Effects of chemical preservation on flux and solute rejection by reverse osmosis membranes

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ABSTRACT

This study investigates the impacts of chemical preservation on the performance of polyamide reverse osmosis membranes with respect to water permeability and solute rejection. Three preservative chemicals, namely formaldehyde, sodium metabisulfite, and 2,2-Dibromo-3-Nitrilopropionamide, were evaluated for membrane preservation at pH 3 and 7. Experimental data show that chemical preservation may change the membrane surface properties, and consequently water permeability and solute rejection efficiency of the membrane are negatively impacted. The impacts of preservation on boron rejection and sodium rejection are similar in magnitude and more significant than those on water permeability. The results indicate that the impact of chemical preservation on the membrane depends on both the preserving chemicals used and the solution pH value. More importantly, the undesirable impacts of chemical preservation can be minimised by appropriate selection of the preservatives and by preserving the membrane in a reducing condition. A near-neutral pH (i.e., pH 7) is necessary to avoid any significant negative impacts on membrane performance due to chemical preservation using either formaldehyde or sodium metabisulfite. Results reported here suggest that the previously recommended minimum pH value of 3 of the preservative solution may be inadequate.

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1. Introduction

In recent years, the demand for clean water has substantially increased due to improved living standards and continuing population growth. At the same time, extreme weather patterns and the uneven distribution of freshwater resources across the globe have further intensified the issue of fresh water scarcity. As a result, a major challenge of our time is to reliably provide adequate clean water for municipal use as well as industrial and agricultural production [1]. This challenge has been progressively addressed by the development of new technologies to purify alternative water resources such as seawater, brackish water, and reclaimed wastewater for various beneficial uses [1,2]. Amongst these technologies, reverse osmosis (RO) has been possibly the most widely used technology for seawater desalination and water recycling [3]. In fact, RO membranes account for about half of the current worldwide desalination capacity [4–6]. Since 2003, in Australia, more than 30 new RO plants have been constructed and commissioned for either seawater desalination or water recycling [7,8]. In addition, the widespread use of small-to medium-scale RO systems has been

seen for brackish water desalination for mine sites [9], remote communities [10], military outposts [11] and a range of industrial applications such as coal seam gas produced water treatment, cooling water demineralisation [12], and wine-making [13].

Although RO membranes are designed for continuous operation, many small scale RO systems are operated on an intermittent basis to match the variations in the supply source and production demand. Some large-scale RO seawater desalination and water recycling plants that are located in regions with extreme climate variability can also be subjected to demand variation. For example, in Australia where the climatic pattern is characterised by intense droughts and flooding rains, several large-scale RO desalination plants, which were built to ensure a secured freshwater supply, have been recently mothballed for energy conservation. This is because seawater desalination is more expensive and energy intensive than the filtration of surface water, which has become abundant during the last few very wet years [14].

The widespread and diversified applications of RO have presented a new challenge to membrane technologists and practitioners. Once the RO plant operation is suspended for more than 48 h, the membrane must be preserved in a chemical solution to prevent biological growth and material degradation [15]. Despite the need to operate small-scale RO systems on an intermittent basis and to occasionally mothball large-scale RO plants, there has been

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very little research work on membrane preservation. The literature review undertaken as part of this study revealed that there has been only one report [16] on this topic in the peer review literature.

Most membrane manufacturers provide only a brief guideline for chemical preservation. Sodium metabisulfite (SMBS) at 0.05–1.5% (wt/wt) is currently the most widely used preservative chemical for RO membranes [15]. Formaldehyde solution at 0.1–1% (wt/wt) has also been recommended as an alternative preservative solution due to its biocidal property. However, because of its toxicity, the application of formaldehyde for membrane preservation is less common compared to SMBS [17]. In addition to SMBS and formaldehyde, in 2013, Hydranautics released a Technical Service Bulletin (TSB 110.11) considering the use of several other biocides including 2,2-Dibromo-3-nitrilopropionamide (DBNPA) and isothiazolin for chemical preservation [17]. Some commercially available pre-mixed solutions (Applied Membranes AM88, Applied Membranes AM225, Perma-Clean PC-55, PermaClean PC-56) have also been designed for RO membrane preservation although their exact ingredients are the proprietary information of the manufacturers. During membrane preservation, SMBS and formaldehyde can be oxidised resulting in a decrease in the preservative solution pH. Thus, several membrane manufacturers have specified that the pH of preservative solutions be regularly monitored and maintained at pH 3 or higher [15].

This study aims to investigate the impacts of chemical preservation of RO membranes on water permeability and solute rejection. In addition to conductivity and sodium, boron is also selected as a model solute since it is a solute of significant concern in many seawater and brackish water desalination applications [18–20]. Boron is a ubiquitous element existing in natural water and wastewater in the form of boric acid. Average boron concentration in seawater is approximately 4.6 mgL^{-1} which is known to be over the tolerance level of many important agricultural plants such as citrus and blackberry [21]. Boron rejection by RO membranes is considerably lower than that of NaCl [21,22]. Previous research has shown that changes in operating conditions such as membrane fouling could exert significant impact on the rejection of boron by RO membranes [23,24].

2. Experimental

2.1. Membranes and chemicals

A low-pressure and a high-pressure RO membranes—namely ESPA2 and SWC5—from Hydranautics (Oceanside, CA, USA) were used. The ESPA2 membrane is used for water reclamation or in the second pass of seawater desalination plants for boron removal. The SWC5 membrane is commonly used for seawater desalination. According to the manufacturer, these are thin-film composite membranes consisting of an ultra-thin polyamide (or polyamide derivative) skin layer on a micro-porous support layer.

Analytical grade SMBS (Chem-Supply, SA, Australia), formaldehyde (BDH Prolabo, VWR, QLD, Australia) and DBNPA (Sigma-Aldrich, MO, USA) were used as membrane preservative chemicals. Analytical grade NaCl, CaCl$_2$, NaHCO$_3$, and B(OH)$_3$ (Ajax Finechem, Taren Point, NSW, Australia) were used to prepare the feed solution. Suprapur HNO$_3$ (Merck Co., Darmstadt, Germany) was used for sample dilution prior to analysis. Milli-Q water (Millipore, Billerica, MA, USA) was used for the preparation of all stock and feed solutions.

2.2. Cross-flow membrane filtration system

A bench-scale cross-flow membrane filtration system (Supplementary Data, Figure S1) was utilised for testing the membrane performance. A detailed description of this system is available

elsewhere [22]. The membrane cell has an active surface area of 40 cm^2 (10 cm × 4 cm) with a channel height of 2 mm.

At the beginning of each experiment, the membrane sample was compacted by using Milli-Q water at 30 bar for 18 h. A stable flux was usually obtained within the first 10 h run. Following the membrane compaction, pure water permeability of the membrane was measured at 5, 10, 15, 20, 25, and 30 bar (at 20 °C). Electrolyte solution was then added to the feed reservoir making up a 10 L feed water containing 10 mM NaCl, 1 mM CaCl$_2$, 1 mM NaHCO$_3$, and 0.43 mM B(OH)$_3$ (or 4.6 mgL^{-1} B). Boron and sodium rejections were obtained at permeate fluxes of 10, 20, 42, 60 Lm^{-2} h^{-1} (LMH), temperatures of 10, 20, 30, 40 °C, cross-flow velocity of 42 cm s^{-1}, and pH values of 7, 8, 9, 11. The permeate flux and the cross-flow velocity were controlled by adjusting the bypass valve and the back-pressure regulator. The applied pressure was linearly proportional to permeate flux, reversely proportional to temperature and independent to the feedwater pH (Supplementary Data, Figure S3). Unless otherwise stated, the standard testing condition is 20 LMH flux, 20 °C, pH 8, and cross-flow velocity of 42 cm s^{-1} (i.e. retentate flow of 120 L h^{-1}). The pH value was adjusted using either 1 M NaOH or 1 M HCl solution. In all experiments, once the target operational parameters had been obtained, the system was stabilised for 60 min before feed and permeate samples of 20 mL each were taken for analysis.

2.3. Membrane preservation protocol

A virgin membrane sample was first evaluated for pure water permeability and salt rejection. The sample was then removed from the membrane cell for preservation. Membrane preservation was simulated by submerging a membrane sample in the preservative solution in a 600 mL air-tight glass bottle for 14 days. SMBS and formaldehyde preservative solutions were prepared at a strength of 5% (wt/wt) in Milli-Q water and were adjusted to either pH 3 or 7. These conditions represent a chemical preservation period from 2 months to up to 2 years. DBNPA preservative solution was prepared at a strength of 1% (wt/wt) in Milli-Q water and was adjusted to pH 7. The bottle was completely filled with the preservative solution to eliminate any head space and was placed in the dark. The pH of the preserving solution was monitored during the preservation period. At the end of the simulated preservation period, the preserved membrane samples were rinsed with copious amounts of Milli-Q water and then evaluated again for water permeability and salt rejection.

It is noted that the permeate flux of different elements of the same membrane name may vary up to 20% due to variation in the manufacturing process [25]. In fact, by testing seven 10 cm × 4 cm membrane samples, variations of 9% and 17% in water permeability of the ESPA2 and SWC5 membrane, respectively, were observed in this study. On the other hand, the mounting and dismounting of the membrane sample to the RO cell did not result in any discernible variation in permeate flux and salt rejection as can be seen from three repeated cycles of filtration after sample mounting and dismounting (Supplementary Data, Figure S2). By using a single membrane sample for evaluating permeate flux and salt rejection before and after preservation, the impact of individual preservative chemicals on the membrane can be accurately examined. However, it is noteworthy that inconsistency among different membrane samples used for different preserving chemicals may still occur. In addition, this study used virgin membranes for the investigation. In practice, chemical preservation would be applied to used membranes, which have been exposed to various chemicals (e.g. cleaning and disinfection agents) and thus their surface properties and separation performance may differ from those under virgin condition [26,27]. As such, changes in the performance of the used membrane due to preservation may be quantitatively different to