



LADDER-LIKE POLYPHENYLSILSESQUIOXANE MEMBRANES FOR DISSOLVED OXYGEN REMOVAL IN LIQUID–LIQUID MEMBRANE CONTACTORS

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Abstract

The main disadvantage of absorption with aqueous alkanolamine solvents is the solvent degradation under process conditions in the presence of oxygen captured from flue gases. In this communication, the direct dissolved oxygen removal from an amine solvent in liquid–liquid membrane contactors is examined. The membranes from ladder-like polyphenylsilsesquioxanes are used for the first time for this process. The membrane deoxygenation is demonstrated in the O₂ removal process from monoethanolamine (MEA) into an aqueous solution of Na₂SO₃. In this case, the O₂ removal efficiency reached up to 40% within 1 h.

Key words: membrane contactor, polyphenylsilsesquioxanes, deoxygenation.

Introduction

Reducing CO₂ emissions is included in the development programs of many countries, including the Paris Agreement [1]. A promising area of research and development to address this global challenge is carbon capture, utilization, and storage (CCUS). One of the most mature technologies that can readily be implemented in different industrial and energy facilities on the immediate horizon is CO₂ capture using alkanolamine absorption [2]. The primary method for regenerating amine solvents is still high-temperature purification of CO₂. However, this method has a significant disadvantage in that it can cause the gradual decomposition of the solvent due to the presence of oxygen in solution [3]. This decomposition is accelerated at elevated temperatures between 100 and 130 °C [4], and the oxidative decomposition can significantly accelerate the degradation process. Oxygen enters the solvent from flue gases directly [5].

A preventive removal of dissolved oxygen from an amine solvent would be a viable option. The potential of membrane contactors for extracting dissolved O₂ has been previously demonstrated in a number of reports [6–8]. However, the commercially available porous membranes used in these studies suffer from the wetting effect in aggressive media containing amine solvents. In particular, the use of modern hydrophobic polypropylene (PP) porous membranes is not practical due to changes in their porous structures that are likely to be caused by the penetration of amine molecules into the PP matrix and its swelling [9]. Additionally, polypropylene membranes have been found to be unstable in the presence of the products of the amine

decomposition [10].

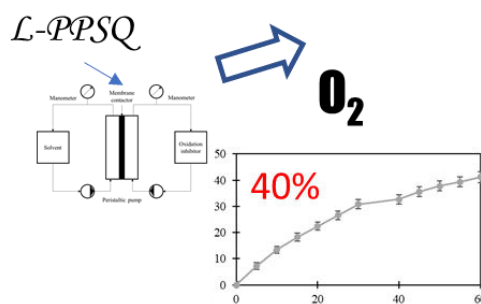
This process, which can be implemented in liquid–liquid membrane contactors, offers several advantages: no phase dispersion occurs, as the membrane serves as a mass transfer surface; the system is modular and compact; the metal capacity of the equipment is low; the energy efficiency is enhanced [11]. The potential for using membrane contactors to extract ions has been demonstrated in a variety of studies [12, 13].

As a membrane for this type of contactors, a porous membrane composed of ladder-like polyphenylsilsesquioxanes (L-PPSQ), high molecular weight polymers (1000 kg/mol) with excellent thermal and oxidative stability (>500 °C), able to form stable, transparent films seems to be of significant interest [14].

Results and discussion

L-PPSQs synthesized in ammonia have a high molecular weight, which is not achievable using other modern techniques for the synthesis of these polymers. A solution of L-PPSQ in chloroform (1 wt %) was used to produce the films. Dense L-PPSQ films were formed by casting a solution of L-PPSQ in chloroform on polytetrafluoroethylene and then drying at room temperature under ambient conditions for 200 h. The film thickness ranged from 30 to 35 μm. The membrane area was 20 cm².

The study of the process of removing dissolved oxygen was conducted in a setup of the liquid–liquid membrane contactor (the contactor configuration is illustrated in Fig. 1). Using peristaltic pumps, a counter-current mode of fluid flow through the contactor was established. A 30 wt % aqueous solution of



monoethanolamine (MEA) with an oxygen concentration equivalent to the solubility limit at the given temperature (~8.3 ppm) was used as the model solvent. An aqueous sodium sulfite (Na_2SO_3) solution (50 g/L) with a catalytic agent, namely, cobalt nitrate ($\text{Co}(\text{NO}_3)_2$) (0.05 g/L) was employed as an oxidation inhibitor. The linear flow rates of the solvent and antioxidant solutions were 4.5 cm/s; the transmembrane pressure was ± 2 kPa; and the volume of each supplied liquid was 400 mL. The oxygen concentration in the solution was measured using a pre-calibrated oxygen meter with a galvanic sensor (Hanna Instruments, Germany).

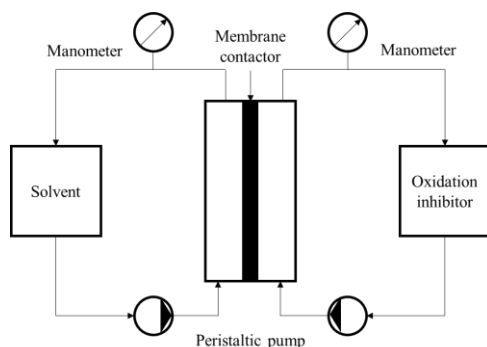


Figure 1. Design of the experimental setup.

The resulting deoxygenation profile is presented in Fig. 2.

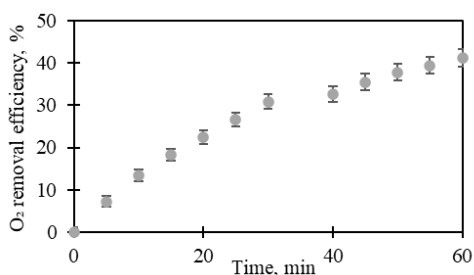


Figure 2. Change in the level of dissolved oxygen extraction over time during the deoxygenation process of the absorbent.

The extraction of 40% of dissolved oxygen is comparable to that achieved by modules based on composite membranes with a polysulfone support and a thin protective layer of PTMSP/PVTMS 70/30. These modules also extract approximately 35% of the gas–liquid interface per hour of operation [15]. This reduces the number of HSS anions formed after 200 days of subsequent storage of the absorbent by a factor of 1.7.

Conclusions

The L-PPSQ membranes obtained in this work allow extracting up to 40% of dissolved oxygen from alkanolamine solvents, which slows the rate of HSS ion formation by 1.7 times for 200 days of operation.

Further research in this field can focus on enhancing the flow in liquid phases, with the in-depth study of the impact of process variables on the efficiency of oxygen extraction, and exploring the potential use of L-PPSQ as the material for constructing continuous layers of composite membranes in both

liquid–liquid and gas–liquid contactor systems.

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