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Foulant analysis of a reverse osmosis membrane used pretreated seawater

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ABSTRACT

This study focused on the characterization of organic and biological foulants on reverse osmosis (RO) membrane and fouled RO membrane characterization with seawater pretreated by submerged membrane hybrid systems (SMHSs). New low pressure membrane based pretreatments namely submerged membrane coagulation hybrid system (SMCHS) and submerged membrane coagulation-adsorption hybrid system (SMCAHS) were investigated. Organic foulants on RO membrane were characterized in terms of molecular weight distribution (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 fluorescence excitation–emission matrix (F-EEM) 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 (adenosine tri-phosphate; ATP). Biological fouling was found to be reduced by organic removal with SMHSs. The fouled membranes were characterized using environmental scanning electron microscopy coupled with energy dispersive spectroscopy, attenuated total reflection-Fourier transform infrared spectrometry, zeta-potential measurement, atomic force microscopy, and contact angle measurement.

1. Introduction

Reverse osmosis (RO) is a leading and a fast growing technology in seawater desalination and is being used in a large number of desalination plants worldwide. In order to operate RO processes successfully, lasting supply of high quality feed water is significant. Poor quality feed water may lead in the decrease of RO desalination process efficiency and increase operation cost due to membrane fouling. Fouling is caused by organic matters (OM), inorganic matters, particulates and colloidal matters, and it affects the performance of RO process [1–3].

Inorganic scale can be easily alleviated by addition of antiscalants and acid prior to the SWRO process. However, organic fouling has more severe effect on RO membrane. It is caused by humics, fulvic acid, carboxylic acid and extracellular polymeric substances (EPS). It is also incorporated with biological growth which may build up to biofouling [4–7]. The key steps in biofouling on RO membrane are adsorption of organic matter to membrane surface, continuous adhesion of microorganisms, growth of adhered cells, and subsequent formation of biopolymer matrix. Thus organic and biofouling developments are mutually related. Even low concentrations of appropriate carbon sources can readily lead to substantial bacterial re-growth on membrane. Only few studies [8–10] showed simultaneous analysis of the OM foulant characterization and its effect on the microbial fouling on RO membrane. Further, the data available in the literature is limited to draw a conclusion on initial fouling development in terms of both organic and biological fouling.

The efforts to alleviate the organics which are more likely to absorb on the membrane surface have to be preceded. By doing that, the reduction of the bacteria growth potential could be also achieved simultaneously. In other words, in order to control the

Abbreviations: AFM, Atomic force microscopy; ATP, Adenosine tri-phosphate; ATR-FTIR, Attenuated total reflection–Fourier transform infrared spectroscopy; CH, Carbohydrate; DAPI, 4′-6-diamidino-2-phenylindole; CLSM, Confocal laser scanning microscope; DI, De-ionized; DOC, Dissolved organic carbon; DOM, Dissolved organic matter; EPS, Extracellular polymeric substances; F-EEM, Fluorescence excitation–emission matrix; FE-SEM, Field emission scanning electron microscope; HP-SEC, High pressure size exclusion chromatography; MF, Microfiltration; MWD, Molecular weight distribution; OM, Organic matters; PAC, Powder activated carbon; PI, Propidium iodide; PN, Protein; PVDF, Polyvinylidene fluoride; RO, Reverse osmosis; SEM/EDX, Scanning electron microscopy coupled with energy dispersive spectroscopy; SMCAHS, Submerged membrane coagulation adsorption hybrid system; SMCHS, Submerged membrane coagulation hybrid system; SMHSs, Submerged membrane hybrid systems; SW, Seawater; SWOM, Seawater organic matter; SWRO, Seawater reverse osmosis; TDC, Total direct cell; UF, Ultrafiltration

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bio-film development at the surface of the membrane, the pretreatment prior to the RO unit has to be carefully optimized to remove microbial cells and growth promoting compounds (nutrients and electron donors) from the feed water.

An increasing number of researchers nowadays apply the use of membrane based pretreatment to meet the expected quality of feed water [1,10,11]. Low-pressure membrane such as microfiltration (MF) and ultrafiltration (UF) are used. They can remove suspended solids, colloids and microorganisms effectively which result in higher RO flux, less fouling and chemical dose reduction. MF alone as a pretreatment cannot remove dissolved organic matter (DOM) in the seawater [12]. On the other hand, when MF is combined with adsorption and coagulation, DOM in the seawater can be removed. In addition, MF has a number of advantages such as low energy consumption and high flux operation when it is coupled with physico-chemical treatment such as adsorption and coagulation. Recently, our previous studies indicated that the small molecular species that are not usually rejected by the MF membrane alone could be absorbed by the powder activated carbon (PAC) and coagulated by the ferric chloride ($FeCl_3$) in the submerged membrane hybrid systems (SMHSs) [13,14]. However, details on the biofouling and its relationship with organic controls on RO membrane fouling at initial stage have not been studied and reported. In seawater RO (SWRO) process, even though the organic concentration is very low (1–3 mg of dissolved organic carbon/L), it still causes severe RO fouling and expects to influence on the initial biofouling. This study deals with the characterization of foulants on a new type of low pressure membrane hybrid system namely the submerged membrane coagulation and adsorption hybrid system as a pretreatment to seawater reverse osmosis, has not been studied in detail. In this study, the effect of membrane hybrid system on the removal of organic foulants was studied in detail.

Membrane foulant characterization (on the fouled RO membrane) is one of the most effective approaches to evaluate the pretreatment and to investigate the fouling behavior on RO membrane [15]. Further, it helps to determine suitable process for pretreatment to control the fouling. The physico-chemical characteristics of organic foulants such as molecular weight distribution (MWD), EPS and fluorescence analysis provide valuable information to understand the complex interactions of organics that occur in the RO membrane. The seawater organic foulants analysis is not straight forward. Only a few recent studies have suggested specific methods to measure the organic foulants [16]. This present study gives the quantitative values of specific groups of organics and detailed information on foulant characterization. This information is essential to assess the initial organic and biofouling. There are also a number of simple microbial methods to identify and measure biofoulants, and the following methods have been used for RO membrane processes: total direct cell (cell/mL or cell/cm^2) and live/dead cells (cell viability). The measurement of adenosine triphosphate (ATP) has also been proposed as an indicator of biomass content on the fouled RO membrane, since ATP is a bimolecule which exists in all living cells. Only a handful reference is available on the fouling analyses especially for seawater [17]. Also, these analyses were not made for the pretreatment system used in this study.

The experimental protocols adopted, provides the practical information on foulants and useful information on organic and biofouling.

In this study, two submerged membrane hybrid systems (SMHSs), namely (i) submerged membrane coagulation hybrid system (SMCHS) and (ii) submerged membrane coagulation adsorption hybrid system (SMCAHS) were used as pretreatment. The effect of pretreatment on the performance of a RO unit was evaluated through the analyses of the fouled RO membrane. Detailed investigations on organic and biological foulant were made using representative analytical methods.

2. Materials and methods

2.1. Seawater sample

The seawater used in this study was collected from Kijang, Busan, South Korea. It was taken from 7 m below sea level and filtered through the centrifuge filtration system to remove the large particles. The dissolved organic carbon (DOC) value of collected seawater was 2.40 ± 0.05 mg/L. The total number of bacterial cells in the untreated seawater was $5.1 \pm 1.3 \times 10^6$ cells/mL. After sampling, it was kept refrigerated at 4.0 °C before utilizing as feed water for the RO test unit.

2.2. Pretreatment method

In this study, SMHSs were used as pretreatment methods to RO. The effect of SMHSs was assessed in terms of the fouling performance and behavior on RO membrane. Untreated seawater (raw SW—prefiltered by 0.45 μm to minimize the effect of particulates in raw seawater) and seawater pretreated with SMHSs (at predetermined conditions) were used as the feed solutions for the RO membrane test unit. In the SMHSs setup, submerged-type of hollow fiber MF membranes (Cleanfil®-S, Polysulfone, Polyethersulfone, Polyvinylidene fluoride (PVDF) of 0.1 μm, Kolon, Korea) were used. The combined effective surface area of MF was 0.1 m^2. The SMHSs were operated at constant permeate flux mode of 20 L/m^2 h (LMH). The filtered seawater through SMHSs was used as feed solution in a RO membrane test unit (Fig. 1). Ferric chloride ($FeCl_3$) and powdered activated carbon (PAC, MD3545WB powder, wood based) were used as a coagulant and an adsorbent respectively in the SMHSs. A high concentration $FeCl_3$ of 3.0 mg Fe^{+3}/L dose was used for the SMCHS while a lower concentration of 1.0 mg Fe^{+3}/L dose was used for the SMCAHS. In addition to the coagulation, 0.5 g/L of PAC was dosed at the initial in the SMCAHS. The details on the adsorbent and the membrane set-up are also given elsewhere [14].

2.3. RO fouling test

A flat sheet polyacrylamide RO membrane (Woongjin chemical, Korea) having an effective area of 140 cm^2 was used. It was soaked in de-ionized (DI) water at 4.0 °C for 24 h prior to use. The test set-up (part no. 1142819, GE Osmonics) comprises of a spacer connected to a 10 L feed-tank with a feed-water volume capacity of 7 L. Fouling tests were conducted at constant flux mode (at a pressure of 5.5 MPa and crossflow velocity of 1.2 L/min at 25 °C). Both permeate and retentate were circulated back to the feed reservoir to enhance the bacterial growth during the short periods of batch test conducted (Fig. 1).

The RO test unit (without membrane) was disinfected before each experiment. Before inserting the RO membrane, the RO unit was disinfected and thoroughly cleaned to remove trace organic impurities using the following procedure: (i) recirculation of 0.5% sodium hypochlorite for 2 h, (ii) cleaning trace organic matter by recirculation of 5 mM ethylene di-amine tetra-acetic acid (EDTA) at pH 11 for 30 min, (iii) additional cleaning of trace organic matter by recirculation of 2 mM sodium dodecyl sulfate (SDS) at pH 11 for 30 min, (iv) sterilizing the unit by recirculation of 95% ethanol for 1 h, and (v) rinsing the unit several times with DI water to eliminate ethanol residues. The RO membrane then went through compaction with DI water at a pressure of 3.5 MPa after