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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.

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

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; IC, ion chromatography; 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.

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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. Sulfuric 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 bisulfite (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 sulfate (primary coagulant). Polymeric coagulant aid and sulfuric 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 (Lp (m^3/m^2 Pa h)), which is defined as seawater flow rate (m^3/h)/(pressure development (Pa) × filtration surface (m^2)) and clogging factor with silt density index (SDI). In fact, DMF is usually operated by set point of Lp value (normally 110 Lp).

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 (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 μg/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 10 kDa 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

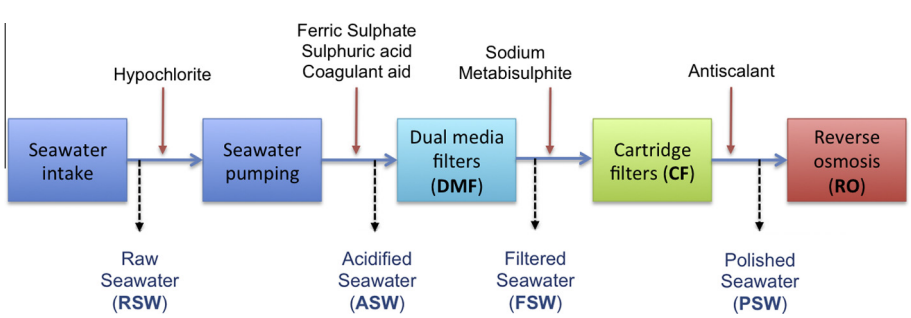

Fig. 1. Flow diagram of processes used at Perth Seawater Desalination Plant (PSDP) in Western Australia.