IOP Conference Series: Materials Science and Engineering

Elucidation of flux decline phenomenon in ultrafiltration of polydisperse silica solution

To cite this article: N H Ramli *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **736** 022097

Energy Security and Chemical Engineering Congress IOP Publishing
IOP Conf. Series: Materials Science and Engineering **736** (2020) 022097 doi:10.1088/1757-899X/736/2/022097

Elucidation of flux decline phenomenon in ultrafiltration of polydisperse silica solution

N H Ramli*, C S Zakaria, M S Mohd Sueb, Sunarti Abd Rahman and N E Badrul Hisham

Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 23600 Gambang, Kuantan, Pahang

*drhanuni@ump.edu.my

Abstract. Ultrafiltration (UF) is widely used in water filtration process due to its ability to operate at low pressure with higher permeate flux. However, fouling is one of the constrains usually occurred in UF, especially when involving colloidal material. Colloidal silica widely used as a synthetic form of colloidal foulant to investigate membrane performance. It has a special characteristic which can change the charge around the molecules easily depending on the surrounding condition. This study was aimed to identify the most significant factor contribute to permeate reduction of UF membrane of polydisperse silica solution that could lead to the fouling issue of this membrane. The factors that have been studied were ionic strength, pH, transmembrane pressure, ratio of feed solution and types of membrane used (modified or unmodified). Fractional factorial design was used to investigate the effect of individual factors and also the interaction factors on the reduction of permeate flux by using Design Expert software. The finding from this study revealed that the factors of fouling was related to each other. In determining the rate of permeate flux, the ionic strength, pH and pressure should not be considered separately. The only independent factor affecting the permeate flux was ionic strength. However, the effect was not prominent compared to interaction factors. Also, surface-modified membrane by using Pebax 1657 has shown opposite trend in terms of pH and pressure effect on permeate flux.

1. Introduction

Membrane widely used especially in water and waste water treatment for the purpose of pollutant removal and purification. Separation process by using membrane offers various attractive advantages in terms of selective separation, free from addition of any chemicals, continuous operation and convenient process. However, there are some drawbacks in membrane operation where it requires higher cost of operating system for the purpose of membrane cleaning and scale inhibition. Basically, the major problem in membrane application is caused by membrane fouling which leads to the rapid decline in permeate flux over time [1].

Fouling can be categorized into two main categories which are reversible and irreversible fouling. Reversible fouling is formed due to cake layer or concentration polarization, and this types of fouling can be solved by means of physical cleaning procedure. While irreversible fouling considered as loss in transmembrane pressure and cannot be fixed through hydrodynamically or chemically cleaning procedure. It happened through complex physical and chemical interactions between various constituents in the feed and the membrane surface [1]. [2] has reported that membrane fouling and characteristic of foulants are determined by concentration of major constituent, chemical properties of water (pH, ionic strength, divalent cation concentration), membrane properties (surface morphology, hydrophobicity, charge, MWCO, temperature and mode of operation for the system. Colloidal silica solution is widely used in literature as foulant model because it exists in has various particle size and surface charged.

The formation of cake layer on membrane surface strongly influenced by the size of particle and charge of the solute constituents. Larger particle size compared to membrane pores can cause pore blockage of the membrane surface and lead to the formation of cake layer which reduce the permeate flux. In some cases, combination of particles with huge size distribution has shown more prominent flux declination compare to solution with less in particle size distribution. In fact, in real problems involving colloidal solution, solution usually consist of solute with different size of particle. For that reason, many studies related to filtration of colloidal silica are using bi-disperse to understand well about the fouling mechanism [3].

Meanwhile, the interfacial properties of silica particles can easily change via the entrapment of ions, molecules through “hairy layer” characteristic exist on the silica colloidal surfaces in presence of water [4]. This unique phenomenon occurs through chemical forces (covalent or coordinate bonding), hydrogen bonding force, electrostatic force, hydrophobic association force or molecular force. This complex interfacial phenomenon specific to silica colloids implies that the fouling strength of these particles is affected by such as pH and ionic strength of the solution [4]. Hence, the general other factor such as transmembrane pressure and characteristic of membrane surface may also contribute to flux decline studies as reported in [5]. Therefore, the objective of this work is to investigate the factor associated with flux decline such as transmembrane pressure, pH, ionic strength, percent of silica composition (particle size variation) and categories of membrane surface (modified and unmodified membrane surface).

2. Materials and method

2.1. Feed solution

In this work, feed solution contained two different types of silica suspension known as W30 and X30 at concentration of 4 g/L purchased from Fison Grades. The filtration process was conducted at various pH, ionic strength, applied pressure and categories of membrane surface according to the condition preliminary set by Design Expert Software by using the range as shown in Table 1. The sample was prepared in 500 mL of glass beaker, by adding a known amounts of electrolyte (NaCl) to a known mass of the silica stock solution in a 500 mL of glass beaker. The pH of the final solution was adjusted to the desired pH value by adding NaOH and HCl (both were from Fison Grades).

2.2. Ultrafiltration experimental set-up

Filtration experiment was conducted by using a membrane rig, which comprised of a nitrogen gas supply, filtration unit cell and balance as shown in figure 1.

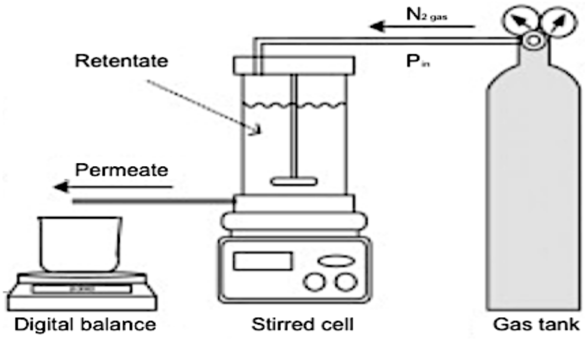

Figure 1. Schematic diagram for simple filtration unit experimental set-up [3].

In this work, there were two categories of membrane. For unmodified membrane, the sample was directly used as provided by manufacturer. In this case, it was referred to NADIR UH004 P and NADIR UP 005 P. Meanwhile, for modified membrane, the sample was prepared through membrane surface modification process as mentioned in Part 2.3. The hydraulic resistance, *Rm* was measured by the filtration of pure electrolyte solution through the membrane. The solvent flux rates were obtained through the filtration of electrolyte alone through a fresh membrane at five different pressures (50, 100. 200, 300 and 400 kPa) until 20 mL of permeate collected at each pressure run. The pressure was controlled by pressure regulator which was installed between the cell and the nitrogen tank.

The filtration of silica solution at various conditions were designed in Design Expert software. In this work, five factors e.g. pH, applied pressure, ionic strength, composition of binary mixture (W30 and X30) and categories of membrane surfaces were investigated using 2^4 fractional factorial design, where all factors were randomized. Table 1 depicts the design factors and levels and they were coded as -1 (low level) and +1 (high level) which indicates the lowest and the highest range of factors. Dead end filtration was implemented to investigate the effect of operating condition of the membrane on the decrease in permeate flux involving colloidal silica solution in binary mixture. 16 runs of experiments were conducted in order to identify the most contributing factors and interaction between the factors. The response of experimental design was analyzed by using analysis of variance (ANOVA). Filtration process was carried out by using a 50 mL dead end filtration cell (Amicon Corp Model 8050). The effective membrane area was 13.4 cm^2 and the system was pressurized with nitrogen gas. The cell was not stirred. The filtration process was carried out until 25 – 30 mL of permeate solution was collected within 1 to 3 hours where the pressure was controlled by pressure regulator. The permeate flux was measured by recording the volume of permeate solution collected at every 5 minutes. The filtration of silica solution at various different conditions were carried out according to Table 2. The condition shown in Table 2 was generated from Design Expert software based on the condition set in Table 1. Ratio of colloid silica was referred to the weight percentage mixtures between two types of silica (W30 and X30).

Table 1. List of selection factors and level.

No	Variables	Coded	Type of factor	Actual values of coded levels		Units
				-1	+1	
1	Ionic strength	A	Numerical	0.1	1	M
2	Ratio colloid silica (W30:X30)	B	Categorical	20:80	80:20	
3	pH	C	Numerical	3	9	pH units
4	Pressure	D	Numerical	1	3	Bar
5	Types membrane	E	Categorical	Modified	Unmodified	

Table 2. Pre-set condition of sample run by Design Expert software.

Run	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
	A: Ionic strength	B: Ratio	C: pH	D: Pressure bar	E: Membrane
1	0.10	80:20	9.00	3.00	Modified
2	0.10	20:80	3.00	1.00	Unmodified
3	0.10	80:20	9.00	1.00	Unmodified
4	1.00	20:80	9.00	1.00	Unmodified
5	1.00	80:20	9.00	1.00	Modified
6	0.10	20:80	3.00	3.00	Modified
7	1.00	80:20	3.00	1.00	Unmodified
8	0.10	80:20	3.00	3.00	Unmodified
9	1.00	20:80	9.00	3.00	Modified
10	1.00	20:80	3.00	1.00	Modified
11	0.10	20:80	9.00	1.00	Modified
12	1.00	80:20	3.00	3.00	Modified
13	0.10	20:80	9.00	3.00	Unmodified
14	1.00	80:20	9.00	3.00	Unmodified
15	1.00	20:80	3.00	3.00	Unmodified
16	0.10	80:20	3.00	1.00	Modified

2.3. Membrane surface modification

The modified membrane was referred to the commercial membrane which undergo surface modification procedure by using Pebax 1657 material. Pebax 1657 pellet contains 60% polyether and 40% polyamide contents, which is suitable for coating layer, was purchased from Arkema France. The preparation of coating membrane was carried out with 100 g of ethanol, water and Pebax that had been diluted. The ethanol used contained 95% of purity. 3 wt % of PEBAX was diluted into 70% of ethanol and 30% water. For the dilution process, the temperature was set at 90 °C with the duration of 2 hours until homogenous clear and solution was obtained. Pebax 1657 was coated on PES membrane for 3 times and each coating was dried in an oven for 10 min or until the coating dried completely.

3. Results and discussion

3.1. Screening of factors affecting on reduction of permeate flux

The factors used to identify the response of the reduction of permeate flux was carried out by using 2^{5-1} fractional design. The factors that contributed to the reduction of permeate flux were ionic strength, ratio of colloidal silica, pH, pressure and type of membrane. The result obtained for permeate flux using Design Expert Software is presented in Table 3 below.

Table 3. Design Expert result of permeate flux.

Run	Factor 1 A: Ionic strength	Factor 2 B: Ratio	Factor 3 C: pH	Factor 4 D: Pressure bar	Factor 5 E: Membrane	Response 1 Permeate flux (min/L)
1	0.10	80:20	9.00	3.00	Modified	-0.0122
2	0.10	20:80	3.00	1.00	Unmodified	-0.0192
3	0.10	80:20	9.00	1.00	Unmodified	-0.0048
4	1.00	20:80	9.00	1.00	Unmodified	0.004
5	1.00	80:20	9.00	1.00	Modified	0
6	0.10	20:80	3.00	3.00	Modified	-0.0034
7	1.00	80:20	3.00	1.00	Unmodified	-0.0074
8	0.10	80:20	3.00	3.00	Unmodified	-0.0004
9	1.00	20:80	9.00	3.00	Modified	-0.0104
10	1.00	20:80	3.00	1.00	Modified	0
11	0.10	20:80	9.00	1.00	Modified	0
12	1.00	80:20	3.00	3.00	Modified	-0.0012
13	0.10	20:80	9.00	3.00	Unmodified	0.0004
14	1.00	80:20	9.00	3.00	Unmodified	0.0012
15	1.00	20:80	3.00	3.00	Unmodified	-0.002
16	0.10	80:20	3.00	1.00	Modified	0

3.2. Statistical analysis for ultrafiltration from colloidal silica

The analysis of variance (ANOVA) for permeated flux was conducted to determine the significance of the model as shown in Table 4. The F-value from the ANOVA shown the statistical significance of regression equation, while p-value was used to investigate the significance of each coefficient. Based on the model, F-value and p-value obtained were 78.17 and 0.0004, respectively. There was only 0.04% of chance that the large F-value could be obtained, which mainly occurred due to the noise. The smaller p-values indicates a more significant corresponding variable. The model term effect of A, C, AD, AE, BC, CD, CE and DE were statistically significant in affecting the permeate flux of the filtration process. However, the model term of B, D and E were not significant as their p-values were greater than 0.05. Based on the p-value, it can be concluded that the interaction factors gave more significant effect compared to individual factor. For individual factor, only A-ionic strength shown more prominent effect towards flux reduction.

Table 4. Test of significance for regression coefficient.

Source	Coefficient estimate	Sum of squares	F-value	p-value, prob>F	
Model	-3.462×10^{-3}	5.438×10^{-4}	78.17	0.0004	significant
A-ionic strength	1.488×10^{-3}	3.540×10^{-5}	55.97	0.0017	
B-ratio	3.625×10^{-3}	2.102×10^{-6}	3.32	0.1423	
C-pH	7.375×10^{-3}	8.702×10^{-6}	13.76	0.0207	
D-pressure	-3.750×10^{-5}	2.250×10^{-8}	0.036	0.8596	
E-membrane	-6.250×10^{-5}	6.250×10^{-8}	0.099	0.7690	
AD	-1.087×10^{-3}	1.892×10^{-5}	29.92	0.0054	
AE	9.875×10^{-4}	1.560×10^{-5}	24.67	0.0077	
BC	-1.587×10^{-3}	4.032×10^{-5}	63.75	0.0013	
CD	-2.488×10^{-3}	9.900×10^{-5}	156.53	0.0002	
CE	2.987×10^{-3}	1.428×10^{-4}	225.77	0.0001	
DE	3.363×10^{-3}	1.809×10^{-4}	286.01	< 0.0001	
Residual		2.530×10^{-6}			
Cor Total		5.464×10^{-4}			

$R^2 = 0.9954$, * Value of p-values greater than 0.05 indicating the model terms are not significant.

The R^2 from the ANOVA was used to identify the closeness of data to the regression line. A good model will give the result of R^2 more than 80%. The satisfactory R^2 value obtained from the analysis was 0.9954, which indicated that the model fits the experimental and predicted values. The final equations in term of actual factors were determined as follows:

Ratio of silica 20:80 (W30:X30) membrane modified

$$\text{Permeate flux} = -8.856 \times 10^{-3} + 5.944 \times 10^{-3}A + 1.437 \times 10^{-3}C + 2.904 \times 10^{-3}D - 2.416 \times 10^{-3}AD - 8.291 \times 10^{-4}CD \quad (1)$$

Ratio of silica 80:20 (W30:X30) membrane modified

$$\text{Permeate flux} = -1.781 \times 10^{-3} + 5.944 \times 10^{-3}A + 3.791 \times 10^{-3}C + 2.904 \times 10^{-3}D - 2.416 \times 10^{-3}AC - 8.291 \times 10^{-4}CD \quad (2)$$

Ratio of silica 20:80 (W30:X30) membrane unmodified

$$\text{Permeate flux} = -0.0367 + 0.0103A + 3.429 \times 10^{-3}C + 9.629 \times 10^{-3}D - 2.416 \times 10^{-3}AC - 8.291 \times 10^{-4}CD \quad (3)$$

Ratio of silica 80:20 (W30:X30) membrane unmodified

$$Permeate\ flux = -0.029 + 0.0103A + 2.370 \times 10^{-3}C + 9.629 \times 10^{-3}D - 2.416 \times 10^{-3}AD - 8.291 \times 10^{-4}CD \tag{4}$$

Whereby;
A: Ionic strength
B: Ratio of colloid silica (W30:X30)
C: pH
D: Pressure
E: Type of membrane (modified or unmodified).

Permeate flux as th response of the ultrafiltration process using colloidal silica 30 wt % and 40 wt % respectively. Factors of A, B, C, D and E were referred as the main effects while AD, AE, BC, CD, CE and DE were the interaction effects.

3.3. *Main effect and interaction effects between factors on reduction of permeate flux*

Figure 2 below shows the Pareto chart representing the main effects and interaction effects of the factors involved in the process. The chart was used to analyse the most significant factors. The height of the bars represents the highest impact of the factors. The t-values of the bars were the values of the square root of the F-values obtained from the ANOVA. The two limit lines; Bonferroni limit and t-value limit line, represent the t-value of the effects. The value of both lines were 6.254 and 2.776, respectively. The Pareto chart below shows that the factors DE, CE, CD, BC, A, AD, AE and C exceeded the t-value limit and gave the significant effect to the reduction of permeate flux.

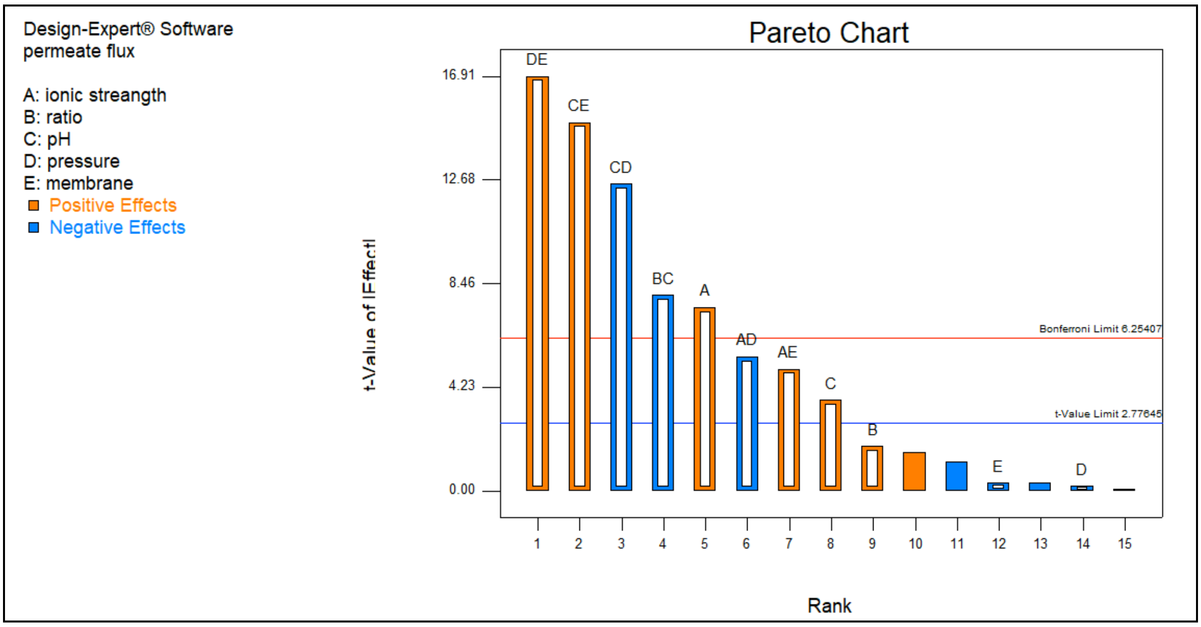

Figure 2. Contribution of independent and interaction effect to reduction of permeate flux.

According to figure 2, the individual factor (B-ratio) and (E-membrane) were plotted below the t-value limit which means both individual factors were not really affecting the flux decline. The only prominent individual factor towards flux decline was given by A which is ionic strength. The interaction factor between DE (pressure and type of membrane surface) and CE (pH and type of membrane surface) has shown the greatest effect towards flux declination. Based on this finding, it can be concluded that the combination of pressure and pH with type of membrane surface can strongly influence the loss in permeate flux. However, B and E alone did not give any significant effect towards the flux decline.

Therefore, it can be summarized that, all the contributing factors should not be considered separately as they were related to each other.

This finding is complied with the concept of UF that allows the separation process to occur even though it was operated at low pressure. This is due to the fact that the pressure was not an independent factor towards the flux decline. Since the solution was considered as polydisperse solution, it was strongly affected by ionic strength. These two parameters can influence the charge around the silica molecule in colloidal solution.

3.3.1. Effect of independent processing parameters on reduction of permeate flux. The effect of two independent variables on the reduction permeate flux is presented in Figure 3. Based on the figure, it showed that, as the ionic strength increased, the permeate flux was also increased. In contrast, the permeate flux was decreased when the pH increased.

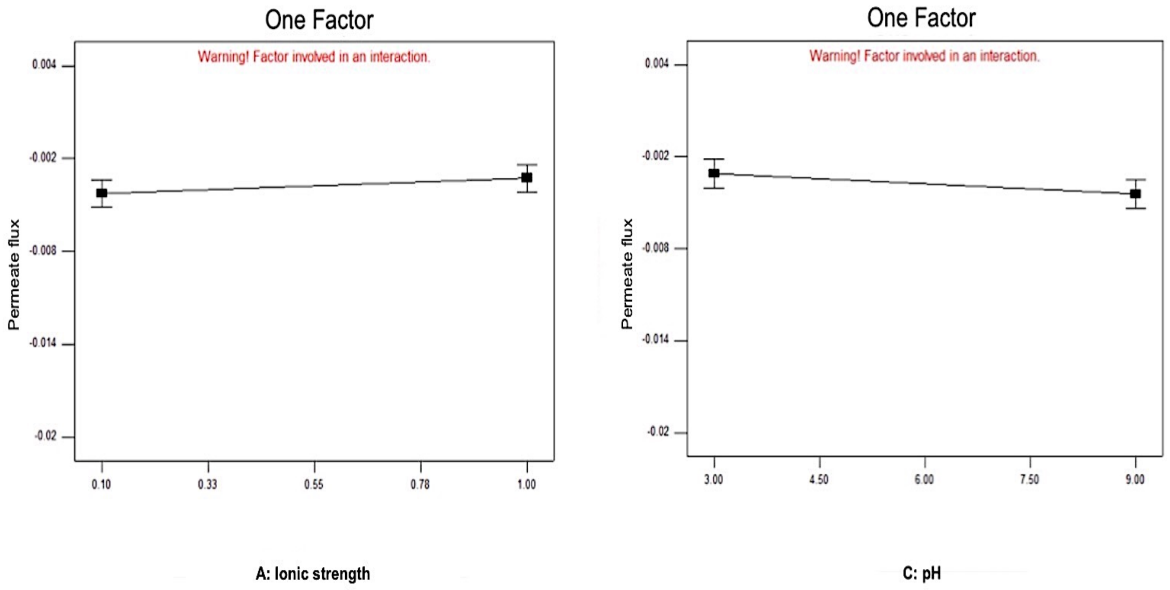

Figure 3. The effect of independent factor to reduction permeate flux.

According to [6], the increase in pH of the solution is resulted in the increase of net negative charge due to the deprotonation of basic group and the ionization of acidic group. Thus, by raising the pH of the solution, the amount of positive charges on silica will be decreased. Hence, this occurrence will reduce the ionic strength and the attraction of silica to the surface of membrane. It will also result in the increase of intermolecular and intramolecular repulsion between silica molecules. As an effect, the permeate flux was decreased as less fluid could pass through the surface of the membrane. While, at lower pH, the attraction forces of the ionic molecules will be dominant over the repulsion forces. This will increase the tendency of silica to pass through the membrane surface of UF and increase the permeate flux. Similar results were reported by [7].

3.3.2. Interaction effects between factors on reduction permeate flux. Figure 4 shows the interaction effect between pressure and type of membrane on the permeate flux at specific condition which were at ionic strength of 0.1 M, ratio of colloidal silica 20:80 and pH of 6. From figure 4, it was observed that the highest permeate flux was achieved for unmodified membrane at pressure 3 bar. While for modified membrane, the highest permeate flux was occurred at pressure 1 bar.

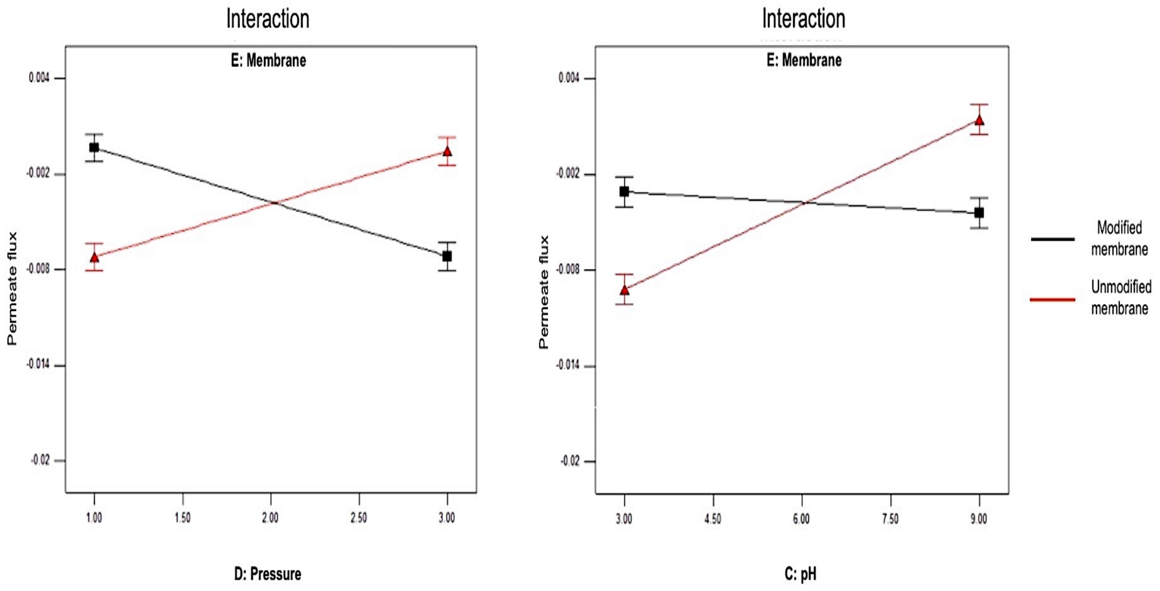

Figure 4. Interaction effect between factors on permeate flux.

Based on Figure 4, for unmodified membrane, the highest permeate flux was observed at pressure 3 bar. As the pressure increased, the permeate flux was also increased which is due to the less resistance on the flow since there was no coating layer on the surface that can obstruct the fluid from passing through the membrane. However, for modified membrane, the permeate flux was decreased as the pressure increased. This is because, the high pressure will clog the surface of the membrane that have been coated with Pebax 1657 and thus, reduced the permeate flux as less fluid can pass through the membrane. There might also be formation of cake layer on the surface of membrane which can also contribute to flux reduction in modified membrane at high pressure as stated in previous research by [8].

For unmodified membrane, as the pH increased, permeate flux was also increased due to the accumulation of negative charge which prevent the particles agglomerate to each other. With the help of pressure, it can enhance the permeate flux as the pressure will force the fluid to pass through the membrane surface in well-dispersed condition. However, for modified membrane, it records the opposite trend in flux reduction compared to modified membrane. This phenomenon might occur due to the existence of pore blockage and charge effect as discussed in Part 3.3.1. Hence, the increase in pressure at this condition will enhance the formation of cake layer and aggravate the condition by preventing the fluid from passing through the membrane.

4. Conclusion

In overall, the operating condition factors should not be considered separately when investigating the reduction of permeate flux in UF. The results obtained in this work indicates that polydisperse silica solution was easily influenced by ionic strength and pH due to the charge effect around the particles. Moreover, the pressure factor alone was not significantly affect the UF system. However, the combination of this factor with other affecting factors may give a significant effect to the performance of UF.

Acknowledgements

The authors are grateful for the financial support from Ministry of Education Malaysia and Universiti Malaysia Pahang through Fundamental Research Grant Scheme (RDU190136) with reference code FRGS/1/2018/TK10/UMP/02/7.

References

[1] Guo W, Ngo H H and Li J 2012 A mini-review on membrane fouling *Bioresour. Technol.* **122** 27–34

[2] Li Q and Elimelech M 2004 Organic fouling and chemical cleaning of nanofiltration membranes: Measurements and mechanisms *Environ. Sci. Technol.* **38** 4683–93

[3] Ramli N H and Williams P M 2012 Experimental study of the ultrafiltration for bi-disperse silica systems *Desalin. Water Treat.* **42** 1–7

[4] Singh G and Song L 2008 Impact of feed water acidification with weak and strong acids on colloidal silica fouling in ultrafiltration membrane processes *Water Res.* **42** 707–13

[5] Ariono D, Aryanti P T P, Subagjo S and Wenten I G 2017 The effect of polymer concentration on flux stability of polysulfone membrane *AIP Conf. Proc.* **1788**

[6] Lim Y P and Mohammad A W 2012 Influence of pH and ionic strength during food protein ultrafiltration: Elucidation of permeate flux behavior, fouling resistance, and mechanism *Sep. Sci. Technol.* **47** 446–54

[7] Zain M and Mohammad A W 2016 Effect of pH on flux decline during fractionation of glucose from cellulose hydrolysate through a polysulfone membrane *Malaysian J. Anal. Sci.* **20** 1413–20

[8] Yunos K F M, Mazlan N A, Naim M N M, Baharuddin A S and Hassan A R 2019 Ultrafiltration of palm oil mill effluent: Effects of operational pressure and stirring speed on performance and membranes fouling *Environ. Eng. Res.* **24** 263–70