong et al. [69] used submerged membrane hybrid systems as pretreatment for RO system and found pretreatment by submerged membrane combining with coagulation-adsorption hybrid system with the low doses of ferric chloride and powder-activated carbon can lead to the best results in terms of organic removal and critical flux. MF and UF provides several advantages and can act as an effective barrier to particulate and colloidal fouling for NF/RO systems in comparison to conventional multimedia filtration [48]. Membrane pretreatment can prolong the aging time and reduce the frequency of chemical cleaning of NF/RO membranes by improving feed water quality.

However, a major issue in membrane pretreatment is that MF and UF membranes are fouled in the process. Both surface cake layer and pore blocking occur in MF and UF membranes. The risk of membrane fouling may result in flux decline and cost raise, especially for feed water with a high organic level. Previous research has shown that hydrophobic materials and cellular or extracellular polymer substances are dominant foulants for UF and MF membranes [1,70]. Pretreatment technologies for MF/UF membranes have been extensively reviewed by Huang et al. [71]. Although membrane technologies are used as the pretreatment of NF/RO systems, fouling control of membrane themselves is a regenerative research issue.

### 2.4. Chemical agent addition

#### 2.4.1. Acid addition

Acid addition is a simple and effective mean to prevent calcium carbonate scale formation. The most

common acid used to lower feed water pH is sulfuric acid ( $\text{H}_2\text{SO}_4$ ) [72]. Moreover, hydrochloric acid (HCl) is used when sulfuric acid addition has the potential to cause sulfate precipitates. Lai et al. [73] found HCl was a better acid agent than  $\text{H}_2\text{SO}_4$  due to the generally lower solubility of sulfate salts as compared to that of chloride salts. However, acid addition will lead to other problems such as corrosion due to lower pH value of the feed water (typical pH range 5–7), transport and storage problems, and safety problems. Moreover, acid addition has no inhibitory effect against other scaling species except calcium carbonate [72].

#### 2.4.2. Antiscalant addition

Adding small amount of effective antiscalants such as polyelectrolytes, polyphosphates, and organophosphorous compounds to alter solution property is known to be a very effective method to control inorganic salt scaling such as  $\text{CaCO}_3$  and  $\text{CaSO}_4$  formed on NF/RO membrane surfaces [74–77]. Effective polyelectrolyte inhibitors are mostly polycarboxylic acids, e.g. polyacrylic acid, polymethacrylic acid, and polymaleic acid. These compounds can prolong substantially the crystallization induction time, and restrain the formation of scale nucleation and development of crystallization at low dosage [75–77]. Adding antiscalant is an attractive selection because it has many kinds of advantages such as operation cost reduction, environmental acceptability, and harmlessness compared to the alternative methods.

Currently, most of the scholars focused on inorganic scale inhibition by antiscalants, but only a few of them paid close attention to effect of antiscalants on organic fouling. For instance, Yang et al. [78,79] investigated the effect of antiscalant on organic fouling mitigation, such as humic acid (HA) and bovine serum albumin. They found that in the presence of polyaspartic acid (PASP),  $\text{Ca}^{2+}$  had positive impact on fouling control within a certain concentration range due to the possible formation of a water-soluble and highly stable complex HA–Ca–PASP or BSA–Ca–PASP via  $\text{Ca}^{2+}$  bridging [78,79]. The interaction mechanisms between organic foulants and antiscalants are needed to be in-depth study in the further.

There are some problems that should be noticed during using antiscalants for scale inhibition. For example, the use of antiscalants is not recommended if the concentration of certain potential precipitates is too high because they do not completely prevent precipitation at high ion concentrations, and as the salt concentration increases, precipitation will eventually

occur [80]. In addition, polyacrylic acid antiscalants would foul membranes in the presence of high iron concentrations, and polyphosphate would hydrolyze to orthophosphate, possibly leading to calcium phosphate precipitation when antiscalant overdosing. Moreover, the presence of aluminum, even at trace levels up to  $100\ \mu\text{g}/\text{L}$ , will significantly reduce the crystallization induction time of calcium sulfate, thereby reducing antiscalant effectiveness [81]. Furthermore, the use of antiscalants precludes the use of coagulants in the same stream because antiscalants are typically negatively charged, while coagulants are cationic polymers so they will complex together to form a more complicated membrane foulant [80]. Therefore, if coagulation is combined with membrane pretreatment prior to NF/RO systems, antiscalants are generally dosed after membrane pretreatment.

In spite of significant roles of antiscalants in restraining membrane scaling, they are prone to enhance biofilm growth on NF/RO membranes by either altering membrane surface properties or by serving as nutritional source for micro-organisms, which is another issue for the optimum operation of NF/RO systems [82,83]. Vrouwenvelder et al. [82] found that biological growth varied with antiscalant type, and some antiscalants can induce biofilm formation in full-scale NF/RO systems by increasing the microbial growth potential up to 4–10 times of their normal growth rate. Recently, Sweity et al. [83] investigated the contribution of antiscalants to membrane biofouling during desalination, and found polyacrylate-based antiscalant enhance initial cell attachment due to rendering the polyamide surface more hydrophobic and polyphosphonate-based antiscalants increased biofilm formation rate by serving as an additional phosphorous source to microbial population. Therefore, it is very important to conduct a wise selection and to use the minimum dosage of antiscalant for scaling control in order to avoid fouling enhancement.

#### 2.4.3. Disinfectant addition

A common method for limiting NF/RO membrane biofouling typically consists of either removal of bacterial growth nutrient sources to limit microbial growth or disinfectant addition to kill bacterial cells. The methods to remove bacterial growth nutrient sources such as activated carbon adsorption and membrane pretreatment have been discussed in Sections 2.2 and 2.3. However, removing bacterial growth factors sometimes does not prevent biofilm growth absolutely as bacteria are able to establish biofilm even in low

nutrient growth environments. Therefore, disinfection is a necessary and effective way to kill bacterial cells, which is achieved through addition of a strong oxidant, such as chlorine ( $\text{Cl}_2$ ), sodium hypochlorite ( $\text{NaClO}$ ), monochloramine ( $\text{NH}_2\text{Cl}$ ), chlorine dioxide ( $\text{ClO}_2$ ), ozone ( $\text{O}_3$ ), or UV irradiation.

Chlorine has been widely used to control microbial growth before reaching the NF/RO systems. Monochloramine and chlorine dioxide show relatively low-antibacterial efficiency and high cost despite less damage on membrane [84,85]. In addition, if chlorine is used as the disinfectant, activated carbon filter or sodium bisulfite will be used at the end of the pretreatment system to remove residual chlorine [86]. The reason is that majority of NF/RO membranes on the market today are made of aromatic polyamides, and such structures are known to be sensitive to chemical attack by chlorine. Excessive chlorine exposure will cause membrane degradation and a decrease in salt rejection by N-chlorination of the amide bonds [87–89]. Therefore, there will be no residual bacterial inhibition at the RO membrane surface.

Ozone oxidation has been chosen for the alleviation of organic fouling of NF/RO membranes, because it is able to react with the hydrophobic parts of organic foulants, i.e. aromatic rings in humic substances, and transforms these functional groups into more hydrophilic groups [90,91]. However, ozone will cause the formation of bromate, a well-known and regulated carcinogen, in waters containing bromide [92]. On the other hand, UV irradiation and ozone perform effective inactivation, but they lack residual effect and the damage to membrane surface structure

is possible as well [93]. Recently, Yu et al. [94] investigated dichloroisocyanurate for bio-fouling control and found DCC has little influence on polyamide RO membranes and possessed better biofilm inactivation than chlorine.

All disinfection processes cause the formation of disinfection by-products, which are potentially toxic oxidation products formed by reactions between the disinfectant and organic or inorganic components in the water. Therefore, research and development of the disinfectant possessing the characteristics of low cost, high efficiency and less damage to membrane surface structure become a hot spot at present. The advantages and disadvantages of chemical agents pretreatment for NF/RO membranes are summarized in Table 1.

In generally, pretreatment processes are not selected solely, and combination of a variety of process together will be chosen depending on the extremes of raw water characteristics since different pretreatment technologies often preferentially remove certain types of aquatic foulants. It also mean that raw water with fluctuating chemistry presents a challenge for designer to select appropriate pretreatment processes.

### 3. Membrane modification

Most of NF/RO membranes are prepared by interfacial polymerization forming an ultrathin separation selective layer on a porous substrate wherein the benefits of two separate polymeric layers could be combined for the desired separation property. As

Table 1  
List of the advantages and disadvantages of chemical agents pretreatment for NF/RO membranes

Types of chemical agent	Advantages	Disadvantages
Acid	Effectively prevent calcium carbonate scale formation	Corrosion Safety problem No inhibition effect against other scaling species except $\text{CaCO}_3$
Antiscalant	Low cost Environmental acceptability and harmless	Possible exacerbation membrane fouling
Disinfectant	Chlorine	Residual effect Effectively inactivation Membrane surface damage
	Monochloramine	Less damage to membrane surface than chloride Relatively low inactivation efficiency High cost
	Chloride dioxide	No damage to membrane surface Relatively low inactivation efficiency High cost
	UV/ozone	Effectively inactivation Formation of bromate Lack of residual effect High cost

Table 2  
List of the advantages and disadvantages of modification methods for NF/RO membranes

Membrane modification methods	Advantages	Disadvantages
Surface coating	Process simplicity No damage to selective layer structure	Permeability decline Poor stability
Surface grafting	More stable than surface coating	Uncontrollable grafting density Cost extra operation step May damage membrane pore structure May cause permeability decline
Incorporation with hydrophilic monomers	Without permeability decline	May cause thermal stability, mechanical properties, dimensional stability, anti-swelling performance decline
Incorporation with inorganic particles	Without permeability decline	Nanoparticle leaching
Modification with zwitterionic materials	With performance altering slightly	Process complex Consumption abundant chemical agents

discussed in Section 1, the membranes with smooth, hydrophilic surface and similar charge to the foulant seem to possess better anti-fouling property. Therefore, a great deal of research efforts have been devoted to improve anti-fouling properties by changing properties of selective layer of NF/RO membranes, generally including surface coating, surface grafting, incorporation of hydrophilic monomers/inorganic particles, and zwitterionic modification. The advantages and disadvantages of modification methods for NF/RO membranes are summarized in Table 2.

### 3.1. Surface coating

Depending on adsorption affinity of membrane surface, the adsorbed coating layer can be stable and this method is feasible. Many scholars have devoted efforts to modify the surface characteristics through coating a thin layer of hydrophilic or antibacterial polymers from solution by physical adsorption so as to improve the anti-fouling property of the NF/RO membranes.

For instance, coating of synthetic polyether-polyamide block copolymer on the surface of thin film composite (TFC) polyamide RO membrane was conducted by Louie et al. [95]. It was reported that the protective coating layer resulted in a smooth, neutral, and hydrophilic surface with improved fouling resistance, but a declined flux [95]. In addition, dendrimer-based coatings for surface modification of RO membranes have been reported to significantly reduce surface contact angles without affecting salt rejection and only moderately reducing their permeate fluxes [96]. Both improved hydrophilicity and dynamic brush-like topology enhanced the fouling resistance

(Fig. 1) [96]. Recently, deposition of hydrophilic polyelectrolytes on a commercial RO membrane was conducted by Ishigami et al. via layer-by-layer assembly [97]. The obtained membranes exhibited anti-fouling properties against various hydrophobic foulants and more hydrophilic and smoother as layer number increased [97]. More recently, Yu et al. [98] modified a commercial TFC aromatic polyamide RO membrane through coating a layer of natural polymer sericin that contains hydroxyl, carboxyl, amino, and amide groups to improve anti-fouling property. The resulting

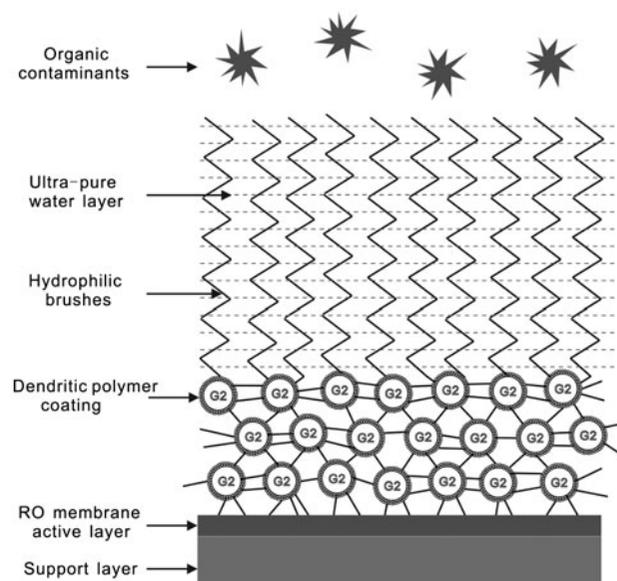


Fig. 1. Schematic diagram of anti-fouling dendrimer-based coating the selective layer of a standard asymmetric RO membrane [96].

membrane showed improved surface hydrophilicity, enhanced surface negative charge, and smooth surface morphology at the cost of pure water permeability [98].

Moreover, selenium is a catalytic producer of superoxide radicals and the superoxide radicals can cause damage to the outer membrane of bacterial cells that results in cell death. Therefore, continuous superoxide production by attached selenium on a surface can prevent bacterial attachment and inhibit biofilm development [99]. Based on this principle, Low et al. [100] proposed that selenium can attach to the RO membrane surface as a biofouling inhibition technique. Furthermore, Kim et al. [101] immobilized a quorum quenching enzyme (acylase) was directly onto a NF membrane to mitigate biofouling and found that acylase-immobilized membrane hindered the formation of mushroom-shaped mature biofilm due to the reduced secretion of extracellular polymeric substances. Recently, Nikkola et al. [102] modified the PVA coating on a commercial RO membrane with cationic polyhexamethylene guanidine hydrochloride polymer to enhance anti-biofouling performance. The modified membrane revealed more hydrophilic, smoother, and higher anti-bacterial property than unmodified one [102].

It can be seen that the materials used for surface coating are usually hydrophilic polymers containing hydroxyl, carboxyl, amino groups, or enzyme. The presence of coating layer could significantly enhance hydrophilicity and reduce surface charge and roughness of membrane, rendering a better anti-fouling property.

Surface coatings are relatively simple to apply and selective layer structure of the membrane is not likely to be affected by the adsorbed layer. However, coating layer tended to offer an additional resistance to water permeation and render flux decline. Moreover, one of

the major concerns is that anti-fouling property of the membrane may be gradually deteriorated, because the coating layer are only attached to the membrane surface by van der Waals attractions, hydrogen bond, or/and electrostatic interaction, which may result in washing away of the coating layer in the chemical cleaning process or long-term operation process.

### 3.2. Surface grafting

Surface grafting has been widely used because of its simplicity, low cost, and breadth field of applications. Free radical-, photochemical-, radiation-, redox-, plasma-induced grafting, and chemical crosslinking are currently used to covalently attach some hydrophilic monomers onto the surface of NF/RO membranes [103].

For example, Cheng et al. [104] performed surface modification of a commercial TFC RO membrane through redox-initiated graft polymerization of N-isopropylacrylamide (NIPAm) followed by acrylic acid (AA) (Fig. 2). Fouling experiments with BSA solution demonstrated that the modification could mitigate the deposition of foulants on the membrane surface through enhancing electrostatic repulsion and lowering hydrophobic interaction between BSA molecules and membrane surface [104]. Although redox-initiated graft polymerization was used to modify polyamide RO membrane, the required reaction time was too long (1 h). In addition, Abu Seman et al. [105] modified polyethersulfone NF membrane by means of UV-initiated graft polymerization technique using the weakly acidic monomer AA and the immersion method. It was found that irreversible fouling by HA molecules was reduced after modification [105]. However, it must be pointed out that the UV-wavelength has a significant impact on the membrane polymer. Short wavelength (254 nm) possessing high energy

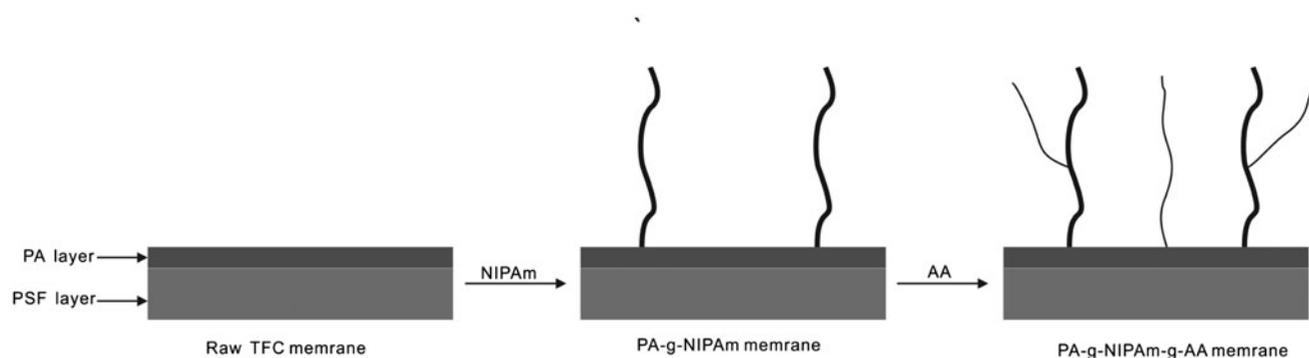


Fig. 2. Schematic diagram of the surface modification of polyamide RO membrane through graft polymerization of NIPAm followed by AA [104].

may damage the membrane support resulting in polymer degradation due to the bond scission of polymer backbone and poor chemical selectivity in the modification reactions. In generally, UV-system with 350 nm wavelength was used to prevent damaging TFC RO membrane. Therefore, it is still a challenge to modify the TFC polyamide membranes for both improved fouling resistance and enhanced separation performance, i.e. increased permeation flux and salt rejection.

In addition, Lin et al. [106] prepared a nanostructured polyamide thin-film-composite (SNS-PA-TFC) membranes via plasma-induced surface activation followed by methacrylic acid and acrylamide surface graft polymerization. The poly(methacrylic acid) and poly (acrylamide) brush layers resulted in RO membranes of significantly lower mineral scaling propensity compared with commercial RO membrane (LFC1) of about the same salt rejection and surface roughness [106]. After that, Varin et al. [107] explored the biofouling resistance of this type of SNS-PA-TFC membranes, as well as cleaning efficiency of the biofouled membranes. Greater resistance to biofouling and flux recovery cleaned by DI water and ethylene diamine tetraacetic acid (EDTA) were observed for this type membranes as compared to the commercial membrane used in the wastewater treatment plant [107].

As discussed in Section 1, some commercial TFC polyamide NF/RO membranes contain carboxylic acid groups on the surface [3]. These reactive groups provide the possibility of membrane surface modification to improve the anti-fouling properties. The activation of carboxylic acid groups by coupling reagent such as 1-ethy-3-(3-dimethyl amidopropyl) carbodiimide (EDC) has been used in chemical grafting to enhance anti-fouling ability of NF/RO membranes. For example, Kang et al. [108] grafted two kinds of poly(ethylene glycol) derivatives with different chains onto the existing carboxylic acid groups on surface of commercial TFC RO membrane by carbodiimide-induced method to improve the anti-fouling property. The modified membranes were more resistant to fouling in protein and cationic surfactant feed water compared to unmodified membrane [108]. More recently, the polyamide RO membrane modified with 6-amino caproic acid (ACA) was fabricated by an interfacial polymerization method and then the antibacterial enzyme, lysozyme, was immobilized onto the ACA-modified polyamide membrane by an amine coupling reaction using EDC and N-hydroxysuccinimide [109]. It was found that the lysozyme-immobilized membrane showed sufficient antibacterial activity at the costs of water flux and salt rejection [109].

In addition to the above mentioned grafting methods, nanoparticles can also be grafted to the surface of polyamide TFC membrane to reduce biofouling through covalent bonding. For example, Yin et al. [110] attached nanosilver (nAg) particles to the surface of polyamide TFC membrane via covalent bonding using cysteamine as a bridging agent. The nAg particles grafted membrane showed a higher water flux and excellent antibacterial properties with slightly lower salt rejection compared to the pristine TFC membrane [110].

Membrane surface modification by grafting hydrophilic or antibacterial ingredients on membrane top layer has been reported to have a positive effect on anti-fouling, but it has uncontrollable grafting density, costs extra operation step, and may damage the membrane pore structure leading to a decline performance. Moreover, covalently attached modifiers to NF/RO membrane surfaces could still leak into the product water if the covalent bond cleavages, for example by reacting with common membrane cleaning agents such as chloride [111]. Therefore, it is important to evaluate the potential toxicity of modifiers in humans with well-established methods such as cytotoxicity assays with mammalian cells [112–114].

### 3.3. Incorporation with hydrophilic monomers

Incorporation of hydrophilic monomers into membrane selective layer is considered to be a convenience and effective strategy to enhance the membrane anti-fouling capacity.

For instance, Abu Seman et al. [115] prepared polyester TFC NF membranes with improved anti-fouling properties by interfacial polymerization using bisphenol A and trimesoyl chloride (TMC) monomers. It was observed that polyester TFC membranes exhibited practically no tendency to be irreversibly fouled by HA molecules at neutral environment [115]. After that, An et al. [116] incorporated PVA into composite NF membranes *in situ* by adding different amount of PVA into piperazine (PIP) during its interfacial polymerization with TMC (Fig. 3). The roughness of these membranes decreased proportionally and the hydrophilicity and flux of the composite NF membranes increased with increasing the mass fraction of PVA to PIP without sacrificing salt rejection [116]. In addition, Wu et al. [117] prepared a novel  $\beta$ -cyclodextrin ( $\beta$ -CD)/polyester TFC NF membrane via *in situ* interfacial polymerization of TMC and triethanolamine in the presence of  $\beta$ -CD (Fig. 4). The  $\beta$ -CD/polyester NF membrane presented a significant enhancement in the anti-fouling performance and high water flux

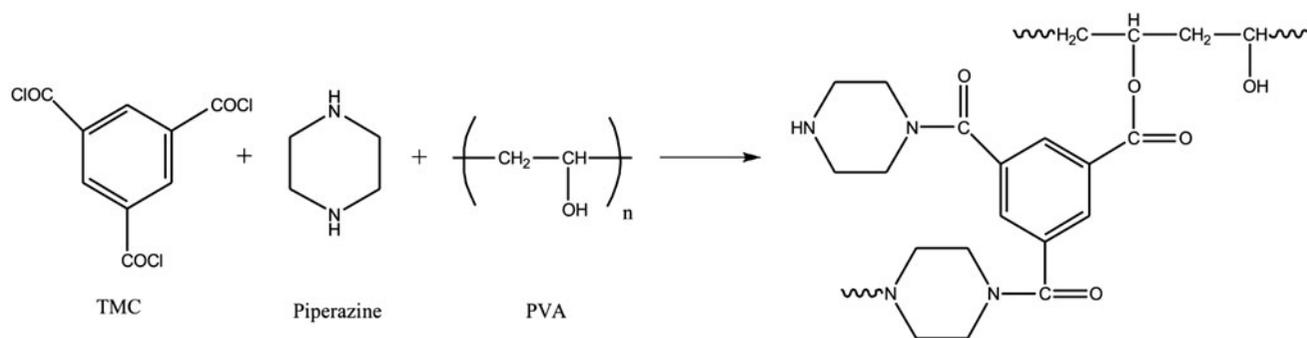


Fig. 3. Schematic diagram of interfacial polymerization between TMC and PIP in the presence of PVA [116].

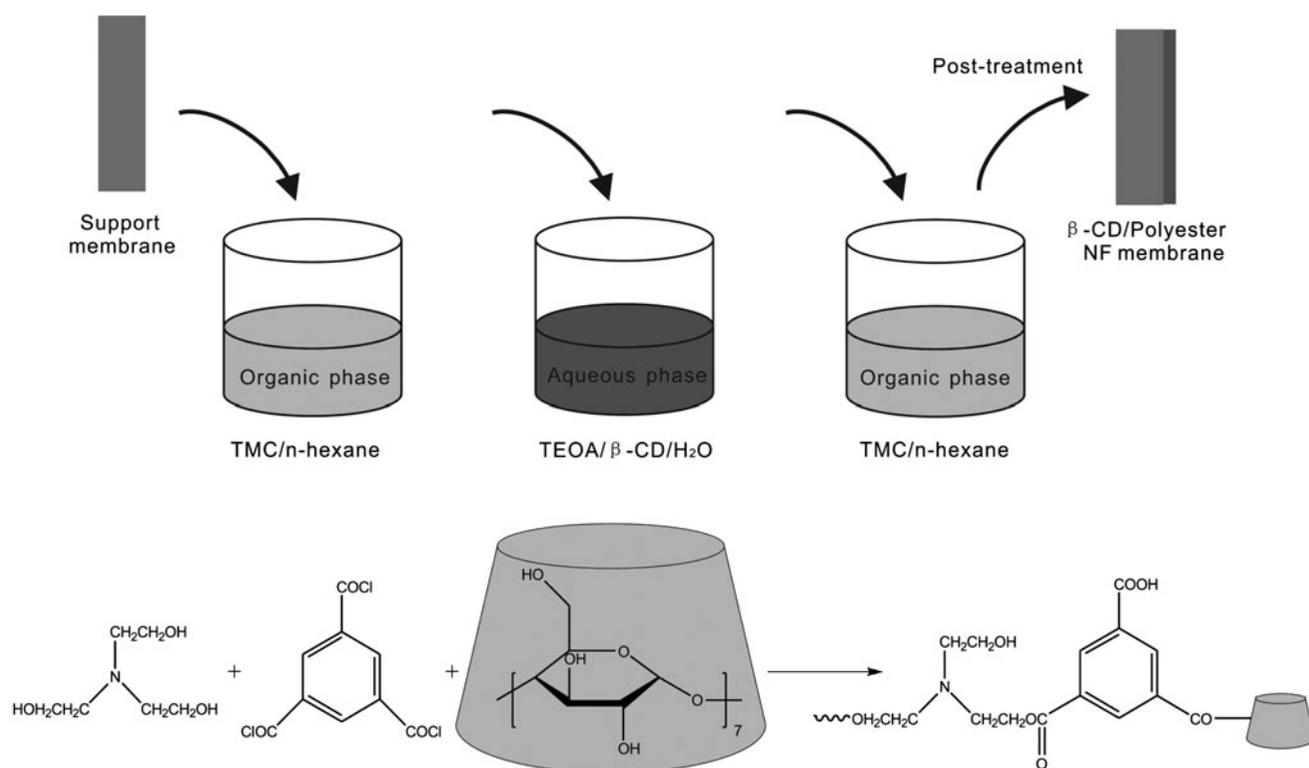


Fig. 4. Schematic diagram of the preparation procedure and reaction formulas of  $\beta$ -CD/polyester NF membrane [117].

compared to the bare polyester membrane [117]. More recently, Zhang et al. [118] selected tannic acid as polyphenol monomer to fabricate a novel composite NF membranes by chemical cross-linking reaction took place between the phenol groups of tannic acid and acyl chloride groups of TMC. Tannic acid and TMC composite NF membranes had low flux decline ratios and high flux recovery ratios without chemical cleaning in the anti-fouling evaluation experiments [118].

Although incorporation with hydrophilic monomers could improve the anti-fouling ability of the

NF/RO membranes, the thermal stability, mechanical properties, dimensional stability, anti-swelling performance, and the ductility of these membranes need to be deeply explored.

### 3.4. Incorporation with inorganic particles

In recent years, many new types of organic/inorganic hybrid materials were explored to combine the desired properties of inorganic and organic, improving the fouling resistance of organic polymers. For

inorganic nanoparticles, which have a higher specific area and lots of negatively charged hydroxyl groups existing on the surface, it can bring new good properties such as thermostability, anti-fouling, and antibacterial properties for the composite materials.

Several types of inorganic materials have been used as additives in organic polymers in NF/RO membrane preparation process, which includes titanium dioxide ( $\text{TiO}_2$ ) [119], silicon dioxide ( $\text{SiO}_2$ ) [120], zeolite [121], carbon nanotubes (CNTs) [122], and nanosilver (nAg) [123]. For example, Jeong et al. [121] created a nanocomposite thin films comprising zeolite nanoparticles dispersed within polyamide films by interfacial polymerization *in situ* on porous polysulfone supporting layer. At the highest nanoparticle loadings tested, the pure water permeability was nearly double that of hand-cast polyamide membranes with equivalent solute rejections [121]. Recently, Vatanpour et al. [119] prepared a nanocomposite polyethersulfone membrane using multiwalled carbon nanotubes (MWCNTs) coated by  $\text{TiO}_2$  nanoparticles. Fouling resistances of the membrane revealed that 0.1 wt.%  $\text{TiO}_2$ -coated MWCNTs membrane had the best anti-biofouling properties due to its lowest surface roughness and synergistic photocatalytic activity induced by incorporated  $\text{TiO}_2$  nanoparticles [119]. After that, Jin et al. [120] prepared a novel NF membrane containing  $\text{SiO}_2$  nanoparticles with poly (amidoamine) dendrimer and TMC by interfacial polymerization. The results showed nano- $\text{SiO}_2$  in the

selective layer can improve thermal stability, hydrophilicity, permeability, and anti-fouling capacity of the membrane without loss of rejection rate [120]. Recently, Vatanpour et al. [122] prepared mixed matrix NF membranes by acid oxidized MWCNTs embedded in polyethersulfone as matrix polymer. The hydrophilicity and anti-fouling capacity of the membrane were enhanced by blending MWCNTs due to migration of functionalized MWCNTs to membrane surface during the phase inversion process [122].

It is well-known nAg particles are an effective anti-bacterial agents. The antimicrobial effects of nAg can be attributed to their capacity to destroy cell membrane functions, to interrupt electron transport chains, and to damage cell protein and DNA [124]. At present, this method was also used in the development of anti-fouling NF membranes. Kim et al. [123] prepared a new type of thin-film nanocomposite membrane that was synthesized by the interfacial polymerization of a support layer containing acid modified multi-walled carbon nanotubes (MWNTs) and a thin-film layer-containing nAg particles (Fig. 5). The anti-bacterial tests indicated greater anti-adhesive and anti-bacterial properties of the resultant membrane compared to similar membranes without nAg particles [123].

However, the compatibility between inorganic particles and polymer phases during preparation and leaching from the bulk polymers in long-term operation still challenges for excellent performance of organic/inorganic hybrid NF/RO membranes.

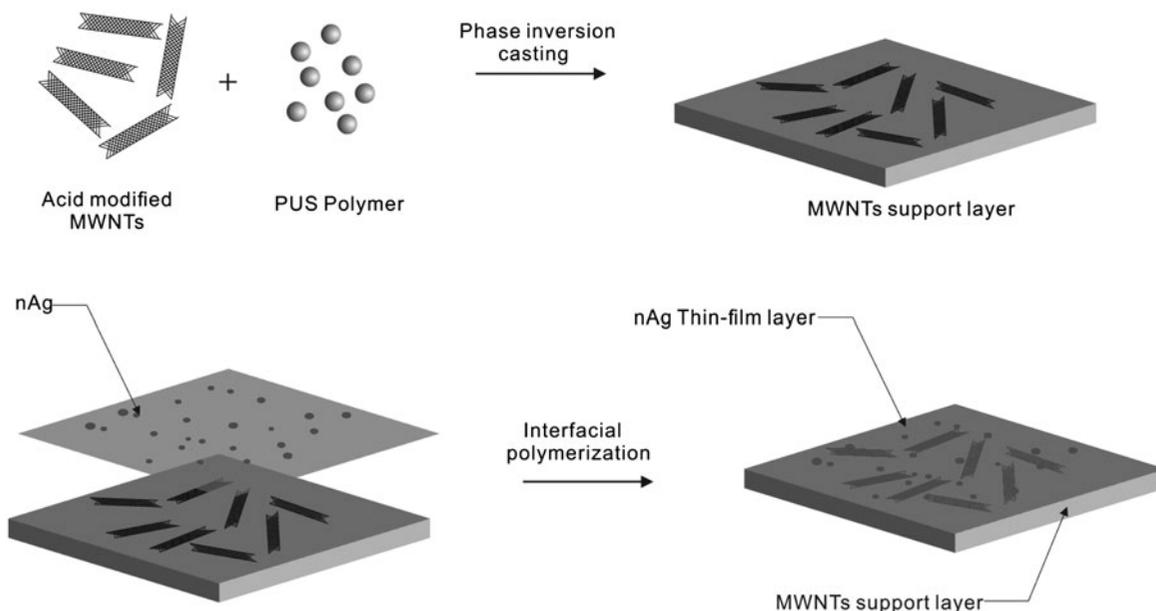


Fig. 5. Schematic diagram of the preparation procedure of polyamide NF membrane containing nAg particles [123].

### 3.5. Modification with zwitterionic materials

It is found that zwitterionic functionalities containing the pendant groups of phosphobetaine, sulfobetaine, and carboxybetaine have been introduced as a new generation of fouling resistance surfaces because of their good resistance to protein adsorption and bacterial attachment [125,126]. They possess both negative and positive charged units and can create stronger and more stable electrostatic bonds with water than hydrophilic materials, resulting in excellent biocompatibility and anti-fouling property [125,126].

Some researchers have commenced the study of modifying NF membranes surface or preparing NF membranes using zwitterionic polyelectrolytes recently. For example, Azari and Zou [127] deposited redox functional poly L-DOPA onto commercial RO membranes to create a zwitterionic surface to resist membrane fouling. After 12 h of coating, the water contact angle of the membrane surface decreased from 55° to below 20° [127]. In addition, Ji et al. [128] synthesized a novel type of polyelectrolyte complexes

(PECs) using quaternary ammonium cellulose ether and sodium carboxymethyl cellulose and prepared composite PECs NF membranes with different ionic complexation degree by chemical crosslinking method. The resultant NF membranes showed a good stability and anti-fouling capability in the long time operation [128]. Recently, Ji et al. [129] synthesized a terpolymers P(DMC-HEA-DMAPS) (PDHD) composed of 2-methacryloyloxy ethyl trimethylammonium chloride, 2-hydroxyethyl acrylate (HEA), and 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS) via aqueous phase free-radical copolymerization. Composite nanofiltration membranes (CNFMs) were prepared with PDHD and glutaraldehyde via the combination of surface coating and chemical cross-linking methods (Fig. 6). The test results revealed that the water permeability and anti-fouling property of CNFMs were significantly improved by incorporating zwitterions into the membranes [129].

The methods mentioned above to prepare composite NF membranes through the chemical cross-linking

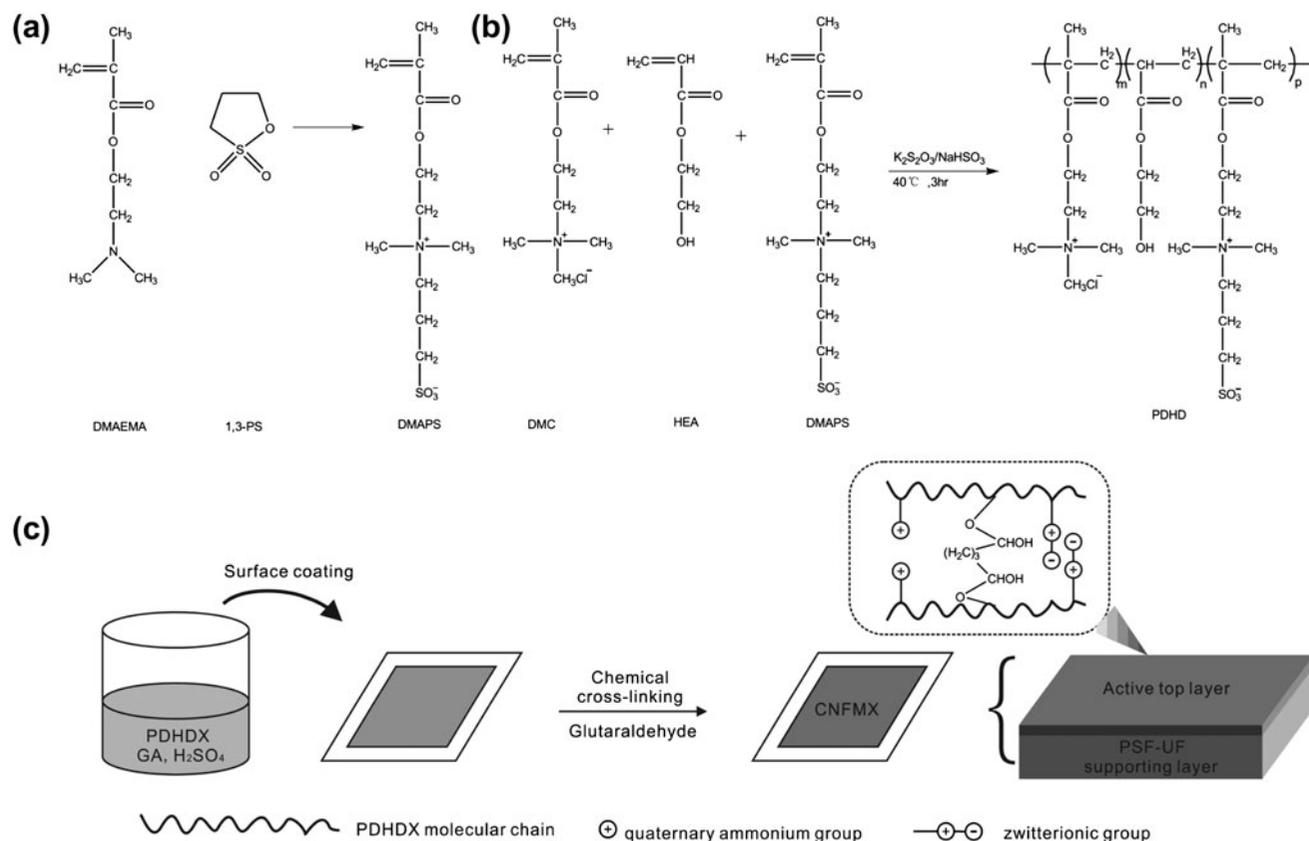


Fig. 6. Schematic diagram of preparation of zwitterionic monomer DMAPS, terpolymer PDHD and NF membrane CNFMX [129].

method, and the zwitterionic PECs layer was used as selective layer directly. Recently, some researchers zwitterionized the membrane surface or utilized zwitterionic polymers as aqueous monomers to modify the NF membranes. For instance, Chiang et al. [130] proposed a new strategy for anti-fouling membrane preparation with zwitterionic surfaces containing carboxybetaine mimetic structures. Polyamide NF membranes were fabricated by interfacial polymerization of Diethylenetriamine and with TMC [130]. A simple N-alkylation procedure by iodopropionic acid is adopted to convert the secondary amine into an anti-fouling zwitterionic functional group. The resulting tertiary amines were further quarternized by iodomethane. The resultant NF membrane has excellent resistance to the adsorption of negatively charged BSA and positively charged lysozyme [130]. In addition, An et al. [131] synthesized a novel zwitterionic amide monomer (N-aminoethyl piperazine propane

sulfonate, AEPPS) and utilized it in conjunction with PIP to perform the interfacial polymerization with TMC (Fig. 7). The flux of the resultant NF membrane increased from 23.4 L/m<sup>2</sup>h to 43.1 L/m<sup>2</sup>h with increasing AEPPS content from 0 to 3.2 mol%, and the resultant NF membrane can resist bacterial adsorption and protein fouling efficiently with permeability and rejection only slightly altered [131].

From the above discussions, we can see zwitterionic polyelectrolytes can improve the anti-fouling of the NF/RO membranes to a great extent with changing other membrane performances slightly. However, the synthesis process of the zwitterionic polyelectrolyte is complicated and the consumption of chemical agents is abundant. Therefore, the future study should focus on the simplification of the synthesis process, optimization of the chemical agent usage and the stabilization of the zwitterionic polyelectrolytes in long-term operation.

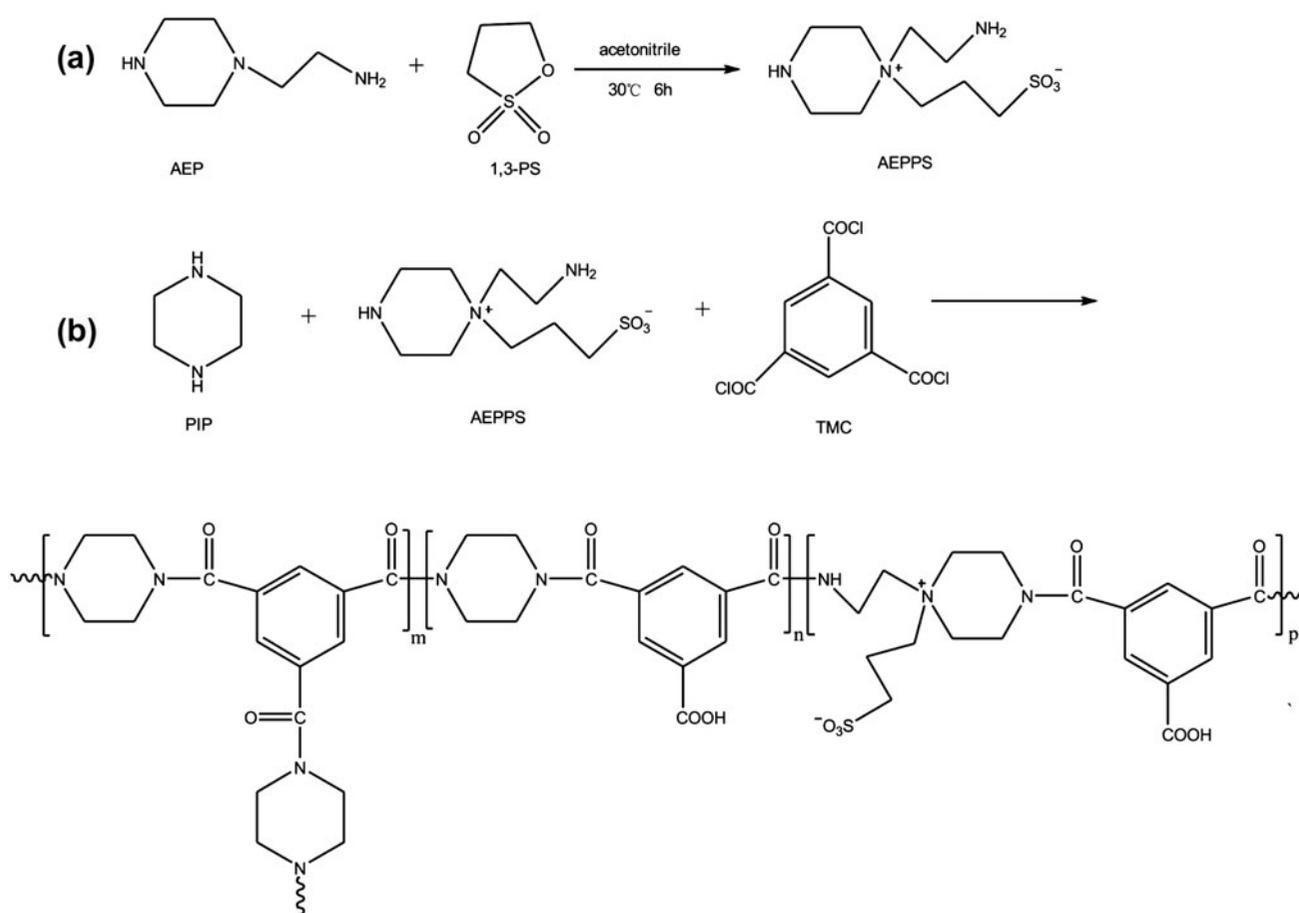


Fig. 7. Schematic diagram of the synthesis process of zwitterionic monomers AEPPS and chemical structure of NF membranes [131].

#### 4. Chemical cleaning

Developing strategies for fouling control have always been a major challenge in membrane research. Although vast research efforts have been contributed to control NF/RO membranes fouling as before discussions, including optimization of operational conditions, feed water pretreatment, and membrane modification, fouling is still inevitable. Consequently, membrane cleaning to remove the fouling layer on the membrane surface is a necessary process to ensure stable operation of membrane systems. The objective of the cleaning processes is to restore membrane performance when it falls below the expected permeate yield or trans-membrane pressure increase above the predetermined value. Membrane fouling includes reversible and irreversible fouling. The reversible fouling can be recovered by simple hydraulic flushing, but the recovery of irreversible fouling needs progressive chemical cleaning. The recovery of irreversible fouling is the main concerned problem in membrane cleaning. In this section, only chemical cleaning is emphasized on.

##### 4.1. Classification and action mechanism of the cleaning agents

Several kinds of cleaning agents are commonly used in chemical cleaning, including acids, alkalines,

inorganic salts, metal chelating agents, surfactants, and enzymes [5,132]. The mechanical stability of fouling layer is overcome in a two-step process which involves both chemical and physical interactions: (1) chemical reaction between the foulants in the fouling layer and cleaning agent, (2) release of the foulants from the membrane surface to the bulk solution by shear forces [5,133]. The cleaning efficiency strongly depended on the chemical reactivity of the cleaning agent since the second step of mass transfer can take place only after the foulant–foulant interactions have been weakened by the chemical reaction which has been confirmed by interfacial force measurement.

Selection of chemical cleaning agents that exhibit favorable chemical reaction with the target foulants in the fouling layer is of great importance. For example, acid cleaning is suitable for the removal of precipitated salts such as  $\text{CaCO}_3$ , while alkaline cleaning is used to remove adsorbed organic foulants [134]. Alkaline solutions detach organic foulants on the membrane surface by hydrolysis and solubilization of the fouling layer, and by enhancing electrostatic interactions between the negatively charged foulants and the membrane surface when the solution pH is elevated [134]. Metal chelating agents remove divalent cations (e.g.  $\text{Ca}^{2+}$ ) from the complexing organic

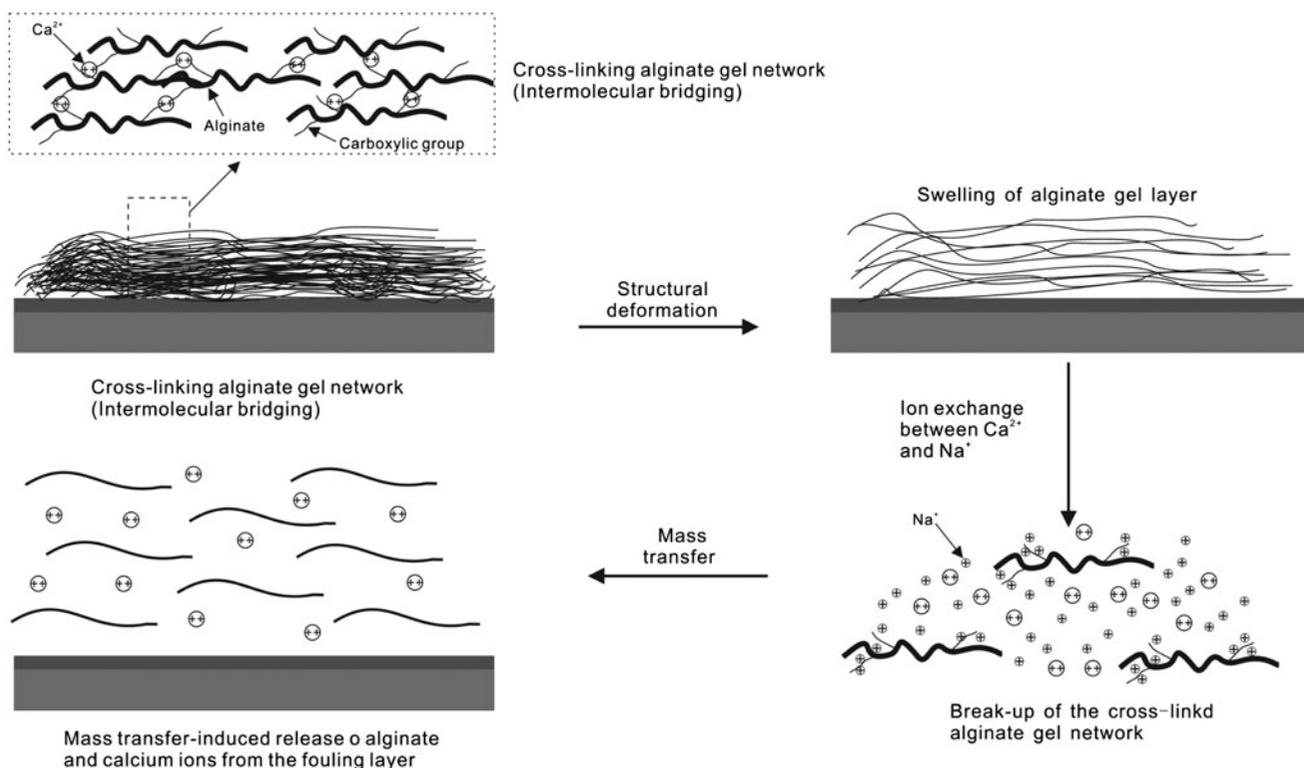


Fig. 8. Schematic diagram for mechanisms of salt cleaning [136].

molecules and weaken the structural integrity of the fouling layer. Li and Elimelech [5] found that cleaning efficiency of EDTA was highly dependent on solution pH of the chemical cleaning agents because the number of deprotonated carboxylic groups of EDTA is a function of pH. Surfactants can solubilize macromolecules by forming micelles around them and help to clean the fouled membrane surface [5]. Moreover, Li and Elimelech [5] found that cleaning efficiency of sodium dodecyl sulfate (SDS) strongly depended on the concentration of SDS since more SDS molecules partition into the foulant layer and the increased hydrophilic interaction results in breakup of some  $\text{Ca}^{2+}$  binding. Ang et al. research results [135] were consistent with that of Li and Elimelech [5]. In addition, Lee and Elimelech [136] showed that inorganic salts were quite effective in cleaning RO membranes fouled by gel-forming hydrophilic organic foulants. The cleaning mechanism for inorganic salts cleaning involved foulant layer swelling, which resulted in the lessening of the structural integrity of the gel network, followed by an ion-exchange reaction between sodium ions and the polysaccharide-calcium complex in the fouling layer (Fig. 8) [136]. In addition, enzymes offer the advantages over traditional caustic or acid cleaning regimes of being biodegradable and posing fewer

pollution problems. They are also less aggressive to the membranes and believed to prolong membrane lifespan due to highly substrate and reaction specificity [134].

#### 4.2. Existing problems in chemical cleaning process

Chemical cleaning can effectively recover permeability of NF/RO membranes. However, chemical cleaning by caustic and acidic cleaning reagents has been reported to result in significant variations in the membrane hydrophilicity, zeta potential, permeability, and salts rejection [137,138]. The variations of the membrane performance are thought to be caused by the enhanced electrostatic repulsion between functional groups of the membrane polymeric matrix and/or by the interaction between the membrane polymeric layer and the cleaning reagents during chemical cleaning [139–141].

Simon et al. [139–141] found that caustic cleaning can change the conformational changes of the polyamide selective layer of NF270, which lead to an increase in permeability and decrease in rejection of conductivity. The conformational changes of the polyamide selective layer can be described by a schematic diagram as shown in Fig. 9. Under caustic solution

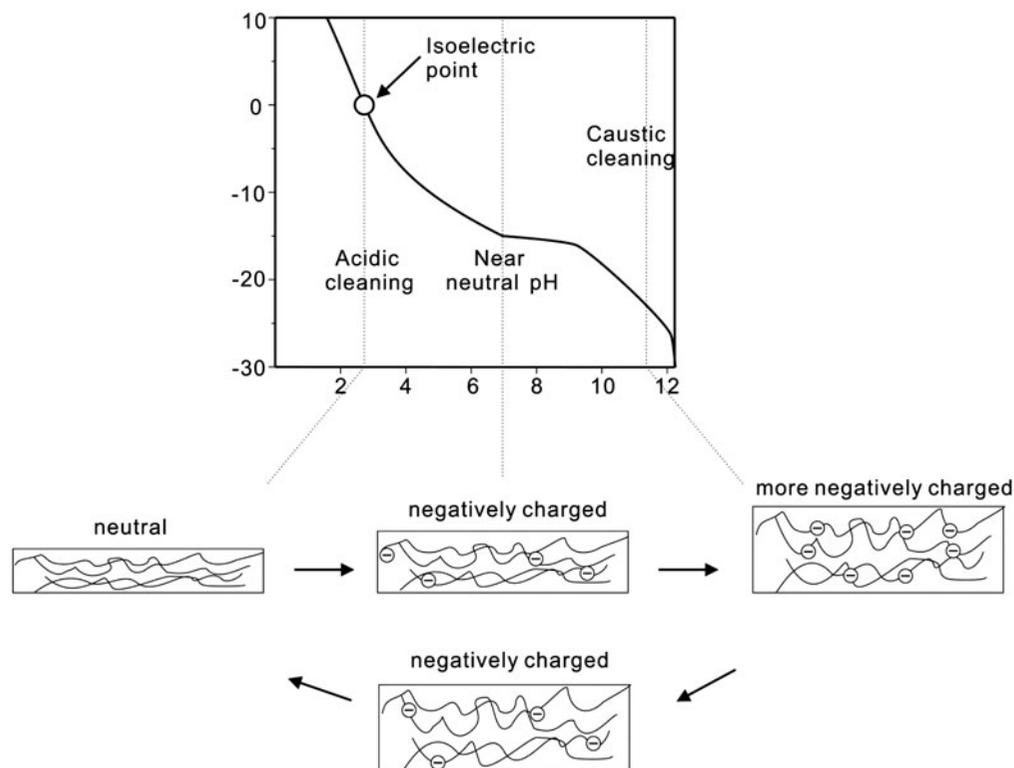


Fig. 9. Schematic diagram of a membrane selective layer as a function of the membrane charge (i.e. background pH) [139].

condition, electrostatic interactions among the negatively charged carboxylic functional groups of the polyamide selective layer can lead to a significant enlargement of the membrane porosity. When the membrane is returned to operation, exposed to a near neutral pH solution, functional groups at the membrane surface can re-protonate. However, the selective layer underneath the membrane surface can experience a hysteresis condition. In other words, a more open surface structure of the membrane resulted in a higher membrane permeability and solute passage [139]. On the other hand, acidic cleaning at the polyamide membranes' isoelectric point (approximately at pH 3) can result in charge neutralization. Thus, the impact of acidic cleaning on both permeability and solute separation efficiency is rather insignificant [139]. Moreover, the author recommended that the sequence of caustic cleaning followed by acidic cleaning can help to minimize the abovementioned hysteresis effect [139]. Espinasse et al. [142] found that HCl removed very little organic matter while sodium hypochlorite and sodium hydroxide at pH 12 could dissolve considerable quantities of organic carbon. However, sodium hypochlorite may have detrimental effect on the membrane surface structure if cleaning conditions are not carefully monitored and controlled.

One important concern regarding these cleaning agents is the detrimental effects on the environment when discharged as waste streams. For example, the EDTA discharged into the water bodies and the environment can extract toxic heavy metal ions that is toxic for biology in relatively high level from the mud and soil [143]. In addition, enzymatic cleaning is expected to be effective for protein-fouled membranes and environmental acceptability. However, the cost and the relatively slower activity rate of enzymes impede its large-scale application [134].

In practice, the composition of the fouling layer is often very complex. Therefore, multiple chemical cleaning mechanisms are usually adapted to mitigate membrane fouling. Enhancing cleaning efficiency can be achieved by combining several cleaning agents either simultaneously or sequentially. Ang et al. [133] investigated the effect of different cleaning modes of RO membranes fouled by wastewater treatment plant effluent and found that sodium chloride adjusted to pH 11.0 can obtain the highest cleaning efficiency (94%) for RO membrane. However, the mismatching of chemical agents would yield the opposite effect, resulting in a drastic decline of cleaning efficiency [133]. Moreover, an optimal cleaning agent concentration can avoid overdosing resulting in unintended detrimental effects on the selective layer of NF/RO membranes and environment. Ang et al. [144] showed

that an optimal concentration of chemical cleaning agent could be obtained from the plot presenting the percent reduction in the foulant–foulant adhesion force with regard to cleaning agent concentration. Optimization of cleaning agents by bench-scale or pilot-scale tests is necessary to maximize cost-efficiency of the process and minimize the harmful chemicals dosage.

## 5. Conclusions and future developments

Apart from feed water pretreatment, membrane modification and chemical cleaning, other measures such as advanced oxidation pretreatment and module and space design optimization to mitigate membrane fouling of NF/RO systems are not involved in this review. For details on these aspects you can refer to references [145–149].

In practice, a combination of multiple pretreatments will be often considered since different pretreatment processes preferentially remove certain types of aquatic foulants. That is to say only relying on one-step pretreatment may lead to failure in effectively mitigating membrane fouling for NF/RO systems. The improper pretreatment processes even have a negative impact on the performance of NF/RO systems. Therefore, selection of appropriate pretreatment processes depending on the extremes of feed water chemistry may be a challenge for the water treatment engineers. Furthermore, future research is needed to pursue new pretreatment technologies that can improve the anti-fouling capacity of NF/RO systems in a cost-effective and environmentally friendly manner.

Membrane modification can effectively enhance anti-fouling capacity by tailoring surface hydrophilicity, surface roughness, zeta potential, and surface functional groups. However, it often bases on sacrificing the flux of membranes, so exploring synthesis of new membrane material to overcome the trade-off effect between anti-fouling capacity and permeability will be pursued in the scientific community. In addition, the chemically covalent linkage between membrane and modifier is more stable than the physical methods in the process of long-term operation, so future research should pay more attention to this method for the target of practical utility. However, covalently attached modifiers to NF/RO membrane surfaces could still leak into the product water if the covalent bond cleavages, for example by reacting with common membrane cleaning agents such as chloride. Therefore, it is important to evaluate the potential toxicity of the modifiers in human with well-established methods. Furthermore, many modification methods

are high cost and complicated and they only stay in the laboratory research stage and large-scale application is also difficult, so future studies should focus on the methods that are cost-effective and simple processes.

In order to recover the membrane flux of NF/RO systems chemical cleaning is inevitable. Selection of chemical cleaning agents that exhibit favorable chemical reaction with the target foulants in the fouling layer is of great importance. However, chemical agents may cause damage to the selective layer of the NF/RO membranes, so future study should focus on the stability of the membrane surface structure during chemical cleaning process. In addition, the mismatching of chemical agents would generate the opposite effect, resulting in a drastic decline of cleaning efficiency. Therefore, optimization of cleaning agents by bench-scale or pilot-scale tests is necessary to maximize cost-efficiency of the process and minimize the harmful chemicals dosage and unintended detrimental effects on the environment.

Due to the presence of various types of foulant in the natural water bodies and secondary effluent, the physical and chemical interaction mechanisms among the various foulants need to be further researched in order to adopt the appropriate strategy to mitigate membrane fouling of NF/RO systems. Furthermore, most of the existing experimental data are obtained by laboratory experiments using the model water and the results may be not suitable for the practical applications, so the pilot-scale or full-scale researches using the real water should be conducted to solve the practical membrane fouling problems.

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