

High Concentration Protein Ultrafiltration: a Comparative Fouling Assessment

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Abstract. In this paper, the predominant fouling mechanism via pH manipulation in gelatin ultrafiltration (UF) at constant operating pressure was studied. Two 30 kDa molecular weight cut off (MWCO) UF membranes with different hydrophilic/hydrophobic properties were tested at solution pH near gelatin isoelectric point (IEP), pH below and above gelatin's IEP. The resistance-in-series model was used to determine quantitatively the contribution of each filtration resistance occurred during gelatin UF. The governing fouling mechanisms were investigated using classical blocking laws. The results demonstrated that concentration polarization remain as dominant fouling resistance in gelatin UF, but exceptional case was observed at pH away from gelatin's IEP, showing that combined reversible and irreversible fouling resistances contributed around 57% and 37%, respectively to the overall fouling resistances. Under all experimental condition tested, permeate flux decline was accurately predicted by all the models studied. Fouling profile was fitted well with "Standard Blocking", "Intermediate Blocking" and "Cake Filtration" model for regenerated cellulose acetate (RCA) membrane and "Cake Filtration" model for polyethersulphone (PES) membrane.

1. Introduction

With the continuous improvement of membrane and the establishment of membrane technology as an efficient separation unit in a wide range of applications in food industry, gelatin is one of the animal products that has benefited greatly by UF process. The application of UF system to perform initial concentration in gelatin production has greatly improved the product quality, reduced emissions and labour costs as well as water usage. In view of the remarkable advantages offered by UF, the application of UF system as an alternative to the classical methods in gelatin concentration has been studied by several authors [1-3]. However, one of the major drawbacks in the application of membrane technology for protein concentration and purification is that the flux declines over time due to membrane fouling. While the instantaneous impact of fouling is observed through decreasing in permeate flux rate and selectivity, the ultimate effect may cause permanent loss in membrane's permeability due to irreversible fouling and the shorter membrane lifetime. Nevertheless, many researchers have studied protein fouling in UF but there is still major discrepancy in regards to the underlying mechanisms governing protein fouling and the fouling rate. Different flux decline mechanisms are suggested in the literatures, e.g., osmotic pressure governed flux decline [4], gel or cake layer controlled flux decline [5] as well as membrane pores blocking, such as, complete blocking, standard blocking and intermediate blocking. [6]. Similar types of fouling mechanisms are researched for other types of solutions, e.g. MF/UF of beer [7], cheese whey [8] and natural organic matters [9]. Hence, by studying fouling behaviour and its associate mechanism, protein fouling could be mitigated by minimizing the attractive forces between membrane-protein and protein-protein. This, in turn, would reveal higher performance characteristics (i.e. retention and flux) and yield higher operational



life during protein UF. Thus, the scope of the present study is to obtain quantitative data on the effect of solution pH on filtrate flux during gelatin filtration through RCA and PES membrane and to develop a more fundamental understanding of the fouling mechanism using these results.

2. Experimental

2.1 Materials

Ultrafiltration experiments were conducted using Ultracel® composite RCA membranes and Biomax® PES membranes, both provided by Millipore Corp. (Bedford, MA). Pharmaceutical grade gelatin (4 % w/v) obtained from Halagel (M) Sdn. Bhd. was used as model protein without further purification. The characteristics of gelatin used were presented elsewhere [10]. The pH of the feed stream was adjusted with dropwise addition of 3 M HCl or NaOH and measured with a Metler Toledo pH meter (model FG2 FiveGo™). All reagents used in the experiments were of analytical grade unless otherwise stated. Pure water was purified with Heal Force® UPW System NW UF Series by Nison Instrument (Shanghai) Limited with resistivity of 18 MΩ-cm.

2.2 Ultrafiltration Experiment

The filtration experiments were carried out by using a dead-end stirred cell filtration system (Amicon model 8200) from Millipore Co., USA at pressure 2 bars and temperature 40°C. Fresh membrane hydraulic resistance (R_m) was obtained by pure water flux measurement (J_o) using Equation (1)

$$J_o = \frac{\Delta P}{\mu R_m} \quad (1)$$

After that, the stirred cell were emptied and rapidly refilled with gelatin solution for UF process and total filtration resistance ($R_t = R_m + R_{cp} + R_{rf} + R_{if}$) was determined using Equation (2).

$$J_v = \frac{\Delta P}{\mu(R_m + R_{cp} + R_{rf} + R_{if})} \quad (2)$$

After 60 minutes, the filtration was stopped and was replaced by ultrapure water (UPW). Pure water flux after release of applied pressure (J_1) was measured using Equation (1) and concentration polarization resistance (R_{cp}) was calculated using Equation (3)

$$R_{cp} = R_t - \frac{\Delta P}{\mu J_1} \quad (3)$$

Next, the cell and the solution reservoir were fully emptied and gently rinsed to remove any labile gelatin. The cell was then filled with UPW and re-pressurized, and pure water filtration was again performed (J_2). The reversible fouling resistance (R_{rf}) was calculated using Equation (4)

$$R_{rf} = \frac{\Delta P}{\mu J_3} - \frac{\Delta P}{\mu J_2} \quad (4)$$

The membrane was then rinsed in a 0.1 M NaOH solution so that weakly adsorbed gelatin on the membrane surface could be desorbed and the pure water flux was again measured (J_3). The irreversible fouling was calculated using Equation (5).

$$R_{if} = \frac{\Delta P}{\mu J_3} - \frac{\Delta P}{\mu J_0} \quad (5)$$

The equation for classical blocking laws as shown in table 1, adapted from [11] was used to identify the predominant fouling mechanism occurred during gelatin UF at different pH. The permeate volume versus time data were fitted into the model using Matlab R2007a and the best fit parameter was obtained by minimizing the sum of square residuals (SSR).

Table 1. Classical Blocking Laws.

Classical Blocking Laws	Equation	Parameters
Cake filtration	$V = \frac{1}{K_c J_o} (\sqrt{1 + 2K_c J_o^2 t} - 1)$	$K_c (s/m^2)$
Intermediate blocking	$V = \frac{1}{K_i} \ln(1 + K_i J_o t)$	$K_i (m^{-1})$
Standard blocking	$V = \left(\frac{1}{J_o t} + \frac{K_s}{2} \right)^{-1}$	$K_s (m^{-1})$
Complete blocking	$V = \frac{J_o}{K_b} (1 - \exp(-K_b t))$	$K_b (s^{-1})$

3. Results and discussion

3.1 Resistance-in-series model

The total filtration resistance (R_t) was maximum at pH 5.3, minimum at pH 4 and intermediate at pH 6.8 as shown in table 2. Particularly, irreversible resistance (R_{if}) was fifth fold higher at gelatin's IEP. At IEP, gelatin molecule has net neutral charge, therefore more easily precipitated or adsorbed and the deposited layer is relatively compact. Kilduff et al. [12] detected that the specific cake resistance was highest at neutral pH due to negligible electrostatic repulsion among foulants, which was in good agreement with our study.

Table 2. Quantification of various fouling resistance at different pH for RCA and PES membrane.

pH	Membrane Type	R_{cp}/R_m	R_{rf}/R_m	R_{if}/R_m	R_t/R_m
pH < gelatin's IEP (pH 4)	RCA	20.3	0.50	0.12	20.9
	PES	3.02	3.48	1.84	8.34
pH near to gelatin's IEP (pH 5.3)	RCA	40.7	0.51	0.55	41.8
	PES	45.30	4.19	3.45	52.9
pH > gelatin's IEP (pH 6.8)	RCA	17.1	0.21	0.11	17.4
	PES	5.14	2.10	1.74	8.98

Generally, the fouling resistance trend is observed at $R_{cp} > R_m > R_{rf} > R_{if}$. R_{cp} contributed to a greater extent (> 91%) to the total filtration resistance during gelatin UF except for PES membrane at pH 4. High R_{cp}/R_m ratio will favor gel forming tendency or increase osmotic pressure at membrane-solute interface and cause decreased in driving force [13]. Thus, it is suggested that improved mass transfer or hydrodynamic conditions at the membrane surface would be beneficial to achieve higher flux. For PES membrane, combination of R_{rf} and R_{if} show contribution of 57% at pH 4 and 38.5% at pH 6.8 to the final global resistance, higher than 7% at pH 5.3. At pH near gelatin's IEP (pH 5.3), R_t/R_m and R_{if}/R_m for PES membrane were significantly higher compared to RCA membrane. The main driving force was hydrophobic attraction between PES membrane and gelatin. At pH 4 and 6.8, R_t/R_m and R_{if}/R_m for RCA were comparatively higher for PES membrane. Similar observations were reported by Luey et al. [14] during bLG adsorption on hydrophilic and hydrophobic silicon surfaces. They found that electrostatic forces play a major role in the protein adsorption on hydrophilic surfaces while non-electrostatic interactions dominate on hydrophobic surfaces. At pH 4, the surface charge of the gelatin was positive and the membrane surface was negatively charged, so electrostatic attraction result in a rigid cake on the membrane surface. Whereas at pH 6.8, electrostatic repulsion induced by the like-charged membrane and gelatin (negative). In addition, the stronger electrostatic repulsion between already adsorbed gelatin fouling layer and freshly transported gelatin from the bulk – further reduces protein deposition on the surface and inside the pores. This explain high R_{cp}/R_m and R_{if}/R_m values at basic pH and indicates that gelatin fouling relies more on electrostatic forces rather than hydrophobic forces at pH away from gelatin's IEP. Therefore, it can be inferred that in electrostatic interactions

controlling scenario, enhancement in membrane hydrophilicity does not beneficial in minimizing fouling phenomena in gelatin UF.

3.2 Classical Blocking Models

An example of fitting experimental data and model prediction is shown in figure 1 and figure 2 for RCA and PES membrane at pH 6.8. Table 3 shows the SSR values and the best fitted parameters for both membranes at varying pH. The bold sign in the table shows the dominant fouling mechanism. In general, membrane hydrophilicity affected the nature of fouling mechanism occurred during gelatin UF. For RCA membrane, it was found that the fouling mechanism is affected by the change in solution pH and the sign of gelatin charge. For the range of pH studied here, gelatin charge changed from positive (at pH 4) to negative (at pH 6.8) passing through neutral at IEP (pH 5.04). Whereas the zeta potential for RCA membrane was -5.4 mV. It is postulated that fouling mechanism changes from external fouling to in-pore fouling in response to protein net charge, and thus it was mainly controlled by electrostatic interactions forces for hydrophilic type UF membrane. As for PES membrane, interaction between gelatin molecules and the membrane surface and inner pores may occur immediately due to the amphoteric nature of gelatin molecules and the hydrophobic nature of PES membrane. Therefore, PES membrane was prone to fouling through solute attachment on the porous surface, resulting in partial pore blockage or cake layer formation. This result was in agreement with higher water flux after external cleaning (showing lower R_f/R_m value) for PES membrane as compared to RCA membrane, indicating that the removal of the major part of fouling (especially surface fouling through cake formation and solute attachment).

Table 3. The model fit error (SSR) and fitted parameters using classical blocking laws.

Membrane Type	pH	Model fit error, SSR ($\times 10^{-4}$)				Fitted Parameters
		Standard	Complete	Intermediate	Cake	
RCA	4	2.79	7.65	1.05	1.82	$K_i = 28.2 \text{ m}^{-1}$
	5.3	0.34	0.54	0.60	1.74	$K_s = 25.1 \text{ m}^{-1}$
	6.8	3.41	8.42	1.08	0.20	$K_c = 1.82 \times 10^6 \text{ s/m}^2$
PES	4	55.0	116	22.0	2.34	$K_c = 3.37 \times 10^5 \text{ s/m}^2$
	5.3	1.52	2.31	1.01	0.46	$K_c = 3.20 \times 10^7 \text{ s/m}^2$
	6.8	15.0	49.0	1.85	4.91	$K_i = 17.2 \text{ m}^{-1}$

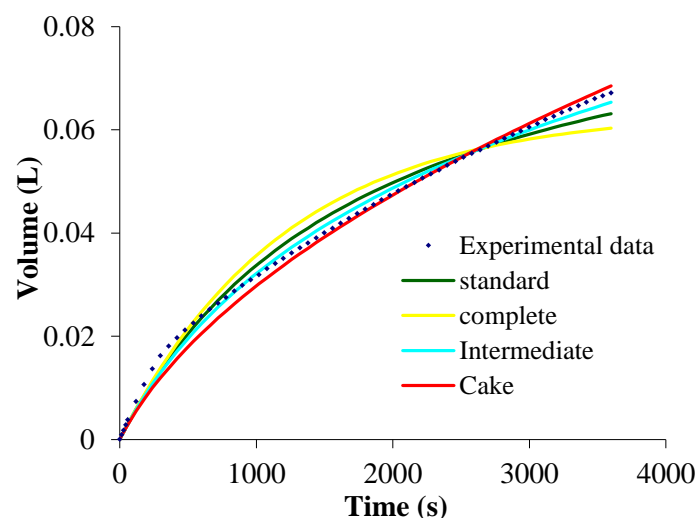


Figure 1. Fitting of experimental data to classical blocking laws for RCA membrane at pH 6.8.

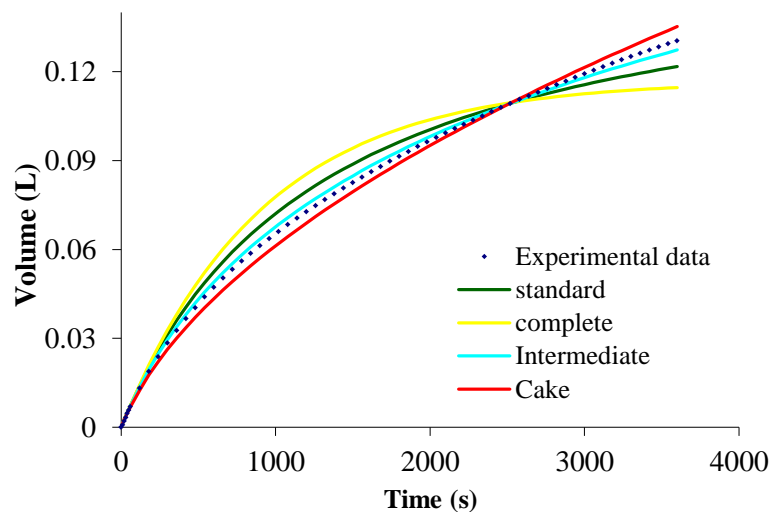


Figure 2. Fitting of experimental data to classical blocking laws for PES membrane at pH 6.8.

From table 3, it was obvious that cake formation, intermediate blocking and standard blocking mechanism were fitted well to all the experimental runs, but complete blocking mechanism displayed the highest deviations. Since gelatin is a type of denatured proteinaceous solution exists with various molecular weights which ranging from 10 kDa to 400 kDa [15], the sizes of the gelatin solutions therefore maybe smaller, same size or even larger than the membrane pore sizes. Therefore, all the blocking mechanisms could happen, but cake formation shall be the dominant fouling mechanism occurred during the filtration process.

4. Conclusion

Quantification of membrane fouling and determination of dominant fouling mechanism during gelatin UF for both RCA and PES membrane were successfully carried out. Generally, effects of membrane hydrophobicity have an impact on the contribution of different fouling resistance. RCA membrane demonstrated that concentration polarization resistance was the main cause for membrane fouling (>90%) at all pHs range. For PES membrane, R_{cp} remain as dominant fouling resistance in gelatin UF at pH 5.3, but exceptional case was observed at pH 4 and pH 6.8, showing that combined R_{rf} and R_{if} contributed around 57% and 37%, respectively to the overall fouling resistances. The best-fitted model for gelatin UF experimental data using RCA membrane was standard blocking, intermediate blocking and cake filtration, depending on pH. Fouling mechanism changes from in-pore blocking to external fouling in response to protein net charge, and thus it was mainly controlled by electrostatic interactions forces. On the other hand, PES membrane was prone to fouling through solute attachment on the porous surface, resulting in cake layer formation. This was confirmed by best fitted cake filtration model to flux decline data in all pH range tested.

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