21R1-08

ปัจจัยที่มีผลต่อการลดลงของฟลักซ์ในกระบวนการนาโนฟิลเตรชันสำหรับน้ำทิ้งโรงงานผลิตแป้งมันสำปะหลัง

Factors Affecting Flux Decline in Nanofiltration Membrane Process for Treated Cassava Starch Factory Effluent

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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาปัจจัยที่มีผลต่อการลดลงของฟลักซ์และผลของความดัน ความเข้มข้นสารป้อน ความแรงประจุ (สารให้ประจุเดี่ยว Na^+ และสารให้ประจุคู่ Ca^{2+}) และการล้างด้วยสารเคมีด้วยกระบวนการแผ่นนาโนฟิลเตรชันสำหรับน้ำทิ้งโรงงานผลิตแป้งมันสำปะหลัง น้ำทิ้งที่ใช้ผ่านกระบวนการบำบัดน้ำเสียด้วยระบบยูเอเอสบี มีค่าซีโอดี (32,35 มิลลิกรัมต่อลิตร) และของแข็งละลายน้ำ (97 มิลลิกรัมต่อลิตร) การทดลองครั้งนี้ใช้ความดัน 3 ระดับ (138, 206.8, และ 413.7 kPa) ซีโอดีเข้มข้น 1500 ถึง 3000 มิลลิกรัมต่อลิตร และค่าความแรงประจุ 0.01 M และ 0.05 M (Na^+ และ Ca^{2+}) กับระบบการกรองแบบแผ่นด้วยระบบการไหลแบบปิดตาย ทำการศึกษาเพอร์มิเอทฟลักซ์ การกำจัดค่าการนำไฟฟ้า (เกลือ) และการกำจัดซีโอดี ผลการศึกษาพบว่า ปริมาณซีโอดีลดลง 82-93% สำหรับเกลือแคลเซียม การกำจัดความนำไฟฟ้าเพิ่มขึ้น (80-90%) ค่าการกำจัดซีโอดี ความนำไฟฟ้าและความดันเมมเบรนมีผลต่อการอุดตันของเมมเบรนอย่างมีนัยสำคัญ พบการอุดตันแบบเค้กและคอนเซนเตรชันโพลาไรเซชันในรูและผิวของเมมเบรน อย่างไรก็ตาม สามารถคืนกลับฟลักซ์ได้ด้วยการล้างด้วยสารละลายด่าง (1 wt% NaOH) และกรดซิตริกเป็น 91% และ 68% ตามลำดับ ดังนั้น เยื่อแผ่นนาโนฟิลเตรชันสามารถประยุกต์ใช้สำหรับการบำบัดน้ำทิ้งจากโรงงานผลิตแป้งมันสำปะหลังและช่วยลดมลสารที่เป็นพิษต่อสิ่งแวดล้อม

คำสำคัญ : แป้งมันสำปะหลัง; ฟลักซ์ลดลง; นาโนฟิลเตรชัน

Abstract

This research studies the factor affecting flux decline and effects of pressure, feed concentration, ionic strength (monovalent Na^+ and divalent Ca^{2+}), and chemical cleaning on NF membrane during treated cassava starch effluent wastewater. The factory effluent is treated by an Upflow Anaerobic Sludge Blanket Treatment plant (UASB) process. This effluent has high values of COD (3,235 mg/L) and TDS (97 mg/L) which make its used in the cassava starch process impossible. In this study, the experiments were carried out at three different pressure (138, 206.8, and 413.7 kPa), COD concentration (1500 to 3000 mg/L), and ionic strength 0.01 M and 0.05 M of two salts species (Na^+ and Ca^2) with a flat-sheet membrane (dead-end) module. The studied responses were permeate flux, conductivity rejection and COD removal. Results showed that, the COD reduction of 82-97% and the highest conductivity rejection (80-90%). The level of COD removal, conductivity rejection and transmembrane pressure were significant affected by fouling (cake formation) and concentration polarization resistance onto pore and surface membrane. Morever, the flux recovery for the chemical cleaning by using 1 wt.% NaOH and citric acid solutions had about 91% and 68% repectively. So that, NF can be applied for treated cassava starch effluent wastewater and reduced environmental pollutant.

Keywords : cassava starch; flux decline; nanofiltration

Introduction

The objective of this research was to quantify the importance of operational conditions on the rejection, membrane fouling and its dynamics was also evaluated by dead-end filtration using the cake filtration model for treated cassava starch factory effluent to obtain tap water quality. Fouling can be defined as a declination in flux with time of operation due to the increment of hydraulic resistance when al operating parameters such as trans-membrane pressure, flow rate, temperature and feed concentration are kept constant. The membrane fouling is dependent on several parameters such as membrane characteristics, feed properties, operational conditions and solution chemistry [1] and [2]. The original membrane filtration properties were characterized with deionized water to provide a baseline of membrane performance.

At desizing wastewater is largely responsible for the chemical oxygen demand (COD) load in the Cassava Starch industry wastewater. A larger portion of COD comes from degraded starch in desizing wastewater. Removing the starch from the wastewater by a nanofiltration process may reduce the environmental problem caused by the cassava starch factory. If the treatment is made in such a way that all starch components are removed from the wastewater, the treated water can be reused by the factory. This will give the factory an economic advantage.

In this study we have studied the fouling mechanisms involved in the nanofiltration of cassava starch effluent wastewater treated solution in order to find the testability of such solutions. The work has mainly been directed to cover how the different fouling mechanisms depend on the operating parameters and the performance of membranes.

Materials and Methods

Industrial effleunt tested

Wastewaters treated were coming from polishing effluent (finishing plant) of Upflow Anaerobic Sludge Blanket Treatment plant (UASB) for the cassava starch production. The charecterization of the effluent has been carried out and is presented in Table 1.

Table 1. Charecterization of cassava starch plant effluent

pH	COD (mg/L)	BOD (mg/L)	Conductivity (μS/cm)	TDS (mg/L)	Turbidity (NTU)	Total phosphate (mg/L)	TKN (mg/L)
9.51	3,235	1,588	2,680	97	158	17	22.4

Experimental device and nanofiltration membrane

Dead-end NF was carried out with an Amicron model 8400 (USA) stirred cell, modified to permit the use of pressures up to 487.63 kPa using compressed nitrogen (Fig. 1). Flat sheet membranes (ESNA1-4040 serial A154052, Nitto Denko, USA) with an effective membrane area of 45.38 cm^2 were employed and membrane sheets were stored with 1% sodium metabisulfite and kept in refrigerator at 4 ^oC to prevent bacterial inactivity. A magnetic stirrer bar was employed at a stirring rate of 300 rpm (LABNCO model LD – 12 Bioculture stirrers (USA) with speeding from 100-990 rpm), adjusted so that the depth of the vortex was no more than one third of the stirred solution level. Feed water was obtained from effluent wastewater treated of cassava starch industry on Ubon Ratchathani province was also studied.

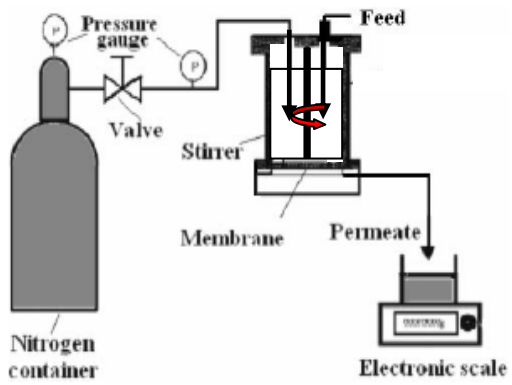

Fig.1 Schematic diagram of NF dead-end unit

Filtration experiments

NF experiments were tested as follow: rapid stirrer at 300 rpm followed with filtration period of 240 min, operating pressure varied at 138, 206.8 and 413.7 kPa. Feed solutions were prepared at a target COD (Chemical oxygen demand) concentration of 1500, 2500, and 3000 mg/L (0.01 M NaCl and 0.01 M $CaCl_2$ for ionic strength adjusted), respectively. Samples were conducted at 0, 5, 15, 30, 60, 90, 120, 180, 210 and 240 min, while flow rate was measured along with filtration period. The removal efficiencies of COD subsequently determined to compare the experimental results. The two type of chemical cleaning which were 1 wt.% citric acid solution and 1 wt.% sodium hydroxide solution for 30 minutes. The membrane permeability was

measured after each cleaning step by filtering DI water to evaluate the cleaning step performance and analysis of organic and inorganic content in both alkaline and acidic extrated solution was investigated in this study.

Analytical techniques

Feed solution used the effluence cassava starch wastewater from another cassava starch factory in Ubon ratchathani province. In the NF experiment, samples of feed solution and permeate were taken for analysis during filtration and the flow rate for permeate was measured when samples were taken for analysis over conditions experiment. The pH, conductivity, Total suspended solids, turbidity, total phosphate, TKN, BOD and COD analysis were performed according to Standard methods [3].

Resistances-in-series model

The parameters in Eqs. (1) and (2) were applied to identify the flux declination and the efficiency of membrane processes:

$$J_v = \frac{Q}{A} \tag{1}$$

where J_v is the flux through the membrane (LHM), Q is the permeate flow rate (LPM) and A is the effective membrane area (m^2). There are five parameters of membrane resistance-in-series model based on Darcy's law which were used to quantify their influences on flux decline [1]:

$$J_v = \frac{\Delta P}{\mu(r_m + r_{irr})} = \frac{\Delta P}{\mu(r_m + r_{cp} + r_g + r_{a1} + r_{a2})} \tag{2}$$

where J_v is flux through the membrane (m/hr), ΔP is the transmembrane pressure (Pa), μ is the dynamic viscosity (Pa-hr), r_m is the membrane hydraulic resistance, r_{cp} is the concentration polarization resistance, r_g is the gel layer resistance, r_{a1} is the weak adsorption resistance, r_{a2} is the strong adsorption resistance (all resistance per m). In this investigation, the osmotic pressure is considered into the concentration polarization.

Results and Discussion

1) Flux decline in the NF dead-end filtration during treated cassava starch factory effluent wastewater

Fig.2 shows the flux decline in the NF dead-end filtration. Before the membrane was introduced to the feed water solution, it was initially flushed with DI water to obtain the intrinsic resistance of membrane (r_m), subsequently, by using the Darcy's law and flux decline was obtained as the amount of total resistances. Based on Fig.2, the permeate flux continuously decrease with operating periods (min) and flux reached a steady state in 90 minutes (our seen at high COD concentration and $CaCl_2$ ionic strength). In this stage, the cake layer has achieved and equlibrium thickness where the hydraulic resistance of the diving pressure (TMP) and pH constanct. Even though the applied pressure was increased, there was still no significant change in the permeate flux at the equilibium stage. In order to recover the initial flux, hydralic and chemical cleaning (used NaOH and Critic acid) or backwash method has been applied onto the fouled membrane.

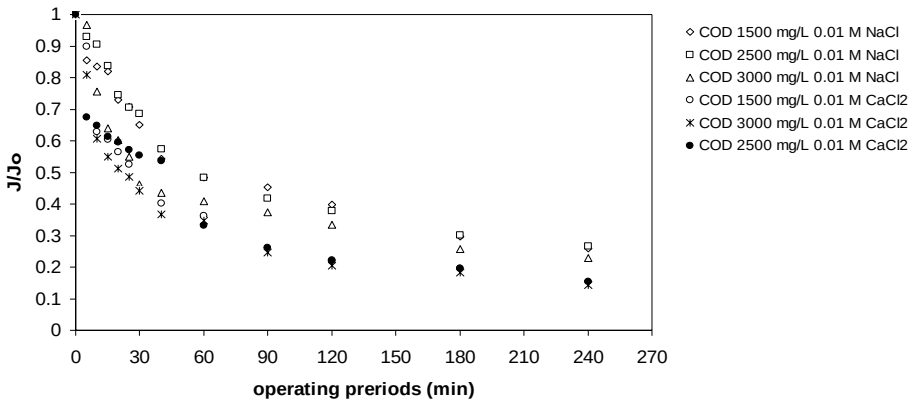

Fig. 2 Normalized flux decline at pH 7 and 413.7 kPa

In this study, flux declines as a function of time were observed at all concentration, pH, ionic strength and transmembrane pressure (TMP) varied during the effluent cassava starch wastewater. TMP is one of the critical operating parameters which influence the efficiency of NF membrane filtration and flux declination due to the effect of compaction of the concentration polarization or gel layer deposited cover the membrane process an important role in the polishig effluent by NF. All the three fouling mechanisms (concentration polarization, adsorption and deposition) were responsible for the flux decline. Initially, the particles from the cassava starch effluent mixture which consists of starch and starch by product (refered to the effluent has a high biological oxygen demand (BOD) and chemical oxygen demand (COD)), reached the membrane surface. These particles tend to occupy the smallest pore of the membrane surface and after all small membrane pores was occupied, then, the big pores of membrane surfaces start to receive foulant particles and the pores become blocked by steric mechanism. Simultaneously, some of the particles were adsorp onto the membrane surface engender to decrease permeate water flow rate. Finally, the cake layer begins to develop. Thus, theoretically, the main foulant found in the concentration polarilation or gel layer was effluent wastewater, whereas the irreversible foulant due to adsorption was mainly cassava starch effluent (residual wastewater after water treated)

The major observed contributors are adsorption and deposition. Adsorption is largely responsible at low-pressure operation while the deposition fouling effect is dominant at higher pressures, near or beyond the limiting flux when used cake formation model ($\frac{dJ_v}{dt} = -k_D J_v^2 J_v^*$) (see Fig. 3) by used sum squared error for prediction opproximate fouling model.

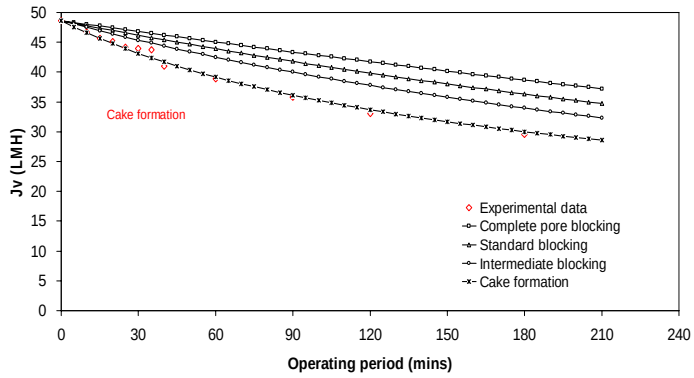

Fig. 3 Fouling model on NF membrane at COD conc. 3000 mg/L 0.01 M $CaCl_2$

2) Resistance-in-series in cassava starch factory effluent wastewater

The resistance – in –series model was used in this study to proposed the hydraulic resistances (m^{-1}) exhibited for chemical cleaning (1 wt.% citric acid and NaOH) during filtration. The total resistance and irreversible resistance are shown in Fig. 4. The membrane resistance, concentration polarization resistance and gel/cake layer resistance were similar for both types of chemical cleaning method (refered to weak and strong adsorption fouling). Feed solution was concentration 3000 mg/L (COD) ionic strength 0.01 M $CaCl_2$ and its adjusted transmembranepressure (TMP) were 138, 206.8 and 413.7 kPa. The total resistancce was about 11.3 m^{-1} (413.7 kPa), 13.22 m^{-1} (206.8 kPa) and 66.14 m^{-1} (138 kPa), respectively, which was probably due to the concentration polarization resistance more than the gel/cake layer resistance exhibited 0.12, 0.12 and 1.18 m^{-1} at 413.7, 206.8 and 138 kPa, respectively. It was presumed that the gel/cake layer resistance was dominant due to contribution by cassava starch effluent that has been dissolved in lower concentration and divalent ions adjusted, while the concentration polarization resistant was dominant due to contribution by suspended colliods or contaminated particles. Furthermore, the concentration polarization can be significantly reduced by regulating the permeate pressure, whereas the cake layer resistance can be significantly removed by hydraulic cleaning [4]. The irreversible fouling can be removed by cleaning with chemical solution for remove the irreversible foulant. The irreversible fouling in this investigation was divided into the weak and strong adsorption. The alkaline solution (NaOH) cleaning shows a higher removal of weak adsorption (not showed in Fig.4), which was 1.3% of the total resistance and its more compared to acidic solution (citric acid) cleaning due to the precipitation of solute onto the membrane surface and pores that and subsequently narrowing off the pores as this component is small enough not to be excluded by steric considerations. So that, the adsorptive fouling increases with concentration and decreases with molar mass of the effluent water, ionic strength, and pH at a given transmembrane pressure. The contribution of the concentration polarization is also dependent on concentration, ionic strength and pressure. However, the relative contribution of the resistance due to concentration polarization increases for the lower range of pressure and decreases for the higher range of pressure ,which it can be reduced by alkaline cleaning rather than acidic cleaning in organic element foulant domination.

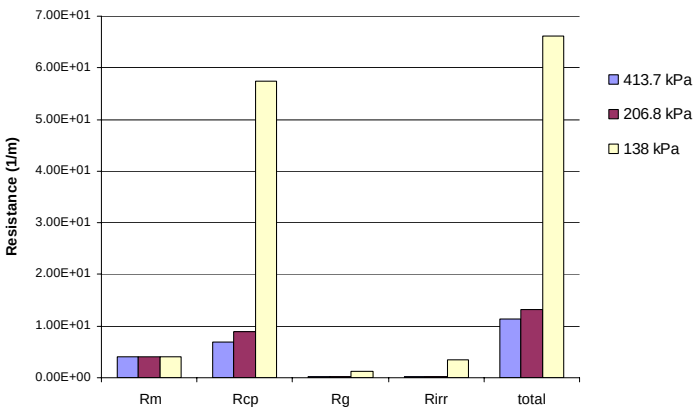

Fig. 4 Resistant in series with different pressure operation during NF filtration process

3) Effect of ionic strength

Fig. 5 shows the effect of salt concentration (mono and divalent ions, Na^+ and Ca^{2+}) on COD rejection at 3000 mg/L, pH 7.0 of permeate flux. With high salt concentration, the COD rejection was relatively low due to increased salt concentration on the membrane surface. Salt species (i.e. divalent Ca^{++}) had significant effects in high rejection more Na^+ ions. At high ionic

strength of 0.05 M, the COD rejection was not different in salt species (i.e. monovalent Na^{+} and divalent Ca^{++}) because the deposited and concentration polarization phenomenon into pore and surface mambrane. Conductivity rejection increased from 72% to 87% (shown in Table 2), indicating reduced charge repulsion between positively charged Na+, Ca++ and negatively charged NF membrane.

Table 2. Rejection of conductivity and COD during NF filtration

	Rejection (%)							
Time (min)	Conductivity	COD	Conductivity	COD	Conductivity	COD	Conductivity	COD
	I.S. 0.01 M NaCl		I.S. 0.01 M $CaCl_2$		I.S. 0.05 M NaCl		I.S. 0.05 M $CaCl_2$	
60 min	76	82	76	87	72	85	75	87
240 min	80	83	92	95	87	90	90	97

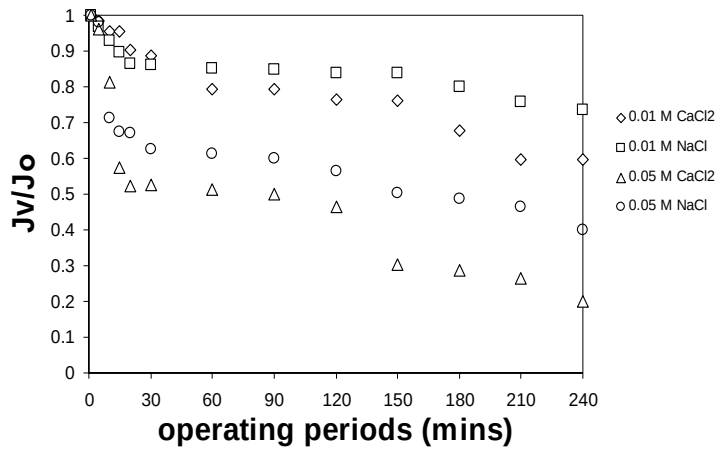

Fig. 5 Effect of salt concentrations on nomarization flux at 3000 mg/L COD feed solution

4) Flux recovery during NF filtration of cassava starch effluent treated

A cleaned membrane was measured through a filtration with DI water after each membrane cleaing step. The ratio of the permeate flux at room temperature (25^{0}C) of the cleaned membrane to the new membrane flux was used to evaluate the flux recovery [4], and the results are shows that cleaning with DI water could recover the membrane flux by about 43%. The hydraulic cleaning was found capable to clean the outmost and loose fouling layer (bulk layer) of the foulant on surface membrane. Furtermore, the flux recovery for the chemical cleaning by using 1 wt.% NaOH and citric acid solutions had about 91% and 68% repectively. Comparision of alkaline and acidic cleaning had an obvious effect on the recovery of the membrane flux. As reported by other researchers, the alkaline solution was more effective in removing the organic foulants both on the external and inner of NF membrane. In this study, the feed solution was rich in organic solutes (Starch, organic carbon, by referring to COD and BOD from). That is why the alkaline cleaning is more suitable in gaining the membrane flux.

Conclusions

A permeate flux was continuously withdrawn and hence, the concentration in the feed water was increased, and the conclusion can be made; 1) based on the steric condition, 2) the reversible foulant was dominated by starch effluent were found to be the major foulant in water modified of cassava wastewater, and finally, the gel/cake layer foulant contained of cassava and its divalent ions salt, and 3) COD concentration, transmembrane pressure and Ca^{2+} ions were important to declination of permeate flux onto NF for treated cassava starch factory effluent.

Acknowledgements

The authors would like to thank the Official of the National Research Council of Thailand (NRCT), for financial support. The authors are also grateful to the faculties for their assistance during experiments at the Ubon Agricultural and Energy Company, department of chemical engineering, Ubon Ratchathani University and Ubon Ratchathani Rajabhat University.

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