Dimensional analysis of steady and unsteady state permeation flux for microfiltration of oil/water emulsion by a ceramic membrane

Amir Vahid[1], Toraj Mohammadi[2*], Afshin Pak[2], Mehrdad Karbassian[2], Masoud Golshan[2]

1- Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, Ohio 44325-3906, USA

2- Separation Research Laboratory, Department of Chemical Engineering, Iran University of Science and Technology, Tehran, P.O.Box 16846, Iran.

Abstract

The main problem in treating oil in water emulsions by membrane technologies is fouling caused by oil adsorption on the membrane surface. Among these technologies, microfiltration has been used in many fields of oil–water emulsions. The effect of operating conditions on a microfilter (home made) with a maximum pore size of 10 ìm was investigated. The results show that by increasing temperature and pressure, the flux factor increases. Also, by increasing oil content, the membrane is fouled rapidly but not significantly and the flux factor decreases. Increasing volumetric flow rate causes an increasing flux factor. While most polymeric membranes are susceptible to fouling, this membrane is not. Steady state and unsteady state dimensional analysis of the mass, length and time shows that the steady state flux and unsteady state flux observed for microfiltration through ceramic membrane can be expressed using three and two dimensionless numbers, respectively. In the case of steady state conditions the three dimensionless numbers were shear stress, resistance and Reynolds number. The shear stress number compares the shear stress against the membrane wall to the pressure, while the resistance number compares the convective cross-flow transport to the derived transport through a layer, whose resistance is the sum of all the resistance induced by the different processes which limit the mass transport. In unsteady state conditions, the two dimensionless numbers were flux factor and dimensionless time. Experimental data obtained in microfiltration of oil/water emulsion were recalculated in terms of these dimensionless groups for the steady state and unsteady state conditions. Straight lines in steady state conditions were plotted whose slope depends solely on the suspension and the membrane and not on the solute concentration. A positive slope of the (NS, Nf) plane means that fouling predominated; this was observed with hydrocarbon emulsion. The results of unsteady state dimensional analysis show that by increasing oil content, the membrane is fouled rapidly but not significantly and the flux factor decreases and increasing volumetric flow rate causes increasing flux factor.

[*] Corresponding author

E-mail address: torajmohammadi@iust.ac.ir, Tel:+98-21-73912732, Fax:+98-21-7896620

1. Introduction

Water quality standards are becoming more and more stringent for all purposes including drinking water or even reclamation in agriculture. Discharge of crude oily wastewater into the sea or rivers has been under increasingly careful scrutiny in recent years. A production separator that separates most of oil from water is usually used to give an initial separation of oil and water. The small quantity of remaining oil in water must be reduced to an acceptable limit before the water can be discharged into the sea or rivers or reinjected for water flooding [1]. Membrane techniques easily meet these standards. For example, cross-flow microfiltration is particularly useful for elimination of suspended solids, turbidity and microorganisms. It is also a promising process for tertiary waste water treatment [1-3] allowing simultaneous clarification and disinfection [4]. Microfiltration membranes may be prepared from a large number of different materials based on either organic materials (polymers) or inorganic materials (ceramic, metals or glasses). Microfiltration membranes, with processing pores in a range of 0.1-2 μm, are relatively easy to characterize. The main techniques employed are Scanning Electron Microscopy (SEM), bubble-point measurements, mercury porosimetry and permeation measurements. The main problem encountered when microfiltration is applied (in a laboratory or an industrial scale) is flux decline. This is caused by concentration polarization and fouling (the latter is deposition of solutes inside the pores of the membrane or at the membrane surface). Quite often considerable flux decline can be observed with values for process flux approximately 1% of pure water flux. To reduce fouling as much as possible it is important that careful control is exercised over the mode of process operation. Basically, two process modes exist, i.e. dead-end and cross-flow filtration. In dead-end filtration, feed flow is perpendicular to the membrane surface, so that the retained particles accumulate and form a type of a cake layer at the membrane surface. Thickness of the cake increases with filtration time and consequently the permeation flux decreases with increasing the layer thickness. In cross-flow filtration, feed flow is along the membrane surface, so that part of the retained solutes accumulates. [2]. The distinction between ultrafiltration, microfiltration and conventional filtration is a little arbitrary. They all operate via the sieving action of membrane itself or a cake or gel layer formed on the membrane surface [1].

An interesting approach was proposed to provide a dimensional analysis giving a basis for design of cross-flow microfiltration of inorganic particles [3]. This paper tries to carefully evaluate the dimensionless numbers derived and to extend the approach to quite different situation: microfiltration of oil/water emulsions by a ceramic membrane.

2. Experimental

2.1. Membrane

The microfiltration membrane was a home made membrane. It was a tubular kaoline membrane calcined at $900^{\circ}C$. The detail of preparation method was presented in previous publications [4, 5]. SEM analysis confirmed that the maximum pore diameter of the membrane is 10 μm.

2.2 Experimental set up

Experimental setup is shown in Fig. 1. The feed was pumped by means of a centrifugal pump into a module. Transmembrane pressure and volumetric flow rate were adjusted by throttling valves V1, V2 and V3 between 0.5 and 2.5 bar. Hot water was pumped through a coil from a hot water bath in order to set the feed temperature. It was varied between 25 and $60^{\circ}C$ by means of the small coil exchanger submerged into the feed tank. The temperature of water bath was $2^{\circ}C$ higher than the set temperature except at 25 $^{\circ}C$. which it was $20^{\circ}C$. In this case, friction in tubes caused the temperature to increase to $25^{\circ}C$. Temperature was measured by a digital thermometer.
Oil/water emulsions were prepared by vigorous mixing of oil and water with adding approximately 0.2 g of an emulsifier (docecyl sulfate sodium) to the mixture. Asaloyeh, Iran, crude oil was used for preparation of oil/water emulsions. The oil/water emulsion was poured into the feed tank. The emulsion was pumped into the membrane module. Some of the feed was bypassed to the feed tank. Inlet and outlet pressures were measured by P1 and P2 manometers, respectively. Permeate was collected every 30 min and then weighted. After weighting, the permeate was recycled to the feed tank in order to keep the concentration approximately constant. Each experiment ran for 270 min.

3. Results and discussion

3.1. Effects of operating conditions

Effects of operating conditions were studied. The results showed that increasing temperature and pressure, increases flux factor. Also, by increasing oil content, the membrane is fouled rapidly but not significantly and flux factor decreases. Increasing volumetric flow rate increases flux factor. In spite of most polymeric membranes the kaoline membrane is not susceptible to fouling, because of its very hydrophilic behavior. After 4.5 h, it showed efficiencies of higher than 50%, therefore, this membrane can be recommended for oily wastewater treatment. This membrane is very cheap because it can be prepared using washed kaoline [4, 5]. It shows good performance for oily wastewater with concentrations of less than 2000 ppm. It is recommended to operate at temperatures lower than 40°C because higher temperatures increase operational costs. A pressure of 2 bar is also recommended for microfiltration of oily wastewaters. Higher flow rates are suitable in order to remove the oil layer from the membrane surface [1].

The results of microfiltration of oil/water emulsions by the kaoline membrane were presented in Figs 2 to 5. Steady flux against pressure with a plateau (limiting flux) reached to an inflection pressure is presented in Fig. 2. This curve is similar to those obtained in microfiltration of inorganic non-interacting particles of magnesia [3]. During microfiltration of oil/water emulsions, the flux reaches to an inflection value, and then a tendency to increase is observed when pressure more increased. This phenomenon is different from those observed by the other researches. For example for filtration of aerobic cells [6] and starch particles [7], a relative decrease at higher pressures was observed. This can be attributed to complicated interactions between the feed and the membrane and needs more investigations.

Steady flux against cross-flow velocity passed through a minimum cross-flow velocity is presented in Fig. 3. This **is showing that steady flux increases as velocity increases, because concentration polarization layer decreases, Also high velocity remove particles form membrane surface and cause increasing permeate flux.**

Steady flux against temperature is presented in Fig. 4. As seen, the flux increases by increasing temperature because of **viscosity reduction and increasing molecular activity.**

Steady flux against concentration reached to a critical concentration is presented in Fig. 5. The flux reaches a **constant value and then a tendency to decrease rapidly at concentration above 2000ppm.**

3.2. Model development

The steady flux J_s is given by the following equation:

$$J_s = \frac{P}{\mu(R_m + R_f)} \tag{1}$$

where P is the pressure (driving force) and μ the feed dynamic viscosity. In Eq. (1), R_m is the membrane resistance and R_f is the overall steady state resistance induced by all reversible or irreversible processes that limit mass transfer, e.g. concentration polarization and fouling (cake or gel formation). R_f is assumed to be a function of the suspension/emulsion density (ρ), pressure (P) and the cross-flow velocity (u). Dimensional analysis of the mass, length and time shows that the following dimensionless numbers $\rho u^2 / P$, $\mu R_f u / P$, $\rho u D_H / \mu$, t / t_S and J / J_w can be derived. The first number is similar to inverse of Euler number sometimes called "number of units of energy" [8]. ρu^2 is the minimum energy per unit volume required to transport the feed through the tubular membrane at a velocity of u, while P is the energy per unit volume dissipated for the permeate transport through the membrane. ρu^2 is linked to the shear stress (τ) against the membrane wall by the following relationship:

$$\frac{f}{2} = \frac{\tau}{\rho u^2} \tag{2}$$

where $f/2$ is the friction factor which is a function of Reynolds number $\mathrm{Re} = \rho u D_H / \mu$, D_H is the filtration hydraulic diameter. The friction factor is then obtained by one of the following relationships [8]:

$$\frac{f}{2} = \frac{8}{\mathrm{Re}} \text{ for } \mathrm{Re} \le 2500 - 4000 \tag{3}$$

$$\frac{f}{2} = 0.023\,\mathrm{Re}^{-0.02} \text{ for } 5000 \le \mathrm{Re} \le 200000 \tag{4}$$

Eq. (4) is valid for a smooth tube; if there is rugosity, the friction factor tends to be almost constant in turbulent flow. Moreover, in this study, assuming the smooth tubular membrane, the friction factor has a mean value of 0.0381 with a standard deviation of 0.0003, which means that it can be considered constant with 4.72% accuracy. $\rho u^2 / P$ can be expressed under the following form:

$$\frac{\rho u^2}{P} = \frac{\tau}{\frac{1}{2}P} \tag{5}$$

$\rho u^2 / P$ compares the shear stress with the pressure; it is then called the shear stress number (N_S). This number can also be expressed using the pressure drop (ΔP) through the tubular module. The number of units of energy (NUE) is defined by the following equation:

$$\text{NUE} = \frac{\Delta P}{\rho u^2} \tag{6}$$

NUE is linked to the friction factor by the following equation [8]:

$$\text{NUE} = \frac{A}{\Omega}\frac{f}{2} = \frac{4L}{d}\frac{f}{2} \tag{7}$$

where $\frac{A}{\Omega}$ is the ratio of the effective surface area over the cross sectional area of the tubular module. *d* and *L* are internal diameter and length of the module respectively.

The shear stress number can then be written under the following form:

$$N_S = \frac{\Delta P}{NUE \times P} \tag{8}$$

N_S compares the overall dissipated mechanical energy to the energy used to drive the permeate through the membrane.

t / t_S and J / J_w are dimensionless time and flux respectively, and t_S is the time which flux reaches to a steady state value.

Also, $\mu R_f u / P$ is equal to u / J_f, where J_f is the hypothetical flux through a layer whose hydraulic resistance is R_f. This is called as the resistance layer. This number compares convective transport in the tubular module with the flux through the resistance layer and can be viewed as inverse of the mass Stanton number also called mass Margoulis number [8]. It is called the resistance number (N_f).

3.3. Experimental results for steady state conditions

All experimental data were recalculated in terms of the dimensionless numbers and they were plotted in Figs 6-10. Fig. 6 present resistance number as a function of shear stress number. It was that the function is almost linear as follows [3]:

$$N_f = a + bN_S \tag{8}$$

where *b* is slope of the straight line, characteristic of the couple (suspension or emulsion)/membrane.

When the resistance R_f due to particle deposition is 0, then:

$$a = -b\frac{\rho u_c^2}{P} \tag{9}$$

where u_c is a critical velocity at which the resistance layer disappears. This property of resistance layers noted by Green et al. [9] can be observed whenever the process which limits the mass transport is reversible, e.g. particles deposition or concentration polarization.

It is also interesting to note that the following rearrangement can be presented [2]:

$$R_f = \frac{a}{\mu}\frac{P}{u} + \frac{b\rho}{\mu}u \tag{10}$$

Since R_f is approximately proportional to the thickness of resistance layer, the first term $aP/\mu u$ on the right-hand side of this equation represents the rate at which the mass transport resistance is induced. The second term $b\rho u/\mu$ is a measure by which the resistance layer is removed by wall shear caused by the feed in the membrane module. *b* is therefore related to the roughness of membrane module and is most probably independent of feed concentration. Fig. 7 shows the resistance number as a function of pressure when the cross-velocity is constant and Fig. 8 shows the resistance number against the cross-velocity when the pressure is constant. A linear dependence of the resistance number on the pressure and cross-velocity is observed in the Figs 7 and 8 respectively. It is noticeable that the slope of the resistance number plateau against the pressure and the cross-velocity is positive.

As shown in Fig. 6 the experimental data of microfiltration of oil/water emulsions give straight lines in with positive slopes. This means that the mass transport is mostly limited by irreversible fouling and R_f is therefore weakly controlled by cross flow velocity.

Fig. 9 demonstrates the variation of resistance number (N_f) against Reynolds number in a logarithmic scale. According to this figure, the resistance number increases as the cross-velocity increases and decreases by increasing in the temperature. In other words, increasing in Reynolds number has two different effects on resistance number. When the cross-velocity in variable and the other parameters are constant, resistance number increases with increasing the Reynold number and when the temperature is variable an opposite result is seen. Again a linear relationship between two dimensionless numbers is observed as follows:

$$R_f = a + b\,\mathrm{Re} \tag{11}$$

Two positive and negative slopes are seen in Fig. 9.

The linear relationship between shear stress number (N_S) and Reynolds number is shown if Fig. 10. It is observed that the shear stress number increases as the cross-velocity increases (increasing in the Reynolds number) and has no change when the temperature increases. In this case the shear stress number is independent of Reynolds number. Again a linear relationship is observed:

$$N_S = a + b\,\mathrm{Re} \tag{12}$$

In the case of increasing temperature the slope of b is approximately zero and a positive slope is seen for increasing of cross-velocity.

3.4. Experimental results for unsteady state conditions

As discussed in section 3.1, in this paper, effect of operation conditions such as concentration, temperature, pressure and volumetric flow rate were investigated on a new microfiltration membrane. Here the functionality of the dimensionless flux (J/J_W) to dimensionless time (t/t_S) is discussed.

3.4.1. Effect of oil concentration

Fig. 11 shows the effect of concentration on permeate flux. Solution with oil concentration of 500, 1000, 2000 and 3000 ppm were prepared. Because of different membrane resistance, flux of oil/water emulsion to flux of pure water at a reference condition was plotted (J/J_W) against the dimensionless time (t/t_S). The reference condition was at a pressure of 1 bar, a temperature of 25°C and a flow rate of 2.5 L/min. By increasing concentration from 500 to 2000 ppm the flux factor or the dimensionless flux (J/J_W) does not change and approximately remains constant. However, when the concentration increase to 3000 ppm, the flux factor decreases suddenly because of a layer of oil forms on the membrane surface. At lower concentrations, an oil layer formed on the membrane surface can be removed by hydrodynamic action of flow. But, at higher concentrations, the hydrodynamic action can not remove the oil layer. By increasing the operation time or the dimensionless time, this layer becomes thicker and the flux decreases. However, because the kaoline is hydrophilic, the bond between kaoline and the oil layer is very week and can be broken rapidly. Therefore, fouling of this membrane is not a major problem and after 270 min (dimensionless time of 1) the flux factor is still above 0.5 even for a concentration of 3000 ppm.

3.4.2. Effect of temperature

Fig. 12 shows the effect of temperature on the flux factor. As shown, by increasing temperature, the flux factor becomes greater than unity because flux of oil/water emulsion (J) is measured at temperatures of 25, 40 and 60°C while flux of pure water (J_W) is measured at a temperature of 25°C. The rate of fouling is higher at higher temperatures because of higher diffusion of oil/water emulsion. All experiments were carried out at a pressure of 1 bar, a concentration of 3000 ppm and a flow rate of 2.5 L/min. It must be mentioned that by increasing temperature, the flux factor increases but higher temperatures increases operational cost of unit. Thus, temperatures of higher than 40°C are not recommended.

3.4.3. Effect of transmembrane pressure

Effect of pressure on the flux factor was also investigated. The effect of pressure is the same as temperature. By increasing pressure, the flux factor also increases. In these experiments, temperature, concentration and flow rate were 25°C, 3000 ppm and 2.5 L/min, respectively.

It can be explained that the higher transmembrane pressure results in droplets to pass rapidly through the membrane pores. Fig. 13 shows that the flux factor initially

decreases with the dimensionless time, however, gradually reaches to a constant value depending on transmembrane pressure. This is also due to the membrane fouling.

Initial flux reduction is due to the fact that the oil layer is formed on the membrane surface rapidly. However, its thickness does not increase with time significantly due to the hydrodynamic action of the flow. Thus after initial reduction, the flux factor remains almost constant. As mentioned before, flux factors of more than unity for pressures of higher than 1 bar is due to the fact that oil water emulsion flux (J) was measured at pressures of 1.5, 2 and 2.5 bar while flux of pure water (J_W) was measured at a pressure of 1 bar.

3.4.4. Effect of flow rate

Effect of volumetric flow rate on the flux factor was also investigated. As shown in Fig. 14, by increasing the flow rate, the rate of flux factor reduction (membrane fouling) decreases because of hydrodynamic effect of the flow on the membrane surface. It means that higher velocities cause the oil layer to remove further. In all experiments, temperature, pressure and concentration were 25°C, 1 bar and 3000 ppm, respectively.

4. Conclusion

1. Steady state dimensional analysis shows that three dimensionless numbers, the shear stress number, the resistance number and the Reynolds number are related to the steady flux in the mass-transfer-controlled region.
2. All the experimental data obtained displayed in the (N_S, N_f), (Re, N_S) and (Re, N_f) planes for steady state conditions give straight lines whose slope depends on the emulsion and the membrane and not on the slurry concentration.
3. Unsteady state dimensional analysis shows that two dimensionless numbers, the flux factor and the dimensionless time are related to the unsteady flux in the mass-transfer-controlled region.
4. The results of unsteady state dimensional analysis show that by increasing oil content, the membrane is fouled rapidly but not significantly and the flux factor decreases and increasing volumetric flow rate causes increasing flux factor.
5. The kaoline membrane previously prepared, is not significantly susceptible to fouling in spite of most ceramic membranes because of its very hydrophilic behavior.
6. After 4.5 hr, it showed efficiencies of higher than 50%, therefore, this membrane can be recommended for oily waste water treatment.
7. This membrane is very cheap because it can be prepared by extruding and calcining washed kaoline which comes Zenoos mine [4, 5] and it showed good performance for oily waste water with concentrations of lower than 2000 ppm.
8. It is recommended to operate at temperatures lower than 40°C because higher temperatures increase operational costs. A pressure of 2 bar is recommended for microfiltration of oily wastewaters. Also, high flow rates are suitable in order to remove the oil layer from the membrane surface.

Nomenclatures:

a	intercept with the N_f-axis
b	straight line slope
d	internal diameter of tubular membrane (m)
$f/2$	friction factor
J_f	flux through resistance layer (m s^{-1})
J_S	steady-state flux
J_W	flux of pure water
L	tubular membrane length (m)
N_f	resistance number
N_S	shear stress number
NUE	number of unit energy
P	driving pressure (Pa)
Re	Reynolds number
R_f	overall reduced resistance (m^{-1})
R_m	membrane hydraulic resistance (m^{-1})
t	chronological time
T	temperature (°C)
u	cross-flow velocity (m s^{-1})
ΔP	pressure drop (Pa)
μ	dynamic viscosity (kg $m^{-1}s^{-1}$)
ρ	density (kg m^{-3})
τ	shear stress (Pa)
Ω	cross-section area (m^2)

References:

[1] T. Mohammadi, A. Pak, M. Karbassian, M. Golshan, Effect of operating conditions on microfiltration of an oil–water emulsion by a kaolin membrane, Desalination, 168 (2004) 201–205.

[2] S. Elmaleh, L. Vera, R. Villarroell-Lopez, L. Abdelmoumni, N. Ghaffor, S. Delgado, J. of Membr. Sci., 139 (1998) 37-45.

[3] M. Asaadi, D.A. White, A model for determining the steady state flux of inorganic microfiltration membrane, Chem. Eng. J. 48 (1992) 11.

[4] T. Mohammadi, A. Pak, Making zaolite A membrane from kaoline by electrophoresis, microporous and mesoporous materials, 56 (2002) 81-88.
[5] T. Mohammadi, A. Pak, Effect of calcination temperature of kaoline as a support for zeolite membranes, Sep. Purifi. Sci., 30 (2003) 241-249.
[6] B. Lacoste, PhD dissertation, Montpellier, 1992.
[7] O. Mahamadou, Etude des Transferts d' Eau et de Suspensions d' Amidon sur Membranes Minerals en function des Conditions Operatoires, PhD thesis, ENSUIT, Dakar, 1992.
[8] P. Le Goff, Energetique Industrielle, Technique et documentation, Paris, 1979.
[9] G. Green, G. Belfor, Fouling of ultrafiltration membranes: lateral migration and particle trajectory model, Desalination, 35 (1980) 129.

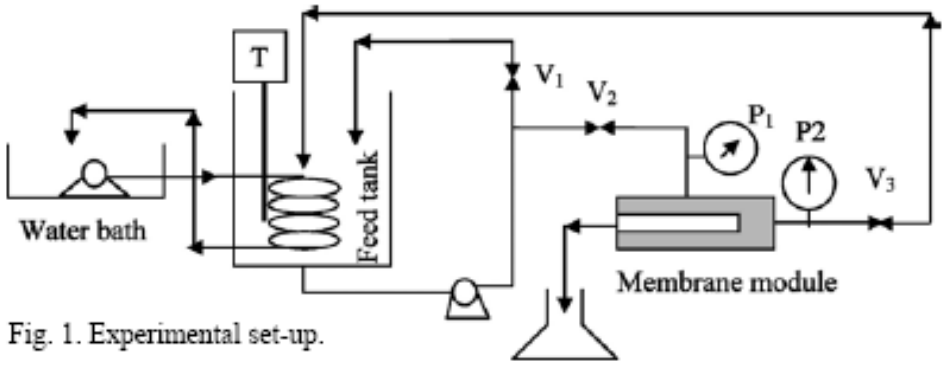

Fig. 1. Experimental set-up.

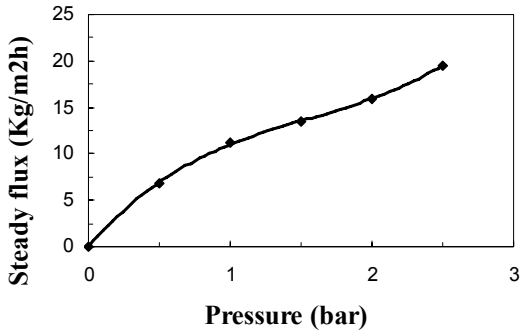

Fig. 2. Steady flux against pressure at u = 1.47 m/s, C = 3000 ppm and T = 25°C.

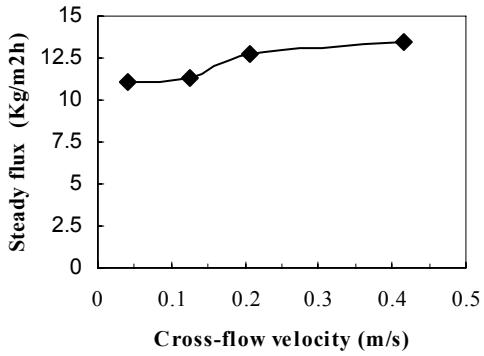

Fig. 3. Steady flux against cross-flow velocity (P = 1 bar, C = 3000 ppm and T = 25°C).

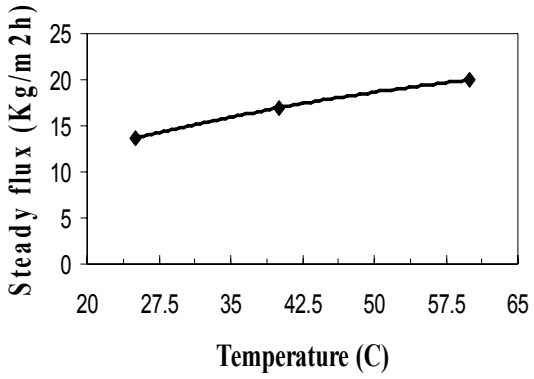

Fig. 4. Steady flux against temperature at P = 1 bar and u = 1.47 m/s.

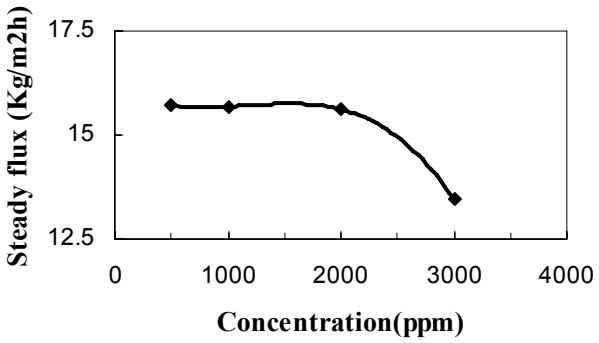

Fig. 5. Steady flux against concentration (P = 1 bar, T = 25°C and u = 1.47 m/s).

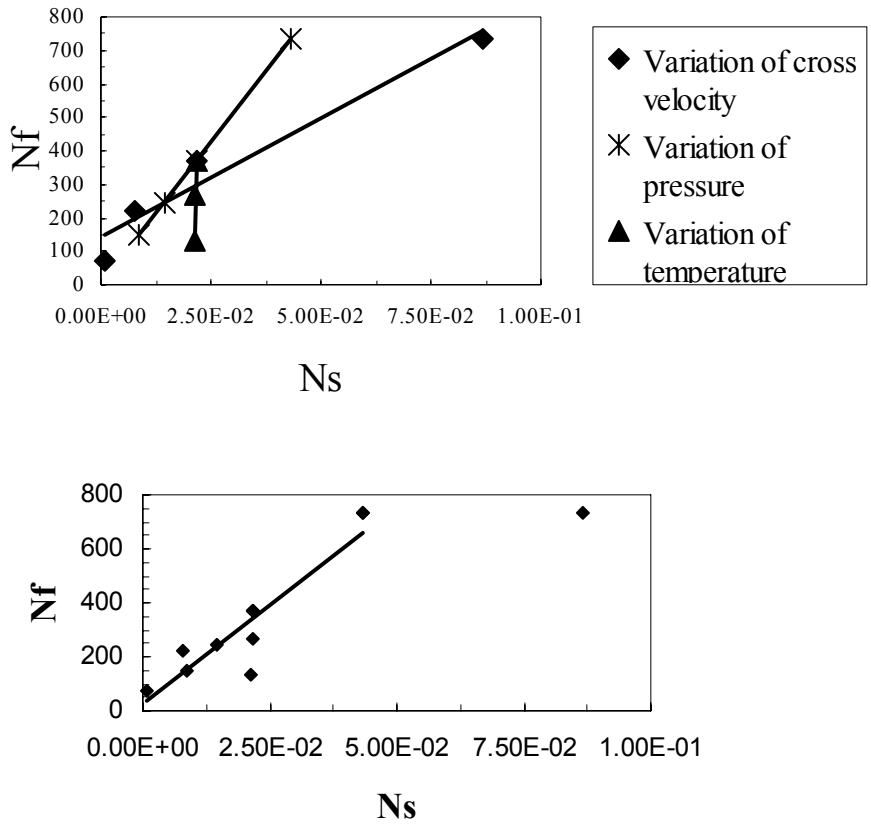

Fig. 6. N_f as a function of Ns.

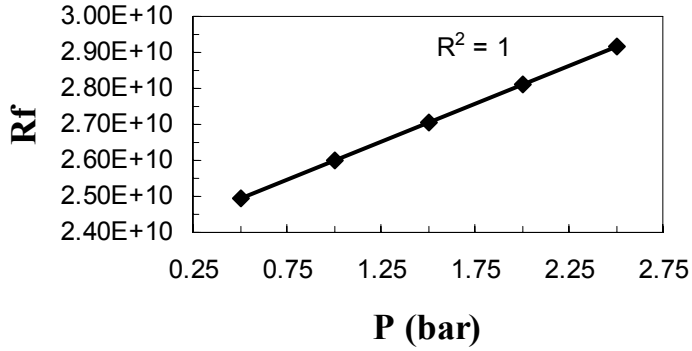

Fig. 7. R_f as a function of pressure when constant cross flow velocity

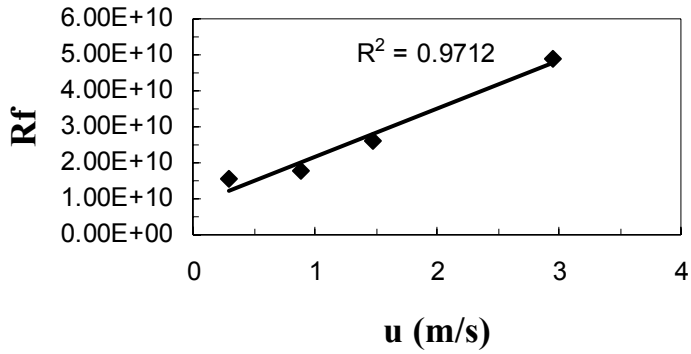

Fig. 8. R_f as a function of cross-velocity when the pressure is constant

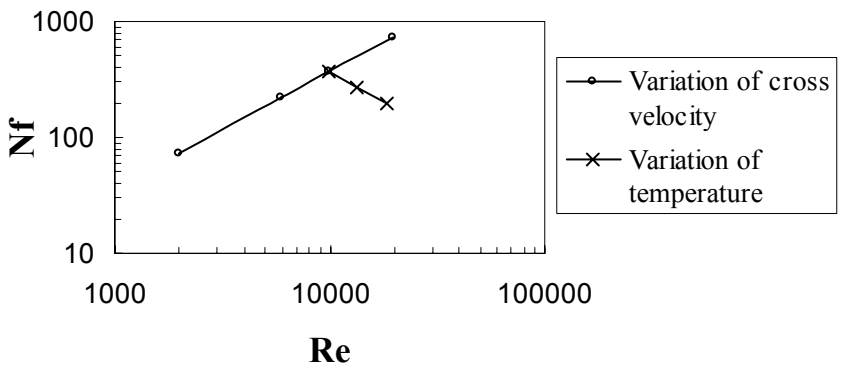

Fig. 9. The plot of N_f versus Reynolds number.

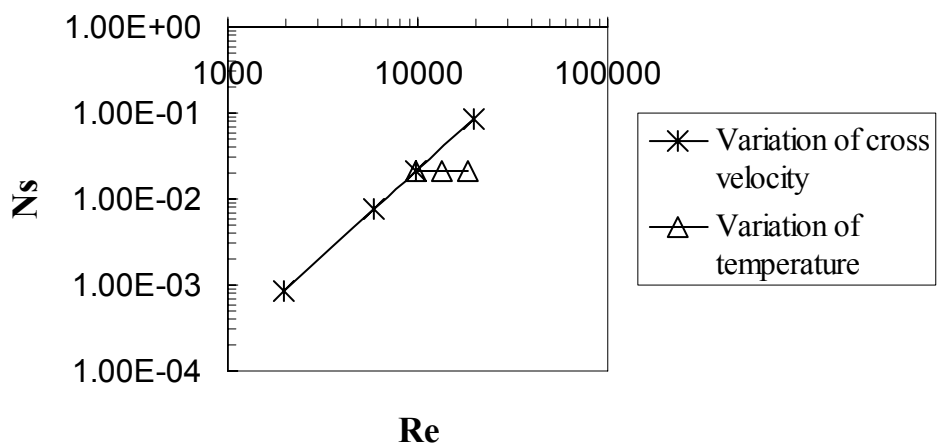

Fig. 10. The plot of N_s against Reynolds number

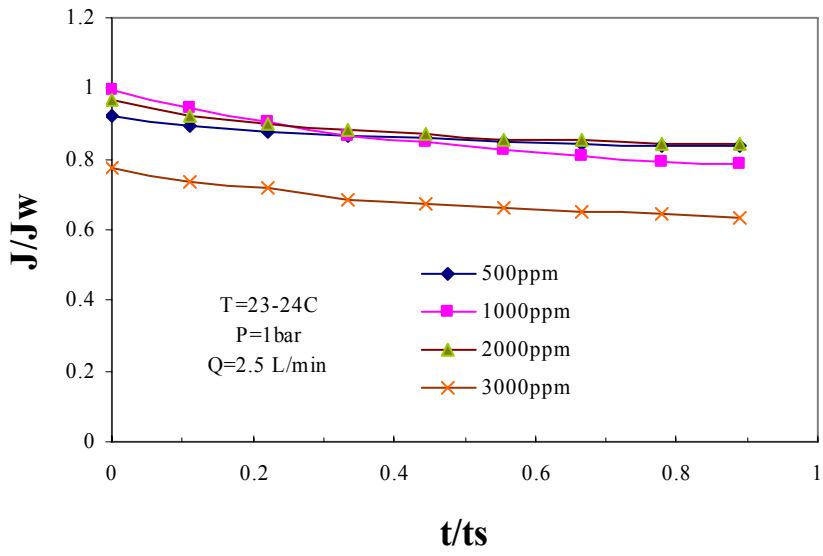

Fig. 11. Effect of concentration on flux factor

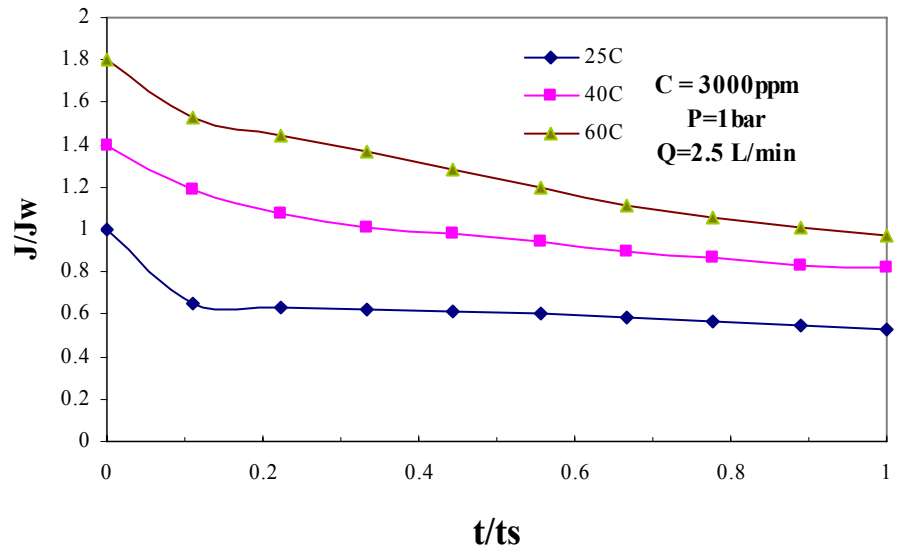

Fig. 12. Effect of temperature on flux factor

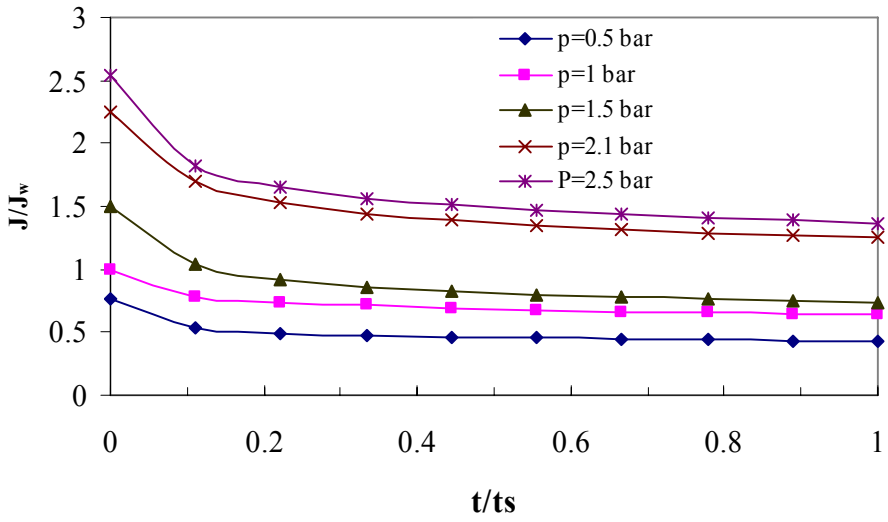

Fig. 13. Effect of transmembrane pressure on flux factor

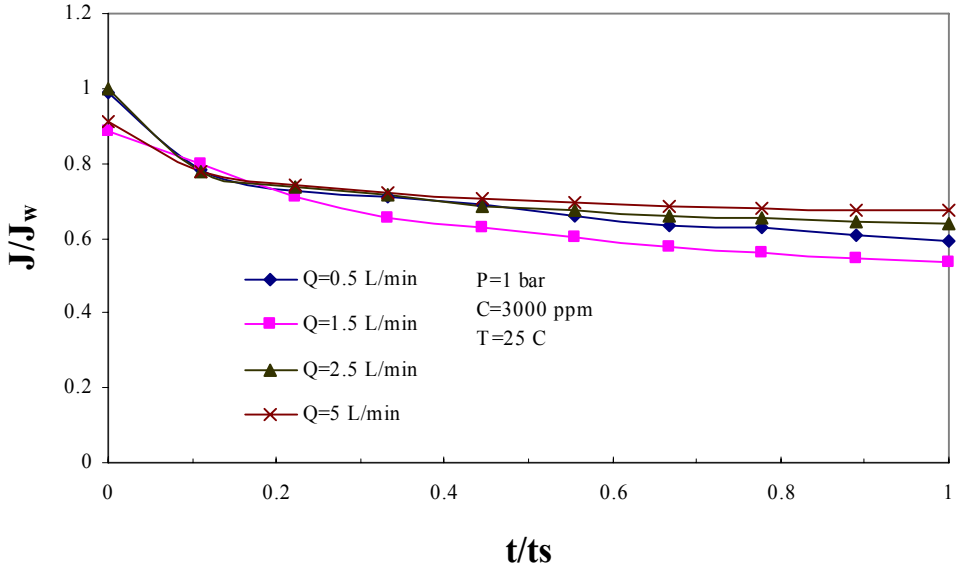

Fig. 14. Effect of flow rate on flux factor