

# **NOVEL MEMBRANE HYBRID SYSTEMS AS PRETREATMENT TO SEAWATER REVERSE OSMOSIS**

by

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**Doctoral of Philosophy**



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## **CERTIFICATE OF AUTHORSHIP/ORIGINALITY**

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Candidate

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1. \*Jeong, S., G. Naidu, S. Vigneswaran, C.H. Ma, S.A. Rice. (2013) A rapid bioluminescence-based test of assimilable organic carbon for seawater. Desalination 317: 160-165.
2. \*Jeong, S., G. Naidu, S. Vigneswaran. (2013) Submerged membrane adsorption bioreactor as a pretreatment in seawater desalination for biofouling control. Bioresource Technology (DOI: <http://dx.doi.org/10.1016/j.biortech.2013.01.021>).
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\*Articles related to the Thesis.

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## Conference papers and presentations

1. \*Jeong, S., T.V. Nguyen, S. Vigneswaran. Submerged membrane coagulation hybrid system as pretreatment to organic matter removal from seawater. The 3rd International Seawater Desalination Workshop. 3-6 November 2010, Jeju, Republic of Korea.
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## LIST OF ABBREVIATIONS

|          |   |
|----------|---|
| AFM      | : Atomic force microscopy   |
| AOC      | : Assimilable organic carbon  |
| ASW      | : Artificial seawater   |
| ATP      | : Adenosine tri-phosphate   |
| ATR-FTIR | : Attenuated total reflection–Fourier transform infrared spectroscopy |
| BB       | : Building blocks   |
| BCA      | : Bicinchoninic acid  |
| BDOC     | : Biodegradable dissolved organic carbon                              |
| BFR      | : Biofilm formation rate  |
| BOM      | : Biodegradable organic matter  |
| BP       | : Biopolymers   |
| BPP      | : Biomass production potential  |
| CDOC     | : Chromatographic dissolved organic carbon                            |
| CFF      | : Contact flocculation-filtration                                     |
| CFU      | : Colony forming unit   |
| CH       | : Carbohydrates   |
| CLSM     | : Confocal Laser Scanning Microscopy                                  |
| COD      | : Chemical oxygen demand  |
| DAPI     | : 4'-6-diamidino-2-phenylindole                                       |
| DBF      | : Deep bed filter   |
| DBPs     | : Disinfection by-products  |
| DI       | : De-ionized  |
| DO       | : Dissolved oxygen  |
| DOC      | : Dissolved organic carbon  |
| DON      | : Dissolved organic nitrogen  |
| EBCT     | : Empty bed contact time  |
| EDTA     | : Ethylene-diamine-tetra-acetic acid                                  |
| EDX      | : Energy dispersive spectroscopy                                      |
| EPS      | : Extracellular polymeric substance                                   |
| FEEM     | : Fluorescence excitation–emission matrix                             |
| FE-SEM   | : Field emission scanning electron microscope                         |
| FI       | : Fluorescence index  |

|          |  |
|----------|--|
| GAC      | : Granular activated carbon                      |
| HOC      | : Hydrophobic organic carbon                     |
| HPC      | : Heterotrophic plate count                      |
| HPI (HF) | : Hydrophilic                                    |
| HP-SEC   | : High pressure size exclusion chromatography    |
| HPO (HB) | : Hydrophobic                                    |
| HRT      | : Hydraulic retention time                       |
| HS       | : Humic substances                               |
| LC-OCD   | : Liquid chromatography-organic carbon detection |
| LMW      | : Low molecular weight                           |
| LN       | : Low molecular weight neutrals                  |
| MBR      | : Membrane bio-reactor                           |
| MF       | : Microfiltration                                |
| MLSS     | : Mixed liquor suspended solids                  |
| MTC      | : Normalized flux                                |
| MWCO     | : Molecular weight cut-off                       |
| MWD      | : Molecular weight distribution                  |
| NF       | : Nanofiltration                                 |
| NMR      | : Nuclear magnetic resonance                     |
| NOM      | : Natural organic matter                         |
| NPD      | : Normalized pressure drop                       |
| OM       | : Organic matter                                 |
| OUR      | : Oxygen uptake rate                             |
| PAC      | : Powder activated carbon                        |
| PBS      | : Phosphorus buffer solution                     |
| PCR      | : Polymerase chain reactions                     |
| PI       | : Propidium iodide                               |
| PN       | : Protein  |
| PS       | : Polysaccharides                                |
| PSS      | : Polystyrene sulfonates                         |
| PVDF     | : Polyvinylidene fluoride                        |
| PWP      | : Pure water permeability                        |
| Py-GC/MS | : Pyrolysis gas chromatography/mass spectrometry |
| RMSE     | : Root mean square error                         |

|        |   |
|--------|---|
| RO     | : Reverse osmosis   |
| SADm   | : Specific Aeration Demand                                |
| SDI    | : Silt density index                                      |
| SDS    | : Sodium dodecyl sulfate                                  |
| SEC    | : Size exclusion chromatography                           |
| SMAHS  | : Submerged membrane adsorption hybrid system             |
| SMCAHS | : Submerged membrane coagulation-adsorption hybrid system |
| SMCHS  | : Submerged membrane coagulation hybrid system            |
| SMABR  | : Submerged membrane adsorption bioreactor                |
| SMHSs  | : Submerged membrane hybrid systems                       |
| SMS    | : Submerged membrane system                               |
| SPE    | : Solid phase extraction                                  |
| SS     | : Suspended solids  |
| SUVA   | : Specific ultraviolet absorbance                         |
| SW     | : Seawater  |
| SWOM   | : Seawater organic matter                                 |
| SWRO   | : Seawater reverse osmosis                                |
| TDC    | : Total direct cell count                                 |
| TDS    | : Total dissolved solids                                  |
| TEP    | : Transparent exopolymer particles                        |
| TMP    | : Trans-membrane pressure                                 |
| TOC    | : Total organic carbon                                    |
| TPI    | : Transphilic   |
| TSS    | : Total suspended solids                                  |
| UF     | : Ultrafiltration   |
| UF-MFI | : Ultrafiltration-modified fouling index                  |
| UV     | : Ultraviolet   |
| VSS    | : Volatile suspended solids                               |
| XRD    | : X-ray diffraction                                       |

## LIST OF SYMBOLS

|                |  |
|----------------|--|
| $A_b$          | : Membrane area blocked by particles                                     |
| $A_m$          | : Initial membrane area  |
| $\alpha$       | : Complete blockage model constant                                       |
| $\beta$        | : Pore constriction model constant                                       |
| $b$            | : Constant (L/mg)  |
| $C_b$          | : Concentration of deposits in bulk phase                                |
| $C_e$          | : Equilibrium concentration of solute in the bulk of the solution (mg/L) |
| $C_{PAC}$      | : PAC concentration within the reactor (g/L)                             |
| $\gamma$       | : Cake formation model constant  |
| $d$            | : Internal diameter of the tube (cm)                                     |
| $\delta$       | : Pore length  |
| $\delta_{PAC}$ | : Age of PAC (d)   |
| $\Delta P(0)$  | : Initial trans-membrane pressure  |
| $\Delta P(t)$  | : Trans-membrane pressure  |
| $G$            | : Velocity gradient (/s)   |
| $g$            | : Gravitational acceleration (cm/s <sup>2</sup> )                        |
| $H$            | : Headloss through the flocculator (cm H <sub>2</sub> O)                 |
| $J/J_0$        | : Permeate flux decline  |
| $J_0$          | : Initial permeates flux (kPa)   |
| $J_c$          | : Critical flux  |
| $J(t)$         | : Operating permeate flux  |
| $J_w$          | : Water flux (L/m <sup>2</sup> h)  |
| $K_F$          | : Freundlich constant indicative of the adsorption capacity              |
| $k_H$          | : Ho rate constant for adsorption, function of temperature (g/mg. min)   |
| $m_d$          | : Deposited mass of foulants   |
| $m_{PAC}$      | : Mass of PAC in reactor (g)   |
| $n$            | : An experimental constant indicative of the adsorption intensity        |
| $N$            | : The number of pores on the membrane                                    |
| $N_0$          | : Initial cell concentration (Cells/L)                                   |
| $N_{max}$      | : Maximum cell concentration (Cells/L)                                   |
| $q$            | : The amount of adsorbate at equilibrium (mg/g)                          |
| $q_e$          | : The amount of solute adsorbed per gram of adsorbent (mg/g)             |

|             |  |
|-------------|--|
| $q_m$       | : Saturation amount of organic adsorbed (mg/g)           |
| $q_t$       | : The amount of adsorbate at any time $t$ , (mg/g)       |
| $Q$         | : Flow rate ( $\text{cm}^3/\text{s}$ )                   |
| $Q_R$       | : Replaced volume (L/d)                                  |
| $\rho_d$    | : Density of the deposit                                 |
| $R_c(t)$    | : Cake resistance  |
| $R_m$       | : Sum of the intrinsic membrane resistance               |
| $r_p$       | : Pore radius  |
| $r_{p,0}$   | : Pore radius before fouling                             |
| $R_t(0)$    | : Initial filtration resistance                          |
| $R_t(t)$    | : Total filtration resistance                            |
| $S_I - S_0$ | : Consumed substrate concentration ( $\mu\text{g-C/L}$ ) |
| $t$         | : Operating time   |
| $\mu$       | : Solution viscosity                                     |
| $V$         | : Volume ( $\text{cm}^3$ )                               |
| $V_r$       | : Reactor volume (L)                                     |
| $v$         | : Linear flow rate (cm/s)                                |
| $Y$         | : Growth yield (cells/ $\mu\text{gC-acetate}$ )          |

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## **CHAPTER 5**

### **MEMBRANE HYBRID SYSTEM AS PRETREATMENT TO SWRO; DETAILED CHARACTERIZATION OF EFFLUENT AND FOULANTS**

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## ABSTRACT

In this study, novel submerged low pressure membrane (microfiltration) systems coupled with physico-chemical treatment such as coagulation/flocculation or adsorption, termed in this study, as “submerged membrane hybrid systems (SMHS)” were investigated as pretreatment for seawater reverse osmosis (SWRO).

***Coagulation as pretreatment:*** In recent years, coagulation and subsequent media-filtration as well as low pressure membrane-based system such as microfiltration (MF) and ultrafiltration (UF) have been used as pretreatment methods for seawater reverse osmosis desalination. Coagulation can remove colloidal matters and dissolved organic compounds which cause irreversible membrane fouling. In this study, a commonly used ferric chloride ( $\text{FeCl}_3$ ) was used as coagulant for removing organic compounds from seawater. The coagulation by  $\text{FeCl}_3$  at optimum dosage removed a majority (95%) of hydrophobic compounds. In addition, the ultrafilter modified fouling index (UF-MFI) decreased considerably from  $15,848 \text{ s/L}^2$  with raw seawater to  $3,025 \text{ s/L}^2$  with seawater after coagulation. It was observed that critical flux was increased from  $20 \text{ L/m}^2\text{-h}$  in the conventional submerged membrane system to  $55 \text{ L/m}^2\text{-h}$  in submerged membrane coagulation hybrid system (SMCHS). The SMCHS led to a high DOC removal efficiency (more than 70%) while keeping the development of trans-membrane pressure (TMP) significantly lower than that of conventional submerged membrane system (SMS).

***Prediction of DOC removal by  $\text{FeCl}_3$  coagulation using mathematical modeling:*** Coagulation removes colloidal matters and dissolved organic carbon (DOC) which can cause irreversible membrane fouling. However, how DOC is removed by coagulant is not well-known. Jar test was used to study the removal of hydrophobic and hydrophilic

DOC fractions at various doses (0.5-8.0 mg-Fe<sup>+3</sup>/L) of FeCl<sub>3</sub> and pH (5-9). Natural organic matter (NOM) in seawater and treated seawater were fractionated by liquid chromatography-organic carbon detector (LC-OCD). Compared to surface water, the removal of DOC by coagulation was remarkably different. Majority of DOC could be easily removed with very low coagulant dose (<5.0 mg-Fe<sup>+3</sup>/L) and the removal efficiency did not significantly deteriorate with pH, but remaining DOC composition has changed. Hydrophobic fraction (HB) is better removed at high pH while hydrophilic fraction (HF) is better removed at low pH. A model which assumes that the removal occurs by adsorption of un-dissociated compounds onto ferric hydroxide was formulated and successfully validated against the jar test data.

The effect of flocculation on the performance of MF in SMCHS was also investigated with modified poly ferric silicate (PFSi- $\delta$ ). Both PFSi- $\delta$  and FeCl<sub>3</sub> were found to be suitable in removing organic compounds. The results show that PFSi- $\delta$  was better than FeCl<sub>3</sub> in terms of removing turbidity and DOC, particularly in removing hydrophilic compounds. It was observed that PFSi- $\delta$  (1.2 mg Fe<sup>3+</sup>/L) and FeCl<sub>3</sub> (3.0 mg Fe<sup>3+</sup>/L) led to an increase of critical flux from 20 L/m<sup>2</sup>·h to 35 L/m<sup>2</sup>·h and 55 L/m<sup>2</sup>·h, respectively.

The removal of different fractions of organic matter in seawater was investigated using titanium tetrachloride (TiCl<sub>4</sub>) as flocculant and compared with that of FeCl<sub>3</sub>. The hydrophobic compounds removal was predominant by both flocculants. However, the removal of hydrophilic organic compounds, such as humics and low-molecular weight neutral compounds of seawater was superior with TiCl<sub>4</sub> compared to FeCl<sub>3</sub>.

This study also investigated the effect of powder activated carbon (PAC) dosed in a submerged membrane adsorption hybrid system (SMAHS) in removing organic matter from seawater. The addition of PAC into submerged microfiltration reactor not only

improved critical flux from 20 L/m<sup>2</sup>.h to 40 L/m<sup>2</sup>.h but also helped reduce the TMP of the system. The analyses of organic matter fraction showed that PAC was able to remove most of hydrophobic compounds (more than 96%) and a significant amount of hydrophilic compounds (78%).

***Submerged membrane adsorption hybrid system with flocculation as pretreatment:***

Biofouling on RO membranes is the most serious problem which affects RO process efficiency and increases its operation cost. The biofouling cannot be effectively removed by the conventional pre-treatment traditionally used in desalination plants. SMS coupled with adsorption and/or coagulation can be a sustainable pre-treatment in reducing membrane fouling and at the same time improving the feed water quality to the seawater reverse osmosis. The addition of PAC of 1.5 g/L into SMAHS could help to remove significant amount of both hydrophobic compounds (81.4%) and hydrophilic compounds (73.3%). When this SMAHS was combined with FeCl<sub>3</sub> coagulation of 0.5 mg of Fe<sup>3+</sup>/L, dissolved organic carbon removal efficiency was excellent even with a lower dose of PAC (0.5 g/L). It should be noted that PAC addition was only at the start and no further PAC addition was made during experiment. The SMAHS and the submerged membrane coagulation–adsorption hybrid system (SMCAHS) can significantly remove the total bacteria which contain also live cells. As a result, microbial adenosine triphosphate (ATP) concentration in treated seawater and foulants was considerably decreased. These led to a significant reduction of assimilable organic carbon (AOC) during the initial stage of RO operation. In this study, AOC method was modified to measure the growth of bacteria in seawater by using the *Pseudomonas* P.60 strain.

***Application of fouling model in SMAHS:*** The application of three different membrane fouling models namely pore blockage, pore constriction, and cake formation models

showed that cake formation was the predominant fouling mechanisms causing fouling in SMHSs.

***Characterization of SMAHS effluent:*** Organic matter in seawater before and after pretreatment was characterized in terms of XAD fractionation, molecular weight distribution (MWD) and fluorescence. A detailed study on the seawater organic matter (SWOM) structure was made through  $^1\text{H}$ -nuclear magnetic resonance ( $^1\text{H}$ -NMR),pyrolysis-gas chromatography mass spectrometry (Py-GC/MS) and liquid chromatography mass spectrometry-ion trap-time of flight (LC/MS-IT-TOF). The three dimensional-fluorescence emission-excitation matrix (3D-FEEM) showed a removal of humic-like materials by SMHSs. In addition, a humic-like relative to protein-like compounds was reduced significantly but aromaticity of humic-like materials was increased. After pretreatment by SMHSs, humics and biopolymers of over 900 Da. were found to be reduced and their structure associated with element composition was also changed.

***RO membrane foulant characterization:*** The organic and biological foulants on RO membrane operated with seawater pretreated by SMHSs were characterized. Organic foulants on RO membrane were characterized in terms of MWD, fluorescence and extracellular polymeric substance (EPS) analyses. The organic foulants were mainly composed of high molecular weight matters representing biopolymers in the foulants. The 3D-FEEM analysis showed that protein-like materials were dominant with samples pretreated by SMHSs. Humic-like materials which have lower aromaticity were also present in the foulant. Biological foulants were investigated in terms of total direct cell (TDC) count, cell viability and biomass activity (in terms of ATP). Biological fouling was found to be reduced by organic removal with SMHSs. The fouled membranes were characterized using environmental SEM/EDX, attenuated total reflection-Fourier

transform infrared spectrometry, zeta-potential measurement, atomic force microscopy, and contact angle measurement.

**Development of a rapid AOC test:** One strategy to minimize biofouling is the pre-treatment of seawater prior to RO application. In this regard, there is a need for tools that can be used to assess the influent water which allows for the subsequent selection of the optimum pretreatment methods. One parameter that is directly linked to biofouling potential is the concentration of AOC in the feed-water, where high nutrient levels are associated with increased growth potential of the microbial fouling community. A rapid and accurate of AOC method was developed for marine (sea) waters. This method is based on quantifying the bioluminescence response of the marine bacterium *Vibrio fischeri* MJ-1. Compared to previous methods, this new *V. fischeri* method was rapid (within 1h), sensitive (detection limit=0.1 µg-C glucose equivalents/L) and highly suitable for seawater samples. *V. fischeri* method was evaluated using real seawater samples. The results showed positive reproductive AOC values. The new *V. fischeri* AOC method developed has a highly promising potential to be practically adopted as a rapid indicator of AOC concentration and hence biofouling potential of influent marine water.

**Submerged membrane adsorption bioreactor (SMABR)** as sustainable pretreatment was investigated. SMABR removed organic matter by adsorption and biological degradation. At a PAC residence time of 66 d (1.5% of daily PAC replacement), higher organic removal was achieved with a high removal of biopolymers, humics and hydrophobic organics. A continuous MBR operation with the optimal PAC residence time of 66 d was conducted and compared with MBR with no PAC replenishment in terms of the removal of organic and microbes. High removal of organics of up to 72% was maintained with only a marginal increment of trans-membrane pressure and stable

bioactivity (TDC and ATP) during the 50 d of operation. The SMABR was found to be a sustainable biological pretreatment to RO with only a small amount of PAC requirement (2.14 g of PAC/m<sup>3</sup> of seawater treated).

***Contact flocculation filtration as pretreatment:*** Deep bed filtration has traditionally been used as a pretreatment in seawater desalination. The performance of contact flocculation–filtration (CFF) as pretreatment of SWRO was evaluated in terms of pressure drop through the filter and removal of organics and turbidity. The performances of CFF were experimentally evaluated with different flocculant doses (0.5–3.0mg Fe<sup>3+</sup>/L) and rapid mixing times (1.7–14.4s). The headloss also significantly decreased when the flocculant dose was reduced from 3.0 to 0.5 mg Fe<sup>3+</sup>/L. However, the organic matter removal was lower at a lower dose of ferric chloride.

In this study, it was also investigated the potential of CFF acting as a biofilter in addition to its major function of flocculation and particle/floc separation. Two different media (sand; S-CFF and anthracite; A-CFF) were tested. Bacterial activity in the filter bed was assessed in terms of cell number, ATP measurement and microbial community over the filter run of 90 d. With the growth of an active microbial population on the filter bed medium, significant removal of organic compounds, especially low molecular weight (LMW) organics, from the seawater was achieved. It was found that CFF functions both as flocculation and separation unit and also as biofilter with moderate efficiency in reducing biofouling potential. A-CFF needed longer time to achieve bio-stabilization but it showed more effective biofiltration potential than S-CFF.