Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Selective removal of multivalent ions from seawater by bioelectrochemical system

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HIGHLIGHTS

• Ca^{2+} and Mg^{2+} in seawater can be removed using a bioelectrochemical system.

• External energy input and alkali addition are not required to remove Ca²⁺ and Mg²⁺.

• Wastewater treatment is also possible during removal of Ca²⁺ and Mg²⁺.

ARTICLE INFO

Article history: Received 28 July 2014 Received in revised form 30 November 2014 Accepted 18 December 2014 Available online xxxx

Keywords: Bioelectrochemical cell Calcium Magnesium Precipitation Seawater Wastewater

ABSTRACT

Energy and cost effective pretreatment of seawater is essential for any desalination plant to convert seawater into clean water successfully. This study shows a way to pretreat seawater without excessive input of electrical energy or high pressure; it uses a bioelectrochemical cell with two chambers, divided by an anion exchange membrane (AEM). When bacteria attached on the anode produce current using organic matter as a source of fuel, hydroxyl ions can be generated in the cathode chamber, which can increase the alkalinity of the catholyte (seawater); scale-forming ions such as Ca^{2+} and Mg^{2+} in seawater can be removed by forming precipitates in the cathode chamber. Our results show that 84% of Ca^{2+} and 37% of Mg^{2+} in seawater can be effectively removed while treating wastewater in the anode chamber. These results indicate a new method to pretreat seawater without external energy input since the cell accomplishes selective removal of divalent cations using an electrochemical cathode reaction. This study provides evidence that this new method can be a viable option for membrane based seawater pretreatment and desalination processes to significantly mitigate scale problems of membranes. @ 2014 Elsevier B.V. All rights reserved.

1. Introduction

It is essential to use pretreatment prior to seawater desalination and, in particular, seawater pretreatment is a key component of membrane desalination plants, such as reverse osmosis (RO) plants, because reducing membrane fouling is critical to the reduction of maintenance and operational costs. The main purpose of the pretreatment system is to remove particulate, colloidal, organic, mineral, and microbiological contaminants contained in seawater and to prevent their accumulation in the downstream seawater reverse osmosis (SWRO) process [1].

Traditionally, seawater foulants are removed using a series of source water conditioning processes (coagulation, flocculation, and pH adjustment) followed by conventional dual media filtration (DMF). Over the past 10 years, advances in microfiltration (MF) and ultrafiltration (UF) membrane technologies, and their successful application for water and wastewater treatment, have created an impetus for using membrane pretreatment in seawater desalination plants [1–3]. However,

* Corresponding author. *E-mail address: jynam@kier.re.kr* (J.-Y. Nam). suspended solids, particles, turbidity, microorganisms, and some natural organic matter (NOM) from seawater but cannot remove scaleforming ions such as calcium, magnesium, and sulfate: alkali must be added to form precipitates with calcium and magnesium [4,5]. Nanofiltration (NF) membranes can remove low molecular weight organic substances and the major portion of scale-forming ions, so that lower fouling water can be fed directly to the RO [6,7]. However, a delicate problem concerning the performance of NF membrane technology for seawater pretreatment is the serious inorganic fouling of membranes, which leads to an increase of the hydraulic resistance, a reduction of the recovery factor, and flux; thus, it is essential that inorganic fouling be preferentially paid attention to when membrane technology is used for seawater pretreatment prior to seawater desalination [8]. Therefore, scale-forming ions should be eliminated before seawater pretreatment and desalination steps to prevent inorganic fouling on membranes, which can have many negative cost impacts on UF/MF, NF, and RO plants.

these low-pressure membrane pretreatment systems can remove

We propose here a new type of seawater pretreatment method to selectively remove scale-forming ions without addition of electrical









Fig. 1. Schematic diagram of a bioelectrochemical cell for removal of divalent cations in seawater.

energy input. Selective calcium and magnesium removal can be implemented using a bioelectrochemical cell (BEC) that consists of two chambers with an anion exchange membrane (AEM) between the anode and the cathode chambers. In the anode chamber, microorganisms convert organic matter into electrical current and the electrons and protons catalytically combine by reducing oxygen to water at the cathode. Proton consumption at the cathode increases pH at the cathode surface and could induce calcium and magnesium precipitations through the reactions below (Fig. 1).

$$Ca^{2+} + HCO_3^{-} + OH^{-} \rightarrow CaCO_3 \downarrow + H_2O$$
⁽¹⁾

$$Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_{2}\downarrow$$
 (2)

Increased pH at the cathode surfaces in BECs has been used for different purposes such as struvite formation [9,10] but calcium and magnesium removal from seawater in BEC have not been explored before. Therefore, the objectives of this study were to show that calcium and magnesium could be precipitated by alkali production from the cathode in BEC without electrical energy input. Using this BEC, it is demonstrated that it is possible to achieve high calcium and magnesium removal during a single batch cycle; this process can be further applicable as a seawater pretreatment method for membrane based processes.

2. Material and methods

2.1. Reactor set up

Cube-shaped chambers (3 cm diameter inner chamber, 4 cm in length) were made of polycarbonate and the anode chamber (wastewater treatment chamber) contained a graphite fiber brush anode (25 mm diameter × 25 cm length, Mill-Rose, Mentor, OH); an air-cathode in the cathode chamber (seawater pretreatment chamber) was made using wet proofed carbon cloth (Type B, E-Tek, USA) coated with a platinum catalyst layer (5 mg Pt/cm² 10% Pt on Vulcan XC 71 with 33.3 μ L/cm² of 5% Nafion solution as binder, projected cross sectional area of 7 cm²). The air side of the cathode had 4 diffusion layers of polytetrafluoroethylene (PTFE) coating to allow oxygen diffusion to the catalyst and to prevent water leakage [11]. The anode and the cathode chambers were separated by an AEM (Selemion AMV, Asahi glass, Japan).

2.2. Experiments and measurements

The anode was inoculated with activated sludge taken from a wastewater treatment plant in Jeju City, South Korea. The anode chamber was supplied with a solution containing 1.5 g/L sodium acetate and a 50 mM phosphate buffer solution (PBS) to provide some buffering capacity in the anolyte solution. PBS contained 4.58 g/L Na₂HPO₄, and 2.45 g/L NaH₂PO₄·H₂O (pH = 7.04), 0.31 g/L NH₄Cl, 0.13 g/L KCl, and trace vitamins and minerals [12]. During inoculation, 100 mM PBS was used as a catholyte; then, the catholyte was shifted to artificial seawater. The artificial seawater contained 24.53 g/L NaCl, 11.11 g/L MgCl₂·6H₂O, 4.09 g/L



Fig. 2. (a) Current generation and (b) electrode potentials at 1 k Ω of external resistance.

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