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Minimizing flux decline in surimi wash water ultrafiltration for protein recovery

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ABSTRACT

The constriction in implementing membrane technology in large scale operation is mainly due to fouling which resulting in flux decline. By applying possible combinations of operating conditions, such as transmembrane pressure and cross flow velocity, it is possible to minimize the flux declination. In this study, statistical experimental design was used in obtaining the maximum flux during surimi wash water ultrafiltration. The experiments were carried out in a low pressure continuous mode applying commercially purchased tubular polyvinylidene fluoride (PVDF) membrane. Various transmembrane pressures of 0.2, 0.3 and 0.4 bar and cross flow velocities of 0.0014, 0.0021 and 0.0028 m/s were implemented all through the study. The favourable condition was obtained using response surface methodology (RSM) as a tool. The best combination of operating conditions for minimum flux decline was found to be at a transmembrane pressure of 0.3 bar and cross flow velocity of 0.0021 m/s.

Keywords: Flux decline; Ultrafiltration; Fouling; protein-recovery

1. Introduction

Surimi wash water is the liquid waste obtained from surimi manufacturing process. Like fish meal production, surimi production also requires huge amount of water, the mean consumption of fresh water for washing purposes being about 27 m^3 per ton of surimi. The organic load of these waste waters is also fairly high as a result of the high protein content leached from fish flesh during washing. This wash water contains element which is recoverable and portentous enough in converting waste to wealth such as concentrated myofibrillar protein that can be obtained from mechanically deboned fish flesh washed with cold water [1].

Surimi process water carries several types of protein which are water soluble sarcoplasmic proteins, myofibrillar proteins, proteases, hemipigments and other potentially bioactive substances [2]. Reported, at least 5000 tons (on a dry-mass basis) of sarcoplasmic proteins are estimated to have been lost to wash water during washing of the 200,000 tons of surimi that were produced in Japan in 1990 which believed worth millions of money if the proteins were fully recovered to be applied in other technologies and industries [3]. The wastewater was reported to contain approximately 2–5 g/L of water-soluble proteins, being the total protein loss during the washing and dewatering about 30% of the deboned meat mass. It was estimated 2.5% of dry weight protein can be recovered from the total surimi production in which the proteins possess high commercial value [4].

Discarded wash water gives significant environmental impact as a result of direct waste water discharge to surface water. Recovering proteins from surimi wash water will decrease the negative environmental impact and the cost of waste disposal while at the same time, generate potential profits. Food and nutritional products, pharmaceutical products and industrial catalyst are several of many miscellaneous applications of protein based product which makes it very important to purify protein products in larger quantities [5]. The raising concerns on the negative impact of

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direct waste water discharge have led to research in protein recovery from surimi wash water.

Ultrafiltration is a pressure-driven membrane process. Driving force on the other hand, is a resultant of chemical potential difference or electrical potential difference which leads to transportation process across a membrane. In order to use ultrafiltration as an efficient bioseparation technique, all factors influencing solute transmission through the membrane need to be taken into account and properly utilized since the significant role of non-sized-based factors in ultrafiltration greatly widen its scope of application; therefore, separation depends on a large number of factors that makes process optimization essential [6].

Fouling can be simply indicated by flux reduction. In most cases, flux decline in protein ultrafiltration is ascribed to two major sources: concentration polarization and membrane fouling. During filtration process, fouling may occur in both inner pores and on the surface of membranes. This is because when a protein solution is pumped across the membrane surface, interaction between protein molecules with the membrane surface and inner pores may occur instantly as a result of the amphoteric nature of protein molecules and the hydrophobic nature of membrane material [7].

Fouling can affect the performance of filtration process by decreasing the quantity and quality of permeate. The quantity of permeate can generally be determined by computing flux and on the hand, quality of permeate can be determined using membrane rejection. Fouling itself, includes several phase of adsorption, pore plugging and irreversible fouling [8]. Adsorption occurs when attractive interaction between the membrane and the solutes or particles exists forming a monolayer of particles and solutes which can grow even in the absence of permeation leading to an additional hydraulic resistance. Pore plugging phase is mainly attributed by the relative size of the solute and membrane pore as well as the operating conditions.

Since optimization of this protein based ultrafiltration process is vital, the need to closely understand the fouling phenomena is essential. In accurately determining the effects of operating conditions, Rai et al. [9] used resistance in series model to analyse and predict the flux decline behaviour during ultrafiltration of mosambi juice. This model was used to quantify the resistance for each fouling stages.

Response surface methodology (RSM) provides essential information regarding the optimum level of each variable along with its interaction with other variables and their effects on product yield [10]. By applying RSM, the number of experiments was depleted without ignoring the interactions among the parameters. It is widely utilized since the multivariate approach of RSM enhances the possibilities of statistical interpretation and evaluates the relative significance of various factors affecting the process. Therefore in this study, RSM was implemented for multivariable optimization of surimi wash water ultrafiltration in recovering proteins during low pressure continuous mode.

2. Materials and methods

In this study, data were collected from experiments and statistically analysed for optimization. The simplified overall experimental and statistical processes that took place throughout this study are portrayed in flow diagram as shown in Fig. 1.

2.1. Feed solution

Surimi wash water used as feed was prepared from Shark Catfish (*Pangasius sp.*). The fish was minced and washed with icy water with a ratio of chilled distilled water (3): fish minced (1). The mixture of water and fish mince were later pretreated at pH 6 and centrifuged. The supernatant obtained was filtered using GF/C glass microfiber filter before been used as feed in ultrafiltration separation system. The raw, pretreated and ultrafiltrated surimi wash water was characterized for its physico chemical properties such as pH, total suspended solid (TSS), turbidity, chemical oxygen demand (COD) and total protein content.

2.2. Ultrafiltration equipment and procedures

Experiments were conducted using tubular cross flow filtration mode. This system was supported by SW-120 centrifugal pump which can withstand up to 100°C of pumped liquid and resist slightly acidic solution. Commercial tubular membranes made of polyvinylidene fluoride (PVDF) with molecular weight cut-off (MWCO) of 100 kDa, fiber diameter of 63.5 mm, flow length of 30 cm and effective area of 0.024 m^2 were used. The temperature of feed was controlled at about 40°C by simple heat exchanger apparatus.

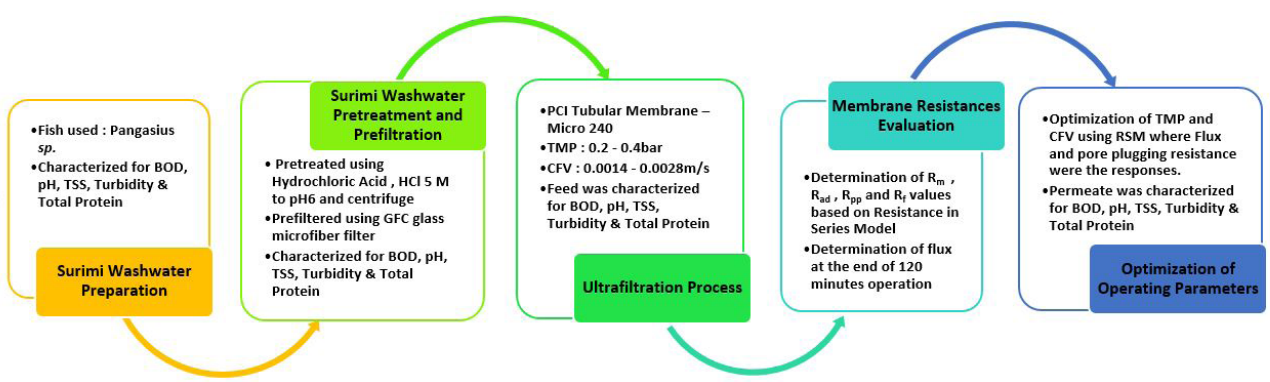

Fig. 1. Flow diagram for overall method in minimizing declination.

2.3. Determination of flux and pore plugging resistance value

From the ultrafiltration, flux decline analysis was carried out. Surimi wash water was filtered for 120 min and the total flux during the period was calculated. In extending the knowledge on the effects of operating parameters, pore plugging resistance, R_{pp} was quantified as an addition of responses besides flux, J_w. Based on resistance in series model, few resistances were determined along the filtration process; membrane resistance, adsorption resistance, concentration polarization resistance and cake resistance. This model has been widely used for the analysis of flux decline in UF and MF of proteins-based solutes which contain many macromolecules.

The overall flux decline is presented by the following phenomenological equations:

$$J_w = \frac{\Delta P}{\mu(R_m + R_{ad} + R_{pp} + R_c)} \tag{1}$$

2.3.1. Membrane hydraulic resistance (R_m)

The membranes were compacted through the filtration of distilled water under different pressure. The permeate flux was plotted against the operating pressure. The plots of J_w vs. pressure through origin will give the value of membrane permeability, L_p, which is represented by the slope of straight line. The membrane hydraulic resistance was calculated from the following equation:

$$R_m = \frac{1}{\mu Lp} = \frac{\Delta P}{\mu vw} \tag{2}$$

2.3.2. Adsorption resistance (R_{ad})

Adsorption on membrane surface by solute particles is dependent on the membrane-solute interactions. The surimi wash water was loaded in the membrane system without applying any pressure. After 120 min time interval, the cell was dismantled and the membrane was rinsed by distilled water several times such that loosely bound particles were washed off. From the slope of the flux versus pressure, the resistance of the membrane was calculated in which the new membrane resistance was.

$$R_m' = \frac{\Delta P}{\mu v \text{ad}} \tag{3}$$

From Eq. (3), the value for adsorption resistance was evaluated at the end of the particular time interval fixed. The values can be determined by:

$$R_{ad} = R_m' - R_m \tag{4}$$

2.3.3. Pore Plugging Resistance (R_{pp}) and cake formation resistance (R_c)

Degree of pore plugging is mainly contributed by the relative size of the solute and membrane pores as well as the operating conditions. In this experiment, the sizes of the solutes were varied from macromolecules to small molecules. The operating conditions analysed were TMP and CFV. These two main operating parameters influenced the intensity of turbulence flow and the effective driving force.

The value of permeate flux at the end of the interval was noted as, J_w. At the end of the experiments, the membrane was dismantled and rinsed with distilled water to discard any deposition on the membrane surface. By doing so, the magnitude of in Eq. (1) was eliminated. The rinsing took place with the same operating conditions; a transmembrane pressure, TMP of 0.2 bar and cross flow velocity, CFV of 0.0021 m/s to obtained the water flux, v_w.

$$v_w = \frac{\Delta P}{\mu(R_m + R_{ad} + R_{pp})} \tag{5}$$

All resistances were all computed at the end of the filtration processes. Pore plugging resistance was selected as response in RSM since it gives significant magnitude compared to other resistance which are believed to mainly contribute to the occurrence of fouling.

2.4. Experimental design and optimization

Four major steps in RSM namely experimental design, model fitting, model validation and condition optimization were all carried out. Based on these steps, RSM was used in studying the effects of various factors at different level and their influence towards each other. Table 1 summarizes the operating condition studied.

3. Results and discussion

3.1. Feed solution characterization

The surimi wash water used was characterized throughout the experiments. The physico-chemical properties for surimi wash water prepared are tabulated in Table 2.

From the table, it was clearly indicated that approximately 48.74% of total protein content in surimi wash water can be possibly recovered using ultrafiltration. Thus, based on our study, it was estimated that for every liter of wash water used, 155 mg of protein is recovered. It has been reported that at least 5000 tons (on a dry-mass basis) of sarcoplasmic proteins are estimated to have been lost to wash water during washing of the 200,000

Table 1
Experimental range and levels of the independent variables

Feed factors	Code	Variation levels		
		–1	0	1
Transmembrane Pressure, bar	X_1	0.2	0.3	0.4
Crossflow velocity, m/s	X_2	0.0014	0.0021	0.0028

tons of surimi that were produced in Japan in 1990 which is believed to worth millions of money if the proteins were fully recovered to be applied in other technologies and industries [11]. Recovery of protein will not only decrease the significant environmental impact of organic waste discarded but also improve the value of waste to potential wealth.

3.2. Permeate flux and all resistances values

Resistance in series model was adopted in ultrafiltration process because it is widely applied in the ultrafiltration of the mixtures of micromolecule solutes since it is particularly applicable for the flux decline analysis in ultrafiltration and also in microfiltration [12]. In this study, resistance in series model that considers membrane resistance, adsorption resistance, pore plugging resistance and fouling resistance had been applied to describe the effect of operating parameters of surimi ultrafiltration process. In addition, Tansel, Bao, and Tansel [13] developed a simple flux model to estimate the characteristics of fouling by resistances in series model. The model was used to estimate the characteristic of fouling in a laboratory ultrafiltration system with respect to fouling kinetics]. Values of resistances are tabulated as shown in Table 3.

Table 2
Results for characterization of raw, pretreated and ultrafiltered surimi wash water of *Pangasius* sp.

Parameter	*Pangsius* sp. Surimi washwater		
	Raw	Pretreated and prefiltered	Ultrafiltered
BOD, mg/L	631.00	272.00	1.50
pH	6.72	6.00	6.02
Total suspended solid, mg/L	12.31	2.32	0.01
Turbidity, NTU	1049.00	38.00	2.02
Total protein content, ppm	318	194	155

R_m is membrane resistance. Considering the fact that the system was deployed with specific crossflow velocity, membrane place in the system creates a magnitude of resistance. Since membrane was commercially purchased, the membrane characteristic was claimed as declared by the manufacturer. In evaluating the magnitude of membrane resistance, membrane resistance acted as baseline for all other resistance magnitude. Therefore, every resistance was divided with membrane resistance value so that the value of each resistance was all normalized.

R_{ad} is adsorption resistance. It existed due to deposition of foulants onto the membrane surface as soon as the filtration process started. Deposition of foulants took place throughout the whole process. The build up of foulants led to fouling resistance and pore plugging resistance – R_f and R_{pp}. R_{pp} occurred when foulant was deposited in membrane pore and later significantly reduce flux. R_f in contrast, is the irreversible fouling that engenders more resistance which is known as fouling resistance.

It can be clearly seen from Table 3 that the highest resistance magnitude was R_{pp}. This explained the behaviour of foulants which were embedded in the membrane pores and created a resistance which rapidly decreased the flux since resistance values were obtained by quantifying flux in the first place. When CFV was increased, the driving force which drove protein molecule increased. This made the protein molecules to accumulate on the membrane surface. Protein molecules acted as foulants that were deposited in membrane pores. This explained the higher magnitude of R_{pp} at higher CFV at 4.0 bar TMP.

Additionally, the second highest resistance in the ultrafiltration of protein recovery was R_{ad} followed by R_c and R_m. R_f is the resistance when irreversible fouling occurred. Irreversible fouling began when foulants were impregnated in the membrane which limits the membrane performance. Ironically, at higher TMP and CFV, R_f was not at its utmost magnitude. It was believed that foulants which accumulated onto membrane were scoured out by the higher driving force. The results on effect of operating parameters towards flux were investigated. Flux decline analysis of each operating conditions were computed to closely examine the fouling occurrence during ultrafiltration. Total flux for each combination of studied operating parameters – transmembrane pressure and cross flow velocity were computed and tabulated as shown in Table 4.

Table 3
Values of all resistances with respect to membrane resistance

TMP, bar	CFV, m/s	R_m / R_m	R_{ad} / R_m	R_{pp} / R_m	R_c / R_m	R_{total} / R_m	Flux, $m^3/m^2 \cdot s$
0.2	0.0014	1	1.961497	2.029691	1.504745	6.495933	2.35E-04
	0.0021	1	1.922858	2.079311	1.615984	6.618153	4.60E-04
	0.0028	1	1.939805	2.822804	1.450515	7.213124	3.17E-04
0.3	0.0014	1	1.961497	2.307619	1.325108	6.594225	3.47E-04
	0.0021	1	1.922858	1.952007	1.583582	6.458514	4.72E-04
	0.0028	1	1.939805	1.925298	1.570499	6.435602	2.37E-04
0.4	0.0014	1	1.961497	1.995323	1.736307	6.693126	3.30E+01
	0.0021	1	1.922858	1.771421	2.074837	6.769116	3.38E-04
	0.0028	1	1.939805	2.355748	1.666079	6.961632	2.19E-04

Table 4
Experimental design and result of central composite design

Run	TMP, bar	CFV, m/s	Total Flux, E-04 $m^3/m^2 \cdot s$	Pore Plugging Resistance, E+10 m^{-1}
	X_1	X_2	Y_1	Y_2
1	0.3	0.0021	4.72	2.88
2	0.4	0.0014	3.30	2.94
3	0.4	0.0021	3.38	2.61
4	0.3	0.0021	4.72	2.88
5	0.2	0.0014	2.35	2.99
6	0.3	0.0028	2.37	2.84
7	0.3	0.0021	4.72	2.88
8	0.3	0.0021	4.72	2.88
9	0.4	0.0028	2.19	3.48
10	0.2	0.0028	3.17	4.16
11	0.3	0.0014	3.47	3.40
12	0.2	0.0021	4.60	3.07
13	0.3	0.0021	4.72	2.88

3.3. Effects of operating conditions on flux

Effects of operating variables was studied using RSM and optimum operating condition of minimum fouling or flux decline was determined. The quadratic regression describes the effect of operating conditions towards flux and the relationship portrayed as shown in Eq. (6) below:

$$flux = -45.84\,TMP^2 - 3.12E06\,CFV^2 - 6892.86\,TMP.CFV + 39.90\,TMP + 148837.8\,CFV - 16.26 \quad (6)$$

Using Eq. (6), a 3D plot was built to show the main effect of the studied parameters and their interactions towards flux. The 3D plot is shown in Fig. 2.

Interactive effect of operating parameters towards membrane process optimization was clearly portrayed. Permeate obtained from the filtration process produced the clarified wash water with satisfactory physical and physico-chemical quality. With respect to flux, a complete factorial design and central composite design of response surface methodology can be used to determine the significant variables and optimum condition for ultrafiltration of surimi wash water which can be simply upscaled for industrial purposes.

3.4. Effects of operating conditions on pore plugging resistance

Based on all the resistances evaluated, pore plugging resistance was chosen as one of the response in RSM. This is as a result of the magnitude of pore plugging resistance which consist of up to 50% of total resistance throughout the filtration of surimi wash water. It was also stated that critical flux decline occurred due to pore plugging phenomena. The quadratic regression equation describing the effect of the process variables on the pore plugging resistance in terms of coded level is as follows:

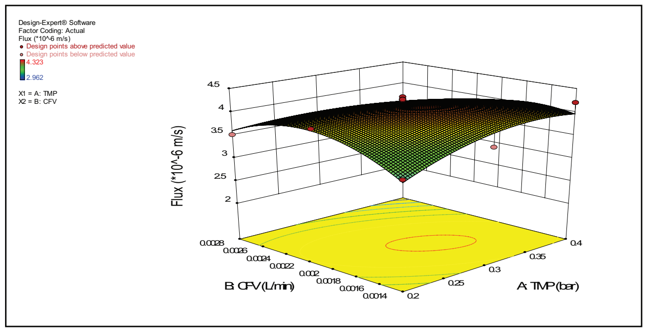

Fig. 2. 3D response surface with contour plot for total flux using surimi ultrafiltration.

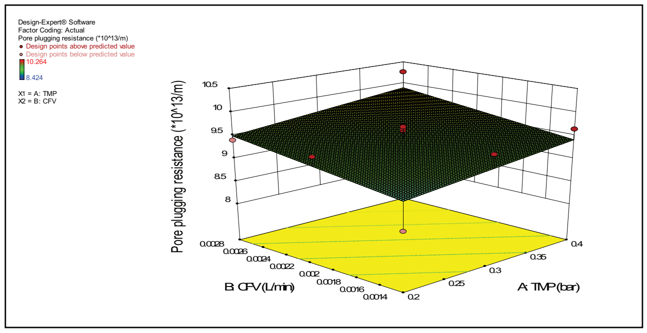

Fig. 3. 3D response surface with contour plot for pore plugging resistance.

$$R_{pp} = 1.97667\,TMP + 341.42857\,CFV + + 8.14938 \quad (7)$$

The relationship of operating parameters studied towards pore plugging resistance was determined to be a linear regression. Thus, for operating parameters optimization purposes, R_{pp} was not significant to be considered as response. The 3D plot for the equation is shown in Fig. 3.

It is believed that membrane fouling is a dynamic process starting with pore blocking which is a fast process observed at the beginning of UF for a clean membrane due to its high initial permeate flux, followed by continuous cake formation on membrane surface when accumulation and deposition of particles on the membrane surface begin and oil or gelatine layer is formed [14].

4. Conclusion

The effect of operating variables of transmembrane pressure and cross flow velocity towards the performance of surimi ultrafiltration precisely overall flux and pore plugging resistance was studied using response surface methodology. As the response surface methodology was used to investigate the interaction between operating conditions towards flux and pore plugging resistance, the optimum operating parameters were 0.3 bar TMP and 0.0021 m/s CFV. A significant relationship of these parameters studied was observed. Optimization of these multiple responses permitted the establishment of the operating conditions in giving maximum flux and minimum pore plugging occurrence. In the long run, fouling can be minimized and controlled whereby the ultrafiltration process can produced a high desired output.

In UF, a protein layer or dynamic membrane is formed on the membrane surface which dominates the subsequent behaviour of the membrane. The structure of the protein layer is affected by: the protein type and changes in pH or ionic strength that affect the apparent size of the protein; hydrodynamic conditions that increase concentration polarisation; the properties of the membrane [15]. In this particular study, the effects of hydrodynamic conditions namely transmembrane pressure, TMP and cross flow velocity, CFV were studied simultaneously.

In summary, increase of TMP and CFV values would significantly raise the production of permeate by increasing the flux at the beginning of filtration. Subsequently, acute fouling occurred as a result of larger driving force exerted on the membrane surface. The fouling mechanisms were then closely studied by quantifying the resistance magnitude that existed due to fouling. Resistances which are divided into few categories were portraying different phases of fouling and foulants behaviour during the filtration process.

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