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Phenol rejection by cellulose triacetate and thin film composite forward osmosis membranes

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ABSTRACT

This study aims to elucidate the separation of phenol by reverse osmosis (RO) and forward osmosis (FO) modes and propose strategies to enhance phenol rejection by these two processes. The results show that phenol rejection was strongly influenced by water flux, membrane materials, membrane structure, modes of operation, and feed solution chemistry (i.e. pH). The relationship between phenol rejection and water flux was demonstrated by the irreversible thermodynamic model which could accurately simulate phenol rejection as a function of water flux. At pH 7, phenol rejection by cellulose acetate (CTA) membranes was negligible while the thin film composite (TFC) polyamide (PA) membranes exhibited much higher phenol rejection. Through a systematic static adsorption experiment, results in this study show that phenol adsorption to CTA material was about 20 times higher than that to PA material. Thus, the observed higher phenol rejection by TFC PA compared to CTA membranes was attributed to the significantly higher affinity of phenol toward CTA and the sorption diffusion transport mechanism of phenol through the membrane. In particular, a TFC PA membrane specific for FO operation was prepared in this study. In FO mode, the tailor-made TFC PA membrane showed a slightly higher phenol rejection and a much higher water permeability compared to the commercial membrane. At the same water flux and solution pH, phenol rejection in FO mode was consistently higher than in RO mode. This observation could possibly be attributed to the reverse diffusion of draw solutes in the FO mode which hinders the forward diffusion of phenol through the membrane. A significant increase in phenol rejection was achieved by increasing the feed pH above the dissociation constant of the compound.

1. Introduction

Phenol is both an important precursor material and a toxic by-product in many industrial processes including paper manufacturing, oil refining, coking, petrochemical, and pharmaceutical production [1,2]. If released into the environment, phenol can accumulate in ground water, soil, or surface water [3]. Phenol compounds and derivatives are harmful for living organisms even at a low concentration, thus are considered as priority pollutants [4]. Many chemical, physical-chemical, and biological methods have been utilized in treating phenol-containing wastewater, such as chemical methods including chemical oxidation, photo-oxygenation, supercritical water oxidation, and physical-chemical methods including solvent extraction, incineration, adsorption, steam stripping processes, and biological method including activated sludge process [4]. To determine a suitable technology for treating the phenol-containing wastewater, several criteria should be considered: operational cost and capital investment, treatment efficiency, generation of secondary waste streams or solid, and footprints. Taking these criteria as guidelines, current chemical, physical and biological processes are not optimal yet.

Membrane technologies, mainly reverse osmosis (RO), nanofiltration (NF), have been challenged for phenol separation. Cellulose acetate membranes have been studied by several researchers in reverse osmosis process [5,6]. Negative rejection was reported at an operational pressure ranging from 34 to 104 bars at 30 °C [7]. Higher rejection was found for TFC membranes [4,8,9]. In a pressure driven RO process, the rejection of small molecules was affected by several factors: size and geometric constraints, charge repulsion, and "solute-membrane affinity". The phenol compound may interact with the active coating layer based on hydrophobicity, hydrogen bonding capacity, and dipole moment [10–12]. The rejection mechanism for the low molecular weight organic solutes such as phenol

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and its derivatives was markedly different from that of simple aqueous salt solutions [13–17]. This strong affinity between the organic solute and the membrane material resulted in absorption of phenol and its derivatives into the membrane rather than being rejected. Recent work demonstrated that the “solute-membrane affinity” played a critical role in the rejection of trace organic contaminants [18–20], leading to a negative rejection on phenol of cellulose acetate (CA) or cellulose triacetate (CTA) [21].

RO and NF are pressure driven membrane processes [22]. For an osmotic pressure driven process, highly concentrated draw solution attracts water across the FO membrane, first the active separation layer followed by a porous support layer [23]. Very recent research work reported that FO process yielded higher phenol rejection due to the contribution of reverse salt diffusion [24]. Another work compared the rejection of CTA and TFC membranes treating 0.47 ppm phenol in FO and RO processes. The results indicated the rejections of CTA membranes were lower than TFC membranes in FO and RO modes, and the adsorbed mass by the CTA membranes (1.07 μg/cm^2) was higher than that by TFC membranes (0.75 μg/cm^2) in FO mode. However, the reported static adsorption experiment of TFC membranes included both the top layer and the support layer of TFC membranes, thus the results were actually an average of the polyamide (PA) active layer and the support layer [25]. Besides, the rejection of phenol by currently available RO and FO membranes were not sufficiently high and thus further treatment might be required (e.g. integral of membrane technologies and other conventional chemical and physical treatment approaches). An improved phenol removal rate in the primary treatment stages is highly desirable to achieve the overall treatment efficiency.

Different driving forces may have different effects on phenol removal, and in turn reflecting in the removal efficiency. It is thus necessary to further understand and improve the separation performance of membranes. The correlation between retention and adsorption of phenol-like chemicals in NF membrane has been investigated before [26]. It was found that the increased adsorption of the organic matter lead to accelerated the diffusion of phenol across the membrane, hence decreased retention [26]. Based on the adsorption experiments using NF/RO membrane, the hydrophobic attraction was found to enhance the adsorption of phenolic compound on the membrane surface, and alter the rejection performance [27]. In this paper, we intended to systematically correlate the sorption of phenol in the active separating layer to the rejection in FO process. The actual rejection of phenol by both RO and FO membranes could be further improved. In this paper, we focus on further improvement of the removal rate of phenol using FO membranes based on the understanding of the adsorption and mass transfer of phenol in the active layer of both types of membranes. The feed was a synthetic phenol/NaCl/H_2O mixture, representing the typical wastewater from the oil/gas industry. The commercial TFC FO, CTA FO, and tailor-made TFC FO membranes were selected for investigation. Irreversible thermodynamics model was utilized to simulate the performance of membranes in RO mode. Significant improvement in phenol removal in FO mode and high pH was found. Sorption of the active layer to the phenol was investigated based on both tailor-made TFC FO membrane and commercial membranes. Hypothesis for the increased removal performance was provided. The research provides a methodological approach for increasing the removal rate of phenolic matters from a mixture via FO membranes.

2. Experimental

2.1. Chemicals and membrane materials

Flat sheet CTA and TFC membranes were kindly supplied from Fluid Technology Solutions (Albany, Oregon, USA). They are denoted as FTS-CTA and FTS-TFC, respectively. Phenol, N,N-dimethyl acetamide (DMAc), polyethylene glycol (PEG400), n-hexane, sodium hydroxide (NaOH) and sodium chloride (NaCl) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). M-phenylenediamine (MPD) and trimesoyl chloride (TMC) were obtained from Sigma-Aldrich (Shanghai, China). These chemicals and solvents were of reagent grade. Polysulfone (PSf, P3500) was purchased from Solvay.

2.2. Fabrication and characterization of TFC-FO membranes

The PSf support and PA active layers were prepared by phase inversion and interfacial polymerization, respectively, as previously described in the literature. Briefly, the PSf support layer was prepared from a mixture of PSF (18 g)/PEG-400 (8 g)/DMAC (74 g). The mixture was stirred at 65 °C until a clear solution was obtained [28,29]. After filtered, de-gassed, a film was cast (Elcometer 4340, Elcometer Asia Pte. Ltd) using a casting knife of 150 μm and immersed into a water bath of 30 °C. The resulting support PSf membrane was rinsed and stored in DI water. For preparation of TFC FO membrane, an interfacial polymerization was adopted as follows: a water phase (MPD 2 wt.%) and organic phase (TMC in hexane 0.15 wt.%) were brought to contact at the PSf membrane top surface for 2 and 1 min, respectively; the TFC PA membrane was cured in an oven at 95 °C for 3 min, and stored in DI water before further analysis [28–31].

Key membrane transport parameters include salt rejection (R, %), pure water permeability coefficient (A, L/m^2 h bar), salt permeability coefficient (B, L/m^2 h) were determined using the standard protocol described by Cath et al. [32]. A laboratory scale cross-flow reverse osmosis system (Sterlitech Corporation) was utilized [32]. The effective membrane area was 24 cm^2. The cross-flow velocity was maintained at 0.25 m/s. All experiments were conducted at 25 ± 1 °C. The intrinsic water permeability, A, was determined by:

$$A = J_W/\Delta P \tag{1}$$

The pure water flux, J_w, was measured by dividing the volumetric permeate rate by the membrane surface area with DI feed water under an applied trans-membrane pressure of 10 bar. Salt rejection was measured using 1000 ppm NaCl as the feed solution at 10 bar. The observed NaCl rejection, R, was determined by Eq. (2):

$$R = 1 - \frac{C_p}{C_b} \tag{2}$$

And the bulk feed (C_b) and permeate (C_p) were the salt concentrations.

2.3. Surface characterization

The membrane morphology was examined by a ZEISS SUPRATM 55 scanning electron microscope (SEM). Cross section samples were prepared by breaking the membrane under a cryogenic condition, followed by vacuum drying overnight at 30 °C and then gold coating.

The membrane surface charge was characterized by a streaming electrokinetic analyzer (Surpass Anton Paar, Austria). The area of each sample was 0.2 × 0.1 cm^2 and the membranes were immobilized to the adjustable gap cell (100 ± 2 μm). KCl solution (1.0 mmol/L) was used as the electrolyte. HCl and NaOH were used for pH adjustment.

2.4. Membrane performance in FO mode

A stainless steel FO membrane cell with length, width and channel height of 80, 30, and 2 mm was used. Two variable speed gear