

MODELLING OF DISPLACEMENT WASHING OF PULP: COMPARISON BETWEEN MODEL AND EXPERIMENTAL DATA

SHELLY ARORA and FRANTIŠEK POTŮČEK*

Department of Mathematics, Punjabi University, Patiala – 147002 (Punjab), India

**Institute of Chemistry and Technology of Macromolecular Materials,*

Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic

Received May 21, 2009

A mathematical model assuming an axial dispersion mechanism, based on two dimensionless criteria, namely the Peclet number and the Biot number, was proposed for the displacement washing of a packed bed of porous, compressible and cylindrical particles. Bulk fluid concentration, intrapore solute concentration and concentration of the solute adsorbed onto the fiber surface were considered as a function of both washing time and position in the bed. Displacement washing experiments performed on pulp beds formed of unbeaten, unbleached kraft fibers were simulated with a laboratory washing cell. The model predicted values of the breakthrough curves, and the average alkali lignin concentration in the bed and displacement ratio were compared with those obtained experimentally. A close agreement was found between the experimental data and the ones calculated from model equations.

Keywords: mathematical modelling, displacement washing, softwood pulp

INTRODUCTION

If the solid particles, such as pulp fibers, are porous, the washing process may be considered as including two operations – displacement and leaching – occurring simultaneously. The solute to be removed is contained in the liquor, in the interparticle voids and within fibers. An unpredictable labyrinth of pores of various tortuosity degrees forms a complex network of voids in the pulp bed. The solute present in the interconnected pores can be removed by a simple displacement by the washing liquid. The transport of the solute from within the fibers to the bulk liquid involves several steps. The solute must diffuse out of the internal structure of the fiber to the external surface of the liquid film immobilized on the external surface of the fiber, prior to its becoming available for displacement.

To predict the behavior of miscible fluid displacement in the packed beds, several mathematical models have been proposed. Assuming that longitudinal mixing between

the displacing and the displaced fluids is described by an equation including the dimensionless Peclet number, derived on the basis of the material balance in unsteady state, Brenner¹ calculated the time dependencies of the concentration of a solute leaving the bed and of the average solute concentration in the bed of finite length. For an unmovable bed of randomly oriented porous particles, Sherman² and Pellet³ modified the usual one-dimensional differential equation for longitudinal dispersion by taking into account the sorption phenomenon, *i.e.* the accumulation of the solute sorbed by the fiber walls and/or the depletion of the solute, in opposite directions, from the fiber walls into the washing liquid flowing through intrapore voids. The absorption equilibrium relationship, expressing the intraparticle solute concentration as a function of the external solution concentration, was assumed to be linear.

Grähs⁴ has divided the packed bed of fibers into three different zones, namely, the zone of flowing liquid, the zone of stagnant liquid and the fiber material. Mass transfer was thought to occur between the flowing and the stagnant liquid, and between the stagnant liquid and fibers. However, the solution was restricted only to axial dispersion. Moreover, some physical features of the fibers, such as fiber porosity and fiber radius, were ignored. An extended mathematical model for the displacement washing of a packed bed of porous, compressible and cylindrical particles, proposed by Arora *et al.*,⁵ is related to diffusion-dispersion and adsorption-desorption phenomena, including, besides axial dispersion, pore diffusion in porous fibers. The sorption relationship is considered to be non-linear.

In this paper, the results attained from a mathematical model⁵ were applied for the displacement washing of a packed bed of kraft pulp fibers and compared with those obtained experimentally in a laboratory washing cell.

Model formulation

A complete mathematical description of the displacement washing of pulp fibers (Fig. 1) ought to include three basic equations, namely an equation, along with the boundary and initial conditions, describing the overall movement of a solute in the bulk liquid, an equation expressing mass transfer in pulp fibers and another equation embracing sorption phenomena. As displacement washing is an unsteady process, a set of partial differential equations should be derived.

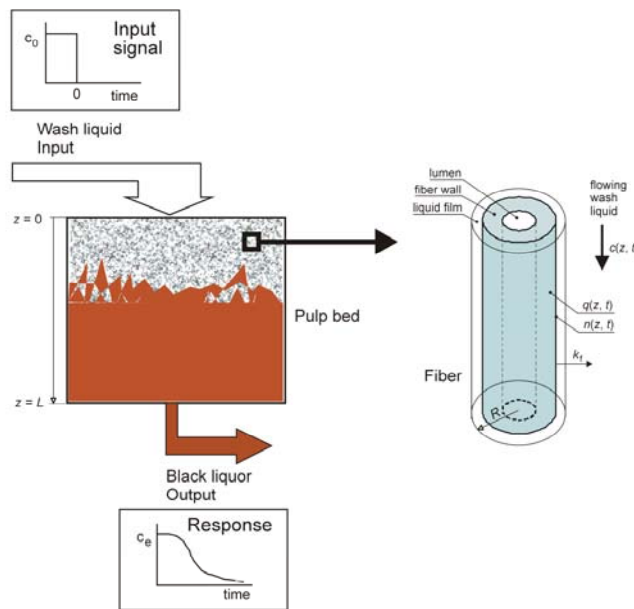


Figure 1: Simplified model of displacement washing of a packed bed of porous particles

Model equation for the bulk liquid phase

For a bed of non-porous granular particles, the basic material balance involving both convective and diffusive transport in an elementary bed volume may be written as:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} \tag{1}$$

In the equation above, the longitudinal dispersion coefficient D_L , which has the same dimension and is analogous to the molecular diffusion coefficient, is a function of the flow pattern within the bed. If the solid particles are porous, then an additional term should be added to equation (1), to account for the mass transfer through the liquid layer immobilized on the particle surface, as long

as a driving force exists. With this assumption, equation (1) becomes:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} - \frac{2(1-\varepsilon)k_f}{\varepsilon K R} (c - q) \quad (2)$$

If the concentration of the solute to be balanced in the washing liquid entering the pulp bed is zero, the boundary condition at the inlet to the bed may be written as follows:

$$uc - D_L \frac{\partial c}{\partial z} = 0 \quad \text{at } z = 0 \text{ for all } t > 0 \quad (3)$$

This condition is imposed by the requirement of no solute loss from the bed through the plane at which the displacing liquid is introduced.

For bed exit, the second boundary condition may be expressed as:

$$\frac{\partial c}{\partial z} = 0 \quad \text{at } z = L \text{ for all } t > 0 \quad (4)$$

The initial condition is:

$$c = q = c_0 \text{ and } n = n_0 \text{ at } t = 0 \text{ for all } z \quad (5)$$

Model for mass transfer in porous particles

Assuming an average fiber porosity β and a liquid side mass transfer coefficient k_f , which is reciprocal to the mass transfer resistance, when a solute is transported from the fiber surface to the bulk flow through the liquid layer immobilized on the fiber surface, the mass transfer from inside the fibers to the bulk liquid may be presented as:

$$\frac{\partial q}{\partial t} + \frac{1-\beta}{\beta} \frac{\partial n}{\partial t} = \frac{k_f}{K R} (c - q) \quad (6)$$

Adsorption isotherm

The sorption phenomena affecting the mass transfer in the system studied have been expressed by the following equation:

$$\frac{\partial n}{\partial t} = \frac{qk_1}{c_0} (n_0 - n) - k_2 n \quad (7)$$

where, at a given initial solute concentration c_0 , the solute concentration inside the fibers q and the solute concentration on the fiber surface n depend on two volumetric mass transfer coefficients k_1 and k_2 , assumed to be of the second order, for adsorption, and of the first order, for desorption. At equilibrium, equation (7) is reduced to the Langmuir adsorption isotherm:

$$n = \frac{q \kappa n_0}{q \kappa + c_0} \quad (8)$$

Basic dimensionless equations

Using the dimensionless variables given in Symbols, equations (2)-(7) have been converted into the following dimensionless form:

$$\frac{\partial C}{\partial \tau} = \frac{1}{Pe} \frac{\partial^2 C}{\partial \xi^2} - \frac{\partial C}{\partial \xi} - \theta Bi (C - Q) \quad (9)$$

boundary conditions:

$$C - \frac{1}{Pe} \frac{\partial C}{\partial \xi} = 0 \quad \text{at } \xi = 0 \quad (10)$$

$$\frac{\partial C}{\partial \xi} = 0 \quad \text{at } \xi = 1 \quad (11)$$

initial condition:

$$C = Q = N = 1 \quad \text{at } \tau = 0 \quad (12)$$

for mass transfer in the bulk liquid:

$$\frac{\partial Q}{\partial \tau} + \frac{1-\beta}{\beta} v \frac{\partial N}{\partial \tau} = Bi (C - Q) \quad (13)$$

for mass transfer in the porous fibers, and:

$$\frac{\partial N}{\partial \tau} = \pi \left[Q(1 - N) - \left(\frac{N}{\kappa} \right) \right] \quad (14)$$

for sorption.

Dimensionless equations (9), (10) and (13) include two dimensionless numbers, the Peclet number Pe and the Biot number Bi . The Peclet number, depending mainly on the flow pattern within the packed bed, characterizes the ratio of the convective to dispersion transport mechanisms. Its value lies within the limits of infinity to zero for plug flow and perfect mixing chamber, respectively. In contrast to the Peclet number, which can be also interpreted as a hydrodynamic parameter of bulk flow, the Biot number expresses the ratio of mass transfer intensity from the fiber surface to the bulk liquid to the mass transfer intensity inside the fibers. When the Biot number is low, most of its resistance is external to the porous particle and the rate of the mass transfer can be approximated by an overall mass transfer coefficient, quite equal to the liquid film mass transfer coefficient.

To solve the system of partial differential equations in dimensionless form (9)-(14), the method of orthogonal collocation on finite elements was selected. This method was first proposed by Carey and Finlayson⁶ to solve the stiff system of ordinary differential equations. According to this method, the axial domain is divided into small elements and then orthogonal collocation is applied within each element. The convergence of numerical solutions does not depend on the number of collocation points, but rather on the number of elements to be taken in the domain of interest. Details on the method of orthogonal collocation on finite elements, on the selection of the collocation points and convergence criterion are given in earlier studies.^{5,7}

EXPERIMENTAL

Stimulus-response experiments, using a step input, have been carried out in the displacement washing cell consisting of a vertical glass cylinder (110 mm high, 36.4 mm inner diameter) closed at the lower end by a permeable septum. The experimental apparatus is described in detail elsewhere.^{8,9}

Unmovable beds of about 4 g of pulp made from a blend of spruce and pine wood were formed by filtration of a dilute suspension of unbeaten, unbleached kraft pulp in the black liquor. In all runs, the beds were compressed to a final desired thickness of 30 mm. To characterize the pulp fibers used in the experiments, the physical properties of kraft pulp were also determined. The Schopper–Riegler freeness had a value of 13 SR. The degree of pulp delignification was expressed in terms of a kappa number equal to 17, while fiber length was determined from measurements in wet state, on a Kajaani FS-100 instrument. The weighed average length was of 2.45 mm, while the arithmetic

average length was of only 1.42 mm. The coarseness of the pulp fibers had a value of 0.217 mg/m. The effective specific volume of the fibers had a value of 2.55 cm³/g and the specific fiber surface was of 1.06×10⁴ cm²/g. Special mention should be made of the fact that the specific volume, as well as the specific surface, were determined for pulp fibers in wet state, when the layer of water immobilized on the surface of the fiber walls should be taken into account.¹⁰ The measurements of the physical properties are described in detail.^{8,9}

To start the washing experiment, distilled water maintained at a temperature of about 20 °C was distributed uniformly *via* the piston to the top of the bed, on approximating a step change in concentration. Depending on the permeability of the pulp bed formed in the washing cell, the wash liquid was forced through the pulp bed, under a pressure drop to 7 kPa. The samples of the washing effluent, taken at different timed intervals, until the effluent was colourless, were analyzed for alkali lignin on an ultraviolet spectrophotometer operating at a wavelength of 295 nm. The initial bed liquor concentration was of 50 g of alkali lignin per litre.

RESULTS AND DISCUSSION

To compare time dependencies of the dimensionless exit solute concentration, the average solute concentration in the bed and the displacement ratio, obtained experimentally, with those calculated according to the proposed mathematical model, four displacement washing runs were performed, *i.e.* runs 1 and 2, differing particularly by their Peclet number, and runs 3 and 4, differing particularly in the pulp consistency of the bed. Some measured and calculated characteristics utilized to determine the breakthrough curves are listed in Table 1.

Table 1
Measured and calculated characteristics for displacement washing runs

Runs	Consistency, %	Peclet number Pe	Biot number Bi	Mass transfer coefficient $k_f \times 10^7, \text{ m s}^{-1}$	Volume equilibrium constant K
1	12.09	12.3	7.4	8.216	0.6042
2	13.14	20.8	10	7.487	1.1884
3	7.96	13.0	6.3	7.859	0.9504
4	16.60	16.9	7.5	8.344	0.6313

Breakthrough curves

A response to the step change in concentration provided time dependencies, known as washing or breakthrough curves. To normalize the breakthrough curve ordinate, each concentration of alkali lignin in the outlet stream c_e was divided by the initial solute concentration in the bed c_0 to give a dimensionless exit concentration C_e . The abscissa was normalized in terms of the dimensionless time τ , defined in Symbols. For a better optical comparison of the breakthrough curves and of the further time dependencies in the following figures, the range of the time axis is limited to $\tau = 4$, although the washing runs were finished at a dimensionless time of 9 to 10, when the alkali lignin concentration in the output stream was less than one thousandth of the initial lignin concentration in the pulp bed.

The typical breakthrough curves measured for the first two runs, characterized by Peclet numbers of 12.3 and 20.8, respectively, are shown in Figure 2. The displacement washing of softwood pulp fibers was non-ideal, lying between the ideal limits of the plug flow, when the Peclet number approaches infinity, and of perfect mixing, when the Peclet number is equal to zero. According to Figure 2, the concentration profile for a higher Peclet number appears as a steeper drop in the second washing period, in which the washing water penetrates through the pulp bed to the exit stream. The calculated data, in close agreement with those obtained experimentally, confirm that, in accordance with a previous paper of ours,⁷ the higher the Peclet or Biot number, the steeper the drop in the exit solute concentration. It should be

noted that both the Peclet and the Biot number are higher for run 2, compared to run 1.

Figure 3 plots the dimensionless exit solute concentration as a function of the dimensionless time, at two values of bed consistency: 7.96 and 16.60%. Both breakthrough curves have a similar profile, although the first segment of the breakthrough curve for the dimensionless exit solute concentration equal to unity is longer at a higher consistency. Displacement washing of pulp fibers is a combination of two mechanisms: displacement and leaching. At a low consistency, the bed has a large effective flow porosity, defined as the ratio of volume available for flow to the total volume of the bed.¹⁰ Thus, larger amounts of liquor can be displaced by the washing water, while a relatively low amount of liquor is removed by leaching, based on the diffusive mechanism developed relatively slowly, as depending on the driving force. Therefore, at high bed porosity, the breakthrough curve falls rapidly and passes to the third segment, in which the leaching operation prevails. Pulp bed porosity is an important factor as the hydrodynamics of the filtrate is highly influenced by the porous path through which the fluid is shifted.

It is worth mentioning that the data obtained experimentally for softwood pulp were satisfactorily fitted by the proposed mathematical model, while the relative error did not exceed 1.3%. The relative errors, along with the mean relative quadratic errors δ , (defined in Symbols) for all washing runs here discussed are summarized in Table 2.

Table 2
Relative errors and mean relative quadratic errors

Runs	Interval of relative error, %	Mean relative quadratic error, δ , %
1	(-0.86; 0.85)	0.45
2	(-0.99; 0.79)	0.51
3	(-1.27; 1.14)	0.59
4	(-0.80; 0.51)	0.31

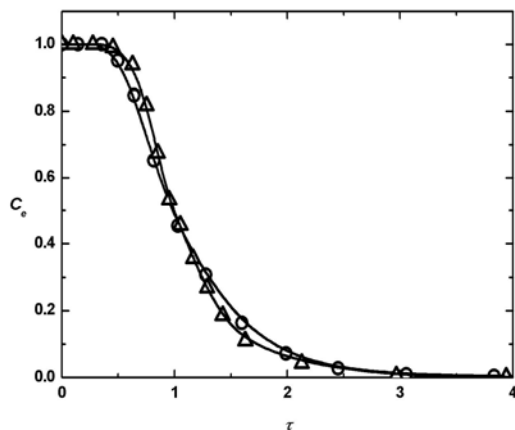


Figure 2: Time dependencies of the dimensionless exit solute concentration calculated for the variables given in Table 1. Experimental data: \circ $Pe = 12.3$ (run 1), Δ $Pe = 20.8$ (run 2).

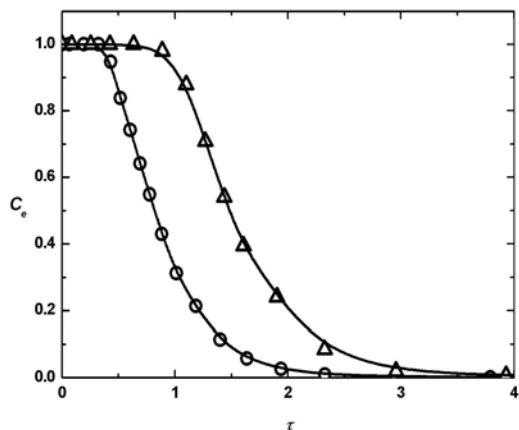


Figure 3: Time dependencies of the dimensionless exit solute concentration calculated for the variables given in Table 1. Experimental data: \circ $C = 7.97\%$ (run 3), Δ $C = 16.60\%$ (run 4)

Average concentration in the bed

Even if the experimental conditions were strictly identical, the fiber bed was always different, owing to the natural source of the material used for bed forming. The pulp fiber bed may be characterized as an unmovable bed containing compressible porous particles of different sizes. Deviations from the plug flow, known as channeling or fingering, due to local inhomogeneities with different porosity, can be assumed during displacement washing. Therefore, the solute concentration in the pulp bed should be expressed as average concentration, in our case calculated from the following relationship:

$$C_{avg} = \frac{\int_{\tau=0}^{\tau \rightarrow \infty} C_e d\tau - \int_{\tau=0}^{\tau} C_e d\tau}{\int_{\tau=0}^{\tau \rightarrow \infty} C_e d\tau} \quad (15)$$

Figures 4 and 5 show the effect of the Peclet number and of bed consistency on the average solute concentration in the bed. As expected, at first, average concentration exhibits almost linear characteristics with the decreasing trend, after which a non-linear

decrease in concentration, approaching zero with increasing time, becomes evident. As follows from Figure 4, the higher the Peclet number, the lower the solute concentration in the bed at a given dimensionless time. Higher Peclet numbers, when the exit solute concentration profile approaches the plug flow, increase the amount of solute removed from the pulp bed.

According to Figure 5, the dimensionless solute concentration decreases as the dimensionless time increases for both consistencies, although a 16.60% consistency gives higher values than a consistency of 7.97%, which is possibly related to the amount of liquor present in the interparticle voids and available for displacement, on the one hand, and to the amount of liquor adsorbed and/or absorbed in the fibers from which a solute should diffuse out to the wash liquid surrounding the fiber surface, on the other. Since the amount of liquor accumulated by the fiber increases with increasing consistency, the average concentration in the bed drops more slowly than in the pulp bed with a 7.97% consistency.

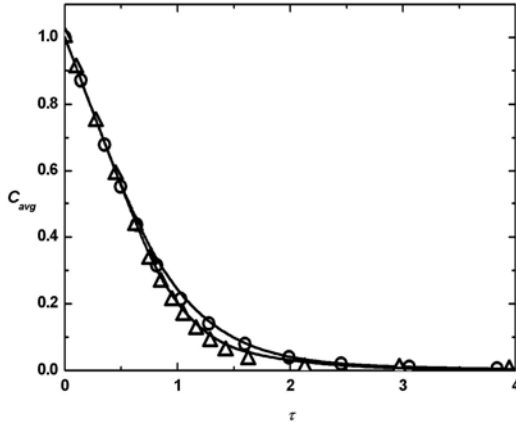


Figure 4: Time dependencies of the average solute concentration in the bed calculated for the variables given in Table 1. Experimental data: \circ $Pe = 12.3$ (run 1), \triangle $Pe = 20.8$ (run 2)

Displacement ratio

One of the commonly used performance parameters describing the amount of a solute removed from the pulp during washing is the displacement ratio. For counter-current washing, the displacement ratio is defined as the reduction in the concentration of dissolved solids from the pulp stream, divided by the maximum reduction in the concentration of the dissolved solids, when the liquor in the pulp stream leaving the washing stage and the wash water stream entering this washing stage are in equilibrium.¹¹ This parameter is not suitable for comparing the washing systems operating at different inlet and discharge consistencies. However, if the inlet and discharge consistencies are identical, the displacement ratio is directly proportional to the quantity of dissolved solids to be removed. In our case, when pulp bed consistency remains unchanged and no solute is dissolved in the washing water entering the pulp bed, the

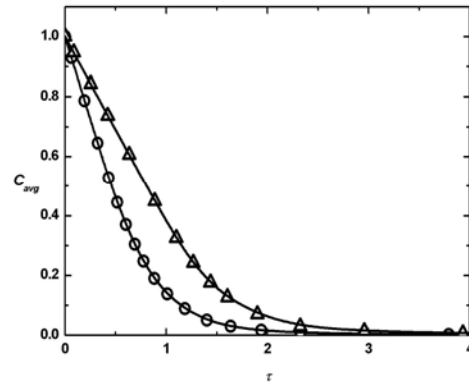


Figure 5: Time dependencies of the average solute concentration in the bed calculated for the variables given in Table 1. Experimental data: \circ $C = 7.97\%$ (run 3), \triangle $C = 16.60\%$ (run 4)

displacement ratio may be calculated from the following relationship:

$$DR = \frac{C_{avg}(\tau = 0) - C_{avg}(\tau = \tau)}{C_{avg}(\tau = 0)} \quad (16)$$

The effect of the Peclet number on the time dependence of the displacement ratio is shown in Figure 6. At first, the displacement ratio increases almost linearly with increasing time, and then asymptotically approaches unity. As expected, the displacement ratio data for a higher Peclet number are slightly higher than those for a lower Peclet number.

Figure 7 shows that the displacement ratio curves are distinctly different for various consistencies. Similarly with the time dependencies of the average solute concentration in the bed, it is evident that a more efficient displacement of a solute is achieved when a large amount of liquor is present in the bed pores, at low pulp consistency.

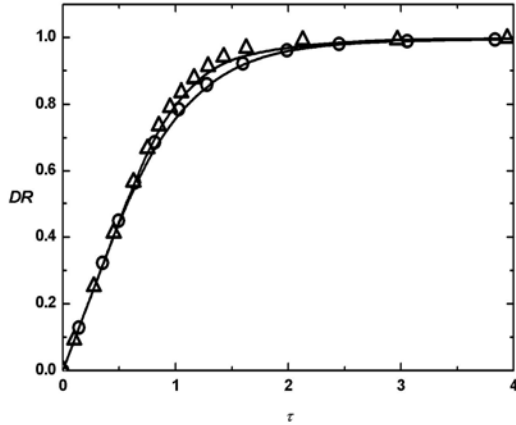


Figure 6: Time dependencies of the displacement ratio calculated for the variables given in Table 1. Experimental data: \circ $Pe = 12.3$ (run 1), \triangle $Pe = 20.8$ (run 2)

In conclusion, all the above experimental and theoretical findings suggest that the present mathematical model agrees quite well with the experimental data, considering many of the important aspects of diffusion, dispersion, adsorption-desorption and different porosity values in the system here studied. The time dependencies of the exit solute concentration, the average concentration in the bed and the displacement ratio reveal a satisfactory fit between the experimentally obtained and the calculated data, according to the proposed mathematical model.

ACKNOWLEDGEMENTS: This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, under the Research Project MSM0021627501.

SYMBOLS

- Bi ($= k_f L \beta / (K R u)$) Biot number
- c solute concentration in the liquor, kg/m^3
- c_e exit solute concentration, kg/m^3
- c_0 initial solute concentration, kg/m^3
- C ($= c/c_0$) dimensionless solute concentration
- C_{avg} average solute concentration in the bed (dimensionless)
- C_e ($= c_e/c_0$) dimensionless exit solute concentration
- D_L axial dispersion coefficient, m^2/s
- DR displacement ratio

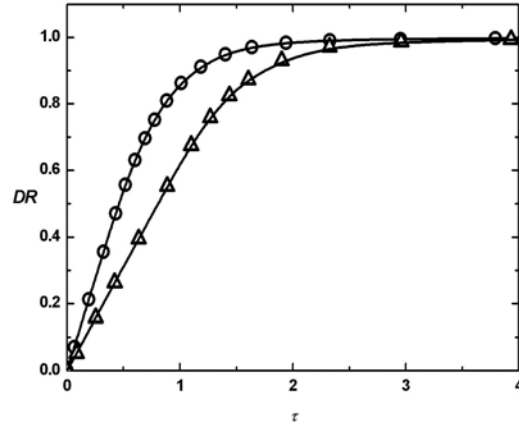


Figure 7: Time dependencies of the displacement ratio calculated for the variables given in Table 1. Experimental data: \circ $C = 7.97\%$ (run 3), \triangle $C = 16.60\%$ (run 4)

- k_f liquid film resistance mass transfer coefficient, m/s
- k_1 volumetric mass transfer coefficient for solute adsorption, $1/s$
- k_2 volumetric mass transfer coefficient for solute desorption, $1/s$
- K volume equilibrium constant (dimensionless)
- L bed thickness, m
- n concentration of solute adsorbed on fibers, kg/m^3
- n_0 initial concentration of solute adsorbed on fibers, kg/m^3
- N ($= n/n_0$) dimensionless concentration of solute adsorbed on fibers
- Pe ($= u L/D_L$) Peclet number
- q intrapore solute concentration, kg/m^3
- Q ($= q/c_0$) dimensionless intrapore solute concentration
- R fiber pore radius, m
- t time, s
- u interstitial washing liquid velocity through the bed, m/s
- z distance from the point of solvent introduction, m

Greek letters

- β fiber porosity, dimensionless
- δ ($= \sqrt{\frac{1}{n} \sum_{i=1}^{i=n} \left(\frac{C_{exp} - C_{calc}}{C_{exp}} \right)^2}$) $\times 100$, where n is the number of measurements) mean relative quadratic error, %
- ε bed porosity (dimensionless)

θ	(= $2(1 - \varepsilon)/\varepsilon$) dimensionless
parameter	
κ	(= k_1/k_2) dimensionless parameter
ν	(= n_0/c_0) dimensionless parameter
ξ	(= z/L) dimensionless axial distance
π	(= $k_1 L/u$) dimensionless parameter
τ	(= $t u/L$) dimensionless time

REFERENCES

- ¹ H. Brenner, *Chem. Eng. Sci.*, **17**, 229 (1962).
- ² W. R. Sherman, *AIChE J.*, **10**, 855 (1962).
- ³ G. L. Pellet, *Tappi J.*, **49**, 75 (1966).
- ⁴ L.-E. Gråhs, *Svensk Papperstid.*, **12**, 446 (1975).
- ⁵ S. Arora, S. S. Dhaliwal and V. K. Kukreja, *Comput. Chem. Eng.*, **30**, 1054 (2006).
- ⁶ G. F. Carey and B. A. Finlayson, *Chem. Eng. Sci.*, **30**, 587 (1975).
- ⁷ S. Arora and F. Potůček, *Braz. J. Chem. Eng.*, **26**, 385 (2009).
- ⁸ F. Potůček, *Collect. Czech. Chem. Commun.*, **62**, 626 (1997).
- ⁹ F. Potůček and M. Marhanová, *Cellulose Chem. Technol.*, **36**, 527 (2002).
- ¹⁰ F. Potůček and M. Pulcer, *Chem. Pap.*, **60**, 365 (2006).
- ¹¹ R. H. Crotagino, N. A. Poirier and D. T. Trinh, *Tappi J.*, **70**, 95 (1987).