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Dynamic membrane filtration using powdered iron oxide for SWRO pre-treatment during red tide event

Byeong-Cheol Kim, Jong-Woo Nam, Ki-Hoon Kang*

Technology R & D Institute, Daelim Industrial Co., Ltd., Yulgok-ro-2-gil 25, Jongro-gu, Seoul 110-140, Republic of Korea

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ABSTRACT

Shut-down or reduced treated water supply of a seawater reverse osmosis (SWRO) plant due to membrane fouling during a red tide event is currently an important issue in regions where red tide frequently occurs. Algal organic matter (AOM) released by algae through metabolic activity is known as a major membrane foulant and the primary cause of the suspension of SWRO plants. In this study, iron oxide was utilized to develop an AOM removal process in seawater since activated carbon and advanced oxidation process (AOP) have limited removal efficiencies due to the high ionic strength of the seawater. Dynamic membrane filtration was applied as an iron oxide application method because additional process is not required for temporary operation during only algal bloom. The results showed that the dissolved organic carbon (DOC) removal efficiencies of the iron oxide were improved at high ionic strength compared to organics removal in fresh water. Although only a partial adsorption rate (below 50%) was achieved using iron oxide, significant reduction of the ultrafiltration (UF) membrane fouling was observed through the continuous operation of dynamic membrane filtration since relatively high molecular weight faction of organics was more readily adsorbed in the oxide surface. Given the continuous lab-scale experimental results and economic aspect, dynamic membrane filtration using powdered iron oxide can be a potential option as an emergency plan during a red tide event.

1. Introduction

Red tide is currently an important issue in the seawater reverse osmosis (SWRO) industry since it has forced the reduction or shut-down of the operations of several SWRO plants [1,2]. During a red tide event, membrane fouling becomes more severe due to the increased organic concentration by algae-derived substances, known as algal organic matter (AOM) [2–4]. About 300 algal species have been reported from seawater during red tide event, and marine algal blooms take place with various cell concentrations depending on the algal species [2,5]. Many previous studies have reported that AOM is the main cause of membrane fouling rather than the algal cells [2–4]. AOM consists of 60–70% of bio-polymer (50–60% of polysaccharides and 10–20% of protein) and 30–40% of low molecular weight organic matter [6,7]. Of the various forms of AOM, high molecular weight bio-polymers cause serious microfiltration (MF), ultrafiltration (UF), and reverse osmosis (RO) membrane fouling [4,8,9]. Particularly, serious fouling in the pretreatment process by AOM leads to frequent chemical cleaning and shortage of RO influent water.

The importance of the application of the dissolved air flotation (DAF) (which is shown to effect the high removal efficiency of algal cells without cell destruction, and thus intercellular organic matter (IOM) is not released) has been gradually increased to deal with the red tide problem [1,10]. However, since organic removal efficiency by DAF through the coagulant injection (~30%) is insufficient [11,12] during severe algal bloom, the remaining organics bring about MF/UF fouling which is a subsequent process in the SWRO system.

Recently, low pressure membrane filtration has been increasingly applied as a SWRO pretreatment since it can guarantee a low silt density index (SDI) of the treated water. AOM results in a significant increase of transmembrane pressure (TMP). AOM strongly adheres to the MF/UF membrane surface and does not easily detach by hydraulic backwashing due to its sticky characteristics. Also, the relatively low molecular weight fractions of the AOM, which allow it to pass through the MF/UF membrane pore, possibly also cause RO membrane fouling. Organics are known as a major contributor to RO membrane fouling, although the concentration of organic matter in seawater is relatively low (below 2 mg/L) [1,8,10].

Many processes generally used for organics removal in fresh water such as activated carbon adsorption and advanced oxidation processes (AOP) are not suitable for organics removal in seawater due to the extremely high ionic strength of seawater. Activated carbon has only

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* Corresponding author.
E-mail address: khkang@daelim.co.kr (K.-H. Kang).

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limited organic removal efficiency in seawater due to inhibition by several ions [13] and the fouling reduction effect is not significant when removing only low molecular weight organics [14–16]. AOP is also not efficient because generated $OH^{\cdot}$ through various types of AOP operations is consumed by the reaction with chorine ions (scavenging effect) [17].

As an alternative process, iron oxide is a natural adsorbent and its organic adsorption ability has been proven for some time [18,19]. The adsorption reaction mechanisms between the iron oxide surface and the organic matter are known as a surface complexation-ligand exchange reaction, hydrophobic interaction, entropic effect, hydrogen bonding, and cation bridging [18–21]. The maximum possible amount of adsorbed organic matter on an iron oxide surface increases with the increasing ionic strength of the solution due to the screening effect of the electrostatic interaction, in contrast to activated carbon [20,22,23].

Iron oxide can be applied in many different ways. The column type process using granular iron oxide has the advantages of easy separation and regeneration [24]. For the practical application, however, granular iron oxide has a relatively low organic removal efficiency due to the lower surface area and rapid reaching of the breakthrough point, which results in frequent regeneration. Also, in terms of economic aspects, the increase of capital expenditure (CAPEX) should be minimized for the development of the process that operates temporarily during only algal bloom periods. From this point of view, a column type process requires a greater footprint and more backwashing/regeneration equipment. On the other hand, dynamic membrane filtration using powdered iron oxide can be a viable option as an emergency plan during a red tide event in a SWRO plant since it does not require an additional lengthy process for organic removal and is relatively inexpensive as it is a natural occurrence. For dynamic membrane filtration, a cake layer is directly formed onto the MF/UF membrane surface to protect the membrane by preventing foulants from accessing the membrane surface.

In this study, analysis of the effects of ionic strength on the adsorption ability of the iron oxide, molecular weight distribution, and Fourier-transform infrared spectroscopy (FT-IR) before and after iron oxide adsorption was carried out to investigate the properties of the adsorption reaction at the seawater condition between the iron oxide surface and organics. In addition, the lab-scale continuous operation of dynamic membrane filtration using powdered iron oxide as one of the proposed operational methods during algal bloom was evaluated in terms of fouling trends and organic removal efficiency.

2. Experiments

2.1. Batch test for analysis of the effect of ionic strength on organic removal by iron oxide

As a reference AOM material, sodium alginate was purchased (99%, Sigma-Aldrich, USA) and used in this study. Sodium alginate is a linear polysaccharide consisting of α-L-guluronic acid (G-block) and 1,4-linked β-D-mannuronic acid (M-block) as shown in Fig. 1. It is refined from brown algae and is widely used as a model biopolymer. Alginate molecules with divalent ions such as Ca^{2+} and Sr^{2+} are able to be complexed by cross-linking, which results in the formation of alginate gel. To prevent this effect, 35 g/L of pure sodium chloride (99.9%, Sigma Aldrich) was used as artificial seawater (NaCl-ASW) since monovalent cations such as Na^+, K^+, and Mg^{2+} do not induce alginate gel formation. Goethite (Sigma-Aldrich, USA) was also purchased and used as a natural iron oxide adsorbent.

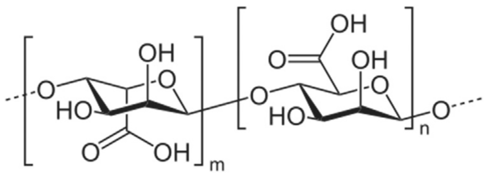

Fig. 1. Molecular structure of the alginate used as a reference AOM material.

In order to investigate the effects of ionic strength on organics adsorption, 100 mL of sodium alginate standard solution (12 mg/L as DOC) was prepared with deionized (DI) water and NaCl-ASW. The solution was placed in 150-mL serum bottles with various iron oxide loadings (0.5–5.0*g*/L). The bottles were mounted on an end-over-end rotary shaker at 50 rpm, and periodic samples were taken (10, 20, 30, 60, 120, and 180 min) from the bottles. Samples were filtered using a 0.45 µm syringe filter for DOC analysis (TOC-L_{CPH} Shimadzu, Kyoto, Japan). DOC was measured using 680 ℃ catalytically-aided combustion and non-dispersive infrared detection (NDIR).

2.2. Analysis molecular weight distribution and FT-IR before and after iron oxide adsorption

Molecular weight distribution analysis before and after iron oxide adsorption was investigated using NaCl-ASW with alginate (6.7 mg/L) and real seawater sampled in Geoje-si, South Korea. Analysis via size exclusion chromatography (SEC) is problematic as the seawater sample is diluted by mixing with DI water or eluents during analysis [25,26], resulting in a change in the physical structure of organic matter due to varying ionic strength. Therefore, in this study, molecular size distributions of the dissolved organic matter in NaCl-ASW and real seawater were determined using membranes with various pore sizes (10, 50, 100, and 300 kDa) in stirred cells to investigate the actual ionic strength state of seawater. The relative fraction was calculated by measuring the organic matter concentration in each filtered solution. Also, to investigate the molecular weight distribution after adsorption, 2 g/L of the goethite was mixed with each sample, with 1 min rapid mixing (200 rpm) and 30 min slow mixing (60 rpm). The molecular weight distribution of the supernatant which is separated by centrifugation (3,400*g*, 30 min) was analyzed using the same method.

FT-IR analysis (Vertex 70, Bruker) was conducted for 3 samples, virgin iron oxide, organic adsorbed iron oxide, and sodium alginate powder, all of which were purchased from Sigma-Aldrich. The organic adsorbed iron oxide sample was prepared using NaCl-ASW with alginate (10 mg/L) and goethite (2 g/L). After adsorption of 1 h reaction time, goethite was centrifuged and washed with DI water three times and then freeze-dried for FT-IR analysis.

2.3. Dynamic membrane filtration system

The dynamic membrane filtration system using powdered iron oxide utilized in this study is shown in Fig. 2. Two membrane units were simultaneously operated to compare the membrane fouling trend with and without iron oxide addition. A model of the new outside-in type pressurized hollow fiber membrane was used in the two units. The model was made of polyvinylidene fluoride (PVDF) and has a nominal pore size of 0.1 µm with an effective surface area of 0.1 m^2. Artificial seawater for normal seawater condition was prepared using 35 g/L bay salt (Bay-ASW), which has a similar composition as that of real seawater, in a 2 m^3 feed tank. The DOC of the artificial seawater was 1.3–1.5 mg/L. However, the artificial seawater during the red tide event was simulated using 35 g/L of pure sodium chloride (99.9%, NaCl-ASW) with alginate to prevent the decrease of raw water DOC by settlement of alginate after reaction with divalent ions. The DOC was adjusted to 5.5 ± 0.1 mg/L. The feed solution was agitated to allow sufficient time before membrane operation. Prepared raw water was pumped using an adsorption reactor with a level switch control, and the hydraulic retention time (HRT) was maintained to 30 min at room temperature (20 ± 2 °C). Bulk powdered iron oxide (Goethite) purchased from Ewic (Korea), which has a specific surface area of 37.5 m^2/g through Brunauer–Emmett–Telle (BET) measurement and a particle size range of 3–20 µm analyzed by a particle image analyzer (flowCAM