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Why is the film model fundamentally wrong but still able to correlate the experimental data in membrane processes?

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ABSTRACT

The film model that predicts a logarithmic dependence of permeate velocity on feed solute concentration in membrane separation processes is fundamentally wrong because the primary mass balance equation in the model is inapplicable to the total solute. Based on mass balance relationships on the retained solute, The permeate velocity in crossflow membrane separation processes can be rigorously shown to be a cube root function of the retained solute concentration. Furthermore, the reported good fitness of the film model to the experimental permeate velocities can be shown just to be a delusion of curve fitting mainly due to the adjustable parameters in the model.

1. Introduction

One essential property of a membrane for separation is the semipermeability that retains solute (or other components such as ions or particles) in solutions but allows water (or other solvents) to pass through. The retained solute accumulates and forms a layer of higher concentration than that in the bulk solution adjunct to the membrane surface. This phenomenon is termed "concentration polarization" and is universal in all membrane separation processes.

Concentration polarization stimulates enormous interests and studies because it profoundly affects the performance of the membrane separation processes [1,2]. The retained solute in the concentration polarization layer remains stationary perpendicular to the membrane surface and water has to penetrate through it to reach the membrane. Its impact on the membrane separation processes can be treated either as an increase of total resistance to the permeation flow by creation of an additional resistance layer or a reduction of the driving force for permeate flow by an increase in osmotic pressure. Either way, the net consequence is a reduced permeate velocity in the membrane processes. Under certain conditions, most likely in microfiltration and ultrafiltration, the permeate velocity in the membrane separation processes is completely controlled by the retained solute and becomes independent of the driving pressure and membrane resistance. This permeate velocity occurs at sufficiently high pressure and is often called the "limiting" permeate velocity.

The film model is the most widely used theory to calculate the permeate velocity controlled by concentration polarization [3,4]. The model predicts a logarithmic dependence of permeate velocity on feed solute concentration. Though the film model is reported to fit well to certain experimental data, its theoretical basis is also noted to be fundamentally weak or inadequate. For instance, the mass transfer coefficient and wall solute concentration in the model are virtually fitting parameters because there is no clue at all on the quantifications of these two parameters in the film theory. Because concentration polarization is such an important phenomenon in the membrane separation processes, every effort should be made to ensure that it is appropriately portrayed and assessed.

In this paper, the mass balance equation as the foundation of the film model was first scrutinized for its inapplicability to membrane separation processes. A different relationship between permeate velocity and feed solute concentration was then rigorously derived from a more appropriate mathematical description of concentration polarization in membrane processes. Finally, the "well agreement" of the calculated values to the experimental permeate velocities was discussed and disqualified as a support to the film model.

2. Inapplicability of the film model for concentration polarization in membrane separation processes

2.1. The film model

The film model is a simple but widely used model for permeate velocity (or flux) in a membrane process controlled by concentration polarization, which is [5].

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$$v\ (or\ J) = k \ln \frac{c_w}{c_0} \tag{1}$$

where v is the permeation velocity of water (m/s) through the membrane, k is the mass transfer coefficient, c_0 and c_w are the solute concentrations in the feed solution and at the surface of membrane, and J is water permeate flux ($m^3/m^2 \cdot s$). Permeate velocity and permeate flux are completely exchangeable when they are used for the permeate production rate through the membrane. However, when mass balance of solute in a membrane channel is concerned, the term velocity is preferred because it represents the convective movement and transport of solute. For this reason, the term "permeate velocity" and the symbol "v" will be used exclusively from now on to quantify water permeation rate through the membranes and flow velocity inside membrane channel perpendicular to membrane surface.

The film model is derived from a one-dimensional mass balance relationship in the direction perpendicular to the membrane surface as depicted in Fig. 1. During membrane separation, the solute is brought to the membrane by the permeate flow and retained by the membrane. The retained solute accumulates in a boundary layer over the membrane surface with the highest concentration (c_w) at the membrane surface. The retained solute diffuses back from membrane surface back to the bulk solution driven by the resultant concentration gradient. The film theory further assumes that a steady state is reached when the convective solute flux toward the membrane is counterbalanced by the diffusive solute flux back to the bulk solution.

The cornerstone of the film model is the governing equation for solute in the concentration polarization layer, which is

$$vc + D\frac{dc}{dy} = 0 \tag{2}$$

where D is the diffusion coefficient of solute. The permeate velocity is a constant in the entire thickness of concentration polarization layer. The positive direction of permeate velocity is toward the membrane, which is opposite to the y-axis as indicated in the figure. The boundary conditions for Eq. (2) are

$$c = c_w\ at\ y = 0 \tag{3}$$

and

$$c = c_0\ at\ y = \delta \tag{4}$$

where δ is the thickness of the concentration polarization layer. The definite integral of Eq. (2) with the boundary conditions Eqs. (3) and (4) is

$$v = \frac{D}{\delta} \ln \frac{c_w}{c_0} \tag{5}$$

Eq. (5) becomes Eq. (1) when the parameter of mass transfer coefficient for the membrane process is introduced as

$$k = \frac{D}{\delta} \tag{6}$$

2.2. A fatal misconception of the boundary layer

As the foundation of the film model, Eq. (2) states that there is a boundary (concentration polarization) layer in which solute is stagnant or stationary perpendicular to the membrane surface. However, it will be shown that such a stagnant layer of solute does not exist in any membrane processes. The use of this misconception in derivation of the film model and other related models virtually disqualify these models for the membrane separation processes from the very beginning.

Let us have a close look at the concentration boundary layer. The lower border of the concentration boundary layer is the membrane surface. Eq. (2) is applicable in the boundary layer as it approaches the lower border because the membrane is impermeable to the solute. The upper border of the boundary layer is imaginary at a distance from the membrane surface where the solute concentration can be treated as equal to the bulk concentration. It is supposed to be arbitrarily chosen dependent on the required accuracy of the problem without significant impact on the magnitude of concentration polarization.

There is a problem when Eq. (2) is applied in a region approaching the upper border of the boundary layer in the membrane separation processes. The derivative of solute concentration does not reduce to zero at the upper border as do in most other boundary layer problems. The concentration derivative on the upper border can be determined by rearranging Eq. (2) with solute concentration c_0 at the upper border,

$$\frac{dc}{dy} = -\frac{vc_0}{D} \neq 0 \tag{7}$$

The nonzero derivative at the upper border means there is an abrupt turn on the profile of solute concentration at the upper border from a horizontal line in the bulk to a line with a slop of $-\frac{vc_0}{D}$, which is represented with a solid line in the boundary layer in Fig. 2. This hard bending of the solute concentration profile at the upper border is weird because there is no physical border to force it. The solute concentration is expected to connect smoothly to the bulk concentration at the upper border as depicted by the broken line in the figure.

The abrupt turn of concentration profile at the upper border may be argued to be tolerable or acceptable here because boundary analysis after all is a method of approximation to the real problems. Indeed, a fatal problem of Eq. (2) is the violation of the principle of mass conservation. The stagnant film of solute is unphysical in any membrane separation processes. As shown in Fig. 2 with the thick arrow, the solute

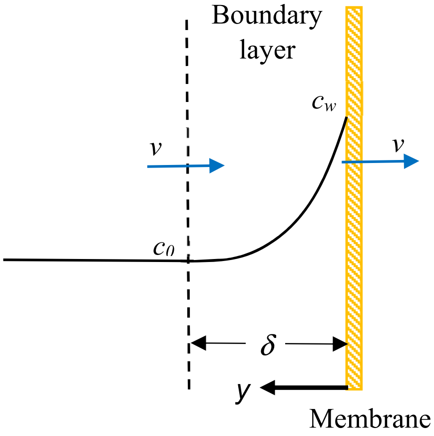

Fig. 1. Boundary (concentration polarization) layer in the adjunct of membrane surface.

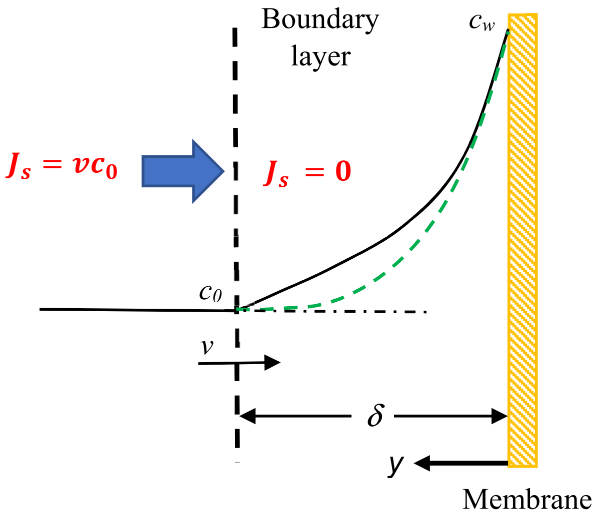

Fig. 2. Mass is unbalanced at the upper border of the boundary layer in film model.

comes from the bulk to the upper border of the boundary layer at a nonzero flux of vc_0. But the solute flux is zero moving down from the upper border because it is in the stagnant layer. Therefore, mass is unbalanced and solute must accumulate at the upper border of the stagnant film. Is there another concentration polarization layer on the top of the concentration polarization layer currently under consideration? This is against the concept of concentration polarization layer, which by definition contains all the retained solute.

To avoid this paradox, at least one of solute concentration and permeate velocity has to vanish at the upper border of the stagnant film. But both parameters have to be nonzero in any membrane separation process. Otherwise, zero solute concentration means nothing in the solution to be separated while zero permeate velocity means no separation by the membrane (no permeate)! A stagnant boundary layer of solute over the membrane surface does not exist in the membrane separation processes. Therefore, the logarithmic dependence of permeate velocity on feed solute concentration predicted by the film model Eq. (1) is fundamentally baseless.

3. True dependence of permeate velocity on solute concentrations

Song and Elimelech [6] indicated that the development of concentration polarization is due only to the retained solute, not all solute in the boundary layer. Therefore, concentration polarization is more appropriately described by the distribution of the retained solute concentration, which is defined as

$$C = c - c_0 \tag{8}$$

where C is the concentration of retained solute. The permeate velocity in a crossflow membrane process is rigorously derived below based on mass balance relationships of the retained solute.

3.1. Mass balance on retained solute in the vertical direction

The retained solute is stationary perpendicular to the membrane surface because it cannot move further. The convective movement of retained solute to the membrane must be counterbalanced by diffusive movement back to the bulk. Therefore, a mass balance relationship on the retained solute on the vertical direction of the membrane channel can be safely written as

$$vC + D\frac{dC}{dy} = 0 \tag{9}$$

Eq. (9) is the same as Eq. (2) in form but it is for the retained solute.

However, the similar boundary conditions for Eq. (2), which specify solute concentrations on the lower and upper borders of the concentration polarization layer, cannot be used for Eq. (9) with the retained solute. This can be shown by looking at the solution of Eq. (9) coupled with such boundary conditions. Supposed the lower and upper boundaries could be specified with

$$C = C_w \; at \; y = 0 \tag{10}$$

and

$$C = C_0 \; at \; y = \delta, \tag{11}$$

the solution of Eq. (9) with Eqs. (10) and (11) would be

$$v = \frac{D}{\delta}\ln\frac{C_w}{C_0} \tag{12}$$

where C_w is the wall concentration of retained solute, i.e., the concentration of retained solute on the membrane surface. However, because $C_0 = 0$ for the retained solute at the upper border, Eq. (12) is invalid. In other words, there is no solution of Eq. (9) coupled with Eqs. (10) and (11). It is obvious that Eq. (11) is an ill-posed boundary condition for the retained solute and cannot be used.

A careful inspection of the problem will find that two boundary conditions are over-posed. Because Eq. (9) is a first order ordinary differential equation, one boundary condition is sufficient. The problem would be thus completely defined, which means the concentrations of all points in the domain would be prescribed by the solution. One more boundary condition is redundant that may lead to wrong solution or make the problem unsolvable. For the same reasoning, it is questionable to use two boundary conditions of Eqs. (3) and (4) for the first order ordinary differential equation Eq. (2) in the film model.

The general solution of Eq. (9) with boundary condition Eq. (10) defines the concentration distribution along the vertical direction to the membrane surface as

$$C(y) = C_w e^{-\frac{v}{D}y} \tag{13}$$

As anticipated, the concentration of retained solute in the vertical direction is fully defined with Eq. (13). It can be seen that the concentration of retained solute naturally dies out as the distance from the membrane surface increases, as

$$C \to 0 \text{ as } y \to \infty \tag{14}$$

Eq. (14) is valid when the height of membrane channel is much larger than the thickness of concentration polarization layer, which is true for most microfiltration and ultrafiltration membrane processes. A forced boundary condition at a definite distance from the membrane surface for the upper border of the concentration polarization layer can distort the problem unreasonably (ill-posed).

The wall concentration C_w in Eq. (13) represents the highest concentration of retained solute in the vertical direction and can be used as a measurement of concentration polarization. It would be premature to use Eq. (13) to quantify concentration polarization in crossflow membrane processes because concentration polarization is also affected by the longitudinal flow in the membrane channels because the amount of retained solute increases downstream.

3.2. *Mass balance of retained solute in the longitudinal direction*

Feed water flows longitudinally along the crossflow membrane channel from the entrance to the exit. The retained solute is brought downstream and is eventually carried out of the membrane channel by this longitudinal flow. As shown in Fig. 3, the thickness of concentration polarization layer grows as the amount of retained solute increases along the membrane channel. The coordinate x is used to indicate the distance from the entrance of the membrane channel in the longitudinal flow direction. A profile of permeate velocity is shown underneath the membrane in the figure.

Considering per unit width of the membrane channel, the accumulation rate of retained solute from the entrance to any distance x in the channel due to permeate flow is

$$N_1 = c_0 \int_0^x v(x')dx' \tag{15}$$

where N_1 is the accumulation rate of retained solute from the entrance to the point x, and x' is the dummy integration variable.

The rate of retained solute carried downstream at the point x by longitudinal flow is

$$N_2 = \int_0^\infty C(x,y)u(y)dy \tag{16}$$

where N_2 is the rate of retained solute carried downward by longitudinal flow across a vertical plat at the point x, and u is the longitudinal flow velocity in the membrane channel. Please note that another independent variable x is added to C because the retained solute concentration is also a function of x in the membrane channel.

At steady state, the rate of solute retained by the membrane from the entrance up to point x, N_1, must be equal to the rate of retained solute moved downstream across the point x, N_2, i.e.,

$$c_0 \int_0^x v(x')dx' = \int_0^\infty C(x,y)u(y)dy \tag{17}$$

Eq. (17) plays a central role in the analysis of concentration polarization because it quantitatively relates the concentration of retained solute to the permeate velocity in crossflow membrane processes.

The concentration polarization layer in crossflow filtration is very thin compared to the velocity boundary layer. Therefore, a shear flow can be assumed in the concentration polarization layer

$$u(y) = \gamma y \tag{18}$$

where γ is the shear rate. The profile of the shear flow is graphically shown on the right side in Fig. 3.

Substituting Eqs (13) and (18) for u and C in Eq. (17) on the right side of the equation and carrying out the integration, the wall concentration of retained solute can be expressed as [6,7].

$$C_w(x) = \frac{c_0}{D^2\gamma} v(x)^2 \int_0^x v(x')dx' \tag{19}$$

Eq. (19) represents the intrinsic link between wall concentration of retained solute and permeate velocity, which is generally valid for the crossflow membrane separation processes.

3.3. *Permeate velocity in crossflow membrane separation processes*

Both wall concentration and permeate velocity in Eq. (19) are variables along the membrane channel in the general cases. Another quantitative relationship is needed to decouple them from each other. Usually, a quantitative relationship can be derived from force balance for permeate flow in the membrane separation process. The general cases will not be discussed further here because they are not particularly relevant to the film model. Interesting readers can find the detailed derivations and discussions of concentration polarization in the general cases elsewhere [6].

A special case that is relevant to the film model is the "limiting permeate velocity" in the crossflow membrane separation processes. The limiting permeate velocity is obtained at sufficiently high pressure when the maximum wall solute concentration (gel concentration) is reached. In this case, because the wall concentration becomes a constant at its highest possible value throughout the whole membrane channel, the permeate velocity becomes the sole variable in Eq. (19). Therefore, permeate velocity is sufficiently defined by Eq. (19) without the need for any additional equation.

With the constant wall concentration of retained solute, the local permeate velocity along the membrane channel can be rigorously derived from Eq. (19) as

$$v(x) = \left(\frac{2}{3}\right)^{1/3} \left(\frac{D^2\gamma}{x}\right)^{1/3} \left(\frac{C_w}{c_0}\right)^{1/3} \tag{20}$$

The detailed derivation was presented elsewhere [7] and is not repeated here. Eq. (20) shows that the local permeate flux declines downstream with cubic root function of the distance ($x^{-1/3}$). The average permeate velocity in a membrane channel of length L is then determined as

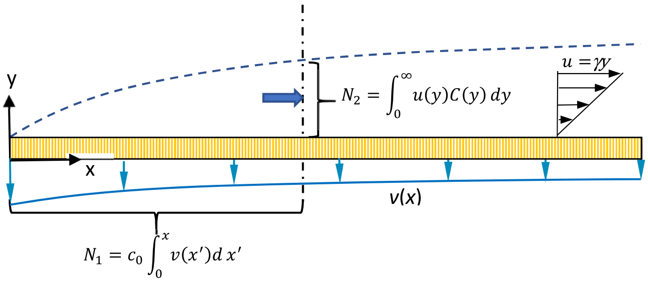

Fig. 3. Mass balance on the longitudinal direction in a crossflow membrane channel.

$$V = \frac{1}{L}\int_0^L v(x)dx = \left(\frac{3}{2}\right)^{2/3}\left(\frac{D^2\gamma}{L}\right)^{1/3}\left(\frac{C_w}{c_0}\right)^{1/3} \cong 1.31\left(\frac{D^2\gamma}{L}\right)^{1/3}\left(\frac{C_w}{c_0}\right)^{1/3} \tag{21}$$

where V is the average permeate velocity.

Attention is called on two important features of Eq. (21). Frist, the Leveque factor $(D^2\gamma/L)^{1/3}$ naturally appears in Eq. (21), which is justified to exist in the expression for permeate velocity in crossflow membrane processes by the rigorous derivation of Eq. (21) from the first principles. Second and more importantly, the average permeate velocity depends on the cube root of the wall concentration of retained solute and feed solute concentration.

Substituting Eq. (8) into Eq. (21) for the wall concentration of retained solute C_w, the average permeate velocity can be written in terms of the wall concentration of total solute as [7].

$$V = 1.31\left(\frac{D^2\gamma}{L}\right)^{1/3}\left(\frac{c_w}{c_0} - 1\right)^{1/3} \tag{22}$$

Comparing the new expression of average permeate velocity Eq. (21) or Eq. (22) to the film model Eq. (1), it can be seen that there are almost nothing in common. The leading coefficient k in the film model is vaguely defined mass transfer coefficient while it is a result of rigorous derivation from the first principles in the new expression. The average permeate velocity is a logarithmic function of solute concentration in film model but a cube root function of retained solute concentration in the new expression.

It should be mentioned that the dependence of permeate velocity on the cube root of solute concentration was previously reported in the literature [8–10] although it was not exactly in the same form as Eq. (21) or Eq. (22). Anyway, the cube root dependence was obtained, though with various analytical methods, all based on two dimensional description of the solute transport for concentration polarization in crossflow membrane processes, which is definitely superior to the improperly formed one dimensional mass balance in the film model.

4. Delusion of experimental support to the film model

The popularity of the film model is not because of its fundamental soundness, but largely because of its good fitness to the experimental data [11,12]. However, the good fitness can be a delusion due to the coincidence between logarithmic function and cube root function under certain conditions. An important reason for the good agreement of the film model to the experimentally observed permeate velocity is that the mass transfer coefficient and wall concentration in the film model are virtually fitting parameters. By properly choosing these two parameters, the film model happens to agree with Eq. (22) well in the common range of feed solute concentration. This can be demonstrated by the following procedure.

First, for a pair of given Leveque factor $(D^2\gamma/L)^{1/3}$ and wall concentration c_w, Eq. (22) is used to generate permeate velocities for a series of feed concentrations. Secondly, Eq. (1) is used to fit the generated data series. The mass transfer coefficient k and wall concentration c_w in Eq. (1) are treated as adjustable parameters for the best fitting. For this purpose, Eq (1) is rewritten as

$$v = -k \ln c_0 + k \ln c_w \tag{23}$$

In this study, curve fitting was done in MS Excel by adding the trendline to the permeate velocities generated with Eq. (22). The equation of the trendline and the coefficient of determination R^2 for the curve fitting are automatically generated in Excel. By the way, the coefficient of determination R^2 is a statistical measurement of the goodness of the data fitted by the model, with $R^2 = 1$ being the perfect fit. Finally, the mass transfer coefficient and wall concentration in the film model are determined from the equation of the trendline.

Fig. 4 presents a curve fitting result for Leveque factor of 1×10^{-6} m/s and wall concentration of 0.4 in the unit of volume fraction. It can be seen that the trendline (film model) fits well to the points generated with Eq. (22). The trendline equation and coefficient of determination are shown in the Figure. The mass transfer coefficient k is the slope of the trendline (which is the leading coefficient before lnc_0 without the negative sign). Then the wall concentration c_w in the film model is calculated from the constant in the trendline equation. The results are

$$k = 1.05 \times 10^{-6} m/s$$

and

$$c_w = \exp\left(\frac{-5.24 \times 10^{-7}}{k}\right) = \exp\left(-\frac{5.24 \times 10^{-7}}{1.05 \times 10^{-6}}\right) = 0.61$$

It is interesting to find that the mass transfer coefficient in the film model is smaller than the leading coefficient in Eq. (22), which is $1.31 \times 10^{-6} m/s$. But the wall concentration is more than 50% higher in the film model than that used in Eq. (22).

The coefficient of determination $R^2 = 0.99$ indicates that the two models agree to each other excellently. This procedure to check the agreement of the film model to Eq. (22) was repeated for various combinations of Leveque factor and wall concentration. Excellent agreements between these two expressions were obtained for all cases with $R^2 = 0.99$. It is also noted that the film model consistently needs higher wall concentration than that used in Eq. (22) for the best fitting.

Therefore, when the experimental permeate velocities follow Eq. (22), it is not a surprise that the film model can match these velocities well with mass transfer coefficient and wall concentration being treated as fitting parameters. It does not mean that concentration polarization is described correctly with the film model. In contrast, the extraordinarily high wall concentrations required for the best fitting to the experimental permeate velocities evidence the failure of the film model in portraying concentration polarization in membrane separation processes.

5. Conclusions

The film model is fundamentally wrong because the stagnant film of total solute does not exist in membrane separation processes. The ultimate cause for concentration polarization to develop is the accumulation of retained solute. With proper quantification of mass balances of retained solute in vertical and longitudinal directions in a crossflow membrane separation process, the permeate velocity controlled by the accumulation of retained solute is rigorously determined to be a cubic

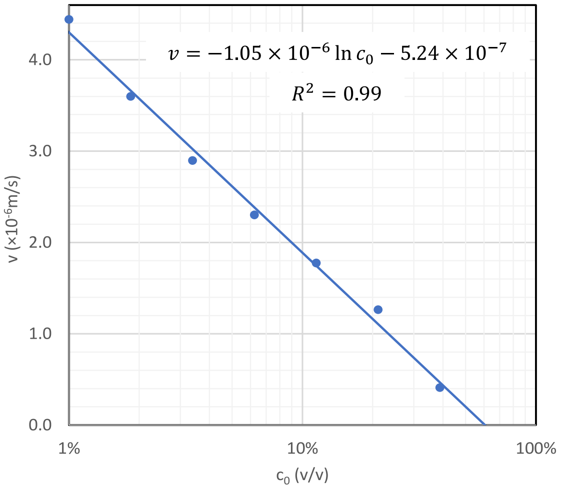

Fig. 4. The best fitting of film model (line) to the data generated with Eq. (22) (points) using Leveque factor $(D^2\gamma/L)^{1/3} = 1 \times 10^{-6} m/s$ and wall concentration (v/v) $c_w = 0.4$.

root function of solute concentrations. The agreement of the film model to some experimental permeate velocities happens just because of the similar trends of the logarithmic function and the cubic root function in the common feed concentration range. Besides, because the film model does not provide any clue to quantify mass transfer coefficient and wall concentration, they are practically treated as fitting parameters for the best fitting to the experimental data. The requirement of extraordinarily high wall solute concentration to fit the experimental permeate velocities virtually disapproves the film model.

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Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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