Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.0266

60 (2017) 11–38
January

Reverse osmosis desalination system and algal blooms
Part III: SWRO pretreatment

Hassan K. Abdulrahim[a], Abdulsattar M. Al-Rasheed[b], Ashraf S. Hassan[a], Abdel-Nasser A. Mabrouk[a], Basem Shomar[a,*], Mohamed A. Darwish[a]

[a]*Qatar Environment and Energy Research Institute, HBKU, Qatar Foundation, P.O. Box 5825, Doha, Qatar, Tel. +974 4454 2892; email: bshomar@qf.org.qa (B. Shomar), habdelrehem@qf.org.qa (H.K. Abdulrahim), ahassan@qf.org.qa (A.S. Hassan), aaboukhlewa@qf.org.qa (A.-N.A. Mabrouk), darwish738@gmail.com (M.A. Darwish)*
[b]*Qatar Electricity and Water Company (QEWC), Doha, Qatar, Email: alrashid@qewc.com*

Received 8 March 2016; Accepted 5 June 2016

ABSTRACT

This study is the third part of a comprehensive review on the effect of algal blooms (ABs) on seawater reverse osmosis (SWRO) desalination plants. The first part covered in depth the physical situation of the Arabian Gulf (AG), the occurrence of AB events, the major technical challenges of the existing and proposed reverse osmosis desalination plants (RODPs), and taxonomy and toxicity of ABs. The second part covered the seawater intake technologies affecting SWRO systems with respect to the ABs. This part covers the different SWRO pretreatment methods and issues arising from ABs. All countries of the Gulf Cooperation Council (GCC) are moving to implement energy efficient SWRO desalination technologies and are facing its main challenge: membranes fouling. The degree, level and complexity of fouling are proportional to the feed-seawater pretreatment methods. A robust pretreatment is the key factor for reliable continuous SWRO plant operation and performance. This paper reviews the available pretreatment methods for SWRO desalination including disinfection (mainly chlorination), coagulation and flocculation or dissolved air flotation (DAF), sedimentation, granular media filtration (GMF), low pressure membranes ultrafiltration (UF), and microfiltration (MF). Effective integration among these processes can be highly effective in enhancing the removal of ABs and their toxins and in protecting the SWRO membranes.

Keywords: Harmful algal blooms; Reverse osmosis; Seawater pretreatment; Membrane fouling

1. Introduction

Thermal desalination processes require little pretreatment of feed seawater (SW), which mainly are limited to screening and chemical additions to prevent scaling, and are widely used in the Gulf Cooperation Council (GCC). Nowadays, GCC states are expanding the use of SWRO desalination systems, which have much lower consumed energy and lower product water cost when compared with thermal desalting systems. SWRO plants require extensive pretreatment of feed SW after the intake and before undergoing SWRO membrane separation, so pretreatment is crucial to any successful operation of SWRO process [1]. Algal bloom (AB) events that have happened recently in the GCC countries raise more concerns about SWRO pretreatment. There are several processes involved in SWRO pretreatment: chlorination, coagulation, flocculation, sedimentation, DAF, GMF, UF, MF, and factors affecting the removal of contaminants from the feed SW before reaching the membranes. These factors include algae, bacteria, total organic carbon (TOC), particulate and colloidal transparent exopolymer particles (TEP), and the biopolymer fraction of natural organic carbon (NOC).

Several forms of algal organic matter (AOM) are produced by AB with varying concentrations, including

---

* Corresponding author.

intracellular organic matter (IOM) formed due to autolysis consisting of proteins, nucleic acids, lipids and small molecules. Extracellular organic matter (EOM) is formed via metabolic excretion and is composed mainly of polysaccharides. Polysaccharides are complex carbohydrate polymers consisting of more than two mono-saccharides that are linked together covalently by glycosidic linkages in a condensation reaction [2]. This paper reviews the different applied technologies for seawater pretreatment and highlights advantages and disadvantages of each technology. Recommendations are provided regarding the best pretreatment technology for dealing with the seawater feed when AB occurs.

Why SWRO desalination plants in the Gulf would need special pretreatment?

- The Arabian Gulf is the main source of feed water to all desalination plants in Qatar and most of the GGC region;
- The GCC countries are moving to membrane desalination technologies where (bio)fouling is the key challenge and technical investment should be given to pretreatment;
- The physical characteristics of the Gulf water, current, depth, nutrient loads, temperature, etc. enhance occurrence and incidence of ABs;
- Serious attacks of ABs on desalination plants were recorded in the Gulf for 2007/2008, which left most of them inoperable and unable to produce water (the main source in this region);
- Attacks of ABs have raised the urgency to invest in pretreatment technologies by policy makers at the highest level of each country in the Gulf;
- Seawater pretreatment processes are not limited to water intake (discussed in detail in part II) but should extend to cover technologies of disinfection, coagulation/flocculation, sedimentation and several filtration procedures;
- Pretreatment technologies given below are not limited to combating ABs, but could also help in the response to other unexpected attacks of turbid water caused by the seasonal sand and dust storms. They can also aid in minimizing any risk associated with oil spills in the Gulf which represents the main terminus of more than 35% of the oil and gas market routes.

2. Seawater contents affecting pretreatment

2.1. Salt ions

Seawater is not just a solution of water and salt. Rather, it is a complex habitat where innumerable organisms live, and serves many critical roles in our lives. It contains several organic and inorganic components that largely depend on location, depth, weather and time. SW has high total dissolved solids (TDS), expressed by salinity (S) on mass basis grams/liter (g/kg or g/L) or milligrams/liters (mg/L), where one mg/L is equivalent to one part per million (ppm). Standard SW has an average salinity of 35 g/L (=35,000 mg/L or ppm), specific gravity of 1.025 (i.e., denser than freshwater), and a pH range from 7.5 to 8.4. Its main salts constituents are shown in Fig. 1 and Table 1. Salinity varies by location, e.g., it reaches up to 57 g/L on the Qatar western coast (due to confined circulation and high evaporation), but is as little as 7 g/L in the Baltic Sea. Salinity mainly depends on direct fresh water inputs from rivers or rain precipitation and evaporation rates. Although salinity is different from one location to another, relative ion compositions are fairly constant in most surface SW [3].

The six major ions making up more than 99% of the TDS in SW are sodium ion (Na^+), chloride (Cl^-), sulfate (SO_4^{2-}), magnesium ion (Mg^{2+}), calcium ion (Ca^{2+}) and potassium

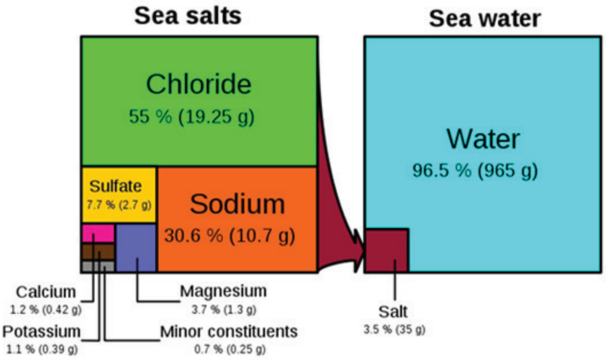

Fig. 1. Diagram showing concentrations of various salt ions in seawater: Cl^- 55%, Na^+, 30.6%, $SO2^{-4}$ 7.7%, Mg^{+2} 3.7%, Ca^{+2} 1.2%, K^+ 1.1%, Other 0.7%. Note that the diagram is only correct when in units of wt/wt, not wt/vol or vol/vol [3].

Table 1
The main salt ions in seawater [3]

Chemical ion	Valence	Concentration mg/L	Part of salinity %	Molecular weight	mmol/Kg
Chloride Cl	–1	19345	55.03	35.453	546
Sodium Na	+1	10752	30.59	22.99	468
Sulfate SO_4	–2	2701	7.68	96.062	28.1
Magnesium Mg	+2	1295	3.68	24.305	53.3
Calcium Ca	+2	416	1.18	40.078	10.4
Potassium K	+1	390	1.11	39.098	9.97
Bicarbonate HCO_3	–1	145	0.41	61.016	2.34
Bromide Br	–1	66	0.19	79.904	0.83
Borate BO_3	–3	27	0.08	58.808	0.46
Strontium Sr	+2	13	0.04	87.62	0.091
Fluoride F	–1	1	0.003	18.998	0.068

ion (K^+). The World Health Organization (WHO) sets TDS of 1,000 mg/L for drinking water while it is of 500 mg/L for the USEPA. Water with TDS concentrations higher than that of drinking water and less than 15,000 mg/L is considered brackish water (BW), while concentrations above 15,000 mg/L are designated as SW.

While TDS in SW has a relatively minor effect on desalination by thermal methods, membrane desalination processes including SWRO are strongly affected. The TDS of an aqueous solution largely determines its osmotic pressure, which affects the pressure that must be applied on the feed SW to enable water permeation through the membranes, and thus the energy consumed by the SWRO process. The TDS is closely related to and often represented by electrical conductivity (EC). Natural waters have an EC (in µS/Cm) that is approximately double that of TDS (in g/L): an average TDS of the seawater 35 g/L corresponds to an EC of 70 µS/Cm.

2.2. Organic matter and colloids

Besides dissolved solids and gases, SW contains particulates including organic and inorganic substances. Organic compounds may contain elements such as sulfur, nitrogen and phosphorus in addition to carbon and hydrogen. Organic matter (OM) encompasses many substances, ranging from food to toxins. Total OM (TOM) is classified as dissolved OM (DOM) or particulate OM (POM). DOM is defined as all organic materials that can pass through 0.2 to 1.0 micrometer (µm) filters, and POM consists of materials that are retained by such filters. The main organic substances are microorganisms, biological debris (plant and animal), polysaccharides (gums, slime, plankton, fibrils), kerogen (aged polysaccharides), lipoproteins (secretions), bacteria, carbohydrates, fats, oils, grease, and polyphenolic aromatic complexes such as humic acids, fulvic acids, lignin, and tannin [4, 5].

Humic acids are the product of OM biodegradation and are a mixture of long-chained organic acids containing several carboxyl and phenol groups. Fulvic acids are similar to humic acids but with smaller molecular weights (MW) and higher oxygen contents. Polysaccharides constituting cell walls of microorganisms and plants are also prominent [6].

Particles are characterized by size. Among the most important are colloids, which are loosely defined as fine particles whose characteristic size is roughly in the range of 1 nm to 1 µm. Colloids can cause membrane colloidal fouling, by depositing in membrane pores (known as pore blocking) or form a cake as suspended particles accumulate, Fig. 2 [7]. Other important characteristics of colloids, besides the size, in relation to the pretreatment process and ability to foul the RO membranes, are shape, charge, and specific interaction with ions in the feed SW [8]. Table 2 gives some of these properties for different classes of colloids.

2.3. Algae

Phytoplankton, the principal source of food for sea life, can multiply exponentially and cause ABs. ABs can severely increase the SW turbidity and release OM known as algogenic organic matters (AOM). The ABs are considered harmful (HABs) if they are:

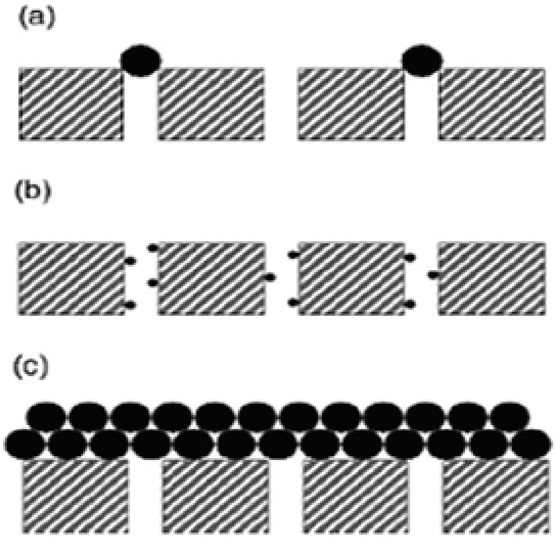

Fig. 2. Three types of fouling mechanisms: (a) external pore blocking, (b) internal pore blocking, (c) cake filtration [7].

a. Toxin producers, which can contaminate seafood, kill fish, or cause health problems in humans through direct exposure to the toxins;
b. High-biomass producers, which can kill or damage marine life after reaching dense concentrations, for example, by causing anoxia after collapse of a bloom or by chronically shading benthic vegetation. They can discolor coastal waters and generate noxious foams, slimes and odors.

Some of the HAB species occur in seawater are dinoflagellates, *Karenia brevis* and *Noctiluca scintillans*. These are associated with red tides, while *Auerococcus anophagefferens* is associated with brown tides. An AB may have algae counts that range from 10^3 to 10^6/mL; typical concentrations are less than 10^3/mL [9].

3. Seawater constituents related to pretreatment

The most common inorganic particles are clay (hydrous aluminum oxides and iron silicates), ranging in size between 0.3 and 1 µm, sands, and colloids of iron oxide, alumina, silica, manganese oxides, calcium carbonate, sulfur and sulfides. Particulates (organic or inorganic) in SW can be classified as settable solids (>100 µm), supra-colloidal solids (1–100 µm), or colloidal solids (0.001–1 µm), while dissolved solids are <0.001 µm [5]. The main SW components, their size distribution and their matching filtration spectrum are shown in Fig. 3 [6]. Distinction between “particulate” and “dissolved” matter is based on pre-filtration of water samples with 0.45-µm membrane filters.

3.1. Natural organic matter (NOM)

The NOM content in SW is indicated by TOC and dissolved organic carbon (DOC) concentrations. The concentrations of both TOC and DOC are expressed by mg/L and

Table 2
Summary of colloid composition and properties that may affect pretreatment and lead to membrane fouling [8]

Types of colloids	Examples	Size and shape	Charge
Inorganic	Silica	Round	Negatively charged (pH_{pzc}~3)
	Aluminum silicate minerals	Angular	Negatively charged at pH~7
	Ferric oxide-hydroxide	Varies depending on crystalline or amorphous	Positively charged. pH_{pzc} for goethite ~9
Humic acid	International Humic Substance Society (IHSS) standards	MW of a few kDa to a few hundred kDa. Globular molecule (linear under high pH, low ionic strength, and low concentration)	Negative charged (pH_{pzc}~3), Typical total acidity: 5–10 meq/g
Polysaccharides	Schizophyllan,	400–500 kDa, rigid rod-like	Neutral
	Xanthan	100–2,500 kDa, linear	Negatively charged
	Gellan	200–2,000 kDa, extended random coil	Negatively charged, ~3 meq/g
	Alginate		(up to 6 meq/g)
Proteins	Bovine serum albumin	67 kDa	$pH_{IEP} = 4.7$ (total acidity 1.5 meq/g including both carboxylic and amine groups)
	Bovine immunoglobulin	G 155 kDa	$pH_{IEP} = 6.6$
	Bovine hemoglobin	68 kDa	$pH_{IEP} = 7.1$
	Bovine pancreas	A 13.7 kDa $pH_{IEP} = 7.8$	$pH_{IEP} = 7.8$
	Lysozyme	14.4 kDa $pH_{IEP} = 11.0$	$pH_{IEP} = 11.0$

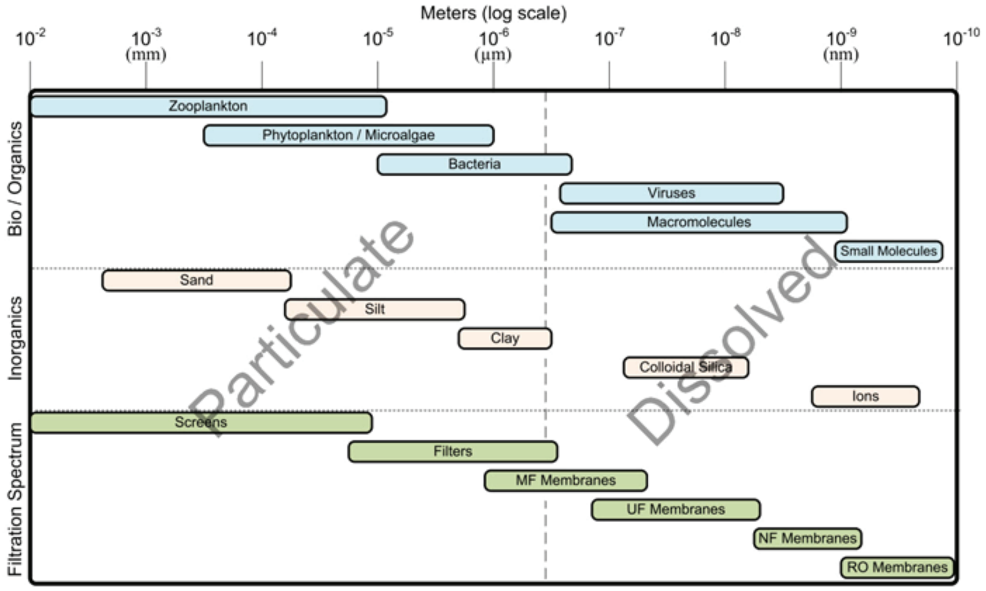

Fig. 3. Seawater contents and the matching filtration spectrum [6].

are determined by passing through 0.45-µm filters. The most common method for TOC and DOC analyses involves acidification and oxidation of total carbon content into CO_2, stripping it out of the solution and measuring its concentration [6]. When the bacteria, algae and inorganic carbon contents are low, the TOC ≅ DOC.

NOM are dominated by humic substances and AOM, mainly consisting of extra cellular macromolecular and cellular debris. Humic substances result from OM degradation and are a mixture of long chained organic acid (MW of 1,000–20,000 gm/mole) representing significant fraction of the TOC in water, and mostly consist of humic acids (HA) and fulvic acids (FA) in natural water. Both HA and FA have significant negative charge density, and can be removed in pretreatment by coagulation and separated by precipitation. They also have bulky macromolecular shapes, and are not as easily adsorbed onto such a membrane. NOM exhibits relatively high specific UV absorbance (SUVA) value and contains relatively large amounts of aromatic carbon. It is known that the organic fouling rates are accelerated with decreasing pH, increasing ionic strength and increasing divalent cation concentrations.

When OM in water is disinfected by chlorine, carcinogenic disinfection byproducts are formed. In non-AB conditions and clean SW, the quantities of NOM in SW may not cause membrane fouling. In the AB events, biodegradable OM are released during their growth and respiration, known as extracellular OM (EOM), and high NOM content is usually observed. At the end of the AB season, algae die and their cells break down, to release IOM into SW. AOM consists of a combination of EOM and IOM from algae, which is easily biodegraded and provides a food source for bio-growth of bacteria on the RO membrane surface. HA combines with iron ions (say from Fe coagulant used in pretreatment process) to form a gel-like layer of chelates on the membranes' surface and to cause fouling. When HA is oxidized with chlorine or other oxidants, it can be easily degraded to serve as a food source for aquatic bacteria growing on the RO membrane surface. Continuous chlorination of SW containing large amounts of HA often causes more membrane bio-fouling problems than it solves [10].

The NOM most responsible for fouling are the polysaccharides, organic colloids, and proteins, followed in size by humic substances, organic acids, and low MW organics of neutral charge. These compounds have the potential to cause membrane fouling, but to different degrees. Polysaccharides excreted by living bacteria on the membrane surface have the highest potential to cause RO membrane bio-fouling, and therefore they are classified as a separate group of microbial foulants.

NOM is analyzed indirectly by filtering SW sample through 0.45 μm membrane filters and measuring the filtrate absorbance by ultraviolet (UV) spectrophotometer at 254 nm. Ultraviolet light at 254 nm is absorbed especially by aquatic humic matter, which absorbs more light per unit concentration of DOC (called the SUVA) than other types of NOM such as hydrophilic acids, hydrophobic bases (e.g., proteins and aromatic amines), and hydrophobic neutrals (e.g., aldehydes). Therefore, the UV_{254} absorbance is based on the fact that specific molecular structures (chromophores) within the NOM molecules absorb UV light. This parameter may not reflect the content of microbial foulants if the NOM contained in SW is not easily biodegradable. If the specific molecular structure is below 0.5 L $mol^{-1}cm^{-1}$, the SW has low potential for organic fouling and biofouling. Other measurements of OM are illustrated in [11]. Gaid [11] demonstrated that the Liquid Chromatography-Organic Carbon Detection (LC-OCD) is used to characterize dissolved organic carbon (DOC) and identifies the constituents causing organic fouling. Table 3 gives typical sizes of dissolved organic carbon detected by LC-OCD.

SUVA can be used as an indirect indicator of the occurrence of AB in SW. If the SUVA is higher than 4, then NOM in SW consists predominantly of aquatic humic matter and does not exhibit AB. If the SUVA is between 2 and 4, the SW's NOM is a mix of assimilable OM and aquatic humic matter, and SW is in the early stages of formation the AB. When the SUVA is less than 2, the NOM in SW consists predominantly of assimilable OM and the SW is experiencing an AB [10]. For SW containing aquatic humic matter, the NOM is a mixture of aquatic humic and fulvic acids of fairly high MW, carrying negative charge, and can be removed in pretreatment by coagulation and separation of the precipitated solids as mentioned before.

3.2. Total organic carbon (TOC)

The TOC contains both NOM and easily biodegradable organics, such as polysaccharides, released during AB events. The TOC is relatively easy to measure, and high TOC indicates the tendency of SW to cause organic fouling and bio-fouling of SWRO membranes. The TOC of SW contains low MW organic compounds (at least 40%), with limited fouling potential. A combination in SW of a high percentage of compounds from the "other low MW" category, low TOC, and low polysaccharide content is a strong indication of low fouling potential. An example of TOC in Ashkelon SWRO plant surface water is 1.2 mg/L which includes 14% of polysaccharides, 39% of humic substances and building blocks, 25% of low MW acids and neutrals, and 22% of other low MW compounds [10]. If TOC is below 0.5 mg/L, biofouling is unlikely, and if above 2 mg/L, biofouling is very likely.

Table 3
Typical sizes of DOC fractions detected by LC-OCD [11]

DOC fractions	Molecular weight (Da)*	Composition	Properties
Biopolymers	> 20,000	Polysaccharides (e.g., TEP) and proteins, biogenic organic matters	Not UV-absorbable, hydrophilic
Humic substances	~800–1,000	Humic and fulvic acids	Highly UV absorbable, hydrophilic
Building Blocks	300–500	Breakdown products of humic substances by oxidation	UV-absorbable
Low molecular weight organic acids	<350	All aliphatic low MW organic acids, biogenic organic matters	Negatively charged**
LMW neutrals	<350	Alcohols, aldehydes, ketones, amino acids, biogenic organic matters	Weakly or uncharged hydrophilic

*One Dalton is equal to 1.666×10^{-24} g. SW membranes would reject 90% of compounds having MW > 200 Da.

**Negatively charged NOM has tendency to adhere on thin film RO membrane that has slightly positive charges.

Colloids (size range 0.001–1 μm) are dispersed solid or liquid particles (mostly of organic nature) could be included as "Macromolecules." Other important SW indicators relevant for SWRO operation and its pretreatment are as follows: Silt Density Index (SDI), and Nephelometric Turbidity Units (NTU), Modified Fouling Index and TEP substances.

Methods of determining SDI, NTU, TEP, Chlorophyll-*a*, particulate organic carbon (POC) and dissolved organic carbon (DOC) were given by [12]. Chlorophyll-*a* is a standard method to evaluate algae concentrations, while TEP are microscopic (0.4–300 μm), organic gelatinous particles consisting mainly of acid polysaccharides, detected by staining with Alcian Blue, and are important components of the NOM pool [12].

3.3. Turbidity

Turbidity, expressed by NTU, indicates the foulant contents of clay, silt, suspended OM, and microscopic aquatic life, such as phytoplankton- and zooplankton. While turbidity represents the overall foulant content, it cannot indicate adequately the potential for particulate or other fouling. Most RO membrane manufacturers require feed SW turbidity less than 1.0 NTU (although this is high) and preferably less than 0.1 NTU. Spikes above 50 NTU for more than 1 h would require sedimentation or dissolved air flotation (DAF) treatment prior to filtration in the pre-treatment process.

3.4. Silt Density Index (SDI)

The SDI is a parameter expressing the fouling potential of water. The particulate, colloidal matter and micro-organisms in water have natural tendency to deposit on the membrane and thus impair its effectiveness. SDI is one of the most important parameters for the design and operation of SWRO process. The SDI indicates the flux rate decline through standard size (0.45 μm membrane pore size) and diameter (45 mm) filter operated at constant pressure (30 lb/in^2 or 2.07 bar) for a given period of time (say 15 min). The time required to filter a clearly defined volume of water (500 ml) with a new test membrane is compared with the time required to filter the same volume after 15 min of filtration. The increase in the time required for filtration of the second 500 ml is used to calculate the SDI. Therefore, SDI_{15} is the percentage of the flow rate decrease of water flowing through the filter, averaged over a period of time such as 15 min. It is determined by measuring the time (t_o in seconds) to collect a 500-mL sample through the filter paper at the start of the test, wait for n = 15 min, and measure the time (in seconds t_n) to collect another 500 L that flow through the filter. The two sample durations (t_0 and t_{15}) are used to calculate the SDI_{15} (indicating particulate fouling potential) by using Eq. (1):

$$SDI_{15} = 100 \times \left[1-\left(t_o / t_n\right)\right] / n \quad (1)$$

Considering the potential for SW particulate fouling, SDI_{15} lower than 2 gives very low fouling. Pretreatment may not be necessary if SDI < 2 is kept for 2 years. For $SDI_{15} > 4$, additional filtration is needed.

3.5. Total suspended solids (TSS)

Total suspended solids (TSS) concentration is a measure of the total weight of solid residuals contained in SW; and is expressed in mg/L. TSS is measured by filtering a known volume of water (typically 1 L) through a pre-weighed glass-fiber filter, drying the filter with the solids retained on it at 103°C–105°C, and then weighing the filter again after drying, taking the salinity of SW in consideration. By knowing TSS, the amount of residuals generated during pretreatment can be assessed.

3.6. Chlorophyll-a

Chlorophyll-*a* concentration indicates the content of algae with green pigmentation in water and is measured using fluorometer or a spectrophotometer. The content of chlorophyll-*a* is proportional to the light transmission through the water sample at a given wavelength, which is detected by the instrument and converted into concentration units, typically either μg/L or mg/L. Concerning fouling potential, water with chlorophyll-*a* content below 0.5 μg/L (indicating non-algae blooms conditions) has low fouling potential, while chlorophyll-*a* levels exceeding 10 μg/L (indicating high content of algae) indicate high fouling potential.

3.7. Algal count

Algal count is expressed by the total number of algae cells per milliliter of water. Concerning the intensity of AB, algae counts below 1,000-cells/mL refer to normal non-AB conditions; more than 2,000-cell/mL refer to AB concern; 2,000–20,000 cells/mL refer to mild AB; between 20,000 and 60,000 cells/mL refer to medium intensity AB; and more than 60,000–cells/mL refer to severe AB. It is critical to determine the type and size of the dominant algae species to determine the best pretreatment.

3.8. Polymers used in flocculation

Generally, flocculants are used in combination with coagulants. Examples of well-known flocculants used in seawater pretreatment include inorganic or organic cationic flocculants. The soluble polyquaternary amine flocculant is one of the common types. The performance of flocculants depends on SDI, potential flocculant fouling at the membrane surface, membrane characteristics, and so on. Polymers used in flocculation of seawater before filtration process in pretreatment can cause colloidal fouling if it is overdosed or not properly mixed.

3.9. Hydrocarbons

Hydrocarbons derived from crude oil (e.g., oils and greases) are not normally present in clean open SW. Their existence in polluted SW, for example, even small quantities that are discharged from ships or seeps from wells, can cause accelerated fouling and should be kept below 0.02 mg/L at all times. Total hydrocarbon concentrations are measured in most SWRO plants using open sea intakes with online total hydrocarbon analyzers.

4. Membrane fouling

Membrane fouling is a major concern in SWRO desalting plants. Fouling reduces the permeate output, increases the required feed pressure to the membranes, and thus raises the consumed energy and cost of produced water. Membrane fouling may even result in the complete shutdown of the plant. Fouling can be by scale deposits from sparingly soluble salts, particulate matter deposits, OM adsorption, and biological fouling by growth of organisms on membranes' surface.

4.1. Scale deposits

Scale deposits occurs on SWRO membranes when the concentration of certain salts (e.g., $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, etc.) exceeds the solubility limits, see Figs. 4(a)–4(c) [13]. This can be controlled by adjusting the pH of the feed water and/or by using anti-scalants. However, some anti-scalants contain biodegradable OM (BOM) that can promote biological fouling [14]. Since microfiltration (MF) and ultrafiltration (UF) do not concentrate salts in the effluent, very little to no scaling occurs on MF and UF components. Scale deposits are common on SWRO membranes, where salts are concentrated. Anti-scalant chemicals that are used in RO applications typically have two or more phosphonate groups, called poly-phosphonates. Concentrates containing phosphates have impacts in areas of discharge that may be associated with AB. Thus, anti-scalants can increase the bio-fouling potential, and the impurities contained in the treatment chemicals are also potential nutrient sources. Mitigation of inorganic scale fouling without creating an environment for biological fouling is very important and needs to be addressed.

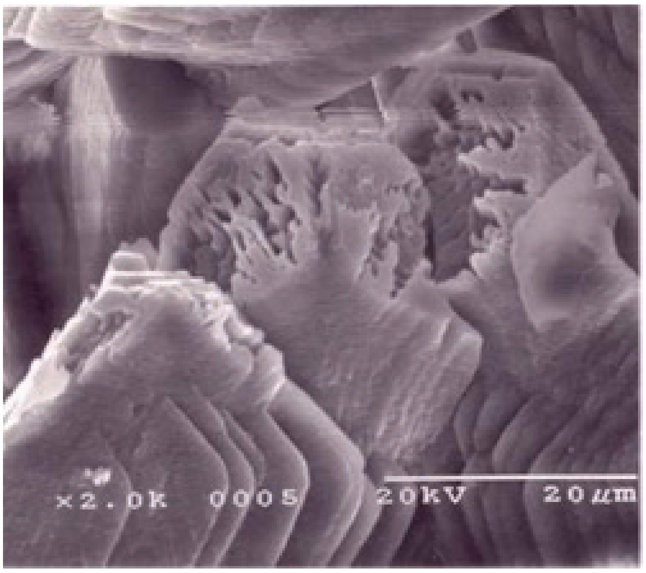

Fig. 4(a). Calcium carbonate precipitated on an RO membrane [13].

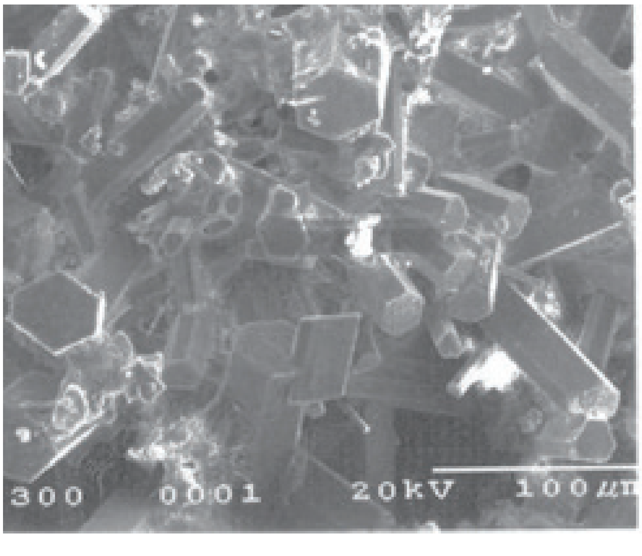

Fig. 4(b). Calcium sulfate precipitated on an RO membrane [13].

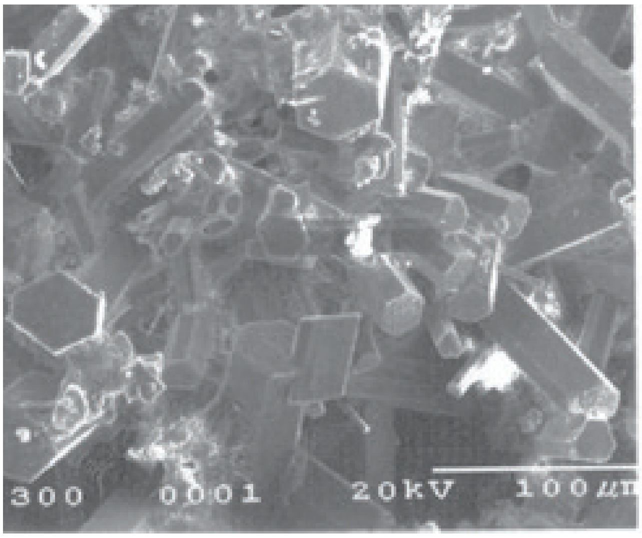

Fig. 4(c). Calcium phosphate precipitated on an RO membrane [13].

4.2. Particulate fouling

Suspended colloids that lead to particulate fouling can be inorganic or mixed inorganic/organic particles that did not settle out by gravity in pretreatment. Colloidal matter contains some major components such as iron, aluminum, silica, sulfur, and OM such as plankton. When suspended (or colloids of size range from 0.001–1.0 µm) organic or inorganic compounds are not removed by pretreatment before the RO membranes, particulates fouling is formed by colloid materials. These can be deposited on membrane pores (i.e., pore blocking) or form a cake of accumulates, as shown in Fig. 2 [15]. Particulates fouling may occur due to suspended particulate and colloidal, and that colloids can form aggregates either by reaction-limited colloid aggregation (RLCA) or by diffusion-limited colloid aggregation. Biopolymers are often involved in aggregate formation. Iron colloidal fouling on RO membranes may result from improper application of iron-based coagulants, and may act as a fouling catalyst, causing damage of membranes by fed water with even very low doses of residual chlorine.

4.3. Organic fouling

Organic fouling (with major dissolved organic components being either HA or FA) occurs by adsorption of OM onto the membrane surface, and may be irreversible. Organic fouling is among the most common fouling mechanisms in SWRO desalting plants, with approximately 40% of permeability decline in RO membranes attributed to the interrelated organic and biological fouling. While OM can be directly responsible for organic fouling, the OM provides substrate for biological growth. The DOC, UV absorbance, and color are related to organic fouling. Dissolved organic carbon fractions in SW were given as 24% of high MW (1–100 nm), and 75% low MW (<1 nm), besides 1% of particulate organic carbon [9]. Since the pore size for SWRO membranes is on order of 1 nm, the high MW DOC fraction is too large to be passed through these membranes and is retained. The pore sizes for UF membranes (0.01–0.05 μm) and for MF membranes (0.1–0.5 μm) are considerably larger, do not have significant retention of marine NOM, so other approaches should be used to deal with the problem [9].

4.4. Biological fouling

Biological fouling is caused by the growth of microorganisms into a biofilm on the membrane surface, as shown in Fig. 5. Formation of biofilm starts with an attachment phase of colloidal biopolymers, TEPs, and proto-biofilm on membrane surfaces. This is followed by a growth phase of micro-organism and by the formation of biopolymer matrix, and then by a dispersed phase for biofilm equilibrium and partial shed-off from the membrane to create a space for a new attachment [7]. Biological fouling decreases the permeate flux, increases the pressure drops in the RO modules, increases the salt passage and can cause irreversible damage to the RO membrane. Bacterial communities in the biofilms release extracellular polymeric substances (EPS), which provide an area for additional bacteria proliferation. The EPS in biofilm account for 50%–90% of biofilm TOC, and assimilable organic carbon (AOC) provides food source that enable bacteria to proliferate. Chemicals added in pretreatment, such as phosphate based anti-scale inhibitors and oxidants, can contribute to biological fouling. AB severely increases turbidity of SW; and release of organic material, AOM. AOM is composed of acids, proteins, simple sugars, anionic polymers, negatively charged and neutral polysaccharides. Although pretreatment can prohibit algal cells from entering the RO membrane modules, greater problems may occur when AOM facilitates favorable conditions for bacterial attachment on the RO membrane. AOM provides a rich substrate for bacterial growth, thereby exacerbating membrane bio-fouling. In general, harmful ABs are being increasingly recognized for their often detrimental impacts on RO desalination facilities.

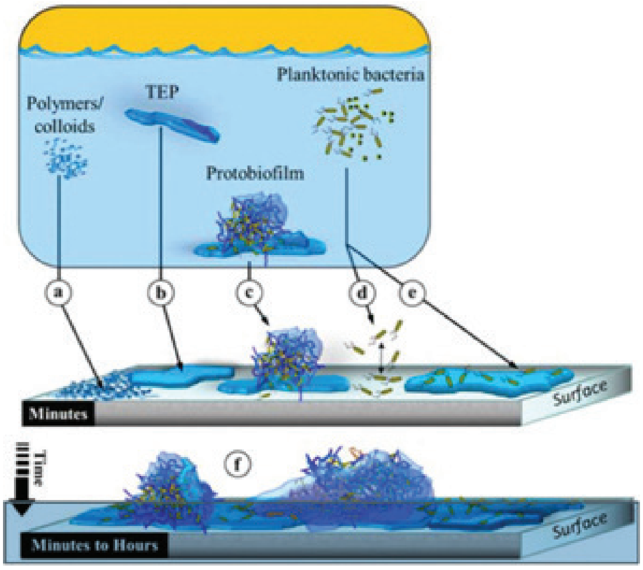

Fig. 5. Schematic illustration of the possible involvement of (a) colloidal biopolymers, (b) TEPs, and (c) protobiofilm in the initiation of aquatic biofilms. A number of planktonic bacteria (first colonizers) can attach (d) reversibly on clean surfaces or (e) irreversibly on TEP-conditioned surfaces. When nutrients are not limited in the water, (f) a continuous coverage of mature biofilm can develop within a short period of time (minutes to hours). Adapted from [16, 17].

5. Seawater pretreatment

Pretreatment of SW is a necessity for SWRO desalting system to prevent (or reduce) fouling of membranes. The SWRO membranes are designed to remove dissolved salts, and are vulnerable to particulate matter that should be minimized before the feed SW entrance to the RO membranes. Voutchkov [15] summarized the purpose of SWRO pretreatment: to remove over 99% of all suspended solids in SW and to reduce the content of the much finer silt particles by several orders of magnitude. The pretreatment facility is designed to give targeted SDI values rather than to target the level of removal of turbidity or pathogens. Pretreatment can account for a good share of the total water production cost. Conventional pre-treatment includes disinfection, screening, hardness removal, alkalinity reduction, antiscalant addition, coagulation, flocculation, sedimentation or DAF and GMF. Advanced pretreatment (membrane filtration) includes low-pressure membranes filtration such as MF/UF, and final particles removal by cartridge filters, as shown in Fig. 6(a). Screening can remove large debris, marine organisms, and small items of silts, sand, plankton, and so on. Coagulation and flocculation enhance the removal of colloidal foulants before sedimentation, and are essential for better performance of GMF filters. In membrane filtrations, MF, UF, and rarely NF replace the GMF. GMFs completely remove the suspended solids of size larger than 50 μm and improve the feed water quality by lowering the SDI. Better pretreatment can be gained by adding UF and MF membranes that also remove suspended solids particles (as fine as 0.1 μm for MF or 0.01 μm for UF) by direct physical separation, large bacteria, dissolved macromolecules, colloids, and smaller bacteria. GMFs were not successful in preventing particulate fouling during AB, and the efficiency of removing the algae released biopolymer (organic macromolecules) was low [15]. The SWRO pretreatment is a key factor to ensure good performance of DPs in terms of reliability, water quality, energy use, and long

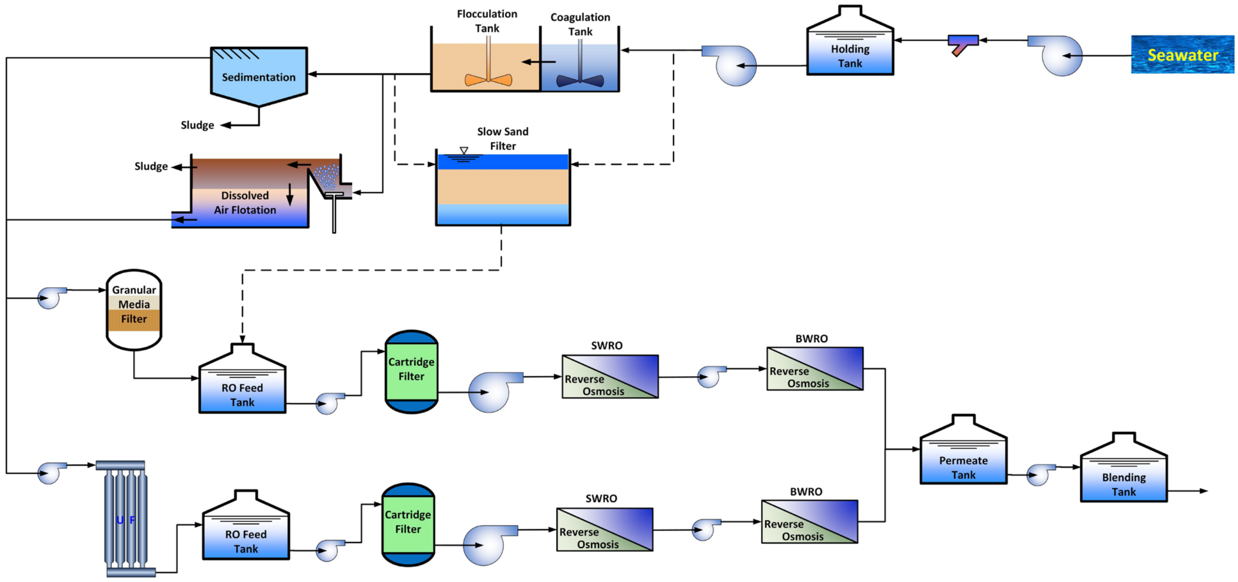

Fig. 6(a). Flow diagram of two pretreatment, conventional and membrane.

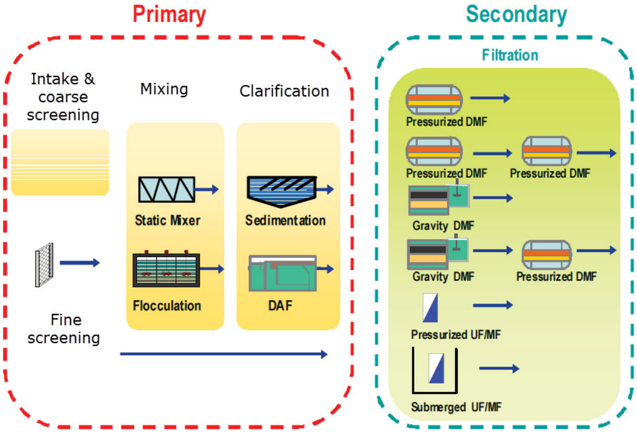

Fig. 6(b). Pretreatment alternatives in desalination systems. Modified from [13].

Fig. 6(c). A cartridge filter in a horizontal vessel (upper left) and a vertical vessel (upper right) with a differential pressure measurement (Perth) [13, 6].

life membranes. Membrane manufacturers typically require maximum allowable turbidity of 1.0 NTU; SDI of 3.0 or 4.0; oil and grease ≤1.0 mg/L to give their warranty [15].

The pretreatment can be classified, after preliminary treatment (chlorination/de-chlorination) as follows: (a) primary pretreatment, including particulates coagulation and clarification processes such as sedimentation and DAF; and (b) secondary pretreatment, including conventional filtration processes using GMFs and advanced membrane filtration using MF/UF membranes, Fig. 6(b).

A cartridge filter is often installed after pretreatment process and just before the RO membranes in Fig. 6(a), to serve as a protection measure against micro-particles that can foul or damage the membrane rather than active pretreatment. The cartridge filters are typically woven, polypropylene micro-filters operated in closed vessels with a particle removal capability of 1–25 µm elements, Fig. 6(c). They are operated at a typical pressure difference of 0.1 bar and are replaced once this pressure drop is increased to 0.8–1.0 bar. The pretreatment should be carefully designed and a pilot test study may be necessary to study the effect of possible heavy AB and other contaminants such as oil from production facilities or shipping.

5.1. Preliminary treatment: chlorination and de-chlorination

Chlorine treatment is among the options commonly used to manage biological activity in seawater intake. Biocides (e.g., sodium hypochlorite and chlorine dioxide) dosing are applied in desalination plants equipped with open intakes, where concentrations of OM and the biological activity are high compared with subsurface intakes. The basic principle of oxidation is when an oxidizing agent, like chlorine, diffuses through the cell wall of an organism, it oxidizes enzyme groups, thereby preventing further metabolic activity and ultimately bringing about death to the organism. In macro-organisms, death can be caused by growth reduction due to the decrease in filtration rate and consequently decrease in food availability, combined with pathological effects. It is believed that chlorine reacts with the OM in water and breaks it down to more biodegradable fragments.

A recent study of Kim et al. [18] provided a comprehensive list of disinfection byproducts that are formed during seawater desalination. The study listed different disinfection technologies, dosing and application, efficiency based on location/source of water/availability, cost, and disinfection byproducts. We limit this third part of our review to the chlorination technology, which represents more than 80% among all being used today and which exceeds 90% in the GCC region.

Preliminary pretreatment starts with pre-chlorination at or even before the intakes, to prevent the uncontrolled growth of microorganisms on surfaces. That growth typically includes a preliminary formation of slime, which gives a biofilm that is produced by the living cells plus their metabolic byproducts. The term "fouling" here refers to the final deposit resulting from the mixture of biofilm:microbial masses and their EPS, suspended solids, corrosion products, and macro-organisms finally adhering and growing on the surface. The fouling layer reaches the maximum development with the adhesion of marine animals such as *Crustacea* (barnacles), Molluscs (mussels and clams), Annelids (Serpulids) and Coelenterates (hydroids) [19]. Chlorine (Cl_2) has the capacity to inactivate most pathogenic microorganisms quickly, and its effectiveness depends on the chlorine concentration, time of exposure/contact time, and water pH. The results of not treating seawater by biocides are shown in Figs. 7(a)–(c) [19, 20]. Considerable amounts of settlement of barnacles, green mussels, and ascidians were observed in coastal waters on the long-term panels [19].

Chlorination cannot destroy all forms of biofouling organisms, so it does not serve as an absolute barrier to RO membrane biofouling. Chlorine and other oxidants break down non-biodegradable NOM into biodegradable organic compounds and destroy the outer walls of bacterial cells thus causing the release of IOM into the feed SW source. The IOM released from algal and bacterial cells due to oxidation is rich in easily biodegradable organics, and serves as a food to bacteria that have already colonized the RO membranes or survived the chlorination process.

Chlorine is a very powerful disinfectant that also oxidizes the membrane material. Polyamide (PA) membranes in particular do not tolerate chlorine, while cellulose acetate (CA) membranes have some tolerance. To minimize damage to membranes, chlorine disinfection should be followed by removal of the residual chlorine (called de-chlorination) in the water before its entrance to the membranes by sulfite (SO_3^{2-}) treatment or carbon adsorption. The free residual chlorine includes sodium hypochlorite (NaClO), hypochlorous acid (HClO), and hypochlorite ions. This is the reason that the term pre-chlorination is sometimes used in place of chlorination.

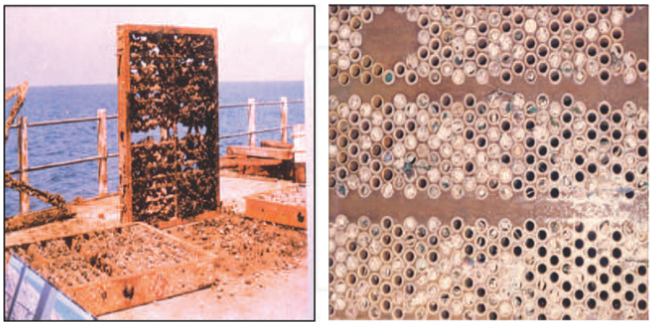

Fig. 7(a). Blockage of intake screen by fouling organisms (left) and blockage of condenser tubes by green mussels and barnacles (right) [19].

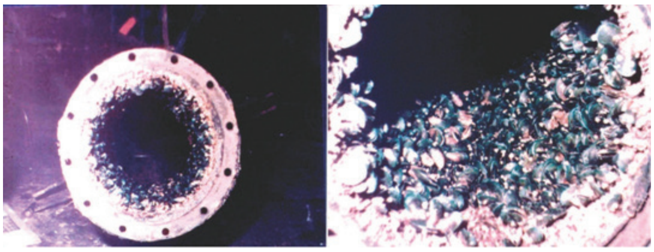

Fig. 7(b). A view of bio-growth inside seawater pipe lines from Madras Atomic Power Station [19].

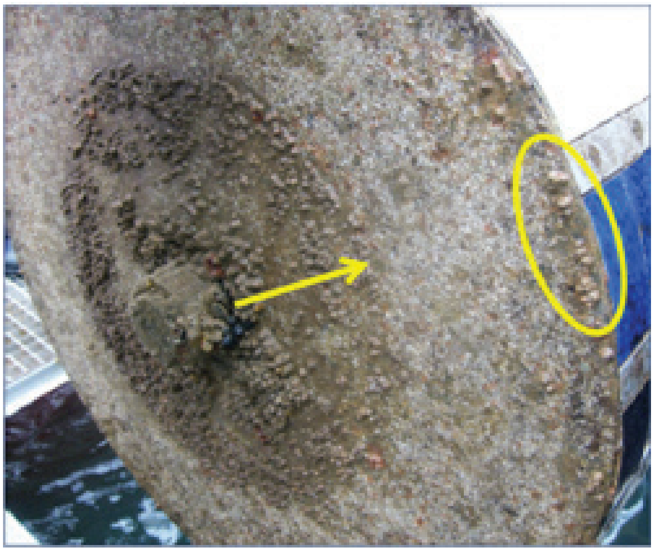

Fig. 7(c). A rotor operated continuously in the Mediterranean sea with surface colonized by barnacles [20].

Chlorines are available as chlorine gas (Cl_2), sodium hypochlorite (NaOCl) and calcium hypo-chlorites $Ca(OCl)_2$. The NaClO, the most commonly used oxidant, is composed of a sodium cation (Na^+) and a hypochlorite anion (ClO^-), and can be formed by reacting sodium chloride (NaCl) with oxygen gas (O_2), according to:

$$2NaCl + O_2 \rightarrow 2NaClO \tag{2}$$

Calcium hypochlorite is made by reacting $Ca(OH)_2$ with Cl_2, similar to sodium hypochlorite. It is a white solid, although commercial samples appear yellow.

All Cl_2, NaOCl and $Ca(OCl)_2$ hydrolyze in water and produce HClO as:

$$Cl_2 + H_2O \rightarrow HOCl + HCl \rightarrow HOCl + H^+ + Cl^- \tag{3}$$

$$NaOCl + H_2O \rightarrow HOCl + NaOH \tag{4}$$

$$Ca(OCl)_2 + 2H_2O \rightarrow 2\ HOCl + Ca(OH)_2 \tag{5}$$

HClO dissociates in water to hydrogen ions $(H)^+$ and hypochlorite ions $(OCl)^-$:

$$HOCl + H_2O \rightarrow H^+ + OCl^- \rightarrow H_3O^+ + OCl^- \tag{6}$$

The OCl^- falls apart to chlorine and oxygen atoms: $OCl^- \rightarrow Cl^- + O$.

The HClO is much more reactive and is a powerful disinfectant than hypochlorite ClO^-. The HOCl splits into hydrochloric acid (HCl) and oxygen atoms (O). The HOCl and $(OCl)^-$ exist in an equilibrium that is pH dependent. The equilibrium is also slightly affected by temperature. The level of HOCl decreases with the increase of pH. When the pH value is less than 5.5, the HClO reaches its peak effectiveness. The disinfecting properties of chlorine in water are based on the oxidizing power of free oxygen atoms and on chlorine substitution reactions. Disinfection with chlorine takes place optimally when the pH is between 5.5 and 7.5. Fig. 8 [21] illustrates distribution of HClO and hypochlorite ion in water at different pH values and temperatures.

Chlorination for RO pretreatment is applied by adding usually chlorine (Cl_2) continuously at the intake location, and by allowing 20–30 min reaction time. A free residual chlorine concentration of 0.5–1.0 mg/L is to be maintained through the whole pretreatment line. Chlorination is useful in several pretreatment steps, e.g., aiding in coagulation, algae control in basins, odour reduction, controlling, and so on. However, it is noticed that the longer contact time provided by pre-chlorination allows chlorine to react with organics in SW and produces carcinogenic byproduct substances such as trihalomethanes (THMs) [22]. The THMs are predominantly formed as a byproduct when chlorine is used to disinfect water for drinking. Many governments set limits on the permissible amounts of total THMs in drinking water, e.g., the EPA in USA limits the total concentration of the four chief constituents (chloroform, bromoform, bromodichloromethane, and dibromochloromethane), referred to as total THM (TTHM), to 80 parts per billion (ppb or μg/L) in treated water. More on the subject of chlorination are given in [11, 23, 24].

De-chlorination upstream of the membranes is required to protect the membranes from oxidation. Biofouling problems commonly appear downstream the point of de-chlorination [22]. Since there is no chlorine present on the membranes, microorganisms can grow with an enhanced nutrient offering, unless the system is sanitized very frequently. Therefore, the continuous chlorination/de-chlorination method is becoming less popular.

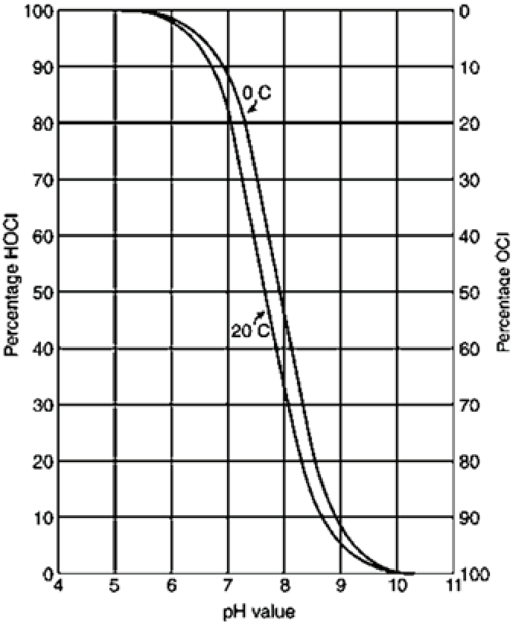

Fig. 8. Distribution of hypochlorous acid and hypochlorite ion in water at different pH values and temperatures [21].

Instead of continuous chlorination, chlorine is preferably applied off-line to the pretreatment section periodically. During offline chlorination, the feed water has to be sent to drain prior to reaching the membranes. Before the system goes into operation again, all chlorine containing feed water has to be rinsed out carefully, and the absence of chlorine must be verified. Sodium metabisulfite ($Na_2S_2O_5$) is commonly used for removal of free chlorine.

Voutchkov [10] stated that chlorine dioxide (ClO_2) is a weaker oxidant than chlorine, fairly effective for most aquatic microorganisms, and not as aggressive in terms of RO membrane oxidation. When chlorine dioxide is used intermittently and in low dosages (0.2–0.5 mg/L) and at low pH, de-chlorination may not be required, and may not cause RO membrane degradation. However, reverse osmosis membrane manufacturers differ in their views regarding the use of chlorine dioxide without subsequent de-chlorination. More on continuous and intermittent chlorination are given in [11].

Chlorine can kill algae species during the AB incidents by damaging the algae cells. This can prevent the cells from entering the desalination plant, but the destroyed cells produce high levels of sticky AOM-containing polysaccharides and proteins, TEP, and biopolymers. These materials are more difficult to remove than the algae cells and cause major SWRO fouling problems. These materials also create an environment where bacteria thrive and exacerbating biofouling issues in the SWRO [25].

As mentioned before, chlorine does not provide 100% barrier to all organisms causing biofouling.

5.2. Primary treatment

Voutchkov [10] has summarized filtration processes and technologies needed for SW before its entrance to the SWRO membranes, based on SW characterization by NTU, SDI, and chlorophyll-*a*, as shown in Table 4.

5.2.1. Coagulation and flocculation

The feed SW to the SWRO desalting plants has suspended particulates, contributing to turbidity that should be removed before SW inlet of the RO membranes. These particles can be inorganic such as clay and silt or organic such as algae, bacteria, viruses, protozoa and natural OM, and can have several sizes. Naturally, the sizes of 100 μm can be settled if sufficient retention time is provided, while particles of 10 μm in size tend to float. Therefore, small size particulates in SW have to be agglomerated to large particles for easily sedimentation or filtration. These include emulsified oil and grease and finely divided solid suspension in SW. Some of the suspended particles may have naturally negative charges (as shown in Table 2), repel each other electrostatically, and would not join to form larger particles that settle more quickly. A coagulant, such as ferric chloride ($FeCl_3$), can be added to SW to overcome repulsion between the particles. Many of the coagulant chemicals react with water to form insoluble hydroxides which, on precipitation, link together to form long chains or meshes, physically trapping small particles into the larger floc.

Coagulation usually precedes other pretreatment processes such as flocculation, DAF, sedimentation, GMF, and low pressure membranes filtration. It encompasses all reactions and mechanisms involved in the chemical destabilization of particles and in the formation of larger flocs by the aggregation of particulates of sizes range from 0.01 to 0.1 mm. The use of coagulation before GMF enables it to remove fine particles and micro-plankton of small sizes up to 0.2 μm, while GMF without coagulation removal is likely for large particles of 50 μm. Coagulation can be followed with or without clarification (e.g., sedimentation tanks or DAF) or filters. Flocculation involves gentle mixing of water to allow small particles to combine and form larger particles by particle collisions. In sedimentation, larger particles sink gradually to the bottom of the tank where they can be removed.

Chemicals coagulants used in SWRO pretreatment include ferric chloride ($FeCl_3$) and less used ferric sulfate [$Fe_2(SO_4)_3$]. They assist in removing the suspended particles by enabling them to agglomerate and settle. Inorganic coagulants and polymeric flocculants have positively charged molecules that interact with the negatively charged particulates, neutralize these charges, and allow the particles to come closer together. Ferric chloride and aluminum sulfate [$Al_2(SO_4)_3$] have trivalent cations that are effective in promoting coagulation. Coagulation is applied either in full scale or inline mode. Once added to SW, the iron coagulants are hydrolyzed and form ferric hydroxide [$Fe(OH)_3$] with a positive charge, depending on the coagulant dose and the pH of SW. The ferric sulfate is less used to limit possible calcium sulfate ($CaSO_4$) precipitation.

Alum [$KAl(SO_4)_2\cdot 12H_2O$] and polyaluminum chloride coagulants are often used in other water treatment processes, but are less common in SWRO pretreatment. These coagulants have high solubility that is encouraged by SW's high ionic strength, and can be carried to the RO membranes, leading to precipitation of ferric sulfate [$Al_2(SO_4)_3$] [6]. Although polyaluminum chloride is similar in performance to alum, its use leads to higher basicity than alum, contains Cl instead of SO_4 and contain up to three times the aluminum content. Limited SWRO plans are using aluminum-based coagulants due to cost and potential toxicity.

The NOM can be removed by coagulation through phase change, converting dissolved NOM into particles directly by precipitation or by adsorption onto particles produced by the coagulant. Other added chemicals in the pretreatment of the SWRO desalting process are shown in Fig. 9.

Voutchkov [10] gave typical dosing amounts for iron salt coagulants between 0.5 and 20 mg/L, depending on water pH, which were obtained from onsite jar tests or pilot plants for the site-specific conditions of a given application. The dosage is also temperature dependent. Coagulants overdosing cause SWRO membrane mineral fouling, and fast-rate fouling of

Table 4
Needed filtration processes based on SW characteristics (NTU, SDI, and chlorophyll-*a*) [10]

Turbidity (NTU)	SDI_{15}	TOC (mg/L)	Pretreatment process	Remarks
<0.1	<2	<1	Cartridge or bag filters only for grit removal may be needed if intake wells are used.	MF/UF may be cost competitive for 7–10 years life membranes.
>0.1 and <5	<5	<1	Single-stage dual-media filters plus cartridge filters are needed, and coagulant addition may not need.	
≥5 and <30	>5	<4	Single-stage dual-media filters plus cartridge filters, or MF/UF are recommended; and coagulant addition may be needed.	Moderate algal blooms
≥30 and <50	>5	≥4	Sedimentation or DAF plus single stage dual-media filters plus cartridge filters, or sedimentation or DAF plus MF/UF are recommended.	Severe algal blooms and/or high oil spill potential
≥50	>5	≥4	High-rate sedimentation or DAF plus two-stage dual-media filters plus cartridge filters, or high-rate sedimentation or DAF plus MF/UF are recommended.	

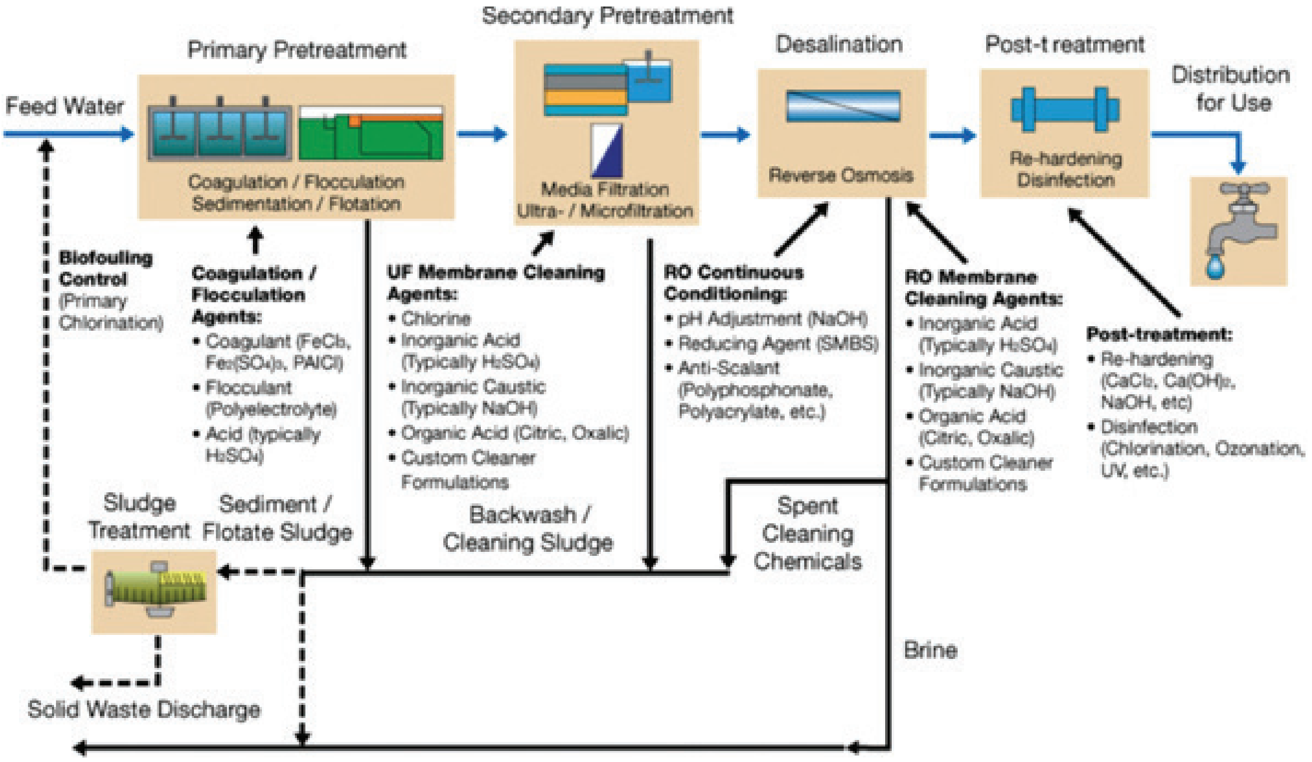

Fig. 9. Chemical conditioning in SWRO desalting plant [13].

Table 5
Reported removal efficiencies of algae for various treatment processes [26]

Treatment	Source water	Remarks	Removal (%)
GMF	E. Mediterranean Sea	Rapid sand filter (no coag.)	76 ± 13
	E. Mediterranean Sea	Coag. + mixed bed filter	90 ± 8
	E. Mediterranean Sea	Coag. [1 mg $Fe_2(SO_4)_3$] + RSF	79 ± 8
	W. Mediterranean Sea	Press. GMF (anthracite-sand)	74
	Algae-spiked seawater	Dual media filter (no coag.)	48–90
DAF	Algal culture	Coag. = 0.7–3 mg Al/L	98
MF	Algal culture	No coagulation	>99
UF	W. Mediterranean Sea	PVDF; pore size = 0.02 μm	99

Note: Removal efficiency calculated based on chlorophyll-*a* concentration or cell count.

the cartridge filters and SWRO membranes. Voutchkov [10] reported that, if TOC in seawater is reduced to 0.5 mg/L or less, then biofouling is unlikely, but TOC levels above 2 mg/L, biofouling is likely. Good coagulation would decrease the TOC to 1–2 mg/L, and then GMF is needed. Coagulation allows the granular filtration process to also remove finer particulate debris and micro-plankton from the source water. Properly operating filters can remove particles as small as 0.5 μm.

Tabatabai [26] showed that coagulation followed by sedimentation was effective in lowering biopolymers concentration and fouling potential by up to 70% and 80%, respectively. AOM comprises IOM formed due to autolysis consisting of proteins, nucleic acids, lipids and small molecules as well as EOM formed via metabolic excretion and composed mainly of polysaccharides. The biopolymer is part of the AOM of high molecular size, while low MW fractions (<1 kDa) are further sub-classified into humic-like substances, building blocks, acids and neutrals [26].

Coagulation followed by sedimentation was also effective in removing more than 80% of TEP for a coagulant dose of more than 5 mg Fe(III)/L [27]. Again, TEP was a significant fraction of the exo-polysaccharides, and was characterized by being highly surface active and sticky and was found to play an important role in the aggregation dynamics of algae during bloom events. The TEP can therefore adhere strongly to the surfaces of filtration systems and provides substantial resistance to filtrate flow during filtration. Table 5 shows that coagulation is only effective (with 99% removal efficiency) if combined with DAF for seawater loaded with algal culture.

Dual coagulants (low MW high charge-density cationic polymer and ferric coagulant) are usually used for SW in which NOM from algae or humic substances exists. The cationic polymer provides positive charge to satisfy partially the negative charge associated with particles and more importantly the dissolved NOM. The high charge-density cationic polymers can satisfy some of the negative charge associated with aquatic humic matter and algae thus reducing metal coagulant dosages. Their use in SW coagulation to complement ferric coagulation can be advantageous, especially because pH of SW is fairly high, limiting the fraction of positively charged Fe species available for charge neutralization [27].

Sometimes, coagulation by ferric chloride ($FeCl_3$) is not enough to create large and stable enough flocs, due to short residence times (typically a few minutes) as in SWRO pretreatment. Thus, coagulation is usually followed by flocculation to promote aggregation of the destabilized (coagulated) particles and as an aid to sedimentation and filtration. Flocculation is the bridging of particles by a polymer chain, causing them to form flocs or larger aggregates. Aggregation of coagulated particles into bigger and more robust flocs can be achieved by either extending the contact time while lowering the turbulence, or adding organic polymers.

The added organic polymers as flocculants can be of cationic, anionic and non-ionic types. Cationic polymers, such as poly-diallyldimethyl ammonium chloride (poly-DADMAC), have positively charged side groups and mostly serve as secondary coagulants following iron coagulant and act to further neutralize the colloids' negative charge. Anionic and non-ionic polymers (such as polymerized and copolymerized acrylamides) act as flocculants aids. By means of adsorption and inter-particle bridging, they create large stable flocs, as shown in Fig. 10 [6].

These flocs either float (flotation) or sink (sedimentation), depending on the relative density of the solute and the identity of the contaminant, making them easier to remove from the system. The large heavy flocs settle at the bottom of the clarifier and form a sludge layer that can be easily collected and removed.

The two types of flocculation are as follows: (1) micro-flocculation (or perikinetic flocculation), in which particle aggregation is brought about by the random thermal motion of fluid molecules known as Brownian motion; and (2) macro-flocculation (or orthokinetic flocculation), in which particle aggregation is brought about by inducing velocity gradients and mixing in the fluid containing the particles to be flocculated [28].

Coagulation and flocculation improves SW quality both in conventional GMF, MF and UF of SWRO, as well as in reducing MF/UF fouling. Prihasto et al. [29] reported, from work of others, that:

a. The use of potassium polymer ferrate (VI) as a coagulant and pre-oxidant can give excellent removal of algae and microbial, which can reach more than 98%.
b. The adsorption of humic acid by powdered, activated carbon (PAC) can be significantly greater in saline water compared with freshwater. The addition of the PAC prior to the coagulant was found to give the greatest removal of humic acid.

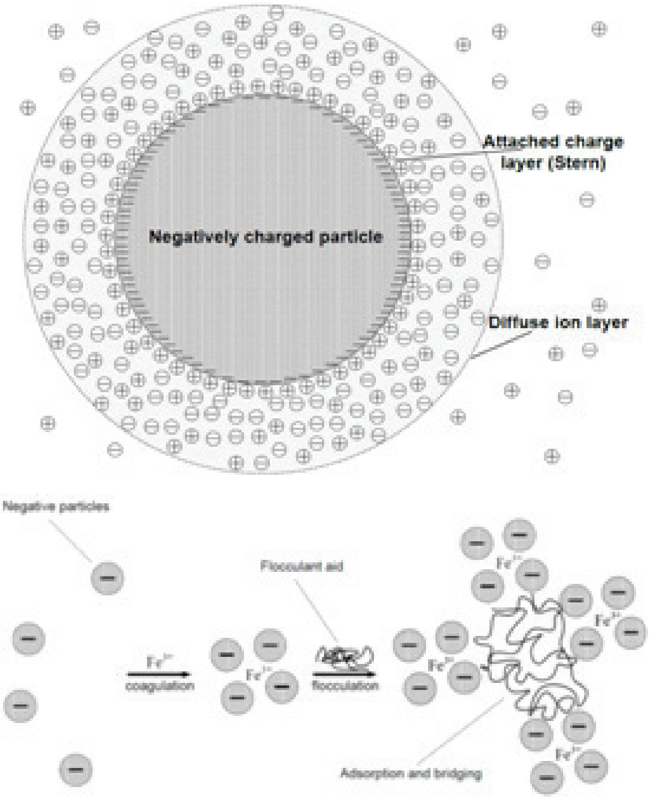

Fig. 10. Coagulation and flocculation of colloids with Fe(III) and an organic polymer [6].

c. Coagulant residuals from the pretreatment process may negatively affect RO membrane performance using either aluminum sulfate (alum) or ferric chloride coagulants and chloramines. The use of alum showed rapid deterioration in specific flux (up to 60% over 100 h of operation), and also progressive reductions in salt rejection.

5.2.2. Sedimentation

After coagulation and flocculation, the effluent SW is directed to the sedimentation tank. Within sedimentation, the suspended solids particles in feed SW are removed by gravity through moving the water to a settling tank at very low velocity. The settling tanks are called clarifiers, and built with mechanical means for continuous removal of solids being deposited by sedimentation. As pointed out by Voutchkov [10], sedimentation tanks are to be designed to produce water of turbidity less than 2.0 NTU and a measurable SDI_{15} below 6 by using both coagulant (most frequently iron salts) and flocculants (polymer) for the feed systems. The water flowing with low velocity in the settling tanks allows floc to settle to the bottom, and this tank should be close to flocculation tank to avoid floc break up. After the clarifier, water is directed to the filtration process, see Fig. 11(a). Typical sedimentation tanks have four zones: inlet zone, settling zone, sludge zone and outlet zone, see Fig. 11(b).

The inlet zone distributes the incoming water and controls its velocity as it enters the basin; and prevents

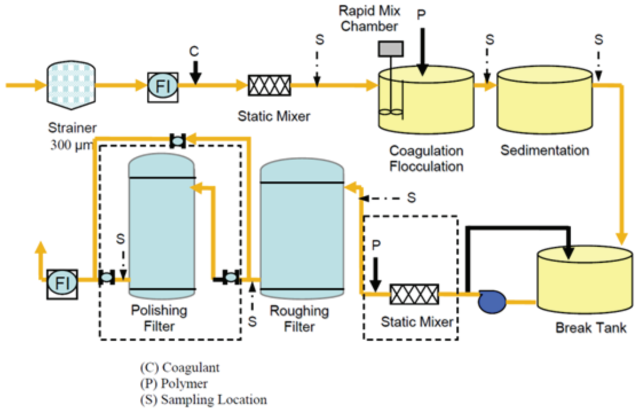

Fig. 11(a). Classical coagulation sedimentation filtration (CSF) pretreatment system [30].

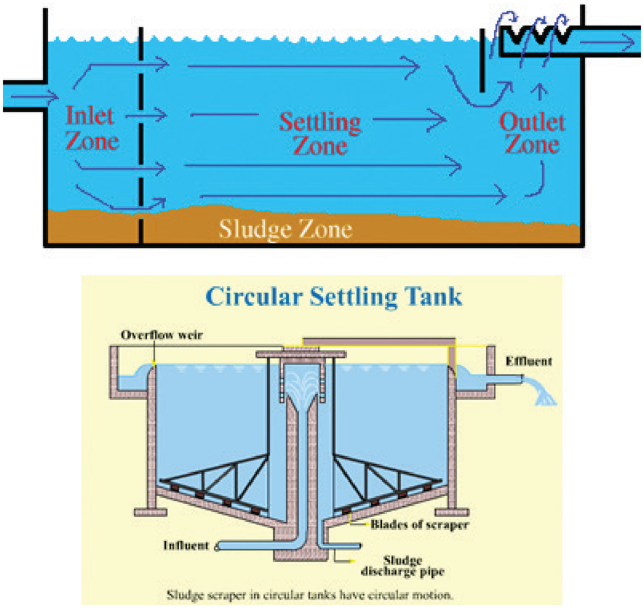

Fig. 11(b). Sedimentation tanks of horizontal and circular shapes [30].

turbulence of the water. In the settling zone, as water velocity is greatly reduced, the bulk of settling occurs. The settling zone requires a slow rate and even flow of water. The performance of sedimentation tanks is a function of settling velocity, flow through the tank and the surface area of tank, but not on the retention time or the depth of the tank. Typical retention times for sedimentation vary from 1.5 to 4 h and basin depths vary from 3 to 4.5 m. The particles settled at the sedimentation basin's bottom form a layer of sludge on the floor of the tank, which must be removed and treated. The amount of sludge generated is significant, often 3% to 5% of the total volume of water to be treated. A typical horizontal sedimentation tank configuration is the Lamella type tanks, as shown in Fig. 12, which is followed by single stage granular media filter that issued in 40,000 m^3/d (10.6 MGD) SWRO desalination plant with 43% recovery ratio [10].

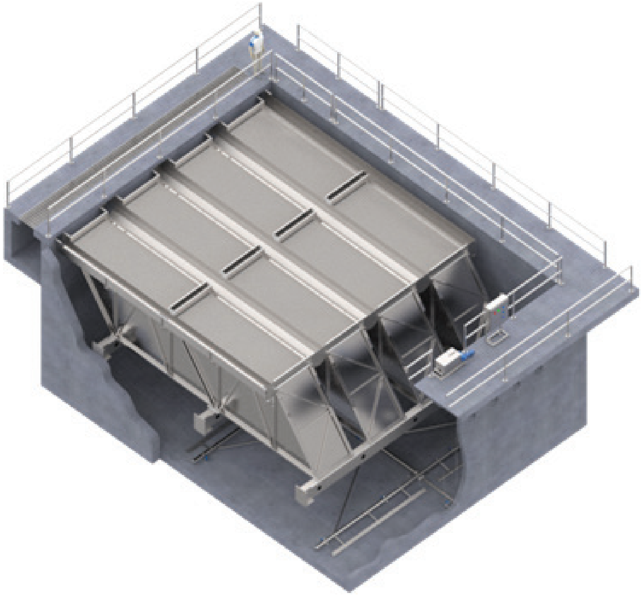

Fig. 12. Lamella sedimentation tanks [10].

5.2.3. Dissolved air flotation

The DAF tank, Fig. 13, has a front (contact) zone separated by a baffle from a separation zone. The contact zone receives the flocculated SW and air bubbles, forming floc-bubbles aggregate (called float) that flow vertically and provides opportunity for collisions and attachment among floc particles and air bubbles. Air bubbles are aggregated with floc. The water carrying the suspension of floc-bubble aggregates, along with free bubbles and unattached floc particles, flows vertically to enter the separation zone. The size of the air bubbles is directly related to the predominant size of algae cells in SW, which can be determined by the completion of algae profiles during AB and non-AB conditions.

The bubble-floc aggregates (called the float) rise to the surface of the tank, producing sludge that is skimmed from there. Clarified water is withdrawn from the bottom of the tank, where part of it is recycled (Qr). Air is introduced within a pressurized recycle water stream and is separated as small bubbles by passing the recycled water through nozzles in the tank that lower its pressure. The recycle flow has a typical 10% times Qr, and the micro-bubbles have typical sizes between 10 and 100 μm. The DAF is particularly good in removing algae from SW, after coagulation by ferric chloride and flocculation by cationic poly-electrolytes. It also removes the precipitates caused by coagulants and flocculants.

The DAF process is increasingly applied in SWRO pretreatment process to remove low-density particles that can float, e.g., algae cells, oil and grease contained in seawater. It is usually followed by conventional GMF or low pressure membranes filtration, i.e., MF and UF. The DAF removes the particles naturally present in the feed SW, particles produced by processes prior to the DAF, or those from oxidation processes [31]. The DAF technology can produce effluent turbidity of <0.5 NTU. Haarhoff and Edzwald [32] modeled the DAF processes, and compared its performance with seawater and freshwater. Fig. 14 shows a schematic diagram of a

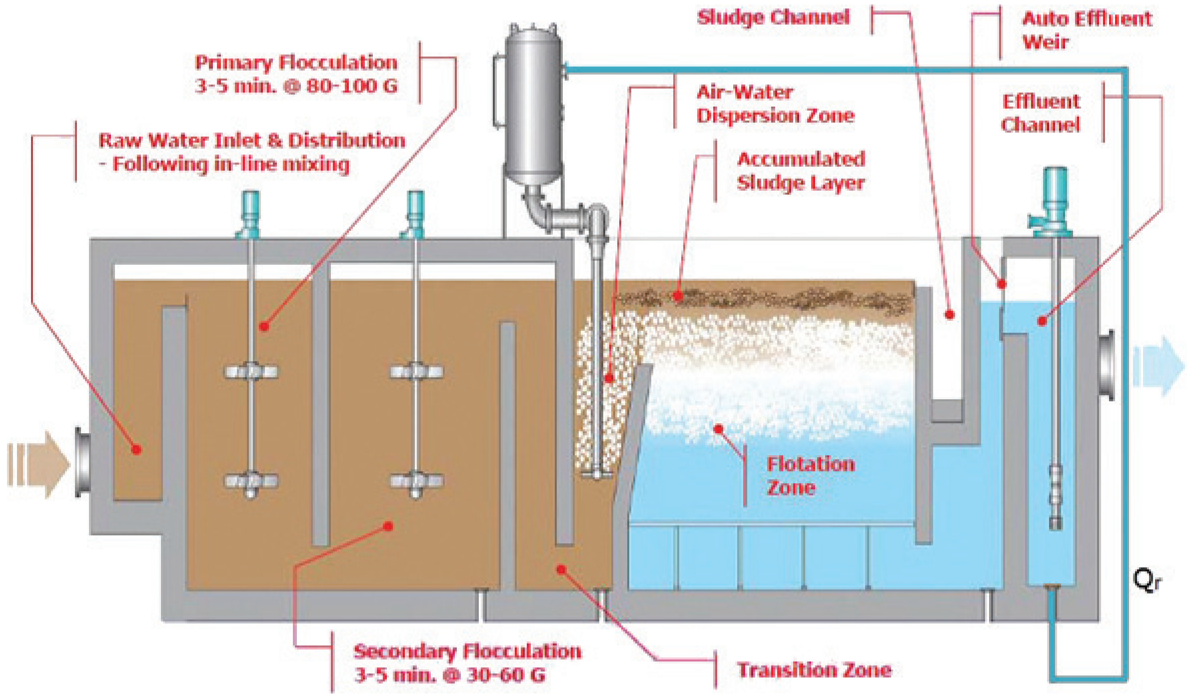

Fig. 13. Clarification by dissolved air flotation [13].

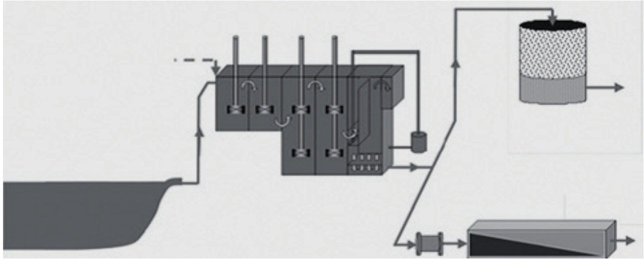

Fig. 14. Schematic representation of the pilot plant [33].

pilot plant used to compare the effect of using DAF upstream GMF or UF systems [33]. One of the most significant features of the DAF is the low surface loading rate (about one tenth, compared with the conventional sedimentation), and thus low foot print. Sludges formed by DAF processes are also of high density.

The DAF may not be suitable for treatment of SW sources of high turbidity (beyond 50 NTU). The SW turbidity during most ABs does not exceed 50 NTU, and thus the DAF can handle practically any AB condition. The problems with the DAF, compared with conventional sedimentation, include the added equipment to provide saturated air, partial recirculation of treated water, and higher consumed energy. Commercial DAF units were primarily designed for fresh and wastewater applications, and new designs were developed for SW having smaller plankton with smaller bubble sizes, increased air pressure of saturated air to account for SW high density and viscosity compared with freshwater. In addition, low-charge particles require longer contact time and better mixing in the coagulation and flocculation chambers, in order to form large enough flocs for effective removal in the flotation zone of the DAF [10]. An example of the DAF clarifier design was given [10], for 40,000 m^3/d SWRO desalting plant having 43% recovery ratio and DAF clarifiers is combined with GMF. The maximum algal count in the source water is 60,000 cells/mL, and the hydrocarbon levels can reach 0.5–1 mg/L. The pretreatment system was designed to operate with addition of coagulants and flocculants and adjustment of pH of the source water flow.

Examples of DAF followed by GMF applied in large SWRO pretreatment plants are [10]:

- Al Dur SWRO plant (Bahrain) of 240,000 m^3/d (63 MGD) permeate capacity, with DAF loading of 25–30 m/h, followed by horizontal pressure filters of filtration rate of 18–24 m/h filter loading rate, and using an open intake of shallow water in an area prone to ABs.
- Barcelona SWRO plant (Spain) of 200,000 m^3/d (53 MGD) permeate capacity, with DAF loading 25–30 m/h followed by 20 dual media gravity filters of 8–10 m/h filter loading rate and 20 horizontal pressure filters of 15–20 m/h filter loading rate, and using deep off-shore open intake.
- Fujairah II SWRO plant (UAE) of 140,000 m^3/d (37 MGD) permeate capacity, with DAF loading of 15–20 m/h followed with 16 single-stage dual-media pressure filters of 37–49 m/h filter loading, and using open intake of shallow water.
- El Coloso SWRO plant (Chile) of 45,400 m^3/d (12 MGD) permeate capacity, with DAF loading 22–33 m/h and followed by 13 two-stage dual-media horizontal pressure filters of 25 m/h filtration rate, and using a deep off-shore open intake in an industrial port with frequent red tides.

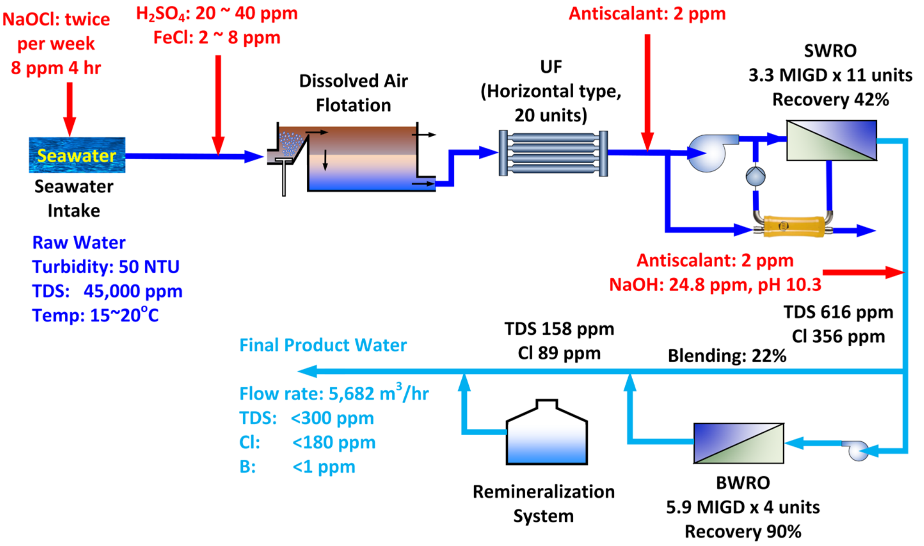

Fig. 15. General configuration of Shuwaikh SWRO plant in Kuwait built and operated by Doosan [34].

DAF also was installed upstream low pressure UF membranes in Shuwaikh (Kuwait) SWRO plant, as shown in Fig. 15 [34]. The use of DAF became a common practice in areas where AB occurs. The DAF subsystems performed well, as shown in Fig. 16, which compared the SW turbidity at the intake and DAF effluent.

When the feed SW contains a measurable amount of algae species, which is greatly increased during red tides, some algae species cells are easily fragmented under pressures as low as 0.3–0.6 bar. When these cells are broken, they release cytoplasm into the source water that has a very high content of easily biodegradable polysaccharides. When the amount of polysaccharides released by the broken algae cells exceeds a certain level in the filtered water, it typically triggers accelerated biofouling on the RO membranes. Therefore, it is preferable to gently remove algae cells and prevent their breakage. Another solution is to include a layer of granular activated carbon (GAC) on the top of granular media filter that followed the DAF to remove some of the polysaccharides and other organics from the water [10]. Operating pressures required for GMF processes are often higher than the threshold at which algal cells break, and thus may cause accelerated biofouling when the filtered water has very high algae content, usually during ABs in summer. In this case, a coagulant of 1–2 mg Fe(III)/L or higher is required to keep this process effective. In addition, coagulants might be required upstream of the GMF to ensure an acceptable SDI in the effluent.

The DAF proved to be more robust than sedimentation in handling large concentrations of suspended matter (e.g., algae), and now is often used upstream the GMF to avoid its rapid clogging with algae in the case of AB incident similar to that happened in the GCC in 2008–2009. In this incident, when a coagulant was used with GMF without using DAF, the population of decayed organic and bacterial matter increased and often passed through GMF. This raised the SDI at both inlet and outlet of cartridge filter beyond 5, leading to down times at some plants that exceeded 40%. Fig. 16 shows thick floating sludge or scum accumulated on top of GMF (right side photograph) during red tide period as compared with clean surface during normal operations (left side photograph) in an operating plant in the UAE. The use of DAF upstream of GMF might be cheaper than having conventional sedimentation units upstream the GMF as the DAF has lower foot print.

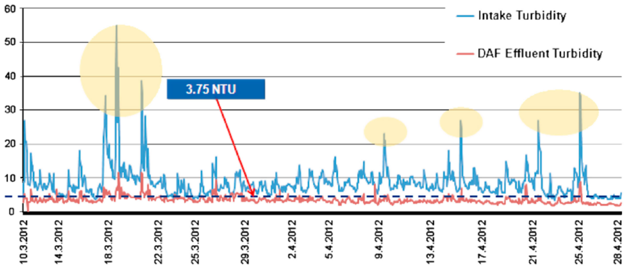

Fig. 16(a). Turbidity peak has been detected during ship movement, torrential rain and low tide with strong wind condition [34].

Fig. 16(b). Thick floating sludge or scum accumulated on top of DMF (right side photograph) during red tide period as compared with clean surface during normal operations (left side photograph) in an operating plant in the UAE [34].

Most of the algae cells (more than 90%) are removed by being floated and skimmed in the DAF tank. It is reported that dosing the SW with a coagulant at around 1–2 mg/L as

Fe^{3+} into the DAF assists micro-bubbles in lifting coagulated cells to the surface of the DAF tank. Coagulant can also aid removal of any extracellular AOM that may have leaked from the algae cells. Notably, toxins are mostly intracellular depending on the species of algae. For example, microcystin is the main intracellular toxin (97%) produced by the algal species *Microcystis aeruginosa* [25]. Thus, DAF can be an additional barrier for removing intracellular toxins. Extracellular toxins are poorly removed by the DAF process and can process to the filtration stage. A pilot plant study conducted at Al Fujairah in the UAE showed more than 97% removal of cells using green algae, *Tetraselmis*, at 100,000 cells/mL [25]. This shows that the DAF process can be effective for cell removal even in very dense AB. Dixon et al. [25] reported that the few algae cells left in the DAF effluent will be adequately removed by pre-filtration, whether that is dual media filtration (DMF) or UF. It is important to mention that *Tetraselmis* is a surface dwelling algae, it exploits the very surface of the water due to the ability to produce its own "sunscreen." Most algae cannot occupy this upper most layer, the UV light is too damaging. Consequently, it is not recommended to use a *Tetraselmis* study as a be all and end all of DAF being effective for removing algae because there are many more types of algae that would need to be investigated.

5.3. Secondary treatment: filtration

5.3.1. Granular media filtration (GMF)

In large conventional SWRO pretreatment plants, GMF is the main water filtration component, where SW is filtered to reduce high loads of particulate and colloidal matter (i.e., turbidity). The GMF is supposed to receive feed SW after being screened, coagulated, flocculated, passed through sedimentation or air flotation tank, which is followed by micron cartridge filter before finally entering the SWRO membranes, see Figs. 5(a) and 10(a). The targeted effluent quality from the GMF before its entrance to the SWRO membranes should have an average turbidity of less than 0.1 NTU or a maximum of less than 0.5 NTU, SDI less than 3 (at least 95% of the time), TOC less than 1 mg/L, and total hydrocarbons of 0.04 mg/L. The main particulate removal mechanism in the GMF is not only due to straining, i.e., removal of particles from liquid by passing the liquid through filter whose pores are smaller than the particles, but rather that of depth filtration or adsorption like effect where particles "stick" to the filter media [35]. Actually the removal mechanisms in filter media rely on sedimentation on media (sieve effect), adsorption, absorption, biological action and straining, see Fig. 17(a) [36]. The media filter should have good hydraulic characteristics (permeable); should not react with substances in the water (inert and easy to clean); should be hard, durable and free of impurities; and should be insoluble in water. Gravel that is used to support the filter sand should have similar characteristics. Typical filter media characteristics are given in Table 6.

Typical parameters of a dual media filters are as follows: anthracite layer thickness of 0.7–0.8 m, grain effective size of 1.0–1.5 mm and uniformity coefficient (UC) ≤1.4. The sand layer thickness should be 0.7-0.8 m, effective size 0.6 mm, UC ≤1.3, and velocity 7–10 m/h. The effective size is defined as the size of a sieve opening through which 10% (by weight) of the particles (sand) will just pass and is given the symbol d_{10}.

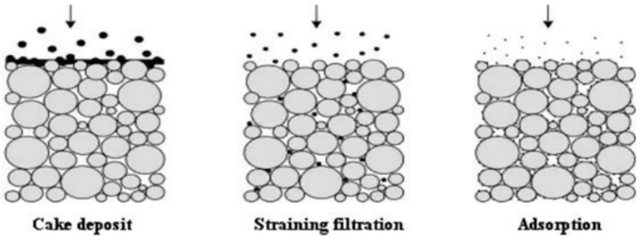

Fig. 17(a). Fouling mechanisms at stake in the granular filtration [36].

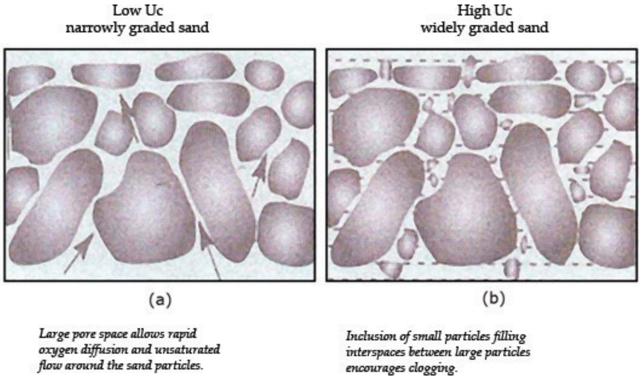

Fig. 17(b). Explanation of how small particles filling the spaces between large particles give high UC [37].

Fig. 17(c). Dual media gravity filtration in Fujairah 2.

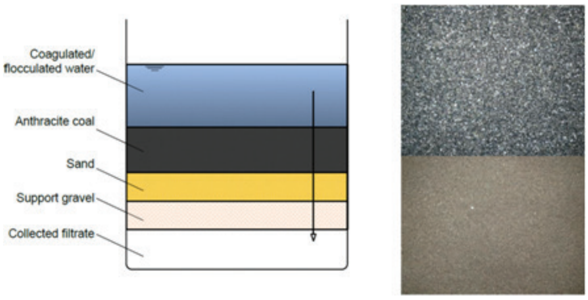

Fig. 17(d). Dual media filtration (left) and schematic of gravity filter (right) sand and anthracite media [6].

Table 6
Typical filter media characteristics [10]

Medium	Typical effective grain size, mm	Specific density, tons/m^3	Uniformity coefficient
Pumice	0.8–2.0	1.2	1.3–1.8
Anthracite	0.8–2.0	1.4–1.7	1.3–1.8
Silica sand	0.4–0.8	2.60–2.65	1.2–1.6
Garnet	0.2–0.6	3.5–4.3	1.5–1.8

In a similar way, the size of a sieve opening through which 60% (by weight) of the particles (sand) will just pass is given the symbol d_{60}. The UC, which is a measure of the grading of the material, is the ratio d_{60}/d_{10} [35]. The UC indicates how similar the media particles are with respect to size. The d_{60} value of the filter media can also be used to determine the filter backwash rate at 20°C. In general, for media of the same size, a higher UC allows for an increased filter cycle length. A schematic diagram of low and high UC is provided in Fig. 17(b).

Single-stage dual-media (separated anthracite and sand of different specific gravities) is typically used in SWRO pretreatment. Water passes through the filter bed (in the down-flow direction in most cases, but up-flow exists also), causing the suspended particles to contact and adsorb (stick) onto the surface of the individual media grains or onto previously deposited material. The anthracite (black coal) layer is sited on the sand layer and allows run times longer than that of sand alone. This top layer with larger void spacing acts as a robust roughing layer that can handle heavy solids loading conditions, such as in the case of an AB incident. The sand lower layer acts as final barrier for the fine particles that would otherwise lead to fouling. The GMF performance depends on the type, uniformity, size, and depth of filter media. Typical layer thicknesses are 0.4–0.8 m for anthracite layer and 0.4–2 m for sand. The performance of GMF is determined by its capability for removing silt and colloids or by reducing the SDI. Many GMF can consistently reduce source water turbidity to less than 0.1 NTU at the same time producing effluent with SDI frequently exceeding 4, and should be designed to capture fine solids, silt, and colloidal organics contained in SW.

The parameters considered in the design of the GMF are the expected quality of filtrate, the size, surface charge, and geometry of both suspended solids and filter media, and choice of operational parameters. The design filtration flow rates are usually 10–20 (m^3/h/m^2) or simply m/h, and the backwash rates are in the range of 40–50 m/h. For feed SW of high fouling potential, flow rates of less than 10 m/h and/or second pass media filtration are used. When SW contains high levels of organics (TOC is higher than 6 mg/L) and suspended solids (monthly average turbidity exceeds 20 NTU), two-stage filtration systems are usually applied. The first filtration stage is mainly designed to remove coarse solids and organics in suspended form. The second-stage filters retain fine solids and silt, and remove a portion (20%–40%) of the soluble organics contained in the saline water by bio-filtration [10]. The use of sand of 0.8–1.2 mm grain size and anthracite of 2–3 mm grain size filter beds provides higher filtration rates, longer runs and require less backwash water, when compared with single media filtration. 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. After the filtration process, the filter media is cyclic backwashed with water and air.

GMFs with water flowing by gravity are reinforced concrete open tanks of similar size operating in parallel, with minimum number of three tanks required to allow for one filter to be standby (e.g., for backwash or maintenance), while the capacity of the other two meets the demand. The size of each tank is limited to 100–150 m^2 to avoid non-uniform backwash. Voutchkov [10] recommended a minimum number of four tanks, even for very small plant, and six to eight tanks for plants with a capacity of more than 5,000 m^3/d (1.3 MGD). For DP of more than 10,000 m^3/d, the tanks are to be divided into two groups that can be operated independently and paired with one-half of the desalination plant RO trains.

Filtration tanks are filled with media of 1.8 and 3.0 m, and water is allowed to flow through them, Figs. 17(c) and 17(d). The water head (pressure) over the filter bed provides the pressure needed to overcome the head loss in the media. Single-stage dual-media down-flow gravity filters are the predominant type of filtration pretreatment technology used in SWRO desalting plants with a capacity of more than 40,000 m^3/d. Typical examples of DP using gravity GMF filters are [10]:

- Ashkelon SWRO plant (Israel) of 330,000 m^3/d (86 MGD) permeate capacity, using 40 single-stage dual-media gravity filters of average and maximum loading of 10/12 m/h.
- Sydney SWRO plant (Australia) of 250,000 m^3/d (66 MGD) permeate capacity, using 240 single-stage dual-media gravity filters of average and maximum loading of 8/12 m/h.
- Fujairah SWRO plant (UAE) of 170,000 m^3/d (45 MGD) permeate capacity, using 14 single-stage dual-media gravity filters of average and maximum loading of 8.5/9.5 m/h.
- Gold Coast SWRO plant (Australia) of 136,000 m^3/d (36 MGD) permeate capacity, by using 18 single-stage dual-media gravity filters of average and maximum loading of 8/10 m/h.
- Tuas SWRO plant (Singapore) of 136,000 m^3/d (36 MGD) permeate capacity, by using 20 single-stage dual-media gravity filters combined with DAF and has average and maximum loading of 6/10 m/h.

Voutchkov [10] gave an example of a gravity type GMF with down-flow dual media operating in large capacity SWRO plant as a guide line, and suggested that final design (media size, depth and configuration) should be based on pilot testing, with a tapered distribution channel to the concrete tanks as follows:

- Velocity in the distribution channel higher than 2 m/s at all times;
- Number of filter cells 8–18;
- Filter cell width 3–8 m, depth 4.5–7.5 m, length-to-width ratio 2:1–4:1 (typically 3:1);

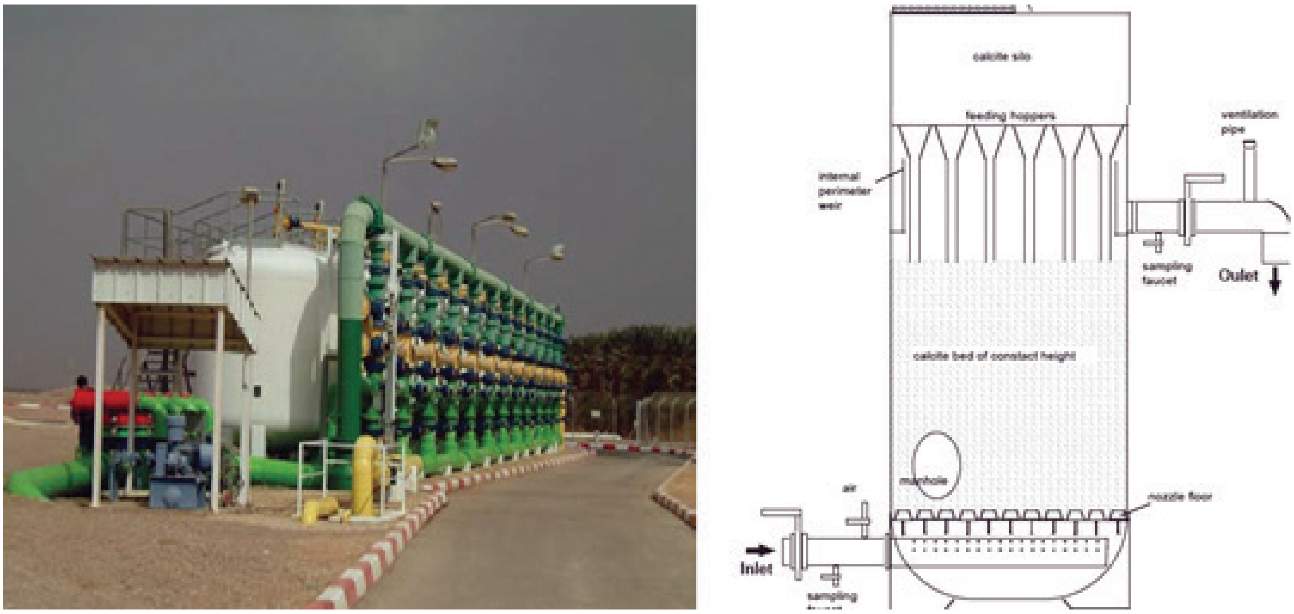

Fig. 18(a). Vertical pressure granular media filters [13].

- Individual filter cell area 25–100 m^2;
- Maximum water depth above filter 2.5 m (should be equal to or slightly higher than filter bed head loss), which is usually 1.8–2.4 m;
- Filtration rate (at Desalination Plant Intake Design Flow) with all filters in service 8–10 m/h, and with two filters out of service 15 m/h;
- Filter Media:
  - *Anthracite/pumice:* top layer depth 0.8–1.8 m for deep bed filters; or 0.4–0.8 m for shallow bed filters used for water of low turbidity (less than 5 NTU) and low organics content (TOC less than 2 mg/L),
  - *Anthracite/pumice:* effective size is 0.8–2 mm (typically 1.2 mm), UC 1.3–1.7 (preferably less than 1.4),
  - *Anthracite bulk:* specific gravity is 1.5–1.6 tons/m^3, and density 0.8–0.85 tons/m^3,
  - *Sand bottom Layer:* depth for deep bed filters 0.8–2 m (recommended), and for shallow bed filters 0.4–0.6 m, effective size 0.4–0.6 mm, UC less than 1.4, and specific gravity 2.65 tons/m^3, and density 1.5–1.9 tons/m^3.
- Air-water filter backwash system
  - *Backwash rates*: maximum 55 m/h and average 40–45 m/ h, and duration (total air plus water) 15–30 min (includes filter cell draining and fill-up);
  - The pressure type GMFs with down water flowing has similar beds as the gravity GMF type, but they are contained in vertical, or horizontal steel pressure vessels, Figs. 18(a) and (b), respectively.

These pressure types GMF were used mainly in small and medium SWRO desalination plants, usually less than 20,000 m^3/d (5.3 MGD) although some large capacity plants use this type. Examples of large SWRO plants using pressure GMF are given by [10]:

- Al Dur SWRO plant (Bahrain) of 63 MGD,
- Barcelona SWRO plant (Spain) of 53 MGD,
- Perth I SWRO plant (Australia) of 38 MGD,
- Fujairah II SWRO plant (UAE) of 37 MGD,
- El Coloso SWRO plant (Chile) of 12 MGD.

Fig. 18(b). Horizontal pressure granular media filters [13].

The pressure type GMFs are prefabricated steel structures. When compared with gravity type, the pressure types have lower volumes and sizes (and smaller foot print) and

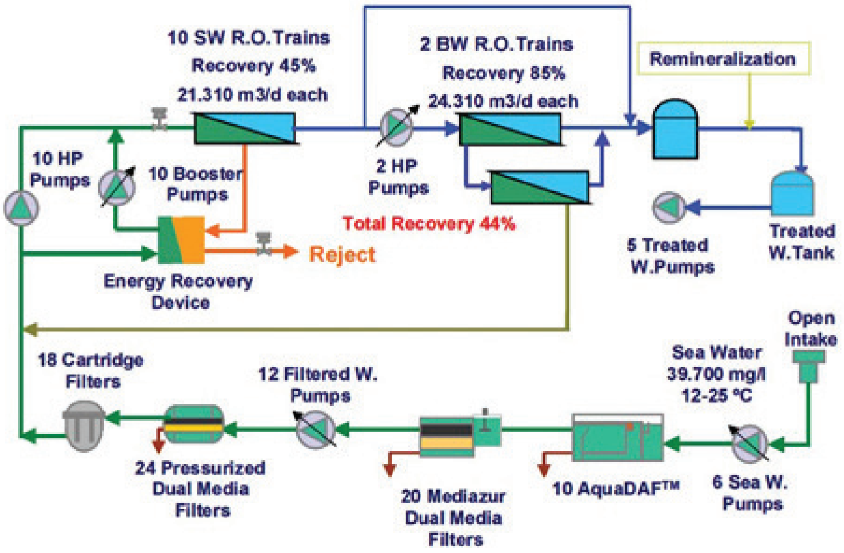

Fig. 18(c). 200 m^3/d ML/d Barcelona SWRO Plant using both pressure and gravity GMF preceded by DAF [13].

thus lower production costs per unit filtration capacity. This is clear from the fact that pressure type GMF have 25–45 m/h surface loading, compared with that of gravity loading of 8–15 m/h. Moreover, it is easier to fill prefabricated vessels with media filters layers in shorter times than building concrete tanks to contain the filer's media. The gravity filters need to be covered in order to avoid sunlight that induces algal growth.

Concerning removal of algae species, the pressure-type GMF is operating at pressures higher than that which breaks the algae cells. Again, the breaking of algae cells releases cytoplasm into SW with high content of easily biodegradable polysaccharides, which can trigger accelerated membranes biofouling. This problem is solved by using DAF before the GMF and by using a GAC media layer (activated carbon layer-cap) on the surface of the filters to remove some of the polysaccharides and other organics in SW. This is usually occurred in the summer and during AB, and when the TOC in SW exceeds 2 mg/L.

Voutchkov [10] gave an example for pressure type GMF of single stage with down-flow dual media operating large capacity SWRO plant as follows:

- Number of filter vessels is 6–20, and each has diameter of 1.2–6 m (typically 3 m), length of 2.5–15 m (typically 6 m), and depth of filter bed 0.6–0.9 m;
- Filtration rate (at desalination plant intake design flow);
  - All filters in service: 12–25 m/h, and
  - Two filters out of service: 30 m/h,
  - For two stage media filtration, the first, coarse media stage using single or dual media down flow, air-water backwash; filtration rate is 15–25 m/h when all filters are operated and 30 m/h when two filters are out of service.
- Head loss across the filter vessel;
  - Total head loss across the filter media 15–30 m (average 20 m), and net head loss available for filtration 7.5–15 m, and average filter cell run length 24–48 h.
- Anthracite or sand filter media;
  - Anthracite layer depth is 0.4–1 m, effective size is 1–2 mm (typically 1.5 mm), and UC is less than 1.5. Sand layer depth is 0.4–1 m, effective size is 0.4–0.6 mm, and UC is less than 1.5.
- Air–water filter backwash system;
  - Backwash rate: maximum 60 m/h, and average 45–55 m/h, and duration (total air plus water) 20–30 min (includes filter cell draining and fill-up).

It is clear that, before GMF, the feed SW should go through some processes such as sand removal, sedimentation and DAF. It is noticed here that the 200 m^3/d Barcelona SWRO Plant (Spain) uses both pressure and gravity GMF preceded by DAF, as shown in Fig. 18(c).

Voutchkov [10] reported low TOC removal rate (15%–20%) when the media filter layer depth is 1.0–1.4 m. The removal rate can reach 25% if the filter media layer is increased up to 2 m. The TOC removal rate can be increased to 40%–50% if a carbon cap is installed on the top of the media filter. Concerning the removal of algae, most of algae species larger than 100 μm are retained by the top anthracite layer. Micro- and pico algae are not well removed by conventional sand media of sizes 0.4–0.6 mm; hence, a third layer of finer filter medium is to be installed. In general, algae removal can typically vary between 20% and 90% depending on the media size. The effluent quality of GMF can be highly changed over time, with reported removal efficiencies of 48%–90% for algae and 17%–47% for biopolymer (algal-released organic macromolecules) [10]. Dixon et al. [25] reported that GMF can have up to 90% algae cells removal efficiency when optimized. Biopolymer removal may be up to 47%. Concerning bacteria and viruses, GMF typically removes 99% of pathogens. Removal of marine bacteria may occur at a lower rate because these organisms are of smaller size than human pathogens and may pass through the filters. Coagulants have to be monitored and optimized by using jar tests in the event of AB, when applied. Filter clogging can occur in case of poor coagulant dosing and insufficient flocculent time.

5.3.2. Low pressure membrane filtration: MF/UF

Low-pressure micro-porous microfiltration (MF) and ultrafiltration (UF) membranes can be used for feed SW filtration, in place of, or with GMF. The MF and UF can be pressure-driven or vacuum-(submerged-)driven, as shown in Figs. 19(a) and 19(b), respectively. The pore size is 0.1–0.4 μm for MF, and 0.001–0.02 μm for UF membranes. The filtration membranes can be an organic type of hollow fiber and plate configuration or a ceramic type of tube or plate configurations. Fig. 15 shows components of the 136,368 m^3/d Shuwaikh (Kuwait) SWRO plant. Particulate, colloidal and some organic foulants contained in shallow SW are successfully removed by using pressurized (Norit) UF of 60–77 $L/m^2/h$ hydraulic loading in the pretreatment [10]. In addition, MF membranes are used for feed SW pre-treatment in Oman 20,000 m^3/d SWRO plant, Fig. 20(a). In this plant, feed SW is taken from shallow lagoon open intake of 4 m depth and is screened, continuously chlorinated before reaching pumping station and directly supplied to MF membranes filtration system, then directed to the RO units without a break tank. This MF system uses Pall Microza UNA-620A, Fig. 20(b), high crystalline crystalline polyvinylidene difluoride (PVDF) membranes, with less than 0.1 μm pore sizes, and outside–inside filtration mode. This system was challenged in September 2013 by an AB event, resulting in SW of very high levels of $SDI_{15} > 35$, and high AB values > 5.8 million cells/L [10]. Consequently, the self-cleaning strainers were partially clogged, a high trans-membrane pressure (TMP) was required due to unexpected SW conditions, and biological fouling on the downstream SWRO units was found due to the high level of DOC that was not removed by the MF pretreatment.

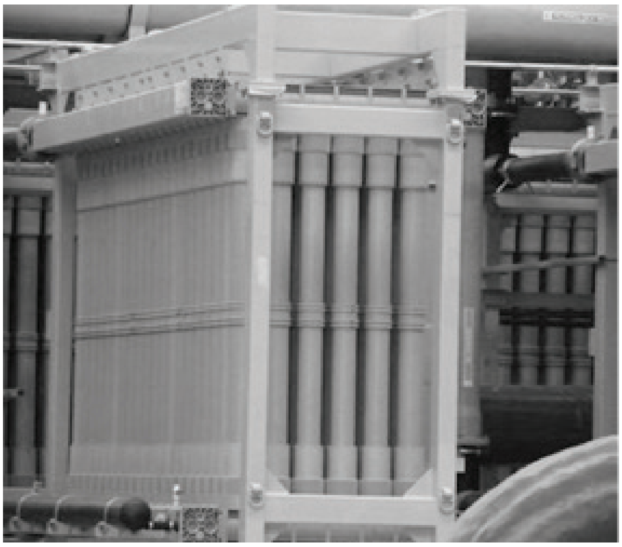

Fig. 19(a). Module of the UF pretreatment system at the Southern Seawater Desalination Plant in Perth, Australia [10].

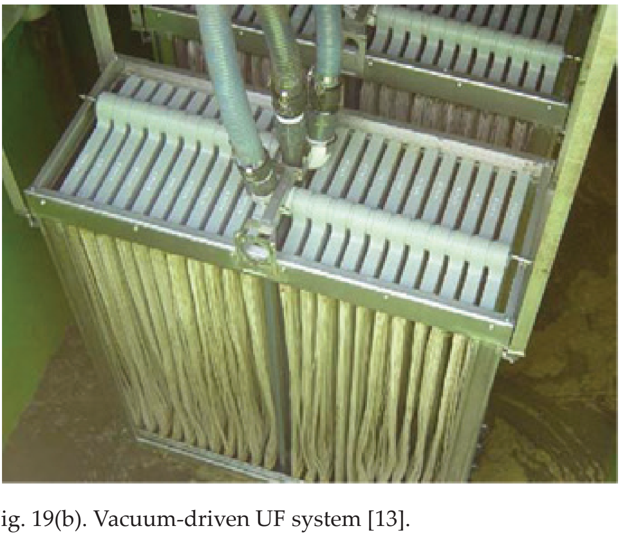

Fig. 19(b). Vacuum-driven UF system [13].

The advantages of using MF and UF, compared with GMF, are the lower footprint, constant high effluent quality (lower SDI), see Fig. 21, higher retention of large MW organics and lower overall chemical consumption. MF and UF are more effective in removing particulate and colloidal matter from SW than GMF [26].

The UF and MF, when compared with GMF, are also superior in microbial removal, give less residuals to handle and are easier to operate. The UF and MF give the SWRO membrane longer life and the potential to operate at higher flux. Thus, less SWRO membranes needed with less replacement and lower cleaning costs. The UF is more reliable in producing low fouling potential SWRO feed SW, even during an AB event.

Fig. 22(a) shows the 300,000 m^3/d SWRO Perth II plant using Siemens pressurized UF membranes (Memcor CP 960) treating shallow open water, using out-in flow type, 2 trains × (4 + 1) units with 912 elements per unit, nominal pore size of 0.04 μm, flux (average/peak) = 52/65 Lmh, and with no chemical addition [13]. Fig. 22(b) shows a schematic diagram of submerged vacuum UF system, and Fig. 22(c) shows vacuum-driven UF system manufactured by GE Zenon system. The largest SWRO plant using vacuum-driven pre-treatment is the 300,000 m^3/d Adelaide, Australia, which has 2 × 14 cells × 900 units/cell, nominal pore size = 0.04 μm, flux (average/maximum) = 52/65 $L/m^2/h$, and no chemical addition.

The UF is increasingly used as substitution for GMF in many large SWRO pretreatment plants in the last decade. Examples of plants with this type of membrane filtration are given in Table 7 [10].

The main performance parameters of the UF filtration process are as follows:

- Membrane flux: volume of treated water per unit membrane area in liters/h per square meters ($L/m^2.h$);
- TMP: difference between the feed pressure and the filtrate pressure across the membrane in bar; and
- Membrane permeability: the membrane flux divided by the TMP difference ($L/m^2.h.bar$).

Typical fluxes of water in pressurized UF units range 40–80 $L/m^2/h$, while typical TMP in UF SW pretreatment ranges 0.2-1.0 bar. The pressurized UF can have TMP

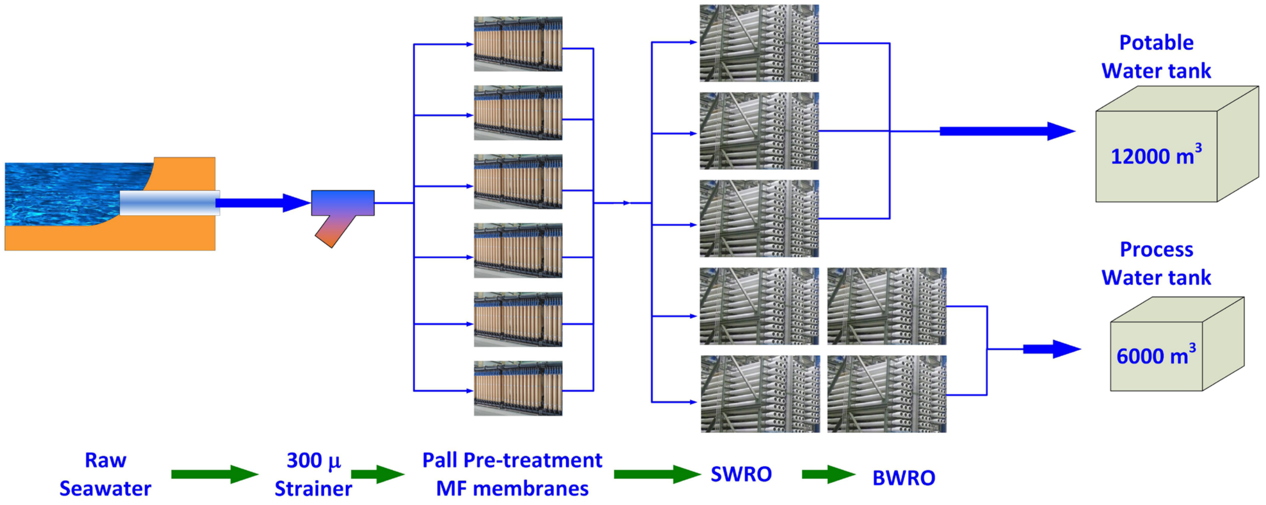

Fig. 20(a). Simplified PFD of Majis 20MLD plant [38].

Fig. 20(b). Microza hollow fiber UNA modules [38].

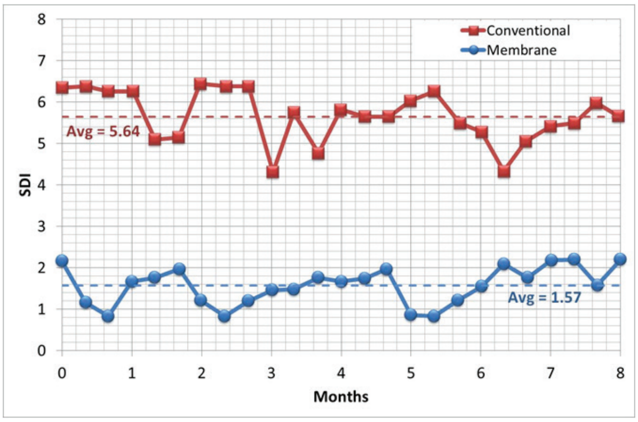

Fig. 21. The effluent SDI of membrane pretreatment compared with GMF along months. Adapted from [13].

exceeding the 1.0 bar, and most of them operate at 2.5 bar. The vacuum-driven (submerged) UF have TMP less than 1 bar (typically 0.7 bar) because of the potential collapse the membrane fibers by for excessive vacuum.

The UF membrane filtration process is followed by periodic backwashing, cleaning, and testing. Backwashing is to be done periodically to remove solids filtered out of the source water accumulated on the feed side of the membrane surface, and by using filtered water or concentrate. Backwashing can be started when the TMP reach a certain value indicating low flux or low quality filtrate. Air–water backwash is applied in sequence and is mainly intended to remove particulates from the UF without using cleaning chemicals. Over time, organic deposits and biofilms are accumulated on the UF membranes, such that chemically enhanced backwash (CEB) becomes necessary. In CEB, the membranes are soaked in chlorine and sometimes other cleaning chemicals (acids, alkalines, or sodium bisulfite) for several minutes and then backwashed. When the TMP increases to a certain pre-set limit, that means that backwashing did not remove all foulants, so the UF module is taken offline and cleaned with combination of low-pH solution of citric or sulfuric acid followed by a high-pH solution of sodium hydroxide and sodium hypochlorite to reduce the TMP to a reasonable level. This cleaning is done every 1 to 3 months. The cleaning chemicals are re-circulated through the membranes for a period of 8–24 h, and then the membranes are flushed and returned to normal operation.

Fouling of MF/UF membranes occurs in SWRO pretreatment systems, particularly due to the increase of NOM present in SW during AB. Algae cells release EOM, resulting in

Fig. 22(a). Perth II – Memcor pressurized pretreatment system [13].

significant increases in fouling rate and indicating the need for additional membrane cleaning. As some fractions of algae EOM are much smaller than typical UF membrane pore sizes, the potential of organic transmission onto downstream processes is also a serious concern. Adding coagulation and DAF prior to UF or MF are very effective to minimize fouling during AB [39, 40].

Resosudarmo et al. [40] indicated significant better fouling performance by adding coagulation or DAF prior to UF compared with standalone UF. They experimented with SW with addition of 25,000 cells/mL *Tetraselmis* algae. The results shown in Fig. 23 indicate significant lower TMP at the end of 10-h filtration after the addition of coagulant. When DAF was added prior to UF, membrane fouling during this period was negligible; TMP increased by less than 2 kPa over 10 h [40].

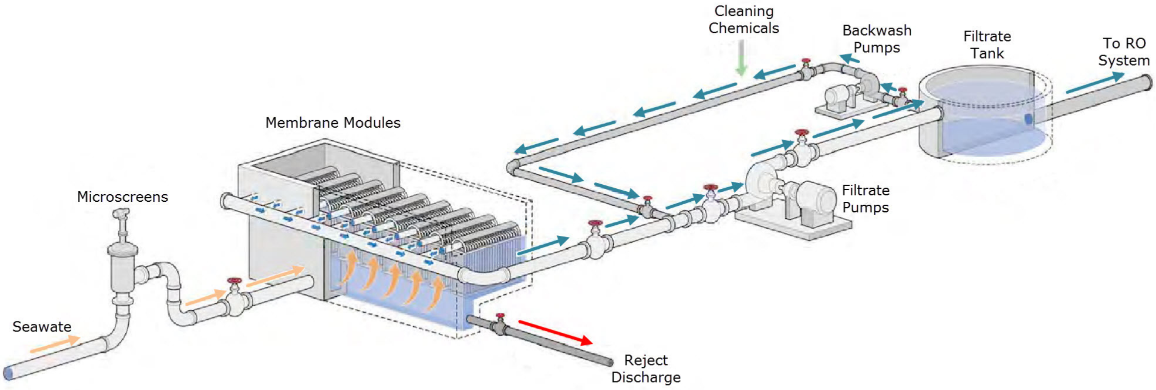

Fig. 22(b). Schematic diagram of submerged UF system [13].

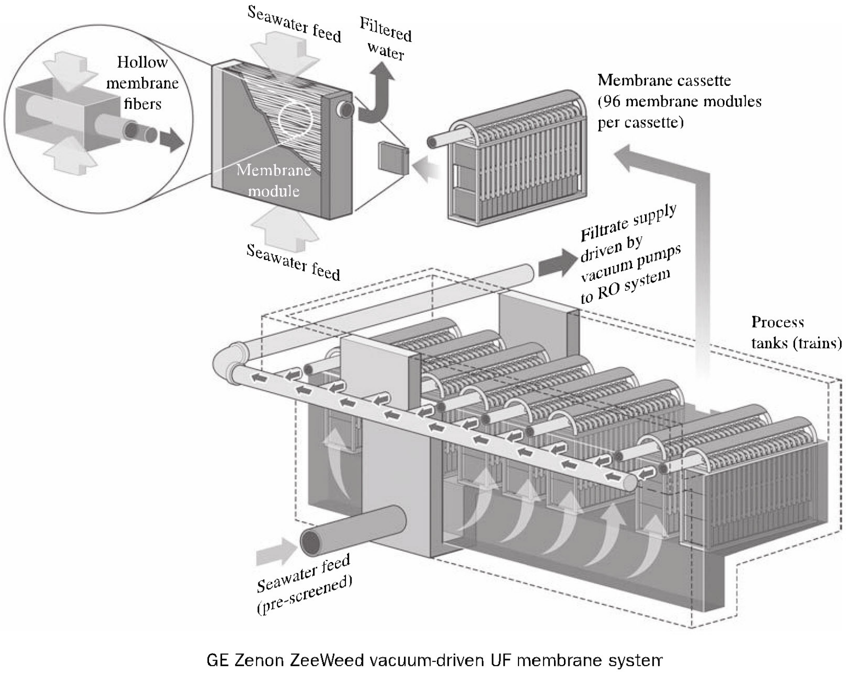

Fig. 22(c). The GE Zenon CP960 vacuum UF system [13].

Table 7
Examples of SWRO pretreatment systems using membranes filtration

Capacity, m^3/d	Location	Intake type	UF type	Flux, L/m^2.h
350,000	Shuwaikh, Kuwait	Shallow SW open intake source	Pressurized	60–77
300,000	Adelaide, Australia	Deep SW open intake source	Vacuum	
300,000	Perth, Australia	Shallow SW open intake source	Pressurized	40–50
232,000	Qingdao, China	SW open intake source	Pressurized	
96,000	Palm Jumeirah, UAE	SW open intake source	Pressurized	60–80
150,000	Beckton, UK	Saline river open intake source	Pressurized	
96,000	Fukuoka, Japan	SW from subsurface intake	Pressurized	
90,000	Kindasa, SA	Near-shore open intake and preceded by GMF	Pressurized	80–100
36,000	Yuhuan, China	Open intake	Vacuum	

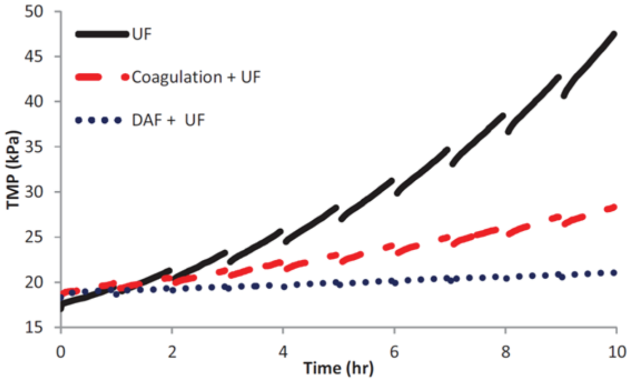

Fig. 23. Effect of inline coagulation and DAF on virgin UF membrane fouling [40].

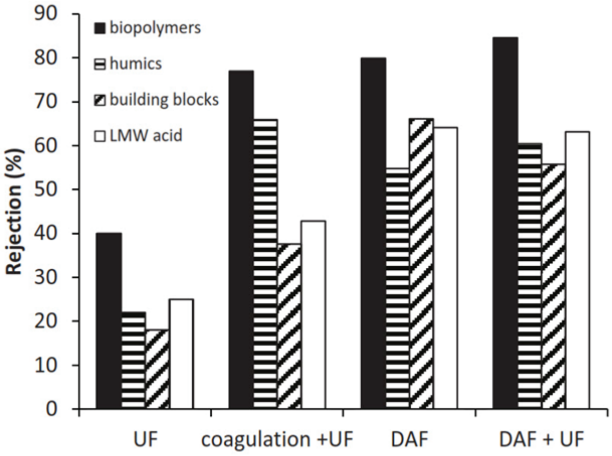

Fig. 24. Rejection performance of virgin UF membranes [40].

Cell count analysis of DAF permeate showed that 90% of algae cells were removed prior to UF, and no algae was present in the membrane permeate.

The rejection rate of organics in the algae feed solution was significantly higher with the use of coagulation and DAF, when compared with stand-alone UF as shown in Fig. 24. The stand-alone UF was able to remove only 40% of biopolymers, and 20%–30% of smaller organics consisting of humic substances, building blocks and low MW acids. This was expected with the large membrane pore size (0.04 µm). When coagulation and DAF are added, significant improvements occurred as shown in the Fig. 24.

Unbroken algal cells are effectively (100%) removed by either the MF and/or UF membranes (absolute barrier to these cells); however, portions of broken cells may pass through the membranes [41–43]. Minimal breakage of algal cells has been reported due to the pressure applied to the UF influent, and even less for dinoflagellate cells (more common in seawater) that have armored siliceous cells (*Theca plates* of armored dinoflagellates are cellulose based, while diatoms have silicate cell coverings).

Villacorte [44] and Villacorte et al. [45] analyzed the removal of algae cells using UF, and showed that AOM can cause severe organic fouling of the UF, leading to higher rate of backwash. The TEP component of AOM can also increase the irreversible component of fouling, leading to a shortening of membrane lifetime. Pre-coagulation can shorten the time between backwashes for UF. They concluded that coagulant overdosing causes fouling downstream in the RO process, particularly if the UF has many broken fibers or rolled seals.

Guastalli et al. [33] compared the performance of DAF preceding GMF or UF, and operating in parallel as shown in Fig. 14, in terms of particles and dissolved OM removal. They concluded that both processes have high elimination of particulate and microbial contaminants. Both treatments have effluent of low turbidity (<0.1 NTU and $SDI_{15} < 2$). UF achieved 100% algae removal, while GMF achieved almost 60% algae cells removal.

Dixon et al. [25] summarized the fate of algae species from their entrance to the SWRO plant to the final product as shown in Fig. 25. They indicated that chlorination can lyse algae and produce AOM, causing fouling to the filtration and membranes; DAF removes more than 90% of cellular biomass and reduce fouling; GMF removes further 90% cells; UF removes almost 100% of all algae cells; and any extra cellular toxins will be removed by the RO membranes.

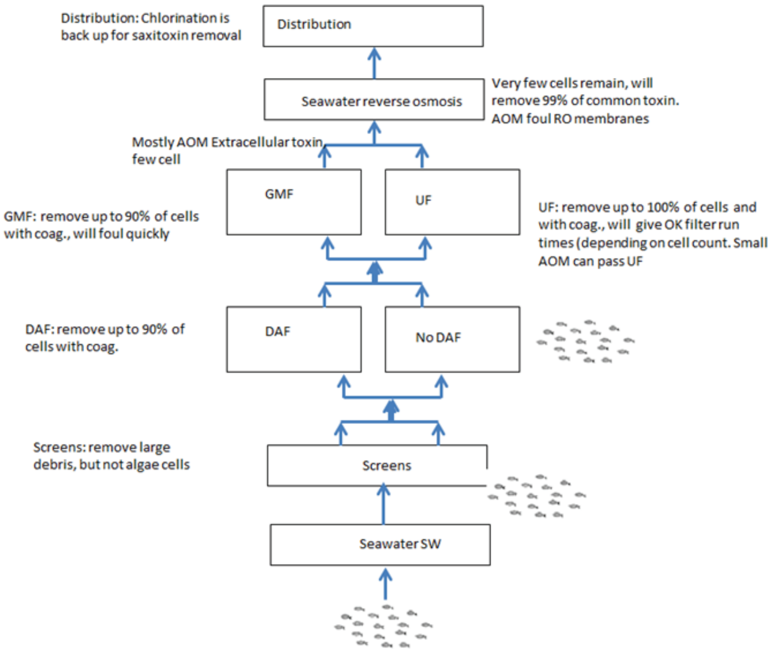

Fig. 25. A summary of cellular biomass, AOM toxin removal through typical SWRO plant [25].

6. Conclusion

Feed SW pretreatment for thermal desalination plants is simple and consists of screening and chemical addition to avoid scaling, when compared with the complex pretreatment of SWRO desalination systems. The main function of SWRO pretreatment is to avoid membranes fouling (inorganic/organic, colloidal and biological fouling). It is required to remove over 99% of all suspended solids in SW and to reduce the content of the much finer silt particles by several orders of magnitude. Achieving such important objectives requires using proper subsurface intakes and the best pretreatment processes. These processes include chlorination, fine screening, coagulation, flocculation, sedimentation, conventional or low-pressure membrane filtration, de-chlorination, and cartridge filters. Since most of the GCC countries including Qatar have begun to deploy SWRO desalination plants, it has become necessary to optimize the pretreatment system, which is very site-specific, to deal with the harsh conditions of the feed SW from the gulf. Such urgent pretreatment technologies are key elements for SWRO desalination, especially in the countries of shallow shore water, high salinity (45,000 in the east and up to 57,000 mg/L), coupled with high summer temperatures (up to 50°C) and a high potential to have AB incidents. This paper illustrates several processes used for SWRO pretreatment and the need for pilot test rigs to optimize these processes in view of increasing occurrence of ABs in the recent years.

Acknowledgment

This work is part of Qatar Environment and Energy Research Institute (QEERI) project 4003, and QEERI support is fully appreciated. Special thanks to Dr. Anne Dare and Dr. Larry Pederson for their continuous efforts in improving the quality and language of the manuscript.

List of abbreviations

AB — Algal bloom
AOC — Assimilable organic carbon
AOM — Algal organic matter
BW — Brackish water
CA — Cellulose acetate
CEB — Chemically-enhanced backwash
DAF — Dissolved air flotation
DOC — Dissolved organic carbon
EC — Electrical conductivity
EOM — Extracellular organic matter
EPS — Extracellular polymeric substances
FA — Fulvic acid
GAC — Granular activated carbon
GCC — Gulf Cooperation Council
GMF — Granular multimedia filter
HA — Humic acid
HAB — Harmful algae blooms
IOM — Intracellular organic matter
LC-OCD — Liquid chromatography-organic carbon detection
MF — Micro filtration
MW — Molecular weight
NF — Nanofiltration
NOC — Natural organic carbon
NTU — Nephelometric Turbidity Unit
OM — Organic matter
PA — Polyamide
POC — Particulate organic carbon
ppm — part per million
PVDF — Polyvinylidene difluoride
RLCA — Reaction-limited colloid aggregation
RO — Reverse osmosis
S — Salinity

SDI — Silt density index
SUVA — Specific UV absorbance
SW — Seawater
SWRO — Sea water reverse osmosis
TDS — Total dissolved solids
TEP — Transparent exopolymer particles
THM — Trihalomethane
TOC — Total organic carbon
TSS — Total suspended solids
TTHM — Total tri halo methane
UF — Ultrafiltration
UV — Ultraviolet
WHO — World Health Organization

References

[1] M.A. Darwish, H.K. Abdulrahim, A.S. Hassan, B. Shomar, Reverse osmosis desalination system and algal blooms. Part I: Harmful algal blooms (HABs) species and toxicity, Desalin. Water Treat., 57/54 (2016) 25859–25880. doi: 10.1080/19443994.2016.1159618.

[2] M.A. Darwish, H.K. Abdulrahim, A.S. Hassan, B. Shomar, Reverse osmosis desalination system and algal blooms. Part II: seawater intake technologies, Desalin. Water Treat., 57/54 (2016) 25881–25917. doi: 10.1080/19443994.2016.1159619.

[3] J.F. Anthoni, The chemical composition of seawater (2006), http://www.seafriends.org.nz/oceano/seawater.htm

[4] R. Y. Ning, Reverse osmosis process chemistry relevant to the Gulf, Desalination, 123 (1999), 157–164.

[5] S.G. Rodriguez, Particulate and organic matter fouling of SWRO systems: characterization, modelling and applications, PhD thesis, Delft University of Technology, Delft, The Netherlands (2011).

[6] M. Berry, Novel sustainable concepts in process design and assessment of seawater reverse osmosis pre-treatment, PhD thesis, Technical University of Berlin (2013).

[7] S. Huang, Investigation of seawater desalination reverse osmosis membrane biofouling, PhD thesis, University of California, Irvine (2012).

[8] C.Y. Tang, T.H. Chong, A.G. Fane, Colloidal interactions and fouling of NF and RO membranes: a review, Adv. Colloid Interface Sci., 164 (2011) 126–143.

[9] L.A. Weinrich, The impact of assimilable organic carbon on biological fouling of reverse osmosis membranes in seawater desalination, PhD thesis, Drexel University (2015).

[10] N. Voutchkov, Desalination engineering, planning and design, The McGraw-Hill Companies, Inc., (2013), ISBN: 978-0-07-177716-2.

[11] K. Gaid, *A large review of the pretreatment*, *Expanding Issues in Desalination*, ISBN: 978-953-307-624-9, InTech (2011), http://www.intechopen.com/books/expanding-issues-in-desalination/a-large-review-of-the-pre-treatment.

[12] E. Bar-Zeev, N. Belkin, B. Liberman, T. Berman, I. Berman-Frank, Rapid sand filtration pretreatment for SWRO: microbial maturation dynamics and filtration efficiency of organic matter, Desalination, 286 (2012) 120–130.

[13] N. Voutchkov, V. Lazarova, Overview of desalination and water reuse technologies, international training course, Water Globe Consulting, 26-28 May (2013), Doha, Qatar.

[14] L. Weinrich, C.N. Haas, M.W. Le Chevallier, Recent advances in measuring and modeling reverse osmosis membrane fouling in seawater desalination: a review, J. Water Reuse Desal., IWA Publishing, (2013), doi: 10.2166/wrd.2013.056.

[15] N. Voutchkov, Considerations for selection of seawater filtration pretreatment system, Desalination, 261 (2010), 354–364.

[16] E. Bar-Zeev, I. Berman-Frank, O. Girshevitz, T. Berman, Revised paradigm of aquatic biofilm formation facilitated by microgel transparent exopolymer particles, Proceedings of the National Academy of Sciences, 109 (2012) 9119–9124.

[17] L.O. Villacorte, Algal blooms and membrane based desalination technology, PhD thesis, Delft University of Technology and of the Academic Board of the UNESCO-IHE, (2014).

[18] D. Kim, G.L. Amy, T. Karanfil, Disinfection by-product formation during seawater desalination: a review, Water Res., 81 (2015) 343–355.

[19] K.K. Satpathy, A.K. Mohanty, G. Sahu, S. Biswas, M. Selvanayagam, *Biofouling and its control in seawater cooled power plant cooling water system – a review*, Nuclear Power, ISBN: 978-953-307-110-7, InTech (2010), http://www.intechopen.com/books/nuclear-power/biofouling-and-its-control-in-seawater-cooled-power-plant-cooling-water-system-a-review-.

[20] S. Dennington, Understanding marine fouling and assessing antifouling approaches, The University of Southampton (2016), https://connect.innovateuk.org/documents/2998699/3676088/Simon+Dennington+Pesentation.pdf/d8ba85fe-a3ab-45b2-affc-aea0ef113749.

[21] S. Kangwen, International overview of seawater desalination plants by reverse osmosis technology, master's thesis, Faculty of Science and Technology, University of Stavanger (2016), http://brage.bibsys.no/xmlui/handle/11250/182519.

[22] S. Jamaly, N.N. Darwish, I. Ahmed, S.W. Hasan, A short review on reverse osmosis pretreatment technologies, Desalination, 354 (2014) 30–38.

[23] G. Petrucci, M. Rosellini, Chlorine dioxide in seawater for fouling control and post-disinfection in potable water works, Desalination, 182 (2005) 283–291.

[24] Chlorination/Dechlorination, FILMTEC™ Membranes water chemistry and pretreatment: biological fouling prevention (2016), http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0039/0901b8038009060.pdf?filepath=liquidseps/pdfs/noreg/609-02034.pdf&fromPage=GetDoc

[25] M.B. Dixon, H. Churman, L. Henthorne, Harmful algae blooms and desalination: an algae cell's journey from sea to SWRO, The International Desalination Association World Congress on Desalination and Water Reuse (2015), San Diego, CA, USA, REF: IDAWC15-Dixon_51571.

[26] S.A.A. Tabatabai, *Coagulation and ultrafiltration in seawater reverse osmosis pretreatment*, Delft University of Technology & UNESCO-IHE Institute for Water Education (2014).

[27] J.K. Edzwald, J. Haarhoff, Seawater pretreatment for reverse osmosis: chemistry contaminants and coagulation water research, 45 (2011) 5428–5440.

[28] Metcalf and Eddy, Inc. (Revised by G. Tchoganologous, F.L. Burton, H.D. Stensel), *Wastewater engineering treatment and reuse*, Tata McGraw-Hill, New Delhi (2003).

[29] N. Prihasto, Q. Liu, S. Kim, Pre-treatment strategies for seawater desalination by reverse osmosis system, Desalination, 249 (2009) 308–316.

[30] C.R. Reiss, C. Robert, J. Dietrich, A. Mody, Pretreatment and design considerations for large-scale seawater facilities, Desalination and Water Purification Research and Development Program Report No. 137, Bureau of Reclamation, Technical Service Center Water and Environmental Resources Division, Water Treatment Engineering Research Team, (2008), https://www.usbr.gov/research/AWT/reportpdfs/report137.pdf.

[31] J.K. Edzwald, Dissolved air flotation and me: a review, Water Res., 44 (2010) 2077–2106.

[32] J. Haarhoff, J.K. Edzwald, Adapting dissolved air flotation for the clarification of seawater, Desalination, 311 (2013) 90–94.

[33] R. Guastalli, F.X. Simon, Y. Penru, A. Kerchove, J. Llorens, S. Baig, Comparison of DMF and UF pre-treatments for particulate material and dissolved organic matter removal in SWRO desalination, Desalination, 322 (2013) 144–150.

[34] K.S. Park, S.S. Mitra, W.K. Yim, S.W. Lim, Algal bloom-critical to designing SWRO pretreatment and pretreatment as built in Shuwaikh, Kuwait SWRO by Doosan, Desal. Water Treat., 51 (2013) 6317–6328.

[35] EPA, *Water treatment manuals filtration*, Environmental Protection Agency, Ireland (1995). http://www.epa.ie/pubs/advice/drinkingwater/EPA_water_treatment_manual_%20filtration1.pdf

[36] S. Plantier, J.B. Castaing, N.E. Sabiri, A. Massé, P. Jaouen, M. Pontié, Performance of a sand filter in removal of algal bloom for SWRO pre-treatment, Desal. Water Treat., 51 (2013) 1838–1846.

[37] B.A. Kocamemi, Filtration and environmental engineering unit operations (2016), http://mimoza.marmara.edu.tr/~bilge.alpaslan/enve301/Lectures/Chp_12.pdf.

[38] S. AL-Sadi, A.E. Ali, Impact of HABs, jellyfish outbreaks and silt contents on membrane pretreatment – challenges and solutions, The International Desalination Association World Congress on Desalination and Water Reuse, San Diego, CA, USA, REF: IDAWC15- Al-sadi_51505, (2015).

[39] E.N. Peleka, P. Mavros, A.I. Zouboulis, K.A. Matis, A hybrid flotation–microfiltration cell for effluent treatment, Desalination, 248 (2009) 881–890.

[40] A. Resosudarmo, W. Cha-Umpong, Y. Ye, P. Le-Clech, V. Chen, Comparison of hybridized membrane pretreatment systems for the removal of marine algae, The International Desalination Association World Congress on Desalination and Water Reuse, San Diego, CA, USA, REF: IDAWC15-RESOSUDARMO_51596 (2015).

[41] M. Dixon, Integrated membrane system for the removal of cyanobacterial toxins and taste and odour compounds, PhD thesis, University of Adelaide, Australia (2010), https://digital.library.adelaide.edu.au/dspace/bitstream/2440/70851/8/02whole.pdf.

[42] A. Resorsudarmo, Proceedings of the Middle East Desalination Research Centre's Workshop on HABs and Desalination, Muscat Oman (2014).

[43] M.B. Dixon, L. Ho, C. Chow, G. Newcombe, J. Croue, H. Buisson, J. Cigana, R. Treuger, *Water Research Foundation Report #4016: Evaluation of integrated membranes for taste and odour and algal toxin control*, Water Research Foundation, Denver, Colorado, USA (2012).

[44] L.O. Villacorte, Algal blooms and membrane based desalination, PhD Thesis Dissertation, Delft University of Technology (2014).

[45] L.O. Villacorte, S.A. Tabatabai, D.M. Anderson, G.L. Amy, J.C. Schippers, M.D. Kennedy, Seawater reverse osmosis desalination and (harmful) algal blooms, Desalination, 360 (2015) 61–80.