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Carbonised template silica membranes for desalination

S. Wijaya, M.C. Duke, J.C. Diniz da Costa*

FIMLab – Films and Inorganic Membrane Laboratory, Division of Chemical Engineering,
School of Engineering, The University of Queensland, Brisbane, QLD 4072, Australia
Tel. +61 7 3365 6960; Fax +61 7 3365 6074; email: j.dacosta@eng.uq.edu.au

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Abstracts

In this work we investigate the performance of inorganic membranes in desalination application using a low pressure pervaporation setup. Inorganic membranes were synthesized via a two-step sol–gel catalysed process employing tetraethylorthosilicate as the silica precursor. In addition, non-ligand surfactants were embedded and carbonized into the silica matrix. Normal silica membranes have typical microporous structural characteristics but were not stable during desalination, as water interacted with the silanol groups and enlarged the silica film pore sizes. On the other hand, the carbon template silica (CTS) membranes were hydrostable and exhibited higher surface area and pore volume as well as improved salt rejection as compared to conventional silica membranes. The longest 16 carbon chain (C16) surfactant derived CTS membrane showed highest NaCl rejection up to 97% with flux in the order of 3 kg m^{-2} h^{-1} at 1 bar pressure difference across the membrane and seawater concentrations. This translated to 1200 ppm of NaCl in the permeate, being close to the standard for drinking water.

Keywords: Inorganic membranes; Silica; Carbonised template; Surfactants; Salt rejection

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1. Introduction

The world is facing global water problems due to population growth and climate change [1]. As a result, in dry continents such as Australia, major cities are already experiencing water shortages. These pressing issues may limit sustainable development, even in currently robust economies. Hence, access to low salinity (10 million m^3) or seawater (1400 million m^3) resources currently available in the world [2] may become a viable option to sustain economic and social stability in the near future. Desalination technologies and process optimization has greatly improved in last two decades, allowing for considerable reductions in capital and operation costs in the production of potable drinking water [3].

Currently, around 43.5% of the world's desalination systems still utilize thermal technology,

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*Corresponding author.

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but this older technology has a high energy requirement for every volume (m^3) of fresh water produced. Membrane technologies have carved up the thermal desalination market [2], mainly due to improvements in water fluxes and reduction in energy requirements. Polymeric membranes are now a mature technology in water treatment and are widely used industrially which stem from major research and development work carried out over the last 30 years. In commercial applications, polymeric membranes have dominated membrane market strongly in liquid separation [4].

Despite their success, polymeric membranes still encounter some limitations, especially related to thermal and chemical stability. Furthermore, crucial improvements for this type of membrane have become more difficult to achieve lately [5]. As a result, research groups have been focusing on inorganic membranes [6], yet little has been reported for desalination application. One example is zeolite membranes employing a high pressure reverse osmosis setup, where fluxes of up to 0.1 kg m^{-2} h^{-1} were achieved after 145 h of operation while NaCl rejection peaked at 77% [7].

Studies by de Lint and coworkers [8] showed both theoretically and experimentally that salt rejection can be obtained with silica layers supported over alumina by a special charge rejection mechanism. Silica membranes have been developed mainly for gas separation for nearly two decades and are still the focus of many extensive studies. One of the major impediments for employing silica membranes in water separation relates to hydro instability of silica films. These membranes have a large concentration of silanol (Si–OH) groups [9] which are essential to produce silica films with pores sizes below 1 nm. As silanols are hydrophilic, water reacts with the silica membrane resulting in pore size enlargement, thus rendering silica membranes ineffective in gas or liquid separation processes. To address this problem, research groups have embedded into silica films covalently ligand templates [10,11] and non-ligand templates such as surfactants [11,12].

Recently, silica membranes have shown superior hydro-stability in water rich environments by carbonizing a non-ligand template into the silica matrix for wet gas streams [12] and desalination [13]. However, these studies have been limited to the carbonization of six-carbon (C6) chain surfactants. In this work, we investigate the effect of carbonizing various non-ligand carbon chain surfactants (C6, C12 and C16) on the fluxes and NaCl rejection for slightly, moderately and highly saline waters. The micro-structural formation of the (CTS) membranes are analyzed and discussed. Results are also compared to a non-templated silica membrane.

2. Experimental

2.1. Membrane preparation and xerogel characterisation

CTS sols were prepared by using two step catalyzed sol–gel process. An initial solution with a molar composition of 1.0 TEOS: 3.8 EtOH: 1.0 H_2O: 7.0×10^4 1 M HNO_3 was refluxed under stirring at 60°C for 90 min. In order to avoid premature partial hydrolysis, water/HNO_3 stock solution was added dropwise to the TEOS/EtOH mixture placed in an ice bath. In the second step, additional water/HNO_3 was added at room temperature resulting in sol with final molar ratio 1:3.8:6:0.1, following by the addition of 0.125 M surfactants at the very end of the sol–gel process. In this work, three different types of surfactant with varying carbon chains were used namely: hexyltriethylammonium bromide (C6), dodecyltrimethylammonium bromide (C12) and hexadecyltrimethylammonium bromide (C16). A blank silica (Blank) sol was prepared using the same synthesis procedures, but without surfactants.