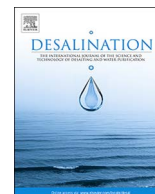




Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Evaluation of a natural polymer-based cationic polyelectrolyte as a draw solute in forward osmosis

Sawanya Laohaprapanon^a, Ywu-Jang Fu^b, Chien-Chieh Hu^{a,*}, Sheng-Jie You^c, Hui-An Tsai^a, Wei-Song Hung^a, Kueir-Rarn Lee^a, Juin-Yih Lai^{a,d}

^a R & D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, Chung-Li 32023, Taiwan

^b Department of Biotechnology, Vanung University, Chung-Li 32023, Taiwan

^c Department of Environmental Engineering, R & D Center for Membrane Technology, Chung Yuan University, Chung-Li 32023, Taiwan

^d Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

ARTICLE INFO

Keywords:

Cationic starch
Forward osmosis
Draw solute

ABSTRACT

We synthesized cationic starch by grafting 2,3-epoxypropyltrimethylammonium chloride onto the backbone of corn starch, and investigated its potential as a draw solute in forward osmosis (FO). The experimental results have shown that the as-prepared cationic starch easily dissolved in water; at 30 wt% cationic starch solution, the osmotic pressure was 11.91 atm. Increasing the solution temperature decreased the viscosity of the draw solution and resulted in a higher flux of water from the feed solution. For the 30 wt% cationic starch at 45 °C, the maximum flux of water from deionized water was 4.10, and that from a 2 g L⁻¹ NaCl feed solution was 2.20 L m⁻² h⁻¹ (pressure retarded osmosis mode). In addition, the cationic starch was satisfactory for protein concentration without protein denaturation. The diluted draw solute was also recovered, and the results indicated that ultrafiltration was effective to reconcentrate the diluted draw solution with a rejection rate > 99% at a concentration < 6 wt% cationic starch. To improve the water flux during the regeneration process, membrane crossflow filtration or other recycling membrane processes, such as membrane distillation, were recommended. Cationic starch was demonstrated to be feasible as a draw solute in FO processes.

1. Introduction

During the past decade, forward osmosis (FO) has drawn great research attention because of its unique features and potential applications in various fields including saline desalination, water purification, power generation, food processing, and drug delivery [1–3]. In FO processes, the water from a feed solution permeates across a semi-permeable membrane to a draw solution on the basis of an osmotic pressure driving force. In the absence of an external hydraulic pressure and without regeneration of draw solute, the total energy consumption and operational cost of FO are much lower than that of conventional pressure-driven membrane technologies such as reverse osmosis [4]. Moreover, FO demonstrates a high separation efficiency and minimum irreversible membrane fouling [5,6] which makes the process more attractive for treating complex feed solutions such as landfill leachate, olive mill wastewater, drilling wastewater, and wastewater effluents from biological treatment processes [7–10].

A sustainable FO in a full-scale application faces a critical challenge—the absence of a suitable draw solute that can generate high water

flux, low salt leakage, and low energy requirements for the easy regeneration of the diluted draw solution. Furthermore, the draw solute should have minimal toxicity with economic feasibility and environmental friendliness.

In early studies, inorganic salts (NaCl, KBr, MgCl₂, MgSO₄, CaCl₂, and ((NH₄)₂CO₃) were the most studied draw solutions for FO applications because they had high degree of solubility and high osmotic pressure, leading to a high water production. However, high reverse salt diffusion and high requirements of reverse osmosis for water recovery and concentration of the diluted draw solution were the major disadvantages that hindered the use of such draw solutes. The diffusion of the draw solution to the feed solution during the FO would reduce the net osmotic driving force and induce membrane fouling on the membrane-supported layer, which ultimately caused a flux decline. Additionally, the accumulation of the draw solute in the feed solution could alter the physical and chemical properties of the feed. For example, ammonium bicarbonate and magnesium chloride were extremely toxic to *E. coli* in the FO membrane bioreactor [8]. Kim et al., [11] found that the reverse flux of KH₂PO₄ and (NH₄)₂SO₄ strongly

* Corresponding author.

E-mail address: cchu@cycu.edu.tw (C.-C. Hu).

<http://dx.doi.org/10.1016/j.desal.2017.04.027>

Received 30 January 2017; Received in revised form 27 April 2017; Accepted 28 April 2017
0011-9164/ © 2017 Elsevier B.V. All rights reserved.

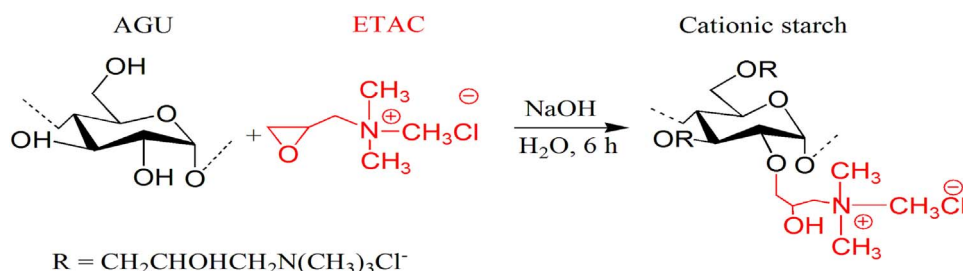


Fig. 1. Schematic representation of the etherification reaction between degraded corn starch and etherifying agent of ETAC.

inhibited the methane production in an FO-anaerobic membrane bioreactor hybrid system.

To overcome salt leakage and recovery problems, various types of new draw solute have been explored during the past few years. Ling et al., [12] proposed magnetic functionalized nanoparticles as a potential draw solute because they could reduce reverse flux and be easily recovered using an external magnetic field; thus, the energy consumption was low during the regeneration of the draw solute. However, the downside was the agglomeration of the particles during the recycling. Strong polyelectrolytes and highly water-soluble organic polymers have been widely utilized for FO applications [3,12–17]. Their large molecular size and flexible chemical structure do not only reduce reversed flux but can also be easily separated from the aqueous solution by nanofiltration, membrane distillation, or ultrafiltration. In addition, organic wastes like lignin sulfonate from paper manufacturing have been employed as a candidate draw solute [18]. The study demonstrated that the lignin sulfonate has osmotic pressure sufficient to draw water from the brackish feed, and the diluted draw solution can directly use to stabilize sand and retain moisture in desert areas without regeneration. Lately, stimuli-responsive hydrogel and polyelectrolytes have received much attention from scientists because of their lower energy requirement for regeneration [19,20]. Although most studied draw solutes exhibit good FO performance, the development of new draw solute is still needed.

Starch is a natural polymer, which has a large molecular weight from 10^4 to 10^7 g mol⁻¹. Because of its complete biodegradability, low cost, and renewability, starch is considered as a promising candidate for developing sustainable materials. A large number of hydroxyl groups on starch molecules provides active sites for chemical modification. Among the modified starch, cationic starch has been intensively used in drug delivery, paper making, and flocculants for water and wastewater treatment [21–25]. Compared with native starch, cationic starch has greater thermal stability and a higher ionic activity. Thus, it may have a potential use as a draw solute in FO processes.

In this study, we synthesized cationic starch and investigated its application as a potential draw solute in FO. Through an etherification reaction, a cationic reagent (2,3-epoxypropyltrimethylammonium chloride, ETAC) was introduced into the starch backbone. The chemical structure of the synthesized cationic starch was characterized by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance spectroscopy (NMR). The physicochemical properties of the cationic starch, including pH, conductivity, osmotic pressure and viscosity, were systematically investigated. The performance of the cationic starch as a draw solute in FO was evaluated in relation to the concentration and temperature using deionized water, salt solution (2 g L⁻¹ NaCl), and bovine serum albumin (0.2 g L⁻¹, BSA) as feed solutions. The recovery of the diluted draw solution after the FO operation was also performed using ultrafiltration membrane.

2. Experimental section

2.1. Materials and chemicals

Corn starch powder (CAS no. 9005-25-8) and a cationic agent

(ETAC) were purchased from Sigma-Aldrich. Initially, the corn starch was pretreated in a methanol/HCl solution at 45 °C. After 4 h of pretreatment, the degraded starch was filtered and washed with acetone three times to remove the excess acid. The products were dried and ground into a fine powder before they were stored in an airtight bag for later use [26]. The other reagents and solvents were commercial grades, and used as received (i.e. without further purification). Deionized (DI) water was used for preparing chemical solutions.

2.2. Synthesis of cationic starch

Cationic starch was synthesized by grafting ETAC onto the backbone of starch. The methanol/HCl-degraded starch (10.0 g, 62 mmol of anhydroglucose unit, AGU), suspended in 50 mL NaOH solution (0.5 mg, 12.5 mmol), was placed in a 250-mL dry three-necked flask, which was heated to 50 °C in an oil bath under stirring. After 1 h, 18.82 g ETAC solution was added to the flask, and the reaction was allowed to occur at 60 °C for 5 h. To terminate the reaction, the suspension was cooled in an ice water bath and neutralized to pH = 7.0 by adding 1.0 M HCl. Then, the resultant product was precipitated by adding cold ethanol, washed with 90% (v/v) ethanol three times, and the waxy light brown cationic starch was purified using cellulose dialysis membrane tubes (molecular weight cutoff = 3 kDa) containing deionized water for 3 days to remove any unreacted residuals. Finally, the purified cationic starch was dried in an oven at 50 °C. Fig. 1 illustrates the conventional etherification reaction between ETAC and starch in an alkaline medium and at a mild temperature.

2.3. Characterizations

To attain the ¹³C NMR spectra, the samples were dissolved in D₂O and the analysis was performed using a Bruker AV 400 MHz Fourier transform spectrometer (Germany) at 25 °C. The FTIR spectra of starch before and after the etherification reaction with ETAC were obtained on a Perkin-Elmer IR spectrometer in attenuated total reflectance mode over a range of 650–4000 cm⁻¹ with 16 scans and a resolution of 4 cm⁻¹.

The apparent viscosity, pH, and conductivity of the cationic starch draw solution were measured using a Brookfield R/S-CPS + rheometer (USA) with the measurement system of CP 75-1, a multiple pH meter, and a conductivity meter (Mettler Toledo, USA), respectively.

The osmolality of the solution was obtained by measuring the freezing point depression osmometry (Micro-Osmometer type 15/15M, Löser Messtechnik, Germany). The osmometer was calibrated using a 290 mOsm solution, and the data were converted to the osmotic pressure by using Eq. (1), wherein π was the osmotic pressure gradient in the FO, m was the measured osmolality of the solution, ρ was the density of water, and R and T were the ideal gas constant (0.0821 L atm mol⁻¹ K⁻¹) and absolute temperature (K), respectively.

$$\pi = m\rho RT \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/4987569>

Download Persian Version:

<https://daneshyari.com/article/4987569>

[Daneshyari.com](https://daneshyari.com)