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A short review

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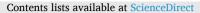
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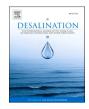
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Biofouling potential indicators to assess pretreatment and mitigate biofouling in SWRO membranes: A short review

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HIGHLIGHTS

• The use of biofouling potential indicators is a promising approach to control biofouling in SWRO systems.

- Few indicators exist to assess biofouling potential during the pretreatment and in SWRO feedwater.
- Low to moderate removal of biofouling potential is observed during SWRO pretreatment processes.
- Preliminary guidelines for controlling biofouling in SWRO membranes are proposed.

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ABSTRACT

Many desalination plants still struggle to control biological fouling in seawater reverse osmosis (SWRO) systems as there are no standard methods to monitor this type of fouling. Strategies to control biofouling in SWRO systems have been proposed such as antifouling coating and lowering biofouling potential in SWRO feedwater through pretreatment processes. Measuring biofouling potential in the pretreatment and SWRO feedwater has gained increased interest due to its direct link to biofouling. Moreover, this approach can be used as an early warning system allowing for taking corrective actions in the pretreatment processes to meet the required SWRO feedwater quality. This article presents the biofouling potential methods/tools developed for seawater, their applications to monitor and assess raw seawater, SWRO pretreatment and SWRO feedwater, and how these methods are employed to control SWRO biofouling membrane systems. The reported removal efficiency of biofouling potential during SWRO pretreatment processes was found to be low to moderate. Threshold values for biofouling potential has provided insight into SWRO pretreatment performance optimisation and biofouling control. Future research is anticipated to determine better pretreatment processes and to identify robust threshold values for mitigating biofouling in SWRO membranes.

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Abbreviations: AOC, assimilable organic carbon; ATP, adenosine tri-phosphate; BDOC, biodegradable dissolved organic carbon; BGP, bacterial growth potential; BRP, bacterial regrowth potential; CDOC, chromatography dissolved organic carbon; CIP, cleaning-in-place; CRISPR, Clustered Regularly Interspaced Short Palindromic Repeats; EPS, extracellular polymeric substances; DAF, dissolved air flotation; DOC, dissolved organic carbon; DOM, dissolved organic matter; FEEM, fluorescence excitation emission matrix; FCM, flow cytometry; GAC, granular activated carbon; HPC, heterotrophic plate count; LC-OCD, liquid chromatography quadrupole time of flight; LMW, low molecular weight; mBFR, membrane biofilm formation rate; MFI, modified fouling index; MFS, membrane fouling simulator; NOM, natural organic matter; RO, reverse osmosis; SUVA, specific ultraviolet absorbance; SWRO, seawater reverse osmosis; TEP, transparent exopolymer particles; TOC, total organic carbon; UF, ultrafiltration; UV, ultraviolet.

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1. Introduction

Desalination of seawater and brackish water has grown rapidly over the last thirty years. Reverse osmosis (RO) membrane is the most dominant technology applied for desalination. Global capacity is now >100 million cubic metres per year and is expected to double by 2030 [1], helping satisfy the growing municipal, agricultural and industrial water demand [2,3]. However, fouling of RO systems, which can be due to suspended and colloidal particles, biomass and biofilm formation, organic matter and sparingly soluble salts, has been the major operational challenge for plant operators.

Over the past twenty years, the knowledge and understanding of biofouling in seawater desalination has advanced extensively and moved away from empirically-based approaches to a fundamentallybased first-principles approach embracing chemistry, microbiology, and physical and bioprocess engineering, often involving experimental laboratory work and techniques. Many of these experimental methods and techniques have matured to the degree that they have been accepted as reliable tools in desalination research and practice.

Biofouling of RO membranes occurs due to microbial growth on membrane surfaces and/or across the spacer-filled membrane feed channels to form a biofilm layer that causes operational issues [4]. Biofilm formation is the accumulation of bacteria and extra cellular polymeric substances (EPS) on the membrane surface [5]. However, biofouling is considered to be taking place only when the accumulation of biomass/biofilm formation exceeds such a level that operational problems occur [5,6]. These operational problems can be: (i) an increase in pressure drop across the elements resulting in a decrease of net driving pressure and increased risk of mechanical damage of the RO elements, (ii) a decrease in permeability of the RO membranes (flux per unit pressure), resulting in a higher required feed pressure (more energy consumption), (iii) an increase in salt passage due to concentration polarisation in the biofilm (higher salinity in permeate), and (iv) an increase in risk of scaling due to concentration polarisation in the biofilm [4,7].

The formation of biofilm in RO systems is inevitable if feedwater contains significant concentrations of easily biodegradable (dissolved) nutrients. Only a very small part of natural organic matter (NOM) in water can be utilised or is assimilable and is referred to assimilable organic matter (AOC) or biodegradable dissolved organic carbon (BDOC) [8–10]. Bacteria adhere to membrane surfaces and utilize easily biodegradable nutrients present in the feedwater to multiply and to produce an EPS matrix, adhering to each other and/or a surface [6,11,12]. Nutrients needed for respiration is the minimum requirement for bacterial survival. When more nutrients are available, bacteria will multiply until a balance between the number of bacteria and available nutrients is achieved. Consequently, an excess of nutrients will promote bacterial growth while a lack of nutrients will cause bacterial numbers to fall [13,14].

To alleviate biofouling in RO systems, plant operators usually perform cleaning-in-place (CIP) interventions using base/acid chemicals, following biofouling occurrence. CIP is usually applied when RO membrane performance is reduced by 10-15% from the initial performance, as typically measured by differential pressure drop or permeability [15]. CIP frequency depends on the biofouling potential of the feedwater and the operational conditions of the plant [16,17]. It should be noted that CIP is applied to restore RO membrane flux but not to prevent RO biofouling [18].

Two strategies are used to minimise biofouling occurrence in RO systems. The first strategy is to lower biofouling potential through feedwater pretreatment, while the second approach targets surface modification of RO membranes (anti-fouling coating) using biocides, polymer- or nanotechnology-based antifouling coatings [19]. The use of membrane modification has shown significant improvement in controlling biofouling and in increasing RO flux. Antifouling RO membranes still face several challenges including stability and durability of the

coated layer and the translation from lab to industrial scale in terms of costs and production [20]. Lowering biofouling potential through pretreatment appears to be the most common and applicable strategy especially because (I) measuring biofouling potential in RO feedwater is directly linked to biofouling and (II) it allows taking corrective actions in the operational conditions of RO pretreatment [21–23]. However, because these are complementary approaches, combining them would be ideal practice to control biofouling development in SWRO systems.

Pretreatment can take place in the form of media filters with or without coagulation, membrane filtration with or without inline coagulation (e.g., ultrafiltration), and dissolved air flotation in combination with the previous mentioned two options [24,25]. Methods and tools to measure biofouling potential can significantly help to (i) monitor pretreatment performance in terms of biofouling potential; (ii) optimise RO pretreatment processes; and (iii) take actions to control biofouling in RO membranes. This work focuses on a review of indicators for assessing biofouling in seawater desalination systems, from source to RO feedwater. This work focuses on the indicators and tools developed to monitor and assess biofouling potential in seawater reverse osmosis (SWRO) desalination systems, from source to SWRO feedwater. Moreover, it summarises the range of biofouling potential reported in literature and analyses the removal efficiency of pretreatment processes. Finally, this work presents the available threshold values to control biofouling in SWRO membranes. To the knowledge of the authors, this is the first database consolidating a wide range of studies on biofouling potential indicators and their applications (full-scale plants and pilotscale SWRO units) in assessing SWRO pretreatment. This work can help plant operators in lowering biofouling potential in SWRO feedwater by taking corrective actions of pretreatment unit operations which, in turn, allows to mitigate biofouling in SWRO systems.

2. Biofouling potential indicators in seawater

Several indicators have been applied to monitor biofouling potential in seawater including assimilable organic carbon (AOC), bacterial growth potential (BGP), orthophosphates, organic matter fractionation, Transparent exopolymer particles (TEPs), etc. However, all these indicators are not standardised as biofouling indicators.

2.1. Assimilable organic carbon

The concept of AOC was proposed for the first time by van der Kooij et al. in 1982 [26] to measure the potential of a water for supporting microbial regrowth in drinking water distribution system based on the growth of Pseudomonas fluorescens strain P17 (P17). AOC is a small fraction (0.1-10%) of dissolved organic carbon [27-29], which is utilised by heterotrophic microorganisms for their growth [30,31]. AOC detection is more complicated than any other chemical methods such as total organic carbon (TOC) and dissolved organic carbon (DOC) because AOC is comprised of different biodegradable organic compounds of natural origin such as low molecular weight (LMW) compounds, amino acids, hydroxycarboxylic acids, and carbohydrates which are difficult to detect at low concentrations [28,32,33]. Van der Kooij et al. [26] originally measured AOC concentration by pasteurising the sample (at 70 $^\circ$ C for 30 min), inoculating it with strain P17, incubating it over 2 weeks and measuring bacterial growth using plate counting [26,34]. AOC concentration is calculated based on a calibration line between the net bacterial growth and carbon concentration as acetate. Further research has been performed on AOC to shorten the test duration and increase the accuracy of the traditional AOC method. For this purpose, different parameters have been employed to monitor bacterial growth during the AOC method such as adenosine tri-phosphate (ATP) [34-36], flow cytometry (FCM) [28], and bioluminescence [37]. The general procedures of AOC are presented in Fig. 1.

The use of one pure strain (P17) cannot completely assimilate AOC due to its lack of *exo*-enzymes and interactions between different

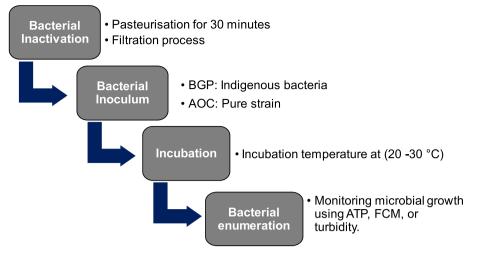


Fig. 1. The general procedures for assimilable organic carbon and bacterial growth potential measurements [10].

bacteria. Thus, van der Kooij and Hijnen later added *Spirillum strain NOX* (NOX) together with P17 as NOX has the ability to utilize oxalic acid for its growth [33,38]. Even though these two strains (P17 and NOX) utilize a wide range of easily biodegradable compounds, they cannot degrade more complex compounds such as polysaccharides and proteins. Therefore, additional bacterial culture (*Flavobacterium Johnsoniaestrain A3*) has been introduced to the AOC test by Sack et al. [39] to target polysaccharides and proteins as nutrients for growth. However, to avoid this limitation (inclusion of all types of biodegradable organic compounds), the use of an indigenous microbial consortium was proposed to further broaden and diversify the substrate utilisation [28,40,41]. Ross et al. [40] showed that bacterial growth of an indigenous microbial consortium was 20% higher than that of a pure strain.

Similarly, in seawater, AOC methods have been developed using one pure strain. Marine microorganisms such as *Vibrio fischeri* and *Vibrio harveyi* bacteria are used as inoculum to measure AOC in seawater since P17, NOX and A3 strains are freshwater bacteria. Vibrio bacteria are used because they grow quickly (2–24 h) and have the ability to produce a high bioluminescence at low substrate concentration [22,42]. However, the use of fast-growing microorganisms (<24 h) may not be representative of the growth of other microorganisms which usually grow within 3–15 days. Moreover, one pure strain cannot utilize all available AOC in seawater which may lead to underestimating AOC concentration in seawater. The detection limits of these methods range between 0.1 and 10 μ g-C/L (see Table 1). However, the extremely low detection limit (0.1 μ g-C/L) reported by Jeong et al. [22] is questionable as it was calculated after subtracting the AOC of the blank, which was >50 μ g-C/L [43].

2.2. Bacterial growth potential

BGP measures the potential of a water sample to support bacterial growth based on all biodegradable organic matter present in a water sample. BGP is derived from the AOC method and it follows the same concept and procedure of AOC method with a few notable differences. These differences are mainly in the terminology, used inoculum, and reported results. The use of the term "AOC" may be misleading since converting bacterial growth in water sample to AOC concentration is not straight forward. Using bacterial growth of one type of carbon source (acetate or glucose) to establish the AOC-bacterial growth calibration curve has clear limitations as one source of carbon cannot represent total AOC which includes a wide range of biodegradable organic compounds (such as LMW, amino acids, hydroxycarboxylic acids, polysaccharides, and carbohydrates) [10,43]. Therefore, Abushaban et al. [44] suggested "BGP" as a term to avoid any misinterpretation of the result. Some researchers use the term of "bacterial growth refers to the regrowth of the added inoculum at the beginning of the test [45].

In comparison to the AOC method, which uses either one pure strain or mixed culture, BGP uses only indigenous bacteria as an inoculum to broaden the utilisation of different biodegradable organic matter. To avoid losing any microorganism, the indigenous bacteria are collected in liquid form from the same seawater source (raw seawater) and added to the sample. Furthermore, the results of BGP can be reported with or without its carbon equivalent. For instance, reporting the maximum bacterial growth (ng-ATP/L, number of cell count/mL, etc.) or as acetate/glucose equivalent microgram per litre [46,47]. The result can be converted to carbon equivalent for the purpose of comparing different samples from different locations. Several BGP methods have been developed employing turbidity, microbial ATP, total ATP, and total and intact cell count by FCM (Table 2).

2.3. Orthophosphates

Phosphate is considered to be a limiting nutrient as it is present in very low concentrations in seawater. Therefore, eliminating phosphate concentration in the SWRO pretreatment could allow for directly controlling SWRO biofouling. Javier et al. [50] found that phosphate limitation in seawater strongly depended on the AOC concentration, indicating that both phosphate and AOC should be limited for better control of SWRO biofouling.

The most interesting fraction of phosphate is orthophosphates (such as H_3PO_4 , $H_2PO_4^-$, HPO_4^{-2-} , and PO_4^{-3-}) because it is biodegradable and

Table 1

Assimilable organic carbon methods in seawater [10].

| 0 | | | | | | |
|-----------------------------|--------------------------------------|----------------------------------|-------------------------|------------------------|---------------|-----------------|
| Reference | Bacterial inactivation | Bacterial strain for inoculation | Growth detection method | Incubation temperature | Test duration | Detection limit |
| Weinrich et al. (2011) [21] | Pasteurisation (70 °C for 30 min) | Vibrio fischeri | Natural bioluminescence | 30 °C | <24 h | 10 µg-C/L |
| Jeong et al. (2013) [22] | Pasteurisation (70 °C for 30 min) | Vibrio harveyi | Natural bioluminescence | 25 °C | 2 h | 0.1 µg-C/L |

Bacterial growth potential methods in seawater.

| Reference | Bacterial inactivation | Culture | Detection principle | Incubation temperature | Expressed results |
|------------------------------------|--------------------------------------|------------------------------|---------------------------------------|---------------------------|-------------------------------|
| Dixon et al. (2012) [45] | Filtration (0.2 μ m) | Indigenous microorganisms | Turbidity | Not available | µg-C as acetate equivalent |
| Abushaban et al. (2017) [44,48] | Pasteurisation (70 °C for 30 min) | Indigenous microorganisms | Microbial ATP | 30 °C | µg-C as glucose equivalent |
| Farhat et al. (2018) [49] | Filtration (0.2 μ m) | Indigenous microorganisms | Total ATP and Total cell count by FCM | 30 °C | μg-C as acetate equivalent |
| Dhakal et al. (2021) [47] | Filtration (0.22 µm) | Indigenous microorganisms | Intact cell counts by FCM | 30 °C | µg-C as glucose equivalent |

the most utilised phosphate by microorganisms [51]. Orthophosphates are not commonly measured through SWRO pretreatment processes due to the lack of methods with low detection limit. However, Abushaban et al. [52] recently measured a concentration of orthophosphates as low as 0.5 μ g-PO₄-P/L in seawater using a 1 m length flow cell. In general, to measure orthophosphates a molybdate reagent and ascorbic acid are added to seawater at a temperature of 37 °C. The added molybdate and the orthophosphates present in seawater form a phosphor-molybdate complex in the acidic environment after reduction with ascorbic acid and in the presence of antimony. This reaction yields a blue coloured complex, which is measured at 880 nm using a cuvette and a spectrophotometer.

2.4. Liquid chromatography of organic matter fractions

Organic matter fractionation using liquid chromatography coupled with organic carbon detection (LC-OCD) is used to determine the composition of natural organic matter (NOM) [53]. LC-OCD combines a size exclusion chromatography column, followed by multi detection of organic carbon, UV_{254} and nitrogen. Organic matter can be fractionated in five different important fractions including biopolymers, humics, building blocks, low molecular weight organic acids (LMW acids) and low molecular weight neutrals (LMW neutrals). The typical size and composition of these fractions are presented in Table 3. An accurate quantification of these fractions in seawater is possible with a variation coefficient lower than 12% [54].

LC-OCD has been widely used to assess raw seawater and pretreatment processes of SWRO systems (see Section 4). However, for better illustration of the results, LC-OCD measurement is usually combined with other methods (such as fluorescence excitation emission matrix (FEEM) and TEP). Fig. 2 shows an overview of organic matter fractions and common analytical techniques that are applied to monitor seawater. Yin et al. [55] characterised DOC in seawater and found the organic composition of seawater to be biopolymers (~6%), humic substances and building blocks (~52%) and LMW (~42%). The authors found that LMW is the main AOC contributor (>70%) and that LMW and biopolymers have the highest impact on SWRO biofouling in terms of flux decline rate (~30%, ~20%, respectively).

| Descriptions of organic matter mattering measured by LC-OCD [30,37] | escriptions of organic matter fractions measured by | LC-OCD | [56,57]. |
|---|---|--------|----------|
|---|---|--------|----------|

| Organic fraction | Typical size (Da) | Typical composition |
|---------------------|----------------------|---|
| Biopolymers | >20,000 | Polysaccharides, proteins, amino sugars, polypeptides, transparent exopolymer particles (TEP) |
| Humic subst. | ~ 1000 | Humic and fulvic acids |
| Building blocks | 300–500 | Weathering and oxidation products of humics |
| LMW neutrals | <350 | Mono-oligosaccharides, alcohols, aldehydes, ketones, amino acids |
| LMW acids | <350 | All monoprotic organic acids |
| | | |

2.5. Transparent exopolymer particles

TEPs are a specific fraction of biopolymers produced by algae in natural waters. It has been identified to be hydrophilic, anionic mucopolysaccharides and glycoproteins [58]. In the literature, the current notion of the role of TEP on biofouling still needs to be further verified and their effect on the operation of RO membranes still needs to be demonstrated. However, a few studies indicated that TEP may cause organic and biological fouling and may enhance particulate/colloidal fouling in RO membranes. Villacorte et al. [59] measured TEP in raw water, pre-treatment processes and RO membrane surfaces of 6 desalination plants and found that 30–70% of TEP from the feedwater were deposited on the RO membrane surface. Moreover, Villacorte [56] reported a significant correlation between TEP_{10kDa} and modified fouling index measured using ultrafiltration membranes (MFI _{UF}).

Several methods have been developed in the literature to quantify TEP. The first TEP method was developed by Alldredge et al. [60] using alcian blue staining and optical microscopic enumeration. However, this method can only detect TEPs larger than 2 μ m. Later, Passow and Alldredge [61] used semi-quantitative spectrophotometric techniques to enable measuring TEP as low as 0.4 μ m (TEP _{0.4 μ m}). A concentration step by filtration through a 10 kDa membrane, known as TEP_{10kDa}, was recently introduced. The method allows size fractionation of TEPs and their precursors (10 kDa – 0.4 μ m) in seawater using a series of membranes with different pore sizes during the extraction step [13,62].

2.6. Other organic indicators

In addition to the above-mentioned parameters, plant operators and researchers have used other parameters as indicators of SWRO biofouling such as TOC, ultraviolet (UV) absorbance, and specific UV absorbance (SUVA). TOC, UV absorbance and SUVA have been commonly used because they are easy to measure and can give indication of the organic matter concentration and character present in the water [63].

TOC measures the total carbon content including both NOM and biodegradable organics. It is usually measured by converting organic carbon to carbon dioxide at high temperature (>700 °C) in the presence of a catalyst. When pre-filtering the sample through a 0.45 µm filter, the measurement is called dissolved organic carbon (DOC).

UV-absorbance is an indirect parameter to measure NOM in seawater. It is measured by filtering a seawater sample through a 0.45 μ m filter and then measuring the absorbance of UV light at a 254 nm wavelength (UV₂₅₄) using a spectrophotometer. The absorbance of UV light in seawater is attributed to the chemical structure of the NOM molecules [64].

SUVA, which is the ratio of UV_{254} absorbance to DOC concentration, has gained attention because it provides insight into the nature of dissolved organic matter (DOM) by combining both UV_{254} absorbance and DOC [65,66].

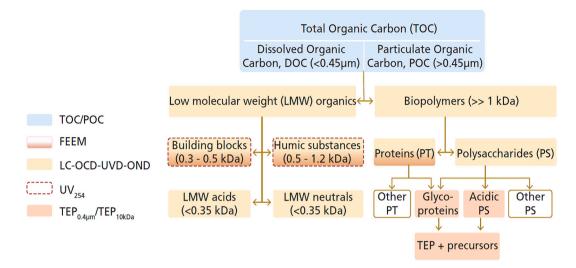


Fig. 2. Overview of organic matter fractions and corresponding analytical techniques for identification and quantification. Legend: LC-OCD-UVD-OND = liquid chromatography with inline detectors for organic carbon, UV absorbance at 254 nm and organic nitrogen; FEEM = fluorescence excitation-emission matrices; TEP = transparent exopolymer particles [58].

3. Biofouling potential using membrane surface

Two tools have been used to monitor biofouling potential through pretreatment and SWRO feed employing a membrane surface. The purpose of having a membrane surface is to evaluate microbial attachment and growth due to organic content in seawater [67,68]. These tools are the biofilm growth monitor and membrane fouling simulator (MFS).

3.1. Biofilm growth monitor

The concept of biofilm growth monitor was developed by Toray [69] to monitor the biofouling potential of a water when it is in contact with a RO membrane surface by measuring the rate at which biofilm forms on the RO membrane surface, which called membrane biofilm formation rate (mBFR). The higher the rate of biofilm formation, the higher the potential of biofouling.

To measure mBFR, a column equipped with O-rings covered with a RO membrane is used (Fig. 3), in which seawater continuously flows. Over time, the O-rings are taken out sequentially to measure biofilm formation and each ring is replaced with a new one to keep a constant flow rate in the water column. Biofilm formation is measured by swabbing the biofilm layer and suspending it in 1 mL of distilled water [70]. ATP concentration is then measured to quantify microbial content. The mBFR value is calculated based on the slope of the linear relationship between biomass and time [68].

3.2. Membrane fouling simulator

The MFS is a tool used to validate fouling of the membrane surface by using the same materials, most critically, under similar hydrodynamic conditions (e.g. velocity distribution and laminar/turbulent flow) as spiral wound RO membranes. The tool was developed by Vrouwenvelder et al. [71] and can be used for many purposes including, but not limited to, characterising the fouling potential of RO feedwater, comparing different pretreatments and testing newly developed membranes [72]. Vrouwenvelder et al. [71] compared MFS and spiral wound membrane modules at pilot and full scale plant and reported that both MFS and spiral wound membrane had the same pressure drop development in time and the same concentration of active biomass. Several types of MFS units have been developed for different purposes. However, for seawater, an MFS unit can be only used without permeate production due to the fact that the maximum pressure on such a unit is 15 bar (1 m length) [73], while the feed pressure needed for seawater application is >50 bar. Thus, the MFS cannot be used to simulate biofouling in SWRO membranes, but only to evaluate the potential of bacterial attachment and growth on the membrane system in a way similar to the mBFR. The drawback of the MFS and mBFR units is that observing biofilm formation on the RO membrane may require up to several months.

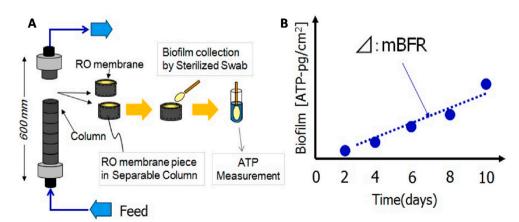


Fig. 3. Schematic representation and measurement using biofilm growth monitor (A), and example of a result (B) obtained [68].

4. Biofouling potential in the intake

4.1. Biofouling potential in raw seawater

Raw seawater quality plays a critical role in the selection of pretreatment processes and controlling fouling of SWRO membrane systems. Poor raw seawater quality requires effective pretreatment processes to protect SWRO systems from frequent fouling, whereas excellent raw seawater quality with minimal fouling potential may not require a pretreatment.

Biofouling potential in raw seawater varies in time, location and

depth due to water characteristics (nutrients, temperature, salinity, pH, oxygen, light, etc.), intake location (depth, closeness to industrial areas/ ships), water circulation (streams, waves, tides, etc.) and sea topography (sea depth, benthic zone, etc.) [74]. Seasonal variation in the BGP, DOC and chlorophyll *a* of the North Sea has been reported, in which low concentrations were measured in the winter and high concentrations were observed in the spring and autumn [10,75]. The high biofouling potential in the spring and autumn was attributed to organic matter originated from algal blooms. Several researchers reported that the uppermost layer of the ocean is enriched with organic carbon, carbohydrates, amino acids, and TEP compared to the underlying seawater

Table 4

Biofouling potential of raw seawater including organic matter and biomass at different locations around the world.

| Water source | Biofouling potential | Temperature | Reference |
|---|---|--------------|------------|
| Coral Sea, Australia | AOC: 160–275 μg-C/L | 20–25 °C | [44] |
| | TOC: <2 mg/L | | |
| Tasman Sea, Australia | AOC: 22.4–26.6 µg-C/L (beach well) | NA | [84] |
| Chowder Bay, Sydney, Australia | DOC: 1.3–1.7 mg/L | ~20 °C | [85,86] |
| | Biopolymers: 350 µg/L | | |
| | Humic substances: 470–700 µg/L | | |
| | Building blocks: 140 µg/L | | |
| | LMW neutrals: 350-800 µg/L | | |
| Indian Ocean, Perth Seawater desalination plant, Australia | AOC: 25–45 µg-C/L | 18.5–23.1 °C | [87] |
| | DOC: 1.3–1.8 mg/L | | |
| | Biopolymer: 90–100 μg/L | | |
| | Humics substance: 500–520 µg/L | | |
| | LMW neutrals: 550–970 µg/L | | |
| Gulf of Oman, Oman | BGP: 280–480 μ g-C/L as glucose equivalent | 22–30 °C | [52] |
| (May 2017) | CDOC: 1528 µg/L | | [] |
| (| Biopolymer: 177 µg/L | | |
| | TEP: 18 μg XG/L | | |
| | Humics substance: 442 µg/L | | |
| | Building blocks: 243 μ g/L | | |
| | LMW acids: 100 µg/L | | |
| | | | |
| Auchieur Culf Courdi Auchie | LMW neutrals: $566 \mu g/L$ | 15 40 00 | [00] |
| Arabian Gulf, Saudi Arabia | mBFR: 63–121 pg-ATP/cm ² /d | 15–43 °C | [88] |
| (Dec 2016–Oct 2017) | | | F (0, 0,07 |
| Arabian Gulf, UAE | BGP: 105–1000 µg-C/L as glucose equivalent | 30–35 °C | [43,89] |
| (Jul & Aug 2018) | (1000–2500 µg/L as glucose equivalent during algal bloom) | | |
| | Orthophosphate: $1.8-11 \ \mu g \ PO_4$ -P/L | | |
| | TOC: 2.9 ± 0.8 mg/L | | |
| | CDOC: 1808 \pm 244 µg/L | | |
| | Biopolymer: 265 \pm 57 µg/L | | |
| | Humic substance: 737 \pm 165 µg/L | | |
| | LMW acids: 157 \pm 47 µg/L | | |
| Arabian Gulf, UAE | BGP: $1.8-3.7 \times 10^6$ intact cell/mL | 22–30 °C | [47] |
| (Sep 2016) | CDOC: 1065 µg/L | | |
| | Biopolymers: 166 µg/L | | |
| | Humic substances: 427 µg/L | | |
| | Building blocks: 188 µg/L | | |
| | LMW neutrals: 161 µg/L | | |
| | LMW acids: 124 µg/L | | |
| North Sea, Netherlands | TEP: 0.01–1.49 mg XG/L | 5–23 °C | [56] |
| (Feb2009–May2012) | Biopolymers: 0.06–0.48 µg/L | | |
| | TOC: 1.35–2.0 mg/L | | |
| North Sea, Netherlands | BGP: 20–385 µg-C/L as glucose equivalent | 5–20 °C | [10] |
| (Nov2016–Oct2017) | 0 | | [] |
| Mediterranean Sea, Barcelona, Spain | CDOC: 1395 \pm 70 µg/L | 15–24 °C | [53] |
| mediteritalean sea, surceiona, span | Biopolymers: $105 \pm 5 \mu\text{g/L}$ | 10 21 0 | [00] |
| | Humic substances: $361 \pm 18 \ \mu g/L$ | | |
| | Building blocks: $220 \pm 11 \ \mu\text{g/L}$ | | |
| | | | |
| | LMW neutrals: $636 \pm 32 \ \mu g/L$ LMW acids: $73 \pm 4 \ \mu g/L$ | | |
| North Pasifia Casar Mantaray Pay Mass Landing California | | 16 00 % | [01 04 00] |
| North Pacific Ocean, Monterey Bay, Moss Landing, California | AOC: 10–155 μg-C/L | 16–20 °C | [21,24,90] |
| Oulf - (Marian Trans Prov Planida | TOC: 1.0–1.8 mg/L | 00.05.90 | [01.01] |
| Gulf of Mexico, Tampa Bay, Florida | TOC: 4–5.7 mg/L | 20–35 °C | [21,91] |
| | AOC: 180–540 μg-C/L | | |
| | Orthophosphate: 12–40 µg PO4-P/L | | |
| | Biopolymers: 35–211 µg/L | | |
| | Humic substances: 879–3305 µg/L | | |
| | Building blocks: 430–1054 µg/L | | |
| | LMW neutrals: 1696–5861 µg/L | | |
| | LMW acids: 6–248 µg/L | | |

NA: not available.

[76–80]. Rimmelin and Moutin [81] reported that the maximum phosphate concentrations measured in the Atlantic and Pacific oceans were 240 and 310 μ g P/L, respectively. However, typical concentrations in seawater are usually below 33 μ g P/L [82].

Table 4 shows some of the gathered biofouling potential data in raw seawater from different locations. The Tampa Bay desalination plant showed the worst raw seawater quality with concentrations of TOC, AOC, orthophosphate, biopolymer, and humic substances exceeding 5 mg/L, 500 μ g/L, 35 μ g P/L, 200 μ g/L and 3000 μ g/L, respectively. Rand [83] reported that the Tampa Bay desalination plant suffered from severe fouling during initial startup due to the high concentration of organics in the raw seawater. The membrane filtration system lasted only a few months instead of years while cartridge filters had to be replaced after a few weeks.

4.2. Biofouling potential in beach well intakes

The intake of a SWRO plant is a critical part of its design and can greatly impact the quality of the inlet water to be treated. Beach well intakes are generally considered to be particularly valuable [92] as they provide a natural filtration barrier and can assure a better water quality than an open sea intake.

Data reported in the literature (Tables 5 and S1), in particular two specific review studies of beach well data [93,94], highlighted the positive impact of such a natural or engineered process on water quality. This was particularly the case for a variety of parameters linked to lifeform activity in seawater (bacterial counts, phytoplankton) but also on the presence of organic matter through decreased concentration of carbon and UV absorbing compounds (DOC, LC-OCD, UV₂₅₄). An increase in TOC (0.2 mg C/L) and UV₂₅₄ (0.2 m⁻¹) following beach well filtration of seawater was reported [94] for a site in Spain though this is likely due to extremely good seawater quality prior to the beach well with values of 0.5 mg C/L and 0.36 m⁻¹ for these two parameters respectively.

The use of an open intake is generally selected based on the need for a large flow of water. However, the data collected from the literature highlights the significant advantage of a plant with a beach well intake in terms of reducing the biofouling risk throughout its treatment line. Thus, there is a need to assess the performance of beach wells with regard to biofouling potential removal (BGP, AOC, etc.).

5. Biofouling potential removal by SWRO pretreatment

Studies evaluating actual SWRO plants were prioritised in this review of pretreatment data. Additional studies, using pilot-scale units on real seawater, were also compiled to provide a wider picture of the performance of the different pretreatment units. Only parameters of interest, related to the biofouling potential of a water were consolidated in the tables presented in this section. It was often found that there was a heterogenous reporting of parameters and performance, some studies focusing only on relative performance (% removal) where others would reference inlet and outlet values for the unit of study to allow calculation of an absolute removal value. This heterogeneity of data reporting translates to some discrepancies in the tables of this section which can also be viewed in graphical format in the supplementary material (Figs. S1 to S7). Finally, the unit processes considered are those that are most represented in actual plants.

5.1. Dissolved air flotation

Dissolved air flotation (DAF) is a separation process that uses the application of air bubbles to separate particles or colloids from seawater. It is generally applied for waters that are highly impacted by potential foulants such as algae, oil and grease [96]. Such a unit is therefore usually considered for plants that treat seawater with a high risk of algae blooms such as those located in the Persian Gulf or those close to an industrial area, increasing the risk of industrial pollution.

Several studies have evaluated the performance of DAF as a pretreatment process for SWRO (Table 6). The detailed data including operational conditions of each process are listed in Table S.2. The results highlight the best removal performance of DAF for algae and chlorophyll *a*, which confirms the process's relevance for resources at risk of algal blooms. This performance also translates well to notable decreases for ATP (27%) and BGP (18–52%) though few studies have evaluated these parameters. One study [89] also showed the potential for DAF, in combination with upstream coagulation, to remove orthophosphates (68%) as a factor for limiting biological potential.

The removal of organic matter was found to be quite variable with no removal observed for very low organic load waters [89] and the highest removals for waters that contain a significant amount of organic carbon [89]. The removal of UV_{254} by DAF was always found to be superior to that of DOC, a result that is well-known in freshwaters where UV_{254} represents compounds much more reactive to treatment.

The evaluation of organic carbon characterisation by LC-OCD revealed that the humic substances and building blocks fractions were the most susceptible to removal by DAF. Low molecular weight compounds and biopolymers, which are often associated with biofouling risk, are not very well removed by DAF with very low performance in the case of biopolymers (0–8%).

Overall, DAF shows interesting results in terms of limiting the risk of biofouling from seawaters, especially for sites concerned with the impact of algae in the raw waters. It also appears to show a limited, though notable, positive impact on the nutrients present in the resources.

5.2. Coagulation

Coagulation as a pretreatment in SWRO plants generally consists of

| Та | ble | : 5 | | |
|----|-----|-----|--|--|
| | | | | |

Removal performance of beach wells.

| Parameter (unit) | Inlet value | Performa | Performance | | |
|-------------------------------|-----------------|------------------|-------------|------------|--|
| | | Quantity removed | Removal (%) | | |
| Total cell count (cells/mL) | 179,837–995,310 | 145,837–919,666 | 81–100 | [92,93,95] | |
| TEP (µg XG/L) | 58-642 | 31–585 | 45–91 | [93,95] | |
| TOC (mg/L) | 0.5–2 | -0.2-0.4 | -40-35 | [94] | |
| DOC (mg/L) | 0.57-1.6 | 0.25-0.76 | 23–76 | [93] | |
| UV_{254} (m ⁻¹) | 0.36-1.4 | -0.19 -0.62 | -53-44 | [92,93] | |
| Biopolymer (µg/L) | 63 | 57 | 90 | [95] | |
| Humic substances (µg/L) | 367 | 195 | 53 | [95] | |
| Building blocks (µg/L) | 131 | 66 | 50 | [95] | |
| LMW neutrals (µg/L) | 230 | 123 | 53 | [95] | |
| LMW acids (µg/L) | 130 | 69 | 53 | [95] | |
| Polysaccharides (mg/L) | 0.12-0.4 | 0.11-0.4 | 92–100 | [94] | |
| Total nitrogen (µM) | 5.7 | -1.4 | -25 | [92] | |

Removal performance of DAF process.

| Parameter (unit) | Inlet value | Perfor | rmance | References |
|--|-------------|---------------------|----------------|--------------------|
| | | Quantity removed | Removal (%) | |
| BGP (μg-C/L as glucose equivalent) | 373–400 | 70–193 | 18–52 | [10,89] |
| ATP (pg/mL) | 75–335 | - | 27 | [10] |
| Algae (cells/mL) | 332 | 251 | 76 | [97] |
| Chlorophyll a (mg/m ³) | 1.8 | 0.8 | 44 | [98] |
| DOC (mg/L) | 0.9-1.1 | 0-0.2 | 0–24 | [97-99] |
| $UV_{254} (m^{-1})$ | 0.7–4 | 0-2.2 | 0–55 | [97–100] |
| CDOC (µg/L) | 1180 - 1808 | 27-135 | 3–7 | [10,89,97] |
| Biopolymer (µg/ L) | 60–265 | 0–13 | 0–8 | [10,89,97,100,101] |
| Humic substances (µg/L) | 410–737 | 10-204 | 3–41 | [10,89,100] |
| Building blocks (µg/L) | 90–160 | 9–35 | 10–22 | [98,100] |
| LWM acids (µg/L) | 10-157 | 0-1.5 | 0–15 | [10,89,100] |
| LMW neutrals (µg/L) | 280–360 | 39–349 | 7–14 | [10,100] |
| Orthophosphate (µg/L) | 5.3 | 3.6 | 68 | [89] |
| Turbidity (NTU) | 2 | 1 | 50 | [97] |

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|-----|-----|---|
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Removal performance of coagulation process.

| Parameter (unit) | Inlet | Perfor | mance | Reference |
|--|-----------|---------------------|----------------|-------------|
| | value | Quantity removed | Removal (%) | |
| AOC (µg C/L) | 29-440 | -3.5 - 290 | -10-93 | [21,87,104] |
| BGP (µg-C/L as glucose equivalent) | 230–305 | 30–43 | 13–14 | [10,44] |
| ATP (pg/mL) | 90 | 35 | 39 | [44] |
| Chlorophyll a (mg/ m ³) | 0.22-0.74 | 0.05-0.43 | 25–59 | [102,103] |
| TEP (µg XG/L) | 214-294 | -120-33 | -41 - 15 | [102,103] |
| TOC (mg/L) | 5.4–5.9 | 0.3-0.36 | 6 | [21,104] |
| DOC (mg/L) | 0.9 - 1.2 | -0.37-0.2 | -31 - 22 | [103,106] |
| $UV_{254} (m^{-1})$ | 17.3 | 4.2 | 24 | [104] |
| CDOC (µg/L) | 1500 | 90 | 6 | [87] |
| Biopolymers (µg/L) | 90-151 | 40–77 | 44–51 | [87,106] |
| Humic substances (µg/L) | 510-1003 | 70–407 | 14-41 | [87,106] |
| LMW neutrals (µg/L) | 150 | -70 | -9 | [87] |

conditioning the raw seawater for the following pretreatment units by dosing coagulants, such as ferric sulphate or ferric chloride. The aim is to remove particulate, colloidal and dissolved organic matter and to enhance their removal in the downstream sedimentation or filtration steps [24]. Coagulation also has the potential to remove natural organic matter and algal content, but coagulant type and dosage optimisation must be carefully carried out.

Tables 7 and S.3 (detailed data) presents the reported removal efficiencies of coagulation steps in various SWRO plants regarding either algal content, biological activity or abundance, natural organic matter (NOM), or organic matter. The data, as far as the authors could gather from the referenced literature, corresponds exclusively to either coagulation followed by sedimentation or direct coagulation without including any subsequent filtration step.

The capacity of coagulation steps to remove algal content, in terms of chlorophyll *a* and TEP, is very heterogenous amongst plants. The coagulant type, dosage applied, and raw water quality can greatly impact the performance. For instance, Fe_2SO_4 is reported to steadily remove both chlorophyll *a* and TEP around 15–25% in one reference [102], but in another [103] showed a greater chlorophyll *a* removal

capacity (59%) accompanied with a marked increase (41%) in TEP concentration.

The impact of coagulation on biological parameters, such as AOC, BGP and ATP, is reported to be low to moderate, with removal percentages ranging from -10% to 39%. Higher removals of AOC were reported for studies in Florida [21,104] with values of 66 and 93% respectively. In this latter case, the coagulant used was ferric acid coupled with hypochlorite, which has been reported to enhance the removal of some biological parameters, such as algal cells, as suggested by Zhu and Bates [105]. In addition, for both studies, the influent AOC measurement was low and its effluent value near or below detection limit (27 and 2 μ g C/L respectively).

Concerning natural organic matter, coagulation is also reported to have a low to moderate removal capacity. The reported biopolymer and humic substances removal capacity of coagulation ranges from 14% to 51%, with rather stable outlet values for the two plants concerned [87,106] with 50 to 74 μ g/L for biopolymers and 440 to 596 μ g/L for humic substances. The only plant that reported the performance of coagulation with regards to low molecular weight-neutrals [87] reported a 9% increase following coagulation.

Table 7 also presents the reported performance of coagulation steps regarding organic matter removal, such as CDOC, DOC, TOC and UV₂₅₄. Its general performance is rather low, ranging from -31% to 24%. It is worth noting that coupling ferric acid with hypochlorite did not impact the removal rate of TOC [104].

Overall, the reported low to moderate impact on algal content, biological parameters, NOM and organic matter removal is not surprising considering the treatment goals of a coagulation step. It is worth noting, though, the high potential for AOC removal reported in one study [104], by coupling the coagulant with hypochlorite. However, this result highlights that any chemical addition must be properly controlled to ensure no adverse downstream effects on the RO membranes which require very low feed levels of elements such as iron or aluminium and are degraded by the presence of chlorine.

5.3. Media filtration

Dual media filtration (DMF) is a ubiquitous part of SWRO treatment chains and therefore provides a wealth of literature references. DMF filters are generally designed with a layer of anthracite of 0.4-0.8 m over a sand bed of 0.8–1.2 m [96]. They are run at velocities that range from 8 to 15 m/h, depending on feedwater quality as well as treatment target. Dual media filtration is used to ensure that the particulate matter present in the water is properly removed ahead of the RO units, targeting such parameters as turbidity and SDI. However, they can also be designed in such a way as to optimise their biological activity or organic matter removal. In such a case, the filtration velocity will be low to increase the contact time in the filter and/or activated carbon media may be used to increase the media's adsorption capacity. The variety of design considerations as well as operational conditions (filtration/ backwash cycles) provide this type of treatment with a wide spectrum of responses which translated to a large heterogeneity of performances found in the literature. The removal performance of media filtration is summarized in Table 8. The full detailed data including operational conditions is presented in Table S.4.

Generally speaking, DMF units showed a positive impact on the various parameters that are considered important towards the risk of biofouling. The parameters that showed consistently lower removal efficiencies were TOC, DOC and UV₂₅₄. These parameters had maximal removals of 0.6 mg C/L for TOC and 2.8 m⁻¹ for UV₂₅₄, which are low and were found in waters with low organic loads. LC-OCD characterisation studies tended to show better performances in terms of organic removals, though it must be noted that studies that reported high removal rates essentially used DMF filters in a biologically active state. Other parameters tended towards the same conclusion, TEP for example showed an 84% removal [84] when using a GAC biofilter while another

Removal performance of dual media filtration.

| Parameter (unit) | Inlet value | Performa | nce | Reference |
|------------------------------------|-----------------------------|-----------------------------|-------------|------------------------------------|
| | | Quantity removed | Removal (%) | |
| AOC (µg C/L) | 1–150 | -40-120 | -200-99 | [21,22,84,87,104,108] |
| BGP (µg-C/L as glucose equivalent) | 106-327 | 14–144 | 8–55 | [10,44,52,89] |
| ATP (pg/mL) | 55-750 | 17-290 | 31-72 | [44,52,89,107] |
| Algae (cells/mL) | 81 | -6 | -7 | [97] |
| Total cell count (cells/mL) | $5.5\times10^460\times10^4$ | $1.6\times10^430\times10^4$ | 8-50 | [95,97,109] |
| Chlorophyll a (mg/m ³) | 0.16-0.3 | 0.14-0.25 | 48-88 | [102,103] |
| TEP (µg XG/L) | 33-414 | 19–211 | 6-84 | [84,95,102,103,110] |
| TOC (mg/L) | 1.7-6.4 | -0.2 -0.6 | -3-35 | [21,89,104,109,110] |
| DOC (mg/L) | 0.7–1.6 | 0-0.5 | 0–30 | [97,103,106,108,110] |
| $UV_{254} (m^{-1})$ | 0.7-13.5 | -0.2 - 2.8 | -2-21 | [97,104,111] |
| CDOC (µg/L) | 1180-1650 | 28-1140 | 2-69 | [52,84,85,87,89,97,107] |
| Biopolymers (µg/L) | 38-470 | 2–180 | 3-51 | [52,84,85,87,89,95,97,106-108,110] |
| Humic substances (µg/L) | 53-651 | -4-350 | -1-74 | [84,85,87,89,95,106–108] |
| Building blocks (µg/L) | 20-140 | -10-70 | -50-52 | [84,85,95,107] |
| LMW acids (µg/L) | 84–149 | -2-5 | -2-3 | [89,95] |
| LMW neutrals (µg/L) | 101–1080 | -84-220 | -83-63 | [85,87,95,107,108] |

study on AOC [22] showed that removals increased from 31 to 99% over 15 days of operations.

It should also be noted that some of the negative values observed in terms of performance (-200% for AOC, -50% for Building blocks) corresponded to studies where the inlet waters of the DMF of interest were of very good quality [104,107], meaning that the observed increase in value following filtration could easily be due to either slight releases of biological or organic material from the filter media into the water or simply to the error of measurement.

Overall, the literature provides ample examples of the significance of DMF units for SWRO treatment chains, though the large variation of observed removals tends to highlight that design selection and proper operation and maintenance is critical to optimising the process's performance.

5.4. Inline coagulation followed by DMF

Inline coagulation is sometimes used instead of full-scale coagulation, especially when the raw seawater is not particularly challenging regarding particulate and colloidal matter. It is generally coupled with DMF and enhances its capacity to remove organic matter. Tables 9 and S.5 present the removal performance of inline coagulation coupled with DMF consolidated from the literature.

The capacity of this coupled pretreatment step to remove algal content is reported to be quite important. The algal cell, bacteria count, the TEP, chlorophyll *a*, picoplankton and pigment content were shown to be removed from 70% to 100%. Only two exceptions can be noted;

one plant in Israel [102] removed only 17% of TEP, while another in the Middle East [47] removed only 25% of the total number of cells. However, these two mitigated results could be due to the very high inlet value reported in these two parameters, with 350 μ g XG/L of TEP reported in the first study and 2 \times 10⁶ cells/mL in the second, which are both much higher than the inlet values reported in the other plants.

The ATP, BGP and orthophosphates values reported in Abushaban et al. [10,52,89] showed a significant impact of inline coagulation and DMF. Indeed, the reported performance of the combined processes ranged from 22% to 60% removal, confirming the biological removal capacity of DMF units.

Concerning NOM removal, inline coagulation combined with DMF showed more mitigated results. The biopolymer removal capacity ranged from 11% to 50% in the five plants reported [10,52,89,101,110]. The humic substances and low molecular weight compounds removal rates results were more consistent, ranging from a few percentage points to 15%. Inline coagulation and DMF treatment thus appear to have a rather significant impact on biopolymers, but a low to insignificant impact on other NOM fractions.

Regarding the other organic matter parameters (DOC, CDOC, TOC and UV_{254}), inline coagulation followed by DMF treatment is reported to have a significant impact, with removal rates ranging from 9% to 68%. The high heterogeneity of these results seems to be linked to either higher inlet values, to low ferric dosage or to high filtration flow rates through the DMF.

DMF coupled to inline coagulation is reported to be quite performant regarding biological parameters, however, it seems less reliable with

Table 9

Removal performance of inline coagulation and DMF process.

| Parameter (unit) | Inlet value | Performance | | Reference |
|------------------------------------|--------------------------------|--------------------------------|-------------|----------------------|
| | | Quantity removed | Removal (%) | |
| BGP (µg-C/L as glucose equivalent) | 180-350 | 70–190 | 22–54 | [10,52,89] |
| ATP (pg/mL) | 75–385 | 45–325 | 60-84 | [52,89] |
| Algae (cells/mL) | 29 | 24 | 83 | [112] |
| Total cell count (cells/mL) | $3.3\times10^{5}2\times10^{6}$ | $2.3\times10^{5}5\times10^{6}$ | 25–70 | [47,92] |
| Chlorophyll a (mg/m ³) | 0.18-1.8 | 0.14-0.8 | 44–79 | [104,113] |
| TEP (µg XG/L) | 350 | 60 | 17–70 | [110,113] |
| TOC (mg/L) | 1.1–2.3 | 0.25-0.3 | 13-40 | [89,110,112,114] |
| DOC (mg/L) | NA | NA | 30 | [110] |
| UV_{254} (m ⁻¹) | 1.0-10 | 0.2–0.7 | 18-68 | [92,104,111,112,114] |
| CDOC (µg/L) | 1500-1673 | 143–200 | 9–17 | [10,52,89] |
| Biopolymers (µg/L) | 120–198 | 21–72 | 11-50 | [10,52,89,101,110] |
| Humic substances (µg/L) | 660 | 9 | 1–14 | [10,89] |
| LMW acids (µg/L) | 157 | 8 | 5–10 | [10,89] |
| LMW neutrals (µg/L) | | | 10 | [10] |
| Orthophosphate (μ g/L) | 1.7 | 0.6 | 35 | [89] |

more challenging inlet waters. It also shows a great potential to remove TEP and biopolymers, although it may not be appropriate for waters with high NOM and organic matter content.

5.5. Ultrafiltration

Ultrafiltration is a membrane-based pretreatment, generally designed to be installed either downstream of the media filtration step or in its stead. UF membranes have pore sizes ranging from 0.01 to 0.05 μ m (or less), and are therefore expected to remove turbidity, particulate and colloidal matter as well as algal cells very efficiently [24]. Studies reported here presented data for the UF unit on its own, without any upstream chemical addition such as coagulation.

Concerning algal content, the reported algal cells removal capacity of UF is indeed very high, reaching up to 96% [97]. Additionally, other cell counts (including non-algal cells) confirm the significant cell removal capacity of UF pretreatment, with 98% to 100% of total cell removal reported in three SWRO plants located in Saudi Arabia (Table S.6) [97,115,116]. On exception was another Middle East plant [104] which showed low UF performance, with only 21% removal of total cells. The capacity of UF pretreatment to remove TEP has been reported to be rather moderate, with 61% TEP removal reported in one study [101].

Studies reported varying degrees of success in the removal of biological parameters. On one hand, UF pretreatment does not seem to remove nutrients, with total nitrogen content shown to have remained stable throughout UF filtration [99]. On the other hand, UF pretreatment seems to have a significant impact on biological growth parameters, such as AOC and BGP, with heterogenous performances, ranging from 13% to 50% removal. The high performance of the pilot scale study [69] is worth noting: the UF pretreatment provided an 80% reduction of mBFR.

Regarding NOM removal, UF pretreatment is reported to have a dual impact: it is reported to remove 38% to 46% of biopolymers, but to have almost no impact on humic substances, building blocks and low molecular weight neutrals and acids, with reported removal capacities of 1% to 8% for each of these compounds. Furthermore, as reported in Table 10, levels of DOC, SUVA, TOC and UV_{254} remained stable throughout UF filtration.

The UF pretreatment's capacity to abate turbidity, particulate and colloidal matter, as well as living cells is reported to be very high,

Table 10

Removal performance of ultrafiltration.

| Parameter (unit) | Inlet value | Performance | | Reference |
|--|--|------------------|----------------|-------------|
| | | Quantity removed | Removal (%) | |
| AOC (µg C/L) | 20 | 10 | 50 | [21] |
| BGP (µg-C/L as glucose equivalent) | 183–330 | 23–130 | 13–39 | [10,48] |
| Algae (cells/mL) | 81 | 78 | 96 | [97] |
| Total cell count (cells/mL) | 19×10^{4} -60 $\times 10^{4}$ | 06×10^4 | 21–100 | [97,98] |
| TEP (µg XG/L) | 0.23 | 0.14 | 61 | [101] |
| TOC (mg/L) | 1.2 - 1.5 | 0-0.12 | 0–10 | [21,115] |
| DOC (mg/L) | 0.9 | -0.01-0.2 | -1-22 | [97,99] |
| $UV_{254} (m^{-1})$ | 0.6-0.7 | -0.2 - 0.2 | -33-29 | [97,99,115] |
| CDOC (µg/L) | 1180 | 108-133 | 9–12 | [48,97] |
| Biopolymers (µg/L) | 72–170 | 29-78 | 38-46 | [10,97,101] |
| Humic substances (µg/L) | NA | 28 | 7 | [10] |
| LMW acids (µg/L) | NA | 2 | 2 | [10] |
| LMW neutrals (µg/ L) | NA | 1 | 1 | [10] |
| Total Nitrogen (mg- N/L) | 0.15 | -0.01 | -7 | [99] |
| mBFR (pg/cm ² /d) | 40 | 32 | 80 | [69] |

reaching above 95% removal in most cases. Its capacity to remove biopolymers is reported to be moderate (38% to 46% removal) but concerning other NOM substances and organic matter in general, its impact is low to non-existent (<10% removal in the vast majority of reviewed SWRO plants).

5.6. Cartridge filtration

Cartridge filtration (CF) is a critical component of SWRO plants and is used directly upstream of the RO membrane units as a final safety barrier to prevent particulate matter from reaching the RO feed. This barrier is particularly critical to maintaining a constant water quality as required by membrane suppliers, generally requiring water that corresponds to an SDI measurement below 3 [24].

Tables 11 and S.7 present the data for the removal of the various parameters of interest. The stand-out result from the consolidation of this data is that the use of cartridge filtration not only yields highly variable results but often increases the risk of biofouling in the water it treats. This can be potentially due to the release of foulants through the injection of antiscalant which often happens upstream of these filters, might also have an impact if the chemical used contains bioavailable nutrients.

Cartridge filtration would be expected, when running properly, to provide a barrier to bacterial presence while having little to no impact on any dissolved nutrients. This translates fairly well with the higher removal performances observed for total cell counts (96%) or ATP (50%) while AOC, DOC, TOC and UV₂₅₄ had low to negative removal values. However, almost all the parameters studied showed potential significant increases following CF.

This result highlights that CF operations is a critical element for biofouling reduction in SWRO plants. If not regularly maintained, these units represent a high risk for increasing biofouling potential of the RO feedwater. When operating properly, it does appear that such units have a positive impact on the water quality above that of being a barrier for particulate matter, though it is unclear what the mechanism or operational conditions are that allow for this.

6. Biofouling potential in SWRO feedwater

The SWRO feedwater quality is the most crucial element in the biofouling occurrence of SWRO systems and thus in the operation of SWRO membrane systems; high biofouling potential of SWRO feedwater leads to a short operating period with frequent maintenance and a shorter SWRO membrane lifespan [25]. Despite the fact that the quality of SWRO feedwater should be significantly improved over that of raw seawater, many SWRO desalination plants have experienced an increase in biofouling potential in the SWRO feedwater due to the addition of chemicals such as antiscalant and/or dichlorination [43,47,52,87,89]. This increase varies depending on the type and concentration of the added antiscalant. The lowest increase in biofouling potential (1.3%) was reported by Jeong et al. [87] in the AOC concentration of the Perth desalination plant, while Abushaban et al. [89] reported a 37% increase in BGP and orthophosphate concentration of a full-scale desalination plant in the Middle East. Tables 12 and S.7 present the reported values of different biofouling potential parameters in SWRO feedwaters and highlights that these can be significantly higher than the reported values in the inlet of cartridge filters (Table 11). This observation implies that special attention should be given to all chemicals added to the pretreatment, particularly antiscalants, regardless of the effectiveness of the pretreatment of SWRO membrane systems.

7. Controlling biofouling of SWRO using biofouling potential indicators

Even though the above-mentioned biofouling potential indicators have not been standardised yet, a few attempts to determine threshold

Removal performance of cartridge filtration.

| Parameter (unit) | Inlet value | Performance | | Reference |
|------------------------------------|----------------------------|------------------------------|-------------|---------------------------|
| | | Quantity removed | Removal (%) | |
| AOC (µg C/L) | 2–33 | -110 | ≪0–66 | [21,87,104] |
| BGP (µg-C/L as glucose equivalent) | 92–235 | -54-45 | -37-32 | [10,44,52,89] |
| ATP (pg/mL) | 17-460 | -180-19 | -39-50 | [44,52,89,107] |
| Total cell count (cells/mL) | $3\times10^4150\times10^4$ | $-2.3\times10^432\times10^4$ | -25-96 | [92,95,101,109] |
| Chlorophyll a (mg/m ³) | 0.02 | 0 | 0 | [102] |
| TEP (µg XG/L) | 42–161 | -17-3.4 | -30-8 | [95,102] |
| TOC (mg/L) | 1.1-6.2 | -0.1-0.34 | -7-31 | [21,89,92,104,109] |
| DOC (mg/L) | 0.68 | -0.42 | -62 | [106] |
| UV_{254} (m ⁻¹) | 1.7–13 | -0.5-0.34 | -5-20 | [92,104] |
| CDOC (µg/L) | 1100-1320 | -100-50 | -9-4 | [52,87,89,107] |
| Biopolymers (µg/L) | 6–140 | -30-10 | -42-17 | [52,89,93,95,106,107,116] |
| Humic substances (µg/L) | 120-635 | -92-13 | -15-8 | [87,89,95,106,107] |
| Building blocks (µg/L) | 30-119 | 5–12 | 0–15 | [95,106] |
| LMW acids (µg/L) | 62–144 | 3–5 | 3–8 | [89,95] |
| LMW neutrals (µg/L) | 133–1040 | -30-83 | -4-45 | [87,95,107] |

Table 12

Biological fouling potential in SWRO feedwater and overall removal in the pretreatment of different seawater desalination plants.

| Parameter | Water quality | Overall removal in pretreatment (%) | Reference |
|--|---------------------|-------------------------------------|----------------------|
| AOC (µg C/L) | 10-210 | -1.5-95% | [21,87,90,104] |
| BGP (µg-C/L as glucose equivalent) | 55–280 ^a | 40–80% | [10,44,46,48,89] |
| mBFR (pg/cm ² /d) | 1.4-106 | 80–99% | [88,117] |
| TEP (µg XG/L) | 20-400 | -10-68% | [91,117] |
| Orthophosphate (µg/ L) | 1.1–10 | 25-81% | [89,91] |
| TOC (mg/L) | 0.9–6 | 3–38% | [21,89,104,114,117] |
| DOC (mg/L) | 0.9–1.6 | 12-15.6% | [53,87] |
| CDOC (mg/L) | 1.2 - 1.7 | 16.5-28.3% | [52,89] |
| $UV_{254} (m^{-1})$ | 0.11-0.63 | 52-68% | [104,114] |
| Biopolymers (µg/L) | 8–187 | -50-70% | [52,53,87,89,91,117] |
| Humic substances (µg/L) | 361–2672 | 0–34% | [53,87,89,91] |
| Building blocks (µg/ L) | 1.32–1162 | -10-12% | [53,87,91] |
| LMW neutrals (µg/L) | 490-4694 | -67-19% | [53,87,91] |
| LMW acids (µg/L) | 12–267 | -7.3-95% | [53,89,91] |

 $^{\rm a}\,$ Up to 950 µg-C/L as glucose equivalent during algal bloom.

values of AOC, BGP and mBFR have been made at full-scale and pilot desalination plants for the purpose of controlling SWRO biofouling.

7.1. Assimilable organic carbon

The relationship between AOC in SWRO feedwater and biofouling of SWRO membrane systems at the Tampa Bay seawater desalination pilot plant was studied by Weinrich et al. [104], in which AOC in the SWRO feedwater ranged between 22 and 161 μ g-C/L. Within nine days of operation, differential pressure increased by 77% (from 3.5 to 6.2 bar) and specific flux decreased by 22%. A significant correlation was found between differential pressure and AOC concentrations measured in the SWRO feedwater. Accordingly, a preliminary threshold concentration of AOC (50 μ g-C/L) was proposed using *Vibrio harveyi* bacteria in seawater [90].

7.2. Bacterial growth potential

The use of BGP to control biofouling of SWRO membrane system was investigated by Abushaban et al. [89]. The BGP in SWRO feedwater and the normalised pressure drop/permeability of a full-scale desalination plant located in the Middle East were monitored for six months. Results showed that higher BGP (from 100 to 950 μ g-C/L as glucose equivalent)

corresponded to a higher normalised pressure drop, suggesting the applicability of using BGP as a biofouling indicator in SWRO systems. Moreover, findings demonstrated that BGP of 100 μ g-C/L as glucose equivalent may still be sufficient to cause biofouling in SWRO membrane systems as it led to a significant increase in the normalised pressure drop within three months.

Furthermore, the relationship between BGP in the SWRO feedwater and CIP frequency of SWRO membrane systems was investigated based on the results of four desalination plants. It was estimated that a BGP value of 70 μ g-C/L as glucose equivalent in the SWRO feedwater requires a frequency of one CIP per year [43,46]. Consequently, a safe level of BGP (below 70 μ g-C/L as glucose equivalent) was preliminarily proposed to control biofouling in SWRO desalination plants.

7.3. Membrane biofilm formation rate

The relationship between mBFR and pressure differential was explored in two SWRO pilot plants fed with the same raw seawater, in which the intake of one pilot plant was chlorinated with 1 mg/L of sodium hypochlorite [117]. Results showed that pressure differential was constant for six months when mBFR in the SWRO feedwater ranged between 1.4 and 7.3 pg/cm²/day (no chlorination), whereas pressure differential increased significantly from 0.04 to 0.12 MPa when chlorination was added and mBFR ranged between 26 and 106 $pg/cm^2/day$. The increase in biofouling potential (when chlorination was added) is attributed to the breakdown of large organic matter fractions present in seawater to smaller and more biodegradable forms of organic matter. Moreover, Kurihara and Ito [67,118] observed a correlation between mBFR of the SWRO feedwater and the chemical cleaning interval based on the results of six SWRO desalination plants. Accordingly, it was proposed to lower the mBFR in SWRO feedwater to $<10 \text{ pg/cm}^2/\text{day}$ in order to ensure a chemical frequency of once or twice per year.

Table 13

Threshold concentrations of biofouling potential indicators in SWRO feedwater.

| Parameter | Criteria | Reference |
|----------------|---|-------------|
| AOC | <50 µg-C/L | [24,90,104] |
| BGP | $BGP < 70 \ \mu g$ -C/L as glucose equivalent, one CIP per year (or less) frequency | [43,46] |
| mBFR | <10 pg/cm ² /day | [67,118] |
| Orthophosphate | <0.3 µg-PO ₄ -P/L | [50] |
| TOC | Biofouling is unlikely when TOC $< 0.5 \text{ mg/L}$ | [119–122] |
| | Biofouling is very likely when $TOC > 2 \text{ mg/L}$ | |
| SUVA | If SUVA <2, high potential of algal bloom in raw seawater and high possibility of biofouling. If SUVA>4 biofouling is unlikely. | [121,123] |

7.4. Other indicators

In addition to the previous research findings, other guidelines of biofouling potential indicators were also proposed to control biofouling in SWRO membrane systems. These guidelines were recommended based on operational experience or by membrane manufacturers. The full summary of these guidelines is listed in Table 13. It is worth mentioning that all of these recommendations are still not standardised guidelines.

8. Future perspectives

Reliable indicators for measuring and predicting the biological fouling potential of SWRO feedwater are important in preventing and diagnosing biological fouling at the design stage, and for monitoring pretreatment performance during plant operation. Besides reliability, robustness of the methods, fast results and low costs are relevant for any method to be successful in end-user adoption. A clear link between the reported values and the impact of these values on SWRO operation is necessary.

Most of the indicators for assessing biofouling in desalination systems have mainly been used for research purposes, applied intermittently or during short testing campaigns, with results taking various days to various weeks to be obtained, and with significant costs for application. An ideal method for assessing biofouling should demonstrate a clear link with RO performance over time, the methodology and procedure should be robust, with a low limit of detection and with a short processing time for obtaining the results. Other aspects are also important such as: availability and cost of consumables, corrosion resistance of the equipment, cleaning and calibration that can be performed on-site by plant operators, automated procedure, etc.

The challenge of biofouling assessment needs to be addressed by all involved parties, namely: desalination plant designers, plant operators and managers, membrane manufacturers, researchers and scientists, and by professionals from various backgrounds including engineers, marine biologists, chemists, and environmentalists, to name a few. The research and development groups of the public and private sector should work together towards a method or product that is able to measure the biofouling potential of water in a short period of time, with a low limit of detection (as for pre-treated water), with relatively low consumables costs (as for being used frequently by plant operators), and able to provide meaningful information to plant operators. An online device that could provide fast and reliable values is an ideal case.

Most of the indicators to date have been focusing on either monitoring biomass or monitoring nutrients present in the water. Examples of such techniques are flow cytometry and ATP used to measure the biofouling potential of water, and assimilable organic carbon. In the last years, we have seen advances in other fields such as metagenomics and the application of techniques such as CRISPR, LC-QTOF in characterisation at the molecular level of living cells and organic matter. Metagenomics may offer another door to tackle the challenge of biofouling development in full scale desalination plants by identifying bacterial populations that may be responsible for biofilm development.

Can the design of plants be improved for controlling biofouling? What can be done differently? Plants with beach well intake structures suffer the least from biofouling in comparison with plants with open intake structures. This may be related to both the physical removal of biomass and nutrients but also to bacteria present in the beach wells degrading assimilable organic matter. Unfortunately, beach wells cannot be applied everywhere, nor should they be.

Are bacterial communities on membrane surfaces the same as those present in the SWRO feedwater? The bacterial community on SWRO membrane biofilms represents a smaller proportion of the bacterial community in seawater. The operational conditions in the plant (intake, pretreatment steps, chemicals addition) and also the increase of salinity on the membranes are likely to influence the selection of a subgroup of seawater bacteria [124]. This finding should influence the type of inoculum used in biofouling potential methods but also in pretreatment technologies that could be tailor-made for removal of specific bacterial types.

9. Conclusions

Biofouling of SWRO membranes is still the most complex operational problem in membrane-based desalination. To control biofouling in SWRO systems, several strategies have been employed including monitoring biofouling potential during the pretreatment and in SWRO feedwater. This paper addressed the known biofouling potential indicators and how they have been applied to assess the pretreatment of SWRO desalination plants and to control biofouling of SWRO membrane systems. The following is a list of the major conclusions of this paper:

- Several new growth potential bioassays were developed to assess and understand the potential of bacterial growth in seawater. The developed AOC and BGP methods in seawater are using the same concept with a few notable differences.
- Raw seawater quality plays a significant role in the biofouling potential of SWRO feedwater and thus in the control of biofouling in SWRO membranes.
- In general, low to moderate removal efficiency of biofouling potential during SWRO pretreatment was reported. However, media filtration coupled with coagulation showed good removal of biofouling potential when media filtration is designed with longer contact time to enhance organic biodegradation.
- Higher biofouling potential was observed in SWRO feedwater due to chemical addition such as dichlorination and antiscalant dosing which contains biodegradable organic matter.
- Several attempts have been made to correlate biofouling potential of SWRO feedwater to biofouling in SWRO membranes and threshold values have been proposed for biofouling risk limitation. However, additional research is needed to ensure the reliability of these threshold values.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2021.115543.

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