Effect of coexisting metal ions on the degradation of polyamide reverse osmosis membrane by hypochlorite treatment

CrossMark

Masaki Ohno [a],*, Cervinia Manalo [b], Laura Rossetto [b], Tetsuji Okuda [a], Satoshi Nakai [b], Wataru Nishijima [a]

[a] Environmental Research and Management Center, Hiroshima University, 1-5-3 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8513, Japan
[b] Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

HIGHLIGHTS

- Hypochlorous acid with metal ions accelerated polyamide (PA) membrane degradation.
- The PA membrane degradation was accelerated by divalent ions in low concentrations.
- The Na^+ has a threshold limit on the acceleration of PA membrane degradation.
- The acceleration of PA membrane degradation was based on metal ion concentrations.
- The divalent ion possibly acts as a catalyst and accelerates amide hydrolysis.

ABSTRACT

Accelerating effect of coexisting metal ions on the polyamide (PA) reverse osmosis membrane degradation by hypochlorite was evaluated. The acceleration mechanism by the metal ions was also examined. The acceleration of membrane degradation by hypochlorite was caused by all monovalent and divalent metal ions used in this study: Na^+, K^+, Ca^{2+}, Mg^{2+}, and Ba^{2+}. Potency of divalent metal ions in PA membrane degradation was shown since divalent ions in much lower concentration than the monovalent metal ions caused membrane degradation. Na^+ did not accelerate the degradation of the PA membrane in concentrations less than 100 mM while Mg^{2+} and Ca^{2+} showed no threshold limits. Accelerated membrane degradation in the presence of both monovalent and divalent metal ions seemed to be influenced by the threshold limit of the monovalent ion within the concentration range of each of the ions present. Membrane degradation below the threshold limit is dominated by the divalent ion while above the threshold limit the monovalent ion dominated the degradation. The degradation mechanism of PA membranes with or without metal ions is the same. However, in the presence of the divalent ion, it possibly acts as a catalyst in the amide hydrolysis, leading to accelerated membrane degradation.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Increased population, industrial expansion, tourism, and agriculture development have triggered an increase in water demand such that many water-stressed or arid regions or countries are supplementing their water supply with desalinated water [1]. The total global desalination capacity is around 66.4 million $m^3\ d^{-1}$ in 2012, and is expected to reach about 100 million $m^3\ d^{-1}$ by 2015 [2]. Moreover, the global needs for water are expected to reach 6900 billion m^3 by the year 2030 which is about 150% increase from the demand in 2009 (4500 billion m^3) [3,4]. In 2012, the source water for desalination is split to about 58.9% from seawater, 21.2% from brackish groundwater sources, and the remaining percentage from surface water and saline wastewater [2]. These percentages are constantly changing because the desalination market is growing very rapidly [1]. Desalination is an increasingly common solution to supply fresh water in many regions of the world where this resource is scarce [5]. Recently, reverse osmosis (RO) is the most widely used desalination technology globally [5,6], with RO technology accounting for 59.9% of the desalination amount in the world [2]. Desalination is no longer a marginal or supplemental water resource in some countries [7]; the desalting supply ratio reached 100% in Qatar and Kuwait. Natural water such as surface water and groundwater can be used as raw water for RO systems in the future, because of worldwide water shortage.

As the most successful commercial RO membrane, thin-film composite (TFC) aromatic polyamide (PA) RO membranes have been primarily used in water recycling and desalination applications from saline water and other wastewater sources due to their ability to withstand wide range of pH values and high recoveries [8–11]. However, among all the types of fouling, an inevitable problem of RO membrane technology is biofouling, which is caused by adhesion and accumulation

of microorganisms, followed by growth and formation of biofilms [12]. With a sterilization or disinfection that is less than 100% effective, complete reduction or removal of biofilm is very difficult to achieve by feed treatment because of the ability of biofouling organisms to self-replicate since some cells remain alive and use the dead cells as nutrient source [13]. Microorganisms are present in nearly all water systems and are capable of colonizing almost any surface forming biofilms [14]. Biofouling is characterized by the presence of a biofilm on the membrane leading to increase in resistance and decline in membrane performance, such as water permeation and rejection of solutes [15] and results to increase in RO operational costs significantly since it is irreversible [16]. Among the different types of biocides summarized in a review by Kim et al. [16], free chlorine (i.e., hypochlorous acid, HOCl or hypochlorite, OCl⁻) injected at the head of a pretreatment process has been the standard practice to control biofilm formation in the RO process [14,16–17]. However, it has been pointed out that PA is very sensitive to free chlorine and, therefore, residual free chlorine in the feed solution can cause the degradation of PA if free chlorine is not completely removed before RO membrane filtration [18–23].

It has been considered that the degradation process of PA membranes mainly involves an initial N-chlorination by substituting the hydrogen on the amide nitrogen with chlorine, followed by ring-chlorination via an intermolecular rearrangement called Orton Rearrangement [18]. Chlorination of the PA has been hypothesized to facilitate C–N bond hydrolysis which leads to additional carboxylic acid groups as a result from the decrease in the number of C–N bonds [22]. It has been also reported that the presence of metal ions with chloramines or free chlorine resulted in the accelerated degradation of PA membranes [24,25]. Fe(III) and Fe(II) ions accelerated the membrane degradation with monochloramine and free chlorine [25]. The effect of chloramine in the presence of several metal ions to the degradation of polyamide membranes was tested and the presence of Cu^{2+} was found to accelerate the reduction of the polyamide (II) peak [24]. Shintani et al. [21] used purified water with 500 mg L^{-1} of Ca^{2+} to evaluate chlorine resistance of PA membrane developed because it was empirically known that Ca ion accelerates PA degradation. However, evidence of acceleration of PA degradation by the addition of Ca ion was not shown.

Different types of water sources are used as raw water for RO processes and the metal ions and their concentrations in the water sources vary depending on the type of water. Understanding the effect to membrane degradation of the presence of main ions in the raw water for RO process is necessary. Feed water for RO processes are usually seawater or brackish water, which contain several metal salts (alkali metal and alkaline earth metal such as Na^+, K^+, Mg^{2+}, and Ca^{2+}), with water qualities in varying degrees: pH values from 6.0–8.2, 7.4–472 mM Na^+, 0.2–56 mM Mg^{2+}, 0.005–10 mM K^+, and 1.9–11 mM Ca^{2+} [26,27]. In seawater, concentrations of trace ions were reported to be 0.11 μM for Ba^{2+} and 74.2 μM for Sr^{2+} [26]. Other various feed water such as secondary effluent water and Colorado River water were also supplied for RO processes [28–30], and the concentrations of the metal ions ranged from 13.5–24 mM Na^+, 0.27–2.1 mM Mg^{2+}, 0.05–0.3 mM K^+, and 3.6–7.3 mM Ca^{2+}. The wastewater from a semiconductor industry also contains trace ions of 5.5 μM Cu, 6.1 μM Zn, 77.6 μM Sr, 139.4 μM Al, and 17.7 μM Fe [28]. Despite the presence of these metal ions in these various feed water sources for RO processes, the effects of these ions or their concentration in the degradation of the PA membrane have not been reported.

Due to increased demand in water supply, RO membrane technology is expected to make drinking water and reclaimed water from various water resources, even with resource waters containing different types and concentrations of coexisting metal ions and with high biofouling potential waters such as secondary effluent water. Chlorine-resistant PA membranes are being developed to allow direct washing of water with free chlorine and chloramines to avoid biofilm formation on the membrane [21,31–36], and are expected to be used in the near future.

In the current state of membrane development research however, the membrane cannot have the perfect resistance to free chlorine as long as polyamide is used as a membrane material, such that research focusing on understanding PA membrane degradation by chlorine is very important. Since water sources and their quality are vital in RO membrane processes, determining the effects of water quality on the PA membrane degradation will be very important in designing and developing chlorine-resistant membranes.

In this study, the enhancing effect of the coexistence of metal ions on PA membrane degradation by hypochlorite was examined using a commercial PA membrane. The mechanism of the PA membrane degradation by hypochlorite was also examined.

2. Materials and methods

2.1. RO membrane and reagents

Commercially available PA RO membrane NTR-759HR, provided by Nitto Denko Co. (Osaka, Japan) was used in the study. Sodium chloride (NaCl), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) and potassium chloride (KCl) were purchased as analytical grade reagent from Kanto Chemical Co. Inc. (Tokyo, Japan). Sodium dihydrogenphosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$), sodium sulfate (Na_2SO_4), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), and calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) were purchased as analytical grade from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Sodium hypochlorite (NaOCl) (approx. 10% available chlorine) was purchased from Sigma-Aldrich Corp. (St. Louis, MO). Other reagents were purchased as analytical grade from Kishida Chemical Co., Ltd. (Osaka, Japan) and Kanto Chemical Co. Inc. (Tokyo, Japan). DPD (N,N-diethyl-p-phenylenediamine) was purchased for free chlorine analysis from Hanna Instruments Japan, Inc. (Chiba, Japan). Pure water was prepared using a Milli-Q Reference Ultrapure Water Purification System (Merck Millipore Corp., Darmstadt, Germany). Phosphate buffer solution of pH 8 was prepared from $NaH_2PO_4 \cdot 2H_2O$ and NaOH.

2.2. Hypochlorite treatment of RO membrane

The membranes were soaked in 300 mL of 2.70 mM (200 mg L^{-1}) NaOCl solution with each metal ion under study for the measurement of the membrane degradation. As control experiment, the membrane was soaked in 2.70 mM NaOCl solution without any metal ion. The soaking of the membrane was conducted at 25 °C in the dark, and was shaken at 45 rpm for 48 h. The pH values of the soaking solutions were initially adjusted to 8.0 using HCl and NaOH, which is within the pH range usually found for seawater desalination plants [23]. Effective free chlorine species of hypochlorous acid (pKa = 7.5, 25 °C) [37] are undissociated (HOCl), dissociated (OCl⁻), and dissolved chlorine (Cl_2), although the effect of Cl_2 which has unstable characteristics such as volatilization can be excluded [38]. The soaking solutions used were either a metal chloride salt or a metal sulfate salt, with metal ion concentrations as follows: 130–469 mM for Na^+, 9.7–300 mM for K^+, 0.5–7.0 mM for Mg^{2+}, 1.0–10.0 mM for Ca^{2+}, and 5.0 mM for Ba^{2+}. Experimental systems were constructed by a combination of these conditions, each metal salt added and the concentrations in the soaking solutions are summarized in Table 1. To maintain greater than 80% residual free chlorine concentration in the solution the soaking solution for the membrane degradation was replaced with fresh solution at 2, 12, 24, and 36 h soaking time for the 48 h duration of soaking. The free chlorine concentration was measured by the DPD absorption photometry using the residual chlorine meter (HI96711; Hanna Instruments Japan, Inc., Chiba, Japan). The soaked membrane was taken out of the soaking solution after 48 h, and then washed with pure water. After soaking, the membranes are subjected to cross-flow filtration to measure membrane performance by determining salt rejection and flux before and after the filtration using an RO test cell apparatus.