

CHARACTERIZATION OF GEL CONCENTRATION IN ULTRAFILTRATION OF OIL-IN-WATER EMULSION

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Processing of oil-in-water emulsions with conventional ultrafiltration membranes leads to rapid membrane fouling and flux decline and it is generally uneconomic because of this problem. The major hurdles to be overcome in the development of a practical industrial unit are concentration polarization and fouling. This paper presented a new model for the calculation of the gel concentration at the membrane surface. The model includes the following influence factors: transmembrane pressure, feed concentration, mass transfer coefficient, membrane resistance and so on. In the present experimental conditions, the gel concentration for FP 055A ultrafiltration membrane is about 30 vol. %.

Keywords: Ultrafiltration, Oil-in-water emulsion, Gel concentration, Concentration polarization

Introduction

Ultrafiltration has been accepted versatile membrane separation process for water purification and wastewater treatment in the last years. Its industrial application is so wide that it is presently regarded as a well established unit process. Using ultrafiltration membrane to separate oil-in-water emulsions many articles have been reported [1-3]. The water removal from wastewater by ultrafiltration is influenced by the membrane material, the physical performance itself and the operation conditions. For a selected membrane it is necessary to choose the best operation parameters in order to assure the membrane works under optimal conditions. As a fundamental study, in our former researches, it was studied that the effects of several kinds of ultrafiltration membranes with different nominal molecular weight cut off (MWCO) and pore size on the treatment efficiency of the oil-in-water emulsions with different oil concentrations [4, 5]. The results show that the tested membranes can be applied to remove water from oil-in-water emulsions with different permeate flux, oil rejection and COD in the permeated fluid. However, there are two significant problems which are always found during the ultrafiltration membrane operation of oily emulsion [6]. (1) Concentration polarization, which is the build-up of a concentrated layer on the membrane surface. The permeate resistance of water increased greatly, and the permeate flux declined. (2) Membrane

fouling, which results from the adsorption of solute in the membrane structure and mainly causes changes in surface chemistry. These effects lead to a decrease in permeate flux with time and limit the separation efficiency.

Many authors have introduced and enucleated the concentration polarization and the ultrafiltration model of gel layer [7-10]. Two typical models, hydraulic resistance model and osmotic pressure model, are widely acceptably [11, 12]. The coefficient of mass transfer at the membrane surface has been studied according to Reynolds number and Schmidt number. However the relationship between models of the concentration polarization and gel layer has been less referred. This research introduces the calculation expression of gel concentration on the basis of understanding concentration polarization and gel layer for the ultrafiltration separation of oil-in-water emulsion.

Theoretical Fundamentals

The permeate flux, J_w , is an important parameter in the design and analysis of the economic feasibility of the ultrafiltration separation process. Hydro-dynamics of membrane modules have an important effect on the mass transfer, separation, and fouling behavior of membrane systems. During ultrafiltration the solutes are

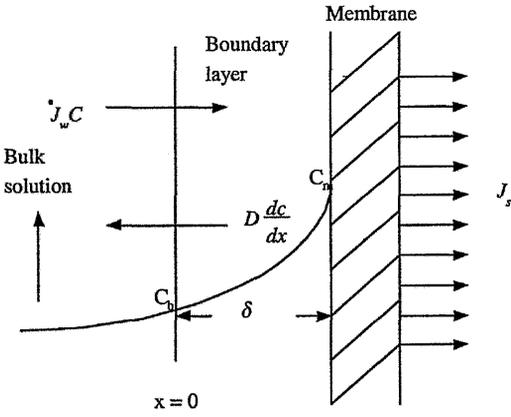


Fig.1 Concentration profile in the boundary layer of UF

carried and accumulated at the membrane surface, and formed a concentration difference between the membrane surface and bulk solution. It leads to the solutes diffusing into the bulk solution backward till a balance situation of concentration is attained, as shown in Fig.1 [10]. The permeate flux can be shown as follows:

$$J_w = \frac{D}{\delta} \ln \frac{C_m - C_f}{C_b - C_f} \quad (1)$$

where J_m is the permeate flux (l/m^2h); C_b is the solute concentration in the bulk solution of feed (g/l); C_m is the solute concentration at the membrane surface (g/l); C_f is the solute concentration in the permeate (g/l); D is the diffusion coefficient of solute (m^2/s); δ is the thickness of the boundary layer (polarization layer) (m).

If the ultrafiltration effect is perfect, there is no solute in the permeate, C_f can be ignored. So Eq.(1) can be simplified:

$$J_w = K \ln \frac{C_m}{C_b} \quad (2)$$

where $K = \frac{D}{\delta}$, coefficient of mass transfer.

Although Eq.(2) does not present the relation between the pressure and other factors, increasing pressure can improve permeate flux of water, and the solute concentration at the membrane surface is also increased. The concentration polarization becomes more severe, which causes the flux of the solute diffusion backward to be increased. As UF process became stable at a specified pressure, the logarithm functional relation between J_w and C_m was keeping with Eq.(2).

In addition, the thickness of boundary layer in Eq.(2), δ , depends on the hydraulic dynamic conditions, such as, the water flow velocity parallel to the membrane surface. The diffusion coefficient D is related with the solute property and feed temperature. If the treated object is a macromolecular solution, the solute concentration at the membrane surface, C_m , increased greatly because of the smaller D , and the backward-diffusion flux of solute is lower as well. It results in

increasing the ratio of C_m/C_b . When the pressure reached the critical pressure, the gel layer was produced. The solute concentration at the membrane surface (C_m) is named of gel concentration (C_g). So Eq.(2) can be changed into:

$$J_w = \frac{D}{\delta} \ln \frac{C_g}{C_f} \quad (3)$$

For a selected solute, the gel concentration can be regarded as a stable value under certain conditions. The gel concentration is related with the solubility of the solute in water. So J_w can also be considered as a determined value. If increasing the transmembrane pressure continually, the backward-diffusion flux of the solute cannot be enhanced. In a short time, the permeate flux might be increased, the enhanced pressure, however, is balanced by the gel layer resistance quickly with increasing the thickness of the gel layer. The permeate flux of water returned to the previous level. So, according to Eq.(3), it can be drawn the following opinions: (1) once the gel layer is formed the permeate flux of water does not increase with the pressure; (2) the permeate flux of water decreased linearly with the logarithm relation of the solute concentration, C_b ; (3) the permeate flux of water still depends on the hydraulic dynamic conditions which defined the thickness of the boundary layer.

On the other hand, there is a polarization layer resistance besides the intrinsic membrane resistance if the polarization layer cannot be ignored. Darcy's law (also known as the resistance-in-series theory) is widely used to relate the permeate flux to the applied pressure and the fouling resistance [10 - 13]:

$$J_w = \frac{\Delta P}{\mu(R_m + R_p)} \quad (4)$$

Here, μ is the solution viscosity (Pa s). ΔP is transmembrane pressure (Pa). R_m is the intrinsic membrane resistance ($1/m$). R_p is the polarization layer resistance ($1/m$). The intrinsic membrane resistance is unaffected by operating parameters whereas the polarization layer resistance is a function of applied pressure. As the gel layer is formed, the resistance of UF includes still the gel layer resistance, R_g ($1/m$), so the permeate flux of water can be expressed:

$$J_w = \frac{\Delta P}{\mu(R_m + R_p + R_g)} \quad (5)$$

Because $R_g \gg R_p$, when R_p is negligible, the filtrate flux is given by the following Eq.(6)

$$J_w = \frac{\Delta P}{\mu(R_m + R_g)} \quad (6)$$

Under certain transmembrane pressure it can be seen that the resistance of gel layer is proportional directly to the solute amounts retentated which is proportional directly to the accumulative water volume, V , permeated according to the general filtration principle, provided

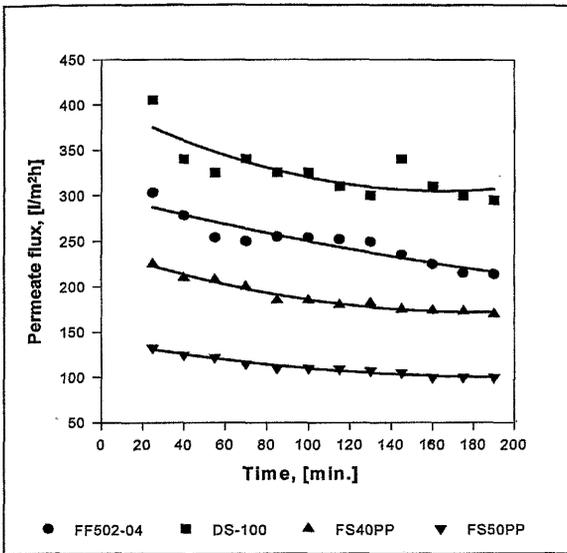


Fig.2 Permeate flux as a function of time for different membranes at feed oil concentration 0.5 vol. %

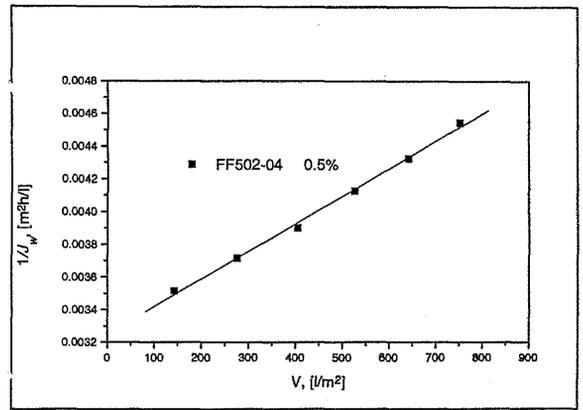


Fig.3 The relation diagram of $1/J_w - V$ for UF membrane FF 502-04 at the feed concentration of 0.5 vol. %

the gel layer cannot be compressed. So the relation between R_g and V can be expressed to $R_g \propto V$.

In addition, the pure solvent transport through porous UF membranes is directly proportional to the applied transmembrane pressure, ΔP . Models that can be used to describe the convective flow, J_w^0 , are the Kozeny-Carman and Hagen-Poiseuille equations [14]:

$$J_w^0 = \frac{\Delta P}{\mu_o R_m} \quad (7)$$

where μ_o is the solvent viscosity (Pa s). Taking Eqs.(6) and (7) together the following equation can be given if the solvent viscosity is nearly equal to solution one.

$$\frac{1}{J_w} = \frac{1}{J_w^0} + \frac{\beta}{\Delta P} V = \frac{\mu_o R_m}{\Delta P} + \frac{\beta}{\Delta P} V \quad (8)$$

where β is coefficient is to be determined.

If taking a plot of $\Delta P/J_w$ with V at a specified pressure, a line can be presented and its intercept is equal to (μR_m) value. According to the slope of the line, the coefficient β can also be attained, and the R_g can be calculated as well ($R_g = \beta V$).

If pressure is variable, the increased pressure can enhance the permeate flux in a shorter time and forces more solute to the membrane surface. Both the thickness and the resistance of gel layer are also increased. So it can be seen that R_g is directly proportion to ΔP at that time, then Eq.(6) can be modified:

$$J_w = \frac{\Delta P}{\mu(R_m + \alpha \cdot \Delta P)} \quad (9)$$

where α is the coefficient to be determined. The equation above shows the relation between J_w and ΔP .

Comparing Eq.(9) with Eq.(2), it can be seen Eq.(9) cannot present the influences of flow velocity of bulk solution and feed oil concentration, and Eq.(2) cannot

show directly the effects of the pressure and resistance. However they erect the relations of $J_w - \Delta P$ and $J_w - C_m$ respectively under the concentration polarization and gel layer. If letting them equal, a novel equation can be obtained.

$$\frac{\Delta P}{\mu(R_m + \alpha \cdot \Delta P)} = K \ln \frac{C_m}{C_b} \quad (10)$$

Subsequently:

$$C_m = C_b \cdot \exp \left\{ \frac{1}{K} \left(\frac{\Delta P}{\mu(R_m + \alpha \cdot \Delta P)} \right) \right\} \quad (11)$$

With respect to the above equation, it can calculate approximately the solute concentration within concentration polarization region under different pressures and the gel concentration under critical pressure at the membrane surface, respectively.

Evaluation of Experimental Results

Calculations of membrane resistance and gel layer resistance

As an example, Fig.2, which plotted the flux with time for different UF membranes [4], was selected to characterize the relationship between $1/J_w$ and V . The operating pressure is 3 bar, the oil-in-water emulsion concentration is 0.5 vol. %. The viscosity of emulsion $\mu = 1.147$ cP = 1.1245×10^{-3} Pa s. At the beginning of operation the flux declines rapidly, and becomes stable gradually. According to the experimental data, the Fig.3 plotted $1/J_w$ with V was presented for FF 502-04 UF membrane.

According to Eq.(8) the relation of $1/J_w - V$ for FF 502-04 membrane can be expressed: $1/J_w = 0.00325 + 1.73 \times 10^{-6} V$ as treating an emulsion with a feed oil concentration of 0.5 vol. %. The intercept of the line is 0.00325, the item of $(\mu R_m / \Delta P)$ is equal to 0.00325 m²/h/l. So after conversion $R_m = 3.12 \times 10^{12}$ 1/m.

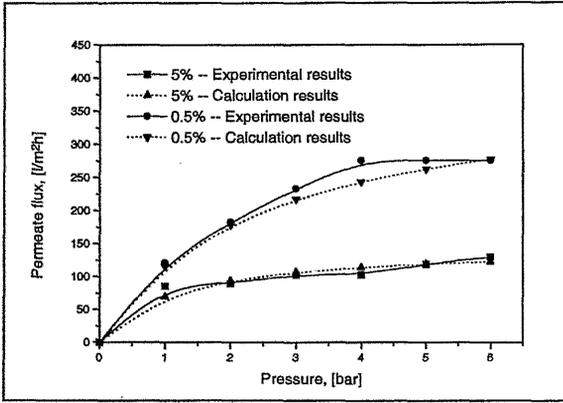


Fig. 4 Permeate flux as a function of transmembrane pressure for FP 055A membrane at different emulsion concentration

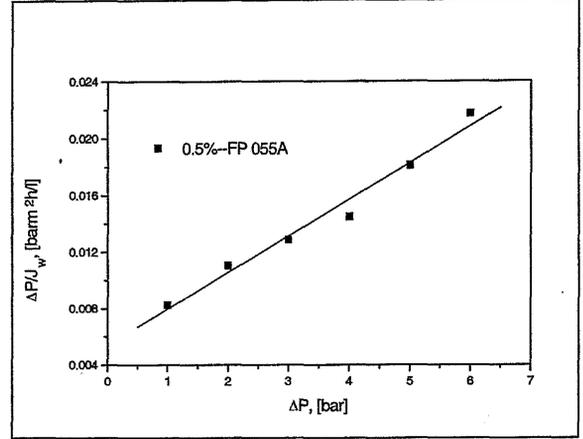


Fig. 5 A diagram of $\Delta P/J_w$ -- ΔP at oil concentration of 0.5 vol. %

In addition, another item of $(\mu\beta/\Delta P)$ is 1.73 h/m^2 according to the slope of the line. $\beta = 1.73 \text{ h/m}^2 \times 3 \times 10^5 \text{ Pa} / 1.1245 \times 10^{-3} \text{ Pa s} = 1.6615 \times 10^{12} \text{ l/m}^2$. $R_g = \beta V = 1.6615 \times 10^{12} V$. With the same methods above, for the other UF membranes DS-100, FS 40PP and FS 50PP plotted in Fig. 2, their expressions between $1/J_w - V$ and their resistances can be shown as follows, respectively:

$$\text{DS-100: } 1/J_w = 0.00088 + 2.1 \times 10^{-6} V \\ (R_m = 8.452 \times 10^{11}; R_g = 2.017 \times 10^{12} V)$$

$$\text{FS 40PP: } 1/J_w = 0.0043 + 10.5 \times 10^{-6} V \\ (R_m = 4.130 \times 10^{12}; R_g = 1.008 \times 10^{13} V)$$

$$\text{FS 50PP: } 1/J_w = 0.0077 + 3.12 \times 10^{-5} V \\ (R_m = 7.395 \times 10^{12}; R_g = 2.996 \times 10^{13} V)$$

From these expressions, it can be seen that the resistance of gel layer increases with the accumulative volume of the permeate water under a specified pressure. Both of the gel resistance and the membrane resistance of DS-100 ultrafiltration membrane are the least among the membranes measured.

J_w -- ΔP expression

The relationship between flux and transmembrane pressure was discussed elsewhere [15]. To increase transmembrane pressure can improve the permeate flux. At lower emulsion concentration (0.5 vol. %), the concentration polarization is not obvious, the permeate flux is almost increased linearly with the transmembrane pressure. At higher emulsion concentration (5 vol. %) the effect of pressure on the permeate flux depends on the magnitude of pressure. Under a lower pressure the flux is also increased with pressure. The flux, however, is controlled by the gel layer at higher pressure, not by transmembrane pressure. So the membrane has a critical flux at higher feed concentration. Fig. 4 showed the permeate flux as a function of operating pressure for FP 055A membrane at 30°C under different emulsion concentrations. The Eq.(9) can be expressed:

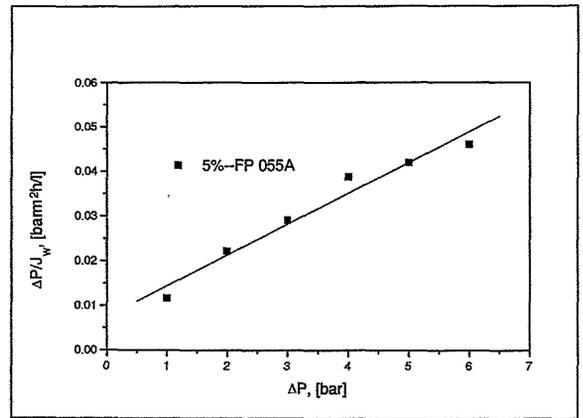


Fig. 6 A diagram of $\Delta P/J_w$ -- ΔP at oil concentration of 5 vol. %

$$\frac{\Delta P}{J_w} = \mu(R_m + \alpha \cdot \Delta P) = \mu R_m + \mu \alpha \cdot \Delta P \quad (12)$$

Taking a diagram of $\Delta P/J_w$ with ΔP at 0.5 vol. %, as shown in Fig. 5., in which the intercept, $\mu R_m = 0.0059$ (bar m²/h/l), the slope, $\mu \alpha = 0.0026$ (m²/h/l).

So for the emulsion with a feed concentration of 0.5 vol. %,

$$J_w = \frac{\Delta P}{0.0059 + 0.0026 \Delta P} \quad (13)$$

Using the same methods, another plot of $\Delta P/J_w$ with ΔP at 5 vol. % is shown in Fig. 6, in which $\mu R_m = 0.0075$ (bar m²/h/l), $\mu \alpha = 0.0069$ (m²/h/l). So, for the emulsion with a feed concentration of 5 vol. %:

$$J_w = \frac{\Delta P}{0.0075 + 0.0069 \Delta P} \quad (14)$$

Both Eqs. of (13) and (14) show the expressions of J_w -- ΔP for FP 055A ultrafiltration membrane under different feed concentrations, respectively. In Fig. 4, the square points symbols the experimental values; the up-triangle points stands for

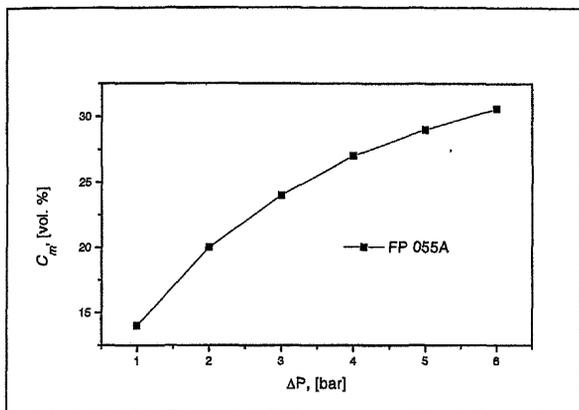


Fig.7 A relation of C_m -- ΔP for FP 055A membrane treated oil-in-water emulsion by calculation

the calculation values at feed concentration of 5 vol. %. The cycle points are the experimental values; the down-triangle points are the calculated values at feed concentration of 0.5 vol. %. From these results, it is seen that the experimental and calculated values are approximately near to each other. The equation above can be used to express the relation of J_w -- ΔP for oil-in-water emulsion.

Expression of C_m -- ΔP

According to data in Fig.4, the critical flux $J_{crit1} = 276$ l/m²h as $C_{b1} = 0.5$ vol. % at a steady state; the critical flux $J_{crit2} = 120$ l/m²h as $C_{b2} = 5$ vol. %. Since the cross-flow velocity was constant throughout, it can be assumed that the mass transfer coefficient (K) was also constant under different feed concentrations and therefore the plot appears linear for the theory to hold true. According to Eq.(2)

$$J_{crit1} - J_{crit2} = K \ln \frac{C_{b2}}{C_{b1}} = K \ln \frac{5}{0.5} = 276 - 120 = 156$$

So $K = 67.75$ m/h. Then taking K into Eq.(2). The relationship between the critical flux and the gel concentration can be expressed:

$$J_{crit1} = 67.75 \ln \frac{C_g}{0.5} \quad (15)$$

Then, C_g can be solved as about 29.4 vol. %. The variation of flux with the concentration at membrane surface can be expressed:

$$J_w = 67.75 \ln \frac{C_m}{0.5} \quad (16)$$

for the feed oil concentration of 0.5 vol. %

$$J_w = 67.75 \ln \frac{C_m}{5} \quad (17)$$

for the feed oil concentration of 5 vol. %

According to Eq.(11) the oil concentration, C_m , at the membrane surface can be calculated by the following Eq.(18) or Eq.(19):

$$C_m = 0.5 \cdot \exp \left\{ \frac{1}{67.75} \left(\frac{\Delta P}{0.0059 + 0.0026 \Delta P} \right) \right\} \quad (18)$$

$$C_m = 5 \cdot \exp \left\{ \frac{1}{67.75} \left(\frac{\Delta P}{0.0075 + 0.0069 \Delta P} \right) \right\} \quad (19)$$

Taking different operating pressures into the Eq.(18) or Eq.(19) above, the oil concentration, C_m , at the membrane surface can be calculated approximately. Fig.7 shows that the oil concentration at the membrane surface varied with pressure. As the operating pressure increases, the C_m is also approaching to C_g (about 30 vol. %).

4. Conclusions

A relation between the permeate flux and transmembrane pressure can be drawn:

$$J_w = \frac{\Delta P}{\mu(R_m + \alpha \cdot \Delta P)}$$

At the same time, it can approximately be calculated the solute concentration within concentration polarization region under different pressures and the gel concentration under critical pressure at the membrane surface with respect to the following equation:

$$C_m = C_b \cdot \exp \left\{ \frac{1}{K} \left(\frac{\Delta P}{\mu(R_m + \alpha \cdot \Delta P)} \right) \right\}$$

Under our present experimental conditions, the gel concentration for FP 055A membrane treated oil-in-water emulsion is about 30 vol. %.

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