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The study of reverse osmosis on glycerin solution filtration: Dead-end and crossflow filtrations, transport mechanism, rejection and permeability investigations

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HIGHLIGHTS

- This work studied water separation from glycerin solution using RO membranes.
- Dead-end and crossflow filtrations were employed in this study.
- Physicochemical property of the membranes affected their rejection and permeate flux.
- TFC-HR in the crossflow filtration achieved the glycerin rejection up to 99.81%.
- The possible molecular movement and transport across the membrane were postulated.

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ABSTRACT

The utilization of recycled water from reverse osmosis (RO) filtration within a production process can be one of the potential solutions to conserve fresh water. In this work, the effect of membrane physicochemical properties on glycerin rejection and water permeability were demonstrated in dead-end and crossflow filtrations. The study showed that RO membrane with high surface roughness, high negative charge in glycerin solution, low water contact angle, high water affinity and small pore radius were favorable in glycerin separation. Crossflow filtration provided better rejection and permeability than that of dead-end filtration using the RO membranes studied in this work. The combination of fundamental knowledge on membrane physicochemical properties and boundary layer theory was used to speculate the molecular movement and transport mechanism across the membrane. The highest rejection of 99.81% was achieved by TFC-HR membrane, along with the permeate flux of 11.86 $kg/m^2 \cdot h$ in the crossflow filtration while in the dead-end filtration, only a rejection of 96.37% and permeate flux of 4.93 $kg/m^2 \cdot h$ were recorded. Lastly, it was found that the membrane surface pattern influenced the membrane performance significantly in terms of rejection and permeability.

1. Introduction

Glycerin is a versatile organic material that is widely used in medical, pharmaceutical, pulp and paper, textile, automotive, food and paint industries [1,2]. Recent studies [3,4] suggested the potential of glycerin to be used as a feedstock material to synthesize acetins, which are a type of transportation fuel additives with good commercial value. Besides that, another study showed that glycerin can be used as fuel directly in modified combustion engine to generate less emission as compared to conventional combustion engine that was driven using fossil fuel [5]. Raw glycerin is a major byproduct in biodiesel processing plant that can account for 10–12% of the total production capacity [6,7]. The byproduct, raw glycerin, can be further purified into pure grade glycerin, and subsequently to be used as glycerin feed for other production processes. In general, the traditional glycerin purification process is able to upgrade the purity of the glycerin up to 99 wt.% purity, which is known as extra pure grade glycerin. This process generally involves glycerin washing, chemical and physical pretreatment, evaporation, distillation and vacuum distillation processes [7–9]. Besides, the pretreatment processes normally involve extensive chemical, water and energy usage. In view of the extensive use of water in the glycerin washing process, there exists the potential to recycle these water for use in other processes within the plant. Membrane filtration is an economical and environmental friendly alternative in replacement of the traditional glycerin purification process. Our previous studies [10,11] have demonstrated that ultrafiltration process using GE PVDF 30 kDa membrane is capable of reducing the concentration of impurities in

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the glycerin solution, which has recorded rejection of palm oil and oleic acid up to 98.59%. Also, the corresponding flux decline due to fouling has been successfully predicted using mathematical model. However, a membrane filtration process of higher efficiency in separating water from glycerin solution is of paramount importance. This is aimed to maximize the recovery of process water and to further concentrate the glycerin solution up to a satisfactory level, achieving two objectives at the same time.

The rapid growth of world population coupled with industrialization and urbanization will eventually result in an increasing demand for freshwater [12]. Therefore, many researches focus on seeking for suitable approaches to obtain freshwater through saltwater desalination and water reuse in order to sustain the future generations [13,14]. The RO process is gaining worldwide acceptance at the present by appearing as a promising way in regenerating freshwater [14,15]. The RO process is also widely used around the world for concentration of process stream and production of ultrapure water [16–18]. To the best of our knowledge, no significant study on RO technology in the separation/extraction of water from glycerin solution and glycerin retention has been reported. Our literature search disclosed that the investigations of process feed and membrane interactions, molecule transport mechanisms, permeation and rejection ability using different filtration configurations and experimental parameters of RO filtration process are not available.

The aims of this present work were to investigate the detailed physicochemical properties for the widely used RO membranes which include TFC-HR, UTC-80LB, X201, ROSE and ROSG as well as to study the possible applications of these membranes in the separation of water from glycerin solution through glycerin rejection processes. The membrane physicochemical properties were determined through several observations and measurements using atomic force microscope (AFM), scanning electron microscopy (SEM), measurements of zeta potential, membrane hydrophilicity and membrane pore radius estimation. The effects of different membrane properties, membrane surface patterns, filtration configurations and process temperature on RO membrane performance were also evaluated. In addition, molecular movement, molecular interactions and molecule transport mechanism during RO filtration process were discussed in detail. The experimental findings from this study are important to determine the suitability of employing RO filtration as a water separation process from glycerin solution in the glycerin purification process.

2. Experimental

2.1. Chemicals and membranes

The analytical grade glycerin with a purity of 99% was provided by ACROS Organics. The model solution of 15 wt.% glycerin solution was prepared using ultrapure water (0.055 μS/cm) that was produced from a TKA smart2pure standard water dispenser (Thermo Electron LED, GmbH). Five flat-sheet reverse osmosis (RO) membranes were selected for this particular scope of experiment, which included ROSE (GE Osmonics), ROSG (GE Osmonics), TFC-HR (Koch Membrane System), X201 (TripSep) and UTC-80LB (Toray). The molecular weight cut off of all these five membranes is 0 Da [19]. In general, ROSE and ROSG have been widely used for concentrating process stream such as fruit juice, starch and sugar and for brackish water desalination [20,21]. TFC-HR and X201 are effective membranes in removing trace organics, reducing water hardness and desalinating brackish water with high salt rejection [22,23]. UTC-80LB has been used for high flux seawater desalination process [19]. The detail properties of the aforementioned membranes were listed in Table 1.

2.2. Membrane characterization

The separation performance of a membrane is greatly governed by its physical and chemical properties such as materials of construction, roughness and hydrophobicity of the membrane surface, shape and size of the pores, pore size distribution and porosity [24–27]. In the present work, the topography of the membrane surface was analyzed using atomic force microscope (AFM). The cross-section of the membranes was examined using field emission scanning electron microscope (FE-SEM). The membrane surface charge property was measured with zeta potential analyzer. The membrane surface hydrophobicity was measured using contact angle goniometer. The water affinity of each membrane was investigated through equilibrium water content calculation, and the mean pore radius, porosities and pore densities of the membranes were obtained from respective water permeation tests.

2.2.1. AFM analysis

The AFM measurements were carried out using Park Systems XE-100 (Park Systems, Korea) atomic force microscope with XE Control Electronics and DSP Board in Controller (Park System, Korea). The cantilever with integrated Super Luminescence Diode Head (Park System, Korea) was used to image the surface topography of membrane. The measurements of surface topography of membrane were performed on dry membrane samples under ambient atmospheric conditions. The membrane surfaces were imaged with non-contact mode. At least three separate scans were conducted on each membrane, covering the area of 3 × 3 μm^2, as to determine the mean roughness values. Roughness parameters were obtained from AFM topography measurement using the instrument software XEP-Data Acquisition (Park Systems, Korea). The three dimensional average roughness (R_a) and root means square roughness (R_q) were determined using Eqs. (1) and (2), respectively. The R_q is the standard deviation of the heights for all the pixels in the topography image from the arithmetic mean, representing the statistical measure of the relative roughness of a surface.

$$R_a = \frac{1}{ML}\sum_{i=1}^{M}\sum_{j=1}^{L}|Zji| \quad (1)$$

$$R_q = \sqrt{\frac{1}{ML}\sum_{i=1}^{M}\sum_{j=1}^{L}Z^2(x_i, y_i)} \quad (2)$$

where M and L are the number of data points in X and Y, respectively, and Z is the surface height relative to the mean plane.

2.2.2. FE-SEM analysis

For the sample preparation, fresh membranes were firstly dried in a desiccator at room temperature overnight to ensure complete moisture removal. The samples were then fractured using liquid nitrogen and later being stored in a moisture free container. Microscopic observation

Table 1
The properties of the RO membranes used in this study [19].

Membrane	Manufacturer	Material	Salt rejection (%)	pH range at 25 °C
ROSE	GE Osmonics	Proprietary thin film	98.9	2–11
ROSG	GE Osmonics	Proprietary thin film	98.2	2–11
TFC-HR	Koch Membrane	Proprietary thin film composite polyamide	99.5	4–11
X201	TriSep	Proprietary polyamide-urea	99.5	2–11
UTC-80LB	Toray	Proprietary polyamide	99.7	2–11