รายงานฉบับสมบูรณ์ของการวิจัย

โครงการวิจัย

การทำเข้มข้นสารละลายโปรตีนด้วยกระบวนการร่วมของระบบฟอร์เวิร์ดออสโมซิส และการกลั่นผ่านเมมเบรน

Hybrid forward osmosis/membrane distillation (FO/MD) for protein concentrated.

ผู้วิจัย

ดร.วัสสา คงนคร

ที่ปรึกษาโครงการวิจัย

รศ.ดร. วิโรจน์ ยูรวงศ์

โครงการนี้ได้รับทุนสนับสนุนจากงบประมาณเงินรายได้ทุนดรุณาจารย์

มหาวิทยาลัยสงขลานครินทร์

ประจำปีงบประมาณ 2555 รหัสโครงการ ENG550348S

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คณะนักวิจัย

1. **ผู้วิจัย** ดร.วัสสา คงนคร

หน่วยงานต้นสังกัด ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์
มหาวิทยาลัยสงขลานครินทร์ วิทยาเขตหาดใหญ่

2. **ที่ปรึกษาโครงการวิจัย** รศ.ดร. วิโรจน์ ยูรวงศ์

หน่วยงานต้นสังกัด ภาควิชาเทคโนโลยีอาหาร คณะอุตสาหกรรมเกษตร
มหาวิทยาลัยสงขลานครินทร์ วิทยาเขตหาดใหญ่

กิตติกรรมประกาศ

ผู้วิจัยขอขอบคุณ รองศาสตราจารย์ ดร. วิโรจน์ ยูรวงศ์ อาจารย์ที่ปรึกษางานวิจัยที่กรุณาติดตามและแนะนำกระบวนการทำวิจัยเป็นอย่างดีให้กับผู้วิจัย ทำให้การทำวิจัยสำเร็จลุล่วงไปด้วยดี

ขอขอบคุณคณาจารย์ เจ้าหน้าที่ ผู้ช่วยวิจัย และนักศึกษาในสถานวิจัยวิทยาศาสตร์และเทคโนโลยีเมมเบรน (Membrane Science and Technology Research Center; MSTRC) ที่คอยช่วยเหลือและสนับสนุนการทำวิจัยในครั้งนี้ ทำให้การทำวิจัยสำเร็จลุล่วงไปด้วยดี

สุดท้ายนี้ขอขอบคุณครอบครัวและเทวดาตัวน้อยที่คอยเป็นกำลังใจให้ผู้วิจัยทำวิจัยสำเร็จลุล่วงไปด้วยดี

วัสสา คงนคร

บทคัดย่อ

การวิจัยครั้งนี้ประกอบด้วยการผสมผสานของเทคโนโลยี 2 ระบบ คือ ระบบฟอร์เวิร์ดออสโมซิสและระบบการกลั่นผ่านเมมเบรนเพื่อนำกลับและทำเข้มข้นโปรตีนจากน้ำนึ่งปลาทูน่า โดยการศึกษาครั้งนี้ได้ศึกษาเงื่อนไขการดำเนินการของทั้งสองระบบที่มีผลต่อประสิทธิภาพการทำงานของระบบ ซึ่งประกอบด้วยความแตกต่างความเข้มข้นของสารดึง อัตราการไหล ความเข้มข้นของสารป้อนและอุณหภูมิ สำหรับระบบฟอร์เวิร์ดออสโมซิส และศึกษาความแตกต่างของอุณหภูมิ อัตราการไหลและความเข้มข้นของสารละลายโซเดียมคลอไรด์ที่ใช้เป็นสารดึงสำหรับระบบการกลั่นผ่านเมมเบรน

ผลการวิจัยพบว่าค่าฟลักซ์สูงสุดของน้ำและอัตราการนำกลับของโปรตีนมีค่าที่เหมาะสมที่ค่าความเข้มข้นของสารดึง 2 โมลของโซเดียมคลอไรด์ ที่อัตราการไหลที่ 100 มิลลิลิตรต่อนาที ที่ความเข้มข้นโปรตีน 200 มิลลิกรัมต่อลิตรของสารละลาย BSA พบว่า ค่าฟลักซ์สูงสุดเป็น 5.57 ลิตรต่อตารางเมตรต่อชั่วโมงและสามารถนำกลับโปรตีนได้ร้อยละ 69 สำหรับระบบฟอร์เวิร์ดออสโมซิส และสำหรับระบบการกลั่นผ่านเมมเบรน ผลการศึกษาชี้ให้เห็นว่าเมื่ออุณหภูมิสูงและอัตราการไหลสูงจะส่งผลให้ได้ค่าฟลักซ์ที่สูงขึ้น โดยการเพิ่มขึ้นของอุณหภูมิที่แตกต่างกันที่เหมาะสมอยู่ที่ประมาณ 50 องศาเซลเซียส โดยมีค่าฟลักซ์สูงสุดที่ 12.80 กิโลกรัมต่อตารางเมตรต่อชั่วโมง สำหรับการใช้พลังงานของกระบวนการได้ทำนายที่ความแตกต่างของอุณหภูมิทางด้านป้อนและความเร็วของของน้ำด้านสารป้อน พบว่า ค่าสัมประสิทธิ์อุณหภูมิ (TPC) แสดงผลที่ดีที่สุดในแง่ของการใช้พลังงานอย่างมีประสิทธิภาพประมาณ 188.6 วัตต์ ที่ค่าความเร็วและอุณหภูมิของสารป้อนเป็น 0.28 เมตรต่อวินาที และ 70 องศาเซลเซียส ตามลำดับ

สำหรับการประยุกต์ใช้กับน้ำนึ่งปลาทูน่า พบว่า กระบวนการฟอร์เวิร์ดออสโมซิสสามารถเพิ่มความเข้มข้นของโปรตีนสูงถึงร้อยละ 9 และมีค่าฟลักซ์เฉลี่ยที่ 2.54 ลิตรต่อตารางเมตรต่อชั่วโมง โดยค่าฟลักซ์มีแนวโน้มที่จะลดลงเมื่อความเข้มข้นของโปรตีนที่เพิ่มขึ้นเนื่องจากผลกระทบจากแรงดันของสารป้อนและการเกิดการอุดตันที่ผิวหน้าเมมเบรน

Abstract

The hybrid FO-MD in this research was composed of consisting of 2 systems that including the forward osmosis (FO) system and the membrane distillation (MD) system. This study was investigated the effect of difference draw solution concentration, velocity, temperature and feed concentration on water flux and BSA concentration.

The results were found that high water flux and high protein recovery rate at 2.0 M DS but high salt leakage as well which limited the process. The optimum flow rate on water flux and BSA concentrate was 100 ml/min. It was found that high flux of feed solution are amount 5.57 L/m^2h and obtained 69 % protein concentrate, respectively. Direct contact membrane distillation (DCMD) process was applied for brine solution recovery. The results can be indicated that highly temperature and velocity obtain higher permeate flux. The flux increases with an increase in temperature difference (ΔT=50). The maximum permeate flux is 12.80 kg/m^2.h The energy efficiency is quite average, the high value obtained for the relative heat lost suggest that this system can be competitive only in situations where some source of waste energy is available. It was found that the flux rate was in function with the temperature, CFV and temperature polarization coefficient (TPC). The best result in terms of energy consumption were obtained 188.6 W at CFV and temperature of 0.28 m/s and 70 °C, respectively.

Forward osmosis (FO) was employed in this work to recover and concentrate tuna cooking juice. FO process could increase the protein concentration up to 9% with an average permeate flux of 2.54 L/m^2h. The permeate flux however tended to decrease as protein concentration increased due to the impact of osmotic pressure of the feed and fouling on the membrane surface.

บทสรุปผู้บริหาร

(Executive summary)

1. บทนำ

ประเทศไทยเป็นผู้ส่งออกที่ใหญ่ที่สุดของอุตสาหกรรมทูน่ากระป๋องของโลกโดยมีอัตราการผลิตกว่า 456.5 ตันทูน่ากระป๋องต่อปี [1] และส่วนใหญ่อุตสาหกรรมกลุ่มนี้ก็เป็นอุตสาหกรรมหลักในภาคใต้ด้วยเช่นกัน ซึ่งในการผลิตแต่ละครั้งจะมีของเสียเกิดขึ้นประมาณ 25-30% เป็นของเสียในรูปของแข็งและประมาณ 35% เป็นของเสียในรูปของน้ำเสีย [2] อย่างไรก็ตามในน้ำเสียซึ่งเป็นน้ำนึ่งปลาทูน่าจะมีองค์ประกอบของโปรตีนประมาณ 4% ซึ่งการนำกลับโปรตีนจากน้ำนึ่งปลาทูน่าสามารถนำมาใช้เป็นโดยผลิตภัณฑ์ที่แหล่งที่มีศักยภาพของเปปไทด์ที่ออกฤทธิ์ทางชีวภาพคือ ต้านอนุมูลอิสระ ต้านจุลชีพ ลดความดันโลหิตสูง ฯลฯ [5-7] นักวิจัยหลายท่านได้คิดค้นและดำเนินการด้วยกระบวนการและวิธีที่หลากหลายในการแยกโปรตีนและทำเข้มข้นจากน้ำนึ่งปลาทูน่า เช่น colloid gas aphrons (CGA) Gel filtration chromatography และเทคโนโลยีเมมเบรน เป็นต้น [3, 4] เทคโนโลยีเมมเบรนเป็นหนึ่งในวิธีการที่นิยมใช้ เนื่องจากสามารถทำเข้มข้นโปรตีนโดยไม่มีการปนเปื้อนจากสารเคมีและความร้อนที่ทำลายคุณภาพของโปรตีน หรือการทำให้บริสุทธิ์ของความเข้มข้นสูง ในที่นี้ กระบวนการฟอร์เวิร์ดออสโมซิส (Forward Osmosis; FO) เป็นกระบวนการที่ถูกนำมาใช้ในการแยกน้ำให้บริสุทธิ์โดยอาศัยหลักการของความแตกต่างของแรงผลักดันที่โดยใช้แรงดันผ่านกระบวนการเมมเบรนกึ่งดูดซึม [10, 11,12, 13] ซึ่งการดำเนินงานของ FO ถูกนำมาประยุกต์ในหลายอุตสาหกรรม เช่น ใช้ในด้านเทคโนโลยีการอาหาร เช่น การเพิ่มปริมาณโปรตีน [14,16] การกลั่นน้ำทะเลให้บริสุทธิ์ [17] บำบัดน้ำเสีย [18] และการผลิตกระแสไฟฟ้า [19] สำหรับข้อดีของกระบวนการ FO คือเป็นการใช้พลังงานต่ำ เมื่อเทียบกับการรีเวิร์สออสโมซิส (Reverse Osmosis; RO) ที่ใช้อยู่ในปัจจุบัน [15]

ในการศึกษานี้เป็นการศึกษาการนำกลับโปรตีนด้วยการกรองด้วยเมมเบรนที่ใช้พลังงานต่ำและให้ผลตอบแทนสูง แต่ประสิทธิภาพของเมมเบรน FO มีข้อจำกัดในเรื่องของการนำกลับของสารดึง (Draw solution) มาใช้ประโยชน์และรั่วไหลของเกลือ (Salt leakage) ที่สูงขึ้นของเมมเบรนด้านสารป้อน ซึ่งการนำกลับของสารดึงนั้นคำนึงถึงใช้ค่าใช้จ่ายในการใช้พลังงานอย่างมีนัยสำคัญในการดำเนินงาน ดังนั้นเทคโนโลยีการกลั่นผ่านเมมเบรน (Membrane Distillation; MD) เป็นเทคโนโลยีทางเลือกที่มีกระบวนการแยกที่มีแนวโน้มในการกลั่นน้ำทะเลและอุตสาหกรรมอาหาร โดยข้อดีของ MD เมื่อเทียบกับกระบวนการแยกอื่นๆ คือ (1) อุณหภูมิที่ใช้ในการทำงานต่ำกว่าเทคโนโลยีอื่นๆ ซึ่งใช้เป็นพลังงานทางเลือก จากความร้อนเหลือทิ้งของ

อุตสาหกรรม (2) ใช้พลังงานต่ำในการขับเคลื่อนโดยอาศัยความต่างของอุณหภูมิ และ (3) สามารถแยกสารกลุ่มอิออน โมเลกุลคอลลอยด์ ได้ร้อยละ 100 ดังนั้นกระบวนการกลั่นผ่านเมมเบรนจึงเป็นกระบวนการที่เหมาะสมสำหรับการนำกลับของสารดึง และต่อกับหระบวนการ FO ได้

2. วัตถุประสงค์

วัตถุประสงค์หลักของการศึกษาในครั้งนี้ คือ

(1) การออกแบบและการติดตั้งระบบไฮบริดเทคโนโลยีเมมเบรนเพื่อนำกลับและทำเข้มข้นโปรตีนโดยใช้เยื่อแผ่นเมมเบรนที่ชอบน้ำและไม่ชอบน้ำสำหรับกระบวนการ FO และ MD ตามลำดับ

(2) เพื่อศึกษาปัจจัยของเงื่อนไขการดำเนินของระบบและผลกระทบที่เกิดขึ้นต่อประสิทธิภาพการทำงานของกระบวนการ FO และ MD ตามลำดับ

3.สรุปผลการทดลอง

การวิจัยครั้งนี้ประกอบด้วยระบบเมมเบรน 2 ระบบ คือ ระบบฟอร์เวิร์สออสโมซิส (FO) และระบบการกลั่นผ่านเมมเบรน (MD) โดยติดตั้งเป็นระบบไฮบริด FO/MD เพื่อศึกษาของผลการดำเนินงานของทั้งสองระบบที่มีผลต่อการแยกโปรตีนและทำเข้มข้นโปรตีนจากน้ำนึ่งปลาทูน่า โดยแบ่งการศึกษาเป็นขั้นตอนและสามารถสรุปผลการทดลองได้ดังนี้

1. การศึกษาผลของความเข้มข้นที่แตกต่างกันของของโซเดียมคลอไรด์ที่ใช้เป็นสารดึง (Draw Solution) ในการทดลองที่ความเข้มข้น 0.5 1.0 1.5 และ 2.0 โมล พบว่า ค่าฟลักซ์สูงสุดของน้ำและการนำกลับความเข้มข้นโปรตีนรูปของ Bovine serum albumin (BSA) สูง ที่ค่าความเข้มข้นของสารดึงที่ 2.0 โมล ของโซเดียมคลอไรด์ อย่างไรก็ตามการรั่วไหลของเกลือ (Salt leakage) ก็เกิดสูงด้วยเช่นกัน โดยพบว่าที่ความเข้มข้น 0.5 โมล ของโซเดียมคลอไรด์ จะแสดงการรั่วไหลของเกลือต่ำและพบว่าคุณภาพโปรตีนมีคุณภาพสูงกว่าที่ความเข้มข้นต่างๆ สำหรับกลไกการเกิดการอุดตันจะเป็นการอุดตันที่ผิวหน้าด้านสารป้อน ซึ่งสามารถใช้การล้างด้วยหลักการไฮโดรไดนามิกส์ คือ ล้างย้อนด้วยน้ำปราศจากไอออน (DI water) สามารถเพิ่มค่าฟลักซ์ได้ดีถึงร้อยละ 50 ของค่าฟลักซ์เริ่มต้น และการศึกษาผลของอัตราการไหลของสารป้อนและสารดึง ที่ 20 50 และ 100 มิลลิลิตรต่อนาที พบว่า การไหลของน้ำสูงและอัตรา

การนำกลับของโปรตีนสูงสุดที่ 100 มิลลิลิตรต่อนาที โดยมีค่าฟลักซ์สูงสุดที่ 5.57 ลิตรต่อตารางเมตรต่อชั่วโมง และสามารถนำกลับโปรตีนได้สูงถึงร้อยละ 69

2. การศึกษาผลของเงื่อนไขการดำเนินการในการนำกลับของโปรตีนจากน้ำนึ่งปลาทูน่าโดยกระบวนการฟอร์เวิร์สออสโมซิส พบว่า อัตราการไหลซึมผ่านได้เฉลี่ยที่ 2.54 ลิตรต่อตารางเมตรต่อชั่วโมง และอัตราการนำกลับของโปรตีนอยู่ที่ร้อยละ 9 ของน้ำหนักต่อปริมาตร โดยค่าฟลักซ์ที่ได้ลดลงจากการเปรียบเทียบกับการแยกด้วย BSA เนื่องจากการอุดตันจากปนเปื้อนจากสารอินทรีย์และอนินทรีย์ที่ละลายน้ำที่สะสมในรูพรุนของเยื่อแผ่นในลักษณะเจลและบนพื้นผิวเมมเบรน อย่างไรก็ตามในการล้างเมมเบรน จำเป็นต้องล้างด้วยน้ำ DI และสารเคมีเพื่อฟื้นฟูสภาพให้เมมเบรนสามารถทำงานมีประสิทธิภาพเท่าเดิม และจากผลของแบบจำลองทางคณิตศาสตร์ของการต้านทานเมมเบรน (Membrane Resistance Model) สำหรับการกรองน้ำนึ่งปลาทูน่าชี้ให้เห็นว่าเจลในรูพรุนเมมเบรนเป็นกลไกสำคัญในการอุดตัน
3. การศึกษาประสิทธิภาพการทำงานของกระบวนกลั่นผ่านเมมเบรนแบบ Direct Contact Membrane Distillation (DCMD) โดยศึกษาผลของอุณหภูมิด้านสารป้อนและอัตราการไหลเพื่อแยกสารประกอบโซเดียมคลอไรด์ที่ใช้เป็นสารดึงในกระบวนการ FO พบว่า ค่าฟลักซ์สูงสุดอยู่ที่ 13.8 กิโลกรัมต่อตารางเมตรต่อชั่วโมง ที่อุณหภูมิด้านสารป้อนมีค่า 70 องศาเซลเซียส และอุณหภูมิด้านหล่อเย็นคงที่ที่ 20 องศาเซลเซียส ที่อัตราการไหล 1.5 ลิตรต่อนาที โดยความสัมพันธ์ของความต่างของอุณหภูมิด้านสารป้อนและด้านหล่อเย็นกับค่าฟลักซ์ พบว่าความสัมพันธ์เป็นแบบเอกซ์โปเนนเชียล และเมื่ออุณหภูมิสูงและความเร็วที่สูงขึ้นจะได้ค่าฟลักซ์ที่สูงเช่นกัน

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Effect of different concentration of draw solution on BSA recovery by forward osmosis

Weerapong Bootluck[1,4] Watsa Khongnakorn[2,4*] and Wirote Youravong[3,4]

[1]Faculty of Environmental Management, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[2]Department of Civil Engineering, Facluty of Engineering, Prince of Songkla University Hat Yai, Songkhla, 90112 Thailand
[3]Department of Food Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[4]Membrane science and Technology Researh Center, Department of Physics, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
Corresponding author e-mail: watsa.k@psu.ac.th*

ABSTRACT

The protein utilization can be applied in medical and pharmaceutical industry. Mainly membrane technology is used for protein recovery and forward osmosis (FO) is proposed for the lower energy consumption and high yield production. The objective of this study is to optimize the draw solution concentration for protein recovery. The cellulose triacetate (CTA) membrane was used in FO unit and supplied with BSA 200 mg/L. The range of draw solution is between 0.5-1.5 M NaCl. The velocity of feed solution and draw solution were kept constant at 0.10 cm/min in co-current mode. The results were found that high water flux, high protein recovery rate and less salt leakage at 0.5 M NaCl. The optimization time for recover protein is 400 min to reduce salt leakage. The fouling behavior in the study is shown the reversible foulant can be enhancing flux for 50% by hydrodynamic force.

Keywords: Forward osmosis, Draw solution, Protein concentration

1. INTRODUCTION

Forward osmosis (FO) is emerging membrane separation process for water reuse and desalination [1, 2]. This process is naturally driving force using osmotic pressure difference across a semi-permeable membrane process [3, 4]. The application of FO membrane is used in food technology such as protein enrichment, and environmental technology such as wastewater treatment and power generation [5]. The advantages of FO process are low energy consumption, low temperature for degradation of food process and less membrane fouling compared with reverse osmosis (RO)[6].

Protein is biopolymer in nature and found in waste from food industry. The protein utilization can be applied in medical and pharmaceutical industry. The protein recovered for bioactive compound is degraded or denatured by heat and chemical reaction. Mainly protein recovery process is UF, NF technology [7]. In this study, FO is proposed for protein recovery under the low energy consumption and high yield production. The objective of this study is to optimize the draw solution concentration for protein recovery.

2. METHODOLOGY

2.1 Forward osmosis set-up and analytical methods

The FO system was set up as shown in Fig1. The membrane unit consisted of cell channels of 20 cm long, 10 cm wide, and 0.3 cm depth on both sides of membrane. The cellulose triacetate (CTA) membrane (HTI, Albanny, OR) occupied the area of 0.02 m^2. The pure water permeability of the CTA membrane tested in an RO mode was 2.1×10^{-12} m/s·Pa. The bovine serum albumin (BSA, purity 98%, MW 66 kDa, Sigma-Andrich) was used as a feed solution (FS) at 200 mg/L. NaCl (purity 99.9%, Ajax Finechem, Pty, Ltd) was used as a draw solution (DS). The range of DS was between 0.5-1.5 M or 29.22-87.66 g/L. The velocity of FS and DS were kept constant at 0.10 cm/min in co-current mode by peristaltic pump (EYELA MP-3N, Japan). The permeate flux was directly measured using digital balance (AND GF-3000, Japan)

connected to computer data record. By measuring conductivity using conductivity meter (WTW, LF318, and Germany), the osmotic pressure was indirectly calculated from eq. (1)

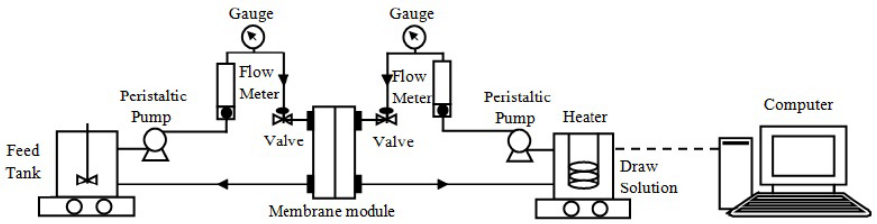

Fig1. Forward osmosis (FO) system.

$$\pi = nCRT \quad (1)$$

Where, π is osmotic pressure of a solution, kPa; n is the number of ions dissociated of one salt molecule; C is concentration, M; R is universal gas constant, 8.314kPa.l.mol^{-1}.K^{-1}; T is temperature, K.

The whole experiment was kept at constant temperature of 25±1°C. The sample was taken every 60 min and protein content was analyzed by Lowry method (1951). The water permeate flux was calculated from the change in weight of draw solution by following eq.(2)

$$J_w = \frac{\Delta \text{ Weight / Time}}{\text{Water density x Effective membrane area}} \quad (2)$$

As shown in Fig 2. the water flow usually flows from low concentration of feed solution to high concentration of draw solution across membrane while salt flows in opposite direction. This salt flow causes fouling.

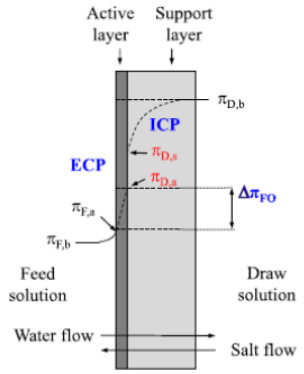

Fig 2. The fouling mechanism in FO membrane [4].

The internal concentration polarization (ICP) in the porous support layer from draw solution is a major problem in this process. The water flux (Jw) in FO can be expressed by the following equation;

$$Jw = A\,(\pi_{D,b} - \pi_{F,b}) \quad (3)$$

Where; A is water permeability coefficient (LMH), $\pi_{D,b}$ is the osmotic pressure of DS, kPa; and $\pi_{F,b}$ is the osmotic pressure of FS, kPa.

2.2 Membrane fouling and cleaning of FO

The BSA was used as feed solution at 200 mg/L. NaCl was used as draw solution at 0.5 M or 29.22 g/L. In order to test fouling, the experiment was run for 9 hours. Deionizer water was feed to clean the process at velocity 4.4 cm/min for 20 min. 1%citric acid and 0.5% NaOH were used as the chemical cleaning agents for 30 min at velocity 4.4 cm/min in both sides of membrane module. Membrane fouling morphology was characterized by scanning electron microscope (SEM-Quanta, FEI Quanta 400).

3. RESULTS AND DISCUSSIONS

3.1 Effect of different concentration of draw solution on water flux

The flux obtained from different concentration of draw solution is shown in Fig3. After BSA filtration, the flux slightly decreased and stayed constant at 650 min. The average of water flux was 3.6 LMH, 4.51 LMH and 5.27 LMH for 0.5 M, 1.0 M and 1.5 M, respectively. The higher the concentration, the higher the flux. The higher the concentration, the greater the osmotic pressure which is a driving force across the membrane [3]. Even though there was the supplement draw solution system was installed, draw concentration decreased with time. High water flux and low membrane fouling can be achieved by varying the operation condition and modified membrane surface [4].

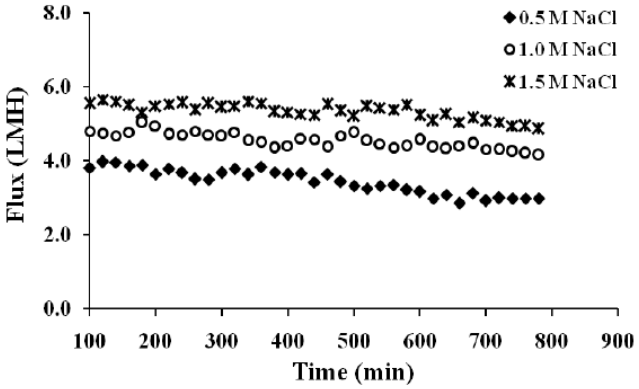

Fig 3. The evolution of water flux in the different concentration of NaCl during the experiments.

The salt leakage was observed in this study. The NaCl concentration in feed side was detected and shown in Fig 4. The lowest the draw solution concentration at 0.5 M causes the lowest salt leakages because the built-up rate of scaling is also the smallest [1]. The salt leakage is contaminated on protein a property that is acceptable at 0.36% (w/w) [8]. The curve shows the sudden increase in slope of the curve is define crisis point. At this crisis point, the scaling will be built up over the limit that the system can be operating. This crisis point is shown here on the curve to be at 400 min.

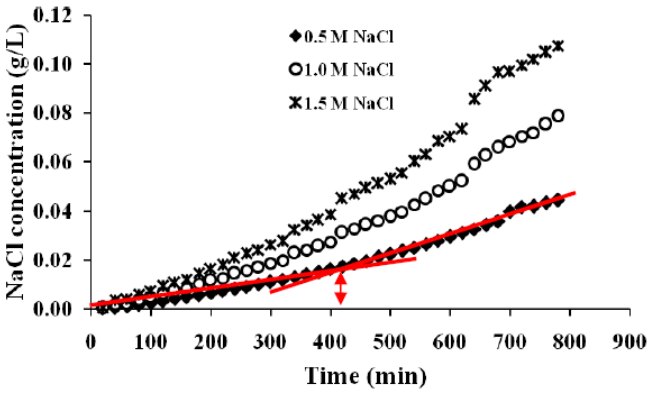

Fig4. Salt leakage concentration in feed solution with the different concentration of draw solution during the experiments.

3.2 Effects of different concentration of draw solution on protein concentration

Protein concentration at the different concentration of draw solution is shown in Fig5. The protein concentration obtained 0.44 g/L, 0.50 g/L and 0.55 g/L for 0.5 M, 1.0 M and 1.5 M NaCl, respectively. The protein concentration is increasing; the similar nearly of protein concentrate all the different concentration of draw solution. The protein recovered rate is increasing to 60%, 63% and 66 % for 0.5 M, 1.0 M and 1.5 M of NaCl, respectively

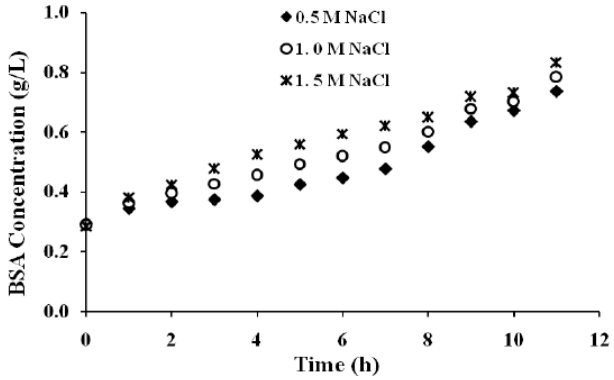

Fig5. The protein concentration at the different concentration of draw solution.

3.3 Fouling behavior and cleaning effect

After DI water was used to rinse the membrane in FO system to test the removal efficiency of foulant by shear force, the flux was enhanced for 50% (data not shown). The SEM images of the virgin and fouled membrane are shown in Fig6. The membrane was fouled by the complex compound from the BSA and NaCl that hardly to remove by shear force [9].

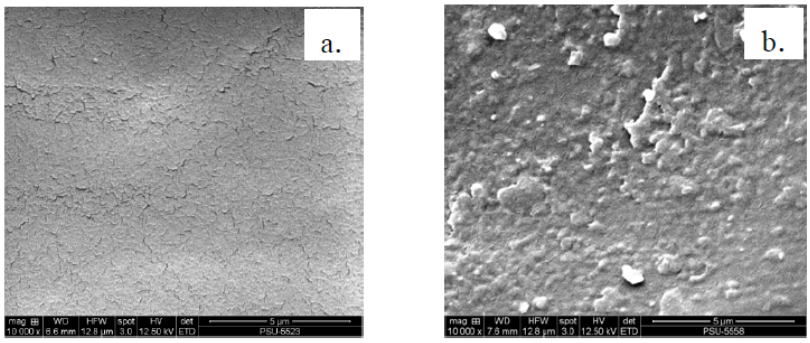

Fig6. Surface image of cellulose triacetate (CTA)
(a) Virgin membrane and (b) Fouled membrane after physical cleaning.

4. CONCLUSION

This study is investigated the effect of the different concentration of draw solution on water flux and BSA concentration. The results are found that the high water flux and high protein recovery rate at 1.5 M DS but high salt leakage as well which is limited the process. The optimize concentration of draw solution in this study is 0.5 M NaCl which shown the lower salt leakage behavior and obtain the good protein properties. The fouling behavior in the study is shown the reversible foulant can be enhancing flux for 50% by DI flushing. The limitation of this study is the salt leakage that will be prevent by the modification membrane surface for the next study.

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Effect of Operating Conditions of Direct Contact Membrane Distillation for Water Purification

Sothyreak Chhun*,***, Watsa Khongnakorn*,***,[1] and Wirote Youravong**,***
Department of Civil Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkla 90112, Thailand

Abstract

In this study, polyvinylidene fluoride (PVDF) hollow fiber membrane was applied with direct contact membrane distillation (DCMD) process on lab-scale, hollow fiber module designs in length of 24 cm with effective area of 0.01 m^2. This membrane also exhibited a mean pore size was about 0.1 µm, with contact angle of 90.4 ± 0.25° with water and the morphology of the hollow fiber membrane analysis by SEM was examined. The effect of operating temperatures and cross flow velocities (CFV) on permeate flux were investigated. During operating of DCMD process with 3.5 wt% of sodium chloride solution, it was found that the permeate flux is about 13.8 $kg/m^2.h$ was obtained with the CFV of 0.42 m/s at feed and permeate temperature 70 °C and 20 °C, respectively.

Keywords

Direct contact membrane distillation, Water purification, Cross flow velocity, PVDF hollow fiber membrane.

Introduction

Nowadays, purify water demand is dramatically increasing due to natural disaster such as flood, drought etc. Many researchers are seeking the new technology to challenge human demand. Membrane distillation (MD) is an alternative separation process with promising in desalination and industrial wastewater treatment. The advantages of MD compared to other separation process are: (1) lower operating temperatures than which applied in conventional distillation. The process performed at feed temperature is lower than the boiling point of water. Moreover, alternative energy such as solar, industrial waste heat and desalination waste heat can be employed to the feed side, (2) lower operating pressures than reverse osmosis, the operating pressure generally near the atmospheric pressure, and (3) over 100% (theoretical) rejections of ionic, macromolecules, colloids and other non-volatiles. MD has been employed for number of applications. Hou et al. [1] used MD to remove fluoride from the blackish groundwater. Gryta et al. [2] prepared capillary of polypropylene membrane in MD for separation of saline wastewater which containing NaCl and protein as well. In case of textile wastewater treatment, Wu et al. [3] studied the possibility of MD process to separate dyes from water and theirs reuse. The MD process was also applied for liquid-low level radioactive waste treatment, and the radionuclide was achieved [4].

The objective of this current research is to study the effect of operating conditions including cross flow velocity and feed temperature on the performance of direct contact membrane distillation (DCMD). The feed solution was 3.5 wt% of sodium chloride.

Experimental

Materials

PVDF hollow fiber was used (Econity, Co.Ltd, Korea). The characteristics of the membrane and the module are shown in Table 1.

* Department of Civil Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkla 90112, Thailand
**Department of Food Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, 90112, Thailand
***Membrane Science and Technology Research Center, Prince of Songkla University, Hat Yai, Songkla 90112, Thailand
[1]Corresponding e-mail: watsa.k@psu.ac.th

Table 1 Characteristics of PVDF Hollow Fiber Membrane

parameters	Value
Contact angle (°)	90.4
i.d of fiber, (mm)	0.7
o.d of fiber, (mm)	1.2
mean pore size (µm)	0.1
thickness (µm)	250
effective length (mm)	240
number of fiber	11
effective area (m^2)	0.01
i.d of module, (mm)	9
o.d of module, (mm)	15

Membrane characterizations

Contact angle

The contact angle of the PVDF hollow fiber membrane was measured by using a tensionmeter (OCA, DataPhysics Instruments Ltd., Germany). The membrane sample was immerged into distilled water before testing. The contact angle was calculating by computer software. Three times reading were measured and an average value was obtained.

Membrane wettability

Membrane distillation can take place whenever the membrane remains in dry which allow only water vapor go through the membrane. Liquid entry pressure (LEP) is the minimum pressure that will be employed onto feed solution before overcome the hydrophobic forces of the membrane and penetrate to the membrane pore size. LEP can be express as shown in Eq. 1.

$$LEP = \frac{2\gamma B\cos\theta}{R} \quad (1)$$

Where γ is surface tension of water, B is geometric factor, R is pore radius, and θ is contact angle.

SEM

Membrane morphology was analyzed for surface inner, outer and cross section structure of the PVDF hollow fiber membrane by Scanning Electron Microscope (SEM-JSM-5800LV, JEOL., USA). The membrane sample were frozen in liquid nitrogen, fractured to obtain fragments, and sputtered with platinum prior the SEM examination.

Direct contact membrane distillation set up

The schematic diagram of DCMD designed is shown in Fig. 1.

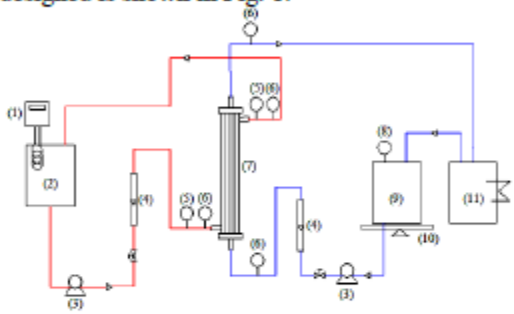

Fig. 1 Schematic diagram of DCMD process: (1) heater with temperature controller, (2) feed tank, (3) pump, (4) rotameter, (5) pressure gauge, (6) temperature indicator, (7) membrane, (8) conductivity meter, (9) permeate tank, (10) balancing, (11) chiller.

The membrane module was installed in vertically to omit the effect of free convection and removal air bubble [5]. NaCl solution 3.5 wt% was used as feed. The feeding pump was diaphragm pump (model UPRIGHT UP-7000, Taiwan). The inlet temperatures in the feed side were varied from 40-70 °C and controlled by heater (model ED JULABO, Germany). Simultaneously, the distilled water was cooled by chiller (model HAILEA HS-66A, Taiwan) to keep temperature constant at 20 °C. The temperatures at inlets and outlets in both feed and permeate side were displayed by temperature indicator. The circulation rate of the feed side was varied between 500-1500 ml/min using the laminar and interstitial flow for Reynolds number (Re) from 1170-2500. On the other hand, distilled water was fed into the lumen side of the membrane by diaphragm pump and controlled at cross flow rate at 500 ml/min corresponding to the Re of 1300. The flow rate of both feed and permeate sides were measured by rotameter (model LZM-15J, ZYIA, China). The ionic conductivity was

measured before and after the testing using Radiometer analytical conductivity meter (model LF 318, WTW, Germany). The distilled was collected in an over level tank sitting on a balance (AND, GF-3000, Japan) with accuracy ± 0.1 g and data record to PC by Data logger.

The permeate flux of the membranes J was calculated by the following equation:

$$J = \frac{\Delta W}{A.\Delta t} \quad (2)$$

Where J is the permeate flux (kg/m².h), ΔW is the quantity of distillate (kg), A is the inner surface area of the hollow fiber membranes (m²), Δt is the interval time (h).

The rejection coefficient R of hollow fiber membranes was determined according to the following equation:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (3)$$

Where C_f is the concentration of the feed side and C_p is the concentration of permeate side.

Calculation of Reynolds number

The Reynolds number normally defined in the following way:

$$Re = \frac{dv\rho}{\mu} \quad (4)$$

Where Re is the Reynolds number, d is the hydraulic diameter (m), v is the velocity (m/s), ρ is density of water (kg/m³), μ is the dynamic viscosity (Pa.s)

The Reynolds number of the feed and distillated introducing through the shell side and the lumen side were defined based on the Eq. (4). The linear velocity was employed for the lumen side based on inner diameter while the Interstitial velocity are used for shell side cross flow based on the outer diameter.

Interstitial = feed flow rate/open area through the shell side (5)

Linear = distilled flow rate / open area for flow through the lumen side (6)

Where Open area for flow through the lumen side A= nπ $(d_i/4)^2$, Open area for flow through the shell side

$$A = \frac{\pi D_l^2}{4} - 4\frac{\pi d_o^2}{4}$$

Result and Discussion

Contact angle

The contact angle measurement confirmed that the membrane used in MD experiment has high hydrophobic property (Table 1). As it was obtained, the highest contact angle as presented in Fig. 2.

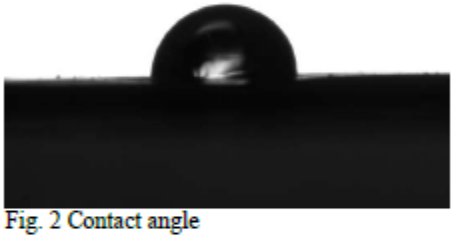

Fig. 2 Contact angle

SEM characterization

The SEM pictures, which show the morphologies of the inner and outer surface and cross section structure of the PVDF hollow fiber membranes, are presented in Fig. 5.

Effects of feed Temperature

Since MD is a selective membrane process driven by vapor pressure gradient across the microporous membrane. Feed temperature is one of the most important process factors. Fig. 3 presents permeate flux obtained in different temperature. Increasing feed temperature is significantly to enhance permeate flux. Wang et al. [6] figure out that the higher feed temperature and feed flow velocity not only help to improve the higher permeate flux but also lead to the stronger temperature polarization coefficient increasing [7].

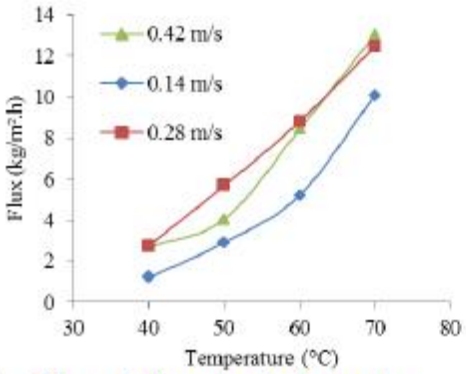

Fig. 3 Permeate flux versus feed temperature

Effects of velocity

Experiment was performed to study the effect of different flow velocities on the permeate flux. Fig. 4 shows the permeate flux as a function of velocities. This presents initially was low and increasing with increased the flow velocity between transient and turbulent. Yang et al. [8] indicated that high flow velocity can help to reduce the temperature polarization of the membrane surface and can be improve the driving force between the feed and permeate side. Otherwise, high flow velocity is in function of pump energy consumption.

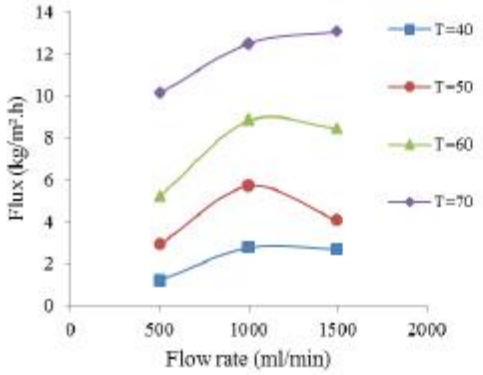

Fig. 4 Permeate flux versus flow rate with feed solution at 40, 50, 60 and 70 °C.

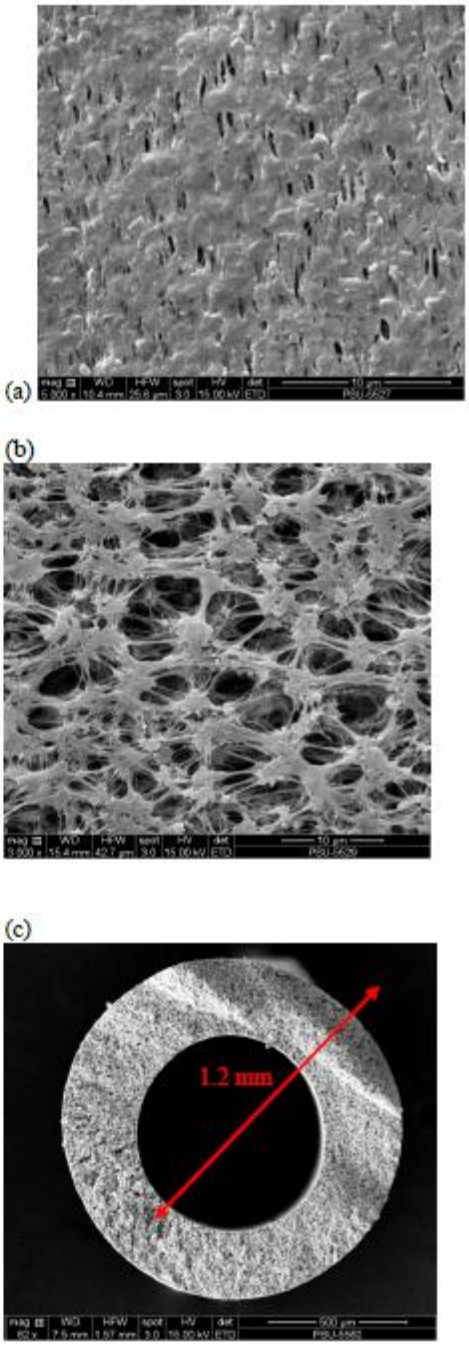

Fig. 5 SEM morphology shows of PVDF hollow fiber membrane, (a) inner surface, (b) outer surface, (c) cross section of membrane.

Comparison with other commercial membranes

Table 2 presents the performance comparison of our study with other reference. It was found that, the PVDF hollow fiber membrane in our work was approximately or even lower performance than other commercial PVDF membrane. Otherwise, configuration and characterization of the membrane also have significant on permeate flux.

Table 2 Membrane performance compared to other references

Ref.	Membrane	Feed side			Permeate side		Flux (LMH)	L/di
		Feed	Flow rate (l/min)	Feed temperature (°C)	Flow rate (l/min)	Permeate temperature (°C)		
[9]	PVDF hollow fiber	3.5 wt % NaCl	-	85	-	20	13.5	20 cm/1.8 mm
[10]	PVDF dual layer hollow fiber	3.5 wt % NaCl	2	90	0.1	16.5	55	17 cm/0.52 mm
[5]	PVDF hollow fiber	3.5 wt % NaCl	1.6 m/s	79.3	0.8 m/s	17.5	41.5	20 cm/0.6 mm
[8]	PVDF hollow fiber	3.5 wt % NaCl	3	50	0.4	25	9.92	22.5 cm/0.92 mm
This study	PVDF hollow fiber	3.5 wt % NaCl	1.5	70	0.5	20	13.8	24 cm/0.7 mm

Conclusions

The performance of the PVDF hollow fiber membrane in DCMD was studied in variations of the feed temperatures and flow velocities. It was found that the highest permeate flux 13.8 kg/m².h was obtained when the feed temperature was reached to 70°C with the flow velocity of 1.5 l/min, respectively. Future work will further to modify the membrane surface to enhance the membrane hydrophobicity which functional of permeate flux and long-terms performance.

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Energy consumption for Brine solution recovery in Direct Contact Membrane Distillation

Sothyreak Chhun[1,2,a*], Watsa Khongnakorn[1,2,b], Wirote Youravong[2,3,c]

[1]Department of Civil Engineering, Faculty of Engineering Prince of Songkla University, Hat Yai, Songkla 90112, Thailand
[2]Membrane Science and Technology Research Center, Prince of Songkla University, Hat Yai, Songkla 90112, Thailand
[3]Department of Food Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, 90112, Thailand
Email: [a*]sothyreakchhun@gmail.com , [b]watsa.k@psu.ac.th , [c]wirote.y@psu.ac.th

Keywords: Direct contact membrane distillation, Hollow fiber membrane, Temperature polarization coefficient, Evaporation efficiency, Energy consumption.

Abstract:

Direct contact membrane distillation (DCMD) process was applied for brine solution recovery. The energy consumption of the process was evaluated as varying feed temperature and cross flow velocity (CFV). The evaporation efficiency and energy consumption were also studied. The experiments was carried out using a hollow fiber PVDF membrane with pore size of 0.1 μm and NaCl 3.5 %wt as feed solution. The operating feed temperature and CFV were in range of 40 °C-70 °C and 0.14-0.42 m/s (laminar and transition flow region), respectively. The temperature and CFV of permeate were fixed at 20 °C and 1.97 m/s respectively. It was found that the flux rate was in function with the temperature, CFV and temperature polarization coefficient (TPC). The best result in terms of energy consumption and evaporation efficiency were obtained at CFV and temperature of 0.28 m/s and 70 °C about 188.6 W and 41.1 %, respectively.

Introduction

Direct contact membrane distillation (DCMD) is a membrane separation process driven by vapor pressure gradient across through the microporous hydrophobic membrane. DCMD has been studied to employ in water purification. It has found to achieve in part of treatment at lower temperature preferred which could be save for energy consumption and higher water quality.

Termpiyakul et al. [1] studied heat and mass transfer in DCMD under differences concentrations of brine solution. They found that the temperature polarization coefficient increased with increasing feed velocity and concentration. In addition, it is also operated at atmospheric pressure without need to supply pressure energy. As a result, feed temperature is considered as an important process parameter to produce vapor pressure. Evaporation efficiency and energy consumption were investigated by Deshmukh et al [2].

The objective of this paper was to determine the energy consumption and heat loss of the DCMD system for brine recovery and desalination for reverse osmosis (RO).

Theory

Polyvinylidene fluoride (PVDF) hollow fiber membrane was used to fabricate in 9 mm of diameter module with fibers diameter 1.2/0.7 mm, length 240 mm, giving an effective membrane area of 0.011 m^2. The membrane module was installed vertically to omit the effect of free convection and to remove air bubble [3]. Brine solution (NaCl solution 3.5 %wt) was used as a feed. The feed temperature and cross flow velocity (CFV, using the laminar and transition flow) were varied in range of 40-70 °C and 0.14-0.42 m/s, respectively. Simultaneously, the temperature of DI water circulated in permeate side was kept constant at 20 °C.

Heat transfer and mass transfer in membrane hollow fiber in DCMD

a. Heat transfer

Heat boundary is shown in Fig.1. Heat flux through the boundary layer due to convection mechanism can be defined as Eq. (1-2) [4]:

$$Q_f = A_o h_f (T_f - T_{fm}) \quad (1)$$

$$Q_p = A_i h_p (T_{pm} - T_p) \quad (2)$$

Where Q_f,Q_p arethe heat flux on feed and permeate sides, T_f,T_p are bulk temperature in feed and permeate sides, respectively. A_o,A_i are the total area based on outer and inner diameter, T_{fm},T_{pm} are the temperature at membrane surface on the feed and permeate sides, respectively.

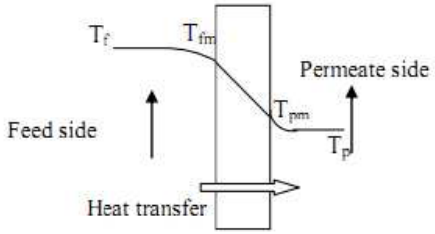

Fig. 1 Heat and mass transfer profile

Heat flux transferring through the membrane Q_m are heat convective heat flux and latent heat of water vapor transferred across the membrane. It can be determined using the following Eq. (3):

$$Q_m = A_i h_m (T_{fm} - T_{pm}) + J\Delta H_v \quad (3)$$

Overall the heat balance of the system

$$Q_f = Q_p = Q_m \quad (4)$$

The temperature of the feed (T_{fm}) and permeate (T_{pm}) at the membrane surface can be estimated as follows;

$$T_{fm} = T_f - \frac{(T_f - T_p)h_m + J\Delta H_v}{h_m + h_{f''}(1 + \frac{h_m}{h_p})} \quad (5)$$

$$T_{pm} = T_p + \frac{(T_f - T_p)h_m + J\Delta H_v}{h_m + h_p(1 + \frac{h_m}{h_{f'''}})} \quad (6)$$

Where $h_{f''} = h_f \frac{r_o}{r_i}$

$$h_m = \frac{k_m}{\delta_m} = \frac{\varepsilon k_g + (1-\varepsilon)k_s}{r_i \ln(\frac{r_o}{r_i})} \quad (7)$$

As seen in Fig.1 the temperature gradient is the temperature difference between the feed and permeate at the membrane surface of both sides. This effect can be defined by temperature polarization coefficient (τ), given by Eq. (8):

$$\tau = \frac{T_{fm} - T_{pm}}{T_f - T_p} \quad (8)$$

In membrane distillation process, heat transfer coefficients are always estimated using empirical correlations known as Nuselt number (*Nu*). For laminar flow (Reynolds number, *Re*<2100) and turbulent flow (*Re*>4000), the *Nu* can be estimated using Eq (9-10), [5] respectively;

$$Nu = 1.86(\mathrm{Re.Pr}.d_{hi}/L)^{0.33} \quad (9)$$

$$Nu = 0.023\mathrm{Re}^{0.6}\mathrm{Pr}^{0.33} \quad (10)$$

Where *Pr* is prandtl number, $Pr = C_p.\mu/k$. Further d_{hi} is the hydraulic diameter, k is the thermal conductivity, C_p is the specific heat capacity, and μ is the viscosity.

b. Mass transfer

The vapor flux can be expressed in terms of the transmembrane temperature difference [6]:

$$J = C\left(\frac{dP}{dT}\right)_{T_m}(T_{fm} - T_{pm}) \quad (11)$$

Where C is the membrane distillation coefficient, T_m is the membrane temperature, By assuming that the temperature polarization effect is similar on both sides of the membrane, T_m can be estimated by $(T_f+T_p)/2$ and $\frac{dP}{dT}$ can be evaluated by using Clausius-Clapeyron equation, combined with the Antoine equation, to calculate the vapor pressure:

$$\left(\frac{dP}{dT}\right)_{T_m} = \frac{\Delta H_v}{RT_m^2}\exp\left(23.238 - \frac{3841}{T_m - 45}\right) \quad (12)$$

Energy consumption

The heat transfer through the membrane was divided into two mechanisms, conduction across the membrane and the heat convective through the membrane. The heat transfer inside the membrane is given by [2]:

$$\begin{aligned} Q_m &= Q_v + Q_c \\ &= J\Delta H_v + h_m(T_{fm} - T_{pm}) \end{aligned} \quad (13)$$

Where, Q_v is the heat flow through the membrane, Q_c is the heat transfer by conduction across membrane as heat lost, ΔH_v is the latent heat of vaporization of water, and h_m is the heat transfer coefficient of porous membrane.

EE is the evaporation efficiency, defined as the ratio between the heat which contributes to evaporation and total heat exchanged by the feed. Thus, the EE can be expressed as Eq. (14):

$$EE = \frac{J\Delta H_v}{J\Delta H_v + h_m(T_{fm} + T_{pm})} \quad (14)$$

Energy consumption for feed, heating side and permeate, cooling side are estimated using the following equations;

$$Q_{hot} = V_f C_p(T_{f.in} - T_{f.out}) \quad (15)$$

$$Q_{cool} = V_p C_p(T_{p.out} - T_{p.in}) \quad (16)$$

Where, Q_{hot}, Q_{cool} are the energy consumption of heating and cooling sides (W), V_f, V_p are feed and permeate flow rate, $T_{f.in}$, $T_{p.in}$ are the feed and permeate inlet temperatures, $T_{f.out}$, $T_{p.out}$ are the feed and permeate outlet temperatures, respectively.

Result and discussion

a. Effect of hydrodynamic

The experiment was performed to study the effect of CFV as corresponded by *Re* on feed side. The outcome of evaporation efficiency (EE) as well as the heat transfer coefficient of feed side as varying Reynolds number is shown in Fig.2. It can be observed that the evaporation efficiency raise (around 26.89 % to 41.1 %) with the *Re* (ranging from 1800 to 2800). The same trend can be seen for the heat transfer coefficient which shows the efficiency of heat transfer from feed inlet to membrane interface. Both heat transfer coefficient and EE dramatically increased with increasing the *Re* in laminar region, and rose slightly until transition region occurred. The increased of *Re* corresponding to trans-membrane flux increase via heat transported through the membrane by convection and as a result, the evaporation efficiency of the process was developed. Ali et al [7] was employed *Re* up to turbulent regime, as a result 13.5 to 19.5 % of evaporation efficiency was improved. They revealed that it was not influence of mixing significantly compared to laminar regime.

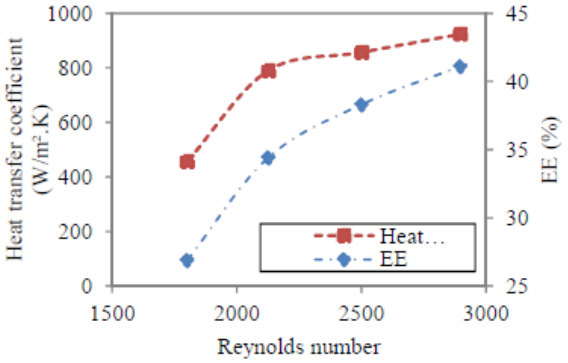

Fig.2 Effect of Reynolds number on evaporation efficiency and heat transfer coefficient

b. Effect of feed inlet temperature

The effect of feed inlet temperature on heat and mass transfer of DCMD was investigated by varying from 40 °C to 70 °C. In Fig.3 indicated the temperature polarization coefficient (TPC) as function of feed inlet temperature. It reveals that TPC decreased with increasing inlet feed temperature due to higher energy consumption to vaporization at the membrane surface at higher temperatures. As well as the total heat flux increased linearly with feed inlet temperature.

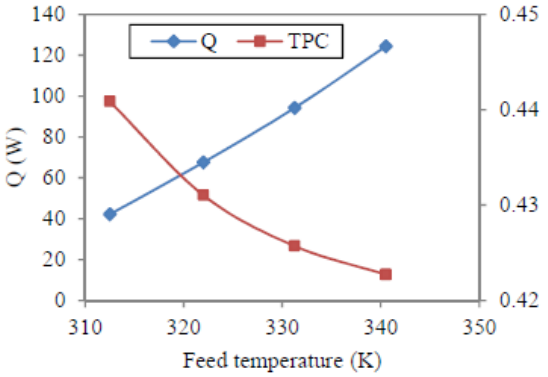

Fig.3 Total heat flux and TPC as function of feed inlet temperature

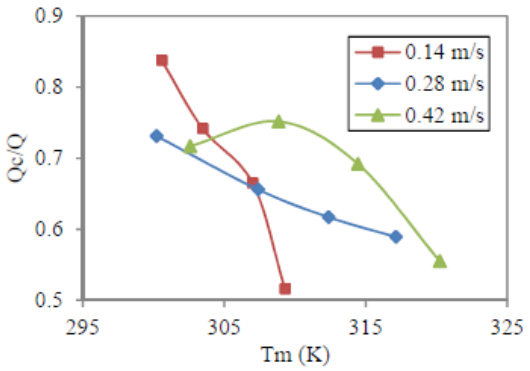

Fig.4 Heat-loss assessment of various velocities at Tm= 300-320 K

Fig. 4 shows that the ratios of the conductive heat loss to total heat flux. It decreased with increasing membrane temperature. These behaviors indicated that the high feed temperature was taken into account for less heat loss. Interestingly, the energy at the velocities with 0.14 m/s and 0.42 m/s were lost higher portion to heat conduct. Meanwhile, the cool side temperature played an important role in determination of energy consumption. Yang et al [6] are also compared conductive heat loss to total heat flux in various membrane properties. It has been reported that curly fibers loses a larger portion of heat to conduction. Table 1 and table 2 are illustrated the comparison of energy consumption, heat loss and evaporation efficiency in different temperatures and velocity. It can be seen that the best result in terms of energy consumption and evaporation efficiency was obtained using the CFV and temperature of 0.28 m/s and 70 °C, respectively.

Table 1 Energy consumption

Solution	CFV (m/s)	T_{fin} (K)	Energy consumption (W)	Heat loss Q_c (W)	%EE	Flux (kg/m².h)	TPC (τ)
NaCl 3.5 %wt	0.14	343	283.052	7586.52	48.45	10.11	0.27
	0.28	343	188.6	12613.52	41.11	12.33	0.42
	0.42	343	240.37	12690.32	44.50	13.8	0.45

Table 2 Evaporation efficiency

$Q_m=Q_v+Q_c$		Evaporation efficiency (%)
$Q_v=J\Delta H_v$	$Q_c=(k_m/\delta)(T_1-T_2)$	
7130.28	7586.52	48.45
8805.28	12613.52	41.11
10173.94	12690.32	44.50

Conclusion

In this study, feed temperatures and velocities were varied to investigate their effects on energy consumption for water purification using DCMD process. The experimental results reveal that the evaporation efficiency values were low, and they were lower continuously when the bulk temperatures decreased. It can be noticed that the best result in terms of energy consumption and evaporation efficiency was obtained at CFV and temperature of 0.28 m/s and 70 °C, respectively. The fluid dynamics studies of this performance would recommended to transition flow regime which could be provide a better flux, thus much lower energy consumption.

Acknowledge

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CONCENTRATION AND RECOVERY OF PROTEIN FROM TUNA COOKING JUICE BY FORWARD OSMOSIS

KHONGNAKORN W.[1,*], YOURAVONG W.[2]

[1]Membrane Science and Technology Research Center, Department of Civil Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[2]Membrane Science and Technology Research Center, Department of Food Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
*Corresponding Author: watsa.k@psu.ac.th

Abstract

Tuna cooking processing plants generate large amount of cooking juice containing a significant content of protein. Recovery and concentrating process of this valuable compound together with a low energy consumption process are of interest regarding full utilization concept and green process approach. Forward osmosis (FO) was employed in this work to recover and concentrate tuna cooking juice. FO process could increase the protein concentration up to 9% with an average permeate flux of 2.54 L/m^{2}h. The permeate flux however tended to decrease as protein concentration increased due to the impact of osmotic pressure of the feed and fouling on the membrane surface. Since tuna cooking juice consists of protein and minerals, membrane analyses indicated that fouling was more severe compared to the fouling caused by standard bovine serum albumin pure protein. However, the presence of minerals rendered it a quicker and lower energy process by comparison. These results indicated that FO is a promising technique in the recovery and concentration of tuna cooking juice protein.

Keywords: Forward osmosis, Protein recovery, Fouling, Tuna cooking juice.

1. Introduction

Canned tuna industry is one of the major industries in Thailand. Among canning industries in the country tuna canning has an almost 80 % share. In 2014 more than 55,500 tons of canned-tuna is exported and its 5-year growth rate is reported to be 19 % p.a. [1]. Hundred thousand cubic meters of tuna cooking juice each year is an unavoidable by-product, and is commonly considered as a liquid waste,

along with some solid waste, producing a very high BOD loading to wastewater treatment. Tuna cooking juice, however, contains approx. 4 % of valuable protein [2, 3] and can be potentially utilized as a source of bioactive peptides, e.g. anti-oxidative, antimicrobial, antihypertensive peptides [4-7].

Methods for protein separation and concentration from tuna cooking juice include: precipitation, colloid gas aphrons (CGA), gel filtration chromatography, freeze-drying, spray-drying, drum drying, and evaporation [8-10]. One common disadvantage of these methods is contamination from chemicals and degradations of protein at high temperature. For protein separation, however, membrane technology is preferred and recommended [4, 8]. Forward Osmosis (FO) is a process of membrane separating in which it establishes one natural driving force called osmotic pressure. FO process is more advanced than other processes in terms of lower membrane fouling, low hydraulic-pressure operation and energy consumption [11-13]. The process has been applied in food industry, desalination, wastewater treatment and power generation [14-17].

The objective of this paper was to recover and concentrate valuable protein compounds in tuna cooking juice by FO process. The process operating conditions were investigated under various draw solution concentrations, feed velocities and temperatures for their effects on bovine serum albumin (BSA) solution. The set of optimum operating conditions derived was employed in the experiment with tuna cooking juice to recover and concentrate protein.

2. Materials and Methods

In this section, the methods used in characterizing the properties of industrial tuna cooking juice will provided followed by description of type of FO membrane and the FO membrane system. Details on how to carry out the filtration experiment to study the effects of several important process conditions such as draw solution concentration, cross-flow velocity, temperature, etc., will also be provided. Experiments regarding the membrane surface fouling caused by protein and its characterization method will be also explained.

2.1. Preparation and characterisation of tuna cooking juice

Tuna cooking juice was obtained from Tropical Caning (Thailand) Public Company Limited, Hat Yai, Thailand. Numerous two-litre samples were prepared as homogeneous feed solutions, and stored at -20°C for further use. Those needed to be investigated would be thawed overnight for pre-treatment before the experiment; details can be found in Section 2.3.2.

Total protein and salt in the tuna cooking juice were determined using AOAC (1999) Method [18]. Total dissolved solids, pH, conductivity and COD were evaluated using the Standard Method [19]. Because of the interference of high NaCl concentration, organic concentrations in the feed solution and in the draw solution had to be measured by total organic carbon (TOC) by TOC Analyzer (Shimadzu TOC Analyzer TOC-L, Japan). Apparent viscosity was measured by capillary viscometer (Schott-instruments GmbH).

2.2. FO membrane and experiment setup

Cellulose triacetate (CTA) FO membranes were purchased from Hydration Technology Innovations (HTI, Albany, OR, USA). Approx. thickness of the flat sheet FO membrane is 50 µm, and the contact angle 64°. Embedded in the membrane is a polyester-mesh support layer. Performance of the membrane was characterized by its water permeability coefficient, pure water flux and salt rejection. The water permeability coefficient, salt permeability coefficient, and salt rejection were tested with RO mode.

Deionized (DI) water was supplied as feed solution at applied pressures ranging between 1-5 bars. The water and 10 mM of NaCl solution were respectively used for water flux testing and salt rejection testing [12]. The water flux (J_w), water permeability coefficient (A), salt permeability coefficient (B), and salt rejection (R) were calculated using Eq. (1) - (3), respectively.

$$Jw = \frac{\Delta\, weight}{water\ density \times effective\ membrane\ area \times \Delta\ time} \quad (1)$$

$$R = 1 + \left(\frac{(B)}{A(\Delta p - \Delta\pi)}\right)^{-1} \quad (2)$$

$$R = \left(1 - \frac{Cp}{Cf}\right) \times 100 \quad (3)$$

where A is in LMH.bar^{-1}; ΔP is the pressure difference across membrane, in bar; and Δπ is the osmotic pressure across membrane, also in bar; C_p and C_f are the salt concentrations, in mg/L of the permeate solution and the feed solution, respectively.

The FO system was set up as shown in Fig. 1. The membrane module unit consists of two c-section cells, one on the permeate - or draw side - and one in the feed side of the membrane, combining into a channel. Each section is 200 mm in length, 100 mm in width (inner side), and 3 mm in the inner depth. Feed solution and draw solution were conducted in co-current mode, each by a peristaltic pump (EYELA MP-3N). The draw solution concentration was maintained constant. Pressure, temperature, flow rate and salt concentration were measured, respectively by a pressure transducer (TR-PS2W-2bar Lutron), Thermo couple (SR100KB1.5S, Caho), flow meters (MR3000, Key Instruments), and a conductivity sensor coupled with its transmitter (M200, Mettler Toledo). Programmable logic controller (PLC) was used to detect and control the system. Signals from all four sensors were translated to digital values and recorded directly to the computer. The permeate flux was weighed by a digital balance (AND GF-3000) connected to the computer.

2.3. FO performance

2.3.1. Effect of operating conditions

Three important variables; draw solute concentration, cross-flow velocity, and temperature, will be investigated in this section. The water solution used for the

membrane feed side was composed of 1 g/L BSA and kept constant under three different variables.

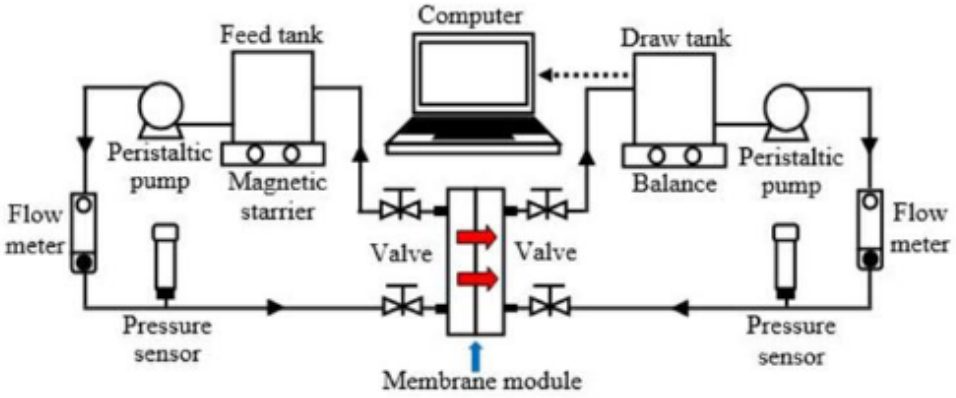

Fig. 1. Schematic of FO experimental setup.

Effect of draw solution concentration

The draw solution used NaCl concentrations of 0.5, 1.0, 1.5 and 2 M to investigate its effect. The FS and DS flows were operated in co-current mode at velocity of 20 mL/min on both sides and tested at a controlled room temperature of 25±0.5°C.

Effect of flow velocity

The draw solution here used a constant NaCl concentration of 2 M, and the temperature was controlled at 25±0.5 °C. The FS and DS flows were operated in co-current mode under varying cross flow velocities of 16.7, 41.5 and 83 m/min.

Effect of temperature

The NaCl concentration for the draw solution was maintained at 2 M, and the FS and DS flows were operated in co-current mode at a fixed 100 ml/min. Temperatures were, however, varied to be at 25±0.5 °C, 35±0.5 °C and 45±0.5 °C.

2.3.2. Concentrate of tuna cooking juice

Before analyses, each sample was thawed at 4°C overnight and then filtrated with cotton fiber (100 µm pore size) to eliminate suspended matters which would increase membrane fouling. The FO process used to filtrate the tuna cooking juice under study employed the maximum 2 M NaCl as draw solution; FS and DS flows at the maximum cross flow velocity of 100 ml/min; and a temperature of 25±0.5°C, since these conditions yielded the optimum result. Protein concentration from the tuna cooking juice was determined using Lowry method employing BSA as a standard.

2.3.3. Membrane fouling and their characterization

In order to test fouling, BSA was chosen as the model for protein without other compounds to compare with the tuna cooking juice. The experiment was run for 9 hours and 36 hours for the tuna cooking juice and the BSA, respectively. In each run, either for the juice or the BSA, when the ratio of flux and the initial water flux (J/J_o) reached 0.5, the experiment was halted. Deionizer water was fed to clean the process at a velocity of 44 m/min for 20 min. The process was then re-filtrated until J/J_o was 0.5 again. Once more the processed was paused to be cleaned by a regenerated chemical (1% citric acid and 0.5% NaOH) for 30 min at the same velocity of 44 m/min on both sides of the membrane module, and stopped finally when J/J_o approached 0.5.

Membrane fouling morphology was characterized by a scanning electron microscope (SEM-Quanta, FEI Quanta 400) coupled with energy dispersive spectrometry (SEM-EDS). Roughness of the membrane was characterized by an atomic force microscope (AFM, NanosurfeasyScan2). Fouling behaviour found was applied to evaluate using the resistance series model according to the method proposed by Zhang et al. [20].

3. Results and Discussion

The findings of this work will be discussed in the following subsections according to the scope of the experiments as described in section 2.0.

3.1. Characterisation of tuna cooking juice

The characteristics of tuna cooking juice are presented in Table 1. The feed solution is mildly acidic, low in viscosity, but high in total organic carbon (TOC) loading. The main valuable component is protein; having approx. 5% concentration. The total solid concentration is still high though it was cotton-filtrated. This high value correlates with high conductivity and high salt concentration.

3.2. Flux permeability and salt rejection of FO membrane

The pure water permeability of cellulose triacetate (CTA) forward osmosis (FO) flat sheet membrane was about 0.74 LMH/bar; and for the salt, 0.68 LMH. The CTA membrane NaCl salt rejection value of 88% is considerably higher than normal mean values of 50% in other RO membranes. In the FO mode experiment, the water flux and the reverse salt flux used DI water as feed solution, and 2 M NaCl as draw solution. The water flux value was 5.08 LMH while that of the reverse salt flux was 0.27 mol/gMH.

3.3. Effect of draw solute concentration

In the FO process operation, systematic experiments were conducted on the effect of draw solution's NaCl concentration, varying between 0.5 M and 2 M, on the water flux and the salt reverse flux. As NaCl concentration increased the water

flux also increased in the feed solutions using either DI water or BSA solution; increasing from 4.34 LMH to 6.63 LMH when using the former, and from 3.93 LMH to 6.11 LMH when using the latter. Greater osmotic pressure resulted from higher concentration rendered the water fluxes high, but it also increased salt leakage from the draw solution across the semi-permeable membrane [21]. The reverse salt when using DI water increased from 1.45 gMH to 3.57 gMH, and from 1.34 gMH to 3.53 gMH when BSA solution was used, and this is one of the phenomena that decreased the water flux. Internal concentration polarization (ICP) in the support layer was reported to be the cause of the decrease of the water flux [12]. From these results, the optimal draw solution concentration was concluded to be the 2 M NaCl because of the relatively higher flux and the salt reverse flux obtained.

Table 1. Physico-chemical characteristics of tuna cooking juice.

Composition	Tuna cooking juice		
	Feed solution	Concentrated	Diluted DS
pH	5.79	5.76	5.57
TOC (g/L)	30.28	60.28	0.24
Protein (w/v %)	5.51	9.02	ND.
Viscosity (mPa.s)	1.11	1.16	1.00
Salt concentration (mg/L)	11,390	19,957	13,357
Total solid (mg/L)	11,450	12,237	350
Conductivity (mS/cm)	16.2	19.0	132.2

Note: DS: Draw Solution and TOC: Total Organic Carbon.

3.4. Effect of flow velocity

Using the draw solution at 2 M NaCl concentration the effect of cross-flow velocity, varying between 16.7 to 83 m/min, was investigated on the water flux, both when DI water and BSA solution were used. Either using DI water or BSA solution, the water flux was observed to increase with increasing cross-flow velocity. However, the flux when using BSA initially increased slightly - from 4.57 to 5.47 LMH (62% to 74%) when flow velocity increased from 16.7 to 41.5 m/min - and then to 6.28 LMH (85%) at 83 m/min. These results when BSA was used are in the same pattern as that reported by P. Zhao et al. [22]. Altaee and Tonningen [23] had found that, in both the feed solution and the draw solution, high feed velocity increased the water flux and decreased fouling since hydrodynamic shear forces increased with increasing feed flow rate. From these results, the optimal flow velocity was concluded to be 83 m/min in order to obtain a higher flux because of high turbulence in the module. Higher cross flow velocity seemed to have decreased the boundary layer thickness and thus the decreased absorption of BSA on the membrane surface.

3.5. Effect of temperature

Temperature plays a significant role in the FO process; influencing the thermodynamic properties of both the feed solution (FS) and the draw solution (DS) [24]. When temperature increased from 25 °C to 45 °C the water flux increased from 6.78 LMH to 8.42 LMH when using DI water and from 6.28 LMH

to 7.63 LMH when using BSA solution. An increase in temperature decreases water viscosity and increases its diffusivity that affects the concentration gradient at the membrane surface. This result is similar to that reported by Phuntsho et al. [24] which studied the effect of working temperature on FO separation performance; that higher temperature induced higher initial flux, higher water recovery and higher concentration factors. These results revealed that BSA recovery and water flux increase with increasing flow velocity, temperature and DS concentration, and decreasing salt reverse flux. High water flux obtained seems to be mainly dependent on crossflow velocity that impacts on the hydrodynamic shear force at the membrane surface. Higher flow velocity decreases the boundary layer thickness and thus decreased absorption of protein at the membrane surface.

3.6. Concentrate of tuna cooking juice

Figure 2 presents the relationship of water flux, protien concentration and viscosity during membrane filtration of the tuna cooking juice. Initially the water flux decreased steeply and then tapered off to be rather constant around 2.54 LMH at time 200 min. At this value of water flux the rising protein concentration with time went up to 9%w/v. The viscosity gradually and slowly rose from 1.11 mPa.s at time zero to 1.16 mPa.s at time 300 min. The decreasing permeate flux with processing time is thus due to the impacts of inceasing protein concentration and increasing viscosity. The increased protein concentration at the membrane surface, concentration polarization, diffusity and fouling consequently increase the osmotic pressure on the feed side. As a result, the effective driven osmotic pressure across the membrane reduces.

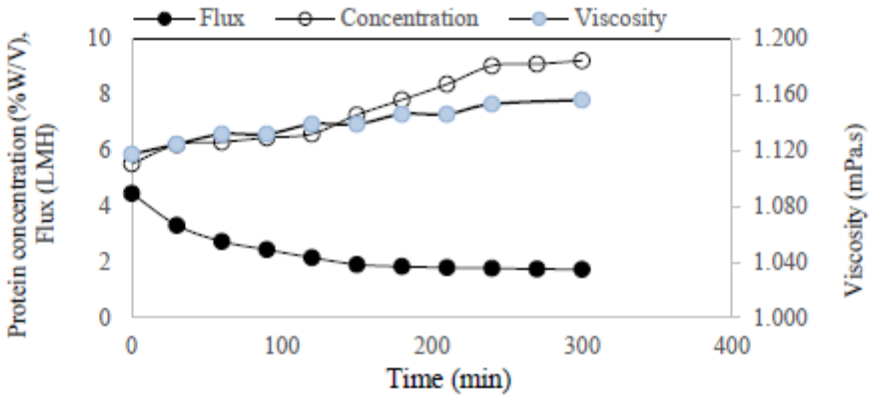

Fig. 2. Relationships of water flux, protein concentration and viscosity versus time of membrane filtration of tuna cooking juice.

3.7. Membrane fouling and their characterization

Figure 3 describes developments of membrane fouling in the FO filtration of BSA (upper part), and of the tuna cooking juice (lower part). The water flux in BSA solution filtration initially declined slightly then decreased more sharply but again tapered off. This behavior is in accordance with published mechanisms on organic fouling of BSA accumulation and adsorption on membrane surface [22, 25]. For

the tuna cooking juice filtration, the water flux decreased steeply from the beginning then became more or less asymptotic. The declining curves are clearly different since the tuna cooking juice contains much more organic and inorganic composites and compounds, and hence fouled up more quickly than BSA that contains only pure protein. The rapid decline in the case of tuna cooking juice was mainly attributed to the decrease of the effective driving force in FO caused by both the increasing salinity and viscosity on the feed side.

The phenomena of membrane fouling on the feed side, with the decline of flux with time, was due to accumulation on the active or selective layer. Membrane fouling from different types of foulant can be comfirmed by the resistance serie model Eq. (4). CTA membrane resistances of FO filtration: Total resistance R_t, Membrane resistance R_m, Pore plugging resistance R_p, and Cake layer resistance R_c, for both the BSA and the tuna cooking juice, are shown in Table 2.

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu(R_m + R_c + R_p)} \quad (4)$$

In Table 2, R_p was found much higher than R_c; indicating accumulation of organic compound (gel) which diffuses some organic molecules and accumulates in the pores while some part of protein is absorbed in the active layer. R_c, presented in inorganic form, and in terms of scaling, accumulates on the surface and blocks the surface pores. On the contrary, Zhang et al. [20] observed, for municipal wastewater treatment, that R_p was lower than R_c; indicating that the cake layer is the dominant contributor to membrane fouling in that case.

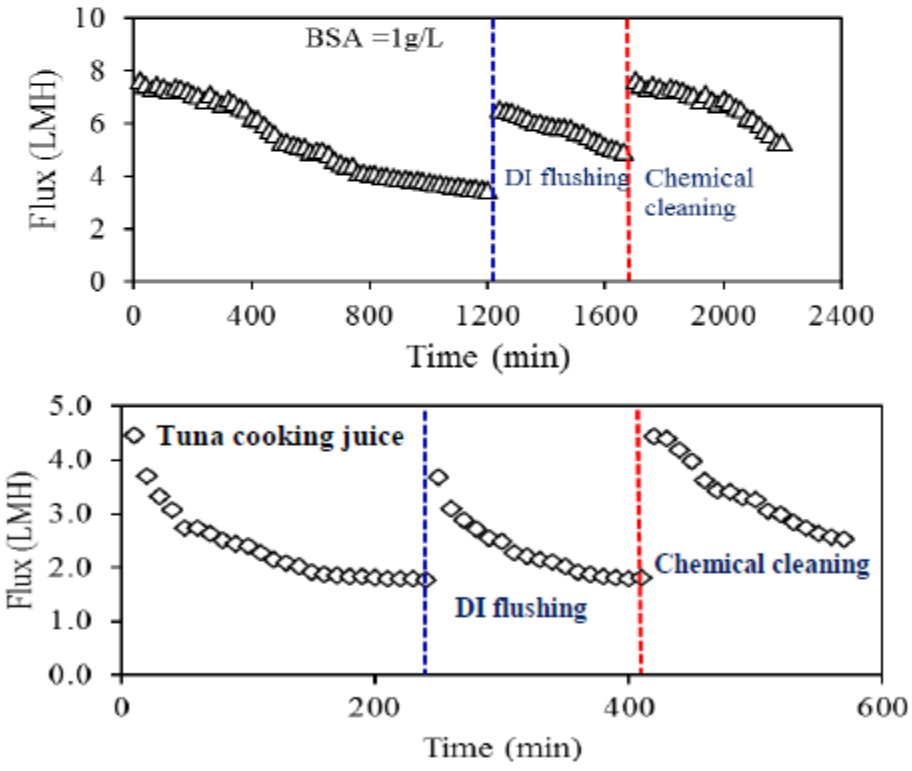

Fig. 3. Evolution of BSA (upper graph) and tuna cooking juice (lower graph) filtration.

The R_p is higher than R_c that indicated the accumulation of organics compound (gel) which diffuse some organic molecule and accumulate in the pore and some part of protein absorb in the active layer. The R_c present the inorganics form in terms of scaling, was accumulated and block the surface pore. In contrary, Zhang et al. [20] observed the R_p is lower than R_c which indicated that cake layer is the dominate contributor to membrane fouling for municipal wastewater treatment. Figure 4 illustrates SEM-EDX results confirming scaling accumulations at the membrane surface. Membrane scaling occurs due to inorganic crystallization of ionic calcium, sodium and magnesium from tuna bone degradation during the process.

Table 2. Membrane resistance of FO filtration for the BSA and the tuna cooking juice.

Type of solution	CTA membrane resistance of FO filtration (x 10^{11} 1/m)			
	R_t	R_m	R_p	R_c
BSA	17.28	6.97	9.29	1.02
Tuna cooking juice	29.53	6.97	21.19	1.37

Note: Subscripts t, m, p, and c for resistance R stand for, respectively, Total, Membrane, Pore plugging, and Cake layer

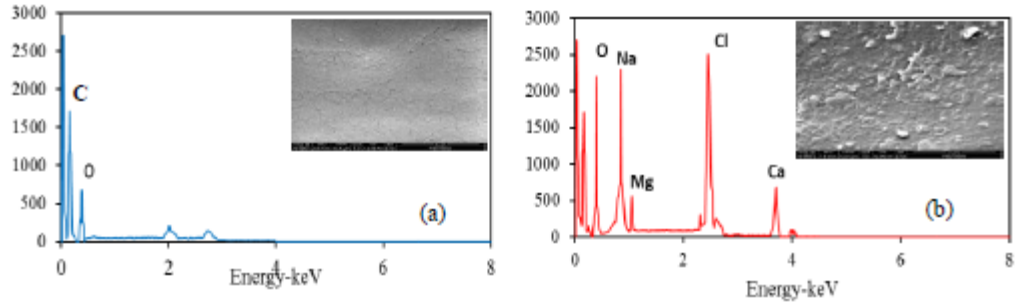

Fig. 4. SEM-EDX results of CTA membrane, (a) before and (b) after tuna cooking juice filtration.

In general, the water flux declines with time because of pore blocking and gel accumulation on the membrane surface; so-called external concentration polarization (ECP). However, membrane ECP fouling from the tuna cooking juice, besides tuna meat scraps, also composed of some water soluble materials such as gelatine and calcium.

The atomic force microscopy (AFM) used to study the characteristic of roughness of membrane surface revealed images of a smooth surface on the top layer, with a mean roughness (Ra) of 5.52 nm for a virgin membrane, and 12.25 nm for the fouled membrane (Fig. 5). Thus, roughness is correlated to accumulation of foulant or scaling; the more roughness value the more clogging, and hence the decrease in water flux.

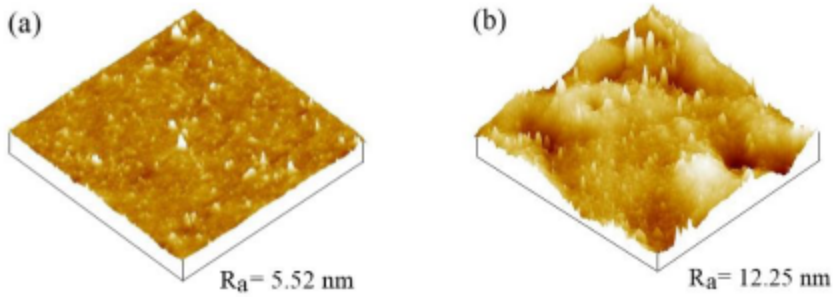

Fig. 5. AFM images of CTA membrane, (a) virgin membrane and (b) fouled membrane.

4. Conclusions

Effects of operation conditions and fouling on protein recovery from tuna cooking juice by FO process were investigated. The average permeate flux obtained was 2.54 LMH; and the protein recovery, 9% (w/v). The water flux output declined due to combined fouling from soluble organic and inorganic compounds, gel accumulation in the pore and scaling on the membrane surface. However, foulants require DI water flushing, and especially chemical cleaning to enhance the water flux. The membrane resistance model results for tuna cooking juice filtration indicated that gel in pore blocking is the dominant contributor to membrane fouling.

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ข้อคิดเห็นและข้อเสนอแนะสำหรับการวิจัยต่อไป

1. ข้อจำกัดของการศึกษาครั้งนี้ คือ การรั่วไหลของเกลือที่ไหลย้อนกลับทางด้านสารป้อน จึงเสนอแนะการพัฒนาเมมเบรนที่ช่วยลดการผันกลับของเกลือ

2. การพัฒนาสารดึงที่มีความเข้มข้นออสโมติกสูงและสารมารถนำกลับได้ง่ายและประหยัด