A detailed organic matter characterization of pretreated seawater using low pressure microfiltration hybrid systems

Sanghyun Jeong [a], Sung-Jo Kim [b], Chang Min Kim [b], Saravanamuthu Vigneswaran [a,*], Tien Vinh Nguyen [a], Ho-Kyong Shon [a], Jaya Kandasamy [a], In S. Kim [b]

[a] Faculty of Engineering and IT, University of Technology, Sydney (UTS), PO Box 123, Broadway, NSW 2007, Australia
[b] School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 261 Oryong-dong, Buk-gu, Gwangju 500–712, Republic of Korea

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ABSTRACT

In this study, two different submerged membrane hybrid systems (SMHSs) namely (i) submerged membrane coagulation hybrid system (SMCHS) and (ii) submerged membrane coagulation-adsorption hybrid system (SMCAHS) were investigated as pretreatment options for seawater reverse osmosis. Organic matters in seawater before and after pretreatment were 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}H-nuclear magnetic resonance (^{1}H NMR), pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS) and liquid chromatography–mass spectrometry-ion trap-time of fright (LC/MS-IT-TOF). The seawater investigated in this study is mainly composed of hydrophilic matter ($57 \pm 3.2\%$). SMHSs removed a significant amount of organic matter. The EEM fluorescence showed a removal of humic-like materials by SMHSs. In addition, humic-like materials relative to protein-like compounds were reduced significantly but the aromaticity of humic-like materials 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. The transformation of the SWOM structure after SMHSs pretreatment may have been due to hydrolyzation or oxidization of the organic compounds such as humics and biopolymers resulting in poly-conjugation to aromatic compounds. SMHSs were effective in improving the RO performance leading to higher RO permeate flux and lower permeate flux decline. The pretreatment reduced the amount of foulants on the RO membrane.

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1. Introduction

In seawater desalination, reverse osmosis (RO) is a leading and a rapidly growing technique with the large number of RO plants in operation worldwide [1]. For a successful RO desalination operation, consistent high quality feed water is important. A poor quality of feed water may shorten the RO membrane operation period and increase maintenance cost. Thus, it is essential to remove or reduce undesirable materials in raw seawater to acceptable levels prior to feeding into RO.

In particular, organic matter (OM) plays a crucial role in formation of RO foulant. Organic fouling is generally acknowledged as a serious problem for membrane processes and limits the widespread use of the membranes [2]. Organic foulants are the precursor to biological growth which progresses to biofouling. Membrane technologies successfully remove particulates and micro-organisms as well as OM from water. Among them, low pressure membrane filtration systems (microfiltration; MF and ultrafiltration; UF) have been widely applied in water treatment. They have a number of advantages over conventional water treatment processes including superior and consistent product water with fewer requirements for chemical and space [3,4]. Moreover, they have the ability to integrate with other physico-chemical technologies such as coagulation/flocculation, and adsorption.

Membrane hybrid systems coupled with physico-chemical processes (coagulation and adsorption) have been recently used

as a pretreatment to seawater reverse osmosis (SWRO). They showed effective alleviation of organic fouling [5]. Our previous results 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 $FeCl_3$ in the submerged membrane hybrid systems (SMHSs) [6,7]. The pretreatment by MF alone removed only 17% of dissolved organic carbon (DOC) and it was not effective in removing hydrophilic organic matter. The submerged membrane coagulation hybrid system (SMCHS), on the other hand, could remove a majority of hydrophobic fraction (95%) of DOC coupled with 3.0 mg of Fe^{+3}/L. SMCAHS (a combination of SMCHS with 1.5 g/L of PAC adsorption) led to remarkable improvement of the hydrophilic compounds removal from seawater (85%). Interestingly, building blocks that were not removed by coagulation with $FeCl_3$ were removed by SMCAHS [8].

Seawater organic matter (SWOM) is removed effectively by membrane hybrid systems; however, only limited information is available on specific properties of SWOM in pretreated water by membrane hybrid systems. Dissolved organic matter (DOM) which is ubiquitous in seawater is a mixture of compounds including humic substances, carbohydrates, proteins and a variety of acidic and lower molecular weight species [9]. Different sophisticated analytical methods have been used during the last few decades to gain insight into the compositions of SWOM. The characteristics of organic matter in seawater are different from those of wastewater or surface water. This study deals with detailed organic characterization of pretreated seawater by SMHSs using qualitative and quantitative approaches including structural studies. It, to our knowledge, has not been studied yet. Our recent studies [6,7] investigated the low pressure membrane hybrid systems based on MF. They have a number of advantages such as low energy consumption and high flux operation when MF is incorporated with physico-chemical treatment such as adsorption and coagulation. However, detailed organic characterization and its relationship with RO performance have not been studied. In SWRO process, eventhough the organic concentration is very low (1–3 mg of dissolved organic carbon/L), it still causes severe RO fouling. In this study, the effect of membrane hybrid system on the removal of organics (which can influence on RO fouling) was studied in detail. This study is also helpful in that it can be used to optimize and select the pretreatment by monitoring carefully the effectiveness of the pretreatment process.

Since the early 1990s, fluorescence techniques (excitation–emission matrix, EEM) have been used to study the nature of seawater, drinking water and sewage [10,11]. The prominent advantage of EEM fluorescence spectroscopy is that information regarding the fluorescence characteristics can be completely obtained by changing the excitation and emission wavelength simultaneously. Since DOM includes organic molecules with chromophoric (light absorbing) and fluorophoric (light emitting) moieties, EEM fluorescence spectroscopy is very useful for studying the physico-chemical characteristics of SWOM [12,13].

In addition, if data on the structural features of SWOM are also available, one can understand the pretreatment process in a better manner. For molecular and structural analysis, adequate extraction, isolation and separation techniques are important. Nuclear magnetic resonance (NMR) spectroscopy such as proton nuclear magnetic resonance (^{1}H NMR) has been used for decades to study the functional groups in SWOM [15,16]. The NMR technique is especially useful in combination with elemental composition, apparent molecular weight or infra-red spectroscopic data of identified SWOM. A recent innovation to the OM structure research is the introduction of high resolution liquid chromatography/mass spectrometry (LC/MS). LC/MS such as quadrupole-time of flight and ion trap-time of flight is a technique that combines the physical separation capabilities of LC with the mass analysis capabilities of MS [17,18]. The possibility of coupling the LC to an advanced technique called electrospray ionization (ESI) with MS makes the requirement for derivatization of OM unnecessary. The ESI-MS is a better and more sensitive method in the characterization of OM. For structural analysis using pyrolysis, macromolecules in SWOM are thermally broken down into more analytically available fragments. Pyrolysis combined with gas chromatography/mass spectroscopy (Py-GC/MS) is useful technique to obtain structural information about molecular building blocks of SWOM [19,20]. As a result, the structural study of the pyrolysates can be of great importance.

The overall aim of this study is to characterize SWOM before and after pretreatment by SMHSs though advanced analytical techniques. In this study, different fractions and molecular weight distribution (MWD) of SWOM were measured by using XAD resin, fluorescence spectroscopic and size exclusion methods. After proper SWOM isolation from salt, structure of SWOM was determined by using ^{1}H NMR, LC/MS-IT-TOF and Py-GC/MS. The results obtained from the characterization by different advanced analysis techniques can provide additional useful information and help in selecting suitable pretreatment methods.

2. Material and methods

2.1. Seawater

Seawater used in this study was drawn from Kijang, Busan, South Korea. It was filtered through the centrifuge filtration system to remove the large particles. The turbidity, pH and dissolved organic carbon (DOC) values of the seawater used in this study were 0.99 NTU, 8.13 and 2.38 mg/L respectively.

2.2. Submerged membrane hybrid systems

In this study, two submerged membrane hybrid systems (SMHSs) were used as pretreatment (Fig. 1). In the submerged membrane coagulation hybrid system (SMCHS), $FeCl_3$ at a concentration of 3.0 mg of Fe^{+3}/L was added in the submerged membrane reactor. In SMCAHS system, both ferric chloride ($FeCl_3$) (at a lower concentration of 1.0 mg of Fe^{+3}/L) and PAC (at a dose of 0.5 g/L) were added. The chemical doses were optimized through previous researches [6,7]. Ferric chloride ($FeCl_3$)·$6H_2O$ was used as coagulant and powdered activated carbon (PAC, MD3545WB powder, wood based) was used as adsorbent in the SMHSs. The detailed characteristics of PAC can be found elsewhere [7]. The MF membrane used in this study was a hollow fiber membrane (Cleanfil®-S, polysulfone, polyethersulfone, Poly-vinylidene fluoride (PVDF) of 0.1 μm, Kolon, Korea) with a
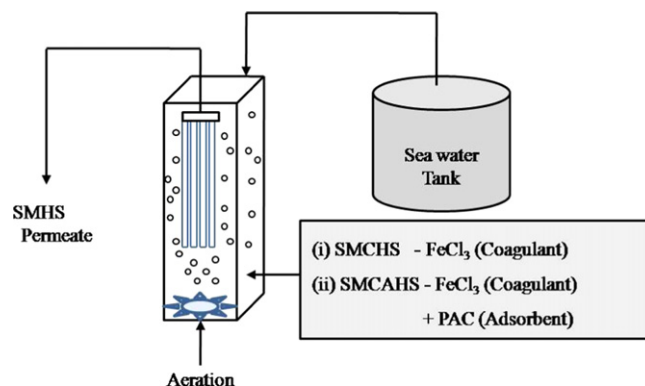
Fig. 1. Flow diagram of SMHSs (SMCHS, submerged membrane coagulation hybrid systems; SMCAHS, submerged membrane coagulation-adsorption hybrid system).