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A review on cleaning of nanofiltration and reverse osmosis membranes used for water treatment

Zailiang Liu[a,b], Jiashun Cao[a,*], Chao Li[a], Hailing Meng[b]

[a]*College of Environment, Hohai University, Nanjing 210098, China, Tel. +86-13956226092, email: liuzailiang2008@163.com (Z. Liu), Tel. +86-13605197619, email: caojiashun1964@163.com (J. Cao), Tel. +86-15380447099, email: lichao0609@163.com (C. Li)*
[b]*School of Energy and Environment, "Water Purification and Utilization Technology of Biofilm Process" Engineering Research Center of Ministry of Education, Anhui University of Technology, Maanshan 243000, China, Tel. +86-13965618381, email: menghlahut@163.com (H. Meng)*

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ABSTRACT

Nanofiltration (NF) and reverse osmosis (RO) membranes are becoming more popular for water purification and reuse application because they are highly efficient, easy to operate and economical. Membrane cleaning is an essential step in maintaining the performance of the membrane for long-term operation because membrane fouling is inevitable. In the past decades, some novel cleaning methods and a great deal of research on high-pressure membranes cleaning have been published. However, a comprehensive review on membrane cleaning in NF and RO membranes is still lacking. This paper reviews the recent developments of membrane cleaning including physical cleaning, chemical cleaning, and biological/biochemical cleaning. The combined cleaning and sequential cleaning process with various chemicals or biological/biochemical agents are also reviewed. A brief conclusion with some recommendations and suggestions is presented at the end of the review.

Keywords: Cleaning; Nanofiltration (NF); Reverse osmosis(RO); Water treatment

1. Introduction

Nanofiltration (NF) and reverse osmosis (RO) are being used increasingly in water purification such as municipal wastewater effluent, industrial wastewater, surface water, brackish water, and seawater desalination with the advantages of high permeate quality, ease of operation, as well as minimal chemical addition [1,2]. However, the successful utilization of NF/RO technology is greatly limited by membrane fouling, which is a major obstacle for the application of membrane technology [3]. It will result in permeate flux drop, salt rejection reduction, power costs increase due to the need to raise the driving force to keep the operating conditions, more cleaning frequency, and reduction of the membrane life [4]. In order to mitigate the problem of membrane fouling and promote the application of NF/RO technology, strategies including appropriate pretreatment [5,6], design of special modules and devices, optimum the operating conditions [7], and development of anti-fouling RO membranes [6] have been examined. However, these preventive strategies can only slow the fouling rate, membrane fouling is inevitable and membrane cleaning is an essential step in maintaining the performance of the membrane.

Membrane cleaning can be categorized into physical cleaning, chemical cleaning and biological/biochemical cleaning. Appropriate selection of the cleaning methods or cleaning solutions can be seen as a critical factor for effective fouling control [8]. In general, physical cleaning such as rinsing or hydraulic flushing is usually adapted to remove reversible fouling (loosely attached foulants) from membrane surface. Chemical cleaning and biological/biochemical cleaning are applied for reducing irreversible fouling (dense fouling layers), indeed, the former is the most important method for reducing fouling with a number of chemicals being used separately or in combination [9], while

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*Corresponding author.

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the latter is mainly target for biofouling (i.e., biofilm matrix and extracellular polymeric substances (EPS)) removal with the use of bioactive agents (e.g., enzyme, biosurfactant, and signal molecules).

However, in recent years, novel physical cleaning methods such as air/water cleaning (AWC), direct osmosis (DO) backwash cleaning, and ultrasonic cleaning have been obtained increasing interest and found to be effective for irreversible fouling removal in NF/RO membrane process. In addition, a large number of papers about chemical cleaning and biological/biochemical cleaning on NF/RO membranes have also been published. Generally, these cleaning methods and/or agents are often used separately, simultaneously or sequentially to regenerate the performance of fouled membranes. It is difficult to select appropriate cleaning strategies due to the various membrane performances and fouling types as well as different cleaning protocol and condition of cleaning agents. Some of the cleaning conclusions may be distinguished from each other, and even contradictory. Therefore, it is necessary to summarize the knowledge of NF/RO membrane cleaning for better understanding and guiding future researches as well as practical operation.

This review presents current cleaning processes and techniques for NF/RO fouling control in various water treatment. After discussion of cleaning principle and evaluation criterions, a comprehensive review about recent advances of physical, chemical, and biological/biochemical cleaning in NF/RO membrane process is performed in terms of cleaning mechanisms, efficiencies, and factors affecting cleaning efficiency. Finally, the appropriate cleaning strategies are also discussed in this review.

2. Principle and evaluation criterion of membrane cleaning

2.1. Definition and principle

Cleaning can be defined as “a process whereby material is relieved of a substance which is not an integral part of the material” [10]. The relieved substance is generally termed “foulants”. Membrane fouling can be classified into organic fouling, inorganic fouling (scaling), and biological fouling based on the characteristics of foulants. These fouling can cause membrane flux and salt rejection rate decline with time, even cause permanent changes in membrane performance [11]. Fouling is still inevitable although various preventive strategies such as pretreatment of the feed water, improvement of the operating conditions, and modification of the membrane properties can slow the fouling rate to a certain extent. Hence a membrane cleaning should be taken to remove foulants by physical, chemical, or biological means [12]. It is a long-term solution to remove foulants and maintain the membrane performance.

The principle of selecting suitable cleaning methods should meet the following criteria: 1) should be effective against several foulants; 2) keeping out corrosion in the system; 3) maintain longer periods of cleaning cycle; 4) being gentle or least damage to membrane so as to maintain its characteristics and prolong the membrane lifetime; 5) being available and cost-effective.

2.2. Cleaning efficiency

Once a cleaning procedure is performed to remove foulants from membrane surface, cleaning efficiency should be used as the quantitative assessment of the cleaning process. Cleaning efficiency can be specified by the flux recovery (FR) and resistance removal (RR) of membranes. FR is defined according to Eq. (1) [13–15]:

$$\text{FR}\ (\%) = (J_{wc}/J_{wi}) \times 100 \tag{1}$$

where J_{wc} is the flux after cleaning and J_{wi} is the initial flux of the virgin or unfouled membrane.

However, if the fouled membrane is flushed with distilled, permeated, or deionized water for a short period of time to remove unbound substances from the membrane surface before cleaning, FR is also defined according to Eq. (2) [9,16,17]:

$$\text{FR}(\%) = \{(J_{wc} - J_{ww})/(J_{wi} - J_{ww})\} \times 100 \tag{2}$$

where J_{ww} is the flux after washing.

There is no significant difference between the two methods of calculation FR, the former is often used for the assessment of the total flux recovery of the whole cleaning procedure. Whereas, if there are an amount of unbound substances on membrane surface can be easily removed at little cost and the cleaning efficiency of some chemical agents should be evaluated, the latter is used more often.

RR is another criterion for cleaning quantification. The resistance is caused by the formation of the cake layer or gel networks on membrane surface. The permeate flux data is used to evaluate the hydraulic resistance (R) of membrane, according to Darcy’s law:

$$R = \Delta P/\mu \text{J} \tag{3}$$

where ΔP is trans-membrane pressure; μ is viscosity of the fluid; J is the permeate flux.

RR can be calculated from Eq. (4) [9,16,17]:

$$\text{RR}(\%) = (R_f - R_c)/R_f \times 100 \tag{4}$$

where R_f is the resistance after fouling and R_c is the resistance after cleaning.

Both FR and RR have been used as the assessment of cleaning efficiency. Al-Amoudi et al. [3] pointed out that there was no difference between the above two methods. Many researchers also proved that the similar tendency was gotten between FR and RR when cleaning NF/RO membrane [9,17]. However, high RR does not necessarily equate with high FR because large RR values are often easily obtained when large amounts of foulants are deposited (e.g., at the isoelectric point) [18,19]. FR is not only easily measured but also has representativeness most compared to RR, thus, in most literatures the cleaning efficiency is mostly evaluated by FR alone [8,20,21] or both [17,19].

Apart from FR and RR, both feed channel pressure (FCP) and mass transfer coefficient (MTC) are also used to quantify the cleaning efficiency. The FCP is the pressure difference between channel inlet and channel outlet due to the hydraulic resistance of the channel. For the FCP, the cleaning efficiency is based on the recovery of the pressure drop to the initial pressure drop [22]:

$$\eta_{FCP} = (\Delta P_{fouled} - \Delta P_{cleaned})/(\Delta P_{fouled} - \Delta P_0) \times 100\% \quad (5)$$

where ΔP_0 is the initial pressure drop at day 0, ΔP_{fouled} is the finial pressure drop just before cleaning, and $\Delta P_{cleaned}$ is the pressure drop after cleaning.

The MTC which is the flux normalized for trans-membrane pressure (TMP) and temperature, is similar to FR. MTC can be calculated by the following Eq. (6) [22]:

$$\eta_{MTC} = (MTC_{fouled} - MTC_{cleaned})/(MTC_{fouled} - MTC_0) \times 100\% \quad (6)$$

where MTC_0 is the initial MTC (clean water permeate during the compaction experiment), MTC_{fouled} is the final MTC before cleaning, and $MTC_{cleaned}$ is the MTC after cleaning.

Wibisono et al. [22] pointed out that using only FCP as an indicator for biofouling removal was insufficient as it could not reflect the biofilms present on the membrane surface, but mainly indicate the presence or absence of fluffy-type biofouling. The MTC gives a better indication about the biofilm present on the membrane surface, thus provides more insight in actual removal rates.

3. Recent advances in membrane cleaning

Membrane cleaning is typically classified into physical, chemical, biological/biochemical cleaning, and combined cleaning, as summarized in Fig. 1, according to fouling removal mechanisms or cleaning agents used.

3.1. Physical cleaning

Physical cleaning such as hydraulic flushing is widely used for NF/RO membrane cleaning, which could easily remove loosely attached foulants called reversible fouling by strong shear force. With the development of physical cleaning, a serial of other physical cleaning strategies such as AWC, DO backwash cleaning, and ultrasonic cleaning have also been proposed and proved to be effective for irreversible fouling removal in NF/RO membrane process. They require no strong chemical reagents, and thus are less likely to cause membrane degradation/damage except for some harsh mechanical cleaning. The detailed researches of physical cleaning on NF/RO membrane are shown as follows:

3.1.1. Hydraulic flushing or rinsing

Hydraulic flushing or rinsing is a process of pouring water onto membrane surface at a high linear speed to thereby wash out substances deposited on the membrane surface by shear force. Flushing with deionized water, permeate, or distilled water is a kind of mostly used physical cleaning, which mechanism is the reduction or elimination of the charge screening effect and has recently been proved to be a good method to control ultrafiltration (UF) membrane fouling [23]. But it is different in NF/RO membrane cleaning. Hydraulic flushing at a high velocity 0.42 m/s [24], 0.44 m/s [22] failed to remove biofouling in spiral wound membranes. It is also ineffective in recovering the permeate water flux when membrane is fouled by organic foulants in the presence of Ca^{2+} (e.g., the recovered flux for humic acid (HA)-Ca^{2+} [20] , alginate-Ca^{2+} [25], combined organic foulant-Ca^{2+} [21] is 5%, 12%, 19%, respectively) and by wastewater effluent (32% cleaning efficiency) [26]. Even with an increment of the tangential velocity over the membrane at longer time and higher temperature, hydraulic flushing results in a lower cleaning efficiency (8%) for RO membrane fouled by secondary-treated olive mill wastewater [27]. However, it can completely recover the flux when the membrane is fouled by HA in the presence of Na^+ or Mg^{2+}, which is mainly controlled by electrostatic interaction, and therefore can be cleaned efficiently with a low ionic strength solution (e.g.,deionized water) [20].

It can be concluded that the cleaning efficiency of hydraulic flushing significantly depends on the nature of the foulants or fouling mechanisms. Because of the ubiq-

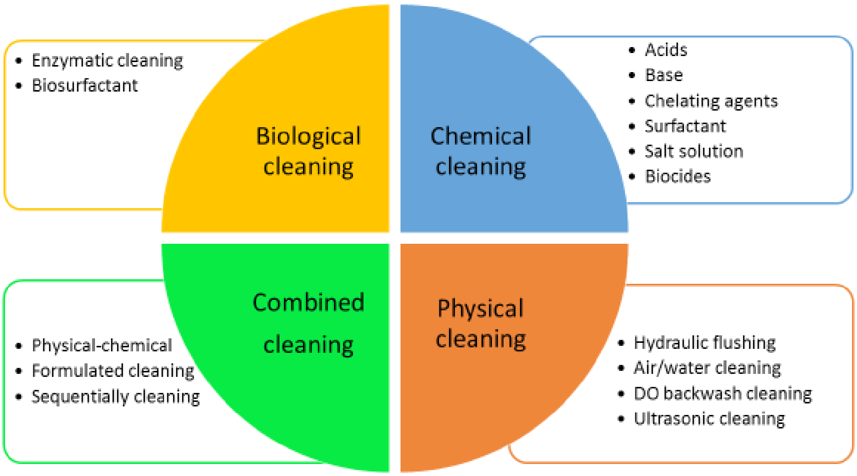

Fig. 1. The category of cleaning for NF/RO membrane.

uitous of organic matters and Ca^{2+} in NF/RO feed water, hydraulic flushing may not be an efficient method to control NF/RO membrane fouling. Thus, it is usually applied to remove the loose foulants from membrane surface before and/or after chemical cleaning for economy.

3.1.2. Air/water cleaning

Air/water cleaning (AWC), a chemical-free technique also called two-phase flow cleaning, is usually carried out at an increased flow velocity of water combined with pressurized air. The literature revealed that earliest studies about AWC are carried out mostly with low-pressure membrane processes (i.e., microfiltration (MF) and UF) applied in membrane bioreactors. Less than 5% of the studies concerns work with spiral-wound membrane elements (i.e., NF and RO) [28]. Despite of the few applications in high-pressure membrane process, it has been proved that AWC is able to prevent or control the NF/RO membrane feed spacer fouling (i.e.,biofouling [29,30], particulate fouling [31,32], organic fouling [29], and inorganic fouling [29]) as demonstrated by an improvement on the permeate flux, a decrease in the FCP drop, and/or a decrease in concentration polarization.

For biofouling: As shown in Fig. 2 (left), AWC was effective both in controlling the FCP drop and in removing biomass. Cornelissen et al. [29,30] used two-phase flow to remove biomass in a pilot-scale spiral-wound RO membrane module. The results showed that daily AWC demonstrated better FCP drop increase and lower biomass concentration compared to that of the reference membrane. Using the same modules, the same author further optimized the AWC process and found that daily AWC was more effective than weekly AWC, expressed as the increase in normalized pressure drop of respectively 5% and 144% after 21 d. At a high air/water ratio of 4:1, biomass removed by about 83% in a vertically positioned pilot-scale flat sheet RO membrane fouling simulator (MFS) [33]. Wibisono et al. [22] also reported that the recovery of FCP and MTC of a biofilm fouled RO membrane was about 90% and 40% respectively after two-phase flow cleaning.

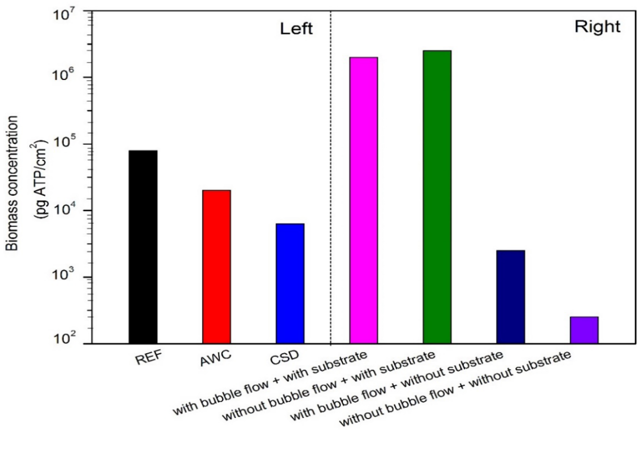

Fig. 2. Left: Adenosine triphosphate (ATP) measurement results at day 110 of membrane elements without (REF) and with (AWC) air/water two-phase flow, and copper sulfate dosing (CSD) combined with AWC (adapted from Cornelissen et al. [30]); right: Biomass concentration ATP after 7.8 d MFS operation. The monitors were operated with and without dosage of a biodegradable compound (0.20 mg acetate-C L^{-1}) to the feed water of the monitor without and with bubble flow (adapted from Vrouwenvelder et al. [24]).

The mechanism of foulants, especially bio-foulants, removal by AWC was graphically summarized in Fig. 3. It can be observed that the loose foulants in feed spacer can be efficiently removed by AWC, resulting in great recovery of FCP. However, the dense foulants which tightly adhered on the surface of membrane may not be removed. In addition, AWC cannot remove biomass when it was conducted during the biofilm growing process (see Fig. 3C). Vrouwenvelder et al. [24] studied biomass accumulation and pressure drop development during biofilm growth in a vertically positioned small scale flat sheet NF MFS with and without bubble flow. They observed that though bubble flow resulted in a much lower pressure drop increase than single water flow in the MFS, it could not remove the biomass growing on the membrane (the same biomass concentration were found with and without bubble flow (see Fig. 2 (right)). Although in a previous study of the same author has shown that there is a strong relation between the biomass concentration and the normalized increase in FCP drop [34], it can be concluded that high FCP recovery efficiency does not always mean high biofilm removing. Because the presence of the air bubbles increasing the shear force not large enough to remove the growing biofilm just resulted in a more compact and less filamentous biofilm structure than single water flow, thus causing a much lower pressure drop increase.

AWC is a good method for efficient biofouling control developed in spiral wound membranes. However, there is a significant amount of biomass remained on membrane after AWC cleaning. As shown in Fig. 2 (left), the combination of periodical AWC with biocide dosage (i.e., daily 1 g/L $CuSO_4$ during 30 min) shows much better advantages. For chemical action can be effective in inactivating biomass, however, being ineffective in removing the inactivated biomass [35], which can be easily removed by AWC.

For other foulants: Ducom et al. [31,36,37] performed two-phase flow cleaning in a lab-scale flat plane NF membrane module aimed to characterize the effects of gas sparging for different kinds of feeds: liquid/liquid solutions (stabilized and non-stabilized oil-in-water emulsions) [36], solid/liquid suspensions [31], and salt/water solution (e.g.,

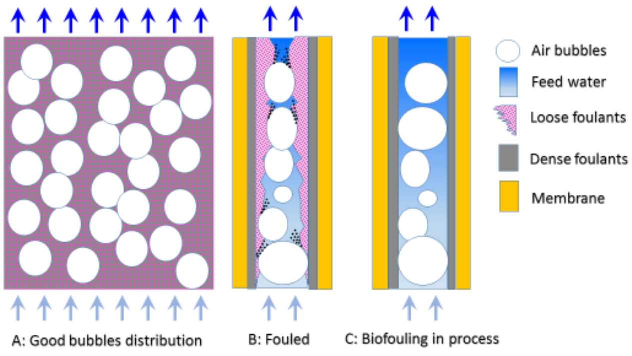

Fig. 3. The mechanism of foulants removal by AWC.

$CaCl_2$) [37]. For the former two feeds, the main fouling phenomenon is respectively drop deposit, and particle deposit. Two-phase flow cleaning allowed significant flux enhancement in both cases: the permeate flux was increased by about 240% with a 10% non-stabilized emulsion by injecting air at a 1 m/s gas velocity [36]; the flux enhancement can reach 170% with a 7 g/L clay suspensions by the lowest liquid velocity (0.08 m/s) and highest gas velocity (0.4 m/s) [31]. Cornelissen et al. [32] also confirmed that particle-type fouling can be removed by two-phase flow in a pilot-scale spiral-wound RO membrane process. These positive effects are due to the presence of air bubbles which increase turbulence and generates recirculation of the concentrate, which can prevent drop or particle deposit. Further hydrodynamics studies of the two-phase flow cleaning using a video system [31,36,38] or particle imaging velocimetry technique [39] revealed: bubbles increase unsteadiness of liquid flow, introduced strong local velocity gradients. Small air bubbles coalesce to form bigger bubbles and an unsteady flow generate liquid recirculate around the air bubbles can generate turbulence near the surface, which can remove foulants and reduce concentration polarization.

But for the latter salt/water solution, the results showed that the two-phase flow cleaning has no effect on permeate flux improvement of the lab-scale flat plane NF membrane due to osmotic effects only and no concentration polarization occurs [37]. Because of the high solubility of $CaCl_2$ no scaling on the membrane surface and the hydrodynamic circumstances in the flat plane membrane is already very good resulting in a very lower concentration polarization, and then no benefits of turbulence increase caused by air sparging can be expected. The experimental results found in this study are not in agreement with experiments done by Verberk and Van Dijk [40], who performed a similar experiment using a distinctive lab-scale capillary NF module at different $MgSO_4$ concentration. They found that the injection of air caused an increase in permeate flux ranging from 11% to 17% and a small increase in retention. It reflected the importance of concentration polarization which decreases significantly when air is injected into the water flow. Both theoretical calculated [40] and experimental estimated [41] concentration polarization for $MgSO_4$of capillary NF membranes are higher than tubular NF membranes and spiral wound NF membranes as well as higher than flat plane NF membranes. These above studies confirmed that capillary NF membrane modules had a good hydraulic cleaning possibility and especially could be easily disrupted by two-phase flow cleaning.

It can be concluded that concentration polarization or fouling needs to be the limiting step in the process for two-phase flow cleaning to be effective, particularly when concentration polarization or fouling is severe [42,43]. The characteristics of the foulants affected the performance of two-phase flow cleaning. When fouling is the flux limiting mechanism, such as oily solution, particles solution, and biofouling, the permeate flux enhancement depends on the gas flow rate. At a given liquid velocity or at identical gas/liquid ratios, the higher the gas velocity, the higher the permeate flux [22,31,36]. However, for non-fouling materials, such as dextran [44], $CaCl_2$ solution [37], and $MgSO_4$ solution [40], the permeate flux enhancement is relatively insensitive to gas flow rates.

Wall shell stress and bubble distribution: Higher wall shell stress and good bubble distribution are responsible for higher cleaning efficiency during the process of two-phase flow cleaning. In order to find some quantitative explanations for the flux enhancement, wall shell stress are widely investigated with experimental and/or numerical approach. Essemiani et al. [38] characterized and simulated the two-phase flow in a lab-scale flat sheet NF module at specific operating conditions in which an isolated spherical cap bubble could be observed. Numerical simulations showed that low pressure areas appear at the bottom of the bubbles. These transient areas of low pressure could play a significant role in the removal of foulants on the surface of membrane. In order to complement these results, authors from the same group used an electrochemical method with nine micro-probes, which were distribute on the lab-scale flat sheet NF membrane surface to measure and characterize wall shear stress [31,45]. Some links could be established between the permeate flux and some characteristics of wall shear stresses (time-averaged value, amplitude), which means the benefit of gas sparging can be related to modifications of local wall shear stresses. In the presence of gas/liquid two-phase flow, the higher the gas velocity, the greater the flux increase and the wall shear stress at the membrane surface. Drews et al. [46] found that wall shell stress not only depend on bubble size (wall shell stress can decrease with bubble diameter) but also on membrane spacing (higher wall shell stress may occur in narrow channel), and liquid velocity (higher shear would be found in moving water). In addition to high shear stress, the good bubble distribution in spacer filled channel is also significantly important.

As shown in Fig. 3, high shear stress and good bubble distribution must be met simultaneously for the efficient use of two-phase flow cleaning in membrane process. It is effected by such factors as: 1) particle characteristics; 2) spacer geometry; 3) bubble size and shape; 4) volume ratio of air and liquid phases; 5) air/water superficial velocity; 6) frequency and duration; 7) applied pressure [22,33,47].

Effect of frequency and duration: The frequency and duration of two-phase flow cleaning is very important for efficient removal of fouling from membrane surface and cost effective should be taken into consideration. Two cleaning strategies, periodical (daily/weekly) or once the FCP had increased by certain value, are often performed. Both Cornelissen et al. [29] and Wibisono et al. [22] pointed out that daily AWC showed higher cleaning efficiency compared to that AWC was carried out only when the FCP exceeded certain values (see Fig. 2 (left)). In a subsequently study, Cornelissen et al. [33] further compared the efficiency of daily AWC and weekly AWC and found that daily AWC was found to be more effective than weekly AWC, expressed as the increase in normalized pressure drop of respectively 5% and 144% after 21d. As to duration of the AWC, visual observation and analysis further revealed that the bulk of the organic and inorganic matter was removed within the first five minutes, and no significant removal took place of organic and inorganic material after 5 min of AWC [29]. Wibisono et al. [22] also confirmed that in five minutes cleaning by two-phase flow the FCP increase was recovered by about 90%, and no significant recovery was found within the subsequently 40 min. It seems that the duration of an effective AWC can probably be shortened from 1 h to a few minutes, and daily AWC superior to both weekly AWC and the cleaning performed when feed pressure exceeded certain values.

Effect of operating pressure: From a practical point of view, the operator of two-phase flow cleaning process would be able to use the same pressure as used for filtration. Furthermore, based on the ideal gas law, an increase of applied pressure should lead to the smaller bubble and possibly a better bubble distribution. However, Wibisono et al. [22] found that operating pressure had no effect on the cleaning efficiency. Visual inspection revealed that the bubbles behaved the same at both pressures, bubble size was identical, following the shape of the feed spacer filaments, regardless of applied pressure.

Effect of gas/liquid ratio: The gas/liquid ratio is one of the most important factors affecting the recoveries of FCP and flux [28]. It can be observed in Fig. 3 that it is required for obtaining a slug flow pattern in the feed channel and a good coverage of bubbles over the full width of the feed channel resulting in the most efficient two-phase flow cleaning. However, there is not an identical gas/liquid ratio for AWC using in either lab-scale flat sheet MFS or pilot-scale spiral-wound NF membrane system. Wibisono et al. [22] tested the effect of different of gas/liquid ratio, 0.25, 1, and 4:1 (equal to the author defined gas/liquid ratio $\theta = \Phi_{gas}/(\Phi_{gas}+\Phi_{liquid})$ = 0.2, 0.5, and 0.8, respectively) on the bubble coverage at a liquid velocity of 0.11 m/s in a lab-scale flat-type NF membrane flow cell simulator. Small discreet bubble with not much coverage was found at a lower gas/liquid ratio of 0.25 (θ = 0.2), when the ratio was increased, a better bubble coverage was obtained, at the ratio 1(θ = 0.5), individual bubble almost filled the width of the channel, increased the ratio to 4 (θ = 0.8), elongated the bubbles in the direction of the flow and enhanced the cleaning efficiency [22]. Cornelissen et al. [29,30,33] performed AWC in a pilot-scale spiral-wound NF membrane system at a gas/liquid ratio of 2:1, obtained a better FCP drop increase and biomass removal by about 57%. The same author also performed a gas/liquid ratio of 4:1 on a flat sheet RO MFS and found a higher biomass removal by about 83% [33]. The difference of gas/liquid ratio made good comparison not possible. However, it can be concluded that higher gas/liquid ratio resulting in higher turbulence, which means the more biomass removal, leading to higher permeate flux recovery. As to cost effective considered, an optimum or a minimum gas/liquid ratio should be further studied, which is necessary to achieve a good bubble distribution, as well as relative high shear stress.

Effect of liquid velocity and bubble velocity: Previous studies showed that a single high liquid velocity 0.42 m/s [24], 0.44 m/s [22], which was higher than practical velocity 0.1~0.2 m/s applied in spiral wound membrane, failed to remove biofouling from the high-pressure spiral-wound membranes. However, increasing liquid velocity within the two-phase flow cleaning process would lead to a higher bubble velocity, which plays an important role in increasing a greater shear force at membrane surface, leading to the increased cleaning efficiency. Wibisono et al. [22] tested three different liquid velocities, i.e., 0.11 m/s, 0.22 m/s, and 0.44 m/s, at gas/liquid ratio of 0.5 for biofouling removal in a vertically positioned lab-scale spiral-wound NF membrane module. The results showed that there is no significant difference in FCP recovery (all between 85% and 90%) with the three liquid velocities. However, increasing liquid velocity leading to a better permeate flux recovery. Increasing liquid velocity from 0.11 m/s to 0.22 m/s, and then to 0.44 m/s, enhanced the MTC recovery from about 10% to 30%, and then to 40%. Visual inspection revealed that more biofouling have been removed from the membrane surface at these greater liquid velocities, because the bubble velocity where found to be approximately 3.5–5.5 times than the liquid velocity at identical gas/liquid ratio. While at decreased gas/liquid ratio [43] (gas flow rate of 26 ml/min and various liquid flows), apart from the lowest velocity studied, the bubble velocity slightly increased with liquid velocity and is much lower than liquid velocity with a similar feed spacer channel thickness of 0.51 mm, 0.52 mm, 0.68 mm. Thus, higher bubble velocity would be obtained by increased liquid velocity at a certain or increased gas/liquid ratio.

Effect of modules type and feed spacer geometry: Spacer geometry influences the local velocity, fouling behavior, and air/water cleaning efficiency. The distribution of the bubbles is improved by the presence of a spacer compared to the empty channel. Wibisono et al. [47] investigated the effect of feed spacer geometries (e.g., shape and thickness) on the efficiency of biofouling and particulate fouling removal by AWC in a pilot-scale flat sheet NF membrane process and found that similar FCP recovery was obtained at the same channel voidage and porosity regardless of spacer types. The relative FCP drop increase before and after AWC were both lower when using a thinner feed spacer (0.432 mm) compared to that of thicker feed spacer (0.711 mm) at a constant channel height (0.7 mm). A larger membrane surface area per unit modules volume will be get with a thinner feed spacer and channel. However, the fouling might be more severe due to the smaller hydraulic diameter of the channel, resulting in a higher FCP and maldistribution of bubbles. The same author further compared the effect of two diamond-shaped feed spacer full filled channel thickness, i.e.,0.51 mm and 0.71 mm, on biofouling removal in a lab-scale flat-type NF membrane flow cell [22,46]. They found that using the thinner feed spacer and channel made the FCP recovery decreases to 65% ,85% compared to that of 90%, 93% of the thicker feed spacer respectively. The MTC recovery became even less than 10%, 15% compared to that of 17%, 18% of the thicker feed spacer respectively [22]. Although higher shear stress may occur in narrow channel [46], a good bubble distribution in the channel is the first requirement. Visual inspection clearly showed that the biofouling caused a preferential trajectory of two-phase flow through regions of lower resistance. Because of the maldistribution of bubbles over the width of the thinner feed channel, it is hard to remove the biofilms from the feed channel. The effect is worse for MTC because a significant part of the membrane surface is not cleaned, limiting the permeate flow. It can be concluded that decreasing the NF/RO membrane spacer thickness does not improve the cleaning efficiency, maintaining good bubble distribution is one of the most important factors. The effect of feed-spacer thickness is only important with regard to whether it improve or worsen the bubble coverage.

Effect of bubble size: Bubble size should match up with feed spacer geometry. Drews et al. [46] pointed out that the bubble size and membrane channels distance were both of a size, which means 3 mm, 5 mm channels with 3 mm, 5 mm bubbles, respectively, appear to be optimized. A relative larger bubble size than membrane channel distance also to be acceptable. Because the bubbles are right or large enough to contact with the channels resulting in the regeneration of a higher shear, which is required for efficient fouling removal (see Fig. 3). The bubble can be easily broken up by the feed spacer and appears to fit the size of the squares of the feed spacer in the flat sheet MFS [33], which appears that it is mainly the structure of the feed spacer that controls bubble flow and bubble size [22]. However, at a given Reynolds the bubble size does not affected by six feed channel spacer types under investigated, with increasing liquid velocity, the bubbles become smaller and more spherical, which are remain large enough (~2 mm) to be contact with both walls of the flow cell feed spacer channel [43].

AWC has several advantages over other cleaning methods. It does not require use of chemical reagents, and also does not damage the membrane. AWC can be performed on-line and automatically. AWC also can be easily combined with other cleaning methods, e.g., chemical cleaning and biological cleaning. It was found that AWC combined with chemical agents could significantly improve the cleaning efficiency. Of course, several issues of AWC should be paid attention to. It is not efficient in removing dense foulants, which needs to combine with other cleaning techniques. The optimization of AWC is also needed to further obtain higher wall shell stress and good bubble distribution, which should be met simultaneously in order to improve the cleaning efficiency. In addition, recent researches are mainly focus on with vertical positioned MFS, while horizontally positioned spacer-filled feed channels are used in practical NF/RO membrane process and AWC does notseem to operate ideally on it. To maintain the uniformity of bubble distribution to membrane surfaces with high wall shell stress is also a key issue in particular for horizontally positioned full-scale applications.

3.1.3. Direct osmosis backwash cleaning

Backwashing is a process of performing washing by pouring water while applying back pressure to the membrane surface in a direction reverse to the direction used at the time of filtration. Spiegler and Macleish [48] may be the pioneer to investigated the DO backwash cleaning of RO membranes. They developed a technique using osmosis to clean and possibly to backwash contaminated cellulose acetate RO membranes about 35 y ago. Recently, The development of forward osmosis and/or direct osmosis technology have been increasingly attractive for backwash cleaning of NF/RO membranes as it is highly efficient and environmentally friendly on-line technique to control fouling [49,50].

In the DO backwashing process, a short injection of high salinity (HS) solution into the feed water provides a wave of process changes from the reverse to the direct osmosis in the section where HS solution contacts the membrane, and, as a result, a wave of permeate backwash streams through the membrane. Then, the fouling and/or scaling components are lifted up vertically from the membrane surface. Meanwhile, horizontal hydraulic forces supplied by high-pressure pump and/or induced by increased velocity of the HS solution due to permeate "up" suction could flush the feed channel. The combination of the lifting up and flushing force provides both stripping and sweeping effects to effectively clean the membrane surface and remove foulants from the feed spacer (see Fig. 4) [50,51].

Apart from fouling lifting and sweeping, Liberman et al. [51] also noted that there are two other cleaning mechanisms: bio-osmotic shock and salt dissolve shock. The former means that a sudden increase of the HS solution can suck up water from the bacteria cytoplasm and dehydrate it, causing the cell membrane shrink and detach from the cell wall, which is fatal for bacteria, algae, and fungi. The latter can able to dissolve microcrystal growing on the membrane surface and feed brine spacer due to the HS solution with high ionic strength. These above four synergetic cleaning effects take place within a few seconds of HS injection, thus can provide high cleaning efficiency.

The most important thing for DO backwash cleaning is to obtain a higher osmotic pressure (driving force) which allow permeate back flow through the membrane. Generally, higher osmotic pressure would result in higher permeate back flow rate and then higher backwash cleaning efficiency. The transport equation of the volume flux in membrane is known as follows [52, 53]:

$$J_v = L_p \times (\Delta P - \mathrm{CP} \times \Delta\pi) \tag{7}$$

where J_v is the permeate flux; L_p is the water permeability constant of the membrane; ΔP is the operating pressure

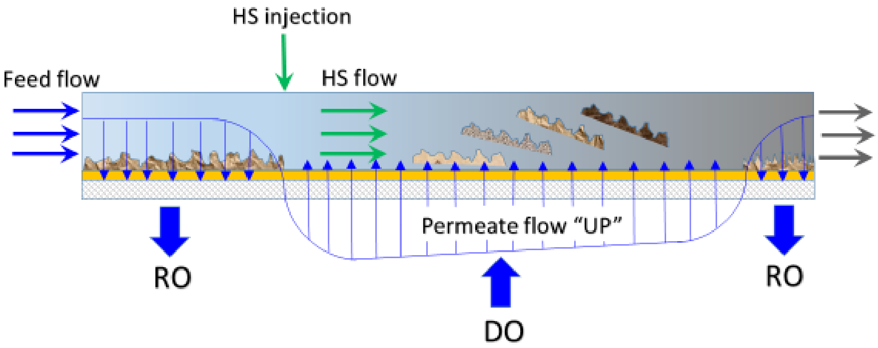

Fig. 4. Schematic of RO and DO with the injection of a HS solution and foulants lifting & sweeping during DO-HS cleaning (adapted from Qin et al. [50]).

difference; CP is the concentration polarization; $\Delta\pi$ is the osmosis pressure differential.

The driving force of NF/RO process is the pressure differential in the brackets of Eq. (7), which can also be denoted as the following expression [50].

$$\Delta P_{\text{driving}} = \Delta P - \Delta\pi = (\text{PF} - \text{PP}) - (\pi\text{F} - \pi\text{P}) \quad (8)$$

where PF is the feed pressure; PP is the permeate pressure; πF is the feed osmotic pressure; πP is the permeate osmotic pressure. There are four forces to determine the driving force. If the feed pressure drop and feed osmotic pressure drop are taken into consideration, Eq. (8) can be changed into Eq. (9):

$$\Delta P_{\text{driving}} = \Delta P - \Delta\pi = ((\text{PF} - \text{PF}_{\text{drop}}) - \text{PP})) - ((\pi\text{F} - \pi\text{F}_{\text{drop}}) - \pi\text{P}) \quad (9)$$

where PF_{drop} is the feed pressure drop; $\pi\text{F}_{\text{drop}}$ is the feed osmotic pressure drop.

A negative value of Eqs. (7)–(9) will cause direct osmosis backwash. It will drive water from the permeate side to the feed side, resulting in the removal of foulants existed on membrane surface. On one hand, this can be achieved by reducing operating pressure either by reducing the feed pressure or by increasing the permeate pressure. However, the former requires the stoppage of RO process, while the latter may cause the damage of the membranes when the pressure on the permeate side above the operating pressure of the feed side. On the other hand, the negative driving force can also be achieved by increasing the salt concentration in the feed side, the higher saline solution means higher πF, resulting in the higher driving force for backwash. The effect of decreasing πP can be neglected due to the permeate osmotic pressure is usually very low compare to πF. It seems that salt concentration and backwash time are the most influential, and the pressure and cross-flow velocity are relatively less important [54, 55].

Obtaining higher driving force by increasing salt concentration

Spiegler and Macleish [48] used 0.01 to 0.03 M NaCl solution as feed while deionized water was supplied at the permeate side to obtained net osmotic pressure as the driving force during DO backwash cleaning. In their lab-scale studies, they found that the DO backwashing improved both the RO flux and in some cases the salt rejection although the RO membranes were fouled with ferric hydroxide and caused significant flux decrease. However, the daily osmotic backwash within 35 min recovered only 50% of the flux loss due to the lower driving force.

Qin et al. [50] summarized the relationship between backwash flux and initial driving force at the backwash time of 20 s. They pointed out that in order to get a net driving force of 15 atm if the actual operating pressure of 5 atm at the RO plant was taken into account, the NaCl concentration could be estimated as at least 0.4 mol/L or 23.4 kg/m^3 with a osmotic pressure of 20 atm. Semiat's group [53,54,56-58] conducted fundamental research on the DO backwash cleaning without permeate pressure using a lab-scale spiral-wound module. They reported that the flux of RO membrane newly fouled by $CaCO_3$ could be all recovered to its original level with good repeatability after several times DO backwashing with 0.5% (5 kg/m^3) NaCl solution over 20 s for every times. They also pointed out that at any time the accumulated backwash water volume increased (indicating driving force increased) with NaCl feed concentration increased from 5.17 to 31.1 kg/m^3 [56] as well as from 18.3 to 31 kg/m^3 [54,57]. Their results indicated that the feed concentration or feed osmotic pressure indeed performed an obvious effect on the DO backwash process as expected. However, several researchers reported different observations: the backwash flow rate decreased with an increase in feed concentration when the feed concentration exceeded a certain level (which could be between 2.76% and 5.03% NaCl) [53], as well as exceeded 31 kg/m^3 in the range of 18.3 to 52.9 kg/m^3 [54,57]. The possible reasons of the decrease of backwash flow rate are: (i) the higher feed concentration results in higher initial flux and higher initial flux drop. Namely, the higher initial driving force results in a higher water flux through the membrane that in turn decreases the concentration difference more rapidly. Consequently, a lower later driving force yields a lower later flux; (ii) the secondary concentration polarization layer at the permeate side may increase with the concentration of the feed and cause the reduction of the backwash driving force. Therefore, the main parameter of NaCl concentration affecting backwash flux and accumulated volume should be carefully selected based on the fouling types and operating conditions.

In order to get higher driving force for backwash cleaning, more higher salt solution are used in recent studies. Different with the NaCl concentration of 31 kg/m^3 [54,57] and 23.4 kg/m^3 [50] suggested by several researchers, Liberman et al. [51] suggested that the concentration of HS solution injected into the feed stream of a full-scale plant during DO-HS backwash cleaning process could be up to 25% NaCl solution with osmotic pressure of 194 bar. They found that 4–5 kg of fouling debris was removed from each membrane by DO–HS backwash cleaning, resulting in a significant decrease in the pressure drop between feed and brine stream and a decrease in the product conductivity. Qin et al. [49] developed a novel backwash method by intermittent injection of the HS solution without stopping of high pressure pump in a pilot-scale UF-RO system used for the reclamation of secondary effluent. They reported that the HS solution (136 kg/m^3) injected within 25 s would create a maximum osmotic pressure πF about 85.5 bar which could lift and sweep the foulants from the membrane surface to the brine, resulting in the turbidity of the brine during DO-HS treatment at 3 NTU was 5 times higher than that (0.6 NTU) before DO-HS treatment. Jiang et al. [59] first studied the effect of DO backwash cleaning without permeate pressure on NF membrane, which was fouled by natural organic matter (NOM), especially HA, in a lab-scale cross-flow test unit for brackish water treatment. They found that the permeate water flux recovery was more than 99.8% by injecting high salinity solution (150 kg/ m^3) in the feed side of the membrane for 10 min. They also pointed out that the back flow rate increased with driving force (osmotic pressure) in the range of 50 to 150 kg/m^3 NaCl solution and kept the same when the NaCl concentration went beyond 150 kg/m^3. In addition, from a view of an economic choice for implementation, the RO brine from seawater desalination plant can also be selected as the HS solution, which usually contains the total dissolved solid about 6% with osmotic pressure over 50 atm.

Obtaining higher driving force by increasing permeate pressure

According to Eqs. (8), (9), a higher driving force can be achieved by increasing the permeate pressure. Liberman et al. [60] suggested that permeate back pressure may be at least 4 bar to make sure DO backwash cleaning is efficient. That is because the typical spiral wound RO membrane modules is a tight multi-layered structure with high resistance for water passage and a very fast back suction of water from the permeate side to the feed side. As a result, the permeate water may not reach the remotes parts of the membranes and the DO backwash cleaning process would be stopped in a few seconds so that the membranes could not be cleaned uniformly. Therefore, increasing the permeate pressure showed some extent importance. However, the permeate pressure should not be higher the feed pressure of the raw saline solution for the membrane modules safety. Moreover, when the permeate back pressure is supplied, the usual low pressure (low cost) equipment at the permeate side has to be replaced by a high pressure system such as high pressure pump, expensive stainless steel pipes, valves etc., which may increase the cost significantly.

Indeed, the DO-HS backwash cleaning process usually performed at a lower permeate pressure (higher than 0.05 MPa but not higher than 0.3 MPa [61,62]) or without permeate pressure (the permeate back flow is driven by the gravity on the permeate side [53,56] or a very low pressure pump [57]) for the membrane modules safety. A high driving force can be implemented by stopping the high-pressure pump and by the injection of higher concentration of NaCl solution.

Obtaining higher driving force by decreasing feed pressure

The feed pressure during DO backwash process opposes the osmotic pressure. So the net driving force for transport the permeate water through the membrane into the feed space decreases with the increase of feed pressure. Sagiv and Semiat [56] found that the backwash permeate flow rate decreased tremendously by increasing the feed pressure from 0 to 10 bar during DO backwash process while the feed concentration was kept at 2% NaCl with osmotic pressure of 13.7 bar. An amount of studies usually performed without feed pressure during DO backwash process, which starts at the stop moment of RO process by stopping the applied pressure as quickly as possible [56,59]. That stoppage would not only result in extra energy cost due to restart the high-pressure pump but also decrease effectiveness of production. Therefore, a novel DO-HS backwash process without stopping the RO pump was developed and studied in recent. Higher saline solution with higher osmotic pressure could compensate the adverse effect of feed pressure caused by without stopping the high-pressure pump, then, relative higher net driving force can also be obtained to lift and sweep the foulants from the membrane surface to the brine. Qin et al. [49] found that the injected HS NaCl solution (136 kg/m^3) during a pilot-scale DO-HS backwash process without stopping the high pressure pump would create a osmotic pressure πF about 85.5 bar for the DO backwash process, resulting in the turbidity of the brine during DO-HS treatment at 3 NTU was 5 times higher than that (0.6 NTU) before DO-HS treatment.

Other factors affecting the DO backwash cleaning efficiency

Apart from osmotic pressure (driving force), other parameters such as backwash time, injection interval, flow rate of the HS solution as well as feed flow rate seems also have significant effect on the backwash cleaning efficiency. These key parameters have to be well calculated in compliance with the feed water chemistry, configuration of the existing RO train and pumps' curves, depending on the applications [50]. Otherwise, improper implementation of the DO-HS backwash process would result in the damage of the membranes due to the high driving force.

Backwash time and injection interval: Sagiv and Semiat [56] reported that there were two distinct stages for the permeate back flow rate vs. time during DO backwash process for newly fouled with inorganic matters ($CaCO_3$). Stage I was characterized by a high backwash flux for a relatively short time, the backwash flow rate was the highest at the beginning and sharply declined with time due to concentration polarization layer dilution. In stage II, the backwash flux was much lower than in stage I and continuously reduces with time until leveled off. Therefore, they suggested that the DO backwash cleaning should be controlled within stage I, maybe less than 20 s. It should be pointed out that the removal of $CaCO_3$ from the membrane surface can be easily made only immediately after precipitation. As times goes on, the removal should be further investigated due to hardening of the scale. Nam et al. [55] also confirmed the two above distinct stages during DO backwash process. Qin et al. [49] found that the optimal HS injection duration (backwash time) of 25~30 s of 136 kg/m^3 salt solution is recommended for DO-HS treatment during the reclamation of municipal secondary effluent by an UF-RO pilot system. They further optimized the DO-HS process and found that daily injection of 8 s of 12% salt solution also has showed good results over two month operation and salt consumption has been reduced by 68% to 0.16 ton for 10000 m^3/d production. They concluded that daily DO-HS treatment showed much lower RO fouling rate compared to every alternate day treatment as well as reduced RO fouling rate by 2.5 times compared to without DO-HS treatment [63].

However, in some cases, a few seconds injection of HS solution was not effective in removing foulants from membrane surface. Jiang et al. [59] suggested that 10 min cleaning by DO backwashing process with 150 kg/m^3 NaCl solution was needed for NF membrane fouled by NOM, especially HA. It should be daily performed based on the flux recovery, which decreased from 99.78% to 86.95% when the filtration time increased from 24 h to 48 h. Park et al. [64] also found that 15 min cleaning by DO backwashing process with 35 kg/m^3 concentration of NaCl solution circulated in the feed side could result in a lower flux recovery rate (only 11–17%) for organic fouled RO membranes, which were used in a lab-scale filtration process for artificial seawater desalination. The lower cleaning efficiency probably may be due to the lower NaCl salt concentration used in the feed side, also probably due to the organic foulants deposited on the membrane surface, which was difficult to be removed. Generally, it is difficult to remove a densely packed fouling layer from membrane surface, thus, in order to remove the foulants more efficiently, a routine daily DO backwash cleaning can be performed with higher concentration of NaCl solution at longer cleaning time.

The pulse concentration and duration of HS solution should be carefully optimized if efficient osmotic cleaning is to be achieved throughout the full length of a membrane train. Due to dilution, a shorter pulse of HS solution is significantly diluted, particularly on the membrane surface and toward the end of the channel, to the point where its concentration may drop below that required for inducing osmotic flow. Therefore, Ramon et al. [65] suggested that the pulse duration of HS solution should be longer than the resistance time for a maximum achievable cycle-averaged permeate rate.

Flow rate of the feed water and HS solution: The thickness of concentration polarization layer is proportional to the inverse of the feed flow rate [52], namely, the concentration polarization layer thickness is thinner at higher velocities. Eq. (7) showed that concentration polarization could affect the driving force, and then affect permeate back flow rate. In a lab-scale spiral-wound RO membrane module, Sagiv and Semiat [56] pointed out that the initial operating conditions of different feed flow rate (200 L/h, 400 L/h, and 600 L/h) under the same TMP (4 MPa) as well as different TMP (4 MPa, 5 MPa, 6 MPa) under the same feed flow rate (400 L/h) have very small difference in the permeate back flow rate during DO-HS backwash process while the high-pressure pump was stopped. However, keeping a higher feed flow rate during DO backwashing would be able to eliminate the foulants on the membrane surface due to turbulence caused by spacer of the feed side and shear force of feed flow. Ramon et al. [65] investigated the effect of crossflow on permeate backflow rate using a numerical simulations method. They pointed out that at shorter time during the DO backwash process the dominant mechanisms responsible for depolarization is osmotic permeate, the backwash process is virtually unaffected by the crossflow velocity, while longer times are controlled by the crossflow. Thus, the presence of crossflow would be beneficial only in cases where the backwash is to be carried out for period greater than the time required for reaching the steady osmotic permeation, and ensuring a maximum cycle-averaged permeate rate. At a higher crossflow velocity the domain-average concentration drops only slightly below the bulk concentration, even upon reaching steady conditions. Recently, in a lab-scale cross-flow RO membrane test unit, Park et al. [64] found that when osmotic backwashing was implemented a longer time about 15 min with feed water total dissolved solid of 35000 mg/L circulated at feed side during DO backwashing, the cleaning efficiency (flux recovery) with the same amount of backwashing water increased from 11.0% to 17.1% when the circulation feed crossflow increased from 0.5 L/min to 2 L/min. Indicating that the increased turbulent crossflow at a higher flow rate of circulation could enhance the physical elimination of the swollen fouling layers on RO membrane surface.

Pressure drop and osmotic pressure drop: In some cases, the impact of pressure drop on net driving force is insignificant (even can be negligible) compared to hydraulic pressure and osmotic pressure due to two reasons: (1) in order to get a higher driving force, the high-pressure pump is usually stopped, which results in the pressure drop can be negligible during the DO backwash cleaning process, (2) in the case of without stopping the high-pressure pump, the pressure drop is approximately equal to the initial pressure drop of clean feed spacer because most of foulants are removed by daily DO backwash cleaning, it may be much lower than osmotic pressure drop resulting from the significant dilution of feed solution, especially in the process of low total dissolved solid water desalination (e.g., surface water, wastewater effluent, and groundwater). However, the pressure drop would be higher in the process of seawater desalination without stopping the high-pressure pump, it should be included to calculate net driving force (see Eq. (9)).

Organic properties of raw water and permeate temperature: Park et al. [64] conducted an analysis of the effects of osmotic backwashing using a lab-scale seawater reverse osmosis (SWRO) process. They investigated the effect of osmotic backwashing on the permeate flux recovery of RO membranes fouled by three different organic type of feed solutions (sodium alginate (SA) 20 mg/L, HA 20 mg/L, and SA 10+HA 10 mg/L). The results showed that the cleaning efficiency in respect to the fouling by hydrophilic organic matters was the greatest. The permeate flux recovery rates of the RO membranes after osmotic backwashing were in the order of SA (17.0%) > HA+SA (13.8%) > HA (11.4%). The lower cleaning efficiency of osmotic backwashing for the fouled RO membranes by HA+SA and HA compared with the fouled RO membrane by SA could be attributed to the hydrophobic properties of HA. The swelling of membrane fouling by hydrophobic organic matter is generally less pronounced than that of by hydrophilic organic matter due to the less diffusion of ions and the hydrophobic interaction between the RO membrane surface and hydrophobic organic matter. They also confirmed that when the temperature of the effluent was high, both the cleaning efficiency and the backwashing volume increased. That is due to the continuous increase in temperature leading to a decrease in viscosity of backwashing water, and leading to an increase in the rate of chemical reactions, and organic fouling layer swells making it easy to eliminate.

Application of DO-HS backwash process

The new DO-HS backwash cleaning technology without stopping the high-pressure pump has been applied in two brackish water full-scale RO plants for commercial operation at Dshanim Factory in Israel in 2005 [51]. The raw feed comes from heavy fouled shallow wells including 0.06 ppm oil. Before implementation of DO-HS treatment, the plant was cleaned by conventional clean-in-place procedure every week, which was not conducted during DO-HS treatment. The results showed excellent performance in cleaning of not only the old and silica scaled RO membranes but also new RO membranes within 50 d of DO-HS cleaning during which injection of 25% concentrated NaCl once a day except for the holidays. A significant decrease in the pressure drop between feed and brine stream, and a decrease in the product conductivity were achieved. The weight of sixteen membranes decreased from 20–23 kg before cleaning to about 17 kg after it. About 4–5 kg of fouling debris was removed from each membrane.

However, recently, Farooque et al. [66] reported different even opposite conclusions. They found that the DO-HS backwashing was not effective in either controlling fouling or significantly removing foulants from a pilot-scale spiral wound seawater RO system. On the contrary, the DO-HS backwashing actually resulted in a higher fouling rate on membranes as can be seen from the rapid performance decline compared to the baseline performance. During the backwashing process, a concentration of 25% NaCl used results in an osmotic pressure about 195 bar. After deducting the feed pressure of about 70 bar supplied by high-pressure pump, a net osmotic pressure of about 125 bar is theoretically available to induce a high backwash flow. But actually the average back flow flux generated was only 11 LMH, which was lower than the average membrane flux of about between 19 and 23 LMH, and was not enough to remove adhering foulants from the membrane surface. Moreover, the tight multi-layered configuration of spiral wound membrane as well as the inherent properties of SWRO membranes apparently places certain constraints on the osmotic backwash process, thus rendering it ineffective in tackling membrane fouling [50,60]. They suggested that the supplied feed pressure in the range of 60–70 bar is expected to significantly reduce the osmotic permeate flux, which could explain the failure of osmotic backwash to restore the SWRO membrane performance. Even without feed pressure supplied during DO backwashing process by circulating a lower concentration of 35 kg/m^3 NaCl solution at feed side, a lower flux recovery rate (only 11.0–17.1%) of artificial seawater fouled RO membranes was obtained [64].

DO backwash cleaning is an environmentally friendly on-line technique. NaCl solution is usually selected as the HS solution. The RO brine from seawater desalination plant can also be selected as the HS solution. It is economic and less harmful to membrane compared to other chemical agents and biological agents. It can be injected automatically even without stopping the high pressure pump which avoids the down time of other cleaning technologies. Of course, several issues of DO backwash cleaning should be paid attention to. NaCl concentration is a key issue and should be carefully calculated to obtain a higher driving force. The optimal operating conditions (e.g., feed pressure, permeate pressure, flow rate, duration, etc.) should also be evaluated to further obtain higher driving force. Otherwise, lower driving force results in a lower flux recovery, a much higher one may cause the damage of membrane. Due to some failure reports of DO backwash cleaning [50,64,66], it seems that DO backwashing process with higher salt concentration and optimal operating conditions should be further researched for fouled RO membranes.

3.1.4. Ultrasonic cleaning

Ultrasonic cleaning technique has been proved a promise method for membrane fouling control as well as for enhancing permeation in membrane process, especially for UF and MF membranes both during membrane filtration and after fouling [67,68]. Studies showed that ultrasonic could significantly enhance permeate flux and this enhancement was mainly caused by cavitation phenomenon (i.e., the formation, growth and implosive collapse of bubbles in the liquid) [68,69]. These bubbles or cavities are formed by ultrasound waves passing through the medium in a series of alternate compression and expansion cycles. Hot spots are created in the liquid where the temperature and pressure of the gas in the cavity rises to enormously high values, owing to the expansion and implosive collapse of bubbles at nucleation sites within the liquid. Further, when a cavitating bubble is oscillating near a solid surface, it does so asymmetrically, resulting in the generation of microjets (microstreams) of high velocity. Fluid flowing at these high velocities can decrease the thickness of boundary layers and diffusional resistance and therefore enhance the rates of mass transfer.

In fact, most researches about ultrasound used in NF/RO membrane process are focused on assessing whether a NF/RO membrane is fouled or has been sufficiently cleaned [70–74]. Relatively few studies have focused on the use of ultrasonication to eliminate or prevent the fouling of NF/RO membranes. Even so, a high cleaning efficiency could also be obtained by ultrasonic cleaning. In a lab-scale installation, Feng et al. [75] performed the study of on-line ultrasonic cleaning to remove fouling from a commercially important polyamide based RO membrane which was immersed into the ultrasonic bath during cross-flow filtration of $CaSO_4$, Fe^{3+} and carboxyl cellulose solutions.The ultrasonic bath was capable of generating ultrasound with a frequency of 20 kHz and a power intensity of 2.8 W/cm^2. They found that On-line ultrasonic defouling of the polyamide-based RO membranes could resulted in a significant increase in the permeate flux, with virtually no loss in rejection. On average, the permeate flux increased by approximately 50.8% for a 500 mg/L $CaSO_4$ solution and approximately 69.7% for a 1000 mg/L $CaSO_4$ solution during 3 h of filtration in the presence of ultrasound. Likewise, the permeate flux increased by about 215% for a $FeCl_3$ solution with 20 mg/L Fe^{3+} during 3 h of filtration in the presence of ultrasound. The permeate flux increased by approximately 264% and 113%, respectively, for a 500 and 1000 mg/L carboxymethyl cellulose solution during 3 h of filtration in the presence of ultrasound. Studies suggested that ultrasonic should be applied at low frequencies in the membrane cleaning process [67,69,76]. It seems that the optimal parameters should be further studied when ultrasonic cleaning is used for NF/RO membrane fouling control. Moreover, cleaning solution treated by ultrasonic bath, and then was pumped into the fouled membrane module could also enhancing the flux recovery. Recently, using this novel method, Luján-Facundo et al. [69] found that an enhancement of 9–12% in the flux recovery of the UF membranes was produced. Likewise, the novel method of supplying ultrasonic bath in the cleaning solution seems also be used in NF/RO membrane fouling control and should be further studied.

3.2. Chemical cleaning

Irreversible fouling removal by the physical cleaning methods mentioned in section 3.1 may be difficult in most cases and hence the chemical related cleaning method is the most widely used [9,77]. Chemical cleaning is the most important method for reducing irreversible fouling with a number of chemicals being used separately or in combination and is a necessary process to ensure successful application of membrane technology. It has been proposed that efficient cleaning involves two important mechanisms: (i) chemical reaction between the cleaning agent and the foulants in the fouling layer, and (ii) mass transfer of the cleaning agents from bulk phase to fouling layer, and foulants from fouling layer to bulk phase [25]. The effectiveness of cleaning chemicals is strongly dependent on the chemical reactivity of the cleaning agents since the second step of mass transfer can take place only after the foulant-foulant interactions have been weakened by the chemical reaction [25]. Therefore, selection of cleaning chemicals that exhibit favorable chemical reaction with the target substances in the fouling layer is paramount importance. Moreover, the chemicals should also (1) keep the foulants in dispersion and solution form, (2) avoid triggering new fouling (secondary fouling) and (3) not attack either the membrane or other parts of the system [7]. Chemical reagents applied in membrane cleaning can be generally classified into five categories: acids, alkalis, cheating agents, surfactants, and other cleaning agents (NaCl solution, disinfectants, and combined cleaning materials, etc.). The major mechanisms of various chemical cleaning processes are summarized in Fig. 5.

3.2.1. Acids

Acid cleaning is targeted to remove precipitated salts (scaling) from the surface of the membrane and from the pore [80]. Table 1 summaries the efficiency of various acid agents used for NF/RO membranes cleaning. As shown in Fig. 5 and Table 1, it can be observed that acid cleaning exhibits some advantages for inorganic fouling and biofouling.

For inorganic fouling: Inorganic fouling such as iron fouling (i.e., iron oxide/Fe(OH)$_3$), carbonate precipitates, Sr, and P can be easily removed by HCl, citric acid, and free nitrous acid (FNA) solution due to the effective chemical reaction between these scaling and acid agents [17,81–84]. Kimura et al. [81] reported that HCl could desorb more amount of Ca, Mn, Al, and Fe than NaOH cleaning from NF membrane in a pilot-scale system for municipal wastewater effluent treatment. Mo et al. [83] conducted chemical cleaning on a lab-scale NF membrane filtrated by simulated municipal wastewater, they found that P, Mg, Ca, and Fe were efficiently removed by citric acid cleaning. Xiao et al. [82] observed that HCl solution could effectively remove the foulant of Sr (the removal fraction between 58.6% and 87.1%) from RO membrane fouled by inorganic deposits (mainly BaSO$_4$ and small amount of SrSO$_4$) during treatment of semiconductor wastewater by a pilot-scale RO process.

However, if the scaling are Si and sulfate based materials, i.e., BaSO$_4$, CaSO$_4$, acid cleaning alone is not effective. The foulants of Si can be effectively removed by caustic cleaning, but with low efficiency by acid cleaning [81], more details would be discussed in section 3.2.2. Fig. 6 summarizes the cleaning efficiency of NF/RO membranes fouled with sulfate precipitates by cleaning of various agents. As for BaSO$_4$, Xiao et al. [82] found that HCl could not remove the foulants of BaSO$_4$, which could be effectively removed by the combined cleaning of HCl–NaOH/EDTA (EDTA: ethylenediaminetetraacetic acid) (see Fig. 6 (left)). After the combined cleaning, the RO membrane permeability

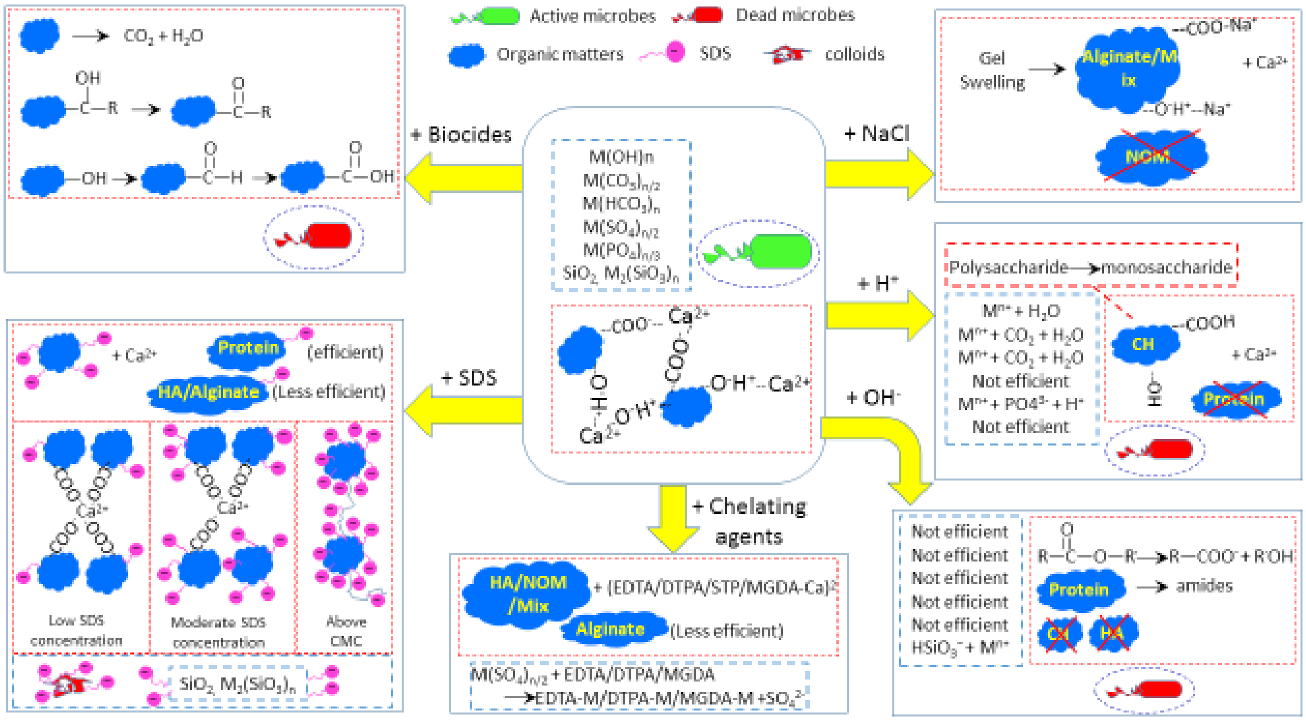

Fig. 5. Mechanisms of chemical cleaning using acids, base, chelating agents, SDS, NCl, and biocides (adapted from Li et al. [20], Wang et al. [78], and Lee et al. [79]).

Table 1
Summary of acids used for NF/RO membranes cleaning

Membrane	Feeding	Fouling time	Cleaning agents	Efficiency	Scale	Ref
NF	Municipal wastewater effluent	40 d	HCl (pH 2) soaking 24 h at 30°C	Si, Ca, Mn, Fe and Al were desorbed at amounts of 10–20 mg/m^2 CH could be efficiently desorbed compared to protein	Pilot-scale	K. Kimura et al. [81]
RO (LFC3-LD)	Semiconductor wastewater effluent (mainly $BaSO_4$, $SrSO_4$)	63 d	HCl 0.5% w/v cleaning 4 h at 35°C	Relatively low permeability recovery (80.45%), foulants is still exist The removal fraction of Sr was 58.6% at the inlet and 87.1% at the outlet	Pilot-scale	Xiao et al. [82]
NF (ESNA1)	Simulated municipal wastewater effluent	24 h	Citric acid 2% w/w Soaking 20 min at room temperature	Mg, Ca and Fe could be completely removed, while the percentage for P decreased obviously from 2.4% to 0.7%	Lab-scale	Mo et al. [83]
NF(Desal-5DK)	Complex pharmaceutical wastewater	180 h	HCl (pH 2)[a] Citric acid (pH 2)[b] Cleaning conditions: 0.1 MPa, 0.24 ms^{-1}, 30 ± 0.5°C, 60 min	Flux recovery was 83.3%[a] Flux recovery was 93.6%[b]	Lab-scale	Wei et al. [86]
RO (SC series)	Secondary-treated olive mill wastewater	20% permeate flux loss	HCl[a] Citric acid[b] HNO_3[c] H_2SO_4[d] Cleaning conditions: 2.7 bar, 4.01 m/s, 22°C, 10 min	The flux recovery was 21.2 ~ 41.2% for 0.1 ~ 0.5% (w/v) dosage[a] The flux recovery was 29.3% upon 0.5% (w/v)[b] The flux recovery was 8.7% ~ 9.9% for 0.25% up to 0.5% (w/v) dosage[c] Similar to HNO_3 cleaning, even poorer when upon 0.25% (w/v)[d]	Lab-scale	Ochando-Pulido et al. [27]
RO (NTR-759HR-S8)	Rolling mill wastewater (64.88% $CaSO_4$ and 16.72% $CaCO_3$	Exhausted	0.5% HCl + 0.1% EDTA Soaking 12 h at room temperature	Flux recovery was 10%, resulting in the membrane were periodically replaced within 6–8 months even cleaning once every 10 days	Lab-scale/ Full-scale	Jung et al. [85]
RO (FT-30) NF (BDX N-90)	Licorice aqueous solutions	30 min	H_2SO_4 0.1 wt.% HNO_3 0.1 wt.% Cleaning condition: 0 TMP, 5 m/s, 5 min, 25°C	Flux recovery both less than 60% (acids were the weakest cleaning chemicals compared to other cleaning agents for the experimental conditions due to the organic nature of the feed solution)	Lab-scale	Sohrabi et al. [9]
SWRO	Raw seawater	10–15 % permeate flux loss	Citric acid (pH 4.0)	killed 100% of all bacterial isolates	Pilot-scale	Farooque et al. [66]
RO	whey	24 h	Acid (pH 2.1) Cleaning 30 min at 50°C	Resulting in 4.54 to 7.90 and 2.09 to 5.02 log reductions of the planktonic and biofilm-embedded cells, respectively. More effective than alkali, surfactant, enzyme, and sanitizer treatment	Full-scale	Anand et al. [87]
RO	Municipal water[a] Industrial water[a] Seawater[a] Coal seam gas water[b]	Collected from full-scale plant	Free nitrous acid (50 mg NO_2–N/L, pH 3.0) cleaning for 24 h	94–95% and 86–96% ATP removal of moderately and heavily fouled membrane respectively[a] Similar to HCl and citric acid, the fouling (mainly composed of $CaCO_3$) removal ranging between 34.3±1.4 and 28.5±4.6 g/m^2[b]	Lab-scale	Filloux et al. [84]

(Continued)

Table 1 *(Continued)*
Summary of acids used for NF/RO membranes cleaning

RO (SWC3)	Seawater (70% were inorganic and 30% were organic fouling)	Retired from full-scale plant	Citric acid 0.2%w/v soaking 1 h at 25°C	The flux recovery was only 24.10%* and the salt rejection index was 93.8% (1.66% recovery)	Pilot-scale	Garcia-Fayos et al. [93]
RO (FT-30)	Industrial wastewater (organic and inorganic fouling (contains of $CaCO_3$ and $Fe(OH)_3$))	9 h	HNO_3 0.3%w/v[a] H_2SO_4 0.2%w/v[b] HCl 0.4, 0.5, 0.6%w/v[c] Cleaning condition: 0.5 bar, 10 min, 25±2°C	Flux recovery was 15%[a] Flux recovery was 12%[b] Flux recovery was 30%, 60%, 112%, respectively[c]	Pilot-scale	S.S. Madaeni et al. [17]

Note: *The calculation of flux recovery was based on the equation: J_p flux recovery = $(J_p - J_{p0})/J_{p0} \times 100$, where, J_{p0} is bank values of permeate flux quantified using distilled water, which is different from Eq. (1) (see section 2.2, FR(%) = $(J_{wc}/J_{wi}) \times 100$) used in this review.

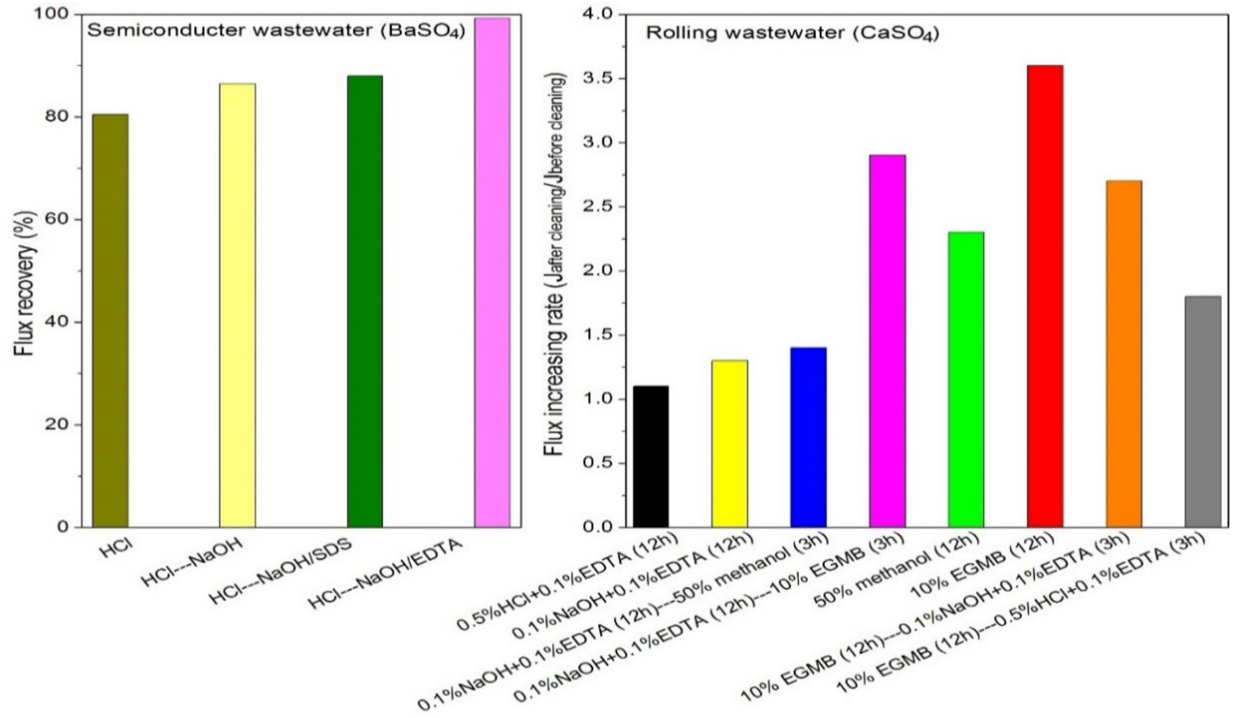

Fig. 6. The cleaning efficiency of NF/RO membranes fouled with sulfate participates by the cleaning of various agents. Left: inorganic foulants (mainly $BaSO_4$ and small amount of $SrSO_4$) [82]; right: inorganic foulants (consisted of $CaSO_4$ (64.88%) and $CaCO_3$ (16.72%)) [85].

was recovered to the fresh one. As for $CaSO_4$, it seems that both HCl and HCL+EDTA cleaning are all not effective (see Fig. 6 (right)). In a lab-scale RO membrane system and full-scale plant, Jung et al. [85] used acidic solution (0.5% HCl + 0.1% EDTA) to clean RO membrane fouled by wastewater from a rolling mill process where a large part of the fouling material consisted of calcium sulfate (64.88%) and calcium carbonate (16.72%).They found that 12h lab-scale soak cleaning using the acidic solution only improved 10% pure water flux. In the previous practical RO process, the acidic solution cleaning of the RO membranes had to conduct once every 10 days, leading to all the membrane modules were periodically replaced within 6–8 months due to the possibility of serious irreversible fouling. As seen in Fig. 6 (right), they also found that alkaline solution (0.1% NaOH + 0.1% EDTA) was not effective as well, while 50% methanol, and 10% ethyleneglycolmonobutyrate (EGMB) could significantly increase the water flux, especially cleaning with these organic solution after alkaline solution was the most effective.

For organic fouling: As shown in Table 1 and compared with other agents summarized in Table 2~4, acid clean-

Table 2
Summary of caustic cleaning used for NF/RO membranes.

Membrane	Feeding	Fouling time	Cleaning agents	Efficiency	Scale	Ref.
NF	Effluent of municipal wastewater	40 d	NaOH (pH 11.0) Soaking 24 h at 30°C	Si was easily desorbed at amounts of 105 mg/m^2 Protein could also be efficiently desorbed	Pilot-scale	K. Kimura et al. [81]
NF 270	Model foulants	18 h	NaOH (pH 11) Cleaning condition: 75 cm/s, 30 min	The flux recovery was almost 70% for BSA-Ca^{2+}, 5% for HA-Ca^{2+}, and 17% for alginate-Ca^{2+} complexes	Lab-scale	Beyer et al. [8]
NF 270	SRHA	8 h	NaOH (pH 11.0) Cleaning condition: 470 rpm, 10 min	The flux recovery was 7% for SRHA- Ca^{2+}	Lab-scale	Li et al. [20]
RO (LFC-1)	Simulate effluent organic matter	17 h	NaOH (pH 11.0) Cleaning condition: 42.8 cm/s, 15 min, 20.0±0.2°C	The flux recovery was 17% for alginate-Ca^{2+} complexes (18% for 60 min cleaning)	Lab-scale	W. S. Ang et al. [25]
RO (LFC-1)	Simulating wastewater effluent	17 h	NaOH (pH 11.0) Cleaning conditions: 15 min; 21±0.5°C; and no pressure.	The flux recovery was almost 79% for combined foulants in presence of Ca^{2+}	Lab-scale	W. S. Ang et al. [21]
RO (LFC-1)	Municipal wastewater effluent	17 h	NaOH (pH 11.0) Cleaning condition: 0 psi, 42.8 cm/s, 15 min, 21.0 ± 0.5°C	The flux recovery was 59.2%	Lab-scale	W. S. Ang et al. [26]
RO (SC series)	Secondary-treated olive mill wastewater	20% permeate flux loss	NaOH 0.5% w/v. Cleaning conditions: 2.7 bar, 4.01 ms^{-1}, 22°C, 10 min,	The flux recovery was 53.1%	Lab-scale	Ochando-Pulido et al. [27]
RO (FT-30)[a] NF (BDX N-90)[b]	Licorice aqueous solutions	30 min	NaOH0.1 wt.% Cleaning condition: 0 TMP, 5 m/s, 5 min, 25°C	The flux recovery was 60%[a] The flux recovery was 88%[b]	Lab-scale	Sohrabi et al. [9]
NF (Desal-5DK)	Complex pharmaceutical wastewater	180 h	NaOH (pH 11); Cleaning conditions: 0.1 MPa, 0.24 ms^{-1}, 30 ± 0.5°C, 60 min	The flux recovery was 60.4%	Lab-scale	Wei et al. [86]
RO (SWC3)	Seawater (70% were inorganic and 30% were organic fouling)	Retired from full-scale plant	NaOH 2% w/v Soaking 1 h at 25°C	The flux recovery was up to 92.04 –95.42%* and the salt rejection index up to 93.02%	Pilot-scale	Garcia-Fayos et al. [4, 93]
RO	Municipal water Industrial water Seawater	Collected from full-scale plant	NaOH (pH 11.0) Cleaning 24 h	59–60% and 62–79% removal of proteins and polysaccharides respectively 85~92% and 42% removal of ATP of moderately and heavily fouled membrane respectively	Lab-scale	Filloux et al. [84]
NF (DK)	Obtained from Saline Water Conversion Corporation (mainly NOM)	9000 h	2 M NaOH (pH 11.3) Soaking over night (18 h) and then stirred for 90 min	Remarkable increment of flux compared to untreated virgin membrane Rejection of monovalent or divalent ions were found to be lower than the control	Lab-scale	A. Al-Amoudi et al. [114]
RO (FT-30)	Industrial wastewater (organic and inorganic fouling (contains of $CaCO_3$ and $Fe(OH)_3$))	9 h	NaOH 0.4% w/v Cleaning condition: 0.5 bar, 10 min, 25±2°C	The flux recovery was 65%	Pilot-scale	S.S. Madaeni et al. [17]

(Continued)

Table 2 *(Continued)*
Summary of caustic cleaning used for NF/RO membranes.

RO (TW30)	Non-chlorinated tap water (Laboratory)^a Acetate enriched tap water (pilot plant)^b	85 d^b	Mixture of NaOH (pH 12) and SDS 1% Soaking for 1 h at 20°C	ATP, CH removal was 65 ± 3.0%, 25 ± 3.0%, respectively (only NaOH cleaning) ATP, CH removal was 69.8 ± 15.0% (average), 33.8 ± 4.9%, respectively^a ATP, CH removal was 98.6 ± 0.9%, 54.2 ±3.0%, respectively^b	Lab-scale/ pilot-scale	Hijnen et al. [103]

Note: *The calculation of flux recovery was based on the equation: J_p flux recovery = $(J_p - J_{p0})/J_{p0} \times 100$, where, J_{p0} is bank values of permeate flux quantified using distilled water, which is different from Eq. (1) (see section 2.2, FR(%) = $(J_{wc}/J_{wi}) \times 100$) used in this review.

ing shows relatively weaker cleaning efficiency for NF/RO membranes fouled by organic foulants and various wastewater. Fig. 7 also schematically shows the same tendency during the cleaning of NF/RO membranes fouled by municipal wastewater effluent, seawater as well as various industrial wastewater.

From Table 1 and Fig. 7, it can be observed that cleaning with HCl and citric acid shows higher efficiency compared to that with H_2SO_4 and HNO_3. In details, Wei et al. [86] found that citric acid showed higher cleaning efficiency (93.6%) than HCl (83.3%) in a lab-scale NF membrane process fouled by complex pharmaceutical wastewater. It is possible due to citric acid is a metal chelating agent, which may have some reactions with calcium ions in organic matter-calcium complexes to form soluble complexes. While Ochando-Pulido et al. [27] found citric acid showed the moderate and HCl ensured the highest cleaning efficiency (between 21.2% and 41.2% for concentration dosages between 0.1% and 0.5% (w/v)) in a lab-scale RO membrane process fouled by secondary-treated olive mill wastewater. A comparable amount of organic matters (mainly carbohydrates) can also be desorbed by HCl, the ratio of carbohydrate (CH) to protein (3.3) in HCl solution indicating that CH can be desorbed more easily by HCl compared to protein [81]. It seems that the difference of acid cleaning between Wei et al. [86] and Ochando-Pulido et al. [27] may be due to the different fouling types and strategies. The former conducted cleaning after 180 h operating time while the latter started at the time of 20% permeate flux loss.

Compared to HCl and citric acid cleaning, Ochando-Pulido et al. [27] confirmed that other acid solutions such as HNO_3 and H_2SO_4 led to minimal cleaning efficiency (less than 9.9% even by increasing its dosage from 0.25 up to 0.5% (w/v), see Fig. 7c). Moreover, increasing the H_2SO_4 dosage above 0.25% (w/v) led to poorer cleaning results due to the fact that high H_2SO_4 concentration can lead to the decomposition of some of the foulants deposited on the RO membrane, triggering more severe secondary fouling. Sohrabi et al. [9] also reported that H_2SO_4 and HNO_3were the weakest cleaning chemicals for RO/NF membrane (lab-scale) fouled by licorice aqueous solution. Glycyrrhizic acid and liquritin are the major bioactive compounds in licorice, under strong acidic conditions (pH < 3), most of the compounds exist as molecular form, which is more hydrophobic than the dissociated form and possibly responsible for the lowest cleaning efficiency.

For biofouling: It is confirmed that acid cleaning is effective to kill bacterias under specific pH values. As shown in Fig. 7a and Fig. 7b. Farooque et al. [66] reported that citric acid, which was ammoniated to a pH of 4.0, was found to kill 100% of all bacteria isolates, and was therefore an effective cleaning agents against biofilm bacteria in a pilot plant for seawater treatment. Anand et al. [87] also pointed out that a lab-scale cleaning in place with acid treatment (pH 2.1 at 50°C for 30 min) was the most effective step compared to alkali, surfactant, enzyme, and sanitizer treatment, which resulted in 4.54 to 7.90 and 2.09 to 5.02 log reductions of the planktonic and biofilm-embedded cells formed on RO membrane surface. Recently, many researchers have found that FNA is a strong biocidal agent, which received increasing attention as a novel low cost acid cleaning agent for both biofouling and scaling removal. More details about FNA would be discussed in the bottom of the section 3.2.6.

For membrane damage and characteristics changes: Acid cleaning is usually operated at or above pH 2, which is consistent with the typical operating pH limits by several membrane manufacturers are reportedly in the range of 2–10, referring to limits of 2–12, 1–12, or 1–13 as harsh cleanings [88], thus, it seems has less adverse effect on the surface properties of polyamide membrane. In general, operating at more conservative values can ensure the best performance and longest lift of the membrane. Tessaro et al. [89] studied the degradation of polyamide RO membrane by cleaning with citric acid at pH 4.0 using a lab-scale RO system. The citric acid solution was recirculated 10 h at 40°C. Such acid cleaning did not change characteristics of retention and permeate flux of new RO membrane, 3-year old operating RO membrane taken from an industrial plant, and new RO membrane previously degraded by free chlorine solution of 500 ppm.

Although acid cleaning showed less adverse effect on polyamide membrane, it could irreversibly alter the charge of membrane. Religa et al. [90] pointed out that the low pH of the model solutions containing chromium(III) used for recovery by a lab-scale NF membrane and subsequently acid cleaning causing an increase in the density of positively charged groups on the surface and in the pores of NF membrane. Hence, the negative chlorides and sulfates ions present in the model solution were 'immobilized' on the surface and inside of the membrane, resulting in formation of ionic adsorption layer causing new conditions in the system, including the strengthening effect of concentration polarization, reducing of permeate flux and scaling of the NF membranes. They also pointed out that HL membrane has a higher density of a mine than carboxyl groups compare to DL membrane in its active layer what causes that

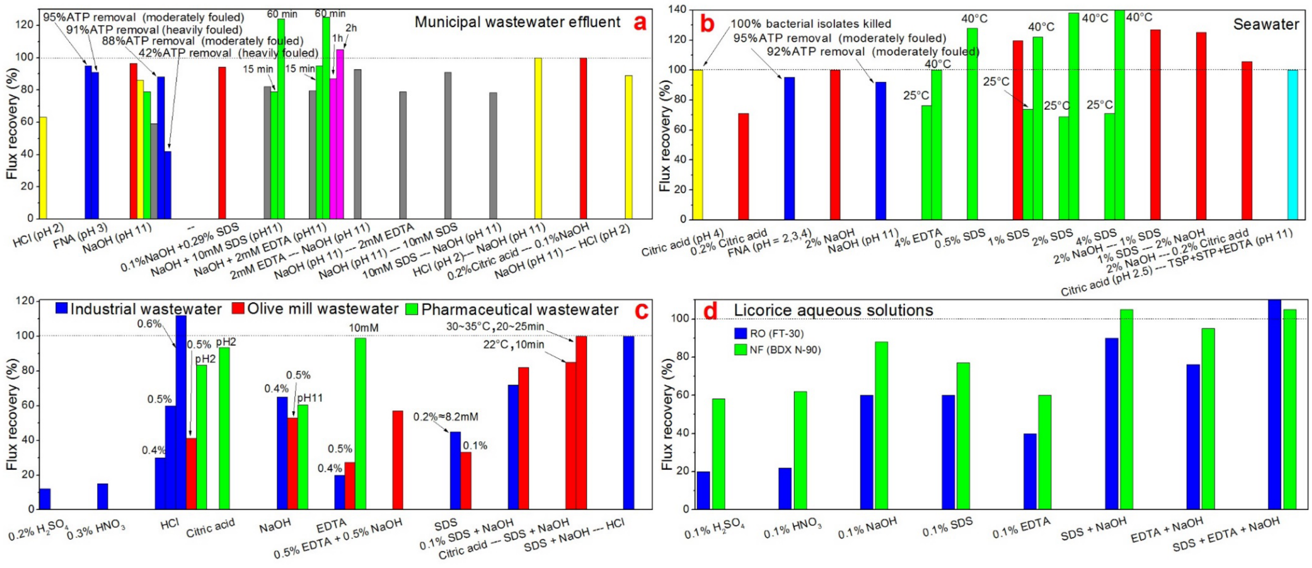

Fig. 7. The flux recovery of NF/RO membranes fouled by: (a): municipal wastewater effluent; (b): seawater (note: the flux recovery of green data are recalculated based on Eq. (1) (see section 2.2, FR(%) = (J_{wc}/J_{wi}) × 100) used in this review.); (c): industrial wastewater, olive mill wastewater, and pharmaceutical wastewater; (d): licorice aqueous solutions by the cleaning of various agents.

Note: (a): yellow data [81]; blue data [84]; red data [83]; greed data [21]; gray data [26]; pink data [94]; (b): yellow data [66]; red data [93]; blue data [84]; green data [4]; cyan data [95]; (c): blue data [17]; red data [27]; green data [86]; (d): blue and green data [9].
The flux recovery that is higher than 100% may be a result of modification to the surface properties (e.g., hydrophilicity) by the cleaning agents [9,17,21] or due to the enlargement of the membrane pores resulting from the adsorption of cleaning agent to the membrane active layer [4,93].

this type of membrane is more susceptible to the adsorption of negative ions and in consequence showed less stable work under experiment conditions. This can be explained according to research conducted by Bandini et al. [91,92] that amine functional groups, becoming active at the low pH and being carriers of positive charges, create convenient conditions for the adsorption of anions both on the surface of NF membranes and in their internal structure. In order to regenerate membrane charge, NaOH cleaning after cleaning with HCl can lead to the recovery of the negative surface charge of NF membranes, thus, significantly improves both the membrane stability and better resistance to mechanical damage in the structure of the DL and HL membranes during nanofiltration of concentrated salt solutions characterized by pH ≈ 4.

The widely-used acids include HCl, citric acid, FNA, HNO_3, and H_2SO_4. In most cases, HCl, citric acid, and FNA can offer a better cleaning efficiency than other acids. Acid cleaning can efficiently remove biofouling and inorganic fouling (e.g., iron, carbonate precipitates, Sr, and P, etc.) from membrane surface. However, the effectiveness of cleaning with acid is limited for Si, sulfate based materials, and organic fouling. From Fig. 7, it can be observed that acid cleaning as one step of two-dual step cleaning would be more efficient. Many researches proved that two-step cleaning with HCl and NaOH [81], HCl and NaOH + EDTA [82], acid and NaOH + Sodium dodecyl sulfate (SDS) [17], etc., are more effective to remove the compounded foulants from membrane surface. More details would be discussed in section 3.4.3.

3.2.2. Base

Alkaline solution is used to remove organic foulants on membranes by hydrolysis, solubilization, and by generating of electrostatic interactions between negatively charged foulants and membrane when the solution pH is elevated [27,96]. NaOH is widely used as the cleaning reagent. At pH 11, the functional groups of the individual organic foulants in the mixture are deprotonated and therefore, the foulants are negatively charged [97–99]. The improved repulsion of the organic deposits on RO membrane could weaken their adhesion to membrane. Moreover, the fouling layer becomes less dense, enabling the penetration of the cleaning reagents and therefore leading to increased mass transfer and thus cleaning efficiency. The repulsive interaction among the foulants within the fouling layer coupled with the shear due to the cross-flow velocity is substantial enough to release the fouling layer and transport the foulants from the membrane surface to the bulk solution. In addition, after deprotonated at caustic condition, the solubility of the organic foulants also increased thus facilitating the removal of organic foulants from membrane surface. For example,when carboxylic functional groups of the organic foulants are deprotonated at caustic condition, solubility increases nearly three orders of magnitude [100].

Table 2 summaries the flux recovery of NF/RO membranes fouled with various organic foulants in the presence of Ca^{2+} by the cleaning of NaOH. As shown in Table 2, NaOH is known to be efficient for organic foulants, colloidal silica, and biofouling removal.

For organic fouling: Organic matters can be hydrolyzed and solubilized into small molecules as illustrated in Fig. 5. The cleaning efficiency of NaOH in removing fouling layer from membrane surface would be affected by organic foulant types. Fig. 8 schematically summaries the cleaning efficiency of NF/RO membranes fouled with various organic foulants by the cleaning of various agents. From Fig. 8a, it can be observed that the cleaning with NaOH is much more effective for protein and combined organic foulants removal compared to that for CH, HA, as well as alginate. Beyer et al. [8] conducted membrane fouling and chemical cleaning experiments by a lab-scale cross-flow NF system. They reported that cleaning with NaOH (pH 11), the flux recovery for protein (almost 70%) was much higher than that for HA (5%)and alginate (17%), because the protein-related fouling was primarily associated with the formation of the hydrophobic cake layer, consequently, the dissolution of protein from the fouling cake layer could be effectively induced at high pH. Kimura et al. [81] also found that the ratios of CH to protein in NaOH solution was 0.61, which was much lower than that in HCl solution (3.3), indicating that more protein was desorbed by NaOH since the amount of TOC desorbed in NaOH cleaning was comparable to that desorbed in HCl cleaning. In most cases, the cleaning efficiency of NaOH cleaning is not enough to be convincing, because NaOH alone is not strong enough to break up the organic foulants-Ca^{2+} bindings.

For inorganic fouling, especially for silica foulants: As for colloidal silica foulants, it can also be easily removed by caustic cleaning but not acid cleaning. Kimura et al. [81] found that Si was easily desorbed at amounts of 105 mg/m^2 by the cleaning of NaOH. Garcia-Fayos et al. [4] also found that the flux recovery was up to 95.4% when they used 2% w/w NaOH to clean a pilot-scale RO membrane apparatus for seawater treatment, which mainly (70%) fouled by colloidal and inorganic fouling consisted of silica, aluminum and iron silicates, and aluminum and iron oxides and hydroxides during seawater desalination. Song et al. [101] pointed out that this is possibly due to the dissolution of silica colloid forming silicate ions ($HSiO_3^-$) more easily at higher pH value.

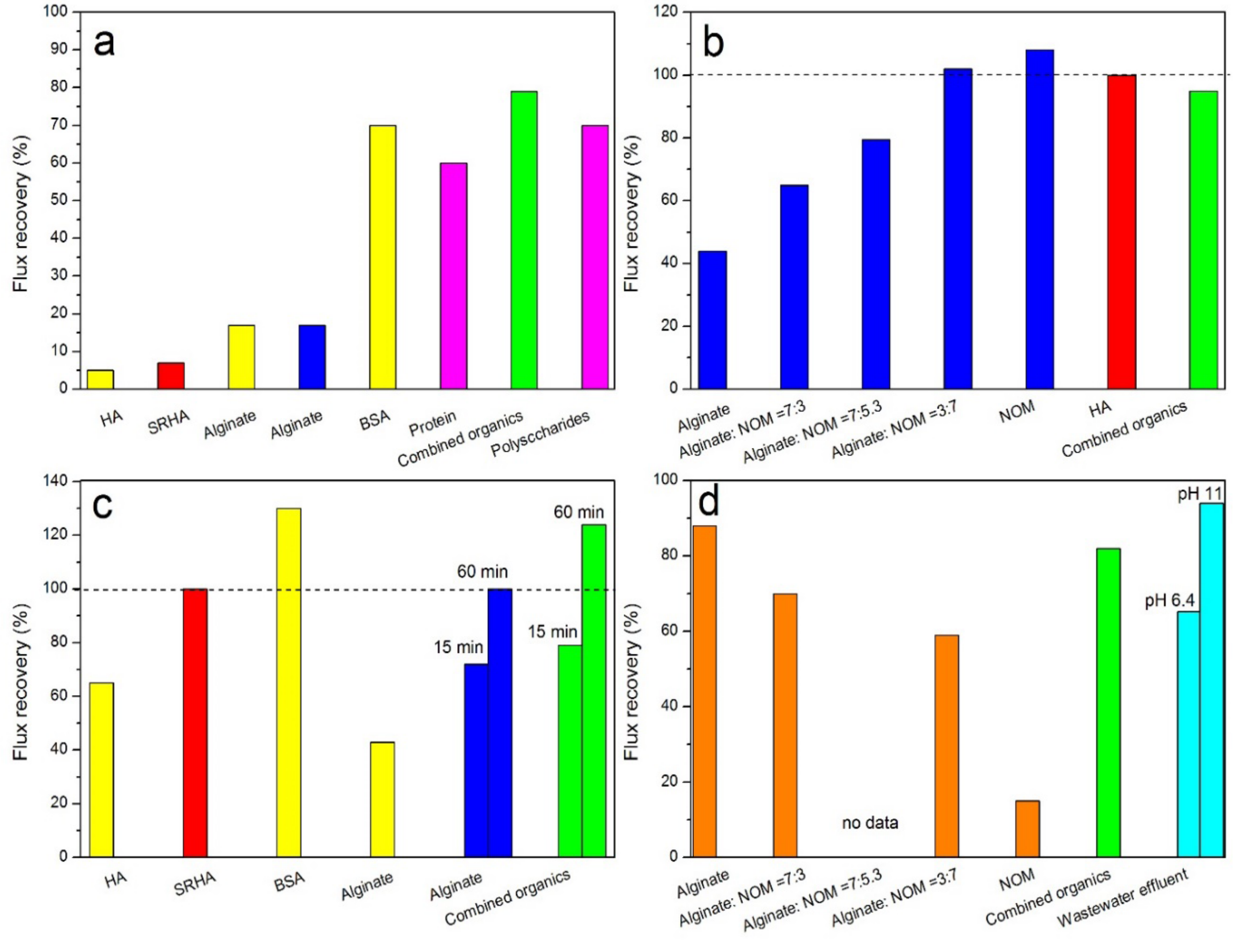

Fig. 8. The flux recovery of NF/RO membranes fouled with various organic foulants in the presence of Ca^{2+} by the cleaning of a: NaOH (pH 11); b: EDTA (pH 11, 0.5 mM (blue and green); 1.0 mM (red)); c: SDS (pH 11, 10 mM); d: NaCl (100 mM (orange); 500 mM (green and cyan)).Note: yellow data [8]; red data [20]; pink data [84]; blue data [25]; green data [21]; orange data [79]; cyan data [26].

For biofouling: NaOH would also be expected to show high biofilm removal. Biomass removal is usually measured by using the parameters ATP and CH, which are well-suited for quantitative assessment of biofouling in high pressure membranes. Removal of bacterial ATP exhibits the impact of cleaning on the active part of the attached biomass, and CH removal represents the effects on the EPS which mainly composed of protein and polysaccharides [102,103]. Filloux et al. [84] carried out lab-scale NaOH cleaning on biofilm fouled RO modules collected from full-scale plants and found that the NaOH solution (pH 11) shows average organic removals of 59~60% and 62~79% of proteins and polysaccharides respectively, and total biomass (ATP) removals of 85~92% and 42% of moderately and heavily fouled membrane respectively (see Fig. 7a). Hijnen et al. [103] also observed that ATP removal was higher than CH removal which was usually ≤40%. The highest and reproducible efficiency was observed for the standard procedure with NaOH + SDS at pH 12.0 (70% ATP and 34% CH on an average) in both laboratory test and clean-in-place of RO membrane pilot plant experiments compared to other regents except for NaOCl. They also studied the influence of biofilm characteristics on cleaning efficiency and observed inverse influence of the CH/ATP ratio on the cleaning efficiency (lower efficiency at higher ratio) presents evidence for the important role of carbohydrates (EPS) in the stress resistance of biofilms against chemical cleaning.

As shown in Fig. 8a, NaOH (pH 11) alone is not an efficient enough cleaning agent for cleaning NF/RO membranes fouled bybiofilms [84,103] and organic foulants in the presence of Ca^{2+} (e.g., alginate-Ca^{2+} [8,25], HA-Ca^{2+} [8,20], bovine serum albumin (BSA)-Ca^{2+} [8], and combined organic foulants-Ca^{2+} complexes [21]) due to the strong complexation between organic foulants and Ca^{2+} ions. In details, the cleaning efficiency of NaOH is higher for membrane fouled by combined foulants (79%, a mixture of alginate, BSA, SRNOM, and octanoic acid) than by alginate (14%) fouled membrane in the presence of Ca^{2+} suggested that the binding among alginate-Ca^{2+} complex was stronger when the fed solution contains alginate as the sole foulant type, and weakened when other foulant types were present in the fed solution [21]. In order to obtain higher cleaning efficiency for NF/RO membranes fouled by organic foulants in the presence of Ca^{2+}, performing acid cleaning followed by NaOH cleaning [81,83] or adding SDS and/or EDTA simultaneously within caustic solution should be considered. This will be discussed in section 3.2.3, section 3.2.4, and section 3.4.3.

For membrane damage and characteristics changes: Compared to acid cleaning, caustic cleaning has a much more adverse effect on membrane surface properties. It can reduce the surface charge (negative charge) [9]. It can also significantly increase the membrane porosity and enlarge the membrane pore size particularly if the membrane has a very thin active skin layer [14,104–107], resulting in a significant improvement of permeability, a decrease of salt and some trace organic compounds (TrOCs) rejection. For example, Liikanen et al. [14] evaluated the effects of several cleaning agents on NF255 membrane in a pilot process and found that NaOH solution (pH 12.2) can modify the NF255 membrane by improving its flux by 50%, but result in a decrease in ion retention. Several researchers investigated the effect of caustic cleaning on the rejection of TrOCs (e.g., N-nitrosamines [104], carbamazepine [106]) using lab-scale cross-flow NF/RO systems. They found that caustic cleaning (pH 12) caused a significant increase in membrane permeability and a notable decrease in the rejection of some TrOCs (i.e., low molecular weight N-nitrosamines, neutral carbamazepine) due to the increase in the porosity of membrane matrix or membrane pore size immediately after caustic cleaning. However, the rejection of negatively charged sulfamethoxazole does not significantly influenced by strong caustic cleaning because it is predominantly by electrostatic repulsion and size exclusion plays a less important role [15,106,108]. Therefore, it seems that membranes with thicker and compact active skin layer (e.g., NF90, TFC-SR100), which pore size was not affected by chemical cleaning, are better to obtain more efficient removal of inorganic salts and TrOCs than that with thinner and loose active skin layer (e.g., NF270), which pore size increased after caustic cleaning [109,110].

As mentioned in section 3.2.1, typical cleaning pH limits by several membrane manufacturers are reportedly in the range of 2–10, referring to limits of 2–12, 1–12, or 1–13 as harsh cleanings. In fact, even a used polyamide membrane was cleaned at conservative pH 10, the permeate flux of the membrane was increased and salt rejection was decreased after alkaline cleaning [111]. Mitrouli et al. [111] attributed such phenomenon to some degradation of polyamide membrane, although the removal of foulants by chemical cleaning may have also significantly influenced this trend. Generally, caustic cleaning was usually performed at pH 11 [26,81] or pH 12 [14,106]. Cleaning at such aggressive pH may result in a more effective cleaning, but can shorten the useful life of the membrane due to hydrolysis, resulting in accelerated membrane deterioration. The hydrolysis of polyamide membrane could be more active during caustic cleaning (pH values > 11) especially when N–Cl species were generated in the active layer due to chlorine exposure at lower pH (acidic) [112]. Excessive hydrolysis occurred while the membrane was treated at pH 13 for the much stronger alkalinity [113]. The comprehensive effect of a possible enlargement of membrane pores and the adsorption of the high pH cleaning agents within the membrane surface or a degradation of the polymer in the active layer maybe responsible for the increase of permeate flux and decrease of salt rejection.

3.2.3. Chelating agents

Metal chelating agent such as EDTA is widely used to remove divalent cations from the complexed organic molecules and improve the cleaning efficiency [21,115]. The mechanisms of chemical cleaning with EDTA are depicted schematically in Fig. 5. In the presence of Ca^{2+}, the organic molecules in the fouling layer are bound to each other by Ca^{2+}. Since EDTA forms a stronger complex with Ca^{2+}, organic molecules originally associated with Ca^{2+} ions are replaced by EDTA via a ligand exchange reaction. The intermolecular bridges among organic molecules as well as those between organic molecules and the membrane surface are then disrupted. Thus, the foulant layer loses its cross-linked, gel-like structure. At the same time, interchain repulsion is resumed and organic molecules return to the original loose conformation due to the destruction of intramolecular organic-Ca^{2+} complexes. These detached individual organic molecules can then be easily rinsed off the membrane surface.

For organic foulants-Ca^{2+} complexes: EDTA presents six molecular positions able to form hydrogen bridges and complexation with calcium ions in both inorganic foulants (e.g., $CaSO_4$) [82] and organic foulants-calcium complexes [20,26,83] deposited on the membrane. Several researches pointed out that EDTA alone is a moderate chemical cleaning as it showed a low cleaning efficiency. For example, only 54.1% and 49.5% cleaning efficiency by addition of 0.1% and 4% w/v EDTA, respectively, when it was used to clean a pilot-scale RO membrane fouled by seawater [93], and only 27.4% cleaning efficiency by the addition of 0.5% w/v EDTA when it was used to clean a lab-scale RO membrane fouled by secondary-treated olive mill wastewater [27]. However, cleaning with EDTA alone at higher concentration with longer reaction time may be efficient for foulants removal from membrane surface. In a lab-scale installation, Wei et al. [86] reported that the cleaning efficiency of NF membrane fouled by complex pharmaceutical wastewater increased in the sequence of NaOH (pH 11) < HCl (pH 2) < citric acid (pH 2) < EDTA (10 mM). After cleaning with 10 mM EDTA for 60 min, the membrane flux recovery ratio reached 99.0%. Indicating that EDTA alone could react through ligand exchange with calcium ions in both inorganic foulants and organic foulants–calcium complexes to produce soluble complexes, which finally resulted in the breakdown of the densely packed fouling layer.

Generally, the mixture of EDTA and NaOH at pH 11 showed cost-effective cleaning efficiency. Table 3 summaries the EDTA cleaning used for NF/RO membranes. From Table 3, it can be observed that EDTA performed better chelating ability at caustic solution than at neutral and acidic conditions, due to the carboxylic groups of EDTA are more deprotonated at caustic solution and available for Ca^{2+} complexation. As shown in Fig. 8b, At pH 11, 0.5 ~ 1.0 mM EDTA is an effective cleaning agent for NF/RO membrane fouled by combined organic foulants-Ca^{2+} [21], SRHA-Ca^{2+} [20], and SRNOM-Ca^{2+} [25,115] complexes, which cleaning efficiency was about 95%, more than 100%, more than 100%, respectively. However, it is less effective in cleaning membrane fouled by feed water with higher alginate content as illustrated in Fig. 5. It is possibly because the alginate fouling layer is much denser and more compact than other fouling layers due to its gel-like structure, which significantly limits the diffusion of EDTA molecules [25]. W.S. Ang et al. [25] found that the cleaning efficiency of alginate fouled membrane was significantly increased by increasing cleaning time, especially by increasing the concentration of EDTA. Varin et al. [94] also reported that 2 h cleaning with 2 mM EDTA at pH 11 enabled complete restoration of membrane permeability in a lab-scale RO membrane system for municipal wastewater effluent treatment. Therefore, the "stoichiometry" and efficient reaction time between the cleaning agent dose and amount of foulants on the membrane surface must be considered.

For calcium ions removal in inorganic fouling: Barium and strontium sulphate are needle shaped crystals which can be removed with alkaline chelants [116]. In a pilot-scale plant for semiconductor wastewater treatment, Xiao et al. [82] also reported that NaOH + EDTA was effective for removing loose inorganic deposits (dominantly $BaSO_4$) under the conditions of biological and organic fouling were ignorable. The authors suggested that the cleaning of HCl–NaOH/EDTA was much more effective to remove foulants from membrane surface than that of HCl, HCl–NaOH, and HCl–NaOH/SDS due to the strong mental ions chelating ability of EDTA. After the HCl–NaOH/EDTA cleaning, the RO membrane permeability was recovered to the fresh one (see Fig. 6 left).

Other chelating agents: Except for the widely used chelating agent of EDTA as well as earlier documented chelating agent of citric acid, other chelating agents such as diethylenetrinitrilopentaacetic acid, sodium tripolyphosphate (STP), and mixture agents comprised of STP, trisodium phosphate (TSP) and EDTA have also been used for membrane cleaning [83,107,117,118]. However, they are not biodegradable leads to the presence of considerable amounts in aquatic systems with serious environmental issues. Pinto et al. [119] reviewed the most relevant studies towards the use of environmentally friendly chelating agents in a large number of applications including detergents and cleaning compositions as well as scale prevention and reduction. They pointed out that Nitrilotriacetic acid, ethylenediaminedisuccinic acid, and iminodisuccinicacid are the most commonly suggested to replace the nonbiodegradable chelating agents. Recently, an environmentally friendly chelating agent (Trilon® M), which is an organic chelating and can be biodegraded, used for lab-scale-polyamide and polyethersulfone membrane cleaning was reported by Kingma [120]. The author found that the chelate (Trilon®M, 0.2%) alone cleans almost 50% of the bacteria cells and more than the double amount of the crosslinked matrix compared to water, surfactant or enzyme alone. The strongest cleaning performance was obtained with a combination of the chelate with surfactant and enzyme where more than 70% of the bacteria cells and of the crosslinked matrix were removed even under mild cleaning conditions at pH 8.

EDTA cleaning at caustic condition shows much more advantages over other cleaning agents. It can form a stronger complex with metal ions, which exist in both inorganic foulants (e.g. $CaSO_4$, $BaSO_4$) and organic foulants-metal ioncomplexes. Thus, organic molecules and inorganic foulants can be easily rinsed off the membrane surface. Attention should be paid to the pH value of the EDTA cleaning solution. Higher cleaning efficiency of EDTA cleaning can be obtained at higher pH values, while the hydrolysis of membrane can also be more active at higher pH values, as discussed in section 3.2.2. Recently, several environmentally friendly biodegradable chelating agents have been received increasing interest. They can be operated at mild conditions without damage the membrane. Further studies are needed to improve cost-effectiveness ratio for full-scale and commercial installations.

3.2.4. Surfactant

Surfactants are generally used as chemical cleaning agents due to their surface-active property. They are amphiphilic compounds that have both hydrophilic and hydrophobic structures. Interaction between the membrane/

Table 3
Summary of EDTA cleaning used for NF/RO membranes

Membrane	Feeding	Fouling time	Cleaning agents	Efficiency	Scale	Ref.
RO (SWC3)	Seawater (70% were inorganic and 30% were organic fouling)	Retired from full-scale plant	EDTA 4% w/v Soaking 1 h at 25°C[a] Soaking 1 h at 40°C[b]	The flux recovery was 49.51 %*, the salt rejection index was 86.8% (–5.26% recovery)[a] The flux recovery was 56.35 %*, the salt rejection index was 97.17% (8.11% recovery)[b]	Pilot-scale	Garcia-Fayos et al. [4, 93]
RO (SC series)	Secondary-treated olive mill wastewater	20% permeate flux loss	EDTA 0.1–0.5%w/v[a] EDTA + NaOH both 0.5%w/v[b] Cleaning conditions: 2.7 bar, 4.01 ms^{-1}, 22°C, 10 min,	The flux recovery was between 11.5–27.4%[a] The flux recovery was 57.1%[b]	Lab-scale	Ochando-Pulido et al. [27]
RO (FT-30)[a] NF (BDX N-90)[b]	Licorice aqueous solutions	30 min	EDTA 0.1 wt.%[I] EDTA + NaOH both 0.1 wt.%[II] SDS + EDTA + NaOH both 0.1 wt.%[III] Cleaning condition: 0 TMP, 5 m/s, 5 min, 25°C	The flux recovery was 40%[aI] The flux recovery was 76%[aII] The flux recovery was 110%[aIII] The flux recovery was 60%[bI] The flux recovery was 95%[bII] The flux recovery was 105%[bIII]	Lab-scale	Sohrabi et al. [9]
NF (Desal-5DK)	Complex pharmaceutical wastewater	180 h	10 mM EDTA Cleaning conditions: 0.1 MPa, 0.24 ms^{-1}, 30 ± 0.5°C, 60 min	The flux recovery was 99.0 %	Lab-scale	Wei et al. [86]
NF 270	SRHA	8 h	1 mM EDTA (pH 4.8)[a] 1 mM EDTA (pH 11.0)[b] Cleaning condition: 470 rpm, 10 min	The flux recovery was 70%[a] The flux recovery was almost 105%[b]	Lab-scale	Li et al. [20]
RO (LFC-1)	Simulating wastewater effluent	17 h	0.5 mM EDTA (pH 4.8)[a] 0.5 mM EDTA (pH 11.0)[b] Cleaning conditions: 15 min; 21 ± 0.5 °C; and no pressure.	The flux recovery was 35%[a] The flux recovery was 95±4.5%. (almost 125% for 60 min cleaning)[b]	Lab-scale	W. S. Ang et al. [21]
RO (LFC-1)	Simulate effluent organic matter (Sodium alginate and SRNOM)	17 h	0.5 mM EDTA (pH 4.9)[a] 0.5 mM EDTA (pH 11.0)[b] 2.0 mM EDTA (pH 11.0)[c] Cleaning condition: 42.8 cm/s, 15 min, 20.0 ± 0.2 °C	The flux recovery was 25% for alginate-Ca^{2+} complexes[a] The flux recovery was 44% for alginate-Ca^{2+} complexes (almost 84% for 60 min cleaning)[b] The flux recovery was almost 100% for alginate-Ca^{2+} complexes[c] The flux recovery was 44%; 64%; 102%; 108% respectively, corresponding to alginate/SRNOM: alginate only; 7:3; 3:7; SRNOM only[b]	Lab-scale	W. S. Ang et al. [25]
RO (LFC-1)	Municipal wastewater effluent	17 h	2 mM EDTA (pH 7.0)[a] 2 mM EDTA (pH 11.0)[b] Cleaning condition: 0 psi, 42.8 cm/s, 15 min, 21.0 ± 0.5°C	The flux recovery was 82.1%[a] The flux recovery was 79.5%[b]	Lab-scale	W. S. Ang et al. [26]
RO	Secondary wastewater effluent (biofouling)	24 h	2.0 mM EDTA (pH 11.0) Cleaning conditions: step one: 1034 kPa, 14.3 cm/s for 1 h, followed by step two: ~138 kPa, 14.3 cm/s for 1 h.	Step one: 93%, 89%, 80% (flux recovery) for PMAA-SNS-PA-TFC, PAAm-SNS-PA-TFC, and ESPA2 membranes, respectively Step two: 2.2–8.5% (flux recovery) higher relative to the native clean membranes	Lab-scale	Varin et al. [94]

(Continued)

Table 3 (*Continued*)
Summary of EDTA cleaning used for NF/RO membranes

RO (LFC3-LD)	Semiconductor wastewater effluent (mainly $BaSO_4$, with small amounts of $SrSO_4$)	63 d	NaOH (0.4%) + EDTA (0.75%) w/v Soaking 7 h at 35°C	The averaged removal fraction values of Ba, Ca, Si, Al, Mg, Fe, Zn and TOC were all more than 50%, and considered to be an effective cleaning agent for all the foulants	Pilot-scale	Xiao et al. [82]
RO (FT-30)	Industrial wastewater (organic and inorganic fouling (contains of $CaCO_3$ and $Fe(OH)_3$))	9 h	EDTA 0.4%w/v (pH 8.0)[a] EDTA 0.4%w/v (pH11.0)[b] Cleaning condition: 0.5 bar, 10 min, 25±2°C	The flux recovery was 20%[a] Not reported[b]	Pilot-scale	S.S. Madaeni et al. [17]
NF270[a] NF 90[b]	Virgin membranes	–	EDTA + NaOH (pH 11.5) Soaking 18 h at 35± 1°C	Led to a small increase in pore size and resulted in a notable increase in the permeability and salt passage[a] The impact on the NF90 membrane was negligible[b]	Lab-scale	A. Simon et al. [109]

Note: *The calculation of flux recovery was based on the equation: J_p flux recovery = $(J_p - J_{p0})/J_{p0} \times 100$, where, J_{p0} is bank values of permeate flux quantified using distilled water, which is different from Eq. (1) (see section 2.2, FR(%) = $(J_{wc}/J_{wi}) \times 100$) used in this review.

foulant and the surfactant is dominated by hydrophilic/hydrophobic reaction. The surfactant can adhere to organic foulants through hydrophobic tails with hydrophilic head orientated towards aquatic phase (water) [19,121], and break up organic foulants-metal ion (e.g., Ca^{2+}) bindings [8,20] through hydrophilic interaction between hydrophilic heads and water molecules, solubilize macromolecules by forming micelles around them [20,121], thereby facilitating removal of the foulants from the membrane surface [25].

SDS is a widely used anionic surfactant for membrane cleaning. The proposed mechanism of SDS cleaning is depicted in Fig. 5. A lower SDS concentration cannot break the intermolecular bridging formed with Ca^{2+}. When a higher SDS concentration is used, more SDS molecules partition into the foulant layer and the increased hydrophilic interaction results in breakup of some Ca^{2+} bindings. Once the SDS concentration exceeds the critical micelle concentration (8.36 mM in deionized water at 20°C [122]), micelles form in the cleaning solution, the solubilization force is then strong enough to break up all the Ca^{2+} bridges, which makes the organic foulants removed easily from membrane surface. Therefore, it is concluded that cleaning with SDS above the critical micelle concentration is the critical factor for efficient SDS cleaning [20,25].

For organic fouling: Table 4 summaries SDS cleaning used for NF/RO membranes. As shown in Table 4, many researchers suggest that the optimum SDS concentration is about 10 mM for the NF/RO membrane cleaning [8,20,21,25]. It is noteworthy that even with the same 10 mM SDS concentration, SDS alone (ambient pH) and/or SDS (pH 11) cleaning mechanisms can be correlated to characteristics of the organic foulant types. There is no significant difference in flux recovery cleaning with both SDS alone and SDS (pH 11) when NF270 membrane in a lab-scale system was fouled by SRHA-Ca^{2+} [20], protein-Ca^{2+} [8], HA-Ca^{2+} [8], alginate-Ca^{2+} [8] complex foulants, and Ludox CL colloidal silica [8], the FR were both more than 100%, more than 100%, about 60%, about 40%, and about 79%, respectively. It can be concluded that both alginate and HA fouling are more quite recalcitrant to SDS cleaning as well as NaOH cleaning than protein fouling (see Fig. 8), which is driven mostly by hydrophobic interaction. However, it is not the case for simulating wastewater [21], industrial wastewater [17], municipal wastewater effluent [26], secondary-treated olive mill wastewater [27], and glutamic acid fermentation broth [123], SDS (pH 11) demonstrated greater cleaning power and cleaning efficiency by about 79%, 73%, 82%, 82.1% and more than 100%, respectively, compared to single cleaning with SDS or NaOH (see Fig. 7). W.S. Ang et al. [26] pointed out it is possibly due to SDS molecules do not interact specifically with Ca^{2+} in the polysaccharide – calcium complex, which is predominantly foulants on wastewater effluent fouled membrane surface, thus, SDS molecules are expected to have more difficulty in breaking down the structural integrity of the fouling layer matrix and removing the foulants. NaOH could facilitate SDS in breaking up the polysaccharide – calcium complex, forming micelles around the foulants, and transporting the foulants from the membrane surface to the bulk solution. Namely, this can be explained on the basis of the detersive action of SDS together with the hydrolysis and solubilization caused by NaOH [17,21,26,27].

For inorganic fouling: The cleaning efficiency of SDS alone [4,93] and mixed with other agents [116] to remove colloidal fouling has been attributed to their emulsifier power, since they modify the interfacial tension of water and facilitate the detachment of fouling materials from the membrane surface [16]. Chesters et al. [116] reported that Genesol 703, a high pH phosphate cleaners with a chelant and surfactant, was effective for clay (alumino-silicates) removal in laboratory tests, which was very difficult to remove by conventional acid and alkaline cleaners. In a pilot-scale cleaning

Table 4
Summary of surfactant cleaning used for NF/RO membranes

Membrane	Feeding	Fouling time	Cleaning agents	Efficiency	Scale	Ref.
RO (SWC3)	Seawater (70% were inorganic and 30% were organic fouling)	Retired	SDS 1% w/v (soaking 1 h at 25°C)	The flux recovery was 136.34%*, the salt rejection index was 97.0% (5.09% recovery)	Pilot-scale	Garcia-Fayos et al. [93]
RO (SWC3)	Seawater (70% were inorganic and 30% were organic fouling)	Retired	SDS 0.5%, 1%, 2%, 4% w/v (soaking 1 h at 25°C)[a] (soaking 1 h at 40°C) [b]	The flux recovery was –, 46.1%, 34.1%, 39.8%*, respectively[a] The flux recovery was 93.0%, 86.1%, 108.7%*, 111.2%, respectively[b]	Pilot-scale	Garcia-Fayos et al. [4]
RO (SC series)	Secondary-treated olive mill wastewater	20% permeate flux loss	SDS 0.1%w/v[a] SDS+NaOH both 0.1%w/v [b] Cleaning conditions: 2.7 bar, 4.01m/s, 22°C, 10 min,	The flux recovery was 33.1%[a] The flux recovery was 82.1%[b]	Lab-scale	Ochando-Pulido et al. [27]
RO (FT-30)[a] NF (BDX N-^{9}0)[b]	Licorice aqueous solutions	30 min	SDS 0.1 wt.% [I] SDS + NaOH both 0.1 wt.%[II] SDS + EDTA + NaOH both 0.1 wt.%[III] Cleaning condition: 0 TMP, 5 m/s, 5 min, 25°C	The flux recovery was 60% [aI] The flux recovery was 77% [aII] The flux recovery was 110% [aIII] The flux recovery was 90% [bI] The flux recovery was 105% [bII] The flux recovery was 105% [bIII]	Lab-scale	Sohrabi et al. [9]
NF 270	SRHA	8 h	10mM SDS (ambient pH ~9)[a] 10mM SDS (pH 11.0)[b] Cleaning condition: 470 rpm, 10 min	The flux recovery >100%[a] The flux recovery >100%[b]	Lab-scale	Li et al. [20]
NF 270	Model foulants	18 h	10 mM SDS (unadjusted pH 6)[a] 10 mM SDS (pH 11)[b] Cleaning condition: 75 cm/s, 30 min	The flux recovery was 118%, 18%, and 62% for BSA-, HA-, alginate-Ca^{2+} complexes, respectively[a] The flux recovery was 130%, 65%, and 42% for BSA-, HA-, alginate-Ca^{2+} complexes, respectively[b]	Lab-scale	Beyer et al. [8]
RO (LFC-1)	Simulating wastewater effluent	17 h	10 mM SDS (pH 11.0) Cleaning conditions: 15 min; 21±0.5°C; and no pressure.	The flux recovery was 79% (almost 124% for 60 min cleaning)	Lab-scale	W. S. Ang et al. [21]
RO (LFC-1)	Simulate effluent organic matter	17 h	10 mM SDS (pH 11) Cleaning condition: 42.8 cm/s, 15 min, 20.0±0.2°C	The flux recovery was 72% for alginate-Ca^{2+} complexes (almost 100% for 60 min cleaning)	Lab-scale	W. S. Ang et al. [25]
RO (LFC-1)	Municipal wastewater effluent	17 h	10 mM SDS (pH 7.0) 10 mM SDS (pH 11.0) Cleaning condition: 0 psi, 42.8 cm/s, 15 min, 21.0 ± 0.5 °C	The flux recovery was 77.4% The flux recovery was 82.0%	Lab-scale	W. S. Ang et al. [26]
RO (LFC3-LD)	Semiconductor wastewater effluent (mainly $BaSO_4$, with small amounts of $SrSO_4$)	63 d	SDS (0.03%) w/v + NaOH (0.1%) soaking 7 h at 35°C	Less than 5% removal fraction of the mainly foulant Ba, but exhibited good removal performance to the foulants Ca, Si, Al, Mg, Fe, Zn and TOC	Pilot-scale	Xiao et al. [82]
RO (FT-30)	Industrial wastewater (organic and inorganic fouling (contains of $CaCO_3$ and $Fe(OH)_3$))	9 h	SDS 0.2%w/v (close to 8.2 mM)[a] SDS 0.1%w/v +NaOH[b] Cleaning condition: 0.5 bar, 10 min, 25±2°C	The flux recovery was 45%[a] The flux recovery was 72%[b]	Pilot-scale	S.S. Madaeni et al. [17]

(Continued)

Table 4 (*Continued*)
Summary of surfactant cleaning used for NF/RO membranes.

NF (DK)	Obtained from Saline Water Conversion Corporation	9000 h	SDS 0.1% (pH 11.3) Soaking over night (18 h) and then stirred for 90 min	Remarkable increment of flux compared to untreated virgin membrane Rejection of monovalent or divalent ions were found to be lower than the control	Lab-scale	A. Al-Amoudi et al. [107, 114]
NF270[a] NF 90[b]	Virgin membranes	–	SDS + NaOH (pH 11.5) Soaking 18 h at 35± 1°C	Led to a small increase in pore size and resulted in a notable increase in the permeability and salt passage[a] The impact on the NF90 membrane was negligible[b]	Lab-scale	A. Simon et al. [109, 131]

Note: *The calculation of flux recovery was based on the equation: J_p flux recovery = $(J_p - J_{p0})/J_{p0} \times 100$, where, J_{p0} is bank values of permeate flux quantified using distilled water, which is different from Eq. (1) (see section 2.2, FR(%) = $(J_{wc}/J_{wi}) \times 100$) used in this review.

system, Garcia-Fayos et al. [4,93] also confirmed that 1 h of SDS static cleaning was the most efficient agent than others for cleaning RO membranes fouled by seawater, which fouling was mainly colloidal and inorganic fouling consisted of silica, iron silicate, and aluminum silicate. After the cleaning the permeate flux recovery and salt rejection index recovery was about 93% and 7.59% (0.5% w/v SDS at a temperature of 40°C) [4], 136.3% and 5.09% (1% w/v SDS at a temperature of 25°C) [93], respectively.

For membrane damage and characteristics changes: After SDS cleaning, the hydrophilicity of polyamide membrane layer can be improved probably because of a very small amount of EDTA and SDS remaining on the membrane surface [109,114]. Increased hydrophilicity make the chemical bonds between the water molecules and the surface groups on the membrane stronger, thereby, reducing the foulants' possibilities to displace the water molecules and adhere on the membrane [124], enhancing the partitioning and passage of water molecules [114], and minimizing membrane fouling [125]. However, the surface hydrophobicity/hydrophilicity is not only dependent on the adsorption of cleaning agent but also due to the remnant of organic foulants on the membrane surface. It would be high hydrophobicity possibly attributed to a small remnant of the organic foulants on the membrane surface, leading to subsequent rapid flux decline after cleaning [8,15]. Just like the laboratory experiments carried by Li et al. [20] and Beyer et al. [8], they both used the same solution (10 mM SDS (pH11)) cleaning the same NF270 membrane fouled with HA, the flux recovery was more than 100% [20], 60% [8], respectively. The later lower efficiency (60%) is probably due to organic foulants remain left on the membrane surface, this is consistent with other literatures which reported that the adsorption of humic-like substances to membrane surfaces has been shown to increase the hydrophobicity of a membrane [126–128]. However, it is noteworthy that different trends in membrane surface hydrophobicity due to organic fouling are also reported probably because of the difference in physiochemical properties of the foulants, chemical cleaning reagents, and the initial hydrophobicity of the membranes [109,129,130].

Apart from the change of hydrophobicity/hydrophilicity, researches further focus on other changes in membrane properties and separation efficiency (e.g., membrane surface charge, membrane pore size,and salt rejection) after chemical cleaning. AL-Amoudi et al. [107] soaked virgin flat sheet NF membrane (DK) in several chemical cleaning agents and found that lowest salt rejection (88%), relative higher permeability and pore size increases was obtained with SDS (pH 11.3) cleaning than that with HCl, NaOH (pH 11.3), and mixed agents (pH 11.3) cleaning. Simon et al. [131] also confirmed that 10 mM SDS improved the highest permeability compared to NaOH (pH 11.5), citric acid (pH 2), and 5.4 mM EDTA when virgin NF270 membrane was immersed in these cleaning chemicals for 18 h. It indicated a possible enlargement of membrane pores and the adsorption of SDS within the membrane surface or a degradation of the polymer in the active layer. Tessaro et al. [89] also reported that the permeate flux of new RO membrane and 3-years old operating RO membrane taken from an industrial plant were slightly increased when they were cleaned with 0.5% v/v of sodium laurel sulfate at pH 11. However, when the membrane was previously oxidized by free chlorine solution, it further suffered strong degradation during cleaning with the surfactant at pH 11, resulting in the saline retention decreased from 96.80% to 84.80% and the permeate flux increased from 2.90 to 5.90 × 10^{-5} $m^3/m^2 \cdot s$. It can be concluded from the above discussion that surfactants could significantly change the surface properties of polyamide membranes, especially of the chlorine-degraded regions of polyamide membrane, and thus should be used carefully.

Other surfactants: Nonionic surfactants are usually not applied on membrane cleaning due to the assumption that they irreversibly adhere to the membrane surface and thereby clog the pores. Some nonionic surfactants (e.g., *Emulan*®AT 9, Triton X-100) shows strong affinity to the polymeric layers even increase the thickness of the soiled layer, resulting in a negative cleaning performance. In laboratory experiments, Kingma [120] studied the adsorption of a wide range of nonionic surfactants to membrane materials and found that the affinity of nonionic surfactants critically depends on their structure. Linear alkyl ethoxylates irreversibly adsorbed to the membrane surfaces, whereas branched alkyl ethoxylates did not. Similar to the results for adsorption, a structure-performance relationship was discovered where several branched alkyl ethoxylates showed excellent cleaning results. He also pointed out that the combinations surfactant such as (*Lutensol XL 60*, 0.025%)/chelate (*Trilon®M*, 0.2%) and surfactant/enzyme (subtilisin, 100 µg/ml) showed synergistic effects, but the strongest cleaning performance was obtained with a combination of all three components where more than 70% of the bacteria cells and of the matrix were removed even under mild cleaning conditions at pH 8. As a nonionic surfactant, Triton X-100 has a lower biofilm reduction capability than SDS [132]. Kim et al. [133] also confirmed that 1,000 mg/l of Triton X-100 demonstrated a 48% lower biofilm reduction than 1,000 mg/l of SDS (total reduction of 79%) in a lab-scale dead-end RO filtration system. In addition, even a negative cleaning performance was reported by Kingma [120] when a soiled polyamide surface was immersed for 10 min in 0.025% Triton X-100 surfactant solutions at pH 12.

Surfactant cleaning shows some advantages over other cleaning agents. SDS is a widely used anionic surfactant for membrane cleaning. It can break up organic foulants-metal ion bindings, which makes the organic foulants removed easily from membrane surface. It can also modify the interfacial tension of water and remove colloidal and inorganic fouling such as silica, iron silicate, and aluminum silicate by emulsifier power. One of the most issue of cleaning with surfactant is that it can change membrane characteristics more severe compared to other cleaning agents. In some cases, it even cause the damage of the polyamide membrane, and thus should be used carefully. Nonionic surfactants should also be used carefully because most of them showed lower or negative cleaning efficiency except for that with the structure of branched alkyl ethoxylates.

3.2.5. Salt solution

NaCl and other common inert salts can be used as an effective alternative for the cleaning of NF/RO membrane fouled by gel-forming hydrophilic organic foulants. It is proposed that gel layer swelling and ion-exchange reaction are the major mechanisms involved during salt cleaning [79], as shown in Fig. 5. The gel layer swells owning to the osmotic pressure difference between the bulk solution and the interior of the gel layer, thus, increasing ionic strength could be useful for the gel layer swelling. Kerchove and Elimelech et al. [134] proved that the alginate layer shows a constant swelling as the ionic strength (KCl) increased. Wang et al. [135] also found that the crosslink density of the alginate gel was reduced as the ionic strength (KCl) increased. The reduction of crosslink density results in the increase of the chain length inside the gel structure, and thus, an increasing of gel network swelling [134,136]. Following the swelling of the cross-linked gel network, ion-exchange reaction between Na^+ and Ca^{2+} could take place, resulting in the breakup of the gel network [137–139].

It is important to note that the rate and degree of both swelling and breakup of the gel network vary depending on the salt type and dose. In a lab-scale cross-flow RO membrane test unit, Lee et al. [79] found that at the lower salt concentration (25 mM), NaCl showing the highest cleaning efficiency (75%) than that of $NaNO_3$, Na_2SO_4, KCl, CsCl, and NH_4Cl, while at the higher salt concentration (100 mM), the cleaning efficiency (87%~89%) was comparable with all above salts, as well as the seawater which was diluted to have a similar ionic strength as 100 mM NaCl. In addition, the efficiency of salt cleaning is also dependent on the types of organic foulants. It has been proved that 50 mM NaCl (at unadjusted pH) is effective in cleaning alginate fouled RO membrane [79] and combined organic foulants (the ratio of alginate: BSA: SRNOM: octanoic acid is 1:1:1:1:1) fouled RO membrane [21]. However, even at a higher concentration, 100 mM NaCl (ambient pH) is much less effective in cleaning the membrane fouled by feed water with higher SRNOM content (see Fig. 8d) [79]. Farooque et al. [66] also reported that 25% concentration of NaCl could not restore the performance of fouled SWRO membranes. W.S. Ang et al. [26] found that 500 mM NaCl at unadjusted pH 6.4 and pH 11 showed the moderate (65%) and highest cleaning efficiency (94%), respectively, in cleaning a lab-scale RO membrane fouled by wastewater effluent. This indicates that the transfer of NaCl from bulk solution to the fouling layer was facilitated at higher pH value due to the ability of NaOH could loosen the fouling layer. The results suggest that the increase of mass transfer and reaction rate by enhancing pH values and increasing NaCl concentration play an important role not only in chemical cleaning applications but also in the DO backwash cleaning process.

3.2.6. Biocides

Biofouling results in severe problems such as higher operating pressure, shorter membrane life, and more frequent chemical cleaning. Biocides can inactivate the biofilms exist on the membrane surface and it appears that biocide-based cleaning is the most reliable option to remove biofouling from membrane surface [140]. Chlorine could sterilize most kinds of microorganisms in water and was used to control biofouling in pretreatment and clean-in-place of RO processes with cellulose acetate based membrane [141]. However, it could damage the polyamine based membrane by oxidizing the polyamine structure [142–144] and/or causing polyamine hydrolysis [145,146], which cause significant changes in surface characteristic and severe reduction in membrane performance such as unstable permeation, lower salt rejection and life-shortening.

Despite the significantly adverse effect of chlorine on polyamine membrane, it is interesting that both cleaning efficiency and membrane performance could be enhanced by using chlorination under certain conditions. In lab-scale cleaning experiments, some researchers showed that NaOCl at pH 11 was more effective in removing CH from biofim matrix [103] and both organic and inorganic foulants from NF 200 membrane compared to other chemicals [147]. Kang et al. [143] reported that the performance of RO membrane in a lab-scale cross-flow test unit was slightly improved after the treatment of alkaline hypochlorite solution for a certain time compared to that of acid environment. Do et al. [146] also confirmed that NF90 membrane chlorinated at pH 9 and moderate total chlorine concentration (100 ppm) had greatly increased water permeability (2.30 $L/m^2{\cdot}h$) and rejection (93.7%) compared to the virgin membrane (1.72 $L/m^2{\cdot}h$ and 87.1%) in a lab-scale cross-flow NF system. In addition, the chlorinated membrane surface is more hydrophilic compared to the virgin NF90 membrane, which tends to minimize membrane fouling [125]. Therefore, more attention should be paid to certain conditions of chlorine-based cleaning. Since even little residual chlorine could cause very negative effect under acid environment (where HOCl is the dominant and most aggressive species) during cleaning cycles, alkaline cleaning conditions may be needed. Solution of NaOCl at elevated pH, where hypochlorite ion OCl^- is the dominant species, does not cause severe damage to the polyamide active layer compared to degradation caused by solutions at low pH values. With reasonable operation and special care, the damage to polyamine membrane can be mitigated. Recently, it has been confirmed that chlorination could also reduce the formation of N-nitrosodimethylamine (NDMA), which may cause cancer risk even exposed to a drinking water containing a very lower concentration of 0.7 ng/L, by deactivating its precursors [148,149]. Ersan et al. [150] investigated the cleaning techniques to minimize leaching of NDMA precursors from different types of NF membranes by a lab-scale cross-flow filtration cell. They found that neither basic nor acid cleaning conditions reduced NDMA formation potential leaching below that of deionized water flushing. However, cleaning with 1 mg/L chlorine containing a distilled and deionized water feed solution that was passed through all three (TS80, TS40, and SB90) membranes, the NDMA precursor leaching potential of TS80, TS40, and SB90 membranes significantly decreased without causing a measurable impact on membrane surface characteristics and significantly altered membrane flux and salt rejection.

Except for chlorine, recent several researches looking for new disinfectants/biocides which have a reliable antimicrobial effect with minimal adverse effect on membrane performance are extensively conducted. Xu et al. [151] reported that 2,4-dinitrophenol, a typical uncoupler, could not only significantly inhibit membrane biofouling but also enhance biofilm detachment from MF membranes during cleaning. It inhibits ATP synthesis and subsequent autoinducer-2 production, which further resulted in reduced microbial attachments on membrane surface and improved membrane performance in terms of water flux. However, it was a toxic chemical agent and harmful to human and environment. Recently, Yu et al. [140,152] investigated two kinds of N-halamines (a group of organic chloramine) such as N-chlorosuccinimide (NCS) and dichloroisocyanurate (DCC) as biofouling control agents in a lab-scale cross-flow RO system, they found that both NCS and DCC are promising new biocides with a reliable antimicrobial efficacy and minimum adverse effect on polyamine membrane. The authors further pointed out that the antimicrobial effect of NCS (10 mg/L with soaking time 15 min and 30 min) against biofilm cells by NCS was slightly greater than that of DCC and far greater than that of chlorine, moreover, there are no significant changes in surface characteristic and membrane performance of polyamine membrane when it is exposed to a high concentration of NCS (5000 mg/L as Cl_2) [140], as well as DCC (5000 mg/L as Cl_2) [152] for 3 h.

As a novel low cost cleaning agent, the FNA is a strong biocidal agent at parts per million concentrations (0.2–2 mgN/L), causing deactivation of microorganisms by inducing substantial cell death and biofilm detachment [153–155]. It is currently being applied mostly for sulphide and methane control in sewer networks,and has been shown that the activities of sewer biofilms were completely suppressed, accompanied by a substantial loss of biofilm after 24 h treatment [156]. Recently, Filloux et al. [84] investigated the impact of FNA on biofouling and scaling removal in a lab-scale filtration system using fouled RO membranes collected from full-scale plants including industrial and municipal water recycling plants and also a seawater desalination plant. They found that FNA cleaning was effective in removing bacteria and organics from membrane surfaces, the best cleaning efficiency (>85% of biomass removal) was observed at an optimum concentration of 50 mg NO_2–N/L(corresponding to 35 mg HNO_2–N/L) and a pH level of 3.0. They further pointed out that for calcium carbonate scale removal, FNA at pH 2.0 and 3.0 was as efficient as the commonly used descaling agents (HCl and citric acid).Therefore, they suggested that one-step cleaning with FNA for both biofouling and scaling removal has much more cost-effectiveness compared to two-step chemical cleaning with alkaline and acidic agents.

It is noteworthy that disinfectants/biocides can only be effective in inactivating or weakening the biofilm matrix. It must be followed by a second-step of removal of the biofilm from membrane surface by high velocity detergent cleaning or flushing [157,158]. Bereschenko et al. [159] investigated the impact of weekly conventional chemical cleaning (sequentially cleaning with: RO permeate, biocide (30% sodium bisulfite solution, pH 10–11) and mixed acid detergent descaler (Divos 2)) on initiation and spatiotemporal development of biofilms on RO membrane in situ using four flow cells placed in parallel with full-scale RO installation. They observed that although the biofilm layer structures were drastically affected by chemical treatment and became more loosely attached, they were not completely removed and often still present on membrane and feed-side spacer surfaces most likely because the flow inside the membrane module cannot exert sufficient friction to flush the biomass away. After cleaning, subsequent rapid biofilm layers re-growth were observed within a relatively short operational time (approx. 1 week).Therefore, biofouling control might be possible only if the cleaning procedures are adapted to effectively remove the dead biomass from the RO modules.

Biocidesis more efficient for biofilm inactivation compared to other cleaning agents. Strong oxidizing biocides (e.g., chlorine and NaOCl) could significantly inactivate biofim matrix from membrane surface. They could also damage the polyamine active layer under acid conditions during cleaning cycles, while the membrane performance could be enhanced by using chlorination under certain alkaline conditions. The optimization of alkaline chlorine cleaning should be carried out in order to further verify its applicability for full-scale and commercial installations. Some non-oxidative biocides and organic biocides have many advantages over other antibacterial agents, including effectiveness against a broad spectrum of microorganisms, less damage to membrane, high structural durability. Further studies are needed to improve cost-effectiveness ratio for full-scale and commercial installations.

Factors affecting chemical cleaning

NF/RO membranes usually require a mild cleaning regime (agents, concentrations, and frequency) compare to low pressure membranes. Consequently, optimizing cleaning procedures is beneficial in the management of spiral-wound membrane filtration. The parameters that have greater influence on the chemical cleaning efficiency are: temperature, cleaning agent concentration, operating pressure, cross-flow velocity, and cleaning step duration [14,160,161]. The knowledge of the effect that these factors have on the efficiency of the cleaning process is fundamental to select and perform the most suitable cleaning procedure.

Effect of cleaning time: The higher cleaning efficiency would be obtained at longer cleaning time when there is a favorable chemical reaction between the cleaning agent and foulants in the fouling layer to lessen the foulant-foulant interactions. In lab-scale experiments, W.S. Ang et al. [21,25] pointed out that increasing the cleaning time from 15 to 60 min, the cleaning efficiency significantly increased for both alginate and mixture organic foulants fouled RO membrane after cleaning with SDS and EDTA. The cleaning efficiency of alginate fouled membrane also increased from 79% to 90% and from 90% to 110% with increasing cleaning time from 15 min to 60 min for 25 mM NaCl and 100 mM NaCl respectively [79]. In the same authors further study, cleaning the wastewater effluent fouled RO membrane with single agents such as NaOH, NaCl, SDS, and EDTA resulted in a higher cleaning efficiency when cleaning time increased from 7.5 min to 15 min [26]. Sohrabi et al. [9] reported that with increasing the cleaning time at a range of 5~20 min the cleaning efficiency was increased for both NF membrane (BDX N-90) and RO membrane (FT30) in a lab-scale filtration system. It is noteworthy that the effect of cleaning time on cleaning efficiency is also depended on membrane types. The cleaning efficiency of NF membrane (BDX N-90) was more than 100% after 10 min cleaning with NaOH and was kept constant within the next 10 min, by contrast, 20 min was needed for RO membrane (FT30) to recover the membrane flux up to 94% only.

Effect of temperature: An increase in cleaning solution temperature results in an increase in the chemical cleaning efficiency. In this case, both the rate of chemical reaction between the cleaning agents and the deposited foulants and the transport of foulants from the fouling layer to the bulk solution, as well as the solubility of foulants, increased [17]. In addition, at higher temperature, the swelling of the organic fouling layer might have also contributed to the weakening of structural stability [162,163], the expanding and relaxation of polymer can lead to increase of permeability due to the increases of pore size [105,118]. Moreover, higher temperature reduces the viscosity of the cleaning solution and a corresponding elevation of Reynolds number [105,164], which all effects the permeability and salt passage of membrane. Lee et al. [79] reported that cleaning efficiency increased from 78% to 86% after increasing solution temperature from 20 to 40°C with 25 mM NaCl solution cleaning the organic-Ca^{2+} fouled RO membranes. Sohrabi et al. [9] found that the flux recovery of RO membrane (FT30) fouled by licorice aqueous solution increased from 42% to 80%, as well as increased from 65% to more than 100% for NF membrane (BDX N-90), when the temperature of cleaning solution increased from 20°C to 35°C during 5 min cleaning with NaOH. However, the sensitivity of membrane materials usually forbids the use of very high temperature. Membrane manufactures recommend that chemical cleaning should be performed at lower than 45°C [3].

Chemical cleaning at a high temperature may also further enhance the modification of membrane properties (e.g., hydrophobicity, surface roughness and permeability) which can be possibly attributed to the conformational changes of the membrane polymeric matrix [105,131]. Nilsson et al. [105] reported that increased hysteresis was seen in the NF/RO membrane performance with increasing temperature. They further pointed out that at 40°C the RO membrane (HR98PP) showed the same performance as the NF90 membrane at 20°C. Simon et al. [131] pointed out that the virgin NF270 membrane surface roughness was significantly enhanced and the membrane surface hydrophobicity was aggravated by caustic and acid cleaning when the cleaning temperature increased. Chemical cleaning using citric acid, SDS or EDTA at a high temperature for the virgin NF270 membrane resulted in a considerable increase in the rejection of salts. It should be note that the NF performance changed not only depending on rinsing temperature but also on the cleaning procedure, showing increased, decreased or unchanged KCl retention when increasing the temperature from 20°C to 60°C after cleaning depending on the experimental history. For example, the NF membrane (Desal-5DK) showed no changes in water permeability due to the combined effect of cleaning and temperature [105].

Effect of cleaning solution pH: As mentioned in early parts of this review, the functional groups of organic foulants would be much more deprotonated and its solubility also increased with increasing solution pH value. It has been reported that cleaning efficiency of EDTA strongly depends on solution pH because the number of deprotonated carboxylic groups of EDTA is a function of pH value. At ambient solution pH (4.8), EDTA is not fully deprotonated to chelate fully with Ca^{2+} from the organic foulant-Ca^{2+} complexes within the fouling layer [20,21,25]. Recent studies have shown that EDTA is only a moderately effective cleaning agent at pH 8 [17], while at pH 11 almost all the carboxylic groups are deprotonated and available for Ca^{2+} complexation, resulting in a more effective ligand exchange reaction between EDAT and organic foulant-Ca^{2+} complexes within the fouling layer [20,21]. However, in some cases, solution pH shows very little effect on SDS cleaning, because the pKa of the sulfate functional group of SDS is 2.12, implying that SDS is in its ionic form at a broad pH range [3,25]. W.S. Ang et al. [25] reported that chemical reaction between SDS and alginate-Ca^{2+} complex is less influenced either by cleaning solution pH 5.7 or by pH 11. Li et al. [20] also confirmed that when NF membrane fouled by SRHA-Ca^{2+}, there was no significant difference in chemical cleaning efficiency between SDS at the ambient pH 9 and at pH 11.

In addition, increment of pH causes higher hydrophilicity and a reduced charge (negative charge) of membrane surface. Sohrabi et al. [9] reported that contact angel decreases with cleaning solution pH increment for both RO membrane and NF membrane. The lower contact angel indicates higher hydrophilicity, increasing hydrophilicity makes the chemical bonds between water molecules and surface groups of the membrane stronger. This break the bonds between the foulants and membrane surface leading to foulants reduction and higher permeability [14,164,165].

Effect of cross-flow velocity (hydrodynamic shear): Cross-flow shear rate has a significant influence on the chemical cleaning efficiency. An increase in cross-flow shear rate enhances the disruption of the fouling layer and the mass transfer of the foulants from the fouling layer to the bulk solution. Cleaning efficiency increased noticeably from 48% to 78% after increasing cross-flow velocity from 0.10 m/s to 0.43 m/s with 25 mM NaCl solution cleaning the organic-fouled RO membranes in the presence of Ca^{2+} [79].

Effect of cleaning solution concentration: In general, the cleaning efficiency elevated with increasing chemical cleaning agents concentration. Results from many researches showed that increasing cleaning agents concentration were effective for flux recovered and/or resistance removal when NF/RO membrane was fouled with HA-Ca^{2+}, alginate-Ca^{2+}, protein-Ca^{2+}, combined organic foulant-Ca^{2+} complexes [21], and licorice aqueous solutions [9]. Li et al. [20] also found that the recovered flux increased from 12% to almost 100% with increasing SDS concentration from 1 mM to 10 mM in a bench-scale NF membrane fouled by SRHA. The same team further studied the effect of salt (NaCl) solution cleaning on a lab-scale RO system fouled by alginate and SRNOM, and found that the cleaning efficiency increased with increasing NaCl concentration and reached about 88% for the cleaning solution of 50 mM NaCl. In lab-scale experiments, Ang et al. [21] reported that the optimum concentration of NaCl, SDS, and EDTA cleaning membrane fouled with combined foulant-Ca^{2+} complexes was 50 mM, 10 mM, and 1 mM, respectively.

It should be note that the optimum concentration is only applicable under specific fouling and cleaning conditions, and thus will change with fouling and cleaning conditions. In addition, it does not improve cleaning efficiency significantly with the more concentration of cleaning agents when it exceeds the optimum concentration, in fact, the increasing cleaning efficiency is small and gradual, even a decreasing cleaning efficiency is found. Madaeni et al. [17] proved that for some acids (e.g., HNO_3, H_2SO_4) the cleaning efficiency is increased with the cleaner concentration, reaches a maximum and decreases afterwards, as well as for SDS, SDS+NaOH, and SDS+NaOH–HCl, during cleaning a pilot-scale RO system fouled by industrial wastewater. Ochando-Pulido et al. [27] pointed out that the cleaning efficiency became enhanced by increasing the SDS dosage up to 0.1% (w/v) but then decreased for 0.2–0.5% (w/v) SDS concentrations. It is probably due to decomposition of some materials by concentrated acids, formation of more foulants, or obstruction of highly concentrated micelles for passage of water through the membrane. In addition, the high presence of micelles may lead to concentration polarization and blockage/plugging phenomena on the membrane surface [3].

3.3. Biological/biochemical cleaning

Despite the widespread use of chemical agents, they are usually in effective in removing or killing the membrane biofilm [166]. Moreover, frequent chemical cleaning would shorten membrane life, further increase operational costs [167]. Recently, new strategies of biofouling prevention have been published to reduce such impacts normally by biological/biochemical cleaning with bioactive agents. Biological agents can be defined as certain chemicals which target specific biological molecules or mechanisms related to biofilm formation, motility or bacterial growth [168].

3.3.1. Enzymatic cleaning

Enzymes are environmentally friendly natural products that not only improve cleaning efficiency, but also reduce the amount of chemicals needed and the energy costs [169]. The use of enzymatic cleaning is of interest because they operate in mild conditions, which is a positive factor for their application to the cleaning of membranes sensitive to chemicals, pH, and/or temperature. Enzymatic cleaners are increasingly considered as potential alternatives from conventional chemical agents [170].

For organic fouling: The primary goal in using enzymes is to hydrolyze organic foulants as well as to remove and kill bio-foulants. Most previous studies of enzymatic cleaning dealt with a particular organic foulants (e.g., protein) from MF/UF membranes [169,171–174], resulting in a better enzymatic performance and has been found to be effective in reducing some irreversible fouling. As summarized in Table 5, the protein fouling on membrane surface caused by whey, BSA and beta-lactoglobulin could be efficiently removed by protease enzymes such as α-chymotrypsin (bovine pancreas) enzyme [175], proteolytic enzymes (i.e., P3-Ultrasil® 62 and Maxatase® XL) [172,173], Terg-A-Zyme and Protease A [169]. However, when a lab-scale UF membrane was fouled by mixtures of organic foulants (e.g., abbatoir effluent comprised of protein and lipid), Maartens et al. [174] found that protease A (type XXIII from *Aspergillus oryzae*) cleaning resulted in a lower protein and lipid reduction rate about 85.8% and 55.0%, respectively. Thus, the combined cleaning should be used to further improve membrane cleaning efficiency. In the same team group's latter research, Allie et al. [171] found that lipases combined with proteases could further remove lipid and protein, resulting in a flux recovery of nearly 100%. In addition, none of α-amylase, lipase, cellulase and protease was found to be not effective (flux recovery less than 12%) for the removal of HA when used alone, while the combined cleaning of α-amylase + NaOH and α-amylase + non-ionic surfactant (Triton X100) could both further increase flux recovery up to 90%[176].

For wastewater effluent: Enzymatic cleaning shows limited cleaning efficiency for membrane fouled with wastewater effluent compared to that with single organic foulants. Puspitasari et al. [170] reported a relatively lower cleaning efficiency when protease and amylase were used either alone or sequentially to clean MF membrane fouled by model wastewater solution consisted of 1 g/L BSA and 1 g/L SA in a lab-scale cross-flow filtration cell. They found that the 0.1% protease and 0.05% of amylase both under pH 6.5 only resulted in cleaning efficiency of 61% and 71.3%, respectively, within a relatively short cleaning duration of 10 min. Moreover, the sequential cleaning with amylase/protease, protease/amylase and amylase/rinsing/protease also resulted in a lower and slight difference removal of protein (64–68%) and polysaccharides (62–70%) from the membrane surface. The combined cleaning of chemical-enzyme solution can further improve cleaning efficiency. Poele et al. [177] performed a pilot investigation about the efficacy of enzymatic cleaning with protease on UF membranes used for the filtration of wastewater treatment plant effluent containing a higher mean protein concentration about 17.3 ± 4.4 mg/l, and confirmed that after applying the new enzymatic cleaning protocol of Divos 110 (commercial alkaline cleaning product) + adjust pH 9.3 by HCl + Protease, the

Table 5
Representative enzymes used to control organic fouling and biofouling formed on membrane surface

Membrane	Fouling type	Enzymes	Dosing	Time	pH	Temp. (°C)	Flux recovery	Foulants removal	Scale	Ref.
UF	Abattoir effluent	Lipase A + Triton X100 → Protease A	1 mg/ml + 0.1% → 1 mg/ml	60 min	7.5	37	>100%	Protein:90.08 ± 4.74% Lipid:64.30 ± 2.5%	Lab-scale	Maartens et al. [174]
UF	BSA[a,b] Whey protein[c,d]	Terg-A-Zyme[a] α-chymotrypsin + CTAB[b] Terg-A-Zyme[c] a-chymotrypsin + CTAB[d]	0.4 wt%[a] 0.01 wt% +0.2 wt%[b] 0.75 wt%[c] 0.01 wt% + 0.2 wt%[d]	60 min	7[a] 5[b] 7[c] 5[d]	40	89.1%[a] 90.2%[b] 91.0%[c] 81.7%[d]	/	Lab-scale	Mufioz-Aguado et al. [175]
UF	Abattoir effluent	Pseudomonas lipase + Triton X-100 → Protease A + Triton X-100	10 mg/ml + 0.1% (v/v) → 0.005 mg/ml + 0.1% (v/v)	/	7–10 → 8–11	20–50 → 20–30	98.38%	Protein: 87.26 ± 3.26% Lipid: 68.83 ± 3.75%	Lab-scale	Allie et al. [171]
UF	Whey protein	Maxatase® XL + NaOH[a] P3-Ultrasil® 62+ NaOH[b]	(30±2.7) × 10^{-9} u/m[a] 35 × 10^{-9} u/m[b]	20 min	9.5–10	50	Almost 100%	/	Standard UF device	M.A. Argüello et al. [172,173]
UF	Wastewater effluent	Divos 110 + Protease	/	26 h	9.3	25–30	100%	/	Pilot-scale	Poele et al. [177]
UF	BSA + BLG[a] Whey[b]	Terg-A-Zyme[a] Protease A[b]	1 wt%[a] 0.0005 wt%[b]	60 min	/	/	90%[a] 65%[b]	Resistance: 91%[a] /	Lab-scale	Chen et al. [169]
MF	BSA and ovalbumin protein	Ultrasil 53	0.1% wt	5 min	10.1	/	75%	/	Lab-scale	Field et al. [188]
UF	BSA	Protease M	0.1 wt%	60 min	9	25 ± 1	/	Protein : > 90%	Lab-scale	Petrus et al. [187]
UF	Biofilm	Reflux® E2001 (protease + lipase)[a] QuatroZyme® (mixture enzymes)[b] Reflux® E1000 (protease) [c]	0.2% (v/v)[a] 0.2% (v/v)[b] 0.3% (v/v)[c]	45 min[a] 45 min[b] 30 min[c]	8.5–9.5[a] 9.0–10.0[b] 7.0–8.0[c]	48	/	Bacteria : >70~80%[a, b] Bacteria: <70~80%[c]	Lab-scale	Tang et al. [180]
UF	HA	α-amylase, lipase, cellulose, and protease[a] α-amylase + NaOH[b] α-amylase + Triton X100[c]	0.1% (v/v)[a] 0.1% (v/v)[b] 0.1% (v/v) + 0.1% (v/v)[c]	2 h	/[a] 11[b] 11[c]	/	<12%[a] 90%[b] 94%[c]	/	Lab-scale	Yu et al. [176]
MF	Biofilm	D-tyrosine	100 ppm/500 ppm	2 h	/	/	18%/28%	Biomass: 56%/60%	Lab-scale	Xu et al. [184]
NF	Biofilm	D-tyrosine	3 μM/30 μM	20 h	6.70–6.83	/	Flux↓:43%/10%	Cell: 50%/50%	Lab-scale	Yu et al. [186]
MF	BSA and sodium alginate	Protease M[a] Purastar® ST L (α-amylase)[b]	0.1%[a] 0.05%[b]	10 min	6.5	50	61% 71.3%	Protein:64%~68%[a] Polysaccharide: 62%~70[b]	Lab-scale	Puspitasari et al. [170]
RO	Biofilm	Acylase I[a] Proteinase K[b] Acylase I + proteinase K[c]	5 μg/mL[a] 100 μg/mL[b] 5 μg/mL+100μg/mL[c]	2 h	/	37	/	Cell: 56.6%; EPS: no[a] Cell: 9.0%; EPS: 33.6%[b] Cell:33.7%; EPS: negative[c]	Lab-scale	Kim et al. [179]
RO	Biofilm	Protease-/lipase-based enzymes	100 ppm	18 h	7	/	/	Biomass: >90%	Lab-scale	Khan et al. [181]
RO	Biofilm (*A. hydrophila and P. putida*)	Acylase I	10, 20, 60, 120 μg/mL	6 h	6.8	30	/	Biofilm formed on RO membrane was reduced by 11%, 18%, 22%, 22% respectively	Lab-scale	Paul et al. [204]

recovery of clean water flux returned to its original level for a new membrane module within total cleaning time of 26 h, which significantly greater than the basic alkaline cleaning method. The difference of cleaning efficiency between Poele's [177] and Puspitasari's [170] research may attribute to the difference of the cleaning conditions (e.g., pH and cleaning duration) and cleaning protocol (the former cleaning with enzyme alone while the latter cleaning with the combination of alkaline and enzyme). It seems that the additional value of the enzyme is to cut protein network chains, whereas the basic alkaline cleaning removes isolated proteins from the membrane surface [177]. Moreover, NaOH appears to modify/dissolve the foulants configuration thus rendering the surface fouling layer less smooth (more rough) and thus creating sites for enzymes to hydrolyze the foulants [176]. After both one times enzymatic cleaning [177] and cyclical cleaning [170], the development of membrane fouling seems even faster due to residual foulants still attached on the membrane, indicating that the applied enzymatic cleaning does not attribute to maintaining the performance of a clean membrane.

For biofilm: Apart from organic foulants, enzymatic cleaning can also remove and kill biofilms from membrane surface. Proteins and polysaccharides are major components of EPS which are major components of bio-foulants and enzymes have been investigated as a common cleaning agent to overcome EPS foulants. Enzymatic disruption of EPS appears to be a promising alternative for high-efficiency control of microbial attachment and membrane biofouling [178]. In fact, cleaning with a single enzyme for biofouling control was not efficient enough. In a lab-scale RO system, it was found that 5 μg/mL of acylase I could remove 56.6% of the bacteria on RO membrane while it could not remove EPS, 100 μg/mL of proteinase K could remove 9.0% of bacteria on RO membrane while it could remove 33.6% of the EPS concentration per cell number [179]. Due to the heterogeneity of EPS, a mixture of enzymes or enzymes treatment combined with other EPS-degrading agents may be necessary for sufficient biofilm degradation. Tang et al. [180] reported that QuatroZyme® (a mixture enzyme of lipase, protease, cellulase, and amylase) and Reflux® E2001 (a mixture enzyme of protease and lipase) performed slightly better, while Reflux® E1000 (protease) performed lower than control clean (Alkaline hypochlorite 200 ppm free available chlorine) which removed 70~80% of culturable bacteria cellsin a lab-scale UF system. In addition, cleaning with the above enzyme cleaners followed by a sanitizer (i.e., MIOX® EW anolyte (120 ppm free available chlorine, pH 6.8)) was found to be much more effective in removing and killing biofilms. Anand et al. [87] also pointed out that enzyme cleaning may be useful for more effective breaking of the complex biofilm matrix, which may help in greater inactivation of biofilm microflora by direct contact with sanitizer. Recently, Khan et al. [181] demonstrated the mode of action of different enzyme-based cleaning agents and their effects on bio-foulants removal as well as membrane properties. They tested eight enzymes using a commercially available polyamide RO membrane without filtration in a lab-scale rotating disk reactor system operated for 58 d. At the end of the operation, they found that the protease-/lipase-based enzymes at 100 ppm and 18 h contact time not only were optimal for removing most of the cells and proteins from the RO surface but also restored the RO membrane surface properties almost to their virgin condition. Moreover, the protease-/lipase-based enzymes were more effectively penetrated the biofilm, resulting in culturable cells inside the biofilm declined by more than five logs even at the lower dose (50 ppm) and shorter incubation period (18 h).They also pointed out that the type/dose of enzymes and the incubation period were the key factors for efficiently removal of bio-foulants. According to the functions of the enzymes, the protease-/lipase-based enzyme hydrolyzed proteins, and dextranase-based enzymes acted upon polysaccharide compounds and carbohydrate components of the EPS in the bio-foluants [182,183].

Dosage: From the economic point of view, the determination of the optimum amount of enzyme required to clean the membrane is very important. Lower amounts of enzyme can result in lower cleaning efficiencies or longer cleaning times. Generally, enzymatic cleaning efficiency increased as well as cleaning times decreased with increasing enzyme dose within a certain range. Khan et al. [181] found that the detachment of biofilms increased with an increase in the enzyme concentration up to100 ppm, while no significant change in thickness for any of the enzymes at concentrations above 100 ppm. In another lab-scale study, Xu et al. [184] reported that 25% of the fixed biomass on a nylon MF membrane was removed when 10 ppm D-tyrosine (a typical d-amino acid) was used, which was increased to 60% at a 500 ppm dose. D-tyrosine can not only promote biofilm detachment from membrane surfaces but also reduce microbial attachment onto membrane surfaces [184,185]. Yu et al. [186] further investigated the effect of D-tyrosine on biofouling control in a lab-scale NF process. They found that the number of attached cells on the membrane was 50% of that on the control membrane when 3 μM D-tyrosine was added, increase in D-tyrosine concentration to 30 mM did not further reduce cells attachment. Several researchers showed that higher amounts of enzyme can increase costs and even result in a decrease in cleaning efficiency, probably due to membrane fouling caused by the cleaning agent itself and/or by re-deposition of solutes on membrane surface [170,172,187].

Cleaning time: As shown in Table 5, with regard to the incubation period of enzymatic cleaning, different observations are found with different type of enzymes. Field et al. [188] reported that the enzymatic cleaners of Ultrasil 53 could rapidly remove protein aggregates in a lab-scale cross-flow MF membrane module and resulted in approximately 75% flux recovery within 5 min. However, the recovery declined after 30 min cleaning due to re-fouling of the membrane by ovalbumin which had previously been removed from the membrane. It confirms that for Ultrasil there exists an optimal cleaning time after which re-fouling becomes significant and cleaning must either be stopped or the cleaning solution refreshed. Another enzymatic agent of P3-Ultrasil® 62 used for inorganic membranes cleaning in a lab-scale UF cell for whey protein fractionation could reach very high cleaning efficiency (nearly 100%) in a short operating time of 20 min [173]. Petrus et al. [187] found that the highest efficiency was observed at cleaning time of 60 min when the protein fouled membrane was cleaned with enzymatic cleaning agent (Protease M) in a lab-scale UF membrane module, while increased cleaning time from 60 min to 120 min resulted in reduced efficiency. However, Poele et al. [177] reported that the total cleaning time of 2 h was needed for full recovery of initial water flux in the case of pilot-scale protease cleaning membrane fouled by effluent from wastewater treatment plant. Recently, in a lab-scale RO membrane enzymatic cleaning process, Khan et al. [181] reported that an incubation time of 18 h was optimal for protease-/lipase-based enzymes at 100 ppm removing most of the cells and proteins from the RO surface.

Although current biological reduction agents have low toxicity and some environmentally friendly properties, problems such as instability, limitations in industrial-scale applications and sensitivity to environmental conditions remains a challenge for biofouling control in membrane systems [189]. Indeed, one of the main concerns in using enzyme as cleaning agent is its potential to foul the membrane, especially using a higher enzyme concentration. Previous researches already reported that the usage of enzymatic cleaning agent can result in foulants and attachment of enzyme on the membrane [170,172,187]. Due to its proteinaceous nature, enzyme can deposit on the membrane surface. Therefore, the inactivation step of the enzyme such as water rinsing might be beneficial. Turner et al. [190] confirmed that water rinsing was able to remove the residual activity of commercial protease Alcalase present on post cleaning surface. The loss activity of enzymes is another prohibitive for its application. Enzymatic activity when enzymes are mixed with protein solutions has to be particularly considered [170], especially for cyclical cleaning. Argüello et al. [172] studied the possibility of reusing the enzyme solutions for consecutive cleaning steps in a standard UF device, they found that a 30% loss in activity was observed during each cleaning cycle, irrespective of the initial activity of the solution. The cost of enzymes is also one prohibitive for large-scale application. Continuous feed of enzymes can be expensive. Further research is needed to develop economic, practical ways to apply enzymes or research new enzymes for biofouling control in membrane systems.

3.3.2. Biosurfactants

Biosurfactants are a structurally diverse group of molecules synthesized by microorganisms [133], composing of one or two rhamnose molecules linked to one or two fatty acid alkyl chains [191]. Rhamnolipids can overcome the disadvantages incurred by conventional biological methods, such as high cost and low stability, and have advantages over chemical reagents in terms of their low toxicity, cost effectiveness, and stability within extreme environmental [192–194]. To date, rhamnolipids produced by *Pseudomonasaeruginosa* have been the most intensively studied biosurfactant [195]. It can be potentially applied in many areas from bioremediation to food additives [196]. The use of rhamnolipids as a fouling reduction agent has been reported in a pilot-scale submerged membrane bioreactor designed for frying oil degradation [197], and in a lab-scale UF system fouled by protein [198]. The cleaning by rhamnolipid under pH 9 could largely remove the protein from the UF membranes post to either short-term or long-term fouling and restore the membrane flux to 94% of initial level, performing much better than the flux recovery of 50–70% for Tween-20 and SDS cleaning [198]. In addition, several reports regarding the effects of rhamnolipids on bacterial adhesion and biofilm reduction on polystyrene plates and glass substrata (strongly hydrophobic surfaces) have been published [199–203].

Recently, Kim et al. [133] performed a lab-scale investigation about the effects of rhamnolipids on bacterial attachment and evaluated the potential of rhamnolipids to be used as a biofilm reduction agent on RO membranes. They found that rhamnolipids affect both the initial attachment of bacteria and the cleaning of biofouled membranes. The highest attached bacteria reduction efficiency and 20% of the water flux was increased after rhamnolipid treatment (300 **μ**g/ml, 6 h exposure time) in a dead-end filtration system. The biofilm reduction efficiency was 77.7% after treatment even with 100 μg/ml of rhamnolipids at a exposure time of 2 h, which was comparable to commercially available surfactants, the biofilm reduction efficiency were 93.2 ± 1.4%, 92.0 ± 2.0%, and 63.2± 8.1% for SDS, surfactin, and Triton X-100, respectively. Surfactin is another biosurfactant that is produced by Bacillus subtilis and promotes antibacterial, antiviral, antifungal, and anti-mycoplasma activities through its incorporation into the lipid bilayer. For pre-formed biofilms, Gomes et al. [201] found that surfactin at 0.1% concentration showed higher biofilms removal compared to rhamnolipids at 0.25% concentration after 2 h contact. They reported the critical micelle concentration of surfactin is 33 mg/L, whereas that of rhamnolipids is 92.4 mg/L [201], which would be responsible for the lower cleaning efficiency of rhamnolipids compared with surfactin [133].

3.4. Physical–chemical cleaning, combined/formulated, and sequentially cleaning

3.4.1. Physical-chemical cleaning

In general, currently applied chemical cleanings are not effective to remove dead biomass from the elements, but only deactivates it. The remaining biomass will still cause operational problems and act as a substrate for newly attached bacteria. Physical cleaning alone also not effective. Thus, the combination of physical and chemical cleaning shows higher efficiency than physical or chemical cleaning alone. Fig. 9 schematically summarizes the physical-chemical cleaning adopted in full-scale NF/RO membrane process.

3.4.2. Combined reagents or formulated cleaning

In practice, combined or formulated cleaning reagents are usually deployed to mitigate membrane fouling due to the composition of fouling layer is often very complex. Enhanced cleaning results can be achieved by combined several cleaning reagents either simultaneously or sequentially [3,9,14,27]. Liikanen et al. [14] reported that caustic chelating reagents in combination with a caustic cleaner resulted in the best cleaning efficiency with respect to both flux recovery and foulants removal. Sohrabi et al. [9] suggested that the combination of EDTA, SDS, and NaOH may be used as cleaning reagents to achieve an optimum cleaning efficiency. Ochando-Pulido et al. [27] found that citric acid cleaning followed by NaOH + SDS (0.1% w/v) provided maximum cleaning efficiency compared to citric

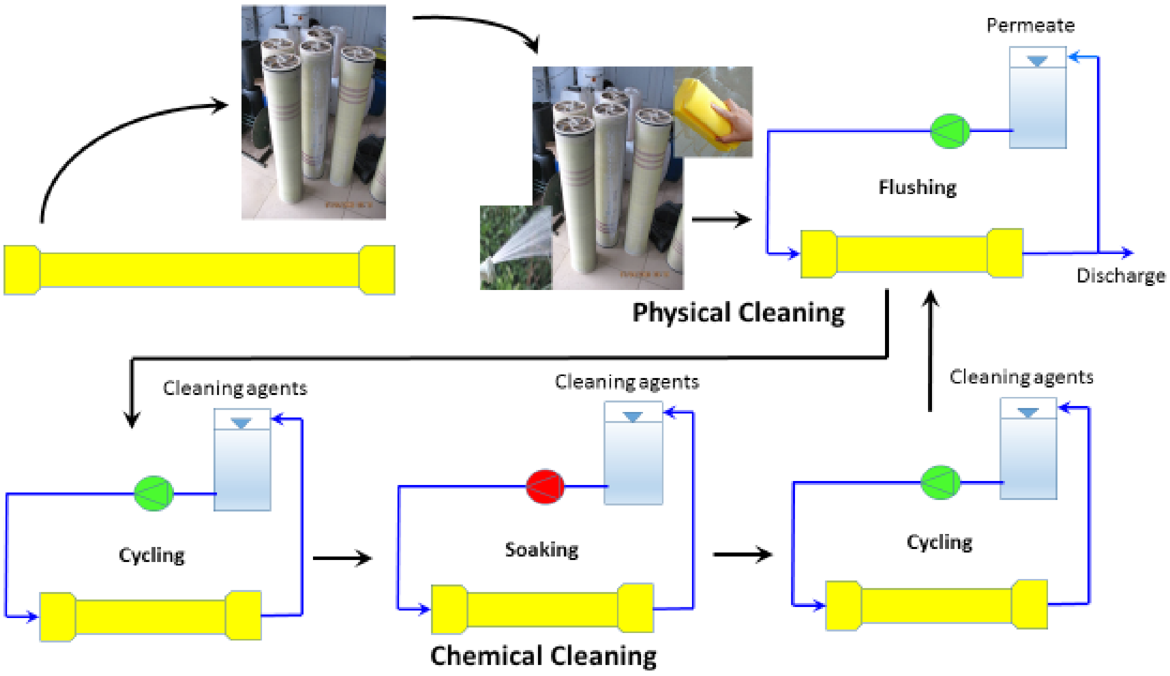

Fig. 9. Physical-chemical cleaning adopted in full-scale NF/RO membrane process.

acid and NaOH + SDS alone. However, W.S. Ang et al. [26] pointed out that combining of cleaning agents either simultaneously or sequentially is only beneficial if their cleaning mechanisms are mutually compatible. Cleaning hindrance can occur between different agents if the respective cleaning mechanisms interfere with each other. They found that both SDS and EDTA for different cleaning orders and combinations negatively impacted the cleaning efficiency of each respective agent during the cleaning of RO membrane fouled by wastewater effluent. It is possibly due to one of the two agents adsorbed onto the fouling layer after the first cleaning stage hinders the cleaning process of the agent used in the second stage. Therefore, the combination of proper cleaning agents and/or the right cleaning order is significant important to obtain a higher cleaning efficiency.

Apart from the combination of EDTA and/or SDS and caustic cleaning mentioned in above sections, the effect and cleaning mechanism of commercially available formulated chemical cleaning reagents, usually a blend of detergent builders, pH buffer, surfactant, and/or chelating reagents, etc., have also been reported in recent years, even though the exact chemistries of the cleaning formulations are proprietary information of the manufactures and are unknown to us. The impact of formulated cleaning reagents on the properties of virgin NF membranes was membranes and cleaning reagents specific [110]. Although Simon et al. [15,106,109,110] reported that caustic cleaning and formulations (namely MC11, and PC98) did not cause any significant modification of both virgin NF270 and NF90 membrane surface charge [106,109,110], caustic cleaning using MC11 and PC98 formulations in a lab-scale NF system could both lead to a significant increase in permeability and a considerable decrease in the rejection of conductivity and TrOCs by NF270 membrane compared to that using acid cleaning formulation (MC 3). By contrast, the above mentioned three cleaning formulations (i.e., MC11, PC98, and MC3) have much less significant influence on NF90 and TFC-SR100 NF membranes [110]. They further calculated the average pore radius of membrane after caustic cleaning based on pore transport model, and confirmed that caustic cleaning (MC11) could lead to a small increase in pore size of virgin NF270 membrane due to its loose and thin active layer, resulting in a notable increase of permeability and salt passage. However, caustic cleaning has no impact on average pore size of virgin NF90 membrane due to its thicker active skin layer, no discernible variations in conductivity rejection could be observed [109]. In addition, when NF 270 membrane was fouled by secondary treated effluent, HA, and SA and then was cleaned by caustic formulation (MC11), the membrane surface became not only more negatively charged but also more hydrophobic due to the presence of organic residuals on the membrane surface, also resulting in flux recovery was higher than that of the virgin membrane [15]. With regard to membrane surface charge, there are some different results from Simon's researches. Al-Amoudi et al. [118] pointed out that SDS induced a highly and uniform negative charge to the membrane surface by hydrophobic–hydrophobic interactions. Sohrabi et al. [9] also found that in the case of NaOH cleaning, the RO membrane (FT30) surface charges changed from positive to negative with the increase of pH value. It seems that differences in membrane properties, cleaning reagents and in the procedure used to simulate chemical cleaning may explain the discrepancy between these studies.

Recent investigations suggests that three mechanisms can be responsible for the increase in permeability and solute passage, either individually or simultaneously: (i) the increase in membrane permeability can be attributed to some extent to adsorption of cleaning additives such as EDTA and/or SDS on the membrane surface, making the active skin layer more hydrophilic, leading to more water passage through the membrane [20, 109], (ii) under strong caustic cleaning environment, the polyamine active skin layer can be hydrolyzed to carboxylic acid derivatives, also resulting in an increase in water permeability due to its hydrophilic properties [205], and (iii) since the functional groups (e.g., COOH and NH) within the membrane active skin layer were deprotonated to form more negatively charged moieties, and/or since the organic residuals made the membrane surface also more negatively charged, the consequently enhanced electrostatic repulsion between the active sites of the membrane as well as between the membrane surface and similarly charged foulants and/or cleaning reagents resulting in an increase in pore size and/or membrane porosity, thus, a considerable increase in permeability and decrease of rejection could be observed [15,109,110,206]. Recently, in a lab-scale NF system, Al-Amoudi et al. [107] reported that SDS and mixed agent of EDTA, TSP, and STP had a profound adverse effect on the virgin NF membranes which pore size increased by 12% indicating an irreversible chemical reaction and adsorption on the membrane surface or a degradation of the polymer in the active layer. In some cases, the interactions between membrane polymeric matrix and cleaning reagents are reversible [110], when exposed to a strong caustic or acid cleaning solution, the membrane porosity can increase or decrease, respectively [106]. It was probably because that acid cleaning could make the membrane tighter by charge neutralization of the remaining OH^- on the membrane surface, resulting in a preservation of the membrane ion retention capacity [14]. Therefore, the impact of caustic chemical cleaning on membrane separation performance could be alleviated by a sequence of caustic cleaning followed by acid cleaning [14,93,104,110].

3.4.3. Sequentially cleaning

Although cleaning with both formulated reagents and combined several cleaning reagents simultaneously showed a higher cleaning efficiency, it is noteworthy that multi-step cleaning with right cleaning sequence can represent a useful tool, since the cleaning efficiency can be improved by means of utilization of different chemicals with complementary cleaning mechanisms [26, 93]. Table 6 summaries the sequence cleaning used for NF/RO membranes. Generally, acid cleaning often followed by caustic cleaning (either by the formulated or by combined reagents) may be the best chemical cleaning protocol (see Fig. 7) for NF/RO membrane fouled by municipal wastewater effluent (HCl or citric acid followed by NaOH) [81,83], secondary-treated olive mill wastewater (citric acid followed by NaOH+SDS) [27], semiconductor wastewater (HCl followed by NaOH+EDTA) [82], and seawater (citric acid cleaning followed by NaOH + STP + TSP + EDTA) [95]. The acid-alkaline cleaning sequence ensures the removal of inorganic fouling (metallic oxides and carbonates) first by acid cleaning and then elimination of the organic foulants by the alkaline-detersive/chelating effect. Moreover, cleaning with acid-alkaline cleaning sequence, NaOH cleaning could also recovery the negative surface charge of NF membrane, which usually be a positively charge after cleaning with HCl, leading to a significant improvement in stability of DL and HL membranes during nanofiltration of concentrated salt solutions characterized by pH≈4 [90]. However, the opposite alkaline-acid sequence of NaOH followed by HCl or citric acid cleaning was not so effectiveness [81,83] due to the increase in permeability by additional acid cleaning conducted after alkaline cleaning was marginal [81]. In fact, the opposite alkaline-acid sequence was attribute to improve salt and TrOCs rejection due to acid cleaning could decrease membrane pore size as just discussed in former second paragraph of this section. It seems that the opposite alkaline-acid sequence or alkaline-SDS sequence becomes more efficient when a significant part of foulants is of organic nature. Garcia-Fayos et al. [93] found that both alkaline-SDS and inverse sequence cleaning resulted in higher permeability recovery during the cleaning of RO membrane fouled by seawater (foulants mainly included silicate materials and NOM compounds).This can be explained by that NaOH could promote the remove of both organic foulants and silicate [4,101]. Madaeni et al. [17] also reported that NaOH+SDS followed by HCl cleaning provided a higher effective recovery compared to that without HCl cleaner as the second cleaning stage for RO membrane fouled with wastewater (may be a kind of industrial wastewater with COD and BOD concentration of 3500 mg/L and 2000 mg/L respectively), but the comparison between NaOH+SDS followed by HCl cleaning and its inverse order could not be conducted due to the author did not reported the cleaning efficiency of HCl followed by NaOH+SDS cleaning.

No matter whatever cleaning agents and cleaning protocol adapted, it is worthy pointed out that the membrane cleaning procedure should be performed before the membrane is densely fouled. Success of the cleaning procedure depends not only on proper selection of the cleaning solution and cleaning operating conditions, but also on the age of the foulant deposits [207]. Higher fouling build-up on the membrane may lead to inefficiency of the cleaning protocol, impeding the penetration of the cleaning reagents within the fouling layer as well as hindering the sweeping of foulants [3]. Therefore, cleaning at an early stage of fouling is more efficient in removing foulants than that at a later stage [84,208]. On the other hand, increasing cleaning frequency could lead deterioration of the cross-linking network of the membrane surface properties, which significantly shorten membrane lifetime. Thus, cleaning frequency (interval) should be given additional attention. The cleaning interval depends on the foulants amount on membrane surface which is indicated by the decrease in flux and salt rejection, or increase in operating pressure. According to the difference of feed water quality, the cleaning interval in full-scale NF/RO system is usually 4–6 months for seawater [95], 3 months to 2 years for groundwater (typical with an average of 6 months) [209], one week to 3 months for surface water. In practical, membrane cleaning is conducted at the time of when the permeate flux drop 10~15%, or salt rejection decrease by 10%, or the feed pressure increase by about 10% /differential pressure increase by 15% to maintaining the same permeate flux [95], or routine cleaning is performed according to manufactures' recommendation.

4. Discussion and conclusion

Several strategies are currently being implemented for the prevention and control of fouling in NF/RO mem-

Table 6
Chemical cleaning protocol used for fouled NF/RO membranes

Membrane	Fouling type	Fouling time	Cleaning protocol	Flux recovery	Scale	References
RO (SC)	Olive mill wastewater effluent	20% permeate flux loss	Citric acid → NaOH + SDS, cleaning conditions: 0.1% w/v, 2.7 bar, 4.01 m/s, 22°C, 10 min^{a} Citric acid → NaOH + SDS, cleaning conditions: 0.1% w/v, 2.7 bar, 4.01 m/s, 30~35°C, 20~25 min^{b}	85.1%^{a} 100%^{b}	Lab-scale	Ochando-Pulido et al. [27]
RO (LFC3-LD)	Semiconductor wastewater effluent	63 d	HCl 0.5% w/v cleaning 4 h → NaOH(0.4%) + EDTA (0.75%) cleaning 7 h, both at 35°C	99.24%	Pilot-scale	Xiao et al. [82]
RO (SWC3)	Seawater	Retired	NaOH 2% w/v → SDS 1% w/v, soaking 1 h at 25°C^{a} SDS 1% w/v →NaOH 2% w/v, soaking 1 h at 25°C^{b} NaOH 2% w/v → citric acid 0.2% w/v, soaking 1 h at 25°C ^{c}	76.13%^{a}# 74.39%^{b}# 44.61%^{c}#	Pilot-scale	Garcia-Fayos et al. [93]
RO (TFC-HR and ESPA2)	Virgin membrane	/	NaOH (pH 12) → citric acid (pH 2.1), soaking 25 h at 30 ± 0.5°C	↓	Lab-scale	Fujioka et al. [104]
NF270*	Virgin membrane	/	18 h MC11 (pH 11.2) → 4 h MC3 (pH 3), soaking at 35°C (compare to caustic cleaning)	↓	Lab-scale	Simon et al. [110]
NF (DL, HL)	Salt mixture solution containing chromium(III) pH≈4	20 h	HCl (pH 2–3) → NaOH (pH 9–11) cleaning at 18 ± 1°C	↑	Lab-scale	Religa et al. [90]
NF (LES90)	Municipal wastewater effluent	40 d	HCl (pH 2) → NaOH (pH 11), soaking 24 h at 30°C	100%	Pilot-scale	Kimura et al. [81]
RO (LFC-1)	Municipal wastewater effluent	17 h	2.0 mM EDTA (pH 7) → NaOH (pH 11)^{a} 500 mM NaCl (pH 6.4) → 2.0 mM EDTA (pH 7)^{b} 500 mM NaCl (pH 6.4) → NaOH (pH 11)^{c} NaOH (pH 11) → 10 mM SDS (pH 7)^{d} Cleaning condition: 0 psi, 42.8 cm/s, 21.0 ± 0.5°C, 7.5 min	92.8%^{a} 91.6%^{b} 91.2%^{c} 91.1%^{d}	Lab-scale	W. S. Ang et al. [26]
NF (ESNA1)	Effluent of Simulated municipal wastewater	24 h	Citric acid 2% w/w, 20 min → NaOH 0.1% w/w, soaking 120 min at room temperature	Almost 100%	Lab-scale	Mo et al. [83]
RO (FT-30)	Industrial wastewater	9 h	NaOH + SDS → HCl, cleaning conditions: 0.075% w/v, 0.5 bar, 1 m/s, 25±2°C, 10 min	100%	Pilot-scale	Madaeni et al. [17]
NF	Seawater	73 d	Citric acid (pH 2.5) → TSP + STP + EDTA + NaOH (pH 11) Cleaning conditions: 1%, 3.5 bar, 7.5 m^3/h, 40°C, 45 min	100%	Full-scale	A1-Amoudi et al. [95]

Note: *Chemical cleaning on NF90 and TFC-SR100 NF membranes was much less significant, possibly because of their thicker and denser active skin layer [110].

#The calculation of flux recovery was based on the equation: J_p flux recovery = $(J_p - J_{p0})/J_{p0} \times 100$, where, J_{p0} is bank values of permeate flux quantified using distilled water, which is different from Eq. (1) (see section 2.2, FR(%) = $(J_{wc}/J_{wi}) \times 100$) used in this review.

branes. Among these, cleaning is an essential step for maintaining long-term operation, since membranes fouling is inevitable. This review focused on the cleaning of NF/RO membrane used for water treatment. Until now, a large number of researches have revealed that membrane cleaning such as physical, chemical, and biological/biochemical cleaning methods are widely implemented in order to remove fouling from membrane surface and regenerate the membrane performances.

For physical cleaning, hydraulic flushing and rinsing are widely used to remove loosely foulants generally called "reversible fouling" from membrane surface, since they failed to remove bio-foulants and organic-Ca^{2+} complexes. Recently, several novel physical cleaning strategies such as AWC, DO backwash cleaning, and Ultrasonic cleaning shows great efficiency for irreversible fouling control in NF/RO membrane with two main advantages – no chemical cost except NaCl solution used in DO backwash cleaning and without membrane damage. The effectively utilized of these new physical cleaning methods depends on the optimum of several factors. Particle characteristics, spacer geometry, bubble size and shape, volume ratio of air and liquid phases, air/water superficial velocity, frequency and duration, and applied pressure could affect the cleaning efficiency of AWC because these factors affect both high shear stress and good bubble distribution, which should be met simultaneous in order to improve the cleaning efficiency. With respect to DO backwashing, the factors of osmotic pressure (NaCl solution concentration), backwash time and duration, and injection interval are every important and should be optimized carefully as well as operating pressure, flow rate of the HS solution and feed flow rate in order to getting a higher and longer time backwash flow to swell and lift up the foulants from membrane surface. However, the possible damage of membrane caused by tremendous inverse driving force should be taken into consideration during DO backwashing. Moreover, innovative methods and researches should be further conducted even the key factors and cleaning mechanism are generally well-known for the most effective cleaning. For example, Cornelissen et al. [33] pointed out that the biomass removal was 83% with horizontal positioned MFS, there are some differences existing in AWC process between the horizontal and vertical positioned membrane. Most researches are focus on with vertical positioned MFS, while horizontally positioned spacer-filled feed channels are used in practical NF/RO membrane process and AWC does not seem to operate ideally on it. In addition, ultrasonic cleaning usually performed with water bath that is difficult to use in huge practical NF/RO membrane process.

For chemical cleaning, five categories of cleaning agents: acids, alkalis, cheating agents, surfactants, and other chemical cleaning agents (NaCl solution, disinfectants, and combined cleaning materials, etc.) are often used singly, simultaneously, or sequentially. Membrane fouling can be classified into inorganic fouling, organic fouling, and biofouling. Generally, acids is used to remove inorganic fouling (scale), alkalis applied to cleaning organic fouling, while biocides was effective for long-term biofouling control in NF/RO membrane process. Indeed, HCl and citric acid are used more effective for removing colloidal iron (e.g., $Fe(OH)_3$) and carbonate precipitates from membrane compared to HNO_3 and H_2SO_4. The complex fouling is inevitable for the ubiquitous of organic matters and Ca^{2+} in the NF/RO feed water, therefore the chelating agents (e.g., EDTA) and surfactants (e.g., SDS) are used to disrupt the organic-Ca^{2+} complexes, especially mixture with alkaline solution under caustic conditions. NaCl solution can also be used as an effective alternative for the cleaning of NF/RO membrane fouled by organic-Ca^{2+} foulants. Several biocides used for biofouling control are also discussed in this review. No matter what kinds of cleaning agents was selected, effective chemical cleaning should meet the following principle: 1) chemical reaction between cleaning reagents and foulants; 2) mass transfer of the cleaning agents from bulk phase to fouling layer, and foulants from fouling layer to bulk phase [25]. Moreover, the chemical cleaning efficiency also depends on key factors such as concentration, pH, cleaning time and duration as well as temperature. The popular concentrations of chemical cleaning with EDTA, SDS, and NaCl are 0.5~2 mM, 10 mM, 100~500 mM respectively, especially under pH 11. Moreover, the cleaning efficiency generally increased with increasing cleaning time and temperature. Changes of membrane performance (e.g., hydrophilicity, surface charge and membrane pore size) caused by chemical cleaning should also be considered since it could affect the removal or retention of human health concerning trace organics such as N-nitrosamines, pharmaceutically active compounds, etc.

For biological/biochemical cleaning, enzymatic cleaning, biosurfactants, and energy uncoupling are commonly used for biofouling control. As a popular biological/biochemical cleaning method, early cleaning researches with enzymes mainly focused on low-pressure membrane (i.e., MF and UF). Although some successful lab-scale experiments about enzymes, biosurfactants, and energy uncoupling used for NF/RO membranes fouling control have been published in recent years. However, they have not been extensively applied in full-scale plants due to the higher cost compared to conventional chemicals.

In particular, the investigation of new agents such as biocides, biodegradable chelating agents, and biosurfactants for NF/RO membrane cleaning process recently received a higher of attention. In addition, due to the complexities of NF/RO membrane fouling, neither physical nor chemical and nor biological/biochemical cleaning agents are enough to remove inorganic, organic and biofouling efficiently, which is very commonly found in practical process of NF/RO. Therefore, combined/formulated cleaning [9,110,181] or sequentially cleaning [27,82] with various agents by using combined (two out of three) or both of the physical, chemical, and biological/biochemical cleaning process [30,87] were conducted for further improvement in membrane cleaning efficiency. The appropriate composition of combined agents or right cleaning orders are significantly important for obtaining higher cleaning efficiency since the combining of cleaning agents either simultaneously or sequentially is only beneficial if their cleaning mechanisms are mutually compatible [26]. Indeed, acid-alkaline sequence may be the best cleaning protocol for NF/RO membrane fouled with both inorganic and organic fouling due to the order could ensure the removal of inorganic fouling first by acid cleaning and then elimination of the organic foulants by the alkaline-detersive/chelating effect, while the inverse (alkaline-acid) sequence may be become more efficient just when a significant part of foulants is of organic nature.

Inspite of all the encouraging findings with regard to physical, chemical, biological/biochemical cleaning, there are several aspects should be further researched. Some of the most notable ones include: (i) the optimization of novel physical cleaning methods such as AWC and DO backwashing and their combination with cleaning agents, (ii) new cleaning agents, especially biodegradable cleaning agents (e.g., biodegradable chelating agents, enzymes, biosurfactants, and biocides) should be developed as a substitute of those traditional agents which affect the environment, (iii) appropriate cleaning protocol for full-scale NF/RO membrane plants, which should be further studied based on the specific fouling types and operating conditions.

Abbreviations

ATP — Adenosine triphosphate
AWC — Air/water cleaning
BSA — Bovine serum albumin
CH — Carbohydrate
DCC — Dichloroisocyanurate
DO — Direct osmosis
EDTA — Ethylenediaminetetraacetic acid
EGMB — Ethyleneglycol monobutyrate
EPS — Extracellular polymeric substances
FCP — Feed channel pressure
FNA — Free nitrous acid
FR — Flux recovery
HA — Humic acid
HS — High salinity
MF — Microfiltration
MFS — Membrane fouling simulator
MTC — Mass transfer coefficient
NCS — N-chlorosuccinimide
NDMA — N-nitrosodimethylamine
NF — Nanofiltration
NOM — Natural organic matter
RO — Reverse osmosis
RR — Resistance removal
SA — Sodium alginate
SDS — Sodium dodecyl sulfate
SRHA — Suwannee river humic acid
SRNOM — Suwannee river natural organic matter
SWRO — Seawater reverse osmosis
STP — Sodium tripolyphosphate
TMP — Trans-membrane pressure
TrOCs — Trace organic compounds
TSP — Trisodium phosphate
UF — Ultrafiltration

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