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A modified rate expression of wet membrane formation from ceramic particles suspension on porous substrate

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Abstract

The formation and growth mechanism of the wet membrane formed in dip-coating process was systematically studied on the consideration of the capillary colloid filtration and the film coating processes as well as an applied pressure. An expression to describe the growth rate of the wet membrane was derived. It can be denoted that the thickness of the wet membrane increases monotonously with the dipping time but a transition would occur due to the saturation of the capillaries in the substrate and the decrease of the capillary suction force. It is also shown that different mechanism has different effect on the thickness of the wet membrane: the wet membrane formed by film coating may dominate while the dipping time is short and the suspension viscosity is high; but for the suspensions with low viscosity, the capillary colloid filtration contributes more to the wet membrane growth, especially for longer dipping time. As long as the wet membrane exhibits a similar structure during the dip-coating process, the wet membrane thickness can be expressed as a function of the parameters, ΔP_p, η, t, etc. And the expression derived in this work has been verified by the experimental data and proved to be valuable for the control of the membrane formation.

Keywords: Fabrication of ceramic membrane; Dip-coating process; Formation mechanism; Capillary colloidal filtration; Film coating

1. Introduction

As an important process for the fabrication of ceramic membranes, dip-coating has been widely used [1–4]. A wet cake is first formed when dipping a dry porous substrate into a particle suspension and subsequently withdrawn from it, and thus the ceramic membrane could be achieved following drying and sintering. The ceramic membranes with different pore size and thickness have found various applications in many areas. The structure and separation property of a ceramic membrane are largely affected by its thickness, which should be large enough to depress the defects formation usually resulting from the substrate surface roughness, such as cracks and voids, but sufficient thickness in order to supply good adhesion to the substrate, great endurance to the mechanical stress during the sintering process and larger fluid permeation rate. The dip-coating parameters, such as the suspension viscosity and dipping time, play a critical role in determining the thickness of the wet cake and subsequently the thickness of ceramic membrane. Therefore, it is very important and necessary to investigate the formation mechanism and the growth rate of the wet membrane prepared by dip-coating process.

Leenaars and Burgraaf [5] proposed a mathematic express of the thickness of wet cake formed by capillary colloidal filtration. Gu et al. [6] in this laboratory made some modification and concluded that the thickness of wet cake should be proportional to the extraction time and reciprocal to the suspension viscosity based on the model from slip-casting process and the consideration of capillary colloidal filtration. According to the film-coating model, Landau and Levich [7] showed that the thickness of the wet membrane increased with the withdrawing velocity of the substrate and the suspension viscosity. Obviously, the above two models just partially describes the mechanism of wet cake formation. Both models play their part in the adhesion of suspension to substrate and in the formation of wet cake. The practical data have showed that the linear plot of the wet cake thickness versus the extraction root of the dipping time does not pass the zero point. This implies that both for-

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mation mechanisms have effect on the thickness of the wet cake. In the dip-coating process, an additional pressure to the capillary pressure caused by the driven flow of suspension should also be considered on the wet membrane thickness; however, there was no complete expression to describe it.

In this paper, a modified model based on the combination of slip-casting model and film-coating model has been developed to describe the formation mechanism and growth kinetics of the wet cake by dip coating, and the effect of applied pressure on cake thickness have been considered at the same time. An equation is achieved to describe the dependence of the wet cake thickness on the dipping time, and some experimental data given to testify its validity.

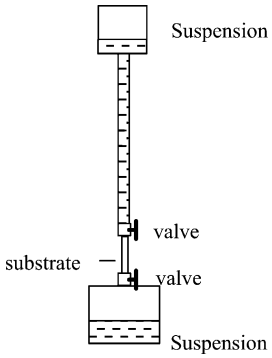

Fig. 1. The sketch of the equipment for dip-coating.

2. Formation mechanism of wet membrane

To prepare a ceramic membrane onto the inner surface of a porous ceramic tubular support by dip coating process, the suspension made of ceramic particles, dispersant and solvent was poured into a dry porous tubular substrate with closed end. Under the driving force of capillary pressure and the applied pressure, a wet membrane is formed by the infiltration of the solvent into the substrate and the non-infiltration of the ceramic particles. After dipping for a desired time, the suspension is allowed to flow out of the tube by opening the lower valve. The thickness of the wet membrane can be enhanced ulteriorly for an additive layer of suspension adhered onto the support surface by the viscous force of the fluent. The instrument was shown in Fig. 1.

The formation and growth of the wet membrane could be divided into four steps according to the different flow status of the suspension:

1. A still boundary layer has formed on the substrate surface when the suspension is poured into the tubular substrate until the tube is completely filled with the suspension.
2. Formation of the wet membrane is driven by the capillary pressure and the applied pressure and membrane thickness increases with the dipping time.
3. After the desired dipping time, the suspension flows out the tube and a new boundary layer forms which protects the wet membrane from peeling off the substrate due to its stillness status.
4. With the lowering of the fluid level, the thickness of the wet membrane intensively increases by the film coating mechanism.

Fig. 2 gives a sketch of those four procedures.

In order to discuss systematically the formation mechanism of the wet membrane, some assumptions were made to simplify its complexity:

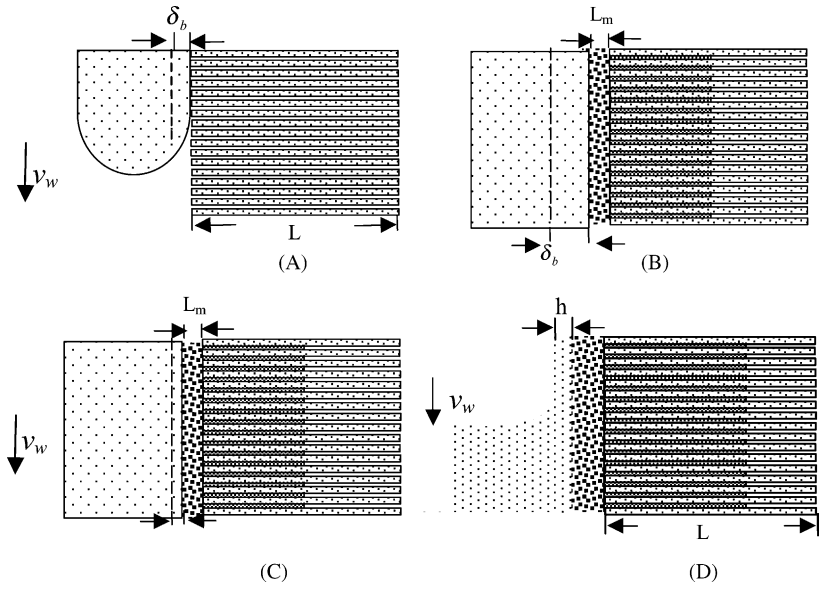

Fig. 2. Sketch of the formation and growth of the wet membrane in dip-coating process. (A) The formation of a laminar boundary as the suspension poured into the tubular substrate; (B) the formation and growth of the wet membrane in still suspension; (C) the formation of the laminar boundary due to the flow of the suspension; (D) the growth of the wet membrane by the film-coating.

1. The inner surface of the tubular substrate is smooth and homogeneous. And the pores in the substrate or in the wet membrane could be treated as a group of capillary with the same diameter and length.
2. The ceramic particles would not agglomerate for its adequately dispersed and stabilized, unless form the wet cake on the inner surface of the substrate.
3. The suspension could spread on the surface of the substrate completely.
4. The distance between the fluid level and the substrate is much larger than the length of the substrate, therefore, the grade of the applied pressure caused by the gravity along the tube substrate could be neglected.
5. The filtration process could be approximately described as planar filtration due to the small thickness of the wet membrane compared with the curvature radius of the substrate inner surface.
6. The flow velocity of the suspension keeps constant when the suspension flow out of the substrate.
7. The density of the suspension keeps constant during the whole process.

The wet membrane formation mechanism and the operational parameters, which may affect the growth of the wet membrane, are discussed below in detail.

2.1. Flow of the suspension on inner surface of the substrate

When viscous suspension flows through the tubular substrate, a velocity grade of suspension is formed due to inherent resistant force with zero velocity on the surface of the substrate known as 'boundary layer'. Though the whole flow could be turbulent, the curve shape of the velocity distribution of suspension would be similar to that of laminar flow. It had been reported that while the turbulent flow went through a smooth tube and its Reynolds coefficient was smaller than 10^5, the thickness of the laminar boundary layer could be estimated by Eq. (1) [8]:

$$\frac{\delta_b}{d} = \frac{B}{Re^{7/8}} \tag{1}$$

where δ_b is the thickness of the laminar boundary, d the inner diameter of the tubular substrate, Re the Reynolds coefficient, B is a constant related to the ratio of the mean flow velocity to the maximum velocity in the center of the tube, such as B equals to 61.5 while v/v_{max} is 0.81.

The Reynolds coefficient is defined as:

$$Re = \frac{\mathrm{d}v\,\rho}{\eta} \tag{2}$$

where η is the viscosity of the suspension, ρ is the density of the flow. And then Eq. (1) could be expressed as:

$$\delta_b = Ad^{1/8}\left(\frac{\eta}{v\rho}\right)^{7/8} \tag{3}$$

To the given suspension and substrate, d and ρ are constant, and Eq. (3) became

$$\delta_b = K_1\left(\frac{\eta}{v}\right)^{7/8} \tag{4}$$

where K_1 is constant affected by the diameter of the tubular substrate and the density of the flow.

As a matter of fact, the laminar boundary layer had no effect on the thickness of wet membrane while the suspension flowed in to fill the substrate. But, the laminar boundary layer could protect the wet membrane from peeling off the substrate while the suspension flowed out of the substrate.

2.2. Formation and growth of the wet membrane

While the suspension contacted with the dry porous substrate, its dispersing liquid passed through the substrate driven by the capillary pressure and some other applied pressures, and wet membrane formed by the aggregating of ceramic particles on the surface of the substrate. And dispersing liquids entered the pores of the substrate by infiltration with a small part of it staying in the wet membrane. Provided that the wet membrane was homogenous and incompressible, the solid volume percentage and the microstructure of the wet membrane were invariable during the whole dip coating process. And at the dipping time dt, the wet membrane of $\mathrm{d}L_m$ in thickness could be formed by the suspension of $\mathrm{d}L$ in thickness, and the growth velocity of the wet membrane would be defined as $\mathrm{d}L_m/\mathrm{d}t$ at time $\mathrm{d}t$. Fig. 3 gives the sketch of the forming of the wet membrane from the dispersing suspension.

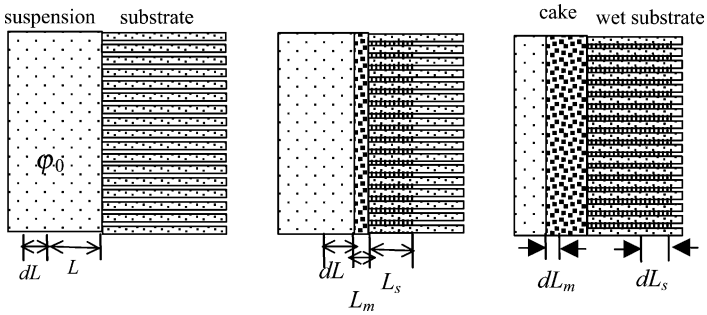

Fig. 3. The formation of the wet membrane on a porous substrate.

According to the mass conservation, the specific flux q of the dispersing liquid that passed through the wet membrane could be described as [6]:

$$q = \frac{\mathrm{d}L - \mathrm{d}L_\mathrm{m}}{\mathrm{d}t} \tag{5}$$

As the amount of the ceramic particles keeps constant in the conversion of $\mathrm{d}L$ suspension to $\mathrm{d}L_\mathrm{m}$ wet membrane, there should be a balance

$$(\mathrm{d}L) \times \varphi_0 = (\mathrm{d}L_\mathrm{m}) \times \varphi_\mathrm{m} \tag{6}$$

where φ_0 and φ_m are the volume fraction of the ceramic particles in the suspension and in the wet membrane, respectively. Combining Eqs. (5) and (6) gives

$$q = \frac{\alpha \times \mathrm{d}L_\mathrm{m}}{\mathrm{d}t} \tag{7}$$

where α is defined as

$$\alpha = \left(\frac{\varphi_\mathrm{m}}{\varphi_0} - 1\right) \tag{8}$$

According to Darcy's law, the specific flux of a liquid flowing through a porous medium at time t is

$$q = \frac{\Delta P_\mathrm{m} K_\mathrm{m}}{\eta L_\mathrm{m}} \tag{9}$$

where K_m is the specific permeability of the wet membrane, η the viscosity of the dispersing liquid and ΔP_m is the pressure drop across the membrane. Combining the Eqs. (7) and (9), the rate equation for the wet membrane formation could be described as:

$$\frac{L_\mathrm{m}\,\mathrm{d}L_\mathrm{m}}{\mathrm{d}t} = \frac{\Delta P_\mathrm{m} K_\mathrm{m}}{\alpha\eta} \tag{10}$$

In the dip coating process, the total driving force (ΔP) for the dispersing liquid into the substrate should be the combination of the specific capillary suction pressure (ΔP_c) caused by the capillaries of the substrate and the applied pressure (ΔP_p) given by potential pressure of the suspension. According to the assumption that the capillaries with radius R are uniformly distributed in the porous substrate, the total driving force is

$$\Delta P = n(\pi R^2)\Delta p_\mathrm{c} + \Delta P_\mathrm{p} = \varepsilon_\mathrm{s}\,\Delta p_\mathrm{c} + \Delta P_\mathrm{p} \tag{11}$$

where n is the number of the capillaries per unit, ε_s the porosity of the substrate and Δp_c the capillary pressure caused by one capillary, which could be given as

$$\Delta p_\mathrm{c} = \frac{2\gamma\cos\theta}{R} = \frac{2\gamma}{R} \tag{12}$$

where γ is the surface tension of the dispersing liquid in the pores of the support, θ the contact angle between the dispersing liquid and the solid surface and assumed to be zero degree to simplify the complexity of the mechanism.

Because of the different microstructure of the substrate and the wet membrane, the total driving force (ΔP) could be divided into two parts: one is the pressure over the whole membrane (ΔP_m), which is used to drive the dispersing liquid passed through the membrane; the other is the pressure drop (ΔP_s) across the substrate, driving the liquid flowing in capillaries:

$$\Delta P = \Delta P_\mathrm{m} + \Delta P_\mathrm{s} \tag{13}$$

From Darcy's law and the mass balance of the dispersing liquid flowing through the wet membrane and the substrate, we have

$$\frac{\Delta P_\mathrm{s} K_\mathrm{s}}{\eta L_\mathrm{s}} = \frac{\Delta P_\mathrm{m} K_\mathrm{m}}{\eta L_\mathrm{m}} \tag{14}$$

where K_s is the permeability of substrate, L_s the length of the capillaries occupied by the dispersing liquid. Combing Eqs. (11), (13) and (14), the pressure over the membrane could be given as

$$\Delta P_\mathrm{m} = \frac{\varepsilon_\mathrm{s}\Delta p + \Delta P_\mathrm{p}}{1 + K_\mathrm{m} L_\mathrm{s}/K_\mathrm{s} L_\mathrm{m}} \tag{15}$$

After a desired dipping time t, a wet membrane with the thickness L_m and a saturated substrate with the length L_s would form from a suspension with thickness L,

$$L - L_\mathrm{m} = \varepsilon_\mathrm{s} L_\mathrm{s} \tag{16}$$

According to mass conservation, the amount of the ceramic particles in the suspension is the same as that in the wet membrane, therefore,

$$L\varphi_0 = L_\mathrm{m}\varphi_\mathrm{m} \tag{17}$$

Substituting Eq. (16) into Eq. (17) gives

$$\frac{L_\mathrm{s}}{L_\mathrm{m}} = \frac{(\varphi_\mathrm{m}/\varphi_0) - 1}{\varepsilon_\mathrm{s}} = \frac{\alpha}{\varepsilon_\mathrm{s}} \tag{18}$$

Thus, Eq. (15) can be also written as

$$\Delta P_\mathrm{m} = \frac{2\varepsilon_\mathrm{S}\gamma + R\,\Delta P_\mathrm{p}}{R(1 + K_\mathrm{m}\alpha/K_\mathrm{s}\varepsilon_\mathrm{S})} \tag{19}$$

According to the assumption in the last section, ΔP_p can be regarded as a constant, though it varies with the vertical position of the solvent. Therefore, the pressure drop ΔP_m across the cake was invariable since its factors, K_m, α and η, keep constant. Eq. (10) then becomes,

$$\mathrm{d}(L_\mathrm{m})^2 = \left(\frac{2\Delta P_\mathrm{m} K_\mathrm{m}}{\alpha\eta}\right)\mathrm{d}t \tag{20}$$

Substituting Eq. (19) into Eq. (20) and integration under the boundary condition that $L_\mathrm{m} = 0$ at $t = 0$ gives

$$L_\mathrm{m} = 2\left[\frac{\varepsilon_\mathrm{S}\gamma + R\,\Delta P_\mathrm{p}}{\eta\alpha R(1/K_\mathrm{m} + \alpha/\varepsilon_\mathrm{S}K_\mathrm{s})}t\right]^{1/2} \tag{21}$$

Considering that the permeability of the substrate (K_s) is much larger than that of the membrane (K_m), Eq. (21) can be further simplified as

$$L_\mathrm{m} = 2\left[\frac{(\varepsilon_\mathrm{S}\gamma + R\,\Delta P_\mathrm{p})K_\mathrm{m}}{\eta\alpha R}t\right]^{1/2} \tag{22}$$

According to the Hagen–Poiseuille equation, the velocity of a dispersing liquid with viscosity η and length l, which flows in a laminar capillary diameter R and L in length, is given as

$$\bar{v} = \frac{\Delta P R^2}{8\eta l} \tag{23}$$

Combing Eqs. (11), (12) and (23) gives

$$\bar{v} = \frac{\varepsilon_s \gamma R}{4\eta l} + \frac{\Delta P_p R^2}{8\eta l} \tag{24}$$

While the length l of the dispersion liquid is equal to the length L of the substrate pores, the capillary of the substrate is saturated, and the time t_0 for saturation gives

$$t_0 = \frac{8\eta L^2}{2\varepsilon_s \gamma R + \Delta P_p R^2} \tag{25}$$

Thus, while the dipping time t is larger than the saturation time t_0, there would be no capillary suction force and it is only the applied pressure to drive the dispersing liquid out of the substrate and the following growth of the wet membrane. Therefore, the equation for the further growth of the wet membrane could be given as follows:

$$L_{mp} = 2\left[\frac{\Delta P_p K_m}{\eta\alpha R}(t - t_0)\right]^{1/2} \tag{26}$$

2.3. The growth of the wet membrane by the film coating

After the desired dipping time, the suspension flowed out of the substrate and a boundary layer formed again which protected the wet membrane from peeling off the substrate due to its stillness, as shown in Fig. 2c. And with the liquid level of the suspension flowing down the wet membrane, some of the suspension would adhere to the wet membrane under the specific surface tension of the suspension and turned into the wet membrane eventually with the filtration or volatilization of the dispersing liquid. Provided that the velocity of the suspension is constant, the intensively growth of the wet membrane formed by film coating mechanism varied with the existence of the capillary [9,10].

1. While the dipping time was shorter than the saturation time, the capillary suction force existed and the thickness of the adhering suspension by film coating could be expressed as

$$h = 0.944\left(\frac{\eta v_w}{\gamma}\right)^{1/6}\left(\frac{\eta v_w}{\rho g}\right)^{1/2} \tag{27}$$

where v_w is the velocity of the suspension which could be regarded as the withdrawn speed, ρg is the gravity force. And the thickness of the wet membrane formed by the suspension with the solid content of φ_0 could be obtained

$$L_{mf} = 0.944\left(\frac{1}{1+\alpha}\right)\left(\frac{\eta v_w}{\gamma}\right)^{1/6}\left(\frac{\eta v_w}{\rho g}\right)^{1/2} \tag{28}$$

(2) while the dipping time was longer than the saturation time, there would be no capillary suction force, and the thickness of the suspension coating should be

$$h = \frac{2}{3}\left(\frac{\eta}{\rho g} v_w\right)^{1/2} \tag{29}$$

Similarly, the thickness of the wet membrane formed by the suspension coating could be written as

$$L_{mf} = \frac{2}{3}\left(\frac{1}{1+\alpha}\right)\left(\frac{\eta}{\rho g} v_w\right)^{1/2} \tag{30}$$

Therefore, on the consideration of the whole dip coating process, the total thickness of the wet membrane formed by slip-casting and film coating could be expressed as

$$L_m = \begin{cases} 2\left[\dfrac{(\varepsilon_S \gamma + R\,\Delta P_p) K_m}{\eta\alpha R} t\right]^{1/2} + 0.944\left(\dfrac{1}{1+\alpha}\right)\left(\dfrac{\eta v_w}{\gamma}\right)^{1/6}\left(\dfrac{\eta v_w}{\rho g}\right)^{1/2}, & \text{for } (t < t_0) \\ 2\left[\dfrac{R\Delta P_p K_m}{\eta\alpha R}(t - t_0)\right]^{1/2} + 2\left[\dfrac{(\varepsilon_S \gamma + R\,\Delta P_p) K_m}{\eta\alpha R} t_0\right]^{1/2} + \dfrac{2}{3}\left(\dfrac{1}{1+\alpha}\right)\left(\dfrac{\eta}{\rho g} v_w\right)^{1/2}, & \text{for } (t > t_0) \end{cases} \tag{31}$$

The Eq. (31) indicated that the growth rate of the wet membrane changed at the saturation time. And the thickness of the wet membrane should be proportional to the extraction root of the dipping time under the combination of the capillary suction force and the applied force, provided that the dipping time was shorter than the saturation time; But while the dipping time was longer than the saturation time, the growth rate of the wet membrane reduced due to the non-existence of the capillary suction force. And it could be clearly seen from the Eq. (31) that the existence of the capillary suction force had an intensive effect on the thickness of the wet membrane due to the different thickness of the wet membrane formed by film coating.

To a given suspension and porous tubular substrate, some factors, such as ε_s, γ, R, ΔP_p, v_w, φ_0, ρ, in the Eq. (31) could be measured by various methods, others, such as α, K_m, could be calculated by fitting the experimental data with Eq. (31). Based on the investigation on the structure of the wet membrane from a deflocculated slip, Haerle et al. [11] obtained the volume fraction of the voids in the wet membrane of 0.425 by an ultrasonic monitoring system, and 0.44 by dimensional measurements, which implied that the volume fraction of the ceramic particles φ_m should be 0.56–0.57. Therefore, α could be calculated by the factors of φ_0 and φ_m. And to the permeability of the wet membrane, Gu et al. [6] gave an equation for calculation, shown as follows

$$K_m = \frac{\varepsilon_s^3}{K_0 K_\tau S_v^2 (1-\varepsilon)^2} \tag{32}$$

where K_0 is the particle shape factor, K_τ the tortuosity of the porous medium, S_v the surface area of the particles per volume solids, and ε_s the porosity of the porous substrate. Thus, Eq. (31) would be very helpful in indicating the dip-coating process and estimating thickness of the wet membrane, since all the factors could be measured or calculated.

3. Experimental procedure

By ball milling of alumina (mean particles size is 2 μm) with proper quantities of dispersant (NH_4PAA, lower molecular) and stabilizer (NH_4PAA, higher molecular), a stabilized alumina suspension was achieved. Changing the content of stabilizer, the stabilized suspension with the viscosity of 37 and 45 mPa s could be achieved, respectively. The tubular substrate with the porosity of 40% and the mean pore diameter of 2.89 μm was made of alumina. As shown in Fig. 1, the fluid level was much higher than the length of the substrate while the suspension was poured into the substrate. The wet membrane with different thickness was obtained by adjusting the dipping time. After drying, the substrate was weighed and the thickness of the wet membrane was estimated as follows

$$L_m = \frac{m_2 - m_1}{\rho A \psi_m} \tag{33}$$

where m_1 and m_2 were the weights of the substrate before and after dip-coating and drying process, respectively, ρ the theoretical density of the membrane, A the surface area of the membrane and ψ_m the concentration of ceramic particles in the wet membrane.

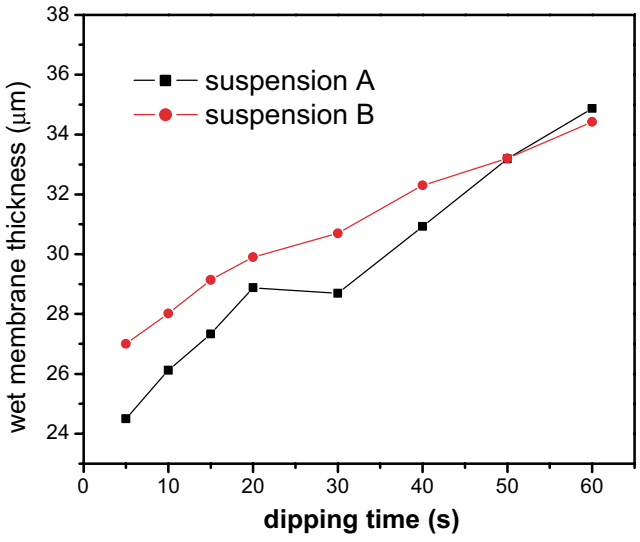

Fig. 4. The effect of the dipping time on the wet membrane thickness (the viscosity of the suspension A was lower than that of the suspension B).

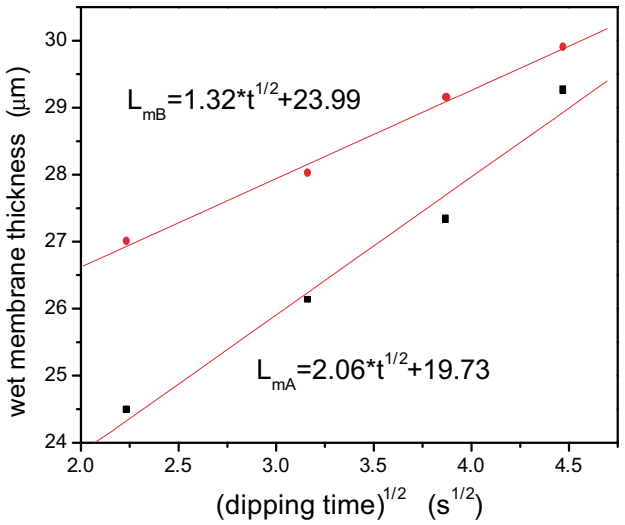

Fig. 5. The linear relationship of the wet membrane thickness with the extraction root of the dipping time.

4. Results and discussion

According to Eq. (31), there is a saturated time t_0 in which the growth rate of the wet membrane had a break resulted from the saturation of the capillaries in the substrate and the decrease of the capillary suction force. Fig. 4 gives the dependence of the wet membrane thickness on the dipping time for suspension A and suspension B, whose viscosity is 37 and 45 mPa s, respectively. The thickness of the membrane increases with the dipping time, and a break occurred in 20–30 s which should be relevant to the saturation time for suspension A and suspension B. By fitting the experiment data, the saturation time is calculated to be 27 s for the suspension A and 28 s for the suspension B. And it could be

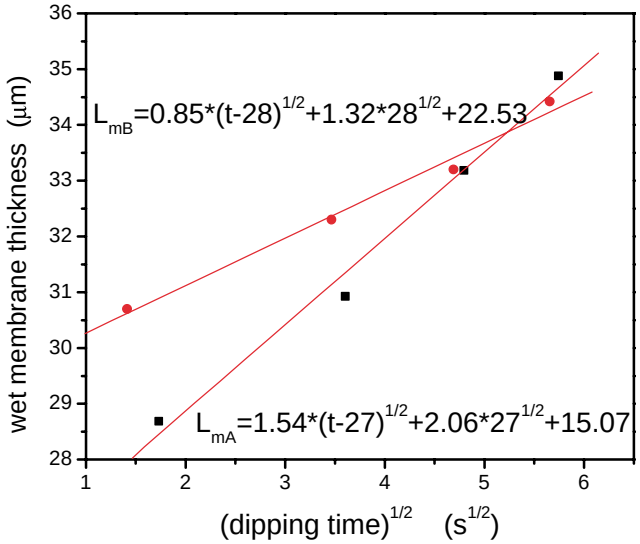

Fig. 6. The linear relationship of the wet membrane thickness with the extraction root of the dipping time following after the saturation time.

clearly seen that the growth rate from the suspension with lower viscosity is larger than that from the higher viscous suspension, which is quite consistent with Eq. (31). It could also be denoted that there is a great difference in the thickness of wet membrane formed by the film-coating process, as illustrated by the intercept of the curves. The higher the viscosity of the suspension, the thicker the wet membrane formed in film-coating.

Fig. 5 presents the linear dependence of the wet membrane thickness on the dipping time for both suspensions, while the dipping time is shorter than the saturation time. And equations have also been simulated from the curves, shown as Eqs. (34) and (36). The growth rate of the wet membrane for the suspension A is larger than that for B which is 2.06 and 1.32 $\mu m\,s^{-1/2}$ for the suspension A and B, respectively, fitting Eq. (31) excellently. And the thickness of the wet membrane formed in film coating process is 19.73 and 23.99 μm from those various suspensions, respectively. While the dipping time is longer than the saturation time, there is also the linear relationship between the wet membrane thickness and the dipping time, as illustrated in Fig. 6. And the equations have also been given as Eqs. (35) and (37). It could be found that the growth rate of the wet membrane reduced from 2.06 to 1.54 $\mu m\,s^{-1/2}$ and 1.32 to 0.85 $\mu m\,s^{-1/2}$ due to the saturation of the capillaries in the substrate, respectively. There is also a drop in the thickness of the wet membrane formed in the film-coating process due to the decrease of the capillary suction, such as 19.73 to 15.07 μm and 23.99 to 22.53 μm, respectively.

$$L_{mA} = 2.06 \times t^{1/2} + 19.73 \quad (34)$$

$$L_{mA} = 1.54 \times (t - 27)^{1/2} + 2.06 \times 27^{1/2} + 15.07 \quad (35)$$

$$L_{mB} = 1.32 \times t^{1/2} + 23.99 \quad (36)$$

$$L_{mB} = 0.85 \times (t - 28)^{1/2} + 1.32 \times 28^{1/2} + 22.53 \quad (37)$$

Substituting ε_s, γ, R, ΔP_p, v_w, φ_0, ρ, η, which are measured by various methods, into Eq. (31), α and K_m, could be calculated by the rate of the slope and the intercept of the equation simulated by the experimental data. The variation of the wet membrane thickness with ΔP_p, η, t could be predicted while the wet membrane had the similar structure. Then the thickness of the wet membrane could be controlled by the operational parameters.

5. Conclusion

The formation and growth mechanism of the wet membrane formed in dip coating process is systematically studied based on a modified model which considered the membrane growth both from the slip-casting process and from the film coating process. An equation has also been given to describe relationship of the wet membrane thickness with the dipping time, shown as follows:

$$L_m = \begin{cases} 2\left[\dfrac{(\varepsilon_S\gamma + R\,\Delta P_p)K_m}{\eta\alpha R}t\right]^{1/2} + 0.944\left(\dfrac{1}{1+\alpha}\right)\left(\dfrac{\eta v_w}{\gamma}\right)^{1/6}\left(\dfrac{\eta v_w}{\rho g}\right)^{1/2}, & \text{for } (t < t_0) \\ 2\left[\dfrac{R\Delta P_p K_m}{\eta\alpha R}(t - t_0)\right]^{1/2} + 2\left[\dfrac{(\varepsilon_S\gamma + R\,\Delta P_p)K_m}{\eta\alpha R}t_0\right]^{1/2} + \dfrac{2}{3}\left(\dfrac{1}{1+\alpha}\right)\left(\dfrac{\eta}{\rho g}v_w\right)^{1/2}, & \text{for } (t > t_0) \end{cases}$$

It is denoted that the growth velocity of the wet membrane have a break at the saturation time. While the dipping time is shorter than the saturation time, the growth velocity of the wet membrane is proportional to the square root of the dipping time under the combination pressure of the capillary suction force and the applied pressure; while the dipping time is longer than the saturation time, the growth velocity reduces with the disappearance of the capillary suction force.

From the equation, it is also shown that different mechanism have different effect on the thickness of the wet membrane: the wet membrane formed by the film coating would be dominate provided that the dipping time is short and the viscosity of the suspension is high; but to the suspension with low viscosity, capillary colloid filtration played more effect on thickness of the wet membrane, specially with long dipping time. All this has been testified by the experimental data.

The variation of the wet membrane thickness with ΔP_p, η, t, etc. could be predicted if the wet membrane have the similar structure. Then the thickness of the wet membrane could be controlled by the operational parameters.

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Nomenclature

A	surface area of the membrane
B	a constant related to the ratio of the mean flow velocity to the maximum velocity in the center of the tube
d	inner diameter of the tubular substrate
dL	thickness of the suspension
dL_m	thickness of the wet membrane
dL_m/dt	growth velocity of the wet membrane
K_1	a constant
K_s	permeability of the substrate
K_m	specific permeability of the wet membrane
K_0	particle shape factor

K_τ	tortuosity of the porous medium
l	length of a dispersing liquid
L	laminar capillary length
L_s	length of the capillaries occupied by the dispersing liquid
m_1	weight of the substrate before dip-coating and drying process
m_2	weight of the substrate after dip-coating and drying process
n	number of the capillaries per unit
Δp_c	capillary pressure caused by one capillary
ΔP	total driving force for the dispersing liquid into the substrate
ΔP_c	specific capillary suction pressure caused by the capillaries of the substrate
ΔP_m	pressure drop across the membrane
ΔP_p	applied pressure caused by potential pressure of the suspension
q	specific flux of the dispersing liquid
R	laminar capillary diameter
Re	Reynolds coefficient
S_v	surface area of the particles per volume solids,
t_0	dipping saturation time
dt	dipping time
v_w	velocity of the suspension which can be regarded as withdrawn speed

Greek letters

γ	surface tension of the dispersing liquid
δ_b	thickness of the laminar boundary
ε_s	porosity of the substrate
ε_S	porosity of the porous substrate
η	viscosity of the suspension
θ	contact angle between the dispersing liquid and the solid surface
ρ	theoretical density of the membrane
φ_0	volume fraction of the ceramic particles in the suspension
φ_m	volume fraction of the ceramic particles in the wet membrane
Ψ_m	concentration of ceramic particles in the wet membrane

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