A review of reverse osmosis membrane fouling and control strategies

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Abstract
Reverse osmosis (RO) membrane technology is one of the most important technologies for water treatment. However, membrane fouling is an inevitable issue. Membrane fouling leads to higher operating pressure, flux decline, frequent chemical cleaning and shorter membrane life. This paper reviews membrane fouling types and fouling control strategies, with a focus on the latest developments. The fundamentals of fouling are discussed in detail, including biofouling, organic fouling, inorganic fouling and colloidal fouling. Furthermore, fouling mitigation technologies are also discussed comprehensively. Pretreatment is widely used in practice to reduce the burden for the following RO operation while real time monitoring of RO has the advantage and potential of providing support for effective and efficient cleaning. Surface modification could slow down membrane fouling by changing surface properties such as surface smoothness and hydrophilicity, while novel membrane materials and synthesis processes build a promising future for the next generation of RO membranes with big advancements in fouling resistance. Especially in this review paper, statistical analysis is conducted where appropriate to reveal the research interests in RO fouling and control.

Graphic Abstract

Keywords: Reverse osmosis; Membrane fouling; Pretreatment; Surface modification; Antifouling
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Abbreviations

AA        acrylic acid
AOM       algal organic matter
BSA       bovine serum albumin
CC        chemical coagulation
CEOP      cake enhanced osmotic pressure
CNTs      carbon nanotubes
DAF       dissolved air flotation
DOC       dissolved organic carbon
DTAB      dodecyltrimethyl ammonium bromide
EC        electrocoagulation
ED        electrodialysis
EDTA      ethylene diamine tetra acetic acid
EfOM      effluent organic matter
EIS       electrical impedance spectroscopy
EPS       extracellular polymeric substances
EXSOD     ex-situ scale observation detector
MF        microfiltration
NF        nanofiltration
NIPAM     N-isopropylacrylamide
NOM       natural organic matter
PDA       polydopamine
PEI       polyethyleneimine
PV        pervaporation
PVA       polyvinyl alcohol
RO        reverse osmosis
SC        surface coating
SDS       sodium dodecyl sulfate
SG        surface grafting
SWRO      seawater reverse osmosis
TEP       transparent exopolymer particles
TFC       thin film composite
UF        ultrafiltration
1. Introduction

Water shortage is one of major challenges in many places around the world (Adeniji-Oloukoi et al., 2013; Avrin et al., 2015; Garcia-cuerva et al., 2016; Hibbs et al., 2016). It is exacerbated by water pollution from agricultural residues, sewage as well as industrial waste (Yao et al., 2016). In order to meet the rising demand for fresh water, strategies like water reuse and seawater desalination have already been applied (Bartman et al., 2011; Gu et al., 2013). Membrane technology is one of the most promising ways to produce high quality water (Lin et al., 2016; Ochando-Pulido et al., 2016; F. Tang et al., 2016).

The common membrane technologies for water treatment include but are not limited to microfiltration (MF) (He et al., 2016), ultrafiltration (UF) (Sun et al., 2015), nanofiltration (NF) (Ribera et al., 2014), reverse osmosis (RO) (Yang et al., 2017), forward osmosis (FO) (Boo et al., 2012), membrane distillation (MD) (Bush et al., 2016), electrodialysis (ED) (Y. Zhang et al., 2015) and pervaporation (PV) (Subramani and Jacangelo, 2015). RO membrane technology is widely used in seawater desalination, drinking water production, water treatment and wastewater treatment. RO is currently the most energy-efficient technology for desalination, with energy cost about 1.8 kWh/m³, which is much lower than that of other technologies (G. R. Xu et al., 2013). Also, RO membrane has the advantages of high water permeability and salt rejection, fulfillment of the most rigorous rules for public health, environmental protection and separation process (López-Ramírez et al., 2006).

However, RO membrane fouling is a main challenge to reliable membrane performance. Fouling is a complicated phenomenon which involves different mechanisms under different circumstances (Khan et al., 2014). For example, a lot of RO projects reusing wastewater with high levels of phosphate are in operation worldwide (Chesters, 2009). In these plants, calcium phosphate scaling on membrane surfaces is a big problem, resulting in poor plant operation and high cleaning and maintenance cost (Chesters, 2009). Membrane fouling could significantly reduce productivity and permeate quality while increasing operation cost due to increased energy demand, additional pretreatment, foulants removal and membrane cleaning, maintenance, as well as reduction in membrane lifetime (Al-Amoudi, 2010; Eric M et al., 2001; Kochkodan et al., 2014; Tang et al., 2011). In order to control membrane fouling, a variety of methods such as pretreatment, membrane monitoring, membrane cleaning, surface modification, as well as developing novel RO membranes have been studied (Al-Juboori and Yusaf, 2012; Brehant et al., 2002; Henthorne and Boysen, 2015; Nguyen et al., 2012; Robinson et al., 2016). The application of different methods could result in different control effects and therefore, in practice these techniques are usually applied together to reduce RO membrane fouling.

Statistical analysis revealed that in the last 25 years, over 3000 papers were published to address the issue of RO membrane fouling (shown in Fig. 1, see Supplementary Information for more details on statistical analysis method), indicating researchers’ great interest in this area. Specifically, the number of SCI papers published in 2016 increased by around 20 times
compared to papers published in 1992 and was around twice as the papers published 5 years ago (i.e., year 2011). A polynomial model was derived to describe the cumulative number of publications from 1992 to 2016, with the equation \( P = 0.3735 Y^3 - 6.881 Y^2 + 67.139 Y - 83.109 \) \((R^2 > 0.999)\), where \( P \) is the cumulative number of publications and \( Y \) denotes the number of years since 1992. Based on this model, and assuming that no revolutionary breakthroughs in RO membrane technology and alternative technologies as well will be made in the next ten years, then it can be predicted that by the year 2022, the cumulative number of papers published will possibly be about twice that of 2016. Although the research trend may not be predicted precisely simply by this model, it can at least give us an indication that research interest in this field will continue to bloom.

Therefore, it is necessary to provide an up-to-date review of RO fouling and its control. This paper reviews membrane fouling and fouling control strategies, with a focus on the latest advances. The first objective of this paper is to elucidate the types of fouling. The second objective is to discuss state of the art strategies for fouling mitigation, including pretreatment, monitoring, cleaning, surface modification as well as novel membrane materials and synthesis process. Especially, statistical analysis (bibliometric method) is adopted where appropriate in this review paper to reveal researchers’ interest in related sub-fields. This comprehensive review may provide an avenue for future research work related to RO membrane fouling.

Fig. 1. Number of publications per year and cumulative number of publications on RO fouling over the past 25 years

2. Membrane fouling

Generally fouling is the accumulation of undesired deposits on the membrane surface or inside the membrane pores, causing decrease of permeation flux and salt rejection (Malaeb and Ayoub,
Since water is the operating environment for most RO applications, it is important to understand the behaviors of water as well as ion transport through RO membrane, which could indicate how RO fouling occurs. Water permeation through membrane could take place in the form of Brownian diffusion, flush and jump diffusion (Gao et al., 2015). The intermolecular interactions of water and ions with membrane are strongly affected by the structure of membrane such as the free volume size in the membrane. In other words, if the membrane structure is more compact, then more energy will be required for water permeation, and as a result, it will be easier for fouling to occur since particles are more prone to accumulate on membrane surface, known as surface fouling which is discussed below.

Fouling can be divided into surface fouling and internal fouling, in terms of the fouling places (Lin et al., 2014; She et al., 2016; Yu and Graham, 2015). The fouling mechanisms of low pressure membranes (i.e., MF and UF) are some kind of different from those of high pressure membranes (i.e., NF and RO). For MF and UF, pore adsorption and clogging are more common while for NF and RO, surface fouling is comparatively more frequent due to the relative compact and nonporous nature of RO membrane (Greenlee et al., 2009). This does not, however, mean that surface fouling is more “dangerous” than internal fouling for RO membrane. Actually, compared with internal fouling, surface fouling is easier to be washed away through improving feed water hydrodynamic conditions or chemical cleaning (Hoek et al., 2008; She et al., 2016). Therefore, it is usually more reversible than internal fouling (Arkhangelsky et al., 2012). Nevertheless, it should be clarified that depending on feed water compositions and their interactions with membrane, both surface fouling and internal fouling can be irreversible.

Fig. 2. SEM of four fouling types on membrane surfaces. (A) Biofouling. (B) Organic fouling. (C) Inorganic scaling. (D) Colloidal fouling. Adapted from (Ho et al., 2016; Hu et al., 2013; Shafi et al., 2017; J. Xu et al., 2013).
In terms of foulants types, fouling can also be classified into biofouling, organic fouling, inorganic scaling and colloidal fouling (Hakizimana et al., 2015; Weinrich et al., 2016; Xu et al., 2010). Fig. 2 shows scanning electron microscope (SEM) images of four fouling types on membrane surfaces. More specifically, Fig. 2A shows the surface of a RO membrane contaminated by bacteria (J. Xu et al., 2013) while Fig. 2B displays the RO membrane surface that is fully covered by an organic foulant, sodium alginate (Shafi et al., 2017). Fig. 2C clearly demonstrates calcium sulfate (CaSO$_4$) scaling on a RO membrane surface (Hu et al., 2013) and Fig. 2D reveals a RO membrane surface fouled by a common colloidal foulant, silica (Ho et al., 2016). In practice membrane fouling is usually caused by a combination of different foulants and membrane autopsy methods are widely used to study the origin and extent of membrane fouling and distribution of foulants because it can provide precise information about foulants compositions and properties (Gorzalski and Coronell, 2014; Kim et al., 2015; Tang et al., 2014; Tran et al., 2007). However, fundamental understanding of formation mechanism of fouling layer could not be obtained through autopsy.

2.1 Biofouling

Biofouling is the process of microorganism adhesion and proliferation on membrane surface. In other words, it is the formation of biofilm to an unacceptable degree which could cause huge operational costs. Biofilm formation is essential in this process (Creber et al., 2010a). Biofouling is more complex than other fouling types. There are two key components of biofilms, namely the bacteria and the extracellular polymeric substances (EPS) which were excreted by bacteria during the metabolism process (Yu et al., 2016). In marine environment, the bacterial community is highly diverse and distinct, with proteobacteria, bacteroidetes, firmicutes and cyanobacteria being the typical ones (Belila et al., 2016; Khan et al., 2013). Depending on different water environment and bacteria community, EPS could have different substances, but are mainly made up of polysaccharides, proteins, glycoproteins, lipoproteins or lipids and nucleic acids (Drews, 2010; Matin et al., 2011; She et al., 2016). The surface morphology of biofouling layers could be different under different environments and it is a good way to observe and analyze the biofouling vividly on a micro level (Karkhanechi et al., 2014; Leterme et al., 2016; Weinrich et al., 2016).

According to Flemming (Flemming, 1997), biofilm development could undergo three stages, namely induction, logarithmical growth and plateau stages. From another perspective, biofilm formation could be briefly divided into three phases in terms of bacteria activity and mobility, and the three phases are bacteria attachment, reproduction, and detachment. Bacteria attachment is a dynamic process consisting of bacteria approaching and then adhering to the membrane surface, which is expected to be the most important stage in biofilm formation. The existence of dead or low flux zone in the pipe system could have an important effect on bacteria growth. A lot of other factors could also affect this process, and these factors could be classified into microbial properties (Camesano and Logan, 1998; B. Tang et al., 2016), membrane surface characteristics (Nguyen et al., 2016), and surface-bacteria interactions (Kang et al., 2004; Walker et al., 2004), as well as operational conditions (Habimana et al., 2014). In brief, as illustrated by Fig. 3, microbial properties include hydrophobicity, surface charge and surface structure, etc. Membrane characteristics include surface hydrophobicity, surface charge,
chemical compositions, roughness, surface morphology, etc. Operating conditions include permeate flux, crossflow velocity, temperature, pressure, pH, salt concentration, presence of certain molecules, feed spacer, etc.

![Fig. 3. Factors affecting bacteria attachment to membrane surface](image)

The next stage is bacteria reproduction, and during this period the attached microorganisms consumes nutrients in the water and undergo proliferation and meanwhile excrete EPS (Matin et al., 2011). The EPS could make the biofilm structure stronger, making it more difficult to clean the biofilm (Ben-Dov et al., 2016; Leterme et al., 2016). Also, EPS could function as a barrier to protect bacteria from bactericide (Belila et al., 2016). The final stage is the bacteria detachment, and during this period the bacteria leaves the mature biofilm due to lack of nutrients as well as the increase of population density. The bacteria finds new sites to grow and the process repeats and new biofilm forms. Later stage of biofouling was more difficult to be removed compared to earlier stage (Creber et al., 2010b).

Biofouling is widely regarded as one of the most formidable fouling (Al-Juboori and Yusaf, 2012; Hibbs et al., 2016; Ni et al., 2014; G. R. Xu et al., 2013). Statistical analysis revealed that around 500 papers were published in the past 10 years to address the issue of biofouling. Unlike other fouling, membrane biofouling is difficult to eradicate by pretreatment methods. As analyzed above, biofouling is formed by microorganism, and microorganism can grow and multiply. As a result, unless pretreatment can remove one-hundred percent of the bacteria, the remaining organisms can grow gradually on membrane surface and cause membrane fouling. On the other hand, for a biofilm to form, two conditions are essential, namely the presence of bacteria as well as the nutrients. So the logic is that if all the nutrients are removed from the water through pretreatment technologies, then the remaining cells could not proliferate due to
lack of food sources. Based on this principle, Weinrich et al. (Weinrich et al., 2016) investigated the relationship between membrane fouling rate and the content of assimilable organic carbon (bacteria nutrient). By observing operational changes such as increased differential pressure and decreased permeate flux, they found that membrane biofouling is more serious when nutrient is higher.

2.2 Organic fouling

Just as its name implies, organic fouling is caused by organic matters. These organic matters usually consist of humic substances, polysaccharides, proteins, lipids, nucleic acids and amino acids, organic acids, and cell components (Cho et al., 1999; Jeong et al., 2016). For surface water or seawater, natural organic matter (NOM) is often used while for wastewater effluent organic matter (EfOM) is often adopted (Kim and Dempsey, 2013). In wastewater treatment, organic fouling is a main problem in RO treatment because the EfOM concentration (10–20 ppm) is much higher compared to typical NOM concentration in surface waters (2–5 ppm) (Malaeb and Ayoub, 2011).

Fig. 4. Cumulative number of publications related to three common RO organic foulants studied in the past 10 years

Fig. 4 shows the cumulative number of publications related to three common RO organic foulants studied in the past 10 years. As indicated by Fig. 4, there are strong research interests in bovine serum albumin (BSA), alginate and humic acid as RO organic foulants. BSA is a type of protein while alginate is a typical representative of polysaccharide. The fouling mechanism of BSA for RO is different with other membranes such as MF. For example, BSA could deposit inside MF membrane pores and cause pore blocking as a result. As RO membrane is non-porous, the fouling behavior of BSA is different. BSA fouling of RO usually occurs on membrane surface, with the first step of depositing on the surface via foulant-surface interactions followed by BSA-BSA interactions, the latter of which could cause more BSA to deposit on membrane
surface and finally resulted in serious membrane fouling if no action (e.g., cleaning) takes place (Ang and Elimelech, 2007). Furthermore, when other pollutants such as alginate exist together, BSA fouling could be intensified due to foulant-foulant interactions (Yu et al., 2012). The fouling behaviors of alginate and humic acid are similar to that of BSA.

Table 1

Some representative work on RO organic fouling under different situations

<table>
<thead>
<tr>
<th>Organic matter</th>
<th>Category</th>
<th>Main findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginate</td>
<td>Polysaccharide</td>
<td>Membrane fouling aggravated with decreasing pH, increasing ionic strength, and addition of calcium ions (Lee et al., 2006).</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>Fatty acid</td>
<td>Both pH and calcium ions could affect the octanoic acid fouling behavior (Ang and Elimelech, 2008).</td>
</tr>
<tr>
<td>Humic acids</td>
<td>Humic substances</td>
<td>Fouling was mainly due to hydrophobic interactions between organic matters and membrane as well as interactions between the organic matters (Yu et al., 2010).</td>
</tr>
<tr>
<td>Hydrophilic carbohydrates, EPS, aquatic humic substances</td>
<td>EfOM</td>
<td>Hydrophilic carbohydrates and EPS made more contributions to membrane fouling than aquatic humic substances (Zhao et al., 2010).</td>
</tr>
<tr>
<td>Alginate, BSA, NOM, octanoic acid</td>
<td>Polysaccharides, proteins, humic substances, fatty acids</td>
<td>Membrane fouling by alginate was dominated by foulant aggregate size. Furthermore, smaller and more compact aggregates could result in more significant flux decline (Ang et al., 2011a).</td>
</tr>
<tr>
<td>BSA</td>
<td>Protein</td>
<td>Membrane properties had no effect on long term flux behavior, the latter was mainly controlled by foulant-deposited–foulant interaction (Wang and Tang, 2011).</td>
</tr>
<tr>
<td>Transparent exopolymer particles (TEP), biopolymers, proteinaceous compounds</td>
<td>NOM in seawater</td>
<td>Concentrations of TEP and proteinaceous compounds were closed related to membrane fouling levels (Miyoshi et al., 2016).</td>
</tr>
</tbody>
</table>

Some representative work on RO membrane organic fouling behaviors under different situations is summarized in Table 1. As revealed by Table 1, the contributions of different organic matters on RO fouling could be different in different situations, with one kind of organic matter being the dominant foulant in one situation but replaced by another organic pollutant in another situation. However, one conclusion that could be safely drawn is that feed water chemistry, foulant-surface interactions as well as foulant–foulant interactions are three important factors affecting organic fouling. Organic fouling could result in significant flux decline of RO membranes and it is hard to eliminate due to the complex structures formed by dissolved organic matters in combination with other substances (Ding et al., 2016; Naidu et al., 2014; Shen and Schafer, 2015). The molecular weight of organic matters is another important factor for membrane fouling (Teixeira and Sousa, 2013). Moreover, organic matters with a low molecular weight are more difficult to be removed through conventional pretreatment technologies such as coagulation compared to high molecular weight organic matters (Fabris et al., 2008). Lee et al. (Lee et al., 2008) found that the initial stage of fouling was caused by medium to low molecular weight components of organic matters, while the majority of fouling
is caused by very high molecular weight organic matters (>50,000 Da).

2.3 Inorganic scaling

Inorganic scaling is the deposition of inorganic substances on membrane surface or inside the membrane pores (Henthorne and Boysen, 2015; Khayet, 2016). As the solubility of some inorganic scalants is pretty small or the concentration of some ions in the water is pretty high, when they exceed the equilibrium solubility product and become supersaturated, they will deposit on the surface or the pores of the membrane, resulting in scaling (Shirazi et al., 2010). To be specific, the inorganic ions in water which exceed the equilibrium solubility product firstly reach the nucleation stage, and then go through homogenous or heterogeneous crystal growth processes (Al-Amoudi and Lovitt, 2007). Both inorganic scaling and the formation of cake layer due to the inorganic precipitation could prevent water from permeating through the membrane (Zhu and Elimelech, 1997).

Statistical analysis revealed that calcium sulfate and calcium carbonate were most studied as inorganic scalants by researchers in the past 10 years, indicating their important roles in causing RO inorganic fouling (shown in Fig. 5). This result is in line with expectations as calcium sulfate and calcium carbonate are really the most common scalants causing RO membrane scaling (Ochando-Pulido et al., 2015). Besides, as revealed by Fig. 5, other common inorganic scalants include calcium phosphate, barium sulfate and so on.

![Fig. 5. Common studied inorganic foulants for RO in the past 10 years](image)

There are many factors which could affect inorganic scaling on membrane, such as membrane traits, compositions and features of feed water as well as operating conditions (Rabie et al., 2001; Shaalan, 2003). According to a study conducted by Lee et al. (Lee et al., 1999), for unstirred batch membranes, surface (heterogeneous) crystallization plays a major role in flux decline, while for crossflow membranes, both surface crystallization and bulk (homogeneous) crystallization could cause scaling on the membranes. Due to the difficulty of removing the scalants on the surface or in the pores of membrane, it is pretty difficult to recover membrane performance only by using physical methods such as backwash (Shirazi et al., 2010).

Different ions may have different effects during the scaling process. Basically, the compositions of salt deposits on RO membranes are determined by inorganic compositions in feed water, chemicals added during pretreatment, as well as the chemical properties of the sparingly soluble inorganic salts (Schneider et al., 2005). Tang et al. (F. Tang et al., 2016) analyzed the
components of inorganic foulants on RO membranes through membrane autopsy and by means of SEM. The result shown that the major inorganic elements found on RO membrane surface were Fe, Ca and Mg. Furthermore, compared to other elements, Fe could deposit on the RO membrane much more easily. Ca and Mg scaling could be mitigated in the presence of scaling inhibitors (F. Tang et al., 2016). On the contrary, the induction time and overall time of calcium sulphate crystallization at lower supersaturation could be shortened when there are iron ions in the solution (Bystrianský et al., 2016). Therefore, removing the iron ions or adding compounds to inhibit the effects of iron ions could also reduce inorganic scaling on the surface or in the pores of the membranes (Bystrianský et al., 2016).

2.4 Colloidal fouling

Colloids are fine suspended particles, the size of which ranges from a few nanometers to a few micrometers, although some references define the size of colloids ranges from one nanometer to one micrometer (Al-Amoudi and Lovitt, 2007; Zhu and Elimelech, 1997). Colloidal fouling refers to fouling of the membrane caused by the colloids or particles depositing on the host materials (Khayet, 2016). The common colloidal foulants can be divided into two types, i.e., inorganic foulants and organic macromolecules. The major inorganic foulants in nature water include aluminum silicate minerals, silica, iron oxides/hydroxides while the organic macromolecules in the water are mainly consisted of materials such as polysaccharides, proteins, as well as some natural organic matters (Tang et al., 2011).

Colloidal fouling could be influenced by many factors such as the colloids size, shape, charge as well as interactions with ions of the colloids (Buffle et al., 1998). Foulant–ion and membrane–ion specific interactions could mightly affect the membrane fouling. For example, the charge properties of polyamide based membranes can be effected by cations such as calcium and magnesium (Wang et al., 2014). The frequency of particle collision and the attachment coefficient could decide the rate of colloidal aggregation, while the coefficient is the reflect of the energy barrier that results from the summation of the van der Waals force and the electrostatic interaction force (Tang et al., 2011). The cake layer formed by deposition of colloids on the membrane surface could lead to an additional hydraulic resistance and a serious concentration polarization, which could cause decrease of permeate flux and increase of operating pressure (Ang and Elimelech, 2007).

Like other types of fouling, the formation of a colloidal cake layer could also be impacted by feedwater characteristics such as the concentrations of the foulants and the physiochemical characteristics, membranes properties as well as operational conditions (Ju and Hong, 2014; Kim et al., 2014; Motsa et al., 2017; Ning et al., 2005). In many published papers, colloidal fouling is integrated into inorganic fouling or/and organic fouling and discussed as a whole.

3. Membrane fouling control strategies

A lot of efforts have been done to address the problem of fouling. For example, through improving hydrodynamics of the filtration process, membrane fouling could be reduced. A
detailed discussion on hydrodynamics can be found in another review paper (She et al., 2016) and is not the focus of this paper. Generally, the difficulty to mitigate fouling is different depending on fouling types. Inorganic scaling could be easily reduced through chemical and physical methods. In contrast, organic fouling and biofouling are more difficult to control and in fact these two kinds of fouling are kind of synergistic (Jeong et al., 2013). For example, bacteria produce EPS during biofilm formation. EPS are organic matters and constitute for supportive and protective structure for bacteria. Meanwhile, organic matters could accumulate in the biofilm (Warsinger et al., 2015). Miyoshi et al. (Miyoshi et al., 2016) reported that organic matters such as TEP and biopolymers play important roles in the formation of biofilms.

3.1 Pretreatment technologies

Pretreatment has been widely used in RO systems and it has the advantage of improving the feed water quality greatly to ensure reliable RO operation as well as to prolong membrane life. Pretreatment methods could be selected based on the source water composition analysis. For example, for feed water that has a high hardness level, pretreatment to reduce hardness is necessary so as to reduce membrane scaling risk. A lot of work has been done by researchers to study the performance of different pretreatment technologies. A statistical analysis was conducted to reveal the common RO pretreatment technologies studied in the past 10 years. As shown in Fig. 6, UF, coagulation/flocculation and MF are the three technologies that have been most studied by researchers as RO pretreatment methods. In fact, UF/MF filtration as pretreatment of RO is gaining more and more popular in recently. Coagulation/flocculation has long been used as a pretreatment method for not only RO but NF and other technologies as well. Fig.7 shows the flow diagram of RO pretreatment processes with their effects in removing contaminants from water and roles in fouling control. While different pretreatment systems are designed in different situations, it illustrates pretreatment processes that are common in RO plants. Below is a detailed discussion and comparison of these techniques.

![Common studied RO pretreatment technologies in the past 10 years](image)

**Fig. 6.** Common studied RO pretreatment technologies in the past 10 years
Disinfection is an important pretreatment method because it can destroy microorganisms that can not only cause diseases but also cause membrane biofouling. There are several commonly used disinfectants, including free chlorine, chloramines, chlorine dioxide, ozone, ultraviolet as well as potassium permanganate (O. M. Lee et al., 2015; Song et al., 2016; T. Y. Zhang et al., 2015). As one of the most widely used disinfectants, chlorine is very effective for the deactivation of a large variety of waterborne microorganisms. When chlorine is added into water, it reacts with water and produces hypochlorous and hydrochloric acids (Al-Juboori and Yusaf, 2012), as shown below:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{HCl} \]

While hydrochloric acids dissociate completely into hydrogen and chloride ions, hypochlorous only dissociates partly and the undissociated hypochlorous has a strong oxidizing property and can inactivate most types of microorganisms (Winward et al., 2008). Chlorination effectiveness is affected by pH and disinfection is more effective at lower pH. While it is effective, chlorine residual should be removed before subsequent water treatment by membrane since it can negatively cause membrane degradation (Hong et al., 2013). Ozone is another powerful oxidizing chemical that has been widely used for water disinfection (H. Wang et al., 2015). Paraskeva and Graham found that ozone can effectively and efficiently remove microbial organisms *E. coli* and coliforms and removal rate is greatly affected by ozonation rates (Paraskeva and Graham, 2005). Unlike chlorine, ozone residual is not adequate to keep a sterile water environment. However, from another perspective, compared with chlorination, ozonation is beneficial for subsequent RO membrane treatment since ozone residual is not a big problem as chlorine residual.
Coagulation is the process of destabilizing suspended solids. Coagulants and colloids possess adverse electrical charges in water and thus when they meet the charges could be neutralized, resulting in fast aggregation of small-suspended particles to form microflocs (Liu, 2014). Generally, there are two types of coagulation, namely chemical coagulation (CC) and electrocoagulation (EC) (Harif et al., 2012; Lee and Gagnon, 2016). The CC process usually requires rapid and high energy mixing to ensure full mixing of coagulants to maximize formation of the microflocs (Koohestanian et al., 2008). Following coagulation is flocculation, which is a slower mixing stage of microflocs to form larger visible particles and then these macroflocs can be removed by sedimentation, flotation or filtration. Dissolved air flotation (DAF) which works by saturating water with air under pressure and then releasing the air into the feed water which then forms air bubbles that can assist to remove suspended particles in the water (Villacorte et al., 2015), is an alternative to conventional sedimentation and has the advantages of effectively reducing coagulant dosages. Coagulation/flocculation is proved to be an effective pretreatment method for improving overall water quality as well as for mitigating membrane organic fouling, colloidal fouling and biofouling. Using ferric chloride as a chemical coagulant, Tabatabai et al. (Alizadeh Tabatabai et al., 2014) investigated the performance of coagulation on removal of algal organic matter (AOM) in seawater and concluded that coagulation substantially reduced fouling potential as well as the compressibility of the AOM cake/gel layer. Peiris et al. (Peiris et al., 2013) found that polyaluminum chloride as a chemical coagulant could reduce hydraulically irreversible fouling caused by humic substances and protein-like matters. EC has been intensively studied recently as an unconventional pretreatment method (Den and Wang, 2008; Millar et al., 2014; Zhao et al., 2014). Hakizimana et al. (Hakizimana et al., 2015) concluded that EC is highly potential in mitigating organic fouling as well as biofouling due to its capacity to reduce dissolved organic matter and microorganisms from water. Sadeddin et al. (Sadeddin et al., 2011) suggested that the removal efficiencies of total suspended solids and turbidity by EC could reach nearly 100%. However, EC is not widely used due to its relatively high operation cost. On the other hand, neither CC nor EC is effective in reducing inorganic scaling. A more effective method is known as scale inhibitors. Scale inhibitors reduce membrane inorganic fouling by changing the chemical and physical properties of the ions (e.g., calcium ion and sulfate ion) that have a very low ion product and thus change the scaling mechanisms accordingly (Pramanik et al., 2017). However, one drawback of using scale inhibitors lies in that new scaling risk (e.g., calcium phosphate scaling) could be brought. Another method for controlling RO inorganic fouling is using ion exchange resins, also known as water softeners. However, additional cations such as sodium cations will be released into water during this process which could place a burden for the following RO process.

Granular media filtration is the process to remove suspended solids, microorganisms and other contaminants when water passes through a porous granular media (Greenlee et al., 2009; Ho et al., 2011; Monnot et al., 2016a; Yu and Graham, 2015). There are many types of granular materials, including but not limited to activated carbon (Delgado et al., 2012; Serpieri et al., 2000; Shanmuganathan et al., 2014), anthracite (Schmidt et al., 2016), sand (Asami et al., 2016), diatomaceous earth (Michen et al., 2011), sponge (Yeom and Kim, 2016; Young et al., 2016), cotton (Ferrero et al., 2014), etc. Among the granular materials, activated carbon is widely used
in commercial water filters as a pretreatment method for the subsequent RO membrane filtration (Monnot et al., 2016a). Activated carbon can reduce the concentration of a variety of substances that are common in water (Derylo-Marcewksa et al., 2017; Karmacharya et al., 2016; Korotta-Gamage and Sathasivan, 2017). For example, activated carbon can effectively remove free chlorine, a common chemical existing in tap water after water chlorination (Jamaly et al., 2014). As discussed before, exposure to free chlorine could cause RO membrane degradation and consequently shorten the membrane lifetime (Surawanvijit et al., 2016). A lot of work has been down on developing novel RO membranes with chlorine-tolerant property (Kim et al., 2016; Kwon et al., 2012; Liu et al., 2014, 2015; Rana et al., 2015; Saqib and Aljundi, 2016). It is another scenario and will not be discussed thoroughly in this review. Besides, powered activated carbon (PAC) and granular activated carbon (GAC) could effectively remove dissolved organic carbon (DOC). However, they played little role in reducing biopolymers (Nguyen and Roddick, 2013; Pramanik et al., 2014). Biological activated carbon (BAC) performed well in reducing organic fouling because it could effectively remove foulants such as biopolymers via biodegradation and adsorption.

In seawater desalination, brackish water and wastewater treatment, membrane filtration especially UF/MF is becoming a popular pretreatment choice to control RO membrane fouling since it could save a lot of space compared with conventional treatment technologies while producing higher quality of effluent for subsequent RO. Firstly, the performance of RO will be improved by utilizing the membrane pretreatment. As discussed in section 2, RO membrane could be easily polluted by substances such as particles, biofilm and organic macromolecules (Janghorban Esfahani et al., 2013). In certain situations, the particles removal efficiency of UF and MF could reach almost 100% (Bonnélye et al., 2008). A constant qualified feed water of RO can be guaranteed by UF with using a small quantity of chemicals or even no chemicals (Teng et al., 2003; J. D. Zhang et al., 2006). Bae et al. (Bae et al., 2011) discovered that the sum of the relative abundance of biofilm-forming bacteria was decreased by about 30% by using the conventional pretreatment, while that sum was decreased by almost 90% by using membrane pretreatment. Therefore, the RO membrane could not be easily fouled, indicating that surface water with poor and/or variable quality could also be treated in that way, and the RO flux could be higher as well (Pearce, 2007). Furthermore, UF/MF pretreatment could be more economical for long-term operation, which could be achieved by reducing energy consumption, use of chemicals, cleaning frequencies as well as replacing of the RO. However, while UF could effectively remove colloids, TEP and bacteria before RO, it is not effective in reducing DOC. GAC is more effective in reducing DOC but less efficient in removing particles and microorganisms (Monnot et al., 2016b). Therefore, coupling GAC and UF could effectively control RO biofouling. Besides, although membrane pretreatment can significantly enhance the performance of RO membranes, the high fouling potential and apparent irreversibility is still a problem in some situations. A combination of membrane pretreatment and conventional pretreatment technique such as coagulation could mitigate this problem, since a lot of foulants could have been removed through coagulation and thus the burden placed on subsequent UF/MF will be greatly reduced (Resosudarmo et al., 2013).

To conclude, pretreatment before RO systems is important to mitigate RO membrane fouling.
As illustrated in Fig. 7, in practical applications, combination of different pretreatment technologies is usually adopted to ensure the best RO performance (Farin and Luis, 2007; Kaya et al., 2015). For instance, Zhang at al. (J. Zhang et al., 2015) used wastewater feed from Melton Wastewater Treatment Plant and found that a combination of ozonation, MF and BAC provided the best protection to RO membrane and the foulants could be easily removed from the RO membrane surface by deionized water. Again, this is because different pretreatment technologies have different preferences and capabilities towards removing different kinds of contaminants from water. If pretreatment combinations and steps before RO are not selected properly, then more contaminants could reach to RO membrane surface. As a result, more frequent membrane cleaning will be needed, which could have an adverse impact on membrane lifespan.

### 3.2 Membrane monitoring and cleaning

#### 3.2.1 Membrane monitoring

In-situ and real-time monitoring of RO performance is necessary to evaluate the severity of fouling on membrane and correspondingly to conduct cleaning timely. Normalization of bulk observations of pressure, flow and conductivity is reported to be the most effective way for in-situ and real-time monitoring the RO performance (Hu et al., 2013). Early detection of scale formation in RO systems remains challenging. Currently, many monitoring techniques are not sensitive enough to detect the subtle changes occurring on the membrane in an early fouling stage. In other words, the signals delivered by these monitoring parameters only show obvious fouling formation (Cobry et al., 2011). For example, RO membrane fouling is usually evaluated through monitoring flux decline with time. And it is generally assumed that the constant flux in early RO operation stage indicates no RO fouling. In fact, the flux decline in early stage could not be discovered until obvious fouling occurs. Besides, as RO membranes developed in recent years possess high permeability and low resistance, it is becoming a less appropriate method to detect fouling by flux decline. It has the same problem for using permeate flux decline as a method to assess membrane cleaning efficiency (Nam et al., 2014). Another example is sacrificing the RO module and performing autopsy to identify RO foulants (Sari and Chellam, 2016). Similarly, it cannot detect RO membrane fouling in the early stage. In order to solve this problem, a number of technologies are developed. For example, the application of ultrasonic time-domain reflectometry (UTDR) for in-situ and real time monitoring in membrane separation process is gaining more popular in recent years (Li et al., 2015, 2014, 2012; Z. Zhang et al., 2006). Fig. 8 shows the principles of UTDR technology. A medium is required for ultrasound waves to go through. When waves are sent out and are reflected at the interfaces (e.g., water/membrane interface, water/fouling layer interface), the return time as well as the magnitude of the waves could be obtained and calculated, through which the thickness of the fouling layer could be determined (S. T. V Sim et al., 2013). Although UTDR has been applied into a variety of membrane separation processes, it should be pointed out that since the acoustic properties at the interfaces is only slightly different, it is not easy to detect membrane biofouling (S. T. V Sim et al., 2013). Besides UTDR, ex-situ scale observation detector (EXSOD), which uses high resolution digital photography to detect scale crystals before flux decline happens, is another real-time monitoring technique that has a great potential for industrial applications (Hu...
et al., 2013; Malaeb and Ayoub, 2011; Uchymik et al., 2007).

![Fig.8. Schematic diagram of UTDR technology](image)

Another monitoring technology gaining popular recently is the electrical impedance spectroscopy (EIS), a novel non-invasive method to monitor the membrane fouling process (Antony et al., 2013; Chilcott et al., 2015; Jing et al., 2016). Compared with conventional fouling measurement methods such as permeate decline and transmembrane pressure, EIS is a more sensitive monitoring method. The main principle of EIS technology is that when membrane fouling starts to form, the electrical properties of the membrane change. In order to do this, usually a typical RO cell is installed with electrodes in conjunction with a high resolution impedance spectrooscope which enable in-situ EIS measurement of the fouling process. Based on the EIS data obtained, Nyquist plots are used to characterize the dynamic fouling process. Kavanagh et al (Kavanagh et al., 2009) found that when RO membrane was fouled by a small amount of deposited calcium carbonate, both the conductance and impedance indicated great changes. Using silica and BSA as the model foulants, Sim et al (L. N. N. Sim et al., 2013) observed that EIS could detect any changes that occurred on the membrane surface in an almost real-time manner. In a recent study conducted by Sim and coworkers, it is revealed that the conductance of all the electrical factors at the beginning decreased with time and then increased as fouling proceeded (Sim et al., 2016). Also, the membrane recovered to its original state after cleaning with sodium chloride solution, as indicated by EIS data (Sim et al., 2016). Zhixin et al (Hu et al., 2013) demonstrated EIS as an effective method to detect nascent stages of calcium sulfate scale formation before permeate flux decline could be observed. Furthermore, the electrical capacitance measured at low frequencies was reported to the most sensitive electrical parameter for signaling the nascent stages of scale formation (Ho et al., 2016). EIS also has the potential as a tool to indicate the membrane fouling types (Cen et al., 2015). While EIS was proved to be an effective method, its tests were mainly conducted in laboratory, and its suitability in industrial applications still need to be field tested and adjusted accordingly.

A number of models for predicting membrane fouling have been developed in recent years.
Sim et al. (Sim et al., 2011) proposed a updated cake enhanced osmotic pressure (CEOP) model to predict the crossflow RO fouling profile under constant flux filtration. Based on CEOP model, when the cake thickness and porosity throughout the filtration changed, the predicted transmembrane pressure profile obviously indicated a two-stage of fouling profile. Further discussion of these models will not be included in this review paper as it is another scenario.

### 3.2.2 Membrane cleaning

Periodic membrane cleaning is of great importance during water and wastewater treatment processes (Sadhwani and Veza, 2001; Yang et al., 2013). There are a variety of cleaning methods (e.g., physical, chemical, biological and enzymatic) and their cleaning efficiency could be evaluated by resistance removal and flux recovery (Koo et al., 2001; Madaeni et al., 2001; Madaeni and Samieirad, 2010; Sohrabi et al., 2011). For chemical cleaning, selecting proper chemical agents is important, which is usually done by considering the fouling types and foulants components, as well as the chemical properties and economic factors. Also, no chemical damages should be produced by the chemical agents. Chemical agents could react with the foulants and as a result, the cohesion forces between foulants as well as the adhesion of foulants to membrane surface could be reduced, making foulants easy to be removed. The commonly used chemical agents include acids, bases, surfactants and chelating agents (Varin et al., 2013). Acids, such as hydrochloric acid, nitric acid and sulfuric acid are effective in removing membrane scaling (Gan et al., 1999) while alkaline solutions such as sodium hydroxide are more effective in removing organic fouling and biofouling (Al-Amoudi and Lovitt, 2007; Filloux et al., 2015). The commonly used chelating agent is ethylene diamine tetra acetic acid (EDTA) (Sohrabi et al., 2011). EDTA cleaning efficiency is very sensitive to solution pH (Ang et al., 2006). Operational conditions that may affect cleaning efficiency include cleaning time, crossflow velocity, and temperature (Ochando-Pulido et al., 2015). However, the impacts are somewhat limited (Madaeni et al., 2001). Surfactants are usually organic compounds that contain both hydrophobic groups and hydrophilic groups. Sodium dodecyl sulfate (SDS) is a common surfactant used in cleaning. As organic matter is hydrophobic, the hydrophobic tail of SDS can adhere to the foulants while the hydrophilic head tends to move toward water (Madaeni and Samieirad, 2010). Furthermore, it is reported that SDS could effectively remove colloidal fouling under proper cleaning conditions (Garcia-Fayos et al., 2015). For physical cleaning, rinsing with water is the most frequent method used in practice. Furthermore, a combination of chemical and physical cleaning can be more efficient, where the former contributing to loosening of the foulant layer while the latter promoting its removal via fluid shear (Ramon et al., 2013).

The cleaning efficiencies by different chemical agents treating different foulants have been investigated widely (Piasecka et al., 2015; Ramon et al., 2013; You et al., 2016). Jung et al (Jung et al., 2006) found that acid and alkaline cleaning could not effectively remove calcium salt scales that were formed on RO membranes used for treating wastewater, possibly because of the presence of trace organic materials in the fouling layer that function as a binding agent for inorganic foulants. Lee and Elimelech (Lee and Elimelech, 2007) found that in the presence of calcium, sodium chloride was a very effective salt in removing the alginate gel layer formed...
on the RO membrane surface where alkaline cleaning was not effective. Structural changes of the gel layer followed by ion exchange were proposed to be the mechanism. Qin et al (Qin et al., 2010) developed a novel backwash cleaning technique (i.e., direct osmosis by intermittent injection of high salinity solution) without interrupting of RO operation. Ang et al (Ang et al., 2011a) revealed that alkaline like sodium hydroxide solution alone was not effective in cleaning organic foulants in the presence of calcium while SDS, EDTA and sodium chloride could remove these foulants efficiently especially under higher pH and longer cleaning time. Higher pH could increase the membrane surface hydrophilicity while reducing the negative charge (Sohrabi et al., 2011). Yu et al (Yu et al., 2012) proposed a novel method using thermo-responsive polymer as the chemical cleaning agent and found that it could effectively clean RO membranes that were fouled by BSA. Filloux et al (Filloux et al., 2015) investigated the one-step cleaning using free nitrous acid and found that it could effectively remove biofouling and calcium carbonate scaling. Li et al (Li et al., 2016) developed a new ultrasonic-chemical cleaning system to control organic and inorganic fouling and found that oxalic acid worked best as the chemical agent. It should be pointed out that while different chemical agents have different cleaning efficiencies towards different foulants, combining chemical cleaning agents are not effective in certain situations (Ang et al., 2011b). Membrane cleaning agents should be selected in terms of the specific RO membrane operation situations.

3.3 Surface modification and novel membrane materials

3.3.1 Surface modification

Membrane fouling in RO systems is closely related to surface characteristics (Saqib and Aljundi, 2016). Among these characteristics, surface smoothness and hydrophilicity are reported to be two important factors affecting membrane fouling (Lee et al., 2008; Louie et al., 2006; Malaeb and Ayoub, 2011). Membranes with smooth and hydrophilic surfaces demonstrated less fouling tendency than those with rough and hydrophobic surfaces. One important reason is that a water layer could be easily formed on a hydrophilic surface and foulants with hydrophobic property are repellent to the surface. But it should be clarified that in certain situations hydrophilic membranes are more inclined to attract hydrophilic substances and thus induce fouling (Kwon et al., 2005).

![Fig. 9. Schematic diagram of membrane surface smoothness and hydrophilicity](image-url)
There are a number of ways to increase membrane surface smoothness as well as hydrophilic property, such as surface modifications, novel materials and synthesis process, etc. Surface modification is a very common strategy used to reduce membrane fouling (Cheng et al., 2013; Jee et al., 2016). For example, using low pressure plasma technique, Reis et al. (Reis et al., 2015) introduced amine functionalities onto the surface of commercial polyamide TFC membranes, and then silver nanoparticles were attached to this amine rich TFC membranes, which shown improved antimicrobial property. Surface modification includes surface coating (SC) which is physical modification and surface grafting (SG) which is chemical modification. Fig. 10 clearly shows the effect of surface modification on membrane anti-fouling performance as the non-coated membrane had more bacterial attached to membrane surface than that of the coated membrane (Saeki et al., 2014).

![Image of microscopic images of bacteria on non-coated and coated membranes](image-url)

**Fig. 10.** Microscopic images of bacteria on non-coated and coated membranes after the bacterial adhesion test. In the CLSM images (C and F), the living and dead bacteria were indicated by green and red color, respectively (Saeki et al., 2014).

A variety of chemicals/polymers have been used to modify RO membranes of different types such as polyamide and polyethersulfone and they are summarized in Table 2. Polyamide membranes are most frequently modified and unless otherwise stated, all the modifications summarized in Table 2 are based on polyamide membranes.
Table 2
RO membrane surface modifications via different chemicals/polymers and methods

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Method</th>
<th>Anti-fouling performance of modified membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(NIPAM-co-Am)</td>
<td>SC</td>
<td>Membrane coated by P(NIPAM-co-Am) demonstrated improved fouling resistance to BSA due to the increased membrane surface hydrophilicity (Yu et al., 2011).</td>
</tr>
<tr>
<td>L-cysteine</td>
<td>SG</td>
<td>The modified membrane displayed higher fouling resistance to BAS and DTAB due to enhanced hydrophilicity and lower surface roughness (Azari and Zou, 2013).</td>
</tr>
<tr>
<td>NIPAm, AA</td>
<td>SG</td>
<td>BSA fouling test shown that the deposition of foulants on the modified surface was reduced through enhancing electrostatic repulsion and lowering hydrophobic interaction and thus fouling resistance was improved (Cheng et al., 2013).</td>
</tr>
<tr>
<td>PVA, PHMG</td>
<td>SC</td>
<td>There were lower number of adhered Pseudomonas aeruginosa bacteria on coated membranes, and antimicrobial performance was also improved (Nikkola et al., 2013).</td>
</tr>
<tr>
<td>HEMA, PFA</td>
<td>SC</td>
<td>The attachment of bacterial cells on the coated membranes was significantly reduced shown by bacterial adhesion tests (Ozaydin-Ince et al., 2013).</td>
</tr>
<tr>
<td>pSBMA</td>
<td>SG</td>
<td>The pSBMA-coated membrane had high resistance to protein adsorption, and the adsorption amount of irreversible proteins on the modified membrane was significantly reduced by ~97% (Y. Zhang et al., 2013).</td>
</tr>
<tr>
<td>ADMH, MBA</td>
<td>SG</td>
<td>The anti-biofouling properties of the membranes modified by ADMH and MBA were greatly strengthened (Z. Zhang et al., 2013).</td>
</tr>
<tr>
<td>PDA, BiBBr, MTAC</td>
<td>SC, SG</td>
<td>There was 93.2% less bacteria on the PDA-g-MTAC modified RO after six days of incubation in nutrient solution (Bloek et al., 2014).</td>
</tr>
<tr>
<td>p(MDBAC-r-Am-rHEMA)</td>
<td>SC</td>
<td>The coated membrane surface could significantly depress the growth of bacteria, and the PMDBAC and PAm were key components to antimicrobial property. Also, the surface hydrophilicity was improved (Ni et al., 2014).</td>
</tr>
<tr>
<td>p(MPC-co-AEMA)</td>
<td>SC</td>
<td>Membrane coated by phosphorylcholine polymer via had high resistance to bacterial adhesion (Saeki et al., 2014).</td>
</tr>
<tr>
<td>HPOEM, PEI</td>
<td>SC</td>
<td>Alginate and BSA were used as protein and a polysaccharide foulants. Membranes coated by HPOEM showed better fouling resistance under brackish conditions while zwitterionic carboxylated PEI-coated membrane showed an inhibitory effect to foulant adsorption under seawater conditions (Choi et al., 2015).</td>
</tr>
<tr>
<td>AUTEAB</td>
<td>SC</td>
<td>Coated polyethersulfone membranes had a higher hydrophilicity and a smoother surface, and shown significant antimicrobial activity (Galiano et al., 2015).</td>
</tr>
<tr>
<td>PVA</td>
<td>SG</td>
<td>The modified membrane had a smoother, more hydrophilic and less charged surface and shown improved fouling resistance to model foulants of BSA, SDS and DTAB (Liu et al., 2015).</td>
</tr>
<tr>
<td>p(4-VP-co-EGDA), pCBAA</td>
<td>SC</td>
<td>Bacterial adhesion tests shown an almost 98% reduction in microorganism attachment onto the surface of modified membranes compared to unmodified ones (Shaft et al., 2015).</td>
</tr>
<tr>
<td>DMAEMA, CBMA</td>
<td>SG</td>
<td>The mortality of Escherichia coli and Bacillus subtilis contacted with the modified membrane could reach to 99%, indicating its capacity to prevent bacterial deposition and growth on the membrane surface (J. Wang et al., 2015).</td>
</tr>
<tr>
<td>PEI</td>
<td>SG</td>
<td>The PEI-modified membranes had high anti-fouling property to the positively charged pollutants (Xu et al., 2015).</td>
</tr>
<tr>
<td>GPPTMS</td>
<td>SG</td>
<td>The GPPTMS-modified membranes shown enhanced resistance to casein fouling (Jee et al., 2016).</td>
</tr>
</tbody>
</table>
To summarize, the essence of surface modification is to change the membrane surface properties (surface charge, morphology, hydrophilicity and chemical groups) to a favorable situation of fouling resistance. Although an abundant of studies have been conducted to modify membrane surfaces, a majority of these studies only focused on certain types of foulants, and thus their applications would be greatly limited. Besides, while the anti-fouling performance was enhanced through surface modification, there might be negative effects on membrane performance, such as decreased water flux. Moreover, a lot of chemicals were used and their side effects to human beings and the environment were less understood. No rules or guidelines have been formed for the application of chemicals or polymers. In other words, any chemicals could be used to modify the membranes. As a result, it is more difficult to compare and quantify the exact anti-fouling performance of different surface modified membranes. It is still challenging but significant to develop a RO membrane with perfect anti-fouling property as well as consistent salt rejection and permeation flux performance by simple surface modification techniques.

3.3.2 Novel membrane materials

Polyamide thin-film composite (TFC) RO membranes have long been the dominant RO membranes used in practice (Cohen-tanugi and Grossman, 2015). Many studies on improving RO membrane anti-fouling performance were carried out by incorporating novel materials onto polyamide thin films (Dumée et al., 2015). In recent years, a variety of novel materials have emerged as potential supplements or even replacements of current TFC membranes, such as nanoporous graphene (Cohen-tanugi and Grossman, 2015), carbon nanotubes (CNTs) (Vatanpour et al., 2011), zwitterionic materials (Ji et al., 2012), metal oxide nanoparticles (Liang et al., 2012), and so on. Fig. 11 shows novel RO materials that are most studied over the past 10 years. The left bar represents publications of related materials without testing their fouling performance while the right bar means publications of related materials whose fouling performance were studied. Nanoparticle ranked as the most popular novel material for RO membrane mainly because nanoparticle itself is a very inclusive term. In fact, CNTs used in RO membranes as additives are usually nano-sized and therefore can be regarded as a kind of nanoparticle. On the other hand, it is indicated that nano-sized particles are the main current of research for developing novel RO membranes. For example, nano-sized silver particles were formed within metal organic framework (MOF) nano-crystals via gamma-ray irradiation, which were then incorporated across the surface of polyamide films. This hybrid membrane shown high anti-microbial properties (Dumée et al., 2017). Besides, the obvious difference between the left bar and the right bar of nanoparticle, CNTs and graphene shown in Fig. 11 indicates that fouling performance study of these novel materials are still at an early stage and therefore there are huge research opportunities in these areas. However, there is no obvious difference between the left bar and the right bar of zwitterion, indicating that addressing the problem of RO fouling was an important reason for studying zwitterion. Zwitterionic polymers are gaining more popular as novel RO membrane materials due to their excellent antifouling properties (Ma et al., 2016).
CNTs have a great potential in increasing membrane surface hydrophilicity and reduce membrane fouling (Vatanpour and Zoqi, 2017). Farahbaksh et al. (Farahbaksh et al., 2017) synthesized a new kind of RO membrane by incorporating CNTs with different concentrations and they found that compared with bare RO membranes, CNTs-embedded RO membranes demonstrated better antifouling performance. Graphene oxide, a cheaper but more efficient graphene source material, is gaining more attention in recent years. He et al. (He et al., 2015) synthesized novel TFC membranes by incorporating graphene oxide nano-sheets into polyamide films through method of interfacial polymerization, which demonstrated excellent anti-biofouling performance. Besides these common studied materials, researchers have been exploring brand-new RO membrane materials as substitute for polyamide, which is of great importance because although improvements on traditional polyamide RO membranes have been achieved, they are not revolutionary since membrane fouling, membrane degradation in the presence of chlorine as well as other problems are still there and serious as well (Cohen-Tanugi and Grossman, 2012; Lee et al., 2011). For example, Falath et al (Falath et al., 2017) synthesized a novel RO thin film membrane using a combination of PVA and Gum Arabic which demonstrated excellent permeation, salt rejection, chlorine tolerance as well as biofouling resistance. However, the development of such membranes is still at the initial stage and there are still many problems to be solved before they can be commercialized.

4. Concluding remarks

RO membrane technology is one of the best technologies for wastewater treatment and desalination. Membrane fouling seems to be an inborn and inevitable problem of membrane
technology. Depending on feed water qualities, operation conditions and membrane characteristics, one or several types of fouling could occur, such as biofouling, organic fouling and inorganic fouling. Although different types of foulants may have different forming processes, sometimes there are no distinct boundaries between these foulants and they are interconnected or synergistic. Ongoing research on fouling behaviors are needed to gain a better understanding of fouling mechanisms, which could provide better foundation for improvement or even revolutionary development of fouling control strategies. Currently there are a variety of fouling control techniques that have been applied in practice (e.g., membrane pretreatment, membrane monitoring and cleaning, membrane surface modification) and these techniques are playing a very important role in RO fouling mitigation. Statistical analysis revealed that there are strong research interests in RO membrane fouling and mitigation. Although there are still many challenges, novel membrane materials and synthesis processes provide a promising solution for solving fouling problem and future research in this topic is expected to produce fruitful findings.

References


Jing, Y., Guo, L., Chaplin, B.P., 2016. Electrochemical impedance spectroscopy study of membrane fouling and electrochemical regeneration at a sub-stoichiometric TiO2 reactive


Khayet, M., 2016. Fouling and Scaling in Desalination. Desalination 393, 1. doi:10.1016/j.desal.2016.05.005


