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In-depth analyses of organic matters in a full-scale seawater desalination plant and an autopsy of reverse osmosis membrane

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Abstract

In order to facilitate the global performance of seawater reverse osmosis (SWRO) systems, it is important to improve the feed water quality before it enters the RO. Currently, many desalination plants experience production losses due to incidents of organic and biofouling. Consequently, monitoring or characterizing the pretreatment step using more advanced organic and biological parameters are required for better operation to lessen fouling issues. In this study, the performance of pretreatment processes (including coagulation, dual media filtration (DMF), polishing with cartridge filter (CF) coupled with anti-scalant) used at Perth Seawater Desalination Plant (PSDP) located in Western Australia were characterized in terms of organic and biological fouling parameters. These analyses were carried out using liquid chromatography with organic carbon detector (LC-OCD), three dimensional-fluorescence excitation emission matrix (3D-FEEM) and assimilable organic

carbon (AOC). Furthermore, the used (exhausted) RO membrane and CF were autopsied so that the fates and behaviors of organic foulants in these treatment systems could be better understood.

Keywords: Autopsy; Cartridge filter; Desalination; Pretreatment; Seawater Reverse Osmosis

Abbreviations

3D-FEEM: Three dimensional-fluorescence excitation emission matrix; AOC: Assimilable organic carbon; ASW: Acidified seawater; ATP: Adenosine tri-phosphate; BB: Building blocks; BP: Biopolymers; CF: Cartridge filter; DMF: Dual media filter; DOC: Dissolved organic carbon; DOM: Dissolved organic matter; FSW: Filtered seawater; HS: Humic substances, humics; Ion chromatography: IC; ICP-MS: Inductively coupled plasma-mass spectrometry; ICP-OES: Inductively coupled plasma-optical emission spectroscopy; LC-OCD: Liquid chromatography with organic carbon detection; LMW-N: Low molecular weight neutrals; MFI-UF: Modified fouling index with ultrafiltration; PSDP: Perth Seawater Desalination Plant; PSW: Polished seawater; RO: Reverse osmosis; RSW: Raw seawater; SDI: Silt density index; SWOM: Seawater organic matter; SWRO: Seawater reverse osmosis; TEP: Transparent exopolymeric particles

1. Introduction

Optimization of pretreatment processes is a critical issue concerning the better performance of seawater reverse osmosis (SWRO) system because its operational efficiency depends heavily on the feedwater quality [1]. For this reason, an advanced pretreatment scheme is required to protect RO membranes from fouling [2]. More effective pretreatment will also reduce the fouling rate and frequency of chemical cleaning of RO. In turn, an improved understanding the role of pretreatment steps and their impact on the produced water quality from individual processes is also necessary [3].

In a SWRO desalination plant, after screening trash from the intake seawater as an initial pretreatment step, what follows – i.e. coagulation, flocculation, media filtration, and cartridge filter (with polishing) - are normally employed prior to the main desalting process (RO). Key concerns in the pretreatment of SWRO desalination plants are: (C-i) removal of suspended particles; (C-ii) destabilization and agglomeration of colloidal particles and dissolved organics; (C-iii) preventing the sudden appearance of particulate matters in the feed water entering RO; (C-iv) preventing bacterial growth and biofouling on the RO membrane; (C-v) regulating the seawater pH to improve the coagulation performance and provide adequate values for the RO membrane; (C-vi) neutralizing the residual active chlorine; and (C-vii) inhibiting scale formation on the RO membrane [4].

In order to resolve the problems mentioned above, the following approaches are recommended; accordingly, (A-i) anthracite (~1 mm) is often applied with sand (as dual media) during the deep-bed media filtration process to remove suspended solids. The media backwashing process with filter effluent and air is followed by the media filtration process to remove captured particles from the filters; (A-ii) ferric or alum salts are often used to coagulate and flocculate colloidal particles and dissolved organics; (A-iii) cartridge filters (CFs) are usually located after media filtration to deal with preventing the sudden appearance of particulate matter; and (A-iv) sodium hypochlorite (NaOCl), Cl_2 , KMnO_4 , or O_3 can be used to control biofouling. Sulphuric acid (H_2SO_4) which may be applied to assist the biocide action of NaOCl ; (A-v) H_2SO_4 can be dosed to regulate the pH for polyamide-type RO membranes; (A-vi) sodium bisulphite (SBS) is primarily used to neutralize the residual active chlorine, especially for a polyamide-type RO membrane; and (A-vii) phosphate-based antiscalant is normally dosed to control scaling. H_2SO_4 can serve to help the action of the scale inhibitors [4].

The Perth Seawater Desalination Plant (PSDP) is located at Kwinana, 25 kms south of Perth in Western Australia, and was commissioned in November 2006 [5]. With a capacity of 144 MLD, the plant is able to produce up to 17% of Perth's drinking water demand. As shown in **Fig. 1**, sodium

hypochlorite (NaOCl) is firstly injected as a biocide to intake seawater. Prior to dual media filter (DMF), seawater (DMF feed) is coagulated with ferric sulphate (primary coagulant). Polymeric coagulant aid and sulphuric acid are added to improve coagulation. Following that, filtered seawater by DMF (or DMF effluents) is polished through cartridge filter (CF) with the addition of anti-scalant (polished seawater) before the RO process. This can, in turn, control particulate fouling (by DMF and CF), inorganic (by anti-scalant) and organic fouling (by DMF with coagulation) and biofouling (by biocide).

However, at present, monitoring of particulate foulants is mainly being conducted at the desalination plant, since the primary function of DMF is to reduce high loads of particulate and colloidal matter (i.e. turbidity), not organic. For this reason, DMF at PSDP currently operates with the guideline of hydraulic permeability (L_p ($\text{m}^3/\text{m}^2 \text{ Pa h}$), which is defined as seawater flow (m^3/h)/(dP (Pa) $\times$ filtration surface (m^2)) and clogging factor with silt density index (SDI). In fact, DMF is usually operated by set point of L_p value (normally 110 L_p).

In many desalination plants, SDI is used for *in-situ* monitoring of pretreatment performance [6]. Despite its limitations in predicting membrane fouling, it is extensively used due to its simplicity. This measures only particulate fouling and is used as an indicator of produced water quality. For example, deteriorating quality of the pretreated water ($\text{SDI} > 5$) at the plant usually requires a higher coagulant dose to enhance treated water quality by reducing the colloidal fouling materials [7]. However, organic and biological fouling is being considered more important to improve SWRO performance. Their control can significantly reduce operating costs [8]. For this reason, several monitoring methods to quantify and qualify organic and biological foulants have been developed and tested in SWRO desalination plants [9]. However, these monitoring methods require complex steps and elaborate laboratorial equipment. Thus, they are not conducive to practical monitoring for organic and biofoulants in plants [10].

Dissolved organic carbon (DOC) is the most commonly used parameter to quantify organic compounds. Recently, many studies have used DOC-LABOR Liquid Chromatography - Organic Carbon Detector (LC-OCD) for analysis of the organic foulants since it can give more detailed information of hydrophilic organic fractions according to their molecular size [11-13]. Additionally, three dimensional-fluorescence excitation emission matrix (3D-FEEM) has been studied for effective characterizing technique of dissolved organic matters (DOM) [14, 15]. This is a rapid (within a few minutes), selective and sensitive analytical technique and generates information regarding the fluorescence characteristics of DOM by changing excitation and the emission wavelength simultaneously. The fluorescence in different spectral regions is associated with different types of functional groups. In the 3D-FEEM analysis, fluorescence signals are basically attributed to protein-like fluorophores and humic-like fluorophores.

Assimilable organic carbon (AOC) is known to be a bio-available DOC fraction that is readily assimilated and utilized by microorganisms resulting in an increase of biomass. Thus, AOC is the main component which influences biological fouling and biofilm formation and it can be an indicator to assess the biofouling potential in feed water entering the RO. Jeong et al. [16] recently developed a direct bioluminescence-based AOC measurement method using *Vibrio fischeri* MJ-1 (*V. fischeri*) for seawater samples. This method analyses the AOC concentration with a low detection limit (~ 0.01 $\mu\text{g/L}$) within a short time of 1 h. Moreover, a recent study [17] showed that standard (pore) blocking coefficient (Ks) obtained from modified fouling index using ultrafiltration (MFI-UF) test using 10kDa PES membrane could be utilized as a preliminary indicator of biofouling potential (instead of AOC).

In this study, various analytical techniques were used to characterize the organic and biofoulants in seawater (intake) and pretreated seawater collected regularly (throughout the 3-year operation) at different pretreatment steps. In addition, to understand fouling behaviors that occur in desalination processes, an autopsy of foulants present on CF and RO membrane (taken from PSDP after 8 years'

operation) was conducted. It is highly vital to establish a fouling control strategy for RO-based desalination plant.

2. Materials and methods

2.1 Monitoring methods

The role and application of advanced analytical methods used in this study to measure the organic and biological foulants are described in this section.

2.1.1 Liquid chromatography-organic carbon detector (LC-OCD)

It was used to measure the DOC and organic fractions. The LC-OCD system separated DOC compounds using a size exclusion chromatography column, a Toyopearl TSK HW50S column (TOSOH Bioscience GmbH, Stuttgart, Germany), with phosphate buffer mobile phase of pH 6.4 ($2.6 \text{ g L}^{-1} \text{ KH}_2\text{PO}_4$ and $1.5 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_4$) at a flow rate of 1.1 mL min^{-1} . To obtain a better resolution for seawater (saline) samples, dual columns were applied in this study with 180-240 minutes retention time (doubled as that used in single column). Two different detectors, an ultraviolet detector (UVD) (absorption at 254 nm) and an OCD detector (after inorganic carbon purging), were utilized to measure the concentration of separated hydrophilic organic compounds. The amount of each organic fraction was calculated using a software program (ChromCALC DOC-LABOR, Karlsruhe, Germany) based on the chromatogram obtained from LC-OCD analysis.

The different organic fractions in seawater organic matter (SWOM) identified and quantified depending on their molecular size from LC-OCD analysis are: i) biopolymers (BP), ii) humic substances (HS or humics), iii) building blocks (BB) and iv) low molecular weight neutrals (LMW-N) [12]. BP has high molecular weight (20,000-100,000 g/mol) compounds such as polysaccharides, amino sugars, polypeptides, proteins, hydrophilic fraction and not UV-absorbing. In seawater, BP mostly exists as colloidal transparent exopolymeric particles (TEP) or polysaccharides and aromatic proteins. HS represents compounds with molecular weights of approximately 1,000 g/mol. BB is

defined as humic-hydrolysates and sub-units of HS with molecular weights between 300 and 450 g/mol. They are mainly weathering and oxidation products of HS. LMW-N consists of LMW weakly charged hydrophilic compounds such as alcohols, aldehydes, ketones and amino acids.

2.1.2 Three dimensional-fluorescence excitation emission matrix (3D-FEEM)

It was used to measure protein-like and humic or fulvic-like organic foulants. For the 3D-FEEM analyses, fluorescence measurements were made with water samples using a fluorescence spectrophotometer (Varian Eclipse Fluorescence Spectrophotometer). FEEMs were acquired by changing and scanning emission (em) wavelengths from 250 to 500 nm repeatedly at excitation (ex) wavelengths scanned from 220 to 400 nm by 5 nm increments and 5 nm bandwidths of both ex and em. In this analysis, the fluorescence spectrophotometer was set at a speed of 3000 nm/min, a PMT voltage of 700 V and a response time of 2 s.

According to previous studies [15, 18, 19], four characteristic peaks were observed in EEMs including Peak A – humic-like (ex/em=250–260/380–480 nm); Peak C – fulvic-like (ex/em= 300–370/400–500 nm); Peak B – tyrosine-like, protein-like (ex/em = 270-280/300–310 nm); and Peak T – tryptophan-like, protein-like (ex/em= 270-280/320-350 nm).

In this study, the average value of fluorescence intensities in the range of ex/em of each peak was used for quantitative analysis, in comparison to relative abundance of standard organic foulants. The selected standard model organic foulants of humic-like, fulvic-like and protein-like were humic acid (HA, Suwannee River), fulvic acid (FA, Suwannee River) and bovine serum albumin (BSA, Sigma-Aldrich), respectively. In order to establish the standard curve, 0.1, 0.25, 0.5 and 1.0 mg-C/L of each model compound were used. Peak T indicated the highest intensity with BSA and a good correlation between fluorescence intensity and BSA concentration was observed. Here, peak T can be considered as BSA or protein-like peak and quantified using the relationship of protein-like mg of BSA/L = 0.51 x peak T's intensity. In terms of HA, peak C showed the highest intensity but peak A has a good correlation with HA concentration. Thus, peak A indicates the humic-like peak and the

following relationship was established: humic-like mg of HA/L = $0.51 \times$ peak A's intensity. Similarly, peak C revealed the highest intensity of FA and fluorescence intensity increased when FA increased. Thus, peak C can be considered to be the fulvic-like peak and the following relationship was established: fulvic-like mg of FA/L = $0.48 \times$ peak C's intensity.

2.1.3 Assimilable organic carbon (AOC)

AOC was used for the direct measurement of biological fouling potential in water. The AOC was measured via the bioluminescence method using *Vibrio fischeri* (*V. fischeri*) MJ-1 strain. A 24-well multi-well, tissue culture treated plate (353047 – BD Falcon™) was employed. Glucose was used as a standard carbon source since better cell growth can be obtained with glucose even at low concentration. Thus, AOC concentration is expressed as $\mu\text{g-C}$ glucose equivalents/L. Details regarding the procedure and information of AOC test have been documented previously [16].

2.2 Foulant analysis

2.2.1 Fouled CFs

DMF filtered seawater flows to CFs. In PSDP, 5 micron (μm) CF (1251-10C, Pall Corporation, USA) is used. It is made of high consistency polypropylene melt blown cartridges. The fouled CFs was taken from CF-14 train of PSDP for further analyses. The CFs was frozen immediately after their ejection from the housing. Several segments were cut from the fouled CF for analysis. Before and after CF replacement, polished seawater was examined to evaluate the fouling on CF and to examine the role of CF as a security filter. The samples include: i) CF feed water (DMF filtered seawater) (*FSW-CF*); ii) polished seawater before changing CF (or discharge water from old CF (*PSW-CF_{old}*); iii) polished seawater after changing CF (discharge water from new CF) (*PSW-CF_{new}*); iv) CF drain-down (*CF-DD*) (seawater from CF when left in a bucket and drained - a significant amount of ferric salt was observed from visual observation).

2.2.2 Fouled RO membranes

The RO membrane used in PSDP is SW30HR LE-400 (DOW FILMTEC, USA). RO membrane has been operated for 8 years. RO modules were taken at three different positions from one of the racks in the 1st pass RO (Rack 7): RO-A (7 Top) (15th element of row A- located at the end of the rack), RO-B (3 Top) (12th element of rack A- located at the middle of the rack) and RO-C (3 Bot) (5th element of row L which is located at the bottom of the rack). RO recovery was 45% and the average conductivity of rack 7 was 523 $\mu\text{S}/\text{cm}$. RO cleaning followed the procedures listed below: i) a low pressure flush with permeate water to remove service concentrate and foulants, ii) cleaning solution prepared was introduced to the first stage and an optional soak and recirculation sequence were then used, and iii) a low-pressure cleaning rinse with permeate water was conducted to remove the traces of chemical from the cleaning skid and the RO skid.

Used RO membranes obtained from PSDP were cut into several small segments. Three layers (from 3 to 1 toward permeate line) at 3 different positions (along the length) were taken randomly for autopsy as shown in **Fig. 2**.

2.2.3 Foulant extraction

Each RO membrane coupon was cut into 2cm x 3cm. In the case of CF, it was cut several pieces into 2cm x 2cm x 2cm for foulant extraction. Inorganic foulants were extracted in 0.1N-HCl (solution). Organic foulants were extracted using 0.1N-NaOH (solution). Extraction was done by agitating them in 10 mL of extraction solution (contained in 50 mL of carbon-free glass tube). The agitation was provided on a shaker at 200 rpm for 24h. Details concerning the foulant extraction procedure have been described in another study [20].

2.2.4 Analytical methods

Thermo Scientific™ Dionex™ ion chromatography (IC), Perkin Elmer OPTIMA 7300 inductively coupled plasma-optical emission spectroscopy (ICP-OES), and PerkinElmer quadrupole Nexion inductively coupled plasma-mass spectrometry (ICP-MS) were used for the inorganic foulant

analysis. The concentration of DOC and detailed organic fractions of organic foulants of CF media and RO membranes were measured using LC-OCD (see section 2.1.1).

3. Results and Discussion

3.1 Pretreated seawater

In this study, pretreated seawater samples - raw seawater (RSW), acidified seawater (ASW), filtered seawater (FSW) and polished seawater (PSW) collected from PSDP (**Fig. 1**)- were investigated in detail in terms of organic and biofoulants. The results are summarized in **Table 1**.

3.1.1 Raw seawater (RSW)

DOM of RSW was characterized from 2012 to 2014. Representative RSW samples are reported. Average DOC value of RSW during the 3 years was 1.50 ± 0.29 mg/L, which comprises 0.09 ± 0.05 mg/L of BP, 0.51 ± 0.08 mg/L of HS and 0.75 ± 0.27 mg/L of LMW-N. DOC of RSW contained about 50% of LMW-N followed by HS (34%). A similar trend was observed in another recent study [21]. LMW-N and HS are the main organic fractions in RSW.

Depending on seawater temperature, RSW is divided into two seasons (warm and cool season: November to April - $19.9 \sim 23.1^\circ\text{C}$ and May to October - $18.6 \sim 19.7^\circ\text{C}$, respectively). As given in **Table 1**, the main difference between seawater collected in the warm season and that collected in the cool season is the LMW-N concentration (i.e. warm season: 0.97 ± 0.25 mg/L contrasted to cool season: 0.55 ± 0.18 mg/L). This increase in LMW-N led to total DOC increase in RSW. In fact, LMW-N accounted for 58.79% of DOC in RSW collected during the warm season. Interestingly, changes in BP and HS concentration of RSW for both seasons were comparatively similar (on average, BP was 0.09 ± 0.05 mg/L (5.93% of DOC) and HS was 0.51 ± 0.08 mg/L (34.02% of DOC)).

The composition of SWOM could be linked to seasonal variation of algal and biological activity in the ocean. DOM is the most abundant form of SWOM and its influences on physical, chemical and biological processes in carbon cycle are widely recognized. In general, HS constitutes a significant

fraction of SWOM and behaves as weakly acidic polyelectrolytes that carry net negative charge at neutral pH. It has been reported MW of HS ranges from 0.5 to 1000 kDa. HS, which is a heterogeneous and complex mixture of high MW BPs, constitutes a significant fraction of SWOM. Possible sources of HS include both river inputs and *in-situ* production by phytoplankton. However, terrestrial input is very marginal (less than 1%). It is therefore regarded as a marine-derived HS from phytoplankton. As temperature increases (occasionally up to 30°C), a higher algal and biological activity can be observed. Thus, during this season the amount of DOM formed by the free radical cross-linking of unsaturated lipids released into seawater increases due to algal/microbial action in the surface seawater [22]. 3D-FEEM results showed a higher contribution of FA-like compounds in RSW than HA-like (0.36 ± 0.01 mg-FA equivalents/L vs. 0.19 ± 0.01 mg-FA-equivalents/L). FA is a smaller MW portion of HS and contains more oxygen but less carbon than higher MW HA [18].

DOM also undergoes a complex series of reactions, which produce photo-degraded or labile DOM with adsorption of sunlight. It can be accessed by phytoplankton and bacterial for growth (chromophoric DOM, CDOM). Therefore one of the dominant fractions of DOM in seawater is actually the LMW fraction (around 50% of DOM in RSW investigated in this study). A previous study also indicated low MW values in the coastal marine DOM [23]. The photolysis of CDOM results in producing LMW organic compounds due to radical and fragmentation reactions arising from the net oxidative flow of electrons from CDOM to O₂. Again, the LMW organic compounds are taken up by bacteria and respired to CO₂. The coupling between photo-degradation of CDOM and uptake of the LMW products by bacteria is an important route for loss of CDOM in the oceans and an important component of the global carbon cycle. Exposure of seawater to sunlight produces higher yields of these LMW organic compounds in the bulk seawater, suggesting that higher photo-production rates in the surface microlayer account for the observed enrichment factor of LMM organics. Thus, the amount LMW organic compounds increased in the warm season as observed in this study.

Dittmar and Kattner [24] attributed LMW-N to amphiphilic DOM recalcitrant to biodegradation such as metabolic intermediates and bacterial membranes moieties that are dependable. Nguyen et al. [25] also revealed that these organic compounds released from algal activity are highly biologically labile. The AOC result supports this phenomenon. High AOC concentration was detected for RSW in the warm season (45.02 ± 19.73 $\mu\text{g-C}$ glucose equivalents/L) while it was nearly half during the cool season (25.18 ± 14.77 $\mu\text{g-C}$ glucose equivalents/L), which indicates that warm season has high biofouling potential in seawater. A recent study [26] has reported the impact of AOC concentration of feed on RO biofouling and the increase in AOC resulted in high growth of biomass on RO membrane.

3.1.2 Coagulation and acidification – Acidified seawater (ASW)

Ferric sulphate solution (Orica Chemicals, Australia) was used as the primary coagulant before the DMF facilitated the flocculation of suspended solids in the raw (feeding) seawater. Ferric sulphate was dosed into a dilute sulphuric acid stream, which flows to the DMFs. pH was adjusted using sulphuric acid to 6.8 (between 6.7 and 7.0) from 8.0~8.1; and polymeric coagulant aid (Floquat FL 4526 PWG, Polydiallyldimethylammonium Chloride; PolyDADMAC) was added to enhance flocculation performance.

This process coagulated and flocculated colloidal particles and dissolved organics present in feed water (RSW), resulting in increased turbidity (up to about 10 NTU) in ASW. With respect to the behavior of organic foulants, DOC reduction by flocculation was only around 6% from RSW. BP reduction was relatively superior and it was roughly 50%, from 0.09 ± 0.05 to 0.05 ± 0.03 mg/L. HS was also slightly reduced (from 0.51 ± 0.08 to 0.44 ± 0.10 mg/L). This pattern was also observed in the 3D-FEEM analysis of organic foulant. In particular the decrease of fulvic-like in HS was observed. However, LMW-N concentration increased by 8.8% by flocculation together with acidification. Similarly, AOC concentration increased by 10% (**Table 1**).

3.1.3 Dual media filter (DMF) – Filtered seawater (FSW)

ASW (as presented in section 3.1.2) was fed into DMF under pressure as opposed to gravity to ensure long runs before the system requires backwashing. The DMF system was operated at a filtration velocity of 14 m/h. Twenty-four DMFs are installed into 2 separate banks (each filter has an effective filtration area of 52 m²). Each DMF consists of a 300mm layer of sand with an effective size of 0.3 mm and 800 mm layer of anthracite with an effective size of 1.6mm. A 100mm gravel bed was provided below the sand medium to protect the nozzles being clogged by the sand. This makes up to a total bed height of 1200mm. As expected, low turbidity of FSW (less than 0.2 NTU) was produced from the DMF. Coagulation followed by DMF reduced BP and HS as well. These organic compounds were coagulated during the coagulation process and DMF captured in the filters. Then, backwashing flushed the captured materials out. The DMF removed LMW-N marginally. This is possibly due to biodegradation of organic materials in the filter. Only 4% of AOC reduction from RSW was observed by DMF.

3.1.4 Polished seawater (PSW)

At PSDP, the polishing process comprised CF and the addition of antiscalant prior to RO. CFs are placed downstream of the DMFs to keep the RO membranes further away from any large items escaping from the DMFs through a broken nozzle. Organophosphate-based antiscalant (PC-1020T Permatreat, Nalco, USA) is dosed before CFs to reduce the risk of scaling on RO membrane. Only a small amount of anti-scalant (0.25 mg/L) was used during the sampling period. The CFs had a filtration capability of 5 microns. The CFs does not have the ability to catch the ferric hydroxide flocs that escape the DMF system. Although CF as final barrier for RO reduced a part of total DOC from RSW, AOC somewhat increased after the polishing process. For this reason, a previous study [27] suggested the necessity of selecting anti-scaling chemicals on the basis of their biological growth-promoting properties.

In summary, pretreatment mainly reduced the particulate fouling potential while the decline in organic fouling was only marginal. It reduced BP and HS contents and led to approximately 16% of DOC removal. Consequently, these pretreatment strategies at PSDP proved to be not effective in lessening organic and biofouling. What is therefore required is an improvement in pretreatment based on reducing organic and biological fouling potential if a desalination plant is to operate efficiently.

3.2 Organic foulants on CF

Table 2 shows the DOC and organic fractions of DMF filtered seawater to CF (FSW-CF), PSW (or CF discharge) before and after CF replacement and CF drain-down water samples. The main function of CF is to prevent RO membrane from the deposition of particulate matters. In this context, large amounts of ferric hydroxide and flocs were found in CF-DD (turbidity of CF-DD water was as high as 28.5 ± 7.5 NTU). The LC-OCD results showed that BP reduction by CF was superior regardless of CF replacement. BP reduction was higher than 80% and BP concentration in CF-DD was 0.157 ± 0.008 mg/L. However, HS reduction was marginal even after changing of CF (HS in PSW-CF_{new} of 0.400 ± 0.028 mg/L as compared to FSW-CF of 0.407 ± 0.089 mg/L). Furthermore, HS concentration in PSW increased when old CF was used (HS in PSW-CF_{old} = 0.572 ± 0.142 mg/L) indicating that HS would have been released from fouled CF. Similar patterns were observed in BB and LMW-N concentrations in PSW. These increased the amount of organic foulants after CF (from 1.184 ± 0.143 to 1.381 ± 0.266 mg-DOC/L), indicating that used CF produced the poor feed water to RO. Thus, it is necessary to change CF based on the quality of organic matter. Schneider et al. [28] also reported that DOC increased after CF. Total cell number increased (based on biodegradable DOC test) for the sample collected after the CF (i.e. CF effluent). In addition, the DOC concentration increased at the CF outlet compared to the CF inlet indicating an increase in biofouling potential. HS

and LMW-N can be the membrane biofouling precursors that provide the nutrients to microorganisms and thus, they are BDOC and AOC compounds [29].

In order to study the organic foulants on CF in detail, foulants were extracted from the used CF media (see section 2.2.3). These foulants were analyzed using LC-OCD and 3D-FEEM and results of these analyses are presented in **Fig. 3a** and **3b**, respectively. As expected, BP and HS were the main organic foulants on the fouled CF (**Fig. 3a**). Especially, fulvic-like organic foulants were found to be the main organic foulants from the 3D-FEEM investigations. Fulvic-like organic foulant was 49.79 ± 27.24 mg-FA/cm³ of fouled CF (**Fig. 3b**).

3.3 Detailed RO membrane autopsy

Autopsy of RO was conducted in terms of inorganic (scalant) and organic foulants. Visual examination revealed a homogeneous brown thin layer on the surface of the fouled RO membranes. More deposition of foulant accumulation was observed especially on the surface of the threads of the concentrate side spacer and the face of the strands facing the water flow. Contamination on the membrane taken near the permeate line (toward water flow) was found to be minimal. Microscopic morphology of fouling layer on the surface of membrane was observed using the optical microscope and the intensities varied at different positions of the membranes (3 Bot > 3 Top > 7 Top) (**Fig. 4**). As can be seen from **Fig. 2a**, 3 Bot represents the front of the rack and 3 Top and 7 Top were taken from the middle and end of the rack, respectively.

3.3.1 Inorganic foulants (or scalants)

The inorganic elements analyzed by using IC and ICP are presented in **Table 2** and **Fig. 5**. As can be seen from **Fig. 5**, higher amounts of inorganic foulants (or scalants) were found with 3 Bot sample (front position of RO rack) compared to 3 Top and 7 Top samples. The contents of inorganic foulants are observed to have the following order: Na > Ca > S > Fe > Mg > Si > K $\approx$ Mn >> Al > Cr $\approx$ B $\approx$ Zn > Cu > Ni > Ba. Sodium (Na) content was the highest and it is due to the high amount of Na in

feed water (seawater) (**Table 3**). In RO system, the inorganic foulant present as dissolved ions are normally concentrated up to 10 times exceeding the solubility at the membrane surface [30]. Since many fouling ions are usually present in raw seawater (RSW), the interaction between salts/ions and the membranes during scale formation is highly complex. Previous studies have shown that CaSO_4 , CaCO_3 , SiO_2 , MgSO_4 and BaSO_4 are some of the most common inorganic salts responsible for scaling on the membrane surface [31-33]. Inorganic scalants such as calcium (Ca), sulphur (S), magnesium (Mg), silicon (Si), potassium (K), manganese (Mn), boron (B) and barium (Ba), etc., may originate in seawater. S may derive from SBS and sulphuric acid (H_2SO_4), which are used for reducing chlorine and adjusting pH during coagulation. Ca may be present as CaCO_3 , CaSO_4 , CaHPO_4 , $\text{Ca}_3(\text{PO}_4)_2$, and $\text{Ca}(\text{OH})_2$. These form inorganic scaling on the membrane. Magnesium (Mg) may be formed as a carbonate and phosphate form, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2$, respectively. Iron (Fe) may exist in hydroxide form, $\text{Fe}(\text{OH})_3$ and phosphate form, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. Fe is found as a high content scalant on fouled RO membranes and it is mainly derived from the iron-based coagulant (ferric sulphate) used in the pretreatment process. Phosphate-based antiscalant may well influence the scalant formation [34]. Minute scalants such as aluminum (Al), chromium (Cr), zinc (Zn), copper (Cu) and nickel (Ni) may come from pipe or plant materials. Thus the inorganic scalants come from three sources: feed water, chemicals used in the pretreatment processes and materials used in the plant construction.

3.3.2 Organic foulants

HS and LMW-N were found to be the major organic foulant components on the used RO membranes (**Fig. 6**). It is noted that these two organic compounds are dominant in feed water (or RSW) (**Table 1**). In other words, these compounds need to be limited to reduce organic fouling on the RO membrane. Amounts of organic foulants (in terms of DOC) were found in the order of 3 Bot (front) > 3 Top (middle) > 7 Top (end): $30.0 \pm 11.3 > 21.2 \pm 2.2 > 18.9 \pm 1.5 \text{ } \mu\text{g}/\text{cm}^2$ of membrane area, respectively. Organic fouling on 3 Bot samples (located at the entrance of RO rack) was higher in

comparison to the other two samples (middle or end of RO rack). This indicates that organic fouling occurred from the front to the end of RO rack.

In RO organic foulants, BP content is relatively low since most of the BP was removed during pretreatment (DMF coupled with coagulation). BP was also low in feed seawater. Relatively higher BP was found in the 3 Bot RO sample ($3.9 \pm 3.0 \mu\text{g}/\text{cm}^2$) as compared to only $1.0 \sim 1.8 \mu\text{g}/\text{cm}^2$ in 3 Top and 7 Top samples. HS constituted the major portion of fouling of RO membranes as reported at desalination plants operated in Middle Eastern region [35]. More than 50% of organic foulants was detected to be LMW-N. For example, 54.7% of organic foulants extracted from 3 Bot sample was LMW-N ($16.4 \pm 5.5 \mu\text{g}/\text{cm}^2$ of LMW-N in $30.0 \pm 11.3 \mu\text{g}/\text{cm}^2$ of DOC). In previous studies, organic foulants on RO membrane present in seawater were 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 [9, 36].

4. Conclusions

Detailed analyses were done on organic foulants in raw seawater (RSW) and pretreated seawater samples (coagulation coupled with acidification; ASW, DMF filtered seawater; FSW and polished seawater by cartridge filter (CF) and the addition of antiscalant). In addition, an autopsy of fouled CF and RO was conducted. The results obtained from this study are summarized below.

- 1) DOC in RSW mainly consisted of HS and LMW-N. What mainly differentiated RSW in the warm season from the cool season was the high concentration of LMW-N. This could be linked to the seasonal degree of algal and biological activity and photo-degradation in the sea.
- 2) Pretreatment steps reduced the particulate fouling potential with a small decrease in high MW organic matter such as BP and HS. Biofouling potential was not reduced by pretreatments used at the current desalination plant.

- 3) BP and HS were the main organic foulants on CF. Fouled CF discharged organic foulants and this resulted in an increase in organic fouling on RO membranes. CF replacement can be determined by organic content in produced water from CF.
- 4) The highest fouling on RO occurred in the front position of the RO rack. Inorganic scalants present on fouled RO membranes originated from the feed water, chemicals used in the pretreatment processes and materials present in the plant. HS and LMW-N were the major organic foulants on the fouled RO membranes. In summary, it is vital to appropriately control these inorganic and organic foulants prior to RO process to effectively limit fouling on the membranes.

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Table 1 Organic characterization of raw seawater (RSW), pretreated seawater samples (acidified seawater; ASW, filtered seawater; FSW, and polished seawater; PSW). (*: Each fraction's composition in DOC, **: N.A – Not available, and ***: R eff. (%) – Removal efficiency compared to RSW.)

Table 2 DOC and organic fractions related to CF samples (unit: mg/L).

Table 3 Composition of inorganic foulants on the used RO membranes (8years operated) (Inlet pressure and flow rate of rack 7 were 5,740 kPa (57.4 bar) and 555m³/hr, respectively.) (Unit: µg/cm²).

Table 1 Organic characterization of raw seawater (RSW), pretreated seawater samples (acidified seawater; ASW, filtered seawater; FSW, and polished seawater; PSW). (*: Each fraction's composition in DOC, **: N.A – Not available, and ***: R eff. (%) – Removal efficiency compared to RSW.)

		LC-OCD (unit: mg/L)				3D-FEEM			AOC
		DOC	BP	HS	LMW-N	Humic-like (mg-HA/L)	Fulvic-like (mg-FA/L)	Protein-like (mg-BSA/L)	(μ g-C glucose equivalents/L)
RSW	Warm season	1.65 $\pm$ 0.18	0.10 $\pm$ 0.06 (6.06)*	0.51 $\pm$ 0.09 (33.94)*	0.97 $\pm$ 0.25 (58.79)*	N.A.**	N.A.	N.A.	45.02 $\pm$ 19.73
	Cool season	1.29 $\pm$ 0.25	0.09 $\pm$ 0.04 (6.98)*	0.51 $\pm$ 0.08 (39.53)*	0.55 $\pm$ 0.18 (42.64)*	N.A.	N.A.	N.A.	25.18 $\pm$ 14.77
	Ave.	1.50 $\pm$ 0.29	0.09 $\pm$ 0.05 (5.93)*	0.51 $\pm$ 0.08 (34.02)*	0.75 $\pm$ 0.27 (50.31)*	0.19 $\pm$ 0.01	0.36 $\pm$ 0.01	0.94 $\pm$ 0.20	34.18 $\pm$ 8.05
ASW	Ave.	1.41 $\pm$ 0.30	0.05 $\pm$ 0.03	0.44 $\pm$ 0.10	0.82 $\pm$ 0.26	0.19 $\pm$ 0.02	0.34 $\pm$ 0.02	0.87 $\pm$ 0.11	37.65 $\pm$ 13.27
	R eff. (%)***	(5.9)	(50.8)	(13.8)	(-8.8)				(-10.15)
FSW	Ave.	1.32 $\pm$ 0.22	0.04 $\pm$ 0.03	0.44 $\pm$ 0.03	0.73 $\pm$ 0.21	0.19 $\pm$ 0.04	0.32 $\pm$ 0.05	0.84 $\pm$ 0.16	32.87 $\pm$ 26.80
	R eff. (%)***	(12.3)	(57.7)	(14.9)	(2.7)				(3.83)
PSW	Ave.	1.27 $\pm$ 0.37	0.05 $\pm$ 0.03	0.44 $\pm$ 0.08	0.76 $\pm$ 0.30	0.20 $\pm$ 0.05	0.39 $\pm$ 0.07	0.87 $\pm$ 0.20	34.97 $\pm$ 16.72
	R eff. (%)***	(15.6)	(50.0)	(14.6)	(-1.4)				(-1.31)

Table 2 DOC and organic fractions related to CF samples (unit: mg/L).

Samples	DOC	BP	HS	BB	LMW-N
FSW-CF ¹⁾	1.184±0.143	0.022±0.002	0.407±0.089	0.002±0.001	0.753±0.052
PSW-CF _{old} ²⁾	1.381±0.266	0.004±0.002	0.572±0.142	0.012±0.004	0.793±0.102
PSW-CF _{new} ³⁾	1.046±0.100	0.002±0.001	0.400±0.028	0.002±0.000	0.642±0.070
CF-DD ⁴⁾	1.806±0.228	0.157±0.008	0.606±0.020	0.017±0.004	1.026±0.204

¹⁾ FSW-CF: filtered seawater to CF, feed water for CF; ²⁾ PSW-CF_{old}: Polished seawater before CF replacement (with old CF); ³⁾ PSW-CF_{new}: Polished seawater after CF replacement (with new CF); and ⁴⁾ CF-DD: CF drain-down water sample.

Table 3 Composition of inorganic foulants on the used RO membranes (8years operated) (Inlet pressure and flow rate of rack 7 were 5,740 kPa (57.4 bar) and 555m³/hr, respectively.) (Unit: µg/cm²).

		<u>Al</u>	<u>Ba</u>	<u>Ca</u>	<u>Fe</u>	<u>K</u>	<u>Mg</u>	<u>Na</u>	<u>Si</u>	<u>B</u>	<u>Cr</u>	<u>Cu</u>	<u>Mn</u>	<u>Ni</u>	<u>S</u>	<u>Zn</u>
7 Top_1	AVE	45	3	1126	498	156	453	3892	419	69	50	19	48	17	899	27
	STEDV	14	0	320	145	68	38	449	31	3	58	5	6	16	194	4
7 Top_2	AVE	44	3	552	393	26	371	3044	429	62	14	13	50	7	698	23
	STEDV	16	1	123	21	44	49	675	75	7	3	1	17	1	130	0
7 Top_3	AVE	30	4	510	468	162	314	2543	426	53	16	14	53	5	526	23
	STEDV	15	1	103	20	189	152	1458	20	8	1	1	6	0	93	4
3 Top_1	AVE	88	5	1392	1012	95	584	4396	428	48	58	20	441	8	923	63
	STEDV	43	0	388	175	80	174	380	11	4	10	2	231	1	272	20
3 Top_2	AVE	66	4	1219	928	95	590	3180	458	41	65	21	417	8	924	30
	STEDV	32	1	303	123	137	115	744	86	8	19	1	218	1	211	4
3 Top_3	AVE	166	3	1308	982	204	580	2903	454	32	72	19	291	5	1064	25
	STEDV	192	1	294	98	119	109	575	94	3	14	1	140	3	362	3
3 Bot_1	AVE	114	5	1378	1065	397	678	4320	455	31	63	22	503	9	1079	45
	STEDV	59	0	322	134	408	15	994	63	3	17	4	254	3	214	9
3 Bot_2	AVE	146	5	1774	1237	287	733	3497	483	31	68	25	603	6	1219	28
	STEDV	75	3	670	91	166	183	694	87	8	10	3	189	1	392	1
3 Bot_3	AVE	186	4	2066	1476	254	721	3122	396	27	88	26	809	7	1440	23
	STEDV	186	1	894	93	238	97	311	83	3	2	1	479	1	776	5

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Fig. 1 Flow diagram of processes used at Perth Seawater Desalination Plant (PSDP) in Western Australia.

Fig. 2 (a) Position of RO membranes in rack 7 at PSDP and (b) sample locations of fouled RO membranes used for autopsy in this study (A-1 to C-3).

Fig. 3 Organic foulants extracted from CF: (a): chromatogram obtained from LC-OCD analysis; and (b): 3D-FEEM ($C=49.79\pm27.24$ mg-FA/cm³, $A=4.57\pm2.71$ mg-HA/cm³, and $T: 9.71\pm6.13$ mg-BSA/cm³).

Fig. 4 SEM images of fouled RO membranes.

Fig. 5 Inorganic composition of the foulants on the used RO membranes.

Fig. 6 Chromatogram of organic foulant on the used RO membranes (obtained by LC-OCD).

Fig. 1 Flow diagram of processes used at Perth Seawater Desalination Plant (PSDP) in Western Australia.

Rack 7	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A												3 Top			7 Top
B															
C															
D															
E															
F															
G															
H															
I															
J															
K															
L					3 Bot										

(a)

(b)

Fig. 2 (a) Position of RO membranes in rack 7 at PSDP and (b) sample locations of fouled RO membranes used for autopsy in this study (A-1 to C-3).

(a)

(b)

Fig. 3 Organic foulants extracted from CF: (a): chromatogram obtained from LC-OCD analysis; and (b): 3D-FEEM (C=49.79±27.24 mg-FA/cm³, A=4.57±2.71 mg-HA/cm³, and T: 9.71±6.13 mg-BSA/cm³).

3 Bot_1

3 Bot_2

3 Bot_3

3 Top_1

3 Top_2

3 Top_3

7 Top_1

7 Top_2

7 Top_3

Fig. 4 SEM images of fouled RO membranes.

Fig. 5 Inorganic composition of the foulants on the used RO membranes.

Fig. 6 Chromatogram of organic foulant on the used RO membranes (obtained by LC-OCD).

Graphical abstract

Research highlights

- This paper deals with pretreatment processes used in a full-scale seawater desalination plant.
- Organic matter in pretreatment was characterized using advanced organic and biological parameters.
- The used RO membrane and CF were autopsied to understand the behaviors of organic foulants.