Seawater reverse osmosis desalination and (harmful) algal blooms

Loreen O. Villacorte, S. Assiyeh Alizadeh Tabatabai, Donald M. Anderson, Gary L. Amy, Jan C. Schippers, Maria D. Kennedy

HIGHLIGHTS
• A review of harmful algal blooms (HAB) from the perspective of desalination.
• Discussion on the impact of HABs on seawater reverse osmosis (SWRO) desalination.
• State-of-the-art of pretreatment technologies for SWRO during HABs.
• Review of indices to quantify effects of HABs on SWRO and pretreatment efficiency.
• Future outlook on pretreatment with regards to HABs and growth of SWRO application.

GRAPHICAL ABSTRACT

This article reviews the occurrence of HABs in seawater, their effects on the operation of seawater reverse osmosis (SWRO) plants, the indicators for quantifying/predicting these effects, and the pretreatment strategies for mitigating operational issues during algal blooms. The potential issues in SWRO plants during HABs are particulate/organic fouling of pretreatment systems and biological fouling of RO membranes, mainly due to accumulation of algal organic matter (AOM). The presence of HAB toxins in desalinated water is also a potential concern but only at very low concentrations. Monitoring algal cell density, AOM concentrations and membrane fouling indices is a promising approach to assess the quality of SWRO feedwater and performance of the pretreatment system. When geological condition is favourable, subsurface intake can be a robust pretreatment for SWRO during HABs. Existing SWRO plants with open intake and are fitted with granular media filtration can improve performance in terms of capacity and product water quality, if preceded by dissolved air flotation or sedimentation. However, the application of advanced pretreatment using ultrafiltration membrane with in-line coagulation is often a better option as it is capable of maintaining stable operation and better RO feed water quality during algal bloom periods with significantly lower chemical consumption.

© 2015 Elsevier B.V. All rights reserved.
1. Background

Seawater reverse osmosis (SWRO) is currently the leading and preferred technology for seawater desalination [43]. The main drawback for cost-effective application of SWRO is membrane fouling [14, 54, 113]. The accumulation of particulate and organic material from seawater and biological growth in membrane modules frequently cause operational problems in SWRO plants. To reduce the (in)organic load of colloidal and particulate matter reaching RO membranes and to minimize or delay associated operational problems, pretreatment systems are generally installed upstream of the RO membranes. Most SWRO plants, especially in the Middle East, install coagulation followed by granular media filtration (GMF) to pre-treat seawater. However, in recent years, low pressure membrane filtration is increasingly being used as SWRO pretreatment.

Over the years, it is becoming more evident that microscopic algae are a major cause of operational problems in SWRO plants [36, 171]. The adverse effect of algae on SWRO started to gain more attention during a severe “red tide” bloom incident in the Gulf of Oman in 2008–2009 (Fig. 1). This “red tide” (hereafter termed as harmful algal bloom or HAB) forced several SWRO plants in the region to reduce or shutdown operation [134] due to clogging of pretreatment systems (mostly GMF) and/or due to unacceptable RO feed water quality. The latter have triggered concerns of irreversible fouling problems in RO membranes which eventually led to shutdown of some plants [22, 111, 118, 134]. This incident highlighted a major problem that algal blooms may cause in countries relying largely on SWRO plants for their water supply, and underlines the importance of adequate pretreatment in such systems.

This article reviews the typical dynamics of (harmful) algal blooms in marine environment, their effects on the operation of seawater reverse osmosis (SWRO) plants, the indicators for quantifying/predicting these effects, and the pretreatment strategies for mitigating operational issues in SWRO plants during algal blooms.

2. Marine algal blooms

All life in the sea depends on the primary producers — the marine algae and other microorganisms that convert CO2 into the biomass that forms the base of the marine food web (Fig. 2). Phytoplankton (floating or swimming marine algae) are a diverse group of organisms comprised of thousands of species. Each has a set of environmental conditions that favour growth and proliferation, and thus there is a continuous succession of species through time in a given area. These are termed “blooms”, and can range from dilute suspensions of cells to dense accumulations that can make the water appear discoloured. Algal blooms are critical to many aspects of marine ecology as well as to human society’s utilisation of marine resources. There are, however, also negative impacts from algal blooms, as detailed in succeeding sections.

2.1. Causative factors

The growth and accumulation of individual algal species in a mixed assemblage of marine organisms are exceedingly complex processes involving an array of chemical, physical, and biological interactions [11]. Given the diverse array of algae from several different classes that cause problems in a variety of oceanographic systems, attempts to
generalize the bloom dynamics of bloom-forming species are doomed to failure. Some common mechanisms can nevertheless be highlighted.

In addition to sunlight, the distribution and concentration of algae in the ocean can be greatly influenced by natural physico-chemical variations (e.g., temperature, current, salinity, nutrient load, etc.; [146]). Nutrients such as nitrogen (N), phosphorus (P) and silicon (S) and many trace metals and vitamins are among the most important of these factors, with two major sources — natural and anthropogenic. Natural phenomena such as storm events can increase river discharges of nutrients to the sea while strong winds can induce mixing and transport of nutrients from the lower water column to the surface where they can be utilised by algae [152,165]. Coastal upwelling, which is driven by the combination of wind, the Coriolis effects, and Ekman drift, is a major factor for the transport of nutrients from the bottom of the sea

Fig. 1. A massive “red tide” algal bloom in the Gulf of Oman spreading to the ‘The Gulf’ as illustrated in this enhanced image based from the satellite image obtained by the European Space Agency MERIS FR satellite on 22 November 2008. The ocean is represented using an RGB combination (bands 9, 5, 3) that emphasises the surface-intensified bloom of Cochlodinium polykrikoides (red). The blue–white colours indicate regions dominated by suspended sediments or shallow waters. Image processed by R. Kudela. Yellow points indicate locations of major SWRO plants in the area. Inset images are screenshots of online news regarding SWRO plant shutdown due to HABs in the region in 2008 and 2013 (www.arabianbusiness.com).

Fig. 2. Typical average annual distribution of algae based on chlorophyll-a concentration in large water bodies on earth. This figure was modified from the composite map generated by Gledhill and Buck [61] based on the Aqua MODIS chlorophyll composite for year 2009 (http://oceancolor.gsfc.nasa.gov/cgi/).
to the surface [15,107]. Wind-driven dust events carrying iron-rich aerosols from the Sahara Desert have been reported to influence the frequency and severity of algal blooms on the Florida coast, on the other side of the Atlantic [184]. A similar scenario may have occurred after dust events around the Yellow Sea [148] and ‘The Gulf’ [69,112].

Human activities can also contribute to algal blooms by increasing nutrient loadings in coastal seawater through direct/indirect discharge of un/poorly-treated wastewater and run-off of untreated livestock wastes and residual fertilisers from agricultural areas. Increased incidence of HABs has been shown to have substantial correlation with growing human populations, and with higher fertiliser use and livestock production [7,146]. Many regions in the world that have implemented stricter environmental regulations to limit anthropogenic nutrient discharges to rivers have observed localised reduction in algal blooms, as in the case of the Seto Inland Sea in Japan [114].

2.2. Harmful algal blooms (HABs)

Virtually every coastal country in the world can be affected by HABs (commonly called “red tides”). This diverse array of phenomena includes blooms of toxic microscopic algae that lead to illness and death in humans, fish, seabirds, marine mammals, and other oceanic life (reviewed in [11]). There are also non-toxic HABs that cause damage to ecosystems, fisheries resources, and to commercial and recreational facilities, often due to the sheer biomass of the accumulated algae. The term “HAB” also applies to non-toxic macroalgae (seaweeds), which can cause major ecological impacts such as the displacement of indigenous species, habitat alteration and oxygen depletion in bottom waters, or societal impacts such as the fouling of beaches and disruption of recreational and commercial activities, including intake of water for cooling or desalination. The frequency, spatial extent, and economic impact of HABs have all expanded in recent decades, in parallel with, and sometimes a result of, the world’s increasing exploitation on the coastal zone for shelter, food, recreation, and commerce [8,11,67].

A common misconception is that HABs are caused by the explosive growth of a single species that rapidly dominates the water column. It is only necessary, however, to have conditions that favour the growth and dominance of a moderately large population of a given species, and the proper hydrographic and meteorological conditions to permit the accumulation of those organisms. In other words, winds, tides, currents, fronts, and other features can create discrete patches of cells of blooms of red water at all scales. In some cases, however, HAB species are able to form nearly mono-specific blooms, benefitting from mechanisms such as grazer avoidance (through swimming, migration patterns, or even cell morphology, for example), or the inhibition of other, competing phytoplankton species, such as through the release of allelopathic substances (see reviews in [38,92]).

HABs in temperate and high latitudes are predominantly spring, summer, and fall phenomena. Some commonly occur during periods when heating or fresh water runoff creates a stratified surface layer overlying colder, nutrient rich waters. This situation favours dinoflagellates and other motile algae, as they are able to regulate their position and access nutrients below the pycnocline. Some of the motile HAB species can swim at speeds in excess of 10 m per day, and some undergo marked vertical migration, in which they reside in surface waters during the day to harvest the sunlight and then swim to the pycnocline and below to take up nutrients at night. This strategy can explain how dense accumulations of cells can appear in surface waters that are devoid of nutrients and which would seem to be incapable of supporting such prolific growth. This vertical migration is a factor of concern to desalination facilities, where intakes might see episodic pulses of algal cells during the daily migrations near intakes.

Horizontal transport of blooms is also an important feature of many HABs, often over hundreds or even thousands of kilometres. Major toxic outbreaks can suddenly appear at a site due to the transport of established blooms from other areas by ocean currents. Advance warning of imminent outbreaks is thus possible with the appropriate tools (e.g., satellite optical sensors and numerical forecast models).

2.2.1. Causative species

All phytoplankton bloom, in the sense that they increase and decrease in abundance through time, are typically preceded and followed by blooms of other species. Some species, however, are noted for their ability to form dense blooms, typically because of the harm those accumulations of cells can cause. About 60–80 species out of ~300 bloom-forming algal species have been reported to cause HABs [150]. Some of these are listed in Table 1 to provide an example of the range of species, cell sizes, cell concentrations, and impacts, but there are many more species that are not listed. There is a wide variety of marine bloom-forming algae, with sizes that range from 2 to 2000 μm. Depending on the species, severe or harmful marine algal blooms can occur with cell concentrations from few thousands cells per ml to several hundred thousand cells per ml.

2.2.2. Toxic blooms

HAB phenomena take a variety of forms, with multiple impacts. One major category of impact occurs when toxic phytoplankton are filtered from the water as food by shellfish which then accumulate the algal toxins to levels which can be lethal to humans or other consumers. The poisoning syndromes have been given the names paralytic, diarrhetic, neurotoxic, amnesic, and azaspiracid shellfish poisoning (Table 2). Therapeutic intervention is primarily limited to symptomatic treatment and life support.

The toxins produced by some HAB species are among the most potent natural poisons known [166]. Saxitoxin, for example, is 1000 times more potent than cyanide, and 50 times stronger than curare. Many of the toxin classes are not single chemical entities, but instead represent families of compounds of similar chemical structure. A single species typically produces multiple derivatives or congeners within a toxin family. Humans are exposed to algal toxins principally by consumption of contaminated seafood products, although several types of toxin (brevetoxin and palytoxin) also cause respiratory asthma-like symptoms because of aerosol formation due to wave action. An emerging concern is the potential for HAB toxins to be retained in treated water during desalination operations, though several studies indicate that >99% removal can be achieved through pretreatment (e.g., [45]) or through direct thermal or reverse osmosis operations [89]. Acute single-dose lethality of seafood toxins has been extensively studied, but chronic and/or repeated exposure to low toxin concentrations, which might be the case with low levels of toxin in desalinated water, has not been adequately examined.

2.2.3. Non-toxic blooms

Non-toxic blooms of algae can cause harm in a variety of ways. One prominent mechanism relates to the high biomass that some blooms achieve. When this biomass begins to decay as the bloom terminates, oxygen is consumed, leading to widespread mortalities of all plants and animals in the affected area. These types of blooms are sometimes linked to excessive pollution inputs, but can also occur in relatively pristine waters.

Another impact from high-biomass blooms is the disruption of desalination operations, as discussed in detail in this work. One example is the massive *Cochlodinium polykrikoides* bloom in the Gulf of Oman in 2008/2009 that affected a large number of RO desalination plants, closing some for as long as two months not because of toxins but mainly due to operational problems caused by the high load of algal cells and algal-derived mucilage in the intake seawater [134]. Other dinoflagellate species, such as *Gonyaulax hyaline/fragilis* (e.g., [100]), are also known to secrete large amounts of mucilage in culture and have been identified as the major cause of massive production of mucilage at some events in New Zealand and the Mediterranean Sea. The diatom *Cylindrotheca closterium* has been linked to major mucilage events in the Northern
Adriatic Sea, stimulated by nutrient loadings from the Po and other rivers [133]. Large standing stocks of phytoplankton build up and extracellular polymers, mainly polysaccharides, accumulate in the stratified water column. Some of the mucilage outbreaks formed by phytoplankton populations have been linked to high N/P ratios and increased stratification in coastal waters, and thus are at least partially reflective of human perturbations to the nutrient balance of coastal waters [40].

### Table 1

Typical characteristics of selected bloom-forming species of microscopic algae and cyanobacteria (blue–green algae) and their recorded bloom concentrations in natural marine environment.

<table>
<thead>
<tr>
<th>Group</th>
<th>Bloom-forming species</th>
<th>Cell shape</th>
<th>Cell size µm</th>
<th>Algal concentration&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Potential impact to marine environment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dinoflagellates</td>
<td><em>Alexandrium spp.</em></td>
<td>RE</td>
<td>25–32</td>
<td>7000 –</td>
<td>Toxins</td>
<td>Selina et al. [145]</td>
</tr>
<tr>
<td></td>
<td><em>Cocchlidium polykrikoides</em></td>
<td>RE</td>
<td>20–40</td>
<td>48,000 –</td>
<td>Toxins, hypoxia</td>
<td>Kim [83]</td>
</tr>
<tr>
<td></td>
<td><em>Karenia brevis</em></td>
<td>RE</td>
<td>20–40</td>
<td>37,000 –</td>
<td>Toxins, hypoxia</td>
<td>Tester et al. [162]</td>
</tr>
<tr>
<td></td>
<td><em>Noctiluca scintillans</em></td>
<td>Sp</td>
<td>200–2000</td>
<td>1900 –</td>
<td>Hypoxia</td>
<td>Fonda-Umani et al. [56]</td>
</tr>
<tr>
<td></td>
<td><em>Procentrum spp.</em></td>
<td>FE</td>
<td>30–60</td>
<td>70,000 – 200 –</td>
<td>Hypoxia</td>
<td>Taş and Oktay [158]</td>
</tr>
<tr>
<td>Diatoms</td>
<td><em>Chamaeceros spp.</em></td>
<td>OC</td>
<td>8–25</td>
<td>30,100 – 14 –</td>
<td>Hypoxia</td>
<td>Booth et al. [31]</td>
</tr>
<tr>
<td></td>
<td><em>Pseudo-nitzschia spp.</em></td>
<td>PP</td>
<td>3–100</td>
<td>19,000 –</td>
<td>Toxins, hypoxia</td>
<td>Anderson et al. [6]</td>
</tr>
<tr>
<td></td>
<td><em>Skeletolemma costatum</em></td>
<td>Cy</td>
<td>2–25</td>
<td>88,000 –</td>
<td>Hypoxia</td>
<td>Shikata et al. [149]</td>
</tr>
<tr>
<td></td>
<td><em>Thalassiosira spp.</em></td>
<td>Cy</td>
<td>10–50</td>
<td>28,000 – 100 –</td>
<td>Hypoxia</td>
<td>Maier et al. [101]</td>
</tr>
<tr>
<td>Haptophytes</td>
<td><em>Emiliania huxleyi</em></td>
<td>Sp</td>
<td>2–6</td>
<td>115,000 –</td>
<td>Hypoxia</td>
<td>Berge [21]</td>
</tr>
<tr>
<td></td>
<td><em>Phaeocystis spp.</em></td>
<td>OC + 0.5 Sp</td>
<td>4–9</td>
<td>52,000 –</td>
<td>Hypoxia</td>
<td>Janse et al. [81]</td>
</tr>
<tr>
<td>Raphidophytes</td>
<td><em>Chattonella spp.</em></td>
<td>Co</td>
<td>0.5 + Sp</td>
<td>10,000 –</td>
<td>Toxins, hypoxia</td>
<td>Orlova et al. [116]</td>
</tr>
<tr>
<td></td>
<td><em>Heterosigma akashiwo</em></td>
<td>Sp</td>
<td>15–25</td>
<td>32,000 –</td>
<td>Toxins, hypoxia</td>
<td>Shikata et al. [149]</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td><em>Nodularia spp.</em></td>
<td>Cy</td>
<td>6–100</td>
<td>605,200 –</td>
<td>Toxins, hypoxia</td>
<td>McGregor et al. [102]</td>
</tr>
</tbody>
</table>

Legend: RE = rotational ellipsoid; Sp = sphere; FE = flattened ellipsoid; OC = oval cylinder; PP = parallelepiped; Cy = cylinder; Co = cone; O2 = dissolved oxygen.

<sup>a</sup> Equivalent geometric dimensions and size range of algal cells based on Olenina et al. [115].

<sup>b</sup> Maximum recorded concentrations reported in reference literature.

2.2.4. Macro-algal blooms

Over the past several decades, blooms of macroalgae (seaweeds) have been increasing along many of the world’s developed coastlines. Macroalgal blooms occur in nutrient-enhanced estuaries and nearshore areas that are shallow enough for light to penetrate to the sea floor. These blooms have a broad range of ecological and societal effects, and often last longer than phytoplankton blooms [10].

Table 2 presents data on the molecular size of the major HAB toxins, and all can be seen to be large enough to be removed routinely by RO membranes. However, it is now clear that algal species can produce organic toxins that pass through pretreatment processes, forming gels or polymers (e.g., transparent exopolymeric particles or TEPs; [23]) or extracellular polymeric substances (EPS; [52]) that are either the direct or indirect cause of organic and/or biofouling in RO membranes. These are discussed in detail in Section 3.0. These compounds can be seriously disruptive, particularly to those plants that use RO to produce fresh water. Since economic considerations are leading to a proportional expansion in RO desalination plants compared to those that use thermal processes, it can be expected that many more impacts of HABs on desalination facilities will arise than have been recorded thus far. It is thus very likely that species that are not generally considered harmful to other sectors of society will be harmful to these plants because they produce disproportionately large amounts of dissolved organic materials. Eventually, a list of species that are prolific producers of harmful organic compounds (that are not toxins) will be generated and used by desalination plant operators to plan mitigation strategies. Table 2 is an example of such a listing with a focus on toxin-producing species, and Table 1 for HABs in general.

Yet another interesting change in the perception of what is harmful comes from countries that are heavily dependent on their coastal waters for aquaculture and capture fisheries, particularly those with very dense operations such as in China, Japan, Korea, and other Asian countries. Here we are seeing a distinction being made between HABs and FABs or “favourable algal blooms” as countries are recognizing that phytoplankton biomass needs to be at a relatively high level to support such
operations [9]. In this sense, algal blooms, even dense, high biomass ones, can be considered beneficial, and thus efforts to reduce pollution or other nutrient inputs as a general bloom mitigation strategy may not be supported by certain sectors of society, such as fishermen. One wonders if this view of favourable, high-biomass algal blooms will become more prevalent as countries and agencies worldwide are under increased pressure to maximize coastal fisheries productivity to feed their growing populations [9], placing two sectors of society (the fishing and desalination industries) at cross purposes.

2.3. Algal organic matter (AOM)

The natural organic matter (NOM) present in the aquatic environment is a mixture of diverse organic compounds originating from both autochthonous (local input) and allochthonous (external input) sources [91]. Algae are a major source of autochthonous NOM in the Earth’s oceans, accounting for about half the organic matter input [51]. These algal-derived substances are collectively known as algal (or allogenic) organic matter (AOM).

Algal blooms, especially diatom blooms, are often responsible for the highest annual pulses of AOM production in the ocean [33]. Algal blooms (harmful or non-harmful) produce various forms and differing concentrations of AOM comprising mainly polysaccharides, proteins, lipids, nucleic acids and other dissolved organic substances [26,41,55,109]. Myklestad [109] highlighted the significance of extracellular polysaccharides as they may comprise >80% of AOM production. A significant fraction of these exopolysaccharides are highly surface-active and sticky and has been suspected to play a major role in the aggregation dynamics of algae during bloom events [106,109].

There are two types of AOM, namely: (1) organic substances released during the metabolic activity of algae known as extracellular organic matter (EOM) and (2) substances released through autolysis and/or during the process of cell decay, termed intracellular organic matter (IOM). Algal cells excrete EOM mostly in response to nutrient stress and other unfavourable conditions (e.g., light, pH and temperature) or invasion by bacteria or viruses [55,95,108]. EOM substances can be either discrete or remained attached (bound) to the algal cell as coatings. Discrete EOMs often contain mainly polysaccharides and tend to be more hydrophilic while bound EOM contain more proteins and tend to be more hydrophobic [130]. On the other hand, IOMs comprise mainly low molecular weight polymers released from the interior of compromised, dying or deteriorating cells, which sometimes carry toxins, and taste and odour compounds [46,97]. Considering the conditions of how they are released, the contribution of IOM to the total AOM production is expected to increase during the stationary-death phase of an algal bloom.

2.3.1. Marine mucilage

Marine mucilage is a phenomenon characterized by the appearance of a sporadic but massive accumulation of gelatinous material at and below the water surface [93]. It is generally a result of excessive production of EOM during an algal bloom in response to low nutrient (P, N, Si) concentrations below the water surface [93]. It is generally a result of excessive production by diatoms (e.g., 

2.3.2. Transparent exopolymer particles (TEPs)

High molecular weight, hydrophilic, anionic muco-polysaccharides and glycoproteins, are essential components of marine mucilage. Such substances are collectively known as transparent exopolymer particles (TEPs; see review by [122]). During an algal bloom, TEPs mainly originate from algal-derived IOM and/or EOM components. Generally, TEPs are highly heterogeneous, both physically and chemically. Their volume and stability largely depends on environmental conditions while their chemical composition is known to be highly variable depending on the species releasing them and the prevailing growth conditions [122].

The observed size range of TEPs is typically 5 to 200 μm as they oftentimes comprise an integral part of marine snow-sized aggregates >500 μm [4,123]. Although TEPs were operationally defined as particles (>0.40 μm), they are believed to form from much smaller colloidal polymers (TEP pre-cursors), perhaps fibrils as small as 1–3 nm in diameter and up to 100 s of nm in length [94,121].

In many aspects of particle dynamics in aquatic systems, TEPs have been associated with the natural coagulation and sedimentation of suspended particles [122,125]. They are known to be highly flexible and sticky, which might explain their tendency to aggregate into large flocs and to adhere to other materials [106]. Their relative stickiness was reported to be 2–4 orders of magnitude higher than most suspended particles in natural waters [122]. Because of their adhesive characteristic, TEPs can accumulate on solid–liquid interfaces and facilitate adsorption of suspended particles, including bacteria. The adsorbed and suspended TEPs can be colonised, degraded and may later serve as a substrate for bacteria [4,123]. Recently, Berman and co-workers proposed a “revised paradigm” of aquatic biofilm formation facilitated by TEPs emphasising the important role of TEPs in the conditioning and bacterial colonisation of surfaces (including reverse osmosis membranes) exposed to seawater [16,20,24,25]. The “revised paradigm” is illustrated and explained in detail in Fig. 3.

3. Impact of algal blooms on SWRO

Caron et al. [36] identified two potential impacts of (harmful) algal blooms on SWRO desalination facilities,

1) Significant treatment challenge to ensure the SWRO system is effectively removing algal toxins from seawater;
2) Operational difficulties due to increased total suspended solids and organic loading resulting from algal biomass in the raw water.

The presence of algal toxins during marine algae blooms is a major concern, since some of these toxins are highly potent neurotoxins [10,11]. Studies on HAB toxin removal by RO are scarce and limited to laboratory bench-scale studies. These suggest that 99% removal can be achieved with RO membranes [28,89] or nanofiltration (e.g., [45]). Given the typical molecular weight size range of marine algal toxins of 0.3–0.9 Da (Table 2), RO is expected to be effective in rejecting these compounds. The adequacy of these rejection levels cannot be justified, as data from operational plants during toxic HABs is not available. The fact that some taste and odour compounds can pass through pretreatment and RO membranes may suggest that some of the smaller HAB toxins might do likewise, albeit in low concentrations. Although there are some WHO guidelines on freshwater algal toxins (e.g., microcystins), no WHO regulations are established for marine HAB toxins in drinking water.
High algal biomass in raw water can cause operational problems in RO membranes. During filtration of algal bloom-impacted waters, particulate matter comprising algal cells, their detritus and AOM – if not effectively removed by the pretreatment process – can accumulate to form a heterogeneous and compressible cake layer on the surface of SWRO membranes. This may result in lower normalised flux and higher feed channel pressure drop, eventually leading to substantial loss of permeability. Considering the lower flux and higher operating pressure in SWRO, the direct relative impact of AOM accumulation on its operational performance is expected to be less severe compared to MF/UF systems. However, the accumulated sticky substances may initiate or promote particulate and biological fouling by enhancing deposition of bacteria and other particles from the feed water to the RO membrane and spacers [24,188].

It is common knowledge that bacteria can adhere, accumulate and multiply in RO systems resulting in the formation of a slimy layer of dense concentrations of bacteria and their extracellular polymeric substances known as biofilm. When the accumulation of biofilm reaches a certain threshold that operational problems are encountered in the membrane system, it is considered as biological fouling or “biofouling” [53,113]. An operational problem threshold can be a significant (e.g., >15%) decrease of normalised membrane flux or increase in net driving pressure and/or an increase in feed channel pressure drop. In the Middle East, about 70% of the seawater RO installations were reported to be suffering from biofouling problems [59]. Generally, biofouling is only a major problem in NF/RO systems because periodic backwashing and chemical cleaning in dead-end MF/UF systems allows regular dispersion or removal of most of the accumulated bacteria from the membrane; thereby inhibiting the formation of a biofilm.

Biofilm accumulation can be accelerated during algal blooms due to higher AOM concentration in seawater [172]. Some AOM components, specifically TEP, are characteristically sticky which make them likely to adhere and accumulate on the surface of the membranes and spacers. The accumulated TEP can serve as a “conditioning layer” – a good platform for effective attachment and initial colonisation of bacteria – where bacteria can effectively utilise biodegradable nutrients from the feed water [24,188]. Furthermore, TEP can be partially degraded and may later serve as a substrate for bacterial growth [4,123]. As illustrated in Fig. 3, TEP (and their pre-cursors) and protofilms (suspended TEP with extensive microbial outgrowth and colonisation) in surface water can initiate, enhance and possibly accelerate biofilm accumulation in RO membranes.

Since bacteria require nutrients for energy generation and cellular biosynthesis, essential nutrients such as biodegradable or assimilable organic carbon (BDOC or AOC), phosphates and nitrates can be the main factors dictating the formation and growth of biofilm. During the peak of an algal bloom, some of these essential nutrients may be limited (e.g., phosphate) due to uptake by algae. However, when the bloom reaches a death phase, algal cells start to disintegrate and release some of these nutrients. Hence, biofouling initiated/enhanced by AOM may likely occur within a period of time after the termination of an algal bloom.

4. Pretreatment technologies for SWRO

To control fouling, most SWRO plants are equipped with one or more pretreatment systems. Pretreatment normally involves a form of filtration and other physical–chemical processes to remove suspended solids (particles, silt, algae, organics, etc.), oil and grease from the source water [186]. Pretreatment is generally categorized as primary pretreatment, consisting of coagulation in combination with a clarification process such as sedimentation or dissolved air flotation (DAF); and secondary pretreatment, consisting of a filtration process. Secondary pretreatment is classified as conventional when granular media filters (GMF) are applied and advanced when micro- and ultrafiltration (MF/UF) membranes are used. The different pretreatment options and process schemes applicable to SWRO are illustrated in Fig. 4.

4.1. Intake systems

The intake system will have a significant influence on the quality of seawater coming into the SWRO desalination plant and therefore dictates the design of the pretreatment system. Currently, majority of SWRO plants operate with an open intake system, which means the pretreatment processes should be designed to handle variations in raw seawater quality while meeting the desired SWRO feed water quality. Over the recent years, various plants have been installed with subsurface intakes to improve the quality of seawater entering the SWRO plant and ultimately reduce process complexity of pretreatment systems in terms of design and operation.

Subsurface intake systems may include wells (vertical, angle, and radial) and galleries, which are either installed on the beach area or in the seabed (see [105]). This type of intake makes use of the natural geological properties of the coastal area to allow seawater to travel slowly through layers of sediments, sands and rocks, providing filtration and possibly active biological treatment before they enter the SWRO plant [104]. Such processes can substantially remove suspended solids, algae, bacteria, and dissolved organic carbon in seawater during algal blooms and therefore reduce the foulant load on the succeeding pretreatment processes [42,105].

Installing subsurface intakes are favourable in coastal and near shore areas where the geological formation comprises permeable rocks, carbonates (limestones and/or dolomites), sand or gravel but they are often unfeasible in areas with low permeability rocky or muddy shoreline [105]. An example of successful large scale application of subsurface intake is the Fukuoka seawater desalination plant in Japan where seabed galleries (103,000 m3/day capacity) of intake pipes were installed to extract seawater (with retention time of ~7 h) followed by UF pretreatment in front of the RO system as illustrated in Scheme 1 in Fig. 4. The capital costs for installing subsurface intakes can be slightly to significantly higher than in open-ocean intake systems, but significant savings in the operational cost of SWRO plant can be expected in the long term [105].
4.2. Primary pretreatment

4.2.1. Coagulation

Coagulation is commonly applied in conventional pretreatment systems, i.e., sedimentation/flotation followed by GMF to improve process performance in terms of turbidity removal and surface loading rates. Coagulation can significantly reduce the average particle size that can be removed by conventional GMF, e.g., as small as 0.2 μm for well operating filters [180]. Mixing intensity and time are essential parameters in the design and operation of coagulation systems [27]. Mixing is accomplished in inline or full-scale mode. Inline coagulation is the application of a coagulant without removal of coagulated flocs through a clarification step. Inline coagulation may also be characterized by the absence of a flocculation chamber [154]. Hence, in most inline coagulation applications, coagulation is achieved by dosing the coagulant prior to a static mixer (for conventional GMF) or directly in the feed line (prior to feed pump of UF membranes). Flocculation is either achieved through in-pipe flocculation or in a flocculation chamber. Flocculation may not be required in UF applications, as enlarging particle size is not an objective and pin-sized flocs are sufficient to enhance UF operation [155]. Various modes of coagulant application and subsequent processes are presented in Fig. 5.

Ferric salts, particularly ferric chloride, are the best choice for seawater coagulation [49]. While aluminium sulphate and polyaluminium chlorides (PACls) have been studied in laboratory and pilot-scale works for RO pretreatment of seawater [58], they are not used in full-scale plants. The primary reason is because of the relatively high solubility of aluminium, which could be carried over to RO membranes leading to precipitative scaling — particularly as aluminium silicate [57]. Ferric chloride is less soluble over a wider pH range, leaving less residual dissolved iron in the water after pretreatment and thus avoiding scaling problems. Furthermore, ferric chloride has a high ratio of cationic charge to total mass [80] that makes hydrolysis products more reactive and adsorptive with emulsified and semi-emulsified organic matter; e.g., oil and grease, natural and synthetic organic matter. The settled sludge volume of the ferric hydroxide formed from ferric chloride is reportedly 30–60% that of sulphate based coagulants (e.g., Fe₂(SO₄)₃). Additionally, the sludge developed from ferric chloride is generally much more dewaterable [35].

4.2.2. Sedimentation

Sedimentation is commonly used upstream of GMF and MF/UF systems to reduce the solids load reaching these systems; typically when feed water has daily average turbidity higher than 30 NTU. For feed waters with very high turbidity (> 100 NTU), conventional sedimentation basins may not be adequate to produce water with low silt and algal content and enhanced solids removal may be required through e.g., lamella plate modules [180]. In the absence of sedimentation, large turbidity spikes may cause GMF to exceed their solids handling capacity, resulting in lower production capacity, shorter filter runs, frequent backwashing and poor permeate quality. Sedimentation basins for seawater pretreatment are typically designed to produce settled water of less than 2.0 NTU and SDI₁₅ below 6 [180]. Enhanced sedimentation technologies that combine lamella plates and fine granular media are used for feed water from open ocean intakes with high turbidity. These technologies allow for high solids removal at high rates (e.g., > 40 m/h).

4.2.3. Dissolved air flotation (DAF)

DAF is a clarification process that can be used to remove particles prior to conventional media filtration or MF/UF systems. Raw water is dosed with a coagulant, typically at concentrations lower than those applied for sedimentation, followed by two-stage tapered flocculation. Removal is achieved by injecting the feed water stream with water that has been saturated with air under pressure and then releasing the air at atmospheric pressure in a flotation tank. As the pressurized water is released, a large number of micro-bubbles are formed (approximately 30–100 μm) that adhere to coagulated flocs and suspended matter causing them to float to the surface where they may be removed by either a mechanical scraper or hydraulic means, or a combination thereof. Clarified water is drawn off the bottom of the tank by a series of lateral draw-off pipes (Fig. 6). Conventional DAF systems operate at nominal
hydraulic loading rates of 5–15 m/h. More recent high rate DAF units are developed for loadings of 15–30 m/h and greater [48].

DAF is suitable for removal of low-density particles that can float, e.g., algal cells, oil and grease, which are not effectively removed by sedimentation or filtration. As such, for handling difficult waters such as algal bloom impacted seawater, incorporating DAF prior to media filtration has been proposed [10]. Flotation is able to reduce the concentration of algal cells to a large extent, protecting media filters from rapid clogging, reduced capacity, and breakthrough. A coagulant dose of 1–2 mg Fe(III)/L or higher is usually required to render the process effective. Additional coagulant might be dosed just before feeding the DAF ef fluent to downstream granular media filters to ensure an acceptable SDI in the RO feedwater. In most DAF units, coagulation concentrations of up to 20 mg/L as FeCl₃ are reported [90,137]. However, storm events that affect water quality may result in substantially higher coagulant concentrations for DAF [90]. Additional coagulant dosage is often required in GMF units downstream of DAF. Installing flotation units in front of media filtration might be cheaper than conventional sedimentation units, as the surface loading rates in high-rate DAF systems can reach 30 m/h resulting in smaller footprint. However, additional equipment is required for air saturation and diffusion, treated flow recirculation, sludge skimmers, etc. of which add to cost and complexity of the overall process.

Several DAF plants in the Netherlands and Great Britain are primarily used for treatment of algal-laden waters [64,99,169]. A review paper on separation of algae by Henderson et al. [72,73] reports DAF removals of 96% to 99.9% when pretreatment and DAF are optimised. In SWRO pretreatment, DAF prior to dual-stage GMF was tested during early pilot testing for the Taweelah SWRO plant in Abu Dhabi, UAE [137]. DAF was suggested to enhance the robustness of the pretreatment scheme in case of oil spills or HAB events, or in case high coagulant concentrations were required during turbidity spikes. Algal cell concentrations were reportedly below 100 cells/mL during this period, which is far below concentrations observed during severe bloom conditions (tens of thousands of cells per mL). Sanz et al. [140] demonstrated the effectiveness of DAF coupled with coagulation prior to dual stage GMF in producing RO feed water with SDI < 4 (typically less than 3) when treating seawater containing various algae, including HAB species. The
authors reported more than 99% removal of total algae after DAF and first stage filtration units. Total cell concentration of various algal species in the feed water was not specified.

The severe HAB event in 2008–2009 in the Gulf of Oman that led to the shutdown of several desalination plants in the region redirected the attention of the desalination industry to DAF as part of SWRO pretreatment schemes. Although the Fujairah 2 desalination plant was still under construction during that period, a pilot plant was fitted with a DAF unit in the pretreatment system continued to operate throughout the red tide bloom [118]. In the Al-Dur plant in Bahrain, more than 99% removal of algal cells was reported during pilot testing of AquaDAF™ combined with coagulation prior to GMF [90]. However, significant bloom conditions were not encountered during the pilot phase with algal cell counts reaching only 200 cells/mL in feed water. The Al-Shuwaikh desalination plant in Kuwait equipped with DAF/UF as pretreatment consistently provided SDI < 2.5 for good quality feed water and < 3.5 for deteriorated conditions during a HAB event [120]. Bloom conditions as measured by cell counts, chlorophyll-a concentrations and/or TEP were not reported for this facility. DAF is now being regularly incorporated in new SWRO plants in the Persian Gulf upstream of GMF or MF/UF. Expansion of the Fujairah plant incorporates DAF as an essential part of the pretreatment scheme [185].

4.3. Secondary pretreatment

4.3.1. Granular media filtration (GMF)

Conventional pretreatment systems for SWRO were developed based on existing technology and most commonly consist of conventional media filtration. Single or dual stage granular media filters comprising sand and anthracite (garnet is sometimes used) are typically applied in conventional pretreatment systems, in gravity or pressurized configuration. Sand and anthracite (0.8–1.2 mm/2–3 mm) filter beds are superior to single media filtration in that they provide higher filtration rates, longer runs and require less backwash water. Anthracite/ sand/garnet beds operate at normal rates of approximately 12 m/h and peak rates as high as 20 m/h without loss of effluent quality. In SWRO pretreatment, the primary function of GMF is to reduce high loads of particulate and colloidal matter (i.e., turbidity).

GMF relies on depth filtration to enhance RO feed water quality. However, when high concentrations of organic matter or turbidity loads are encountered, coagulation is required to ensure that RO feed water of acceptable quality is produced (SDI < 5). Coagulation is applied either in full scale or inline mode in these systems. Coagulation aggregates particulate and colloidal matter in water and can therefore shift filtration mechanism from depth filtration to surface straining (cake filtration). As filtration rates are relatively high (5–10 m/h) in media filters, cake filtration can result in exponential head loss in the filters.

Poor removal of algae can lead to clogging of granular media filters and short filter runs. While diatoms are well-known filter clogging algae, other algae types can clog filters including green algae, flagellates, and cyanobacteria [48]. During the severe HAB event in the Gulf of Oman and ‘The Gulf’ in 2008–2009, conventional pretreatment systems were not able to maintain production capacity at high algal cell concentrations of approximately 27,000 cells/mL [134]. Operation of the media filters was characterized by rapid clogging rates, deteriorating quality of pretreated water, and frequent backwashing, resulting in higher system downtime and reduced capacity [118,141].

At the Fujairah plant in UAE, filter runs were reduced from 24 to 2 h. Reducing filtration rate by 50% can lower the rate of clogging, e.g., by a factor 2–4 depending on the size and characteristics of the foulants. However, higher surface area of the media filters was required to maintain production capacity, resulting in significant investment costs and large footprint of the pretreatment system. Deteriorating quality of the pre-treated water (SDI > 5) at this plant, led to higher coagulant dose required to enhance treated water quality. Increasing coagulant dose may lead to higher clogging rates of media filters as explained above. One way to enhance operation of GMF during such extreme events is to provide a clarification step, e.g., sedimentation or filtration after coagulation/flocculation to reduce the load of particulate/colloidal matter (including coagulated flocs) on the media filters.

The product water of granular media filters can be highly variable over time, with reported algae and biopolymer (algal-released organic macromolecules) removal efficiencies in the range of 48–90% and 17–47%, respectively [129,138].

4.3.2. Ultrafiltration (UF)

Over the last decade, UF membranes have been tested and applied at pilot and commercial scale as pretreatment for SWRO [32,60,62,68,136,167,189] and are reported to offer several advantages over conventional pretreatment systems; namely, lower footprint, constant high permeate quality (in terms of SDI), higher retention of large molecular weight organic, lower overall chemical consumption, etc. [127,187]. Successful piloting has led to the implementation of UF pretreatment in several large (>100,000 m³/day) SWRO plants [34], e.g., Adelaide, Ashdod.

Depending on the driving force for filtration, UF membranes are divided into pressurized and vacuum-driven systems. Both outside–in and inside–out configurations are applied in SWRO pretreatment. The application of UF in SWRO pretreatment is considered a more reliable alternative to conventional GMF (with or without coagulation), as UF membranes are generally more effective in removing particulate and colloidal matter from seawater. As such, they are expected to be more reliable in producing low fouling potential RO feed water even during a HAB event. However, Voutchkov [180] reported that in a submerged vacuum-driven UF system, a driving vacuum higher than 0.4 bar can cause disruption of soft-walled algal cells resulting in the release of easily biodegradable dissolved intracellular substances which might be detrimental to the operation of downstream SWRO. So far, such issue has not been reported nor verified in pressure-driven UF systems.

To the best knowledge of the authors, there is no publicly available literature on the performance (i.e., hydraulic operation and permeate quality) of outside-in membranes in SWRO pretreatment during periods of algal bloom. From published literature, inside-out UF membranes were reported to experience some degree of fouling during algal blooms [44,143,144]. High concentrations of AOM present during a severe algal bloom in the North Sea impaired operation of UF membranes (Fig. 7) at a pilot desalination facility in the Netherlands, resulting in CEBs as frequent as once in 6 h. Under such conditions, coagulant was dosed to control hydraulic performance of UF membranes [143,144]. With optimised inline coagulation, operation was stabilised at relatively low doses of ferric chloride (<1 mg Fe/L) during the bloom period.
Very high numbers of algal cells present in the feed water during algal blooms can adversely affect operation of inside-out UF membranes by:

- depositing along the length of the membrane capillary,
- depositing primarily at the capillary entrance, and
- depositing primarily at the capillary dead-end.

Theoretically, small particles deposit uniformly along the capillary length whereas larger particles tend to deposit primarily near the capillary dead-end [96,117]. This indicates that inside-out UF systems may be clogged at the capillary dead-end with algal cells and associated AOM, resulting in higher flux at the capillary inlet (assuming that the parts of the capillary with algae and AOM deposition are no longer permeable). Villacorte [172] demonstrated that even at very high numbers, algal cell deposition does not severely limit membrane permeability. Heijman et al. [70,71] demonstrated that larger particles might plug the entrance of capillaries. However, applying microscreens with openings smaller than 150–300 µm, which is the current practice, can reduce capillary plugging.

So far, a few studies have investigated the effect of algal blooms on operation of UF membranes [84,87,143,144,172]. These studies agree on the notion that large macromolecules (e.g., biopolymers such as polysaccharides and proteins) produced by algae are the main cause of membrane fouling, and more so than the algal cells as particles. AOM which comprise high molecular weight biopolymers (polysaccharides and proteins) often including sticky TEP [109,174] may cause organic/particulate fouling in UF membranes. TEP can absorb/retain water by up to ~95% of their dry weight while allowing some water to pass through [13,170]. Consequently they can bulk-up to more than 100 times their solid volume and squeeze through and fill-up the interstitial voids between the accumulated solid particles (e.g., algal cells) on the surface of the membrane. It is therefore expected that accumulation of these materials can provide substantial resistance to permeate flow during membrane filtration. In addition, as TEP can be very sticky, they may strongly adhere to the surface and pores of UF membranes, rendering hydraulic cleaning [backwashing] ineffective (Fig. 8a). This scenario has been reported in recent studies (e.g., [130,131,143,144,177,178]), signifying that AOM does not only cause pressure increase during filtration but can also increase non-back washable or physically irreversible fouling in dead-end UF systems.

Coagulation can reduce the adverse effects of AOM on UF operation by reducing the fouling potential and compressibility of AOM layers on the membrane surface (Fig. 8b). This is mainly achieved through partial complexation of algal biopolymers and formation of colloidal Fe–biopolymer complexes at low coagulant dose (< 1 mg Fe/L) and adsorption of algal biopolymers onto and enmeshment in iron hydroxide precipitates forming Fe–biopolymer aggregates at coagulant dose of 1 mg Fe/L and higher [157]. Coagulation of AOM – comprised mainly of hydrophilic, non-UV absorbing polysaccharides – may be governed by mechanisms that are different from coagulation of NOM (i.e., aromatic humic substances). Tabatabai [156] showed that pH did not play a strong role in the coagulation efficiency of AOM in terms of biopolymer removal.

Furthermore, coagulation applied in different modes can enhance the backwashability of sticky AOM layers deposited on the surface of UF membranes [156]. However, if not optimised, coagulation may deteriorate long-term UF operation. Unreacted iron species (monomers, dimers, trimers, etc.), ferrous iron and manganese – present in low-grade coagulants – can foul UF membranes by adsorbing on the membrane surface or within the pores, resulting in gradual irreversible fouling of UF membranes that will require chelation with cleaning solutions based on e.g., ascorbic and oxalic acids to release fouling.

Although extensive operational experience on HABs of different types and severities is not available, it may be proposed that inside-out pressure driven UF membranes are more capable of handling HAB events than conventional GMF. This may be attributed to significant differences in hydraulic operational parameters of the two systems. An overview of operational parameters for GMF and UF is presented in Table 3. Filtration rate fluxes in GMF can be up to 100 times higher than flux rates in UF systems, while total filtered volume prior to backwash may be 2000 times higher. Thus, low filtration rates together with more frequent backwashing favours better UF system performance during algal blooms. Coagulation may be required to stabilise hydraulic performance of UF membranes during severe HAB events.

### 5. Algal bloom indicators for quantifying pretreatment efficiency

Monitoring membrane fouling potential of raw and pre-treated water is important in SWRO plants, especially during algal bloom periods, in order to develop preventive/corrective measures for the potential adverse impacts to RO membranes. Various indicators have been proposed to assess the magnitude of the bloom and the effectiveness of the pretreatment systems. The most relevant indicators/parameters,
namely: algae, biopolymer and TEP concentration and membrane fouling potential, are discussed in the following sections. A review of recent studies on the performance of various pretreatment technologies in terms of reduction of such indicators is presented in Table 4.

5.1. Algae concentration

The magnitude of algal blooms is usually measured either in terms of cell abundance or chlorophyll-a concentration — the former giving an indication of the relative abundance of individual species, while the later is a bulk measure that includes many different, co-occurring algal species. Bloom-forming algae of different species can vary substantially in terms of cell size and chlorophyll-a content. Hence, the relationship between these two parameters also varies. Typical bloom cell concentrations are higher for smaller algae compared with larger algae (see Table 1). To compensate for the size differences, cell concentration can be expressed in terms of volume fraction (total cell volume per volume of water sample) instead of cell number per volume of water. Operationally, this is difficult to calculate, as it requires conversion factors on the cell volume of each species that might be encountered.

Ideally, the pretreatment systems of an SWRO plant should effectively remove algal cells to prevent clogging in RO channels. As shown in Table 4, algae removals in granular media filters (GMF) are highly variable (48%–90%) as compared to more stable and much higher removal efficiencies by MF/UF membranes (>99%). High algal removals (>75%) were also reported for sedimentation and DAF treatments. Cartridge filters, which are typically installed after the pretreatment processes and before the SWRO system, have comparable removal with GMF.

Although algal cell and chl-a concentrations are the main indicators of an algal bloom, these parameters are not sufficient indicators of the fouling potential of the water. Different bloom-forming species of algae can behave differently in terms of AOM production and at which stage of their life cycle AOM materials are released. More advanced parameters that better indicate the concentration of AOM in feed water and the fouling potential attributed to the presence of AOM are therefore necessary, some good examples of which are discussed in the succeeding sections.

5.2. Biopolymer concentration

AOM released by different species of algae may widely vary in terms of size and composition [73]. Recently, it has been demonstrated that the application of size exclusion chromatography, specifically liquid chromatography–organic carbon detection (LC–OCD) technique, allows the quantification of the different size and functional components of AOM in algal bloom-impacted waters [157,174,177]. LC–OCD is a semi-quantitative technique to subdivide the pool of organic matter in a water sample into six major sub-fractions which could be assigned to specific classes of compounds based on their retention time through a chromatogram column (see [76]). The high molecular

![Fig. 8. Graphical presentation of membrane fouling in UF system (a) operated during severe algal blooms and (b) fouling mitigation with optimised inline coagulation.](image)

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Operational parameters for ultrafiltration and media filtration typically applied in SWRO pretreatment. Adapted from [141].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pores [μm]</strong></td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>Filtration rate [L/m² h]</td>
<td>50–100</td>
</tr>
<tr>
<td>Run length [h]</td>
<td>1</td>
</tr>
<tr>
<td>Ratio backwash rate: filtration rate</td>
<td>2.5</td>
</tr>
<tr>
<td>Backwash time [min]</td>
<td>1</td>
</tr>
<tr>
<td>Filtered volume/m² per cycle [L]</td>
<td>50–100</td>
</tr>
<tr>
<td>Pressure loss [bar]</td>
<td>0.2–2</td>
</tr>
</tbody>
</table>
**Reported treatment efficiencies of various treatment processes based on selected algal bloom indicators.**

<table>
<thead>
<tr>
<th>Treatment type</th>
<th>Water source</th>
<th>Treatment condition/remarks</th>
<th>Reduction or removal efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Algae</td>
<td>Biopolymers</td>
</tr>
<tr>
<td>a Subsurface intake</td>
<td>W. Mediterranean Sea</td>
<td>Beach well</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vertical beach wells</td>
<td>&gt;99</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Horizontal wells</td>
<td>77</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>N. Pacific ocean</td>
<td>Infiltration gallery</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Red Sea (Jeddah)</td>
<td>Vertical beach wells</td>
<td>&gt;99</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Oman Gulf</td>
<td>Vertical beach wells</td>
<td>&gt;99</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>N. Atlantic (Turks &amp; Caicos)</td>
<td>Vertical beach wells</td>
<td>&gt;99</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>N. Atlantic (Canary Is.)</td>
<td>Well intake</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Dissolved air flotation</td>
<td>W. Mediterranean Sea</td>
<td>Coag. = 0–6 mg FeCl3/L</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lake water</td>
<td>Coag. = 7–12 mg FeCl3/L</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>River water (Meuse)</td>
<td>Coag. = 4 mg FeCl3/L</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Algae-spiked freshwater</td>
<td>Coag. = 12 mg Al2O3/L</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Algal culture (saline water)</td>
<td>Coag. = 60 mg FeCl3/L</td>
<td>50–60</td>
<td></td>
</tr>
<tr>
<td>Sedimentation</td>
<td>Lake water</td>
<td>Coag. = 90 mg FeCl3/L</td>
<td>87–93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Algal culture (freshwater)</td>
<td>Coag. = 0.7–3 mg Al/L</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Algae-spiked freshwater</td>
<td>Coag. = 20–24 mg FeCl3/L</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Algal cultures</td>
<td>No coagulation</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 0.5 mg FeCl3/L</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 5 mg FeCl3/L</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 10 mg FeCl3/L</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>b Granular media filtration</td>
<td>E. Mediterranean Sea</td>
<td>Rapid sand filter (no coag.)</td>
<td>76 ± 13</td>
<td>51 ± 27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. + mixed bed filter</td>
<td>90 ± 8</td>
<td>27 ± 19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. (1 mg Fe2(SO4)3/L + RSF</td>
<td>79 ± 8</td>
<td>17 ± 28</td>
</tr>
<tr>
<td></td>
<td>W. Mediterranean Sea</td>
<td>Press. GMF ('anthracite-sand)</td>
<td>74</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. + dual media filter</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N. Mediterranean Sea</td>
<td>Anthracite-sand; 1.5 mg Fe3+/L</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Estuarine (brackish)</td>
<td>Coag. + continuous sand filter</td>
<td>17</td>
<td>65</td>
</tr>
<tr>
<td>Micro-/Ultra-filtration (MF/UF)</td>
<td>W. Mediterranean Sea</td>
<td>PVDF; nom. pore size = 0.1 μm</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lake water</td>
<td>PVDF membrane</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Algal culture</td>
<td>PVDF; pore size = 0.02 μm</td>
<td>99</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Algae-spiked freshwater</td>
<td>PVDF; 0.03 μm</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Red Sea</td>
<td>PVDF; 0.01 μm</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>c Micro-/Ultra-filtration (MF/UF) (cont’d.)</td>
<td>Oman Gulf</td>
<td>Ceramic; pore size = 0.08 μm</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>North Sea</td>
<td>PES 300 kDa 0.5 mg Al3+/L</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Seawater (Sydney)</td>
<td>MWCO = 17.5 kDa</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Algae-spiked seawater</td>
<td>Ceramic; pore size = 0.03 μm</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Estuarine (brackish)</td>
<td>No coagulation</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Algae-spiked freshwater</td>
<td>PVC; nom. pore size = 0.01 μm</td>
<td>100</td>
<td>52–56</td>
</tr>
<tr>
<td></td>
<td>Algal cultures</td>
<td>No coagulation</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lake water</td>
<td>PES; MWCO = 100 kDa</td>
<td>65–83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>River water</td>
<td>RC; MWCO = 10 kDa</td>
<td>83–95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>No coagulation</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 0.5 mg Fe3+/L</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 5 mg Fe3+/L</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 10 mg Fe3+/L</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 0.7 mg Fe3+/L</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 0.5 mg FeCl3/L</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 5 mg FeCl3/L</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coag. = 10 mg FeCl3/L</td>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>

(continued on next page)
weight fractions are classified as biopolymers. When coupled with an organic nitrogen detector (OND), this fraction can be further divided to estimate the polysaccharide and protein components. The low molecular weight fractions (<1 kDa) are sub-classified into humic-like substances, building blocks, low molecular weight acids, and neutrals. Considering that the high molecular weight AOM are likely to deposit/accumulate in the RO system, measuring the biopolymer fraction of organic matter in the water is a promising indicator of organic and biological fouling potential of algal bloom impacted waters. Although not proven via LC-OCD analysis, one would expect biodegradable/assimilable low molecular weight acids to contribute to the biological fouling as well. However, a recent study showed that algal-derived organic material extracted from 3 species of bloom-forming algae mainly comprise biopolymers (>50%) while some species also produce substantial amounts of refractory low molecular weight organic compounds which is considered not readily biodegradable [172,174].

As shown in Table 4, biopolymers in seawater can be totally removed through sub-surface intake (specifically vertical beach wells) treatment but substantial removals (>50%) by UF and coagulation-sedimentation–filtration were reported as well. Coagulation followed by granular media filtration typically removes less than 50%. Although very limited information is available regarding biopolymer removal by DAF, removal of more than 70% was reported in freshwater [172].

5.3. TEP concentration

TEPs are a major component of the high molecular weight fraction (biopolymers) of AOM. As discussed in previous sections, these materials are potentially a major cause of organic fouling in UF and biological fouling in RO systems. Over the last two decades, various methods have been developed to measure TEP by microscopic enumeration [4] or by spectrophotometric measurements [12,124,164,173]. The most widely used and accepted method was introduced in 1995 by Passow and Alldredge. This method was based on retention of TEP on 0.4 μm polycarbonate membrane filters and subsequent staining with Alcian blue dye. The reported TEP reduction by different pretreatment processes based on this method are summarised in Table 4. MF/UF can completely remove TEP while subsurface intake systems, GMF, DAF and cartridge filters can remove 34–92%, 17–100%, >70% and 47–82% of TEP, respectively.

Although they are operationally defined as particles larger than 0.4 μm, TEPs are not solid particles, but rather agglomeration of particulate and colloidal hydrogels which can vary in size from few nanometres to hundreds of micrometres [121,170]. Hydrogels are highly hydrated and may contain more than 95% of water, which means they can bulk up to more than 100 times their solid volume [13,170]. A majority of these materials are formed abiotically through spontaneous assembly of colloidal polymers from algae known as TEP precursors [39,121]. These submicron precursors (<0.4 μm), which have similar chemical properties with TEP but not covered by the current established method (i.e., [124]), may agglomerate and form TEP in the RO system after passing through the pretreatment system. Recently, an improved TEP method was developed to cover this previously neglected colloidal fraction and allow better measurement of the efficiency of the pretreatment processes in preventing TEP fouling in RO membranes [173].

5.4. Particulate/organic fouling potential

There are two established methods to measure the particulate/or- ganic fouling potential of RO feed water, namely; the silt density index (SDI) and the modified fouling index (MFI). Currently, the SDI is the most widely used method to measure the fouling potential of the feed water in SWRO plants. It is based on measurements using membrane filters with 0.45 micrometre pores at a pressure of 210 kPa (30 psi). Although this simple technique is currently widely used in practice, it has been known for many years that SDI has no reliable correlation with the concentration of particulate/colloidal matter [2]. Hence, it is often insufficient in predicting the fouling potential of SWRO feed water.

A more reliable approach to measure the membrane fouling potential of RO feed water is the modified fouling index (MFI). Unlike SDI, MFI is based on a known membrane fouling mechanism (i.e., cake filtration). This index was developed by Schippers and Verdouw [142] whereby they demonstrated the linear correlation between the MFI and colloidal matter concentration in the water. Initially, MFI was measured using membranes with 0.45 or 0.05 μm pore sizes and at constant pressure. However, it was later found that particles smaller than the pore size of these membranes most likely play a dominant role in particulate fouling. In addition, it became clear that the predictive value of MFI measured at constant pressure was limited. For these reasons, MFI test measured at constant flux with ultra-filtration membranes (MFI-UF) was eventually developed over the last decade [29,30,193]. A comparison of the reduction of fouling potential as measured by MFI-UF in pretreatment systems is presented in Table 4. In general, UF membranes are superior over GMF in terms of MFI-UF reduction.

5.5. Biological fouling potential index

Measuring biological fouling potential of RO feed water is rather complicated. Over the years, multiple parameters have been proposed as indicators of biofouling potential, namely: adenosine triphosphate (ATP), assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC) [5,182]. So far, these parameters are mainly applied in non-saline waters and still not extensively used in seawater RO plants. Furthermore, inline monitors such as the biofilm monitor and membrane fouling simulator (MFS) have been introduced to measure biofilm formation rate [182,183]. Meanwhile, Liberman and Berman [98] proposed a set of tests to determine the microbial support capacity of water samples, namely chlorophyll-a, TEP, bacterial activity, total bacterial count, inverted microscope observations of settled water samples, biological oxygen demand (BOD), total phosphorous and total nitrogen. Further investigations are needed to assess the reliability of these parameters/monitors to predict the biofouling potential of algal bloom impaired seawater.

6. Strategies to control operational issues in SWRO plants during algal blooms

Regardless of their location, SWRO plants can be adversely affected by algal blooms (see Figs. 2 and 9). Therefore, it is important to establish a robust monitoring programme to measure potential impact of algal blooms and to assess the effectiveness of the pretreatment system in
preventing fouling in SWRO. Measurement of algal bloom indicators (see Section 5.0) can be performed on a routine basis and with higher frequency in seasons when algal blooms are historically known to occur. For instance, in the Gulf of Oman, algal blooms typically occur during the period of January to April and August to September while algal bloom occurrences in the Arabian Sea only peaks during August to October [1]. In the absence of historical records, it is important to perform continuous monitoring during the pilot testing phase to properly design the SWRO plant to continuously operate during algal blooms. Large-scale HAB phenomena off-shore can be monitored using satellite optical sensors coupled with numerical models to forecast the transport and landfall of such blooms [153,190]. Such application is still subject to intensive research and verification but it does have a good potential in developing an early warning system for SWRO desalination plants.

Although the presence of HAB toxins in seawater does not pose a major operational issue in SWRO plants, the possibility of potent toxins reaching the drinking water system (even at low concentrations) can be a major public health issue or may influence greatly the perception of the public regarding the safety of desalinated water. Boerlage and Nada [28] recommended that drinking water SWRO plants should develop a water safety plan (WSP) to define critical control point for algal toxin monitoring. The WSP should include continuous measurement of conductivity (salt rejection surrogate) in desalinated water to monitor the integrity of SWRO process in removing toxins.

Following the 2008–2009 HAB outbreak in the Gulf of Oman, an expert workshop was held in Oman on the impact of Red Tides and HABs on desalination operation. During this workshop, DAF and UF were highly recommended as possible alternatives to GMF for maintaining reliable operation in RO plants during severe algal bloom situations [10]. Moreover, installing a sub-surface intake (e.g., beach wells) instead of an open intake is increasingly being considered as a pretreatment option for SWRO.

SWRO plants operating with sub-surface intakes, especially vertical beach wells, are less vulnerable to HABs as these intakes can serve as natural (slow) sand filters which can substantially enhance removal of algae, bacteria and AOM from raw water entering SWRO plants due to long retention time [105]. Consequently, less-extensive pretreatment processes are needed to maintain stable operation in the SWRO plant. However, sub-surface intakes may not be applicable in some coastal locations where the geology of the area (e.g., high mud content sediments, low permeability rocks) makes it unfeasible to install such structures due to high energy costs.

SWRO plants operating with direct/open source intake require extensive pretreatment of the raw water to maintain or prolong reliable performance and membrane life. As such, primary and secondary pretreatment systems are installed to ensure acceptable RO feed water quality and stable operation during algal blooms. Primary pretreatment typically includes microstraining/screening to remove large suspended materials (>50 μm), coagulation and clarification by sedimentation or DAF. Secondary pretreatment typically comprises (dual) GMF or UF.

A reliable pretreatment system is one that can continuously produce high quality RO feed water while maintaining stable hydraulic operation. In GMF and UF pretreatment systems, stable operation is the ability of the system to maintain acceptable backwash frequency at minimum chemical and energy requirement. GMF might require full-scale coagulation/flocculation followed by clarification to ensure high quality RO feed water and stable hydraulic operation. A flocculation basin or floc removal step may not necessarily be required in UF pretreatment systems. Schurer et al. [144] demonstrated that UF operation could be stabilised during algal blooms when preceded by in-line coagulation without flocculation or clarification. Other operational measures such as decreasing membrane flux and applying a forward flush cleaning may also improve the performance of UF during severe algal bloom situations. These measures in turn translate into higher required filtration area (larger overall footprint) and lower productivity of the UF membranes.

Pre-coating UF membranes with a layer of pre-formed flocs of ferric hydroxide at the start of each filtration cycle, intermittent coating and intermittent coagulation have all shown to be promising approaches in controlling UF hydraulic performance during algal bloom periods with low chemical requirements [156]. Combining such dosing strategies with new generation of UF membranes with low molecular weight cut-off [174] may ensure the production of high quality RO feed water with very low coagulant consumption.

7. Future pretreatment challenges

Currently, biofouling and the associated chemical cleaning of membranes is a major challenge to the cost-effective application of SWRO technology, especially in HAB-prone areas. High cleaning frequencies make RO systems less reliable/robust, i.e., longer downtime and increased risk of membrane damage. This is in particular a concern for large plants. Driven by the increasing global demand as well as the economy of scale on the cost of desalinated water, it is projected that more large-scale RO plants (>500,000 m³/day) will be installed in the near future (Fig. 10). A mega-size SWRO plant, with production capacity of 1 million m³/day, is expected to be completed by year 2020 [86]. If pretreatment systems in these plants are ineffective during HABs, they will likely result to severe organic/biological fouling, which often requires extensive chemical cleanings (i.e., CIP) and premature membrane replacement, leading to high operational costs for such plants. Moreover, plant operators may be charged with penalties if they fail to supply the contracted amounts of water. Consequently, for current and future large and extra-large SWRO plants, it is essential that pretreatment systems are reliable in maintaining RO feed water with very low fouling potential. The increasing number of SWRO plants equipped with UF as pretreatment reflects this expectation.

To minimise the cleaning frequency of SWRO plants affected by algal blooms, the development of a new generation of pretreatment technology should focus on complete removal of algae and their AOM as well as limiting the concentration of nutrients in RO feed water. Removal of algae and AOM (e.g., TEP) in itself can eliminate organic fouling and may substantially delay the onset of biological fouling in SWRO as there would be a minimal “conditioning layer” to jump-start biofilm development and reduced biodegradable carbon as a microbial nutrient. On the other hand, removal of essential nutrients (e.g., phosphate, dissolved AOC) from the RO feed water can further control biological growth in the system [78,79,181]. Integrating the two treatment strategies can delay and potentially eliminate organic/biological fouling in seawater RO systems, even in severe HAB situations.

8. Summary and outlook

Virtually every coastal country in the world can be affected by algal blooms. This phenomenon is mainly triggered by natural processes but human activities have been reported to increase their frequency and severity as well. The recorded algal cell size, cell density and potential consequences during algal blooms can vary substantially, owing mainly to the high diversity of the causative species. Some types of blooms are considered harmful because of their capability to produce toxins and/or their tendency to proliferate in dense concentrations. Toxic and non-toxic HABs produce varying concentrations and types of algal organic matter (AOM) which are either actively exuded by living algae and their tendency to proliferate in dense concentrations. Toxic and non-toxic HABs produce varying concentrations and types of algal organic matter (AOM) which are either actively exuded by living algae and/or released through lyses of compromised cells. A major component of AOM is highly sticky (e.g., TEP) and has been identified as a major initiator and/or promoter of biofilm in marine aquatic environments.

Recent severe HAB outbreaks in the Middle East have resulted in temporary closure of multiple seawater desalination installations in the region, mainly due to breakdown of pretreatment systems and/or
as a drastic measure to prevent irreversible biofouling problems in SWRO membranes downstream. The major specific issues which may occur in SWRO plants during an algal bloom are: (1) particulate/organic fouling of pretreatment systems (e.g., GMF, MF/UF) by algal cells, their detritus and/or AOM, and (2) biological fouling of NF/RO initiated and/or enhanced by AOM. The presence of HAB toxins in desalinated water is a potential concern, but only at very low concentrations considering the >99% removal capability of SWRO membranes. As membrane-based desalination is expected to grow in terms of production capacity and global application, many coastal areas in the world will potentially face a similar scenario in the future if these HAB-associated problems are not adequately addressed.

To tackle serious operational problems of membrane-based desalination plants, a number of pretreatment strategies are currently being proposed. For areas frequently affected by algal blooms, a monitoring programme should be established to measure indicators (e.g., algae, MFI-UF, TEP) of their impact and to assess the effectiveness of the pretreatment system in preventing (bio)fouling in SWRO. When geological conditions are favourable, subsurface intake can serve as a robust pretreatment to protect SWRO plants from the direct impact of algal blooms. Existing SWRO plants with open intake and are fitted with conventional granular media filtration can gain significant benefits in terms of capacity and product water quality if preceded by DAF or sedimentation. As a consequence, coagulant consumption will increase as a result of coagulant dosage prior to DAF or sedimentation. Therefore, particularly in countries with stringent legislation, such schemes should include sludge handling and/or treatment facilities.

If conditions allow, UF pretreatment (with inline coagulation) should be incorporated in the SWRO plant design, either as a one step process or as a secondary pretreatment. To minimise risk of operational failure in the pretreatment system during HABs, the second option is preferred, whereby UF is preceded by DAF or sedimentation or...
subsurface intake. Significant benefits of UF pretreatment can be gained during periods of severe HABs in terms of maintaining pretreatment capacity and RO feed water quality. Moreover, coagulant consumption is significantly lower in these systems compared to conventional pretreatment systems. The future of UF pretreatment for SWRO lies in the development of tight UF membranes (low MWCO) which can completely remove AOM during bloom periods and deliver high quality RO feed water (very low SDI or MFI-UF) at minimal coagulant consumption and high outlet rates.

Acknowledgements

This study was conducted with the financial support of UNESCO-IHE Institute for Water Education, Wetsus Centre of Excellence for Sustainable Water Technology and Water Desalination and Reuse Center (KAUST, Saudi Arabia). Support for D. M. Anderson was provided through the Woods Hole Center for Oceans and Human Health, National Science Foundation Grant OCE-1314642 and National Institute of Environmental Health Sciences Grant 1-P01-ES021923-01.

References


