

Recent advances in measuring and modeling reverse osmosis membrane fouling in seawater desalination: a review

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ABSTRACT

A review of recent literature focuses on the fouling phenomena in membrane systems for desalination, quantification and qualification of parameters related to biological fouling (biofouling), and emerging areas for prevention. In particular, biofouling of seawater reverse osmosis (SWRO) is widely regarded as the most important area for future research on this topic. Reducing membrane fouling is fundamental to seawater treatment but is not well managed. The current state of industry knowledge is evaluated with particular focus on SWRO membrane biofouling, as well as its measurement and mitigation. Specific shortcomings and possible solutions are reviewed regarding the role of assimilable organic carbon, chemical treatment and other components in understanding the fouling process, impacts from pretreatment, level of assimilable nutrients, modeling applications, and real time monitoring. A critical review of recent advances in understanding organic and biological fouling is presented because these are the most difficult to control and least understood.

Key words | antiscalant, biofouling, membrane, organic carbon, reverse osmosis, seawater

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ABBREVIATIONS

α	alpha	FeCl_3	ferric chloride
γ	gamma	g	gram
2- and 3-d	two- and three-dimensional	HEDP	1-hydroxy ethylidene-1,1-diphosphonic acid
ΔP	pressure (applied)	IOM	intracellular organic matter
AOC	assimilable organic carbon	J_w	flux
AOM	algogenic organic matter	k	kilo
ATMP	amino trimethylene phosphonic acid	L	liter
BDOC	biodegradable dissolved organic carbon	LC-OCD	liquid chromatography – organic carbon detection
BOM	biodegradable organic matter	LSI	Langelier Saturation Index
CAS	Chemical Abstract Service	MF	microfiltration
cm	centimeter	mS	millisiemens
CP	concentration polarization	MFI	modified fouling index
CFD	computational fluid dynamics	μGAF	microgranular adsorptive filtration
Da	dalton	μm	micrometer
DMF	dual media filtration	μ	permeate viscosity for calculating pure water flux
DOC	dissolved organic carbon	μ_{max}	bacterial rate of utilization calculated by Monod modeling of AOC
EOM	extracellular organic matter		
EPS	extracellular polymeric substances		

m	meter
mg	milligram
MGD	million gallons per day
MSDS	Material Safety and Data Sheet
mL	milliliter
mV	microvolts
MW	molecular weight
NF	nanofiltration
nm	nanometer
N_{\max}	maximum available substrate in AOC test
NOM	natural organic matter
NTU	Nephelometric Turbidity Units
O&M	operations and maintenance
OND	organic-bound nitrogen detection
π	osmotic pressure
PAC	powdered activated carbon
PBTC	2-phosphonobutane-1,2,4-tricarboxylic acid
PCR	polymerase chain reaction
PVDF	polyvinylidene fluoride
R_m	membrane resistance
RLCA	reaction-limited colloid aggregation
rRNA	ribosomal ribonucleic acid
SHMP	sodium hexa-metaphosphate
SD	Stiff and Davis Index
SDI	silt density index
SEC	size exclusion chromatography
SWRO	seawater reverse osmosis
SUVA	specific ultraviolet absorbance
TDS	total dissolved solids
TOC	total organic carbon
T-RFLP	terminal restriction fragment length polymorphism
UF	ultrafiltration
UV ₂₅₄	UV absorbance at 254 nanometers

INTRODUCTION

A robust review is presented to evaluate the state of industry knowledge on the fouling phenomena in membrane systems for desalination, quantification and qualification of parameters related to biological fouling (biofouling), and emerging areas for prevention. In particular, biofouling of

seawater reverse osmosis (SWRO) membranes is widely regarded as the most important area for future research on this topic. Biofouling, caused by microbial growth on membranes, is not well managed. An essential need exists for better biodegradable organic matter (BOM) monitoring and measurement tools to predict fouling (Voutchkov 2010b; Amy *et al.* 2011; Veerapaneni *et al.* 2011). Some advances in fouling prediction by data modeling show promise but many preliminary membrane applications have not been extensively tested in seawater desalination. Complex modeling approaches for fouling have limitations that result from time and cost associated with advanced computing capability. The goal of this paper is to evaluate the current state of industry knowledge with particular focus on SWRO membrane biofouling, as well as its measurement and mitigation.

In the USA, two-thirds of the desalination capacity is used for municipal water supply (Carter 2011). Desalination is on the rise and the USA is currently leading in the number of desalination projects that are planned or in construction, according to the Desalination Tracker reported by *Global Water Intelligence* magazine (<http://www.globalwaterintel.com>). The rise in desalination has been forecast from the current level of 2,324 million gallons per day (MGD) of contracted desalination capacity up to 3,434 MGD by 2016 in the USA (Report: US desalination market 2010). With this projection, it is more important than ever to address shortcomings in SWRO desalination operations and maintenance (O&M) and to investigate approaches to optimize this process. While reverse osmosis (RO) membrane desalination can be a costly supply alternative, advances in membrane technology and performance, market demand, and energy recovery have driven costs down in the past few decades (WaterReuse Association 2011). Membrane fouling continues to pose a costly challenge for aspects related to prediction, prevention, and, when possible, removal. The following sections will briefly describe the four types of fouling: inorganic, particulate, organic and biological. A critical review of recent advances in understanding organic and biological fouling is presented because these are the most difficult to control and least understood. Evidence of exacerbated fouling from chemicals used in SWRO pretreatment is examined; investigating the effects of chemical pretreatment is emerging as an important area for the reduction of fouling.

The paper also presents recent advances and current applications for understanding, measuring, and predicting fouling through analytical and microbiological techniques for quantification and qualification. Prediction of fouling through computer modeling also shows promise, and prevention is evaluated based on recent reports during the pretreatment process for SWRO.

FOULING

Membrane fouling results from the accumulation of materials on, in, or near the membrane (Taylor & Weisner 1999). The result of this accumulation has long been recognized to be a major problem for RO facilities as it can result in a decline in water production over time for constant pressure operations or an increase in required feed pressures (Zhu & Elimelech 1995). Because fouling issues lead to a significant economic burden on membrane plants, the future of desalination is partly driven by the economic viability of membranes and their application, including low pressure and RO membranes. Therefore, a successful future for membrane applications will be realized by having a clear understanding of fouling mechanisms and developing essential tools for quantification and prevention. Fouling is generally documented as one of four types: scaling from precipitation of sparingly soluble salts, plugging due to deposition of particulate matter, adsorption of organic matter, and biological fouling due to the growth of microorganisms on membrane surfaces (Zhu & Elimelech 1995; Duranceau 2007).

Membrane fouling may be further classified as to whether it is reversible or irreversible. Reversible fouling is caused by physical separation mechanisms that induce cake formation, deposition of particles, and plugging of pores (Hilal *et al.* 2006). Irreversible fouling occurs when dissolved compounds interact with the membrane material and cannot be removed by chemical or physical cleaning.

Scaling

Scaling occurs as dissolved materials increase in salt concentration on the feedwater side of the membrane, until the point at which the solubility of the salt is exceeded in

the reject water, or brine, and precipitation occurs. This type of fouling occurs only in high pressure membranes, nanofiltration (NF), and RO. Low pressure membrane separation microfiltration (MF) and ultrafiltration (UF) do not concentrate salts in the reject stream and therefore scaling does not occur in these membranes. Scaling is often attributed to precipitation of the polyvalent cations (calcium, magnesium, barium, and strontium) and anions (silicate, sulfate, carbonate, and phosphate). Typically, scaling may be managed through feedwater monitoring and mitigated with chemical and physical pretreatment (Yang *et al.* 2009). Chemical pretreatment of inorganic scaling caused by calcium salt precipitates can be managed with pH adjustment or antiscalant addition (Pontié *et al.* 2005). However, impure mineral acids often used as antiscalants have been shown to contain BOM (Amy *et al.* 2011) that can promote biofouling (Vrouwenvelder *et al.* 2000; Vrouwenvelder & Van Der Kooij 2001). Because of this potential for a causal effect, effective fouling prevention will be based on maintaining a universal view in order to appreciate that the effects of mitigation procedures for one event may have adverse effects downstream that exacerbate another issue. Understanding and preventing such secondary effects will be promoted with research specifically targeted for SWRO design and processes.

Colloidal or particulate fouling

Particulate fouling occurs as water permeates through membranes that contain suspended materials. Colloid materials may either deposit within the membrane pores (known as pore blocking) or form a cake as suspended particles accumulate. A recent publication by Tang *et al.* (2011) provides a comprehensive review of the existing literature related to mechanisms and factors controlling this type of fouling. The review is inclusive of membrane filtration for various treatment applications in wastewater and freshwaters. Solution chemistry, hydrodynamic conditions, and membrane properties are the major drivers of membrane fouling with regard to colloids.

Colloidal particles are concentrated by physical membrane separation which causes fouling and a decline in membrane flux. Therefore, SWRO manufacturers recommend that membrane feed turbidity is <0.1 NTU, silt

density index (SDI_{15}) <4 , and zeta potential >-30 microvolts (mV) (Voutchkov 2010b). Depending on particle size, the fouling components are generally referred to as either suspended or colloidal. Colloidal particles are naturally occurring inorganic and organic compounds and range in size from 0.001 to 1 μm . From measurements made in the North Atlantic and Northwest Pacific oceans, small colloids ranging in size from 0.005 to 0.200 μm are identified to be the most abundant particles in seawater and concentrations were nearly 10^9 particles per milliliter (Wells & Goldberg 1993). Particle sizes less than 1 μm are considered 'colloids', but 90% of 'suspended' particulate foulants in SWRO are >1 μm (Voutchkov 2010b). Suspended foulants may include organic and inorganic particles in seawater, for example plankton, silt, and other fine debris. Filtration of the seawater prior to the RO membranes can efficiently remove suspended materials. Recent publications (Voutchkov 2010a, 2010b) categorize fouling into five classes, instead of the four mentioned previously, by separating particulate fouling into two categories: particulate (i.e., suspended) and colloidal. Colloid dynamics vary greatly in seawater, and can form aggregates. Aggregate formation may occur either by reaction-limited colloid aggregation (RLCA) or by diffusion-limited colloid aggregation. RLCA formations have more condensed structures and distribution occurs in both near-shore and offshore environments (Wells & Goldberg 1993). In addition, biopolymers are often involved in aggregate formation. Colloidal aggregates 'package' organic matter as more readily biologically utilizable. Colloids from the Santa Monica basin (California) also share similarities to soil-derived fulvic acids as determined through transmission electron micrographs (Wells & Goldberg 1991). The granular size of 2–5 nm (0.002–0.005 μm) as determined in these studies corresponds to ~ 10 kDa which is in the range for dissolved organic carbon (DOC) fractions measured in seawater. Molecular weights (MW) of proteins, amino acids, sugars, and other biopolymers are in the range 0.2–200 kDa. NF and RO are generally best ranked for removal of similarly sized chemicals.

From open ocean intakes, silica and iron fouling is not as much of a challenge since these foulants are often in dissolved and precipitated form in seawater conditions of 30,000–45,000 mg/L total dissolved solids (TDS)

(Voutchkov 2010b). The exception occurs in areas where the intake is under the influence of river water or groundwater, thereby having elevated silica content. Iron colloidal fouling on RO membranes may also result from pipe corrosion or improper application of iron-based coagulant, and may act as a fouling catalyst causing damage on membranes fed by water with even very low doses of residual chlorine.

The previous discussion has mainly referred to naturally occurring colloids that enter the seawater intake. However, anthropogenic colloid sources may also be problematic, particularly in areas under the influence of urban runoff from storm drains, or a wastewater treatment plant discharge, or point source pollution from ships in port areas. These colloids would be from petroleum derivatives.

Organic fouling

Membrane fouling can occur through adsorption of organic matter onto the membrane surface. Once sorbed, removal is difficult and may lead to irreversible fouling. As mentioned in the previous section, colloidal interactions with natural organic matter (NOM) exacerbate fouling when the sorbed particles block membrane pores, form part of the membrane cake, or become more biologically available. Organic fouling was reported to be most common in SWRO desalination as reported in the recent Water Research Foundation report by Veerpaneni *et al.* (2011). In addition, the study found that 40% of permeability decline in RO membranes is attributed to organic and biological fouling. Organic and biological fouling are interrelated. Membrane foulants only comprise a small fraction of the NOM (Cai & Benjamin 2011) when measured in freshwater. NOM present in seawater was reported to be 24% high MW DOC (1–100 nm) and about 75% low MW DOC (<1 nm); the other 1% was identified to be particulate organic carbon (Benner *et al.* 1997). UF and MF membrane pore sizes are 0.01–0.05 and 0.1–0.5 μm , respectively. RO membrane pore size is near 0.0001 μm . Therefore, the opportunity for organic matter removal in RO feedwater is diminished by the inherent capacity of the membrane. Studies have shown that UF membranes do not achieve significant removal of marine NOM having MW ~ 10 kDa (Tansakul *et al.* 2010). NOM can occur naturally in the

source water, or from anthropogenic sources, specifically wastewater, industrial or agricultural effluents.

Traditional approaches for predicting organic fouling potential include DOC, UV absorbance, and color; however, the measured fouling rates for NOM in seawater do not correlate with these parameters (Amy *et al.* 2011). Discovering the link between potential and realistic fouling rates is critical and additional understanding of organic matter behavior in high salinity, i.e., seawater, environments will be most useful for successful O&M applications at the full scale. Opportunities exist for either breaking NOM down into smaller fractions that can be removed by biological pretreatment, or some other combination of organic absorption and removal. These approaches will be discussed in more detail in the following sections.

Biological fouling

Biofouling is by far the least understood and most problematic type of fouling in RO membrane separation processes (Griebe & Flemming 1998; Vrouwenvelder *et al.* 2000; Vrouwenvelder & Van Der Kooij 2001; Pang *et al.* 2005; Kumar *et al.* 2006). The growth of microorganisms into a biofilm on the membrane surface leads to costly increases in SWRO treatment. Decreasing permeate flux, increasing pressure drops in the RO modules, increasing salt passage, and irreversible damage to the RO membrane are all issues associated with biofouling. Bacterial communities in the biofilms release extracellular polymeric substances (EPS) which provide an area for additional bacteria to proliferate. EPS present in the biofilm (composed of EPS and bacteria) account for 50–90% of the biofilm total organic carbon (TOC). Other naturally occurring or anthropogenic biopolymers can contribute to biofouling, as well as sources of assimilable organic carbon (AOC) that provides a food source for bacteria to proliferate.

Chemicals introduced into the treatment process, such as impure acids or phosphate-based scale inhibitors, may also exacerbate biofouling. Disinfectant addition must be carefully managed. Oxidants are often applied at the seawater intake to control biological growth. This process is not well understood regarding its impact on RO membrane biofouling downstream of disinfection. In addition, it is unknown if the oxidative impact from disinfection on organic matter

may be similar to that of drinking water treatment. Primary oxidation during drinking water treatment through the application of ozone changes the structure of NOM into smaller, polar, oxygenated compounds (von Gunten 2003). Van Der Kooij (1986) showed that AOC concentrations increased in water samples treated with increasing chlorine doses. Similarly, Hamsch & Werner (1993) reported higher biodegradability of humic substances (NOM) after chlorination. LeChevallier *et al.* (1992) found that chlorination may increase AOC levels depending on the point of chlorine application. These effects have been extensively investigated in surface and groundwater matrices used for drinking water, but the effects of disinfection with specific regard to production of BOM is largely unknown in seawater and brackish water matrices used for RO desalination. A recent study using the saltwater bioluminescent-AOC test (Weinrich *et al.* 2011) is underway to help close the gap in knowledge about the oxidation impacts on NOM and chemical impacts in seawater. The ongoing research shows promise for dually estimating the growth rate and the growth potential-induced AOC. The method will be described in more detail later.

Red tides are highly destructive events that can occur when marine algae rapidly increase in concentration, called an algae bloom, and are often recognized by the visible red color and therefore appropriately named. Blooms can severely increase turbidity of seawater; however, the release of organic material, algogenic organic matter (AOM), is also a major concern. Dinoflagellates are generally recognized as most frequently responsible for marine algal blooms. *Karenia brevis* and *Noctiluca scintillans* are examples of algae that occur in seawater and are associated with red tides, and *Auerococcus anophagefferens* is associated with brown tides (Edzwald & Haarhoff 2011). An algal bloom may have algae counts that range from 10^3 to 10^6 #/mL; typical concentrations are $<10^3$ #/mL.

Transmembrane pressure and hydrodynamic shear forces can cause algal cell lysis and lead to release of intracellular organic matter (IOM) in RO treatment, thereby increasing soluble and highly biodegradable AOM (Ladner *et al.* 2010). AOM is composed of acids, proteins, simple sugars, anionic polymers, negatively charged and neutral polysaccharides (Edzwald & Haarhoff 2011). 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 biofouling (Ladner *et al.* 2010). In general, harmful algal blooms are being increasingly recognized for their often detrimental impacts on RO desalination facilities. Future research has been suggested to understand the impacts of algal blooms in geographic regions for RO facility design and operational efficiency (Caron *et al.* 2010).

Antiscalants

Chemicals are added prior to membrane separation to reduce the precipitation of sparingly soluble salts. Antiscalant chemicals in RO applications typically contain two or more phosphonate groups, called polyphosphonates. The ability of a chemical to reduce scale formation is related to its chemical structure, MW, active functional groups, and solution pH (Shih *et al.* 2004). MW are reported to range from 1,000 to 3,500 and typically consist of polycarboxylates, polyacrylates, polyphosphonates, and polyphosphates. Phosphonates contain a carbon-phosphorus bond that must be broken for microbial assimilation, and bacterial degradation pathways have been studied in naturally occurring phosphonates. With the increasing use of artificial phosphonates in industry and natural occurrence in the environment, phosphate-containing chemicals provide an essential nutrient supply. In addition, the presence of phosphate in waste streams and concentrates have impacts in areas of discharge that may be associated with algal blooms. Companies are developing environmentally friendly antiscalants to avoid this issue, some of which are phosphate free (Musale *et al.* 2011). In desalination applications, the potential for microbial growth from the application of phosphonate/phosphate and carboxylate requires additional research. Antiscalants and mineral acids have been shown to increase biofouling potential (Vrouwenvelder *et al.* 2000; Weinrich *et al.* 2011), and impurities contained in the treatment chemicals are also potential nutrient sources. Many of the chemical suppliers reserve proprietary rights to the chemical composition of the antiscalants, and therefore specific chemical formulations are not disclosed. Often, Material Safety and Data Sheets (MSDSs) lack Chemical Abstract Service (CAS) numbers and only provide general information. For example, the MSDS for

VITEC[®] 5100 NSF (Avista Technologies, San Marcos, CA), an antiscalant used at a brackish water desalination plant, provides 'phosphonic acid derivative compound' as part of the mixture. This lack of transparency makes it challenging to predict the biodegradability and potential for biological fouling. Prior desalination configurations used sodium hexametaphosphate (SHMP) as an antiscalant, but it is no longer used because SHMP was shown to be a food source for bacteria and resulted in biofouling (Alawadhi 1997; Voutchkov 2010b). A commonly reported antiscalant in the cooling water industry is 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) and it has been extensively examined on a molecular level (Demadis *et al.* 2005).

PBTC contains phosphate and carboxylic acid functional groups (Figure 1), which are common in other antiscalant chemicals and important nutrient reserves for bacterial growth. Antiscalants are associated with biofouling in membrane elements (Vrouwenvelder *et al.* 2000). Pathways for cleaving the carbon-phosphate bond present in these chemicals have been investigated (Huang *et al.* 2005) and bacteria contain specific genes capable of this degradation, including some *Vibrio* species. Results from a prior study showed that AOC increased in samples collected after antiscalant addition at the Fujairah desalination plant, measured by the bioluminescent test which uses the marine organism *Vibrio harveyi* (Schneider *et al.* 2011; Weinrich *et al.* 2011). The antiscalant application was low at 0.5 mg/L. In general, antiscalant degradation and assimilation by bacteria in seawater matrices has not been clearly elucidated. Ongoing work by the authors evaluates common antiscalants in a seawater matrix using the marine-based AOC test to quantify the biofouling potential of reported antiscalants (Table 1). Other phosphonate chemicals include amino trimethylene phosphonic acid (ATMP), 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), and proprietary phosphino succinic oligomers. For HEDP and PBTC, 0.5–2% of the chemical composition may include phosphoric acid and phosphorous acid ('Phosphonate

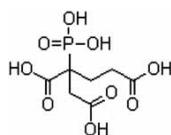


Figure 1 | 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), an antiscalant, molecular weight 270.13.

Table 1 | Examples of antiscalants and chemical cleaning agents referenced in the literature

Location	Antiscalant/Chemical	Type
Fujairah, UAE	PermaTreat PC-1020 (Nalco, Naperville, IL, USA)	Organophosphate
Taunton River, MA, USA (seasonally brackish)	VITEC [®] 5100 NSF (Avista Technologies, San Marcos, CA, USA)	Phosphonic acid derivative compound
Florida	AWC-A102 Plus (American Water Chemicals, Plant City, FL, USA)	Phosphonate
General	Citric acid	Organic acid
California	PermaTreat PC-1020T (Nalco, Naperville, IL, USA) PermaTreat PC-191T (Nalco, Naperville, IL, USA)	Phosphonate
General, known biofoulant (Voutchkov 2010b)	Sodium hexametaphosphate (SHMP)	Polyphosphate

products'). Impure acids and chemicals have already been recognized as potential sources for biological growth that can lead to biofouling in RO membranes used in freshwater matrices. The extent of this relationship between chemicals used in seawater matrices to biofouling potential requires additional understanding. Other common classes of antiscalant chemicals include polycarboxylates, polyacrylates, and organic acids. Citric acid has been used for pretreatment in seawater RO, and has already been shown to be an assimilable food source for *Vibrio harveyi* used in the AOC test (Weinrich *et al.* 2011). Depending on the location of the application and the chemicals used, ongoing research shows promise for providing evidence that biofouling potential of RO feedwater can be better managed by monitoring AOC.

QUANTIFICATION

There are numerous indirect measurement techniques for predicting membrane fouling, though all have their limitations. Traditional fouling potential of a membrane is

measured using SDI or a similar but slightly more advanced modified fouling index (MFI). These tests predict particulate fouling; they are based on plugging of a 0.45-micron (μm) membrane over a defined time interval (often 15 min). However, these test conditions are not predictive of either organic adsorption or biological growth.

The potential for mineral scaling of calcium carbonate to occur may be predicted using Langelier Saturation Index (LSI) and the Stiff and Davis Index (SD) (Voutchkov 2010b). Mineral scaling is fairly easy to manage and there are sufficient indexes for measuring the potential; however, as mentioned in the previous section, preventing scaling via chemical addition of antiscalants or impure acids has the potential to subsequently cause biological fouling. This effect will be discussed in more detail in the section on prevention.

Organic matter and biodegradable fractions

TOC guidelines for pretreated seawater have also been proposed to minimize fouling. TOC levels <0.5 mg/L may be sufficient to avoid biofouling, and seawater above 2 mg/L may certainly result in biofouling (Voutchkov 2010b; Edzwald & Haarhoff 2011). TOC has been reported to range from 2 to 5 mg/L (Edzwald & Haarhoff 2011), although levels can be much greater. In the recent Water Research Foundation report by Schneider *et al.* (2011), TOC ranged from <1 to >10 mg/L measured at desalination intakes from US and international facilities (Schneider *et al.* 2011). Intake TOC has also been influenced by algal blooms and aquatic humic matter found in rivers.

Algae release soluble organic matter during growth and respiration, called extracellular organic matter (EOM) (Edzwald & Haarhoff 2011). EOM and IOM are referred to as AOM, and AOM is soluble and biodegradable. Therefore, if AOM is monitored in red tide events or other algal growth events, it might lead to a better understanding of the biofouling potential at the intake and throughout the treatment process. Cell lysis from the exertion of transmembrane pressure also causes algal cells to release IOM. There are no common measurements for evaluating the presence of AOM, although suggestions for fluorescence-type measurements have been noted (Edzwald & Haarhoff 2011). Obtaining the most appropriate measurement that

represents the biodegradability of the sample is a challenge, and many surrogate or even direct measurements do not provide the needed information about the impact on biofouling in pretreatment.

UV absorbance at 254 nm (UV_{254}) is often used as a surrogate for DOC. Since seawater UV_{254} is often low, and has been reported near 0.01 cm^{-1} , it is recommended to measure absorbance with a longer path-length than the typical 1-cm cell used for freshwater analysis (Edzwald & Haarhoff 2011). Specific UV absorbance (SUVA) has been extensively used in drinking water treatment to evaluate the characteristic of organic carbon in source waters. SUVA is the UV absorbance per unit concentration of DOC. Edzwald & Haarhoff (2011) adapt conventional drinking water guidelines to seawater in the following manner: (1) SUVA >4 indicates that NOM is mainly aquatic humic matter, (2) SUVA of 2–4 indicates that NOM is a mixture of AOM and aquatic humic matter, and (3) SUVA <2 indicates the NOM is composed primarily from AOM.

Liquid chromatography – organic carbon detection (LC–OCD) is an option for determining NOM having lower SUVA (Amy *et al.* 2011). These analyses provide information for NOM present at various MW often characterized from high to low MW: biopolymers, humics, building blocks, low MW acids, and neutrals. Separation is based on size-exclusion chromatography (SEC) followed by multidetection with organic carbon (OCD), UV_{254} , and organic bound nitrogen (OND). LC–OCD was originally used for detecting OM transformation in freshwater treatment, but has been modified for the high ionic strength in seawater.

A critical need exists for a reliable measurement of AOC in a seawater matrix. Other attempts at AOC tests have not determined an appropriate reference organism and use plate counts for measuring biomass, which is time-consuming and costly with a long turnaround time for results (Amy *et al.* 2011). The AOC test is a microbial assay (bioassay) which traditionally uses two strains of bacteria, P17 and *Sprillum* NOX, and monitors their growth in a pasteurized water sample over time, until maximum growth occurs (N_{\max}). The AOC bioassay is considered to be an indicator for the biological growth potential of a water sample (LeChevallier *et al.* 1993), and therefore similar application for SWRO treatment would assist in further understanding biofouling

potential. However, highly saline conditions are not conducive for growth and previous AOC attempts using these traditional strains have had to drastically alter the sample (Ong *et al.* 2002). Using a naturally occurring, bioluminescent marine organism, *Vibrio harveyi*, a saltwater AOC test was developed and recently applied to environmental samples from seawater intake points and from treatment points in full-scale SWRO desalination facilities (Schneider *et al.* 2011; Weinrich *et al.* 2011). Compared to traditional spread plating techniques in bioassays, bioluminescence is used for measuring bacterial growth using a photon counting luminometer. Bioluminescence is the amount of light produced and is the key measurement for this bioassay. Standard curves produced linear relationships between maximum bioluminescence and acetate carbon equivalents. There are numerous advantages to this bioassay, including minimal consumables and short turnaround time. In addition to available substrate (AOC, N_{\max}) determination, it is possible to fit observed data to the Monod kinetic model and thereby determine the bacterial rate of utilization in solution (μ_{\max}). When determined throughout the treatment process, a higher μ_{\max} indicates greater biodegradability, or lability, of that water sample. Alternatively, depressed lability suggests a lowered potential for biofouling, though the extent of this relationship is currently being confirmed through further testing. For example, a consistent pattern of μ_{\max} decrease throughout the treatment system may indicate that treatment rendered organic carbon less labile.

QUALITATIVE UNDERSTANDING

Biofouling in SWRO membranes is not well understood and recent advancements have focused on determining which bacteria cause SWRO biofouling (Zhang *et al.* 2011). Bacterial isolates from a biologically fouled SWRO membrane at a full-scale facility in Carlsbad, California were determined by 16S rRNA to be well-known biofilm-forming bacteria. Isolates matched the genera *Shewanella*, *Alteromonas*, *Vibrio*, and *Cellulophaga*. 16s rRNA terminal restriction fragment length polymorphism (T-RFLP) was used to determine that the bacteria responsible for biofouling in the SWRO were found in the seawater intake.

Samples were analyzed at four points during treatment including the intake, phytoplankton epibionts, cartridge filter, and SWRO membrane. However, a comparison between these locations indicated that microbiology of the cartridge filter was not the same as that of the SWRO which was biofouled. T-RFLP analysis was also conducted on bacterial communities from five separate international SWRO membranes that experienced biofouling. Those results indicated that, while overall profiles were not identical, there was consistent occurrence of dominant bacteria. Zhang et al. (2011) state that determining dominant biofilm bacteria is difficult because >99% of the natural microbial community is not culturable on nutrient-rich artificial medium. This has important implications. *Pseudomonas* and other similar easily cultivable model organisms are typically used for membrane fouling research. However, *Pseudomonas* was not dominant either in SW intakes or on RO biofilms. Bacteria in marine environments are α -proteobacteria from the culture-independent clone library, whereas isolation on nutrient-rich medium favors γ -proteobacteria (e.g., *Vibrio*). The research indicates an important aspect about bacteria colonizing the cartridge filter, which is not actively incubating bacteria responsible for SWRO biofouling. Regardless, bacteria most often observed on SWRO membranes from international locations are often similar and therefore their survival is expanded from oligotrophic to chemolithotrophic conditions. Finally, the study reports that seasonal change has marked impacts on microbial communities in seawater and it was observed that this was more impactful than geographic location (Zhang et al. 2011).

Conventional pretreatment (coagulation by ferric chloride (FeCl_3), sedimentation, and two-stage sand filtration) showed average turbidity removal of 93% in a pilot system operating for 1.7 years in which average turbidity was 3.6 ± 2.9 NTU, but went as high as 20 NTU during the rainy season because of runoff from the coastal area near the plant (Bae et al. 2011). Bacterial diversity evaluated in the conventional system was increased from the raw seawater, while a parallel MF setup decreased bacterial diversity. Carefully managed treatment could use the diversity as an advantage for removing BOM and minimizing bacterial breakthrough. Numerous studies identify α - and γ -proteobacteria to be responsible for biofilm formation in seawater based on the

16S rRNA from both culture-dependent and -independent methods (Lee et al. 2009; Bae et al. 2011; Zhang et al. 2011). Qualitative results from a SWRO pilot system employing MF indicated removal of putative biofilm-forming bacteria, decreasing relative abundance from 98 to 10%. However, the conventional system was also shown to reduce γ -proteobacteria *Alteromonas*, *Cowellia*, and *Glaciecola* from 79.8 to 50%. This qualitative analysis could surely be improved by quantitative measurements of the abundance of biofilm forming bacteria through quantitative polymerase chain reaction (PCR) or other culture-independent tools. While this would definitely aid in the specific knowledge of a system, even qualitative analysis is not practical for most SWRO facilities. The use of a surrogate measurement for determining the growth potential of treated or raw seawater may be more useful in practical application for the reduction and inhibition of SWRO biofouling.

MODELING

Models are important for designing RO desalination processes and are present in two major areas in the literature: (1) mechanistic or membrane transport model and (2) lumped parameter model (Sobana & Panda 2011).

Estimating flux in a membrane that has not yet been fouled can be expressed as $J_w = \Delta P - \pi / (\mu \times R_m)$ where J_w is the pure water flux estimated from resistance-in-series model, ΔP is the applied pressure, π is the osmotic pressure, μ is the permeate viscosity, and R_m is the membrane resistance (Antony et al. 2011).

Very little information exists about the methods for predicting biofouling on RO membranes. Research has focused on biological fouling and modeling bacterial growth in non-seawater matrices. These matrices include drinking water treatment and distribution systems and wastewater treatment. Because there is only limited modeling information in seawater matrices, it is necessary to identify the state of recent advancements using high pressure membranes such as NF or RO in other matrices. Some of this information will be useful for developing models, though specific testing in a saline matrix needs to be completed.

Computational fluid dynamics (CFD) is based on determining fluid flow through the Navier–Stokes equation.

Using CFD in membrane systems is well documented in the literature. For the optimization of feed spacer geometry, CFD has been applied for decreasing pressure losses in the past 10 years (Panglisch *et al.* 2011). Piciooreanu *et al.* (2009) report that the common issue with the previous models is that they do not relate flow and mass transfer to biofilm growth. To account for this, they have developed a model for describing biofilm development in feed channels of spiral-wound NF and RO membranes that includes description of the liquid flow and the mass transport of a soluble substrate. The additional benefit of their model is that it includes changes in the geometry of the feed spacer that occurs from biofilm growth. The resulting flow channeling from biofilm clogging is accounted for by an expanded computational domain of five by three squares, which is an expansion of other three-dimensional (3-d) CFD which have previously only focused on one square element formed by four crossing filaments. The research determined that biofilm growth affects pressure drops on the feed spacer filaments to a greater extent than growth on the membrane only, which is determined from a more uniform drop in pressure over the feed channel length. The study reinforced previous experimental observations about the residence time distribution of solutes and the permitting of dead zones caused by biofouling. These effects, in turn, cause local accumulation of high salinity water which leads to a lower permeate flux.

CFD and biofilm modeling are useful in a 3-d approach for more detailed investigation of feedspacers, and advantages of CFD include a minimization of time, cost, and risk from associated experiments that can be avoided using CFD to predict flow and mass transfer (Panglisch *et al.* 2011). However, there are a few drawbacks that have been reported elsewhere (Radu *et al.* 2010). Validation through experimental data for membranes is still necessary. Also, cost of producing full-scale models is prohibitive, so CFD membrane studies have focused on a small section of the spiral-wound membrane module in 2-d.

3-d was modeled without permeation and therefore concentration polarization (CP) could not be investigated. In addition, more advanced 3-d models would require additional time and resources that are not convenient or cost-effective. A study using brackish water was completed in which biofilm formation was modeled and combined

with CFD to investigate local effects (irregular biofilm distribution) and macro-effects on loss of performance as a result of biofilm-enhanced CP, increased hydraulic resistance to trans-membrane flow and feed channel pressure drop in membranes having feedspacers (Radu *et al.* 2010). Radu *et al.* (2010) had performed the modeling on brackish water and indicated that CP enhanced by biofilm formation was the major contributor to a loss of permeate flux.

Many researchers report that membrane biofouling is a major challenge in the membrane industry. Even though it is one of the most undesirable effects in the membrane separation process, there is substantially little understanding for preventing, measuring, or modeling biofouling. A recent literature review by Matin *et al.* (2011) includes a consolidation of current knowledge on the phenomena and prevention of membrane biofouling. The group concludes that recent advancements in membrane surface modification offer promise for minimizing occurrence, and previous approaches like feed pretreatment and biocide application may not be as applicable as a control strategy. However, while surface modification may be applicable and efficient at the bench scale, manufacture and testing at full-scale facilities must still be investigated. Desalination facilities would benefit from having the proper tools for mitigating biofouling occurrence by monitoring biofouling potential and pressure increases. Current research using the saltwater AOC bioassay by Weinrich *et al.* (2011) suggest that, by understanding the formation and removal of AOC, a facility can better manage its treatment in an effort to mitigate biofouling.

Radu *et al.* (2010) compiled an overview of multiple causes for the deterioration of membrane process performance that occur because of biofouling. These have been defined experimentally and include transmembrane flow studied by McDonogh *et al.* (1994), biofilm-enhanced CP (Herzberg & Elimelech 2007; Chong *et al.* 2008), and increased feed channel pressure drop as reported by Vrouwenvelder *et al.* (2009). CP is the layer of concentrated solutes that remains near the membrane surface as the solvent (water) passes through. Therefore a layer formed by CP has a secondary effect of increasing the osmotic pressure at the membrane surface. Measuring osmotic pressure is a challenge in RO systems and is therefore investigated through CP modeling studies (Subramani *et al.* 2006; Lyster & Cohen

2007). Research presented by Chong *et al.* (2008) is the only effort that has explicitly included the presence of biofilm in the model. The Monod kinetic approach is used in mass balance equations in the model, and reflects substrate consumption by the biofilm. Substrate consumption leads to biological growth in the model, and other accommodations for biomass attachment, transport, and detachment are also considerations in the model (Radu *et al.* 2010). Some of the parameters used for the model are sourced from previously published manuals modeling activated sludge.

A recent report using the bacterial growth rate in solution, μ_{\max} , proposed incorporating growth of the marine AOC test organism and Monod kinetics into a model for application at a full-scale desalination facility that experiences high BOM and RO membrane biofouling (Schneider *et al.* 2011). Using the AOC test in conjunction with the Monod kinetic model will provide metrics for determining treatment effects on biofouling potential, such as chlorination or filtration, which may create (in the case of chlorine) or remove (in the case of slow sand filtration) AOC. The development of the bioluminescent saltwater AOC test (Weinrich *et al.* 2011) produces multiple measurements that can be used to model increased pressure drops along pressure vessels specifically in seawater RO desalination and provide a mathematical model for fouling control. This model was presented in the final report for Water Research Foundation project 4280 (Schneider *et al.* 2011). The model can account for flow rates, AOC concentration, and substrate utilization rates (μ_{\max}). Using data from one train of a full-scale RO facility, the model was calibrated to match existing operational data. The development of this model showed that increased pressures in the pressure vessels can be almost entirely explained by bacterial growth (biofouling) and thus points to the importance of AOC control through pretreatment. This new approach considers the following phenomena:

1. Biofilm growth on the surface of the membrane is non-uniform and is induced by AOC concentrations.
2. Biofilm growth in the spacers of the spiral-wound membrane that induces longitudinal pressure reduction due to a restriction in the effective cross-sectional flow area.
3. Pressure losses along the elements inside the pressure vessel due to friction.

4. Dynamic conditions. The model accepts changes of operational characteristics of the membrane filtration cycle such as changes in influent water quality and changes in crossflow velocities.

This model would use daily measurements of AOC and μ_{\max} along with forecast flow rates to each train in a real-time application. Based on these results, alternative operational strategies, such as pretreatment optimization, flow rate distribution, and the use of biocides, can be identified for balancing flow rates among trains and reducing cleaning times. The model addresses short-term pressure losses due to reversible fouling, assuming that the pressure drops are due to biological growth; however, colloidal fouling would be revealed through increases in pressure drop. However, this phenomenon may not be an issue at all facilities, but where it is significant, colloidal fouling can be accounted for by including a term in the hydraulic radius calculation.

PREVENTION

Strategies for biofouling prevention typically include continuous or intermittent biocide application or nutrient limitation or chemical and physical cleaning programs in SWRO pretreatment, or even membrane surface modification (Yang *et al.* 2009; Mansouri *et al.* 2010). Conventional desalination pretreatment often includes pre-chlorination, coagulation/flocculation, clarification, and filtration. Filtration can be achieved using granular media such as sand or dual media filtration (DMF). Presumably, because of the commercial availability of UF and NF, these membranes are increasingly used in the industry. However, UF and NF exhibit a low degree of removal of fouling substances (Hilal *et al.* 2004). In the interest of sustainability, membrane filters have limited usage and must be cleaned or replaced. In addition, the robustness of membrane filters for pretreatment has not been proven (NRC 2008). Alternatively, proper operation of sand filtration for RO pretreatment has shown that beach wells, i.e., natural sand filters, have lower biofouling potential than in the raw water (Ebrahim *et al.* 2001; Saeed *et al.* 2004; Veza *et al.* 2008). The effectiveness of beach wells as a pretreatment technique can partially be related to the natural

biological activity in the sand. Because of the similarity between slow sand filters and beach wells, this pretreatment technique warrants further investigation for its role in reducing biofouling components.

Limitation of nutrients

Nutrient limitation is a practical approach for reducing the quantity of life-sustaining elements, carbon, nitrogen, and phosphorus, in order to minimize unwanted microbial assimilation and growth. Although this is a fairly simple concept, the ubiquitous nature of these naturally occurring substances and applied usage of treatment chemicals are all sources of growth promoting nutrients. Furthermore, AOC sources are not well understood in seawater matrices.

Effective pretreatment is critical in the efficient operation of SWRO membranes (Kumar *et al.* 2006). There is evidence that biologically active sand filtration prior to polyamide composite RO filters significantly enhanced the membrane performance (Griebe & Flemming 1998), presumably by removing BOM. A study of biodegradable organic carbon in an RO facility that experienced extreme biofouling was conducted by Schneider *et al.* (2005). Very high levels of AOC and biodegradable dissolved organic carbon (BDOC) were created by chlorination of river feedwater. Furthermore, the application of chlorine on the sludge blanket inhibited any microbiologically facilitated AOC reduction. The drinking water industry often practices preoxidation as part of pretreatment, which creates biologically available organic carbon, i.e., AOC. For example, ozone reacts with NOM to form aldehydes and low MW organic acids (Glaze *et al.* 1989; Miltner *et al.* 1992; Schechter & Singer 1995; Siddiqui *et al.* 1997), which can then be removed by biological filtration to increase biological stability and decrease disinfection byproduct formation. Unfortunately, there is no biofiltration research to this extent in desalination, yet there is significant interest in mitigating irreversible biofouling of RO membranes. This issue has been clearly referenced by numerous authors (Flemming *et al.* 1997; Griebe & Flemming 1998; Schneider *et al.* 2005; Fujiwara & Matsuyama 2008; Voutchkov 2010b).

The role of cleaning agents and disinfectants is not fully understood yet in seawater. Acid cleaning, intermittent biocide application and nutrient removal are strategies for

biofouling control (Mansouri *et al.* 2010). Anecdotal results and some limited research have shown that application of disinfectants increases the biofouling potential in seawater, presumably resulting from the reaction between the oxidant and NOM, which produces more easily biodegradable compounds as described above in freshwater. This area of nutrient limitation has not been fully investigated because of the lack of tools for monitoring or measuring biofouling potential. Flemming *et al.* (1997) described biofouling as having a 'biofilm reactor in the wrong place'. Proper pretreatment removal of BOM would limit available nutrients and therefore reduce biological growth on the membranes.

Reducing fouling via membrane amendment

Biofouling control includes various strategies which have been divided into two main categories, 'anti-adhesion' and 'anti-microbial' (Mansouri *et al.* 2010). Research using the model organism *Pseudomonas aeruginosa* has identified predictors of cell adhesion with zeta potential, surface roughness, and hydrophobic character. However, as noted previously, this organism has not been identified as a key member in RO membrane biofilm studies (Zhang *et al.* 2011). Anti-adhesion reduces initial macromolecular adsorption and antimicrobial approaches attack, disperse, or suppress activity of organisms that have already attached to the membrane.

Recent research has identified the importance of mitigating fouling by early detection. A study by Cai *et al.* (2011) investigated antibody-based sensors. These biosensors were attached to cellulose acetate UF membranes using a temperature-responsive polymer film. In combination with a modified film layer, the membrane was capable of detecting bacteria and reducing fouling. In addition, its thermally responsive layer can be exploited to control fouling specifically of the sensor surfaces. Biofouling management at the membrane level is another important strategy for controlling O&M cost, and maintaining membrane performance. This research exhibits the potential for manufacturing membrane components that are inherently resistant to fouling. For instance, feedspacers have also been targeted. Studies have shown that biological fouling can be related to feedspacers in spiral-wound membrane elements (Cornelissen

et al. 2007). Modification of the element using copper-charged polypropylene feedspacers was shown to maintain 75% of the initial flux compared to 30% maintained by an unmodified membrane feedspacer in drinking water experiments (Hausman *et al.* 2010). Although experiments with both modified and unmodified feedspacers exhibited instantaneous flux declines, the unmodified units fouled rapidly over time. Other work has focused on using silver nanoparticles for inhibiting or reducing biological growth on the feedspacers (Yang *et al.* 2009). Specifically, Yang *et al.* (2009) tested a surface modified RO membrane and membrane spacer coated with silver nanoparticles in sand-filtered seawater. The coated membrane was able to better maintain permeate flux than the unmodified membrane; however, initial permeate flux was lower ($0.8 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$) than that of the unmodified membrane ($1.3 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$). Extended operation of the membrane indicated that foulants could have reduced the bactericidal effects of the silver ions, suggested to result from accumulation of foulants on the membrane. This limitation was mitigated by additional testing of silver-coated feedspacers, which showed improvement of the initial permeate flux and were able to minimize a loss of this flux over the duration of the experiment. While advances are made in membrane technology and researchers continue to investigate methods for reducing fouling at the membrane site, investigations may only be based on drinking water or amended freshwater. In desalination, fouling is a pertinent issue because of the increasing usage and inherent expense of treatment. Fouling reduction should not just be targeted at the membrane surface, but investigations into removing and reducing the source of the foulant in the feedwater are also of utmost importance. Application of nanoparticles remains a controversial technique because of the possibility for detachment of silver nanoparticles or disposal of components coated with these substances. Their fate in the environment is still not fully understood.

Recent studies have also prepared membranes with micrometer-sized heated aluminum oxide particles which are referred to as microgranular adsorptive filtration (μ GAF). This approach has been shown to enhance NOM removal (Cai & Benjamin 2011). The adsorbent coating appeared to capture most of the organic matter, and when removed the membrane permeability was nearly fully

recovered, which suggests that fouling did not occur in the membrane material.

Pretreatment using coagulation

Coagulation/flocculation is used in drinking water or wastewater treatment for improving the removal of organic matter and for reducing membrane fouling (Tansakul *et al.* 2010). Recent research identifies fouling minimization on SWRO membranes when pretreatment includes low pressure membrane (UF) following powdered activated carbon (PAC) adsorption (Tansakul *et al.* 2010, 2011). This approach is likely to reduce fouling on the UF as a result of the removal of DOC present in seawater which has characteristic high salinity. Fouling rates were investigated under bench-scale conditions using hybrid processes combining coagulation/UF and PAC adsorption/UF. Source water was from the Mediterranean Sea with 39 g/L salinity and 1.3 mg/L average TOC concentration. Elevated concentrations of PAC between 100 and 200 mg/L reduced fouling rates over a distribution of transmembrane pressures. In particular, PAC chosen for greater surface areas exhibited better performance for removing marine organics and thereby reducing UF membrane fouling (Tansakul *et al.* 2010).

Another study used ferric chloride (FeCl_3) as a coagulant and PAC. With regard to OM, flocculation removed all but the smallest MW fraction of seawater, which could not be removed by PAC adsorption. A dose of 4 mg/L of FeCl_3 was used after determining the optimum dose through jar tests using seawater from Collioure, France. Water quality was as follows: pH = 8.14, conductivity = 48.5 mS/cm, TDS = 32,760 mg/L, and DOC = 1.78 mg/L. MW distribution of the seawater was determined throughout the course of experiments. The greatest response of raw water OM was detected around 280 Da; MW ranged from 280 to 14,160 Da prior to treatment. For reference, typically RO removes 90% of organic matter MW around 200 Da. Comparatively, PAC adsorption removed MW near 280 Da better than FeCl_3 ; however, overall OM removal was better with FeCl_3 (Shon *et al.* 2009).

Pretreatment using low pressure membranes

Low pressure filtration is increasingly used in seawater RO desalination for pretreatment via MF or UF to

provide a barrier for particulates, colloids, macromolecules, algae, and bacteria. However, in protecting the RO membranes from fouling, often these low pressure filters become fouled from water quality fluctuation or ineffective pretreatment. The mechanisms by which fouling occurs are variable as discussed previously, but foulants are typically particles and NOM (Cai & Benjamin 2011). Although UF and MF membranes have been exceedingly popular for RO pretreatment, a recent study has called into question the suitability of these solutions where algal blooms are common (Ladner *et al.* 2010). As algal cells pass through the seawater intake or are pumped into the treatment plant, internal organic material is released through cells broken by hydrodynamic shear forces and results in pore blocking and cake formation. Organic matter rejection was reduced in UF (pore size 0.22 μm) and MF (0.45 μm) membranes. Permeate from crossflow membranes with sheared algal feeds exhibited an increase in organic matter which was confirmed by TOC, carbohydrate, UV absorbance, and fluorescence measurements, which confirmed that DOC was able to pass through the membrane pores. Ladner *et al.* (2010) proposed that an alternative setup to crossflow might be investigated, such as open tank membrane configuration similar to a membrane bioreactor in systems that are prone to algal blooms. This study also investigated adsorptive fouling. Hydrophilic polyvinylidene fluoride (PVDF) membranes were tested and results indicated that without particulate matter the high MW AOM did not cause fouling. This is contradictory to other studies; however, these discrepancies exist in tests conducted with freshwaters in which the chemistry of the NOM is different from AOM in seawater.

The claims put forth by the manufacturer for reducing SDI in the RO feed or other water quality benefits should be carefully considered for low pressure membranes. Switching to UF for pretreatment may not be effective, even though pilot tests can indicate otherwise. Pilot testing may not capture operational parameter variability; a major problem at the Addur SWRO facility in Bahrain. The facility struggled with numerous treatment inadequacies including structural design, process design, operational experience, and, especially problematic, biological fouling (Burashid & Hussain 2004;

Fujiwara & Matsuyama 2008). The SWRO intake is located in the Gulf of Addur, in which TDS ranges from 45,000 to 47,000 mg/L. Besides elevated TDS, other water quality issues were associated with the high water temperature and location. The intake is 1.2 km offshore and 3 m below the surface and immediately downstream of industrial and residential waste effluent discharge. Therefore, a considerable nutrient load led to growth and proliferation of microbial activity. Numerous operational iterations failed to reduce fouling; the system was fitted with a chlorine tolerant, cellulose acetate RO membrane and intermittent chlorine injection for biological growth control. There were fundamental issues with the pretreatment approach and testing procedure, which had not achieved removal of organic matter and reduction of biological fouling. Specifically, the facility had originally utilized DMF (which leaked and allowed media to pass through into the RO feed), which was then switched out to utilize UF pretreatment and non-chlorine operation in order 'to suppress generation of the nutrient (assimilable organic compound) as a micro-organism food', in other words inhibiting AOC formation (Fujiwara & Matsuyama 2008). This is an important point to review; in fact, there was no change specifically targeted to remove AOC and no measurements were reported to measure this parameter. In their defense, there was no test to adequately measure AOC, or components that contribute specifically to the food source for biological growth in the system. However, monitoring organic carbon is critical. The contractor for the facility had designed the retrofit on the basis of SDI measurements, which have often been described to be inadequate for addressing a range of fouling issues based on the limitation of the test itself to only measuring particles, and not BOM that contributes to biofouling. After review of the publications related to this facility, there was no accommodation made to address the detection or removal of nutrients available for biological growth. Although intermittent chlorine injection was included, UF membrane treatment was neither sufficient nor appropriate for removing or reducing the amount of organic carbon, in particular assimilable or biodegradable organic carbon that would be available as a food source for biological growth in

the system. Theoretically, if the UF provides a barrier to the microorganisms that may make it through the sand filter, then monitoring BOM could provide a useful approach to inhibiting the regrowth potential in the RO feed.

CONCLUSIONS

Fouling in SWRO membranes continues to be problematic for O&M efficiency and reducing its occurrence through prediction and prevention is critical. Organic matter, particularly the biodegradable fraction, appears to be a key component for the mitigation and prevention of biological fouling. Although the impacts of chemical interactions with organic matter are well established in freshwater used for drinking, the same level of understanding is lacking for SWRO applications. Understanding the impacts of pretreatment on the biodegradable fraction, specifically AOC, has been previously challenged by the lack of available tools and minimal research geared toward understanding treatment changes and AOC levels. There have been numerous reports of biological fouling; measuring AOC and modeling AOC utilization rates through the recent development of the bioluminescent saltwater AOC bioassay show promise for efficient prediction and prevention of biological fouling. Pretreatment applications have largely been focused on physical separation, but further development of biological treatment to reduce nutrients in RO feedwater would be valuable. Evaluating pretreatment impacts via new methods such as the bioluminescent AOC test will facilitate understanding of the fouling process, impacts from chemical addition, level of assimilable nutrients, and information for modeling applications and real-time monitoring. Other quantitative and qualitative techniques for monitoring water quality and microbiology of seawater intakes and during pretreatment will aid current and future SWRO applications. Additional SWRO research and development is crucial for the efficiency of this growing industry.

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